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1 **Origin and fate of Vanadium in the Hazeltine Creek Catchment following the**
2 **2014 Mount Polley mine tailings spill, British Columbia, Canada**

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24

25 **ABSTRACT**

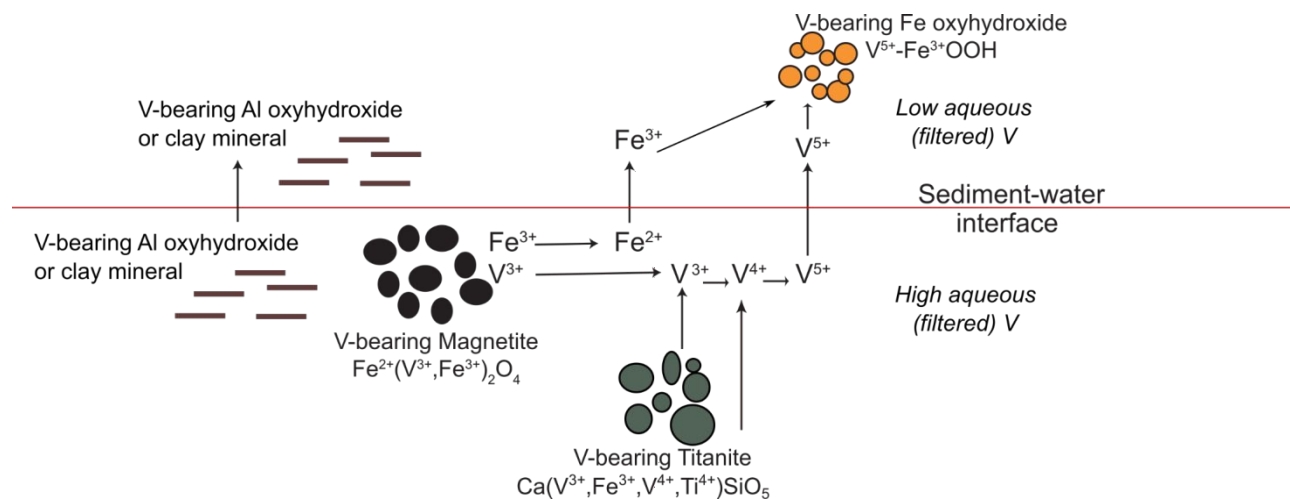
26 Results are presented from the analysis of aqueous and solid-phase V speciation within
27 samples collected from the Hazeltine Creek catchment affected by the August 2014 Mount Polley
28 mine tailings dam failure, Canada. Electron microprobe and XANES analysis found that V is present
29 as V³⁺ substituted into magnetite, and V³⁺ and V⁴⁺ substituted into titanite, both of which occur in the
30 spilled Mount Polley tailings. Secondary Fe oxyhydroxides forming in inflow waters and on creek
31 beds have V K-edge XANES spectra exhibiting E^{1/2} positions and pre-edge features consistent with
32 the presence of V⁵⁺ species, suggesting sorption of this species on these secondary phases. PHREEQC
33 modelling suggests that the stream waters mostly contain V⁵⁺, and the inflow and pore waters contain
34 a mixture of V³⁺ and V⁵⁺. These data, and stream, inflow and pore water chemical data, suggest that
35 dissolution of V(III)-bearing magnetite, V(III,IV)-bearing titanite, V(V)-bearing Fe(-Al-Si-Mn)
36 oxyhydroxides, V-bearing Al(OH)₃ and/or -clay minerals may have occurred. In the circumneutral pH
37 environment of Hazeltine Creek elevated V concentrations are likely naturally attenuated by
38 formation of V(V)-bearing secondary Fe oxyhydroxide, Al(OH)₃ or clay mineral colloids, suggesting
39 that the V is not bioavailable. A conceptual model is presented describing the origin and fate of V in
40 Hazeltine Creek that is applicable to other river systems.

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ToC Art



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47 INTRODUCTION

48 Vanadium (V) is a transition metal which is the 22nd most abundant in the Earth's crust^{1,2} and
49 occurs naturally in four oxidation states (V(II), V(III), V(IV) and V(V)). Although V is an essential
50 element for humans and animals at low concentrations³, intake of high concentrations of V can be
51 carcinogenic and toxic^{4,5}. Generally V(V) is considered to be the most toxic of the V species because
52 it can inhibit or replace phosphate^{6,7}. Vanadium is classed by the United Nations, US Environmental
53 Protection Agency and Chinese Ministry of Environmental Protection as a priority environmental risk
54 element^{2,8,9,10}. In recognition of the potential toxicity of V, Canada has set a Federal Water Quality
55 Guideline of 120 µg/L for protection of aquatic life in freshwater¹¹, and Schiffer and Liber¹² have
56 suggested a more stringent chronic hazardous concentrations endangering only 5% of species (HC5)
57 of 50 µg/L for Canadian freshwater organisms.

58 Humans can be exposed to vanadium mainly through inhalation and ingestion, potentially
59 causing long-term respiratory and digestive problems, respectively¹³. Aqueous vanadate (V(V)) can
60 also be taken up in benthic organisms such as *Hyalella azteca*¹⁴, and have been shown to cause
61 genotoxic and cytotoxic effects in higher plants¹⁵. Vanadium can be distributed in water, soil,
62 sediment and air through the weathering of natural materials and through releases from anthropogenic
63 activities including the burning of fossil fuels, application of pesticides and phosphate fertilizers, steel,
64 aerospace and other industries, and mining^{9,16,17}. For example, mining activities have led to
65 contamination of waters and soils with V (e.g., 76-208 µg/L in groundwaters and 149 to 4800 mg/kg
66 V in soils of the Panzhihua mining and smelting area, China^{18,19}). There is, however, a lack of
67 information on, and understanding of, the geochemical-mineralogical cycling of V in mining-affected
68 environments²⁰, but these are required to determine health effects and to develop management and
69 remediation schemes.

70 Mine tailings dam failures can rapidly add large amounts of V-bearing solid and liquid wastes
71 to the fluvial environment²¹. Globally, failures of mine tailings dams impact significantly in the short-
72 (hours to months) and long-term (years to centuries) on ecosystems and humans that live in affected

73 catchments, through erosion, deposition of tailings sediment and fluids, contamination of soil and
74 water with potentially toxic metal and metalloid elements, and loss of life^{22,23}. The 4th August 2014
75 failure of the tailings storage facility (TSF) at Mount Polley, British Columbia, Canada, is the second-
76 largest by volume on record²³. Approximately 25 Mm³ of material, comprising 7.3 Mm³ of tailings
77 solids, 10.6 Mm³ of supernatant water, 6.5 Mm³ interstitial water and 0.6 Mm³ of, tailings dam
78 construction materials were discharged into the Quesnel River Watershed²³⁻²⁵. The material flowed
79 north into and plugged Polley Lake, then was diverted south-east into Hazeltine Creek for 9.5 km. A
80 significant proportion of the tailings and interstitial water ($18.6 \pm 1.4 \text{ M m}^3$; ²⁵) and eroded soils and
81 vegetation²⁶ were deposited into the West Basin of Quesnel Lake (Figure 1). Deposition of tailings
82 (average 1 m thick, but up to 3.5 m thick in the upper part of the area nearest the TSF) also occurred
83 within the Hazeltine Creek catchment up to 100 m from the channel, especially near Polley Lake and
84 Lower Hazeltine Creek²⁵. Extensive clean-up has been undertaken since the spill (and since the
85 sampling for this study was undertaken), comprising removal of most of the spilled tailings from, and
86 restoration of, the catchment. This was aimed at restoring ecosystem habitats through the
87 establishment of a new rock-lined channel, reducing remobilization of the remaining tailings and
88 exposed natural sediments and decreasing turbidity^{27,28}.

