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4 **Vanadium geochemistry along groundwater flow paths in**

5 **contrasting aquifers of the United States: Carrizo Sand (Texas) and**

6 **Oasis Valley (Nevada) aquifers**

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8 **Katherine Telfeyan***

9 **Karen H. Johannesson**

10 **T. Jade Mohajerin**

11 **C. Dianne Palmore**

12

13 *Department of Earth and Environmental Sciences, Tulane University, New Orleans, LA, 70118-5698 USA*

14 **Corresponding author: Tel.: +1 504 862 3277*

15 *E-mail address: ktelfeya@tulane.edu (K. Telfeyan)*

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17 **Abstract**

18 Vanadium (V) concentrations were measured along the flow paths in two contrasting

19 aquifer systems to study how changing solution composition and redox conditions affect V

20 cycling and transport in groundwater flow systems. The Oasis Valley groundwater system in

21 Nevada is an unconfined system where groundwaters generally remain oxic along the flow path,

22 whereas the Carrizo Sand aquifer is a deep, confined coastal plain aquifer in Texas that contains

23 well-defined Fe(III) and SO₄²⁻ reduction zones along the flow path. Speciation modeling predicts

that in groundwaters from the Oasis Valley, V chiefly occurs as the vanadate oxyanion (e.g., H_2VO_4^- , HVO_4^{2-}), which is mobile along the entire flow path because of vanadate's solubility in oxic and alkaline waters. Furthermore, the data indicate that V concentrations increase in groundwaters along the flow path suggesting that mineral dissolution and/or desorption reactions progressively contribute V to groundwaters of the Oasis Valley system. Geochemical modeling is consistent with dissolution of mafic phenocrysts that are common in the local tuffaceous aquifer rocks as a probable source of V to Oasis Valley groundwaters. Within the Carrizo Sand aquifer, groundwater V concentrations decrease with flow beyond the recharge zone and into the confined portion of the aquifer. Thereafter, total V concentrations remain low and relatively constant along the remainder of the studied flow path, exhibiting no systematic variations across the Fe(III) and SO_4^{2-} reduction zones. Groundwaters from the Carrizo Sand aquifer are generally reducing, and as such, geochemical modeling suggests that both V(V) and V(IV) species occur in Carrizo Sand groundwaters, and furthermore, that the proportion of V(IV) species increases concurrent with the decrease in total V concentrations along the flow path. Results from sequential extraction experiments on Carrizo Sand aquifer sediment samples suggest that V adsorption onto Fe(III)/Mn(IV) oxides/oxyhydroxides acts to decrease the aqueous V concentrations in Carrizo Sand groundwater. Furthermore, geochemical modeling is consistent with complexation of V(IV) with dissolved organic matter (DOM) within the Carrizo Sand aquifer groundwaters, which, owing to the low DOM concentrations, appears to buffer V at low, but relatively constant concentrations within the confined and reducing Carrizo Sand groundwaters. These results support previous reports of V(IV)-DOM binding and imply that aquifer material maintains an essential role in not only determining the availability of V to enter aqueous solution but also in influencing partitioning between solid and aqueous phases.

Keywords: Vanadium; Groundwater; Geochemical Modeling; Oasis Valley; Carrizo Sand

I. Introduction

Understanding the behavior of V in natural waters is important from a number of standpoints. For example, V has many industrial uses, including being a key alloying metal for hardening steel, as pigments and catalysts, and has a history of use in some pharmaceuticals (e.g., Nriagu, 1998, and references therein). Vanadium contents of fossil fuels, including petroleum and coal, are commonly high (Duce and Hoffman, 1976; Barwise, 1990; Hope, 1997), and as such, combustion of fossil fuels can represent an important source of anthropogenic V along with industrial activities to the environment (Nriagu and Pirrone, 1998; Mamane and Pirrone, 1998). Thus, V has been studied for its role both as an industrial pollutant (Hope, 1997) and potential carcinogen (Zwolak, 2014), as well as for use in pharmaceuticals (Nriagu, 1998; Tang et al., 2012; Soveid et al., 2013; Clark et al., 2014). Consequently, the importance of V in industry and pharmaceuticals heightens its potential as an environmental contaminant (Hope, 1997, 2008). However, predicting V mobility in the hydrologic cycle requires a deeper understanding of V behavior along groundwater flow paths. Because of the complexity of V's chemistry, studies of V in aqueous systems necessarily incorporate its redox state, interaction with aquifer solids, and complexation with aqueous ligands.

Vanadium occurs in natural waters in a variety of oxidation states including V(III), V(IV), and V(V) (Cotton et al, 1999). In oxic natural waters, V(V) predominates, occurring as the vanadate oxyanion (e.g., H_2VO_4^- , HVO_4^{2-}), whereas V(IV) predominates in more reducing waters as the vanadyl oxycation (e.g., VO^{2+} , $\text{V}(\text{OH})_3^+$). Under highly reducing conditions, V(III)

species may exist, for example, as $\text{V}(\text{OH})_2^+$ (Wanty and Goldhaber, 1992; Wright and Belitz, 2010; Pourret et al., 2012). Vanadium(V) as the vanadate ion is generally more soluble in natural waters than either V(IV) or V(III) species (Wehrli and Stumm, 1989; Wright and Belitz, 2010). However, vanadyl may persist beyond its predicted stability range (Eh up to 0.4 Volts) owing to complexation with dissolved ligands, especially fluoride, sulfate, and carbonate ions, as well as dissolved organic matter (Wehrli and Stumm, 1989; Breit and Wanty, 1991; Wanty and Goldhaber, 1992; Wang and Sañudo Wilhelmy, 2008). Vanadyl may therefore be common at the transition from oxic to anoxic redox conditions in natural waters (Wehrli and Stumm, 1989). Wang and Sañudo Wilhelmy (2009), for example, determined that V(IV) may account for up to 40% of total dissolved V under summer hypoxic conditions in Long Island Sound, although it typically accounts for less than 5% of total V in most oxygenated waters of the Long Island Sound.

Particle interaction and organic matter may also influence the effective solubility and speciation of vanadium (e.g., Szalay and Szilágyi, 1967; Wehrli and Stumm, 1989; Peacock and Sherman, 2004). Specifically, vanadyl may be removed from solution by adsorption onto positively charged mineral surfaces, particularly metallic hydrous oxides (e.g., FeOOH), despite electrostatic repulsion because the adsorption is still energetically favorable (Wehrli and Stumm, 1989). Moreover, V(IV) may adsorb to clays (McBride, 1979; Manohar et al., 2005). Clays with a constant point of zero charge (e.g., montmorillonite) at low pH (<3) have a negative surface charge in most natural aquifers (Langmuir, 1997), and vanadyl will likely adsorb to such clays under most pH conditions. Vanadyl concentrations may also decline in low Eh waters by reduction from dissolved sulfide to an insoluble V(III) oxide/hydroxide (Wanty and Goldhaber, 1992; Wang and Sañudo Wilhelmy, 2008). Furthermore, although V(V) can be relatively mobile

93 in oxic and alkaline natural waters as the vanadate oxyanion, it exhibits a strong affinity for
94 hydrous metal oxide surfaces, adsorbing via ligand exchange at neutral to low pH (Wehrli and
95 Stumm, 1989). For example, Peacock and Sherman (2004) demonstrated using extended X-ray
96 absorption fine structure (EXAFS) spectroscopy that V(V) adsorption onto Fe(III)
97 oxides/oxyhydroxides occurs as inner-sphere bidentate corner-sharing complexes with
98 stoichiometries of $\text{Fe}_2\text{O}_2\text{V}(\text{OH})_2^+$ and $\text{Fe}_2\text{O}_2\text{VO}(\text{OH})^\circ$. Szalay and Szilágyi (1967) determined
99 that humic substances also strongly adsorb V. Consequently, the geochemical enrichment factor
100 of V in humic materials approximates 50,000:1, and explains, in part, the association of V with
101 fossilized organics (e.g., petroleum, coal) and carbonaceous rocks (Szalay and Szilágyi, 1967).

102 Vanadium mineralogy is complicated by its mutable behavior with changing oxidation
103 potential and acidity levels, and primary vanadium minerals include a diverse suite of silicates,
104 oxides, sulfides and sulfosalts (Evans and Garrels, 1958; Nriagu, 1998). A number of primary
105 vanadium minerals occur in mining regions, including montroseite, descloizite, and vanadiferous
106 chlorite, but most vanadium occurs in association with iron oxides (Wanty and Goldhaber, 1992;
107 Sracek et al., 2014 and references therein). Vanadium(III), the predominant redox state of
108 vanadium in rocks, substitutes for iron in pyroxene and magnetite and is therefore commonly
109 associated with mafic rocks (Goldschmidt, 1954; Nriagu, 1998; Shiller and Mao, 2000; Wright
110 and Belitz, 2010; Cinti et al., 2015). During fractional crystallization of magmas, V behaves
111 similarly to Fe and Ti and is incompatible in most silicic melts (Miyashiro and Shido, 1975;
112 Peccerillo and Taylor, 1976). Vanadium concentrations in granites are therefore much lower than
113 in basalts (e.g., 16 mg kg^{-1} versus 240 mg kg^{-1} ; Reeves and Brooks, 1978). In sedimentary rocks,
114 V concentrations are highest in carbonaceous (i.e., black) shales. Because V is associated with

the organic-rich fraction of black shales, V concentrations can reach 16,000 mg kg⁻¹ in these rocks (Vine and Tourtelot, 1970).

Surface water studies of aqueous V geochemistry in the literature are more abundant than groundwater studies. These surface water studies include quantification of V concentrations in the ocean, streams, and estuaries. For example, V concentrations in the ocean range from about 24 to 55 nmol kg⁻¹ and display a nutrient-type profile (Collier, 1984; Weisel et al., 1984; Jeandel et al., 1987; Middelburg et al., 1988). Vanadium concentrations in United States rivers are typically in the range of 5 to 73 nmol kg⁻¹, and Shiller and Boyle (1987) argue that source rock and weathering rate are the most important influences on vanadium concentrations in rivers. In particular, silicate weathering contributes greater amounts of dissolved V to rivers than carbonate weathering (Shiller and Mao, 2000). In estuarine settings, including surface and in pore waters, V concentrations are reported to range from 13 to 149 nmol kg⁻¹, and researchers highlight the influence of multiple processes, including association with organic matter, adsorption to particulate metal hydrous oxides, and redox-, temperature- and salinity-induced desorption (e.g., Auger et al., 1999; Beck et al., 2008; Strady et al., 2009, Wang and Sañudo Wilhelmy, 2009).

Despite the numerous investigations of V in the ocean and other surface waters, far less effort has focused on studying the geochemistry of V in groundwater flow systems, and in particular, how V concentrations and speciation change along flow paths in response to changing solution composition and redox conditions (Wright et al., 2014). The recent inclusion of V on the US EPA's list of candidate environmental contaminants in combination with our limited understanding of the processes that mobilize and sequester V along the flow paths in groundwater flow systems underscores the importance of systematic investigations of V in aquifer systems (U.S. Environmental Protection Agency, 2009; Wright and Belitz, 2010). The

evolution of groundwater hydrochemical facies along flow paths has long been established, especially with regards to the progression from calcium-rich to sodium-rich bicarbonate groundwaters commonly reported for groundwaters from Coastal Plain aquifers of the United States Atlantic coast (e.g., Foster, 1950; Back, 1960). The approach was then extended to include the evolution of the redox conditions on trace elements along groundwater flow paths (e.g., Champ et al., 1979; Edmunds et al., 1987, 2003). Our study examines how hydrochemical evolution of major ions and redox chemistry along groundwater flow paths contributes to changes in V chemistry. Several studies in the United States have targeted areas of elevated V concentrations (Glenn and Lester, 2010; Wright and Belitz, 2010; Wright et al., 2014), and other investigators have reported high V concentrations in groundwaters from Italy and Argentina (Nicolli et al., 1989; Minelli et al., 2000; Veschetti et al., 2007; Farnfield et al., 2012; Nicolli et al., 2012). These investigators employed statistical and experimental methods to determine the processes controlling V concentrations, such as V content of aquifer source material or comparison of V concentrations in aquifers of different redox and pH values. Here, we utilize two relatively well-studied aquifers to document how V concentrations change due to lithologic controls, changes in groundwater composition owing to interaction with aquifer solids (e.g., pH changes), adsorption/desorption reactions, redox reactions, and the presence of organic matter. Additionally, because of our low analytical detection limit, we are able to examine V geochemistry in suboxic and sulfidic groundwaters, where V is sparingly soluble.

II. Study Site

II. 1. Oasis Valley and Beatty Wash Aquifer, Nevada

The Oasis Valley study site is located near the western boundary of the Nevada Test Site and approximately 190 km northwest of Las Vegas, NV (Fig. 1a). The Nevada Test Site region has been extensively studied due to concern over contamination from past nuclear testing as well as previous plans to build a long-term high-level nuclear waste storage facility at nearby Yucca Mountain (Winograd and Thordarson, 1975; Broxton et al., 1987; Thomson et al., 2002). Geologically, the study area is part of the Timber Mountain-Oasis Valley caldera complex that, when active 16-9.5 mya, encompassed 11,000 km² (Christiansen et al., 1977). Precambrian and Paleozoic marine sediments underlie the Tertiary volcanic rocks of the Timber Mountain-Oasis Valley caldera complex, which are in turn overlain by Quaternary alluvial fill, consisting of weathered volcanics and carbonate rock detritus. The Tertiary volcanic rocks consist of zeolite-rich rhyolitic tuffs and lavas and quartz latites from the caldera complex in addition to minor trachytes and basalts (Christiansen et al., 1977; Broxton et al., 1987; Broxton et al., 1989; Farnham et al., 2000). Paleozoic carbonate rocks constitute parts of the northwestern study area near the Bullfrog Hills as well as Bare Mountain southeast of Beatty, Nevada (White, 1979). The majority of groundwater wells sampled in this study area are completed in the Ammonia Tanks member of the Timber Mountain Tuff (Sawyer et al., 1994; Thomas et al., 2002; Johannesson and Tang, 2009). The area experienced both folding and subsequent thrust faulting during the Mesozoic and extensional faulting during the Cenozoic (Winograd and Thordarson, 1975). Faults and fractures control flow direction, which throughout the study area is predominantly toward the south/southeast. As such, sample sites were chosen along the flow path previously investigated in the Oasis Valley region of the field area (Fig. 1a; Winograd and Thordarson, 1975; Thomas et al., 2002; Koonce et al., 2006; Johannesson and Tang, 2009).

Annual precipitation in the study area averages 97 mm, of which 90% is snow (Western Regional Climate Center, 2008). The area receives recharge from Thirsty Canyon to the north, where waters of the upland regions (e.g., Pahute Mesa) and central Nevada mix and subsequently flow toward the south through Oasis Valley (Davisson et al., 1999; Farnham, 2001; Thomas et al., 2002; Johannesson and Tang, 2009). Additional groundwater that appears to originate as recharge from the Timber Mountain Caldera flows through Beatty Wash before mixing with Oasis Valley groundwater near the end of the studied flow path (Fig. 1a; Thomas et al., 2002; Johannesson and Tang, 2009).

II. 2. Carrizo Sand aquifer, Texas

The Carrizo Sand aquifer is a large, regional confined aquifer composed of Eocene sand that is located in southern and eastern Texas and portions of Louisiana (Hamlin, 1988; Basu et al., 2007). The predominant aquifer material is quartz sand, which is coated with clay-mineral-rich Fe(III) oxides/oxyhydroxides (Basu et al., 2007; Willis et al., 2011). In addition, the Carrizo Sand contains minor occurrences of calcite, clay, and pyrite, and relatively rare sedimentary organic matter in the form of lignite (Pearson and White, 1967; Payne, 1975; Hamlin, 1988). The Carrizo sand is bounded by clay confining units of the Wilcox and Recklaw Formations.

We investigated V in groundwaters from the Carrizo Sand aquifer in southern Texas (Fig. 1b). Here, the aquifer outcrops as a sand ridge in northwest Atascosa County, where groundwater is recharged (Fig. 1b). The groundwater subsequently flows down dip (up to 1.41°) to the southeast into McMullen County at a rate averaging 2 m yr^{-1} (Fig. 1b; Pearson and White, 1967; Stute et al., 1992). Farther down gradient beyond our study region, the Carrizo Sand encounters the Wilcox Geothermal Corridor, a 32-km growth-fault system, where upward leakage of

groundwater occurs owing to high fluid pressure (Bebout et al., 1978; Hamlin, 1988; Castro and Goblet, 2003; Haque and Johannesson, 2006). The thickness of the Carrizo Sand varies from 100 m to 360 m, generally increasing down dip along the flow path, and groundwaters are as old as 27,000 years ~55 km down gradient from the recharge zone (Pearson and White, 1967; Hamlin, 1988; Castro et al., 2000). Aquifer sediment porosity ranges from 30-40% and hydraulic conductivity is on average 8.2 m day^{-1} (Pearson and White, 1967). Groundwaters are of potable quality until the southern portion in McMullen County, beyond the study site, at which point salinity increases above drinking water standards (Payne, 1975; Castro et al., 2000; Castro and Goblet, 2003; Basu et al., 2007).

III. Methods

III. 1. Sample Collection

Samples from the Oasis Valley-Beatty Wash aquifer described in this study were collected in the fall and winter of 1997 and were analyzed within a month of collection (Thomas et al., 2002; Johannesson and Tang, 2009). Details of the field sampling and analysis of the Oasis Valley groundwater samples can be found in Thomas et al. (2002) and Johannesson and Tang, 2009), and will not be repeated here. We note, however, that the sampling and analytical procedures used for the Oasis Valley-Beatty Wash aquifer were similar to those employed for the Carrizo Sand aquifer that are described in detail below.

Samples from the Carrizo Sand aquifer were collected in March 2013, and analyzed within two weeks of the sample collection date. Prior to sample collection, all materials, including high-density polyethylene (HDPE) sample bottles, Teflon[®] tubing, and low-density polyethylene (LDPE) cubitainers[®] were cleaned according to trace-metal clean procedures

outlined in Johannesson et al. (2004). Groundwaters were collected into LDPE cubitainers[®] at each well after rinsing the cubitainer three times with sample water. Water samples were then filtered on site using a peristaltic pump with Teflon[®] tubing attached to a 0.45- μm Gelman Sciences (polysulfone ether membrane) in-line filter capsule, and directly into an HDPE sample bottle. Each HDPE sample bottle was rinsed three times with the filtered sample water before collection of the actual filtered sample. Samples for cation and V analysis were then acidified with ultrapure HNO_3 to $\text{pH} < 2$ (Thermo Fisher Optima[™]) to prevent Fe(III)/Mn(IV) oxide/hydroxide precipitation and loss of V to bottle surfaces via adsorption. Samples for anion analysis were similarly filtered but not acidified. Samples for dissolved organic carbon (DOC) were collected in 2002, at which time they were immediately filtered into pre-cleaned (rinsed with HCl), and pre-combusted amber glass vials, and acidified with ultrapure HCl (Thermo Fisher Optima[™]; Tang and Johannesson, 2005). Because the samples were filtered through 0.45 μm filters, the DOC measurements include the colloidal fraction of DOC in addition to the totally dissolved fraction (e.g., Thurman, 1985). Samples for cation and V analysis were refrigerated until analysis, and samples for anion and DOC analysis were stored frozen until analysis.

A number of ancillary geochemical parameters of the Carrizo Sand aquifer groundwaters were determined on-site using a Hydrolab MiniSonde[®] 5 with a flow-through cell connected with a polyethylene tube to the well to prevent contact with the atmosphere. The Hydrolab MiniSonde[®] 5 measures pH, temperature, Eh (i.e., platinum electrode), specific conductance and dissolved oxygen. In addition, titration (Hach method 8203) using phenolphthalein and bromcresol green-methyl red indicators and 0.16 Eq L^{-1} sulfuric acid was used to determine the alkalinity of groundwaters from both aquifers. A Hach DR 2800 UV/VIS spectrophotometer was

used to measure dissolved concentrations of total iron, ferrous iron, and dissolved sulfide in the reducing groundwaters of the Carrizo Sand aquifer (e.g., Haque and Johannesson, 2006; Tang and Johannesson, 2006; Basu et al., 2007; Johannesson and Neumann, 2013; Johannesson et al., 2013). We measured total iron using the Ferrover[®] method (detection limit 0.36 $\mu\text{mol kg}^{-1}$), ferrous iron by the 1,10-phenanthroline method (detection limit 0.36 $\mu\text{mol kg}^{-1}$; Eaton et al., 1995a), and sulfide by the methylene blue method (two detection limits determined as 0.87 and 0.25 $\mu\text{mol kg}^{-1}$ for the two cuvettes used in analysis; Eaton et al., 1995b). Ferric iron was determined as the difference between total iron and ferrous iron.

III. 2. Sediment Digestion

Samples of Fe(III)/Mn(IV) oxide/hydroxide coated sand from the Carrizo Sand aquifer were digested according to a modified version of the sequential extraction method reported in Tessier (1979) and Tang et al. (2004). The procedure was modified to target the phases of interest, namely V bound to the Fe(III)/Mn(IV) oxide/hydroxide minerals, V bound to organic matter phases, and the total V concentration of the sediment (i.e., the residual V that occurs within silicates and other minerals that are not easily leached). Briefly, to extract the V bound to the Fe(III)/Mn(IV) oxide/hydroxide phase, 0.5 g sediment was digested with 20 mL 0.04 mol L⁻¹ NH₂OH·HCl (Alfa Aesar[®]) in 25% (v/v) CH₃COOH (SeastarTM's Baseline[®]) and heated to 96°C with occasional agitation. The mixture was then centrifuged for 20 min at 3000 rpm, the supernatant extracted for V analysis, and the sediment rinsed. To target the V bound to the organic matter phase, the remaining sediment was digested with 3 mL of 0.02 mol L⁻¹ HNO₃ (Thermo Fisher OptimaTM) in 5 mL of H₂O₂ (30%) (Sigma Aldrich[®]) at pH 2, heated to 85°C for 2 h, then digested again with 3 mL of H₂O₂ (30%) at pH 2 and heated to 85°C for 3 h. Upon

cooling, 5 mL of 3.2 mol L⁻¹ CH₃COONH₄ (Sigma Aldrich®) in 20% (v/v) HNO₃ and 4 mL deionized water (18 MΩ cm) was added, and the mixture was agitated for 30 min. The resulting mixture was centrifuged at 3000 rpm for 20 min, the supernatant extracted for analysis, and the remaining sediment rinsed with deionized water (18 MΩ cm). Aliquots (0.5 mL) of the above supernatants were then diluted to 10 mL with 2% HNO₃ for ICP-MS analysis of V. To determine the V content of the bulk sediment, a separate aliquot of the sediment (0.2 g) was placed in a Teflon® beaker and digested with 10 mL HF (Thermo Fisher Optima™), evaporated to near dryness, followed by 10 mL HNO₃ (Thermo Fisher Optima™), evaporated to near dryness, and redissolved again with 2% HNO₃. All three digestions were performed in triplicate.

III. 3. Analytical Techniques

Anion concentrations in the Oasis Valley groundwaters were measured within 48 h of collection by ion chromatography at the Harry Reid Center for Environmental Studies at the University of Nevada, Las Vegas (HRC-UNLV; Thomas et al., 2002). Major cations (i.e., Na⁺, K⁺, Ca²⁺, Mg²⁺) in groundwaters from the Oasis Valley-Beatty Wash aquifer were measured using atomic absorption spectrometry, whereas V concentrations were measured using a quadrupole inductively coupled plasma mass spectrometer at the HRC-UNLV (Perkin-Elmer Elan 5000; Thomas et al., 2002; Johannesson and Tang, 2009).

Vanadium concentrations in Carrizo Sand aquifer groundwater samples were determined by monitoring ⁵¹V after introduction of the water samples into a Thermo Fisher Element 2, sector field ICP-MS. The medium resolution (MR) mode was selected for easier peak resolution. The minimum detectable concentration was determined as 3 · σ_{blank} (140 pmol kg⁻¹), where the standard deviation of the blank was determined from multiple days (n=7) of analysis with ICP-

MS. Relative standard deviation (%RSD) measurements were between 2 and 7%. Standards were made from SPEX CertiPrep[®] ICP-MS Multi-Element Solution 2 in 5% HNO₃ to concentrations ranging from 19.6 to 4908 pmol kg⁻¹ (i.e., 1-250 ng kg⁻¹). Scandium (⁴⁵Sc) was used as the internal standard (222.4 nmol kg⁻¹ added to all samples and standards) to correct for instrumental drift during analysis. Standards used in calibration were included as a sample to check accuracy. Percent error using the SPEX CertiPrep[®] standards was 8%.

The major anion and cation composition of Carrizo Sand aquifer groundwaters were measured at the Ohio State University (K.A. Welch analyst) by ion chromatography on filtered water samples following the approach of Welch et al. (1996). The DOC concentrations of these water samples were quantified at Old Dominion University by high temperature catalytic oxidation via a Shimadzu TOC-5000 total carbon analyzer (Burdige and Gardner, 1998).

III. 4. Geochemical Modeling

Because we did not directly measure V speciation in the Carrizo and Oasis Valley-Beatty Wash groundwaters, we employed the SpecE8 and Act2 Programs of the Geochemist's Workbench[®] (Version 9.0; Bethke, 2008) to model V speciation. We employed the thermodynamic data from the "thermo.dat" database released by the Lawrence Livermore National Laboratory (Delany and Lundeen, 1990) to compute the predicted V species. Specifically, Eh values measured in the field during collection of Carrizo Sand groundwater samples and dissolved oxygen values measured from Oasis Valley groundwater samples were used to compute the redox conditions of the water samples, from which the software was then allowed to predict the thermodynamically stable V redox speciation of these groundwaters (e.g.,

Willis et al., 2011). It is important to note that we did not consider the kinetics of V redox changes in the modeling.

The possible association of V(IV) with dissolved organic matter was modeled with the Windermere Humic Aqueous Model (WHAM) that employs Humic Ion-Binding Model VII (i.e., WHAM VII; Tipping et al., 2011). The humic ion-binding model is capable of accounting for proton-metal competition, electrostatic effects, and heterogeneity in binding site affinities (Tipping, 1998; Tipping et al., 2011). To the best of our knowledge, binding constants for V(V) and V(III) with humic substances have not been optimized for use with the WHAM VII model, which limited our modeling efforts to V(IV) complexation with DOM, for which binding constants do exist (Table 1; Tipping et al., 2011). The V(IV) concentration was determined from the percent of total V predicted from the speciation modeling, and the model predicted V(IV) concentrations were input into the WHAM VII code to evaluate the amount of V(IV) in Carrizo Sand aquifer groundwaters that occurs as complexes with DOM. Vanadium in the groundwaters from Oasis Valley-Beatty Wash are predicted by the Geochemist's Workbench[®] to exist as V(V), and as such, predicting anion-organic matter binding using WHAM VII is not possible. Simulations using WHAM VII define separate parameters for fulvic and humic acids, and the partitioning of DOC measurements into these two components is therefore necessary. The DOC of natural waters commonly consists of 30-50% humic substances, of which ~40% is fulvic acid and ~10% is humic acid (Thurman, 1985).

Species	ΔLK_2	$\log K_{\text{MA}}$ (fulvic)	$\log K_{\text{MA}}$ (humic)
V(IV)O	1.74	2.51	2.76
UO ₂	1.16	2.28	2.64

Table 1. V-specific constants used in WHAM VII calculations from Tipping et al. (2011). U(IV) constants are listed in order to compare V-DOC and U-DOC complexation.

IV. Results

IV. 1. General geochemistry of the Oasis Valley-Beatty Wash and Carrizo Sand aquifers

Major ion data, redox indicator elements, and field parameters for the Oasis Valley-Beatty Wash and Carrizo Sand groundwaters are presented in Tables 2 and 3, respectively, and Figure 2. The Carrizo Sand aquifer is a confined aquifer and relatively deep as compared to the unconfined, shallow Oasis Valley-Beatty Wash aquifers (Tables 2, 3). Groundwaters from both aquifers are relatively dilute along the entirety of the flow path as evidenced by the general low electrical conductivities (Tables 2, 3; Fig. 2). Nonetheless, conductivity of the Carrizo Sand aquifer generally increases along the confined portion of the flow path, whereas the conductivity of the Oasis Valley-Beatty Wash groundwaters does not vary systematically along the flow path (Fig 2.). Groundwaters of the Oasis Valley-Beatty Wash aquifers are neutral to alkaline displaying a narrow range of pH values between 7.86 and 8.38 (Fig 2b). Alkalinity of the Oasis Valley-Beatty Wash groundwaters also displays relatively narrow range between 2.62 and 4.21 mmol kg⁻¹ (Table 2). Conversely, the pH of the Carrizo groundwaters shows an increase along the confined portion of the aquifer from around 6 to 8.5, accompanied by an increase in alkalinity from a low of 0.22 mmol kg⁻¹ at 4.3 km along flow path (BCW-5) to a high of 5.45 mmol kg⁻¹ at the end of the studied portion of the flow path (SMA74R-2; Fig. 2e, Table 3).

Waters of Oasis Valley-Beatty Wash aquifer are alkali bicarbonate rich, except upon interaction with probably hydrothermal deposits, which increases sulfate concentrations as a result of oxidation of metal sulfide minerals (Fig. 3a; Thomas et al., 2002; Johannesson and Tang, 2009). Sulfate concentrations may also increase as a consequence of gypsum dissolution

(Winograd and Thordarson, 1975), which is predicted to be undersaturated in these groundwaters (Johannesson and Tang, 2009). Beatty Wash samples are more bicarbonate rich, whereas the most up gradient Oasis Valley groundwaters samples in this study (i.e., EROV2 and EROV1) are more sulfate rich, and EROV4, located near the confluence of the Oasis Valley and Beatty Wash flow paths, plots as a mixture of these end members (Fig. 3a). Mixing calculations suggest that where the two flow paths converge near EROV4a, the groundwater composition is roughly a 50-50 mixture of waters from the upper Oasis Valley and Beatty Wash (Johannesson and Tang, 2009). Cluster analysis reveals that the major ion composition of both Oasis Valley and Beatty Wash groundwaters is consistent with chemical weathering of and interaction with the local felsic volcanic rocks (Koonce et al., 2006). More specifically, Johannesson and Tang (2009) predict that volcanic glass and biotite, in addition to gypsum and K-feldspar, are dissolving along the flow path, whereas calcite, Ca-montmorillonite, and Fe oxides/oxyhydroxide precipitate along the flow path.

Groundwater composition in the Carrizo Sand aquifer evolves from Ca-Cl-HCO₃ type waters in northwest Atascosa County (well depths < 200 m), where the groundwaters are recharged, to Na-HCO₃ waters in the southeast (well depths > 500 m; Fig. 3b; Tang and Johannesson, 2005). Chloride concentrations decrease steadily along the flow path for 41 km (Peeler well), at which point Cl concentrations increase for the remainder of the studied flow path. These geochemical changes are consistent with a combination of processes including ion exchange reactions, calcite dissolution, microbially-induced redox reactions, adsorption/desorption reactions, and chemical weathering of alumino-silicates and chloride minerals (Pearson and White, 1967; Hamlin, 1988; Castro and Goblet, 2003; Johannesson et al., 2013).

IV. 2. Redox structure of the Oasis Valley-Beatty Wash and Carrizo Sand aquifers

A major difference between the Oasis Valley-Beatty Wash and Carrizo Sand aquifers is their redox structures. Using the classification scheme of Berner (1981), groundwaters of the Oasis Valley and Beatty Wash aquifer system are oxic, with measured dissolved oxygen concentrations averaging ($\pm \sigma$) $0.14 \pm 0.06 \text{ mmol kg}^{-1}$ (Fig. 2c; Thomas et al., 2002; Johannesson and Tang, 2009). High dissolved oxygen concentrations have likely persisted in these waters as a consequence of their characteristically low dissolved organic carbon concentrations (Table 2), which may hamper microbial activity and subsequent consumption of available dissolved oxygen (Winograd and Thordarson, 1975; Winograd and Robertson, 1982; Johannesson and Tang, 2009). In contrast, dissolved oxygen concentrations of the Carrizo Sand groundwaters are, on average, an order of magnitude lower than in Oasis Valley-Beatty Wash groundwater (i.e., mean $\pm \sigma$ of dissolved oxygen in Carrizo Sand groundwater is $20 \pm 36.5 \text{ } \mu\text{mol kg}^{-1}$). Dissolved oxygen initially increases in Carrizo Sand groundwater, reaching a maximum where the aquifer first becomes confined at well N-3 ($\text{DO}=123 \text{ } \mu\text{mol kg}^{-1}$), and subsequently decreases and remains relatively constant at low concentrations (i.e., mean $\pm \sigma = 7.6 \pm 4.6 \text{ } \mu\text{mol kg}^{-1}$) for the remainder of the confined portion of the Carrizo aquifer studied. Again, the overall average dissolved oxygen concentration of Carrizo groundwaters is nearly an order of magnitude less than that of the Oasis Valley-Beatty Wash aquifers (Fig. 2f).

Furthermore, dissolved iron and manganese concentrations of the Oasis Valley-Beatty Wash groundwaters are low, especially when compared to those of the Carrizo groundwaters (Tables 2,3). Only total dissolved iron and manganese were measured in the Oasis Valley-Beatty

Wash groundwaters (e.g., Table 2). However, considering the high dissolved oxygen concentrations and the relatively low Fe and Mn concentrations in the Oasis Valley-Beatty Wash groundwaters, we expect that Fe and Mn occur in the aquifer chiefly as Fe(III)/Mn(IV) oxides/oxyhydroxides and colloids.

Contrary to the oxic conditions of the Oasis Valley-Beatty Wash aquifer, the Carrizo Sand aquifer becomes progressively reducing along the flow path (Fig. 2c,f, Tables 2,3). Total Fe concentrations in the Carrizo Sand aquifer vary considerably along the flow path, decreasing initially from $14 \mu\text{mol kg}^{-1}$ to $1.1 \mu\text{mol kg}^{-1}$ within the unconfined portion of the aquifer (Fig. 4b). Another peak in both total iron and Fe(II) is observed just after where the aquifer first becomes confined, and total Fe concentrations decrease for the remainder of the flow path to a low of $0.9 \mu\text{mol kg}^{-1}$ at ~60 km down gradient along the flow path (AC74R-1 well). Ferrous iron generally dominates along the flow path, accounting for between 49% and 95% total iron (Fig. 4b, Table 3). Dissolved S(-II) concentrations remain low ($<0.6 \mu\text{mol kg}^{-1}$) for the initial 26.1 km along the flow path, increase to $2.1 \mu\text{mol kg}^{-1}$ between PCW-1 (26.1 km) and Peeler (41.1 km), and then abruptly increase to $\sim 45 \mu\text{mol kg}^{-1}$ by the end of the flow path (Fig. 4a, Table 3)

IV. 3. V concentrations in the groundwaters and sediments of the Oasis Valley-

Beatty Wash and Carrizo Sand aquifers

Vanadium concentrations of the Oasis Valley-Beatty Wash groundwaters are presented in Table 2. Vanadium concentrations range between $21.8 \text{ nmol kg}^{-1}$ and $73.3 \text{ nmol kg}^{-1}$, exhibiting a mean ($\pm\sigma$) of $44.4 \pm 15.0 \text{ nmol kg}^{-1}$ (Table 2). Vanadium concentrations generally increase along the flow path with the lowest concentration ($21.8 \text{ nmol kg}^{-1}$) measured in groundwaters from Coffer's Windmill well and the highest concentrations ($73.3 \text{ nmol kg}^{-1}$) determined in

groundwater from the EROV4a well at the confluence of the Beatty Wash and Oasis Valley flow paths (Fig. 5). Vanadium content of the local felsic volcanic rocks is reported to range from a low of 5 mg kg⁻¹ in the Topopah Spring Rhyolites located southeast of the study site, up to 54 mg kg⁻¹ in the Ammonia Tanks quartz latites located northeast of the study site (Broxton et al., 1989).

Vanadium concentrations in the Carrizo Sand aquifer groundwaters are substantially lower than in the Oasis Valley-Beatty Wash aquifer, ranging from a high of 2.00 nmol kg⁻¹ in the recharge zone (well RF2) to a factor of 10 lower (~0.2 nmol kg⁻¹) by the end of the flow path (Table 3; Fig. 4c). More specifically, V concentrations decrease 6.5-fold over the first 7 kms of the flow path (well RF-1, 0.5 km, to well KS-1, 7.4 km), and remain relatively constant (0.21 ± 0.02 nmol kg⁻¹) along the remainder of the studied flow path (Table 3; Fig. 4c).

Vanadium in the sediments of the Carrizo Sand aquifer predominantly occurs in the Fe(III)/Mn(IV) oxide/oxyhydroxide phase (Table 4). The V content of the organic matter phase is 0.49 ± 0.09 mg kg⁻¹, as compared to the nearly ten-fold higher V content of the iron oxide phase, 4.19 ± 0.37 mg kg⁻¹. Vanadium content of the bulk sediment is 4.02 ± 0.19 mg kg⁻¹, indicating that most of the V in the Carrizo Sand aquifer sediment is associated with the Fe(III)/Mn(IV) oxide/oxyhydroxide phase.

Vanadium concentrations in the Carrizo Sand groundwater are low when compared to other groundwaters where V concentrations have been measured, whereas groundwaters from the Oasis Valley-Beatty Wash aquifer exhibit higher V concentrations that are more comparable to those of other studies (Table 5). The average V concentration of Oasis Valley-Beatty Wash groundwaters is about half the value observed in shallow groundwaters in the Petit Hermitage catchment in Western France, where V association with colloids appears to control the V

speciation (Pourret et al., 2012). Vanadium concentrations in groundwaters from Texas coastal aquifers are much higher than those of both the Carrizo Sand and Oasis Valley-Beatty Wash groundwaters, which has been attributed to high V content of aquifer source material in coastal Texas (Glenn and Lester, 2010). Similarly, in California, groundwaters with the highest V concentrations are associated with aquifers that contain mafic to intermediate source rock compositions (Wright and Belitz, 2010; Wright et al., 2014). Additionally, groundwaters throughout Italy (Minelli et al., 2000; Veschetti et al., 2007) and Argentina (e.g., Nicolli et al., 1989; Farnfield et al., 2012; Nicolli et al., 2012) that drain volcanic terrains have high V concentrations owing in part to the high V content of volcanic source rocks and relatively rapid devitrification rates.

IV. 4. Geochemical modeling speciation of V in Oasis Valley-Beatty Wash and Carrizo Sand aquifers

The geochemical modeling predicts that V exists as the hydrolyzed vanadate oxyanion (i.e., H_2VO_4^- , HVO_4^{2-}) along the entire flow path of the Oasis Valley-Beatty Wash systems (Fig. 6). In the case of the Carrizo Sand aquifer, the modeling predicts that many of the groundwater samples are poised along the redox boundary where H_2VO_4^- is reduced to $(\text{VO})_2(\text{OH})_5^-$ (Fig. 7a). The half-reaction that describes V(V) reduction to V(IV) along this boundary on Fig. 7a is:

Furthermore, the modeling predicts that V(V) species account for between 20 and > 99% of total V species in the Carrizo Sand groundwaters, whereas V(IV) species account for between < 1 and 81% of total V species in solution (Fig. 7b). The first sample displays relatively even partitioning between V(IV) and V(V) species (57 versus 43%, respectively), owing to its relatively low Eh

values compared to the immediate downstream samples. The vanadate oxyanion HVO_4^{2-} then predominates along the flow path from just beyond the point of recharge until the Eh of the groundwater rapidly decreases in the vicinity of the Peeler well (41.1 km). At this point, the hydrated vanadyl species, $(\text{VO})_2(\text{OH})_5^-$, is predicted to predominate over vanadate oxyanions along the remainder of the flow path (Fig. 7b). Further modeling using WHAM VII also predicts that V(IV) is strongly bound to dissolved and/or colloidal organic matter within the Carrizo Sand groundwater (Table 6). Specifically, 100% of vanadyl is predicted to bind with humic material (both fulvic and humic acids). Therefore, the V(IV) ion represented as $(\text{VO})_2(\text{OH})_5^-$ in the redox modeling likely exists as V(IV)-DOM complexes in Carrizo Sand groundwater.

V. Discussion

V. 1. Vanadium Geochemistry of the Oasis Valley and Beatty Wash Groundwaters

Previous investigations of the Oasis Valley and Beatty Wash groundwaters demonstrated generally conservative behavior of oxyanion-forming trace elements like As, Mo, Se, W, and Sb (Johannesson and Tang, 2009). These oxyanions are generally mobile in the oxic and alkaline groundwaters of the Oasis Valley-Beatty Wash aquifer owing in part to ionic repulsion from clays and Fe(III)/Mn(IV) oxides/hydroxides, which are negatively charged at high pH (e.g., Stollenwerk, 1995; Stumm and Morgan, 1996; Goldberg et al., 1996; Goldberg, 2002; Gustafsson, 2003; Johannesson and Tang, 2009). However, V concentrations are not conservative with respect to Cl in Oasis Valley-Beatty Wash groundwaters as clearly demonstrated in Fig 8. With the exceptions of Fran's and Bailey's springs, which have relatively lower V concentrations than adjacent sites, V concentrations increase along the flow path (V vs. distance $R^2=0.728$, $p<0.05$). It is worth noting that Bailey's is a thermal spring (i.e., 34.7°C) and

502 Fran's Spring may also be influenced by hydrothermal inputs as its temperature (28.2°C) is
503 higher than all of the other groundwaters sampled in the Oasis Valley-Beatty Wash aquifer
504 system except Bailey's Spring (mean $\pm \sigma = 21 \pm 2.6^\circ\text{C}$; Table 1). Hierarchical dendrogram
505 clustering demonstrates that Bailey's spring has a distinct chemical signature from the other
506 Oasis Valley-Beatty Wash groundwaters sampled, which again has been attributed to geothermal
507 influences. Furthermore, Fran's spring is located on the western side of Oasis Valley, and
508 discharges from geologic materials that originated, in part, from the Bullfrog Hills (Fig. 1a).
509 Groundwater that is recharged in the Bullfrog Hills is isotopically distinct from the majority of
510 Oasis Valley groundwaters (White and Chuma, 1987), and its contribution to the Oasis Valley
511 groundwater system may affect the groundwater composition in the vicinity of Fran's spring
512 (Farnham et al., 2000). Finally, both Fran's and Bailey's springs have higher arsenic
513 concentrations than other wells sampled in the Oasis Valley-Beatty Wash aquifer system, which
514 may be indicative of geothermal influences and the oxidation of As-bearing sulfide minerals
515 related to local geothermal processes (Table 2; Johannesson and Tang, 2009).

516 Increasing V concentrations along the flow path suggests that chemical weathering of the
517 local aquifer materials progressively adds V to the groundwaters along the length of Oasis
518 Valley-Beatty Wash groundwater flow path. The lack of correlation between V and Cl, which
519 was previously used to calculate conservative mixing curves, further demonstrates that simple
520 mixing of Oasis Valley and Beatty Wash groundwaters plays a less significant role in controlling
521 dissolved V concentrations in the aquifer system than chemical weathering and/or desorption
522 (Johannesson and Tang, 2009). The abundance of V reported in the rocks of the Oasis Valley and
523 Beatty Wash systems is less than the V content reported for the upper continental crust but
524 comparable to the V content of granites (18.1 mg kg⁻¹ for Oasis Valley felsic volcanic rocks, 106

525 mg kg⁻¹ for the upper continental crust, and 16.1 mg kg⁻¹ for granites; Reeves and Brooks, 1978;
526 Broxton et al., 1989; Hu and Gao, 2008). However, despite the relatively lower V content of
527 felsic rocks, the V contents of mafic minerals within felsic rocks are generally higher than in the
528 bulk rock, whereas mafic minerals within mafic rocks have comparable V contents to the bulk
529 rock (Hillebrand, 1898; Turner, 1899).

530 Mafic rocks like basalt, although present in the Oasis Valley region, are comparatively
531 minor in abundance relative to the extensive felsic volcanic rocks (Christiansen et al., 1977).
532 Consequently, it is unlikely that chemical weathering of the minor basaltic rocks in the region
533 contributes substantially to the V concentrations measured in the Oasis Valley-Beatty Wash
534 groundwaters. Nonetheless, within the more abundant felsic volcanic rocks of the Oasis Valley,
535 mafic phenocrysts that include hornblende, biotite, and clinopyroxene occur and account for up
536 to 10% of total phenocrysts, by mode, in the Ammonia Tanks member, the chief aquifer rock
537 material of the Oasis Valley-Beatty Wash aquifer system. All phenocrysts (i.e., including felsic
538 phenocrysts such as quartz, plagioclase, and alkali feldspar) can account for up to 50% of the
539 total felsic volcanic rock of the Ammonia Tanks member, with the remainder being chiefly
540 composed of volcanic glass or devitrified relict glass (Byers et al., 1976). Geochemical modeling
541 indicates that Oasis Valley-Beatty Wash groundwaters are undersaturated with respect to
542 representative mafic mineral such as those that characterize the mafic phenocrysts of the local
543 volcanic rocks. Specifically, Oasis Valley-Beatty Wash groundwaters are undersaturated with
544 respect to biotite (i.e., phlogopite), hornblende (i.e., tremolite and pargasite, both of which
545 bracket the composition of common hornblende; Deer et al., 1983), and the Mg-rich pyroxene,
546 diopside (Fig. 9). The only exception is groundwater from EROV3a3, which is slightly
547 oversaturated with respect to biotite (Fig. 9). Nevertheless, previous geochemical inverse

modeling also suggests that biotite dissolution may be an important process contributing solutes to groundwaters of Oasis Valley-Beatty Wash groundwaters (Johannesson and Tang, 2009). Consequently, the equilibrium calculations indicate that chemical weathering/dissolution of mafic phenocryst minerals such as those that characterize the local felsic volcanic rocks, are energetically favorable in the Oasis Valley-Beatty Wash groundwaters. Because the V contents of mafic phenocryst minerals like biotite, hornblende, and pyroxene are generally higher than the bulk silicic rocks, we suggest that progressive weathering/dissolution of the mafic phenocrysts within the Ammonia Tanks member volcanic rocks are likely the chief source of V to Oasis Valley-Beatty Wash groundwaters.

Vanadium added from chemical weathering is able to accumulate in the Oasis Valley-Beatty Wash groundwaters because it is unlikely to adsorb to aquifer sediment. The pH values that characterize Oasis Valley-Beatty Wash groundwaters (i.e., mean $\pm$ σ pH 8.22 ± 0.14) should favor repulsion of the negatively charged vanadate oxyanions (H_2VO_4^- and HVO_4^{2-}) as mineral surface sites are expected to be predominantly negatively charged for these moderately alkaline conditions (e.g., Dzombak and Morel, 1990; Stumm and Morgan, 1996; Peacock and Sherman, 2004). Nicolli et al. (2012) also suggest that desorption under oxic and alkaline conditions increases the aqueous concentrations of oxyanions like V. Similarly, in oxic groundwaters of California, Wright et al. (2014) observe a positive correlation between pH and V concentrations, and suggest that desorption of the vanadate oxyanion is a dominant process.

V. 2. Vanadium Geochemistry of the Carrizo Sand Aquifer

As mentioned above, and described in detail previously, the redox structure of the Carrizo Sand aquifer is more complex than the Oasis Valley-Beatty Wash aquifer system, changing from oxic conditions in the recharge zone, to anoxic and sulfidic near the end of the studied flow path (e.g., Haque and Johannesson, 2006; Tang and Johannesson, 2006; Basu et al., 2007; Willis et al., 2001; Johannesson and Neumann, 2013; Johannesson et al., 2013). The initial variation in Fe and dissolved oxygen concentrations has been interpreted as a zone of initial Fe(III) reduction (4.3 km along the flow path) followed by reoxidation of Fe(II) (7.4 km along the flow path) (Figs. 2f, 4b; Haque and Johannesson, 2006; Johannesson et al., 2013). Ferrous iron concentrations then increase dramatically from $0.55 \mu\text{mol kg}^{-1}$ where the aquifer first becomes confined near well KS-1 to a factor of nearly 30 higher ($16 \mu\text{mol kg}^{-1}$) roughly 2 km down gradient (well N-3) (Fig 4b). The predominance of Fe(II) over the next ~30 km indicates that Fe(III) reduction buffers the redox conditions in the aquifer along this portion of the aquifer (Basu et al., 2007; Johannesson and Neumann, 2013). Beyond the Peeler well (~41 km down gradient from the recharge zone), dissolved sulfide begins to increase as the Fe(II) concentrations decrease (Fig. 4). These changes in S(-II) and Fe(II) are interpreted to reflect a switch from predominantly Fe reducing to sulfate reducing redox conditions with flow beyond the Peeler well, with the dramatic decrease in Fe(II) in solution being the result of precipitation of iron sulfide minerals like mackinawite and pyrite (Johannesson and Neumann, 2013; Johannesson et al., 2013). Although the composition of the in situ microbial populations have not been determined, previous investigations have inferred their influence on the development of these redox zones from analytical as well as biogeochemical reactive transport modeling (Haque and Johannesson, 2006; Tang and Johannesson, 2006; Basu et al., 2007; Johannesson and Neumann, 2013). Indeed, the biogeochemical reactive transport modeling indicates that once iron reducers

are exhausted (~14.5 km along the flow path), sulfate-reducing microbes are predicted to predominate (Johannesson and Neumann, 2013). The increase in sulfate reduction does not, however, coincide with the increase in sulfide concentrations. The Fe(II) in solution buffers the S(-II) concentrations until all of the Fe(II) is removed as FeS minerals, whereupon S(-II) begins to increase in solution. Once the dissolved ferrous iron is exhausted, sulfide concentrations increase abruptly (59 km along the flow path) (Fig. 4a; Johannesson and Neumann, 2013). Therefore, the modeling results are consistent with interpretations from previous studies that documented a zone of Fe(III) reduction followed by a zone of sulfate reduction along the flow path (e.g., Haque and Johannesson, 2006; Basu et al., 2007; Willis et al., 2011).

The more complex redox structure of the Carrizo Sand aquifer as compared to the Oasis Valley-Beatty Wash groundwater systems plays an important role in controlling V concentrations in Carrizo Sand groundwaters. Specifically, in contrast to increasing V concentrations with flow down gradient as observed in the Oasis Valley-Beatty Wash aquifer system, V concentrations in the Carrizo Sand groundwaters decrease along the flow path (Fig. 4c). The highest V concentration measured in Carrizo Sand groundwaters ($2.00 \text{ nmol kg}^{-1}$) occurs in the most up gradient well (i.e., well RF-2), which is located in the recharge zone (Figs. 1b, 4c). The V concentration subsequently decreases by more than a factor of 8 to $0.244 \text{ nmol kg}^{-1}$ with flow down-gradient along the first 9.4 km of the flow path (well N-3), where the aquifer transitions from unconfined to confined flow and where Fe reduction begins to buffer the redox conditions (Figs. 1b, 4c). For the remainder of the flow path studied within the confined portion of the Carrizo Sand aquifer, the V concentrations remains remarkably constant, varying between 0.188 and $0.244 \text{ nmol kg}^{-1}$, and exhibiting a mean $\pm \sigma$ of $0.215 \pm 0.025 \text{ nmol kg}^{-1}$ along the final 56.4 km of the studied flow path (Table 3, Fig. 4c). Consequently, the average V concentration

of Carrizo Sand groundwaters is a factor of 100 less than its concentration in groundwaters of the Oasis Valley-Beatty Wash aquifer.

The substantially lower V concentrations of Carrizo Sand groundwaters compared to those from the Oasis Valley-Beatty Wash system may reflect, in part, differences in the V content of the corresponding aquifer materials. For example, the V content of the Carrizo Sand (mean $\pm \sigma$ of $4.01 \pm 0.19 \text{ mg kg}^{-1}$) is nearly a factor of 5 less than the average of the felsic volcanic rocks of southern Nevada (mean $\pm \sigma$ of $18.1 \pm 13.5 \text{ mg kg}^{-1}$) where the Oasis Valley-Beatty Wash aquifer is located (Table 5). In addition to differences in the V contents of the aquifer source materials, the substantially lower V concentrations of Carrizo Sand aquifer groundwaters compared to those of the Oasis Valley-Beatty Wash systems are also likely the result of differences in groundwater composition and, particularly, the redox conditions of groundwaters from these aquifers. Indeed, comparison of the groundwater datasets for the Carrizo Sand aquifer and the Oasis Valley-Beatty Wash aquifer systems suggests that V is more mobile in oxic, high pH groundwaters than in suboxic and anoxic groundwaters. This is because V occurs as the vanadate oxyanion in oxic waters of neutral to high pH (Fig. 6), and the vanadate oxyanion favors the solution over mineral surface sites as pH increases above 8 (e.g., Dzombak and Morel, 1990). In contrast, reduction of vanadate to vanadyl in reducing groundwaters leads to adsorption of the vanadyl oxyanion onto aquifer mineral surfaces (Wehