Synchrotron X-ray spectroscopy for investigating vanadium speciation in marine sediment: limitations and opportunities

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21 **Significance to JAAS**

22 Synchrotron-based X-ray spectroscopy has the potential to help resolve the geochemistry of
23 inadequately-studied elements, such as vanadium, in marine sediments. Here we evaluate both bulk
24 and microfocused synchrotron X-ray spectroscopic methods for determining solid-phase vanadium
25 speciation in a marine sediment, containing low concentrations of vanadium, to determine both the
26 opportunities and practical limits of this approach.

27
28 **Abstract**

29 Vanadium (V) exists in a number of oxidation states in the environment, potentially making it a useful
30 chemical tracer of both modern and ancient redox conditions in the Earth's oceans. However, the use
31 of V as a redox tracer relies on a comprehensive understanding of V geochemistry in marine systems,
32 which in turn requires the ability to accurately measure its solid-phase speciation in marine sediments.
33 Here we report the first evaluation of both bulk and microfocused synchrotron X-ray spectroscopy to
34 investigate the speciation of V in a modern coastal marine sediment. Semi-quantitative spectral
35 analysis of pre-edge peak areas, extracted from bulk X-ray absorption near edge structure (XANES)
36 spectra, determined the average oxidation state of V in the sediment samples to be ~3.5, indicating a
37 mixture of V(III) and V(IV). Signal-to-noise ratios of XANES spectra were not sufficiently high to
38 allow accurate quantitative analysis by commonly used linear combination fitting approaches. We
39 also demonstrate that high-resolution element mapping by scanning X-ray fluorescence microscopy
40 (SXFM) provides useful complementary geochemical information for resolving possible V host
41 phases in sediments, but is limited in its ability to distinguish V and Ti due to the proximity of their
42 fluorescence emission lines. This study highlights the practical limitations and opportunities of X-ray
43 spectroscopy for investigating V speciation in marine sediments, and reinforces the importance of
44 comprehensively evaluating X-ray spectroscopic techniques prior to applying them to investigating
45 new elements or sample types.

46

47 **Introduction**

48 Vanadium (V) is a transition metal that can exist in various oxidation states in the environment (i.e.
49 +3, +4, +5) depending on the prevailing redox conditions.¹ Dissolved V(V) (as the vanadate
50 oxyanion) dominates in oxic surface waters, whereas the reduced species that are prevalent under
51 reducing conditions, V(IV) and V(III), interact more strongly with the particulate phase and have
52 lower solubility.¹ Accordingly, the enrichment of V in marine sediment tends to indicate deposition
53 under reducing conditions.² This characteristic relationship with oxygen makes V a potentially
54 powerful chemical tracer for investigating past oxygen concentrations in various compartments of the
55 Earth.² For example, V distributions in 1.4 billion-year-old marine shale from the Xiamaling
56 Formation were integral to determining that oxygen concentrations in the oceans, and therefore the
57 atmosphere, were sufficient to support animal respiration 400 – 800 million years earlier than
58 previously estimated.³ The accuracy of these paleoceanographic applications of V, however, rely on
59 a thorough understanding of its geochemistry in the marine environment. Unfortunately, the early
60 diagenesis of V in marine sediments has been poorly studied to date.

61

62 To investigate the diagenetic processes responsible for V accumulation in marine sediments, it is
63 essential to determine its chemical speciation (i.e. its oxidation state, coordination environment, and
64 primary host phases). Synchrotron X-ray spectroscopy encompasses a number of techniques that have
65 the potential to provide this information, including: 1) bulk X-ray absorption near edge structure
66 (XANES) spectroscopy for determining the average oxidation state and coordination environment;
67 and 2) scanning X-ray fluorescence microscopy (SXFM) for generating elemental maps to investigate
68 the co-localisation of elements at high-spatial resolution (i.e. μm -scale). These techniques require
69 minimal sample manipulation prior to analysis and, therefore, maintain the integrity of the sample.⁴
70 To date, synchrotron X-ray spectroscopy has been applied to determine V speciation in Al-ore
71 processing waste,⁵ tropical soils,⁶ amended soils,^{7,8} pure iron oxide phases,⁹ bitumen,¹⁰ steel slag¹¹

72 and multiple biological sample types.^{12–14} There are no reports, however, of these techniques being
73 applied to study V speciation in marine sediments.

74

75 Marine sediments present specific challenges for studying V speciation by synchrotron X-ray
76 spectroscopy, which require comprehensive evaluation prior to the routine application of these
77 techniques. For example, many marine sediments tend to be dominated by crystalline quartz sand,
78 which can be strongly diffracting. Given that vanadium concentrations in sediments are typically low
79 ($\ll 1$ wt %), X-ray fluorescence detection is used to collect XANES spectra. X-rays diffracted off
80 crystalline phases, such as quartz, can enter the fluorescence detector and lead to artefacts and non-
81 linearities in the spectra that, practically, cannot be removed from the data.¹⁵ At low vanadium
82 concentrations, these artefacts can thus dominate spectra and render XANES infeasible. Marine
83 sediments also typically contain concentrations of titanium (Ti) that can be problematic when working
84 at the V K-edge, due to the proximity of Ti K-beta fluorescence emission lines ($E[\text{Ti-K}\beta_{1,3}] = 4933.4$
85 eV) to the V K-alpha emission lines of interest ($E[\text{V-K}\alpha_1] = 4952.9$ eV; $E[\text{V-K}\alpha_2] = 4945.2$). The
86 energy resolution of modern solid-state energy dispersive fluorescence detectors is typically in the
87 order of 150–300 eV, so V fluorescence is difficult to fully resolve from the Ti fluorescence
88 background due to a separation of only ~ 20 eV. Collectively, these factors are likely to contribute to
89 lower signal to noise ratios and thus higher detection limits when measuring V speciation in marine
90 sediment samples.

91

92 The first step in realizing the full potential of V as a paleoredox tracer is to evaluate the reliability of
93 methods for the measurement of its speciation in marine sediments. This will facilitate the detailed
94 examination of early V diagenesis in modern sediments, and the identification of V speciation in
95 ancient sediments. Here we report the application of synchrotron X-ray spectroscopy, both bulk and
96 microfocused, to determining the solid-phase speciation of V in a marine sediment. The studied
97 sediment was intentionally selected to challenge the technique (i.e. a quartz-dominated sediment with

low total V concentration – 12 mg kg⁻¹) to better elucidate the practical limits of this approach for studying V speciation in marine sediments.

Experimental

Vanadium reference standards. Reference standards were selected to be representative of the V oxidation states relevant to environmental samples (i.e. +3, +4, +5). These included the commercially-available (Sigma-Aldrich) V compounds: vanadium(III) oxide (V₂O₃, 99.99%), vanadium(IV) oxide (V₂O₄, 99%), vanadyl sulfate hydrate (VOSO₄·5H₂O, 99.99%), vanadium(V) oxide (V₂O₅, 99.99%), and sodium orthovanadate (Na₃VO₄, 99.99%). Powders were diluted to ~1000 mg kg⁻¹ V in cellulose (20 µm, Sigmacell) by grinding with an agate mortar and pestle. Goethite-sorbed V(V) (~1000 mg kg⁻¹ V) was prepared by mixing 1 g of goethite (α-FeOOH; Sigma-Aldrich) with 50 mL of 10 mg L⁻¹ V(V) (as Na₃VO₄), prepared in deionized water (≥ 18.2 MΩ cm⁻¹). After ~1 h the suspension was centrifuged, decanted, and the solid material washed in 50 mL of deionized water. The solid material was then recovered by centrifugation and dried at 80°C. To evaluate the accuracy of linear combination fitting to quantify the proportion of various V oxidation states, defined mixtures of reference standards representing the end-member oxidation states (V₂O₃ and V₂O₅) were prepared at ratios of 80:20, 50:50, and 20:80 at a total concentration of 1000 mg kg⁻¹ V in cellulose. Mixtures were homogenized by exhaustive grinding with an agate mortar and pestle.

Sediment collection and characterisation. Five sediment cores (8 cm ID, 60 cm length) were collected by hand from the Gold Coast Broadwater (GCB, 27°57'16.0"S, 153°24'37.4"E), a coastal lagoon located in Queensland, Australia, and transported to the laboratory for processing. Four of the cores were sectioned inside an anaerobic chamber (< 10 ppm O₂, Coy Labs) at 0-1 cm, 1-2 cm, 2-3 cm, 3-4 cm, and 4-6 cm depth intervals, and frozen at -20°C until analysis of moisture content, acid-volatile sulfides (AVS), and chromium-reducible sulfur (CRS) as described previously.¹⁶ Total organic carbon (TOC) was measured by non-dispersive infrared absorption following dry combustion

124 (LECO TruMac CNS analyzer). From the remaining core, four small sub-cores (1.8 cm ID, 10 cm
125 length) were taken and immediately frozen at -80°C. Two sub-cores were transported frozen to the
126 Australian Synchrotron, where they were extruded and sliced inside a nitrogen-filled glove bag, dried
127 under a stream of high-purity argon gas, and sieved to < 75 µm prior to V K-edge XAS analysis. The
128 remaining two sub-cores were extruded, sliced, and dried inside an anaerobic chamber (< 10 ppm O₂,
129 Coy Labs). Dry sediments were sieved to < 75 µm prior to microwave assisted extraction (Mars 6,
130 CEM Corp.) of the < 75 µm and > 75 µm fractions (9 mL sub-boiling distilled concentrated HNO₃
131 and 3 mL high-purity concentrated HCl) and quantification of V by inductively coupled plasma mass
132 spectrometry (ICP-MS, Agilent 7900). Duplicate samples of a certified reference material (PACS-3
133 Marine Sediment; National Research Council Canada) were extracted and analyzed in the same way
134 to determine the efficiency of the extraction procedure.

135

136 **ICP-MS analysis.** Sediment extract solutions were diluted 50-fold in deionized water prior to
137 analysis by ICP-MS. The instrument was externally calibrated using a multi-element standard (High
138 Purity Standards) prepared in 2% (v/v) ultra-pure HNO₃. Scandium was added on-line to the sample
139 flow as an internal standard for the correction of instrument drift. The instrument was fitted with a
140 collision-reaction cell, which was operated in He-collision mode (He flow-rate = 5 mL min⁻¹) to
141 remove polyatomic interferences (e.g. ³⁵Cl¹⁶O⁺ and ³⁴S¹⁶OH⁺) on V (*m/z* 51). The limit of detection,
142 determined by analyzing blank solutions (n=6) taken through all microwave extraction steps, was
143 0.02 mg kg⁻¹ V. An aqueous certified reference material (SLRS-5 River Water; National Research
144 Council Canada) was analyzed to verify the accuracy of the ICP-MS external calibration, and had a
145 measured recovery of 92% (0.291 µg L⁻¹ measured; 0.317 µg L⁻¹ certified).

146

147 **Bulk synchrotron XANES.** X-ray absorption spectra were collected at the V K-edge (5463.76 eV)
148 at the XAS beamline at the Australian Synchrotron (3 GeV storage ring; 200 mA top-up). X-ray
149 absorption near edge structure (XANES) spectra were collected in fluorescence mode using a

monolithic 100-element (i.e. channel) HP-Ge fluorescence detector (CANBERRA, France). Samples were packed into 1 mm-thick plastic (polymethyl methacrylate) sample holders and sealed with polyimide (Kapton) tape prior to being placed into a He-purged sample chamber at room temperature. Cryostat-based measurements were not feasible due to the parasitic absorption of both incoming and fluorescence photons by the cryostat windows. The X-ray energy was controlled by a Si-(111) double-crystal monochromator ($\Delta E/E \sim 1.5 \times 10^{-4}$) and calibrated to an in-line V metal foil ($E_0 = 5463.76$ eV).¹⁷ Higher harmonics were rejected via mirrors (Si, Rh, SiO₂), of which the first two were used to focus the beam. The beam was approximately 3 mm wide and 0.5 mm high, and the duration of sample exposure to the beam was minimized using a fast-shutter system that only exposed the sample to beam during data collection. The photon flux at the XAS beamline is approximately $10^{10} - 10^{12}$ photons s⁻¹. XANES spectra were collected over the pre-edge region (5400-5462 eV) in 3 eV steps, the XANES region (5462-5517 eV) in 0.25 eV steps, and the post-edge region in steps constant in k -space (0.035 Å⁻¹). Typical dwell times at each step ranged from one second for reference standards to two seconds for samples, and the total acquisition time for each sample spectrum was approximately 21 minutes. Reduction of the data collected by the multi-element fluorescence detector was done in Sakura (available free of charge from <http://www.synchrotron.org.au/aussynbeamlines/x-ray-absorption-spectroscopy/sakura>). The limited pre-edge energy range was necessary to minimize the interference from the Ti K-edge post-edge region, due to the close proximity of the Ti K-edge (4966 eV). The potential for beam-induced speciation changes was assessed by a series of six rapid XANES scans (~200 s beam exposure per scan) of a Na₃VO₄ standard (1000 mg kg⁻¹ V in cellulose), and was found to be negligible for typical sample exposure times (standard deviation of main edge position = 0.13 eV; see Figure S1). At least three replicate scans were collected for each reference standard, and at least six replicate scans were collected for each sediment sample. All replicate scans were acquired from the same area of the sample, thus avoiding variation in replicate spectra due to sample heterogeneity. No visible shifts in

175 absorption edge position occurred between the replicate scans of samples, further indicating that
176 beam-induced speciation changes were unlikely.

177

178 **Pre-edge peak and main edge position analysis.** Replicate spectra were energy calibrated,
179 normalized and the background subtracted in Athena (ver. 0.9.25),¹⁸ and then averaged to improve
180 the signal to noise ratio. The pre-edge peak was analyzed using peak-fitting software (PeakFit v4.12,
181 Systat Software Inc.) as described in detail by Chaurand and co-workers.¹¹ Briefly, the pre-edge
182 background was removed using a cubic function and the pre-edge peak fitted using multiple Voigt
183 functions (constrained to share FWHM and Lorentzian:Gaussian parameters). The *pre-edge peak*
184 *area* was determined as the sum of the integrated area of each fitted component, and the *pre-edge*
185 *peak centroid energy* as the area-weighted average of the centroid energy position of each fitted
186 component. The *main edge position* was determined as the energy at 0.5 of the normalized absorption,
187 which was previously found to be a reliable approach for interpreting the edge position of noisy
188 spectra (where the first derivative maxima is difficult to interpret accurately).⁶ To assess the
189 sensitivity of this approach to variations in the normalization procedure, two different pre-edge
190 normalization ranges were evaluated: 15 eV (from -30 to -15 eV) and 40 eV (from -60 to -20 eV).

191

192 **Linear combination fitting analysis.** XANES analysis was done by linear combination fitting (LCF)
193 of the reference standard spectra to the sample spectra in normalized energy space over a 50 eV
194 energy range (~5460-5510 eV). The sum of the fitted components was not constrained to unity, but
195 the individual components were constrained to values between 0 and 1. The *combinatorics* function
196 in Athena was used to determine the best fit (i.e. lowest r-factor) for all possible combinations of
197 reference standards. Only fits where all components contributed greater than 10% of the total were
198 considered, consistent with previous evaluations of linear combination fitting precision.^{19,20} Due to
199 the presence of high relative quantities of Ti in the samples, the pre-edge region of the V K-edge
200 XANES spectra was impacted by the Ti K-edge, resulting in spectra with a variable pre-edge.

201 Preliminary investigation showed that the selected pre-edge normalization range had a substantial
202 impact on the outcome of linear combination fitting. Therefore, to systematically assess the sensitivity
203 of the linear combination fitting procedure to variations in the normalization of the XANES spectra,
204 two different pre-edge normalization ranges were evaluated: 15 eV (from -30 to -15 eV) and 40 eV
205 (from -60 to -20 eV), referred to as small and large normalization ranges, respectively. These values
206 represent the two endmembers of a typical pre-edge normalization range, and therefore provide an
207 estimate of the maximum difference in LCF results associated with varying the pre-edge
208 normalization range.

209

210 **Microfocused synchrotron X-ray fluorescence mapping.** A subsample of the GCB 0-0.5 cm
211 sediment sample ($< 75 \mu\text{m}$) was dusted onto the adhesive side of a strip of polyimide tape and the
212 excess sediment removed using a stream of nitrogen gas. The sample was mapped by scanning x-ray
213 fluorescence microscopy (SXFM).²¹ The incident energy was controlled by a Si-(111) double-crystal
214 monochromator ($\Delta E/E \sim 1 \times 10^{-4}$) and focused using a Kirkpatrick-Baez mirror microprobe to a $2 \mu\text{m}$
215 beam size. The photon flux at this resolution is approximately $3 \times 10^9 \text{ photons s}^{-1}$. A Maia (Rev. C)
216 384-element silicon array fluorescence detector was operated in on-the-fly mode, where data is
217 collected continuously on the x-axis.^{22,23} The sample was placed in an argon-exclusion chamber,
218 constantly purged with nitrogen, to improve the fluorescence signal for light elements (i.e. sulfur).
219 SXFM maps were collected on a $1 \times 1 \text{ mm}$ region with a $2 \mu\text{m}$ pixel-size (8 ms dwell time) at incident
220 energies of 18500 eV (for elements heavier than V) and 5665 eV (for V, Ti, Ca, K, and S) – this was
221 necessary to avoid the interference of silicon escape peaks due to intense Fe fluorescence on V K-
222 alpha fluorescence emission lines, which severely impacted V detection limits (see Results and
223 Discussion for further analysis of this issue). Elemental maps were generated using GeoPIXE 7.4.^{24,25}

224

225

226

Results and Discussion

Sediment characterization. The studied sediment is typical of coastal marine environments in that it contains considerable reduced inorganic sulfur species at shallow depths (i.e. within the first centimeter), and relatively high concentrations of total organic carbon, compared with pelagic sediments. This indicates that sulfate reduction is occurring throughout the studied sediment, and thus it is likely that the redox potential is sufficiently low to favor the reduction of V(IV) to V(III).

Table 1. Moisture content, TOC, AVS and CRS for GCB sediment samples (mean $\pm$ 1 SD; n=4 at each depth).

Depth	Moisture Content (%)	TOC (%)	AVS ($\mu\text{mol g}^{-1}$)	CRS ($\mu\text{mol g}^{-1}$)
0-1 cm	66 ± 22	1.3 ± 0.6	1.0 ± 0.5	90 ± 35
1-2 cm	48 ± 11	1.2 ± 0.4	2.0 ± 0.6	81 ± 26
2-3 cm	36 ± 6	0.9 ± 0.2	2.5 ± 0.3	65 ± 10
3-4 cm	30 ± 3	0.7 ± 0.1	3.6 ± 1.3	64 ± 4
4-6 cm	27 ± 2	0.6 ± 0.2	4.4 ± 1.5	53 ± 14

The sediment contained an average total recoverable V concentration of $30.1 \pm 1.7 \text{ mg kg}^{-1}$ in the $< 75 \mu\text{m}$ fraction (n = 6), and $10.3 \pm 1.4 \text{ mg kg}^{-1}$ in the $> 75 \mu\text{m}$ fraction (n = 6). The $< 75 \mu\text{m}$ fraction accounted for $8.3 \pm 0.9 \%$ of the total sediment weight, resulting in a total recoverable V concentration in the whole sediment of 11.9 mg kg^{-1} . This is considerably lower than the average V concentration in both the crust (97 mg kg^{-1})²⁶ and in shale (130 mg kg^{-1}).²⁷ There was no discernable change in V concentration with depth. It should be noted that the microwave assisted extraction procedure used here is unlikely to completely recover all solid-phase V in marine sediment samples, as it lacks the hydrofluoric acid required to dissolve the silicate matrix. This is confirmed by the results of the analysis of PACS-3 marine sediment certified reference material, for which the microwave extraction procedure recovered 64% (82.6 mg kg^{-1}) of the certified V content (129 mg kg^{-1}).

XAS data pre-processing. During data reduction of the raw XANES fluorescence spectra acquired with the 100-element detector, diffraction contamination of the recorded spectra was found to be

250 severe for the studied sediment samples, due to the large proportion of crystalline quartz and low
251 vanadium concentrations. Fortunately, artefacts from diffraction were not present in all of the
252 individual 100 spectra, and thus the careful removal of impacted spectra allowed acceptable average
253 spectra of each individual scan to be obtained. This allowed spectra to be generated that exhibit a
254 sufficient signal to noise ratio for data analysis (Figure 1).

255

256 **Pre-edge peak and main edge position analysis.** The pre-edge peak region was extracted from the
257 XANES spectra of reference standards and samples, and the baseline removed using a cubic function.
258 Each baseline-subtracted peak was then modelled by up to three Voigt functions (Figure 1).
259 Coefficients of determination (R^2) were between 0.9927 and 0.9997 for fits to reference standards,
260 and between 0.9411 and 0.9803 for fits to samples. It should be noted that previous authors^{11,28} have
261 justified constraining some peak-fitting variables (e.g. the number, FWHM, and Gaussian to
262 Lorentzian ratio of fitted peaks) based on known physical parameters of the electronic transitions
263 responsible for the pre-edge feature (e.g. number of electronic transitions predicted from the $Z + 1$
264 model) and/or beamline-specific factors that can impact the acquired spectra (e.g. Gaussian spectral
265 broadening). However, this relies on knowing the number of electronic transitions expected, which
266 is not possible for samples with unknown oxidation state, as well as knowing the impact of beamline-
267 specific (e.g. energy resolution) and sample-specific (e.g. signal-to-noise ratio) parameters on the
268 measured spectra. Instead, we took an empirical peak-fitting approach, where we allowed the
269 amplitude, center and width parameters to vary during the peak-fitting process to provide the best fit
270 of the model to the experimental data. Given that our objective was to obtain a precise measure of the
271 pre-edge peak area and centroid energy position for semi-quantitative interpretation of unknown
272 samples, and not in modelling the specific electronic transitions responsible for the pre-edge peak in
273 known reference standards, this empirical approach was appropriate to address our objectives.

Figure 1. Normalized V K-edge XANES spectra of reference standards and sediment samples (left panel). Pre-edge peaks of reference standards and sediment samples (open circles) fitted with multiple Voigt functions (dashed lines) to generate the combined model (solid line). Coordination geometry of reference standards is indicated as distorted octahedral (O_h), square pyramidal (P_y), or tetrahedral (T_d). The pre-edge peak centroid energy (vertical dotted line) was determined as the area-weighted average of the centroid energy position of each fitted Voigt function.

A plot of the pre-edge peak area versus the pre-edge peak centroid energy position for reference standards and samples demonstrated the utility of these spectral features for the semi-quantitative determination of the oxidation states and coordination geometry of the GCB sediment samples (Figure 2), as comprehensively demonstrated and discussed previously by Chaurand and co-workers.¹¹ In addition, the choice of a small (15 eV) or large (40 eV) pre-edge normalization range

288 had a negligible impact on the position of sample data points, suggesting that the pre-edge spectral
 289 features (i.e. peak area and centroid energy position) are relatively insensitive to slight changes in the
 290 normalization approach. Overall, this semi-quantitative approach indicates that the studied sediments
 291 consisted of a mixture of V(III) and V(IV), which is consistent with the reduced nature of these
 292 sediments as demonstrated by the presence of reduced sulfur at all studied depths (Table 1).

293
 294 **Figure 2. Normalized (to Na₃VO₄) pre-edge peak area versus centroid energy of reference**
 295 **standards (closed circles), sediment samples (diamonds; mean $\pm$ 1 SD), and defined mixtures of**
 296 **V₂O₅ (P_y) and V₂O₃ (O_h) (squares), determined from peak fitting analysis. Sediment sample**
 297 **spectra were normalized with either a small (S) or large (L) pre-edge normalization range.**
 298

299 Plots of the pre-edge peak area versus oxidation state (Figure 3A) and the main edge position versus
 300 oxidation state (Figure 3B) both showed strong linear relationships ($R^2 > 0.975$), and were used to
 301 calculate the average oxidation state for the GCB sediment samples (Table 2). The pre-edge peak area
 302 method resulted in an average oxidation state of ~ 3.5 , indicating that the studied sediment samples
 303 consisted of a mixture of V(III) and V(IV). Importantly, the pre-edge normalization range (i.e. 15 eV
 304 or 40 eV) of the sample spectra had a minimal impact on the calculated oxidation state, with only 0.1
 305 eV difference between the oxidation states calculated from both ranges. In contrast, the main edge
 306 position method appeared to be more sensitive to the pre-edge normalization range, with calculated
 307 oxidation states differing by ~ 0.4 eV. Based on the results of the pre-edge peak area versus pre-edge

308 peak centroid analysis, it appears that the large pre-edge normalization range provides the most
 309 accurate estimate of the average oxidation state when using the main edge position method, indicating
 310 a mixture of V(III) and V(IV).

311
 312 **Figure 3. Linear regression of normalized (to Na₃VO₄) pre-edge peak area (A) and normalized**
 313 **(to V₂O₃) main edge position (B) versus V oxidation state for the studied reference standards.**
 314 **Gray shaded area is the 95% confidence interval of the fitted linear regression line.**
 315 **Coordination geometry of reference standards is indicated as distorted octahedral (O_h), square**
 316 **pyramidal (P_y), or tetrahedral (T_d).**

317
 318 Chaurand and co-workers¹¹ previously suggested that the relationship between oxidation state and
 319 both pre-edge peak area and main edge position were too variable to permit accurate prediction of the
 320 V oxidation state of unknown samples. However, this assessment was based on relationships derived
 321 from reference standards analysed at multiple beamlines with different energy resolutions, energy
 322 step sizes, and sample preparation methods, all of which can introduce variation into the pre-edge

323 peak area and main edge position. In contrast, we observed that reference standards analysed on the
 324 same beamline, with the same sample preparation procedures, showed very little variation in pre-
 325 edge peak area and main edge position for each oxidation state (Figure 3). This highlights the
 326 importance of analyzing both reference standards and samples in the same way and on the same
 327 beamline.

328

329 **Table 2. Oxidation state of V in GCB sediment samples determined from the linear relationship**
 330 **between the pre-edge peak area or the main edge position, and the oxidation state of V reference**
 331 **standards. Results are shown for spectra with small (15 eV) and large (40 eV) pre-edge**
 332 **normalization ranges.**

<i>Sample</i>	<i>Oxidation state [95% CI]</i>			
	<i>Pre-edge peak area method</i>		<i>Main edge position method</i>	
	<i>15 eV</i>	<i>40 eV</i>	<i>15 eV</i>	<i>40 eV</i>
0-0.5 cm	3.58 [3.29,3.78]	3.45 [3.14,3.67]	4.05 [3.90,4.18]	3.58 [3.37,3.74]
0.5-1 cm	3.42 [3.10,3.65]	3.41 [3.09,3.64]	4.09 [3.95,4.22]	3.83 [3.66,3.98]
1-2 cm	3.52 [3.22,3.73]	3.50 [3.20,3.72]	4.22 [4.09,4.35]	3.96 [3.80,4.10]
2-3 cm	3.52 [3.23,3.74]	3.36 [3.02,3.59]	4.09 [3.95,4.22]	3.58 [3.37,3.74]
3-4 cm	3.48 [3.17,3.69]	3.42 [3.10,3.64]	4.09 [3.95,4.22]	3.66 [3.46,3.82]
4-6 cm	3.42 [3.10,3.64]	3.34 [3.00,3.58]	4.09 [3.95,4.22]	3.70 [3.51,3.86]
Average	3.49 [3.19,3.71]	3.41 [3.09,3.64]	4.09 [3.95,4.22]	3.70 [3.51,3.86]

333

334 **Linear combination fitting analysis.** The quantitative assessment of element speciation in unknown
 335 samples is often done by linear least squares fitting of reference standard XANES spectra to the
 336 unknown sample XANES spectra – typically referred to as linear combination fitting (LCF). This
 337 approach is widely used to analyse XANES data due to its ability to provide quantitative estimates of
 338 the proportion of each species in an unknown sample. However, it is critical that the LCF approach
 339 is thoroughly evaluated for the element of interest, in order to avoid erroneous interpretation of the
 340 data.

341

342 The first step in evaluating the robustness of the LCF procedure for V K-edge XANES was to collect
 343 spectra from a series of known mixtures of reference standards, and determine the accuracy of the

LCF approach for determining the proportions of each component. Mixtures were composed of various ratios of V(III) to V(V) (as V_2O_3 and V_2O_5), the two end-members of the series of three expected V oxidation states (+3, +4, +5). The LCF results agreed well with the expected proportions of each oxidation state (Table 3). The inclusion of V(IV) (as V_2O_4) as a component did result in a significantly improved fit, based on *Hamilton testing*, although it never exceeded 10% of the total. These results are consistent with previous estimates of the precision of LCF of XANES spectra being 5-10%,^{19,20} and therefore justifies our decision to reject fits where any component accounts for less than 10% of the total. Overall, the results indicate that LCF should be capable of accurately differentiating the proportion of V oxidation states in unknown samples. It is important to note, however, that this evaluation was done in a simple matrix (cellulose) at relatively high analyte concentrations (1000 mg kg⁻¹), which is often not the case with environmental samples.

Table 3. Proportions of V(V), V(IV) and V(III) from defined mixtures of reference materials, as determined by linear combination fitting and *Hamilton testing*. Fits that are statistically different from the best fit ($p < 0.05$) are highlighted in bold.

<i>fit no.</i>	<i>V(V)</i>	<i>V(IV)</i>	<i>V(III)</i>	<i>R-factor</i>	<i>p-value</i>
80:0:20 V(V):V(IV):V(III)					
1	0.77 ± 0.005	0.09 ± 0.009	0.14 ± 0.005	0.00022	-
2	0.82 ± 0.003	-	0.19 ± 0.003	0.00036	< 0.001
50:0:50 V(V):V(IV):V(III)					
1	0.45 ± 0.006	0.10 ± 0.010	0.46 ± 0.005	0.00027	-
2	0.50 ± 0.003	-	0.50 ± 0.003	0.00042	< 0.001
20:0:80 V(V):V(IV):V(III)					
1	0.17 ± 0.004	0.08 ± 0.007	0.75 ± 0.004	0.00016	-
2	0.21 ± 0.002	-	0.79 ± 0.002	0.00025	< 0.001

The accuracy of the LCF approach relies on a reproducible normalization procedure for both reference standard and unknown sample spectra. While this is straightforward for reference standard spectra, due to their high signal to noise ratio, it can prove challenging for unknown sample spectra where low analyte concentrations result in poor signal to noise ratios.

364

365 In the case of the sediment samples analyzed in this study, the low concentration of V (i.e. less than
366 50 mg kg⁻¹) coupled with comparatively high concentrations of Ti, resulted in noisy spectra with
367 highly variable fluorescence in the pre-edge region. This variability complicates the pre-edge
368 normalization of the sediment sample spectra, potentially leading to errors in the linear combination
369 fitting analysis. We assessed the impact of two different pre-edge normalization ranges on the linear
370 combination fitting analysis: a small pre-edge normalization range spanning 15 eV, and a large pre-
371 edge normalization range spanning 40 eV (Figure 4 and Table 4). The results clearly show that small
372 changes in the pre-edge normalization range can result in large differences in the results of LCF
373 analysis. For example, the proportion of V(III) almost doubles (from 33% to 61%) from the small to
374 large pre-edge normalization range scenarios, while the proportion of V(IV) more than halves (from
375 67% to 21%).

376

377 **Figure 4. Linear combination fit results for the GCB 0-0.5 cm sediment sample with A) small**
378 **pre-edge normalization range (15 eV); or B) large pre-edge normalization range (40 eV).**

379

380 Based on the results of the LCF analysis of this sediment sample, it is not possible to reliably
381 determine the relative proportions of different vanadium species. This is primarily due to the low
382 concentration of V, and thus low signal-to-noise ratio of the acquired spectra. It is possible that the
383 incorporation of additional reference standards may improve the LCF results (e.g. V(III) and V(IV))

silicates), and may improve the minor misfit observed in the post-edge region, as there is likely to be some V present in the silicate phase of sediment samples. However, this would not address the unacceptably large uncertainties (i.e. up to 70%) in the LCF estimates of the proportions of vanadium species in the studied sample. Overall, caution is needed with LCF analysis of V K-edge spectra in unknown samples with low V concentrations, and a rigorous quality control assessment is required before reporting quantitative speciation information (i.e. relative proportions of each component used in the fitting analysis). At a minimum, we recommend that the uncertainty of the LCF results should be assessed by systematically varying normalization parameters and assessing their impact on the results. If the proportion of each component remains consistent to within a predetermined range of uncertainty (e.g. within 20%), then the results should be reported along with their uncertainties. However, if the proportion of each component varies beyond the accepted uncertainty range, the results of the LCF analysis should not be reported and the speciation data limited to the semi-quantitative oxidation state and coordination geometry information provided by pre-edge peak fitting analysis.

Table 4. Proportion of each V oxidation state in the GCB 0-0.5 cm sediment sample determined by linear combination fitting analysis of spectra with different pre-edge normalization ranges.

<i>Species</i>	<i>Pre-edge normalization range</i>	
	<i>A - small (15 eV)</i>	<i>B - large (40eV)</i>
V(V)	-	0.20 ± 0.02
V(IV)	0.67 ± 0.07	0.21 ± 0.05
V(III)	0.33 ± 0.03	0.61 ± 0.03
sum	1.00	1.02
r-factor	0.011	0.0098

Microfocused synchrotron X-ray fluorescence mapping. Scanning X-ray fluorescence microscopy (SXFM) was applied to image the distribution of elements in a subsample of the studied sediment (GCB 0-0.5 cm). Initial attempts to image V simultaneously with other geochemically relevant elements (e.g. Fe and Mn) resulted in poor data quality, likely due to the degradation of detection

limits associated with silicon escape fluorescence. This is due to elements present in the sample at high concentrations (i.e. Fe in this case) causing the emission of a Si K-alpha X-ray (1.74 keV) from the silicon detector, which is recorded as fluorescence at 1.74 keV lower than the incoming X-ray energy (e.g. an escape peak due to Fe is recorded at ~4.66 keV). In the case of measuring both V and Fe in a sample simultaneously, this results in poorer sensitivity for V due to the presence of escape peaks overlapping the V K α fluorescence emission line at ~4.95 keV (Figure 5). GeoPIXE attempts to remove the influence of escape peaks on the X-ray spectrum, however, the increased uncertainty in the fitting of the spectrum results in degraded detection limits compared to when no overlapping escape peaks are present. To address this issue, we mapped the sample using an incident energy of 5.67 keV, which is 200 eV above the V K-edge and lower than the Fe K-edge (Figure 5). This avoids the issue of Si escape peaks overlapping the V K α fluorescence, and thus provides improved sensitivity for V. This approach necessitates SXFM mapping at multiple incident energies to acquire maps for all elements of interest, but it provides a more reliable measurement for the element of interest. It should be noted that the element concentrations reported here should be interpreted with caution, as they are likely to be influenced by the varying sample thickness (due to particles of different sizes) and, therefore, varying fluorescence yield.

Figure 5. Average X-ray fluorescence spectra from SXFM maps of the GCB 0-0.5 cm sediment sample at different incident beam energies (18.5 keV and 5.67 keV). Solid black line is the XRF spectrum and solid gray line shows the Si escape fluorescence. Vertical dashed line shows the position of the V and Fe K-alpha fluorescence lines.

SXFM elemental mapping revealed highly heterogeneous distributions of Ca, Ti, Fe, Mn, S, and V (Figure S2). There was clear evidence of a strong association between Fe and S, consistent with the presence of Fe-sulfide minerals (i.e. FeS and FeS₂) (Table 1). Titanium was present at high concentrations throughout the sample, which raises the question of how reliably the V K-alpha fluorescence can be measured in the presence of Ti K-beta fluorescence given that the proximity of their emission lines (within 20 eV) is much smaller than the energy resolution of the fluorescence detector (~240 eV). In this case, the strong colocalisation of Ti and V is evident from the linear relationship between these two elements. This indicates that V is either genuinely associated with Ti, or that the spectral deconvolution routine is not capable of accurately discriminating V K-alpha and

437 Ti K-beta fluorescence peaks. The latter is certainly the most simple and plausible explanation for the
 438 observed relationship between V and Ti, given the proximity of their fluorescence emission lines.
 439 Unfortunately, this means that the accurate interpretation of V by SXFM is partly confounded by the
 440 presence of high concentrations of Ti typical of geological materials. One approach to investigating
 441 this issue is to use the *element associations* analysis tool in the GeoPIXE software, where all the data
 442 for two elements is plotted on a scatter plot, and can be selected and highlighted on the SXFM map
 443 (Figure 6). This function can be used to identify areas where there is a comparatively high ratio of V
 444 to Ti, which may enable accurate quantification of V, by selecting data points that deviate from the
 445 linearly correlated data (shown in Figure 6 as a green circle). These data points can then be highlighted
 446 on the 2D SXFM map, and the fluorescence spectra extracted for verification of the presence of V.
 447 Using this approach, five areas of interest (AOI) were identified for further investigation (Figure 6).
 448 These areas of interest can also be identified using the *three element RGB image* analysis tool in
 449 GeoPIXE, which can be used to generate a 2-colour image to highlight regions where V is present at
 450 high concentrations and Ti is present at low concentrations (Figure S3).

451
 452 **Figure 6. SXFM map of V in the GCB 0-0.5cm sample (left) and a scatterplot of V versus Ti**
 453 **concentration (right). Green circle shows selected subset of data that was subject to further**
 454 **analysis, which is represented as five areas of interest on the SXFM map.**
 455

456 To verify that the selected areas of interest contain V, their fluorescence spectra was extracted and
 457 analysed in GeoPIXE (Figure 7). Least squares fitting of the fluorescence spectra was done with and
 458 without V as a possible element, and showed that V was required to allow a satisfactory fit of the
 459 spectra. Without V included in the fit, the peak at approximately 4950 eV is considerably
 460 underestimated. This is confirmation that the areas selected using the *element associations* tool
 461 contain V. We recommend that this verification procedure be done for all areas of interest in any 2D
 462 SXFM map where V and Ti co-occur in the sample.

463
 464 **Figure 7. X-ray fluorescence spectra (grey circles) extracted from selected areas of interest**
 465 **identified using the *element associations* tool in GeoPIXE. Least squares fitting of the spectra**
 466 **was done with and without V.**

468 The utility of SXFM for investigating trace element speciation in sediments lies in its ability to
 469 measure colocalised elements, such as S, Ca, Ti, Mn and Fe, which are often associated with trace
 470 element host phases. Average element concentrations were extracted from the identified areas of
 471 interest (Figure 6; Table 5) to investigate possible V host phases. From this data, two broad categories
 472 of elemental composition could be identified: type 1) represented by AOI 1, 3 and 5 and consisting
 473 of relatively high Fe, Mn and Ca but low S; and type 2) represented by AOI 2 and 4 and consisting
 474 of comparatively low Fe, Mn and Ca, but high S. All AOIs contained 480-620 $\mu\text{g g}^{-1}$ V and 0.17-0.25

wt % Ti. The type 1 phases are likely to consist of a mixture of Fe/Mn (oxyhydr)oxides (e.g. ferrihydrite, goethite, lepidocrocite), Fe/Mn carbonates (e.g. siderite), and Ca carbonates (e.g. calcite). In contrast, the type 2 phases are more challenging to identify, but given the comparatively high S and low Fe content (thus excluding Fe-sulfide minerals), they could consist of detrital organic material. Given that bulk XAS spectroscopy indicated this sample contained a mixture of V(III) and V(IV) (with an average oxidation state of ~ 3.5), the colocalisation of V with these solid phases is consistent with our existing, albeit limited, understanding of V geochemistry.^{2,29,30} Unfortunately, the mapping of elements lighter than phosphorus, which could further assist with identifying host phases, is not possible using the Maia (Rev C.) fluorescence detector on the XFM beamline at the Australian Synchrotron.

Table 5. Elemental composition in areas of interest of GCB 0-0.5 cm sediment sample

<i>Area</i>	<i>Concentration</i>					
	<i>S (wt %)</i>	<i>Ca (wt %)</i>	<i>Ti (wt %)</i>	<i>V ($\mu\text{g g}^{-1}$)</i>	<i>Mn ($\mu\text{g g}^{-1}$)</i>	<i>Fe (wt %)</i>
1	0.7	12	0.2	480	1400	6.7
2	4.4	0.2	0.2	510	-	0.7
3	0.6	14	0.2	610	1000	6.6
4	3.0	0.8	0.2	500	-	0.5
5	0.7	7.8	0.2	620	270	2.1

Given the high degree of chemical heterogeneity often observed in coastal sediments on a fine (i.e. sub-mm) scale,^{31–33} it is quite possible that the particles/phases in these AOIs experienced different geochemical environments during early diagenesis. For example, it would not be unexpected for a surficial sediment in a productive coastal system to contain discrete microniches of Fe reduction, sulfate reduction, and Fe and sulfide oxidation, thus providing micro-environments with a variety of redox potentials and potential sorption phases.^{33–35} Indeed, this chemical heterogeneity represents one of the primary reasons why spatially resolved geochemical analysis is needed in the study of sediment diagenesis. Further insight could be gained from microfocussed XANES imaging,⁴ which would allow the determination of spatially resolved oxidation state information for both V and host phase

497 elements (e.g. Fe and S), as well as scanning electron microscopy (SEM), which could assist with
498 further identifying solid phases based on their morphology.

499

500 The high degree of sample heterogeneity observed in sediments, however, also imposes some
501 important caveats to this analytical approach, which should be carefully considered during the
502 interpretation of SXFM data. Firstly, the element concentrations determined via SXFM are influenced
503 by the thickness and composition of the sample, as they both impact the intensity of the measured
504 fluorescence. While these parameters are accounted for in the dynamic analysis approach
505 implemented in GeoPIXE,³⁶ they are typically specified as averages for the entire sampled area, and
506 thus thicknesses and compositions that deviate from this average will impact the measured
507 concentrations. This is of particular importance when analysing whole particulates mounted on tape,
508 as was done in this case, as the thickness and composition of the sample can vary substantially. As a
509 result, reported concentrations are best interpreted as semi-quantitative. The issue of varying sample
510 thickness can be partially addressed by embedding sediments in resin and preparing thin sections,
511 however, particles smaller than the thickness of the thin section (i.e. typically 30 µm) will still be
512 subject to higher uncertainty in the measured concentrations.

513

514 **Conclusions.** Our comprehensive evaluation of synchrotron X-ray spectroscopic methods for
515 investigating V speciation in marine sediments has revealed that the application of these methods,
516 although potentially powerful, require cautious interpretation and rigorous quality control measures.
517 Specific recommendations include:

- 518 - Assess the effect of XANES normalisation parameters on the results of linear combination
519 fitting analysis. This should be done by systematically varying normalisation parameters and
520 determining the effect on the fit results. If the uncertainty exceeds an acceptable threshold
521 (e.g. 20%), analysis should be limited to pre-edge peak or main edge position approaches.

- 522 - Interpret SXFM maps of V in marine sediments with caution. The relatively high
523 concentration of Ti in geological samples complicates the accurate measurement of V due to
524 overlapping fluorescence emission lines, which cannot be fully deconvoluted. Rigorous 2D
525 data analysis can be used to identify areas of interest without overlapping Ti fluorescence, but
526 this means that areas where V and Ti genuinely co-occur are at risk of being overlooked. At
527 high V concentrations (e.g. from anoxic or euxinic systems that often contain high
528 concentrations of V), reliable measurements are certainly possible, but this should be assessed
529 on a case-by-case basis.

530
531 While the measurement of V speciation by synchrotron X-ray spectroscopy is relatively
532 straightforward at high concentrations, at the lower concentrations typical of some marine sediments
533 the poor signal-to-noise ratios result in data that is prone to erroneous interpretation. This can be
534 countered somewhat with increased dwell time to improve signal-to-noise, but becomes less practical
535 with limited synchrotron experiment times. With appropriate recognition of the limitations outlined
536 in this study, however, synchrotron X-ray spectroscopy can be a powerful tool for investigating V
537 geochemistry in marine sediments.

538
539 **Conflicts of Interest.** There are no conflicts to declare.

540
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