89 Mount Polley is a Cu-Au porphyry deposit, and the tailings comprise mostly silicate minerals
90 (feldspars, ferro-magnesian and Ca-Ti-silicates, muscovite), oxides such as magnetite and rutile,
91 carbonates, Cu sulfides and pyrite. Although the Mount Polley tailings have low sulfide (0.1 – 0.3
92 wt. %) and trace metal and metalloid concentrations²⁹ relative to other tailings^{22,30,31}, they have
93 elevated concentrations of V (86 – 295 mg/kg) compared to local background soils (40.2 – 133
94 mg/kg²⁶). Vanadium was also initially identified, in addition to Cu, Se and Mo, as a contaminant of
95 potential concern in Hazeltine Creek soils³². The cycling of Cu in Hazeltine Creek has been
96 previously examined in detail^{26,29,33-37}, but detailed geochemical and mineralogical studies of V, Se
97 and Mo have not been conducted.

98 In this paper we focus on V due to its high environmental risk potential^{2,8,9,10} and to the relative
99 lack of data on its behavior in mining-affected environments²⁰. We aim to understand the geochemical
100 cycling of V in the Hazeltine Creek catchment and its implications for the origin, transport, fate and
101 potentially toxicity of V in other river systems. The objectives of the study are to determine (1) V
102 concentrations and speciation in stream, inflow and pore waters using aqueous composition data and
103 PHREEQC modeling, (2) solid-phase V concentrations and speciation in the deposited tailings and
104 secondary Fe oxyhydroxides using electron microprobe, automated mineralogy analysis and X-ray
105 absorption spectroscopy (XAS) analysis, (3) the environmental origin, fate and potential hazard of
106 the deposition of V-bearing tailings in mining-affected catchments following tailings dam failures
107 and remediation. We present, for the first time to our knowledge for natural systems, evidence that
108 dissolution of V-bearing magnetite and titanite may contribute to aqueous V. The results will also
109 inform restoration and management schemes for river systems receiving V from other natural and
110 anthropogenic sources.

111

112 MATERIALS AND METHODS

113 **Field Site.** The Mount Polley porphyry Cu-Au mine³⁸ is located in British Columbia, Canada,
114 275 km south-east of Prince George (Figure 1). Hazeltine Creek drains an area of 112 km², including
115 Polley Lake (Figure 1), and flows 9.5 km in a south-easterly direction before discharging into Quesnel
116 Lake. Hazeltine Creek has an alkaline pH (average 8.2 prior to the spill³⁹; 7.0-9.3 from 30th July to
117 2nd August 2015³⁷). The catchment is underlain by Late Triassic alkali intrusions, including the
118 porphyry Cu-Au orebody, and by Mesozoic basaltic and andesitic volcanics, and glaciofluvial and
119 glaciolacustrine deposits³⁸.

120 **Water Sampling, Analysis and Speciation-Solubility modelling.** Details of water sampling
121 analysis and quality control are presented in Byrne et al.³⁷ and are summarized briefly here. In August
122 2015 sample collection comprised from 10 stream waters from Hazeltine Creek, 12 inflow waters
123 seeping from riparian tailings into the creek, and 3 stream channel pore water sites collected at 10

124 and 20 cm depth through deposited tailings, natural stream sediments and bank materials (using a
125 3/8" stainless steel piezometer and peristaltic pump). The piezometer design used in this study was
126 developed by the U.S. Geological Survey and has been used extensively to sample trace metals in
127 pore waters. Standard practice for operating the piezometer is to flush with deionized water before
128 and after pumping to ensure that the drive point itself is clean and not contaminated. Furthermore, it
129 is unlikely that metal leaching would occur over the timescale of pore water pumping / sampling (2
130 – 3 min). Thus, we believe that there was no contribution of V or other metals to the pore water
131 samples. The sampling took place when spilled tailings were being excavated and removed from the
132 creek valley, creek turbidity was high and a new channel was being constructed. Thus, the results
133 reported here could be considered to represent conditions that might be encountered during a spring
134 freshet³⁴. The concentrations of total and filtered (<0.45 μm) major (Al, Ca, K, Mg, Na, Si) and trace
135 elements (As, Cd, Cu, Cr, Fe, Mo, Mn, Ni, Pb, Se, V, Zn) were determined by inductively coupled
136 plasma – optical emission spectroscopy (Thermo Scientific iCAP 6500 Duo) and – mass spectroscopy
137 (Thermo X-series 1), respectively. Ion chromatography (Dionex ICS-2500) was used to determine
138 filtered anion (Cl, F, SO_4) concentrations. Equilibrium modeling, using the measured aqueous
139 concentrations and other aqueous parameters of the Hazeltine Creek stream, inflow and pore water
140 samples, were carried out using the PHREEQC code and the minteq.dat.v4 thermodynamic database
141 distributed with the code^{40,41}. Alkalinity was estimated for the stream and inflow waters as
142 bicarbonate by ion sum calculation (i.e., charge balanced was forced with bicarbonate). We carried
143 out calculations to check if the modelled V speciation and saturation indices were sensitive to
144 bicarbonate activity using different HCO_3 concentrations and found no significant differences in our
145 results. Ferrihydrite and amorphous $\text{Al}(\text{OH})_3$ were allowed to precipitate during the equilibrium
146 modeling, as the waters are not likely to be very much oversaturated with respect to these minerals.

147 **Tailings, Sediment and Fe oxyhydroxide Sampling and XRF V Analysis.** In August 2016
148 samples of deposited tailings and a secondary Fe oxyhydroxide sample deposit scraped from a seep
149 draining a re-profiled stream bank (Supplementary Table S4) were also collected in clean

150 polyethylene bags. These were air-dried and stored at 4 °C until used. A proportion was crushed and
151 pressed into powder pellets for V analysis by XRF (Bruker S4 Pioneer). Sub-samples of deposited
152 tailings (ST 09-02-01-140915 and WT 17-08-02-140912; Supplementary Table S4) collected in 2014
153 following the dam failure by consultants of Mount Polley Mining Corporation, and described in SNC-
154 Lavalin Inc²⁶, were donated by the mine for comparison to samples collected by the authors.

155 **Electron Microprobe and Automated Mineralogy Analysis.** Polished blocks of all solid
156 samples were examined with a Jeol 8100 Superprobe (WDS) with an Oxford Instrument Inca System
157 (EDS). Spot analyses and X-ray chemical mapping were carried out by collecting energy data
158 between 0 and 20 eV using a 15 kV accelerating voltage, 2.5 mA current and a spot size of 1 µm. The
159 analyses were calibrated using a ZAF (atomic number, absorption, fluorescence) matrix correction
160 with standards of oxides and Specpure metals. To quantify and further characterize and quantify the
161 bulk mineralogy and those minerals identified with the Superprobe as containing V, the polished
162 blocks were investigated using an Mineral Liberation Analysis automated mineralogy system on a
163 FEI Quanta 650 FEG ESEM equipped with twin Bruker XFlash EDS detectors at Queen's University,
164 Canada. Spectra were collected at 25kV, with a minimum of 2000 counts per analysis, collecting
165 250,000+ X-ray spectra on each sample to calculate total area percentages of each mineral detected,
166 then a further 800,000 spectra at higher resolution searching and targeting V-bearing minerals at fine
167 detail.

168 **X-ray Absorption Spectroscopy (XAS) Analysis.** Microfocus XANES V K-edge spectra
169 (5465 eV) for individual magnetite, titanite and Fe oxyhydroxide grains were collected on beam
170 line I18 at the Diamond Light Source operating at 3 GeV with a typical current of 300 mA, using a
171 nitrogen cooled Si(111) double crystal monochromator and focusing optics. Kirkpatrick-Baez
172 mirrors were used to produce a focused beam of 3 µm diameter at the sample. For samples and
173 standards (V metal, V₂O₃, VO₂, V₂O₅, V(V) sorbed to FeOOH (see SI for preparation method)), K-
174 edge spectra were collected in fluorescence mode at room temperature (~295 K) using a 4 element
175 solid state Si detector. Because we analyzed V-bearing titanite we checked that the V K α emission

176 line could be resolved, despite its overlap with the Ti K β emission line. On beamline I18, the Ti K α
177 emission at ~ 4510 eV is resolvable in XRF detectors from the V K α emission at ~ 4950 eV (250-300
178 eV separation is required for effective windowing of I18's XRF detectors). The lower intensity Ti
179 K- β emission at 4932 eV is not resolvable by any XRF detector but the binding energy of the V-K
180 edge (5465 eV) is about 500 eV above the Ti K-edge (4966 eV). Therefore, interference of the Ti
181 K- β XAS spectra and V K- α XANES spectra was minimal and limited to long wavelength, low
182 amplitude EXAFS oscillations, by 4950 eV Ti k-edge oscillations that would be not be apparent in
183 V-XANES. After collecting the XANES data, multiple scans were then averaged to improve the
184 signal to noise ratio using Athena version v0.8.061⁴². XANES spectra absorption data were also
185 normalized in Athena over the full data range and plotted from approximately -15 eV to +30 eV
186 relative to the edge position with no correction required for drift in E_0 . Vanadium data were
187 calibrated using E_0 measured from thin metal foils inserted downstream of the samples and
188 measured simultaneously. The V-metal K-edge was detected and the E_0 position did not drift
189 between spectra. The V pre-edge peak energy was determined by calculation of the area normalized
190 centroid energy position (i.e., the peak intensity is normalized to the height of the main V K-edge
191 step on the y-axis of the resultant graph, plotted against the area normalized pre-edge centroid peak
192 energy position on the x-axis) following the method of Chaurand et al.⁴³, and used previously for
193 solid-phase V speciation in bauxite residue⁴⁴.

194

195 RESULTS AND DISCUSSION

196 **Aqueous V geochemistry and speciation.** Filtered V concentrations (mean: 9 $\mu\text{g/L}$; range:
197 7 – 12 $\mu\text{g/L}$) in the Hazeltine Creek stream waters were slightly elevated compared to pre-event mean
198 concentrations (1 $\mu\text{g/L}$ ²⁹), higher than mean global filtered river concentrations (0.71 $\mu\text{g/L}$ ⁴⁵), but
199 lower than chronic hazardous concentrations recently identified for freshwater organisms¹².

200 Overall, filtered V concentrations declined with distance downstream of the Polley Lake weir
201 (Figure 2). Filtered V concentrations in the stream waters were generally lower than those of the

202 inflows seeping from tailings (mean: 17 $\mu\text{g/L}$; range: 4 – 41 $\mu\text{g/L}$), but the inflow waters do not
203 appear to have affected V concentrations downstream, likely because of their low volumes and flow
204 rates (Figure 2). Unfiltered V concentrations in stream (mean: 15 $\mu\text{g/L}$; range: 11 – 21 $\mu\text{g/L}$) and
205 inflow waters (mean: 59 $\mu\text{g/L}$; range: 4 – 303 $\mu\text{g/L}$ ¹) were either similar to (within 7 $\mu\text{g/L}$; 62% of
206 samples) or higher than (up to 278 $\mu\text{g/L}$; 38% of samples) their respective filtered concentrations³⁷.
207 Unfiltered V concentrations were highest in the inflow waters in the upper part of the catchment
208 within approximately 2000 m of the Polley Lake weir (Figure 2).

209 Filtered V concentrations in the Hazeltine Creek stream waters at 0 cm in the sampled profiles
210 (8 – 11 $\mu\text{g/L}$) were similar to those of the other stream waters collected. At 10 cm depth all filtered
211 pore water V concentrations peaked (132, 1200 and 53 $\mu\text{g/L}$ for PW-1, PW-2 and PW-3, respectively;
212 Figure 3), but concentrations declined at 20 cm depth (83, 231 and 43 $\mu\text{g/L}$ for PW-1, PW-2 and
213 PW-3, respectively). Peaks in filtered V concentrations at 10 cm depth coincide with peaks in filtered
214 Al, As, Ca, Cu, Fe, K, Mg, Mn, Ni, Zn and Si, and declines in ORP and pH (Figure 3). The fact that
215 PW-2 has higher V concentrations than those in PW-1 and PW-3 might be due to its position at the
216 downstream end of upper Hazeltine Creek (Figure 1), where the greatest amount of spilled tailings
217 were deposited following the tailings dam failure, and still remained at the time of sampling in August
218 2015³⁷.

219 Filtered V concentrations for most of the pore waters are positively correlated with filtered
220 concentrations of Fe, Al, Cr, Ni and Si, and slightly positive but flatter correlations with filtered Ca
221 concentrations (Figure 4). By contrast, filtered concentrations of inflow waters are poorly correlated
222 with Fe, Al and Ni, but show good correlations with Si, Ca and Cr, together with some of the pore
223 water samples.

224 The PHREEQC modeling suggested that no minerals with V as a major component were
225 oversaturated in any of the Hazeltine Creek waters (Supplementary Table S1). Calcite, diaspore and
226 gibbsite were predicted to be slightly oversaturated in many of the samples (Supplementary Table
227 S1). Pentavalent V was predicted to form 100% of all of the aqueous V species in all but one (HC9)

228 of the stream waters. By contrast, the inflow and pore waters are modeled to contain varying amounts
229 of V(III) and V(V) (Supplementary Table S2. V(III) is modelled to dominate in some of the inflow
230 waters and in the pore waters at 20 cm depth, and V(V) is predicted to dominate in the majority of
231 the inflow waters and in the pore waters at 0 and 10 m depth (Supplementary Table S2). The
232 modelling suggests that HVO_4^{2-} was the dominant species (50-86%) in all but one (HC9) of the stream
233 waters, with lesser amounts of H_2VO_4^- (14-50%; (Supplementary Table S3). The inflow and pore
234 waters have relatively low calculated proportions of HVO_4^{2-} (inflow 23-63%, pore 21-46%) and
235 relatively high proportions of H_2VO_4^- (inflow 37-77%, pore 54-77% Supplementary Table S3). The
236 highest V concentrations recorded in this study occur in inflow and pore waters with $\text{pH} < 8.1-8.3$,
237 which is the equilibrium point between the weak acid and conjugate base (pK_a) ($\text{pH} 8.1$ to 8.3)
238 between HVO_4^{2-} and H_2VO_4^- at 25°C ^{9,46}.

239 We did not measure DOC concentrations and thus were not able to develop a V-organic
240 complexation model. However, we acknowledge that V is known to bind with DOC in the form of
241 humic acids and EDTA in aquatic environments^{47,48,49} and therefore, that DOC may have played a
242 role in V cycling in the Hazeltine Creek catchment.

243 **Solid-phase V geochemistry and mineralogy.** Concentrations of V in the study samples
244 from 51 to 231 mg/kg (Supplementary Table S4), which are mostly within the range for Mount Polley
245 tailings collected in 2014²⁶. The V concentrations are lower than concentrations reported for some
246 mine wastes (e.g. 860-963 mg/kg for red mud from the 2010 Ajka, Hungary, alumina processing
247 repository failure⁴⁴), but are within the same range as others (e.g., 135 mg/kg V for abandoned Au
248 mine tailings, Nova Scotia, Canada⁵⁰; 40.7 mg/kg V for polysulfide tailings, Boliden, Sweden⁵¹). The
249 spilled tailings (samples POL-5- to 7, POL-9; Supplementary Table S5) are dominated by orthoclase
250 and albite (both 32-41 area %), with lesser amounts of hornblende/augite (3.9-5.1 area %), epidote
251 (3.5-4.9 area %), muscovite (3.2-3.8 area %), plagioclase (1.6-2.5 area %), quartz (1.3-2.4 area %)
252 and chlorite (1.3-1.5 area %), similar to proportions found by Kennedy et al.⁵². Magnetite abundance
253 is ascribed to Fe oxides in the automated mineralogy analysis, forming 1.2-3.1 area % of the total

254 mineralogy, while titanite forms 0.5-1.7 area %. A Cu-bearing Fe oxide phase containing >0.1 wt. %
255 Cu was added to the automated mineralogy library³⁴, and this phase forms 0.5-2.3 area % of the
256 tailings. The remaining samples (POL-12 to -14; Supplementary Table S5) contain higher proportions
257 of quartz (20-50 area %), suggesting dilution by catchment soils.

258 Magnetite and titanite in the Mount Polley tailings both contain V (Figure 5), but no other
259 tailings minerals were found to contain V at the detection limit of the microprobe (0.001 wt. %).
260 Average V concentrations for 11 magnetite grains are 0.28 wt. % (range 0.16-0.37 wt. %), and for 14
261 titanite grains are 0.25 wt. % (0.14-0.35 wt. %). The latter are within the same order of magnitude to
262 those determined by Celis⁵³ for 57 titanite grains from the Mount Polley deposit (mean 0.15 wt. % V,
263 range 0.06-0.29 wt. % V). The magnetite also contain trace amounts of Si (mean 0.045 wt. %), and
264 magnetite and titanite contain trace concentrations of Al (0.045 wt. % and 0.037 wt. %, respectively),
265 Cr (0.042 wt. % and 0.001 wt. %, respectively) and Mn (0.13 wt. % and 0.042 wt. %, respectively).
266 Vanadium concentrations in the Fe oxyhydroxide collected from a seep draining a re-profiled stream
267 bank are low, at or below the limit of detection of the microprobe (≤ 0.001 wt. % V; 10 grains).

268 **Vanadium XANES Analysis.** Charaund et al.⁴³ proposed an elegant system for interpreting
269 V K-edge XANES spectra based on the detail observation of pre-edge peak intensity and energy
270 position. In this system, data are described in terms of variation in both co-ordination symmetry and
271 valance state. Data are provided from multiple V(V) standards as V K-edge XANES is sensitive to
272 changes in both valance and the mode of structural incorporation (e.g. V(V) on FeOOH is
273 tetrahedral and V(V) in V₂O₅ is square pyramidal⁵⁴⁻⁵⁶). The multiple V(V) standards are therefore
274 desirable in order to investigate the mode of V occurrence in samples. When the Mount Polly
275 magnetite and titanite data are plotted in this scheme the sample data plots between the octahedral
276 V³⁺ and V⁴⁺ standards. The magnetite samples appear to contain primarily V³⁺, suggesting
277 incorporation of V³⁺ via substitution for octahedral Fe³⁺ within the structure. This is consistent with
278 other studies on magnetite⁵⁷⁻⁵⁹, although Balan et al.⁵⁸ also found minor (<10 %) V(IV) occupying
279 octahedral sites. The Mount Polley titanite V plots between octahedrally co-ordinated V³⁺ and V⁴⁺

280 (Figure 6), suggesting that it most likely substituting for octahedrally co-ordinated Fe^{3+} , Al^{3+} or Ti^{4+}
281 in the mineral structure. Celis⁵³ found that Mount Polley titanite contained almost equal
282 concentrations of Al and Fe, substantiating the possibility of V^{3+} substitution for Fe^{3+} and Al^{3+} . Pan
283 and Fleet⁶⁰ also reported that octahedrally co-ordinated V^{3+} and V^{4+} had similar radii to octahedrally
284 co-ordinated Al^{3+} (0.64, 0.58, 0.535 Å, respectively⁶¹) and could therefore substitute for the latter
285 within the vanadian titanite of the Hemlo gold deposit.

286 The V-bearing iron oxyhydroxide sample plots between V^{4+} (O_h) and the V^{5+} absorbed to
287 FeOOH standards. It is possible that V in these samples is present as a mixture between the primary
288 V^{4+} and V^{5+} in absorption complexes on hydrous iron oxyhydroxides. However, adsorbed V^{4+} does
289 not persist in oxygenated environments as it is readily oxidized to V^{5+} ⁶², and most of the scientific
290 literature reports the strong affinity of Fe oxyhydroxides such as goethite and ferrihydrite to V^{5+}
291 ^{54,64,65}. Kaur et al.⁶⁵ attempted to make samples of V(III)-containing goethite, but found that some
292 oxidation occurred, and that V(III), V(IV) and V(V) were also present. The resultant XANES
293 spectra are intermediate between V(III) and V(V), similar to our spectra (Figure 6). Kaur et al.⁶⁵
294 also provided data that suggested that oxidized V was not readily incorporated in the goethite, and
295 therefore are likely present as adsorbed V(V) that was more easily removed by protons than more
296 reduced forms.

297 **Vanadium Cycling in Hazeltine Creek Following the Mount Polley Tailings Dam Failure**
298 **and Remediation.** V(III)-bearing magnetite and V(III) and/or V(IV)-bearing titanite (Figure 5, 6)
299 were deposited within remobilized tailings and together with a large number of uprooted trees in the
300 Hazeltine Creek catchment following the 2014 Mount Polley dam failure. It is also possible that lesser
301 amounts of these minerals occurred within Hazeltine Creek channel and floodplain sediments and
302 soils prior to the failure, given the relatively high V concentrations of some background soils²⁶. A
303 year after the tailings dam failure high filtered concentrations of V in pore waters occurring at 20 cm
304 and especially 10 cm depth in Hazeltine Creek, coincide with peak concentrations in Al, As, Ca, Cu,
305 Fe, K, Mg, Mn, Ni, Zn and Si, and declines in ORP and pH (Figure 3). It is possible that these high

306 concentrations reflect those in initial tailings dam pore waters transported with the spilled tailings,
307 but this is unlikely for the following reasons. First, most of the tailings and interstitial water went into
308 Quesnel Lake rather than Hazeltine Creek²⁵, second, we sampled in a very disturbed mixed river
309 sediment rather than undisturbed layers of tailings and third, we sampled a year after the spill and the
310 nature of the channel (high gradient, gravelly substrate) encouraged flushing by hyporheic exchange.
311 Therefore, we propose that the high filtered V concentrations at 10 and 20 cm depth arose from
312 dissolution of V-bearing phases containing these elements just below the water-sediment interface⁶⁶.
313 Positive trends between concentrations of V and those of Al, Fe, Cr, Mn and Si (Figure 4) suggest
314 that one of the phases undergoing such dissolution could be the Mount Polley magnetite which
315 incorporates these elements. The dissolution of vanadium titano-magnetite with similar
316 concentrations of V (0.28 wt. %) has been demonstrated experimentally by Hu et al.¹⁰, who showed
317 that V is released from magnetite between pH 5.9 and 8.8 under dissolved O₂ ranging from 5% to
318 80%. Other possibilities for phases undergoing dissolution to produce these positive trends could be
319 V-bearing clay minerals, Al(OH)₃ or Fe-Al-Mn-Si oxyhydroxides whose V concentrations were
320 below detection limits of our microprobe analysis and which were small enough to pass through the
321 0.45 μm filter.

322 Vanadium concentrations in inflow waters are mostly lower than those in pore waters, and
323 those up to 50 μg/L correlate well with Ca, Si, Fe and Al, while those up to 25 μg/L correlate with
324 Cr and Mn (Figure 4). The released Ca and Si can be attributed to the weathering of epidote or feldspar
325 which occur in the tailings, and that of Ca, Si, Fe and Al, to the weathering of hornblende
326 (Supplementary Table S5), but none of these minerals were found to contain V. Ca and Si are two of
327 the major components of titanite, and Mount Polley titanites contain trace amounts of V, Fe, Al, Cr
328 and Mn. It is proposed that titanite weathering in the tailings piles from which the inflows emanate is
329 responsible for these trends and modest enrichments in V. Although they did not analyze for V, Tilley
330 and Eggleton⁶⁷ have shown that titanite can weather, likely under supergene conditions, to beidellite
331 and anatase at neutral pH, resulting in loss of all of the Ca but retention of Ti. The reason for the

332 different V-trends shown by the inflows and pore waters (Figure 4) is unknown but may be related to
333 different proportions of these minerals in the spilled tailings.

334 Positive saturation indices for ferrihydrite and goethite (Supplementary Table S1), the
335 presence of Fe oxyhydroxides forming along the inflow waters and the sampled V-bearing Fe
336 oxyhydroxide (POL-13, Supplementary Table S5, Supplementary Figure S3; Figure 5) show that
337 some of the mobilized V is taken up by secondary Fe precipitates. Iron oxyhydroxides were observed
338 in 2015 at the sediment-water interface in Hazeltine Creek, especially in the riparian area downstream
339 of the second gorge where the gradient shallowed and the valley widened (near HC-9; Figure 1).
340 These, and the declines in Fe concentrations in the Hazeltine Creek stream waters at 0 cm in the depth
341 profiles collected (Figure 3) suggests that the high Fe pore waters at 10 cm depth were attenuated
342 either by diffusion of aqueous V and Fe, and/or by precipitation of Fe oxyhydroxides at this interface.
343 The V in these Fe phases is most likely to be V(V), given the dominances of this species in the stream
344 waters, in most of the inflow waters and in the pore waters at 0 and 10 cm depth in the PHREEQC
345 (Supplementary Table S2), and in the XANES modeling (Figure 6). The fact that filtered V
346 concentrations for samples with pH values between 7.5 and 8.3 are higher than those with pH values
347 greater than 8.3 (Supplementary Figure S1) is consistent with experimental studies. Dzombak and
348 Morel⁶⁸ and Naeem et al.⁸ demonstrated that V sorption to Fe oxides and hydroxides was highest
349 between pH c. 3 and 3.5 and then decreased as pH increased from 4 to 11.6. Naeem et al.⁸ attributed
350 this decrease to competition between OH⁻ and aqueous V anions for Fe oxide/hydroxide surface
351 binding sites. Similarly, positive saturation indices for the Al oxyhydroxide diaspore and Al
352 hydroxide gibbsite, and positive trends between total Al, Si and V concentrations (Supplementary
353 Figure S2), also suggest that the formation of secondary phases such as (Al-Si-bearing) Fe
354 oxyhydroxides, Al oxyhydroxides and hydroxides or clay minerals (see above) may attenuate aqueous
355 V concentrations that show a decline downstream in Hazeltine Creek (Figure 2).

356 The association of V with Fe oxyhydroxides has been observed for streams throughout
357 Sweden affected by natural and anthropogenic inputs of V⁶⁹, with other studies showing that

358 considerable transport occurs in the colloidal phase⁷⁰. Concentrations of total V in Hazeltine Creek
359 are higher than those of filtered V (Figure 2), and apart from three inflow water samples, total Fe, Al
360 and Si concentrations correlate well with total V concentrations (Supplementary Figure S2),
361 suggesting that fine particulate transport of V is significant in the catchment.

362 The significance of the Mount Polley tailings spill on water quality and V transport are
363 illustrated in Figure S4 where V flux (kg yr^{-1}) and yield ($\text{kg km}^{-2} \text{ yr}^{-1}$) are compared to unaffected
364 regional watersheds in British Columbia and other mining-affected watercourses around the world.
365 Transport of V in the stream is elevated compared to nearby regional streams, even when the flux
366 data are weighted by watershed area. In addition, under high flow conditions, V yield (measured at
367 HC-9 in 2016) was comparable to (low flow) yield values recorded in Torna Creek, Hungary,
368 following the 2010 Ajka bauxite residue tailings spill⁷¹. The V transport data reported here show a
369 larger departure from background concentrations and fluxes than those reported for Cu at Mount
370 Polley³⁷. Particulate transport of V appeared to be more dominant under high flow than low flow,
371 suggesting physical mobilization of residual tailings could be an important transport mechanism for
372 V during spring freshets and summer rainfall-runoff events. However, the bulk of the tailings
373 remaining after our sampling in 2015 and 2016 were removed from the Hazeltine Creek watershed
374 and returned to the tailings storage facility (L. Anglin, pers. comm., 2018), suggesting that the effects
375 of such physical mobilization could be minimal in the future.

376 The weathering of mine tailings derived from dam failures such as Mount Polley can play a
377 major role in V cycling in surficial environments. We have presented evidence that deposition of V-
378 bearing tailings can lead to enhanced pore and inflow water V concentrations, especially when
379 deposited or stored in environments where dissolution of primary (e.g. V-bearing magnetite and
380 titanite) and secondary (V-bearing Fe and Al oxyhydroxides or clay) minerals also leads to greater V
381 mobilization. However, these enhanced V concentrations can be naturally attenuated, and their
382 potential ecotoxicity reduced, by formation of secondary colloidal Fe oxyhydroxides that reduce
383 aqueous V to near background levels.

384

385 **Supporting Information**

386 Detailed water sampling and XANES methods and mineral results, pore water geochemical data,
387 PHREEQC modelling results and plots, automated mineralogy data and V flux and yield plot. This
388 material is available free of charge via the Internet at <http://pubs.acs.org>.

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394 **Notes**

395 The authors declare no competing financial interests.

396

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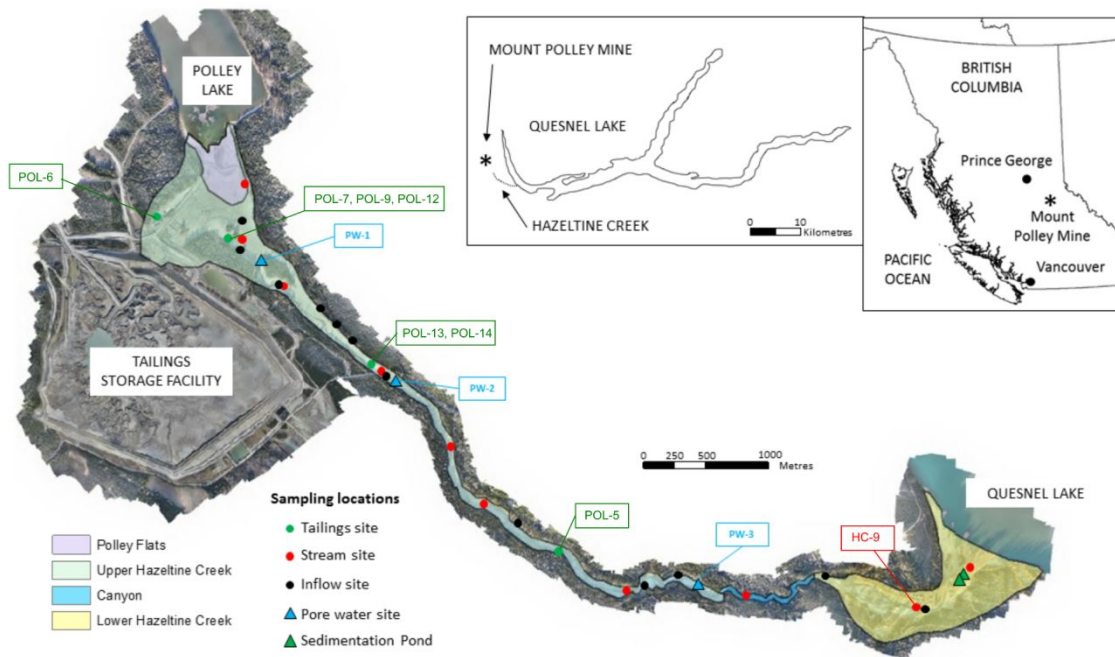
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607 **Figure 1.** Location of study area showing Hazeltine Creek stream (HC-), inflow sample, pore water
 608 (PW-) and tailings, sediment and Fe oxyhydroxide (POL-) sample sites for materials collected in
 609 2014 and 2015. Labels shown are for those samples discussed in this manuscript; sample locations
 610 for the remaining stream, inflow and pore water samples are shown in Byrne et al.³⁷.



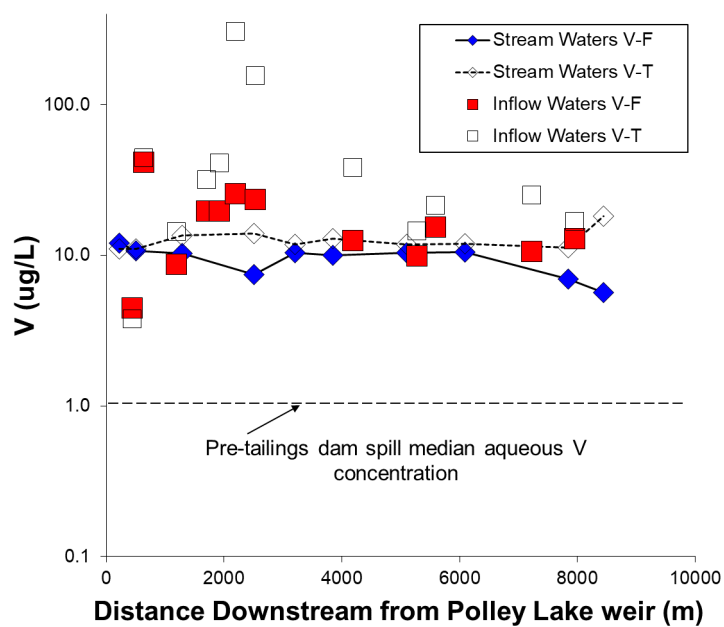
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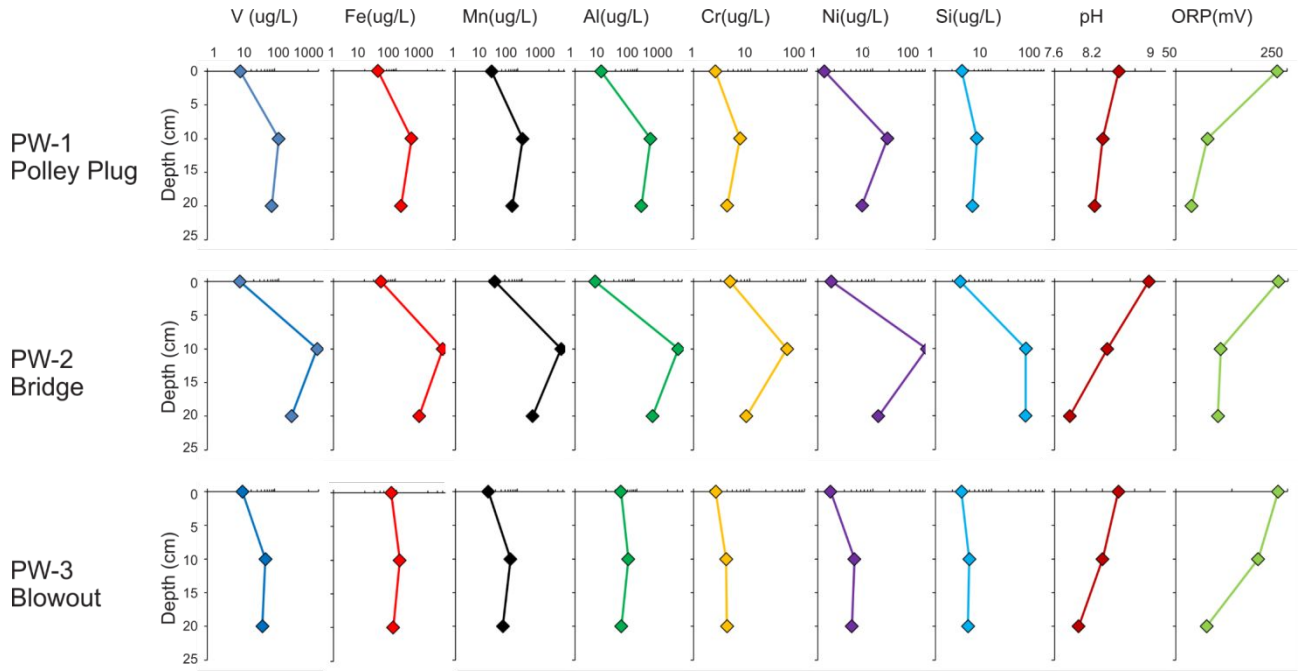
615 **Figure 2.** Spatial profile of Hazeltine Creek stream and inflow filtered (V-F) and unfiltered (V-T) V
616 concentrations. Samples were collected in August 2015. Pre-tailings dam spill median V
617 concentration of 1 $\mu\text{g/L}^{29}$ is shown for reference.



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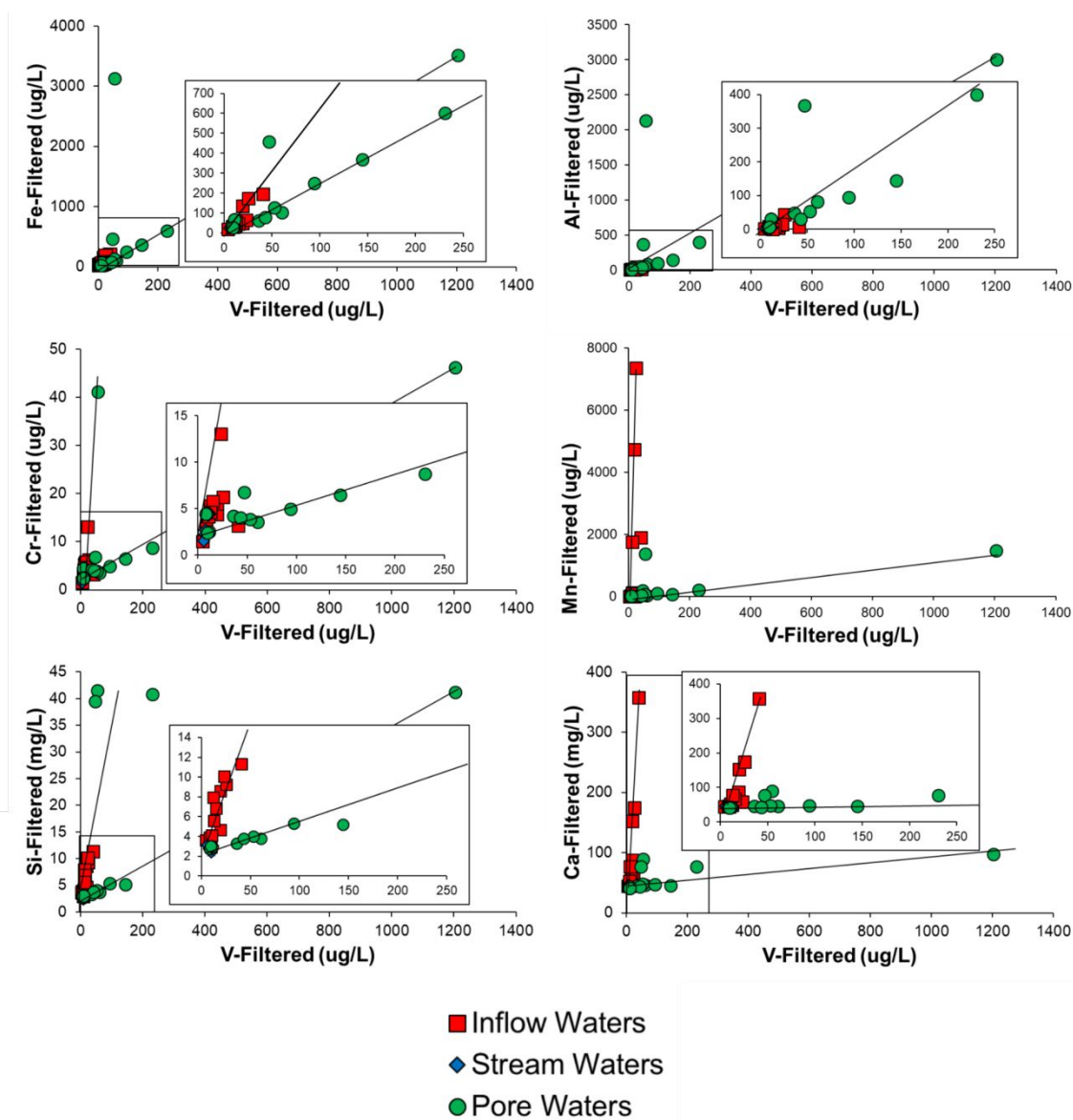
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620 **Figure 3.** Geochemical profiles for pore water profiles PW-1, PW-2 and PW-3.
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625 **Figure 4.** X-Y plots showing relationship between filtered V ($\mu\text{g L}^{-1}$) and other filtered element
 626 concentrations in stream, inflow and pore waters. Stream water sample concentrations are mostly <
 627 $10 \mu\text{g/L}$ so are masked by the inflow and pore waters. Trends shown for the inflow waters (red
 628 squares) and for most of the pore water data (green circles).



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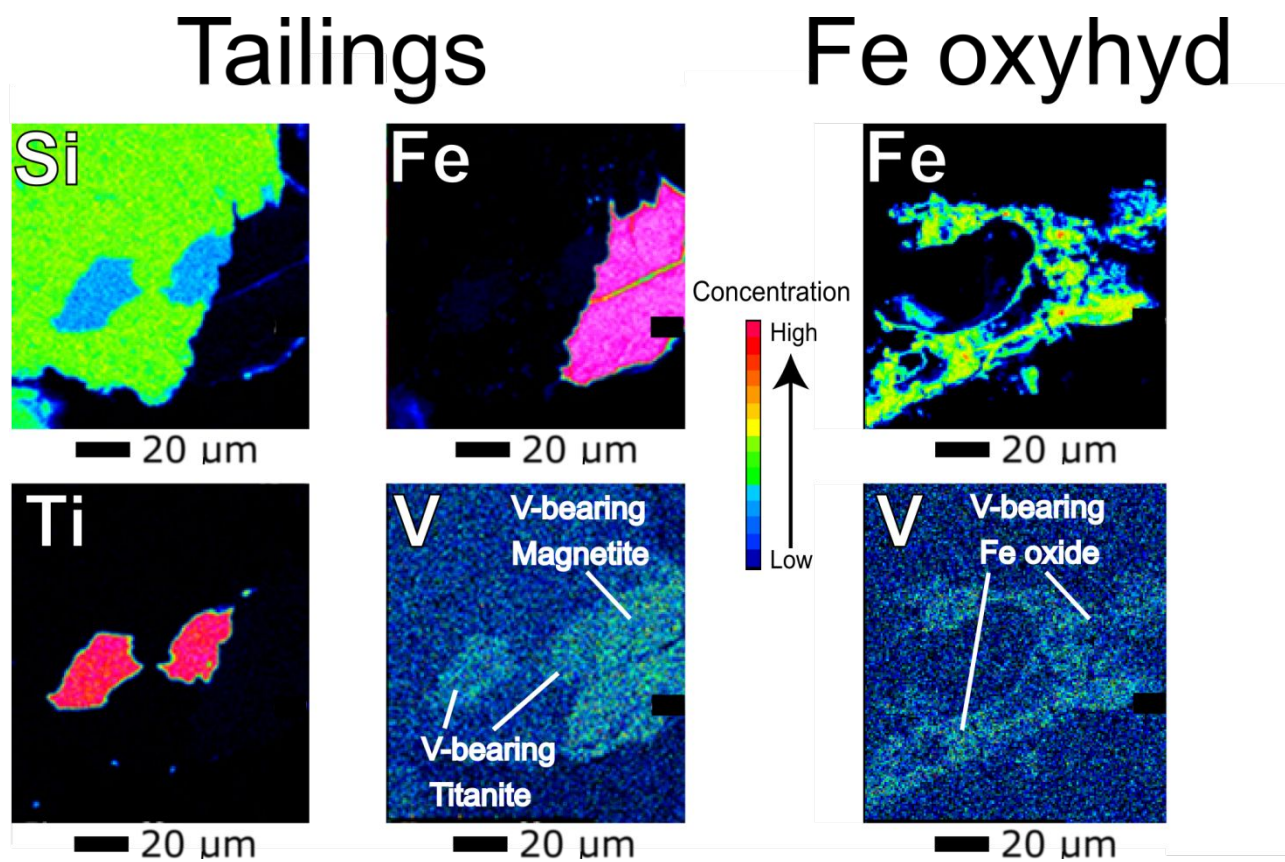
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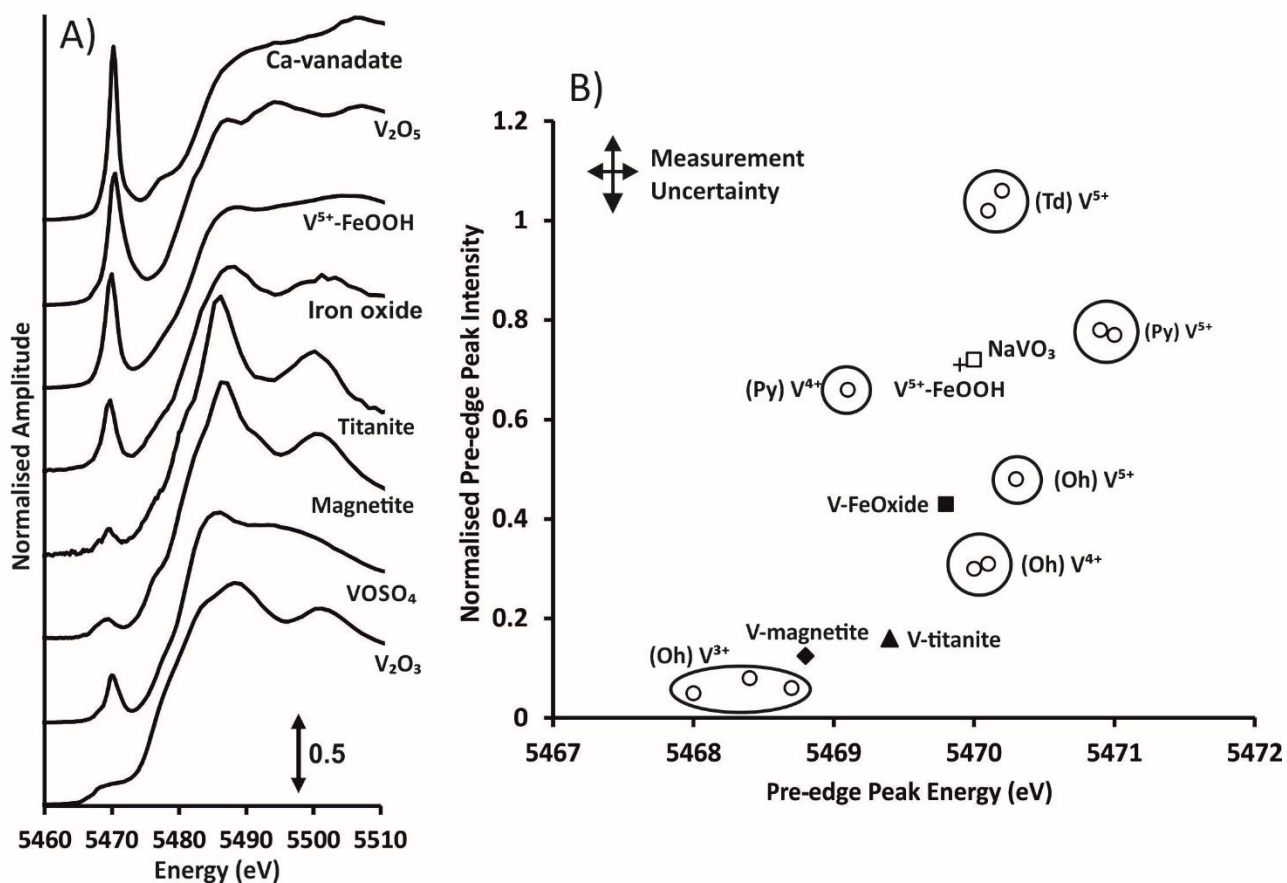
635 **Figure 5.** Electron microprobe X-ray maps showing V-bearing titanite and magnetite in Mount
636 Polley tailings (POL-5), and V-bearing Fe oxide in the Fe oxyhydroxide (Fe oxyhyd) (POL-13).

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640 **Figure 6.** (a) K-edge XANES spectra collected from Mount Polly mineral samples and selected V-
 641 containing standards. (b) Plot of pre-edge intensity vs. pre-edge peak energy derived from V K-edge
 642 XANES spectra. V standard data from Hobson et al.⁷², Burke et al.^{21,44}, Charaund et al.⁴³, Bronkema
 643 and Bell⁷³ and Wong et al.⁷⁴. (T_d), (P_y) and (O_h) refer to tetrahedral, square pyramidal and
 644 octahedral co-ordination, respectively.

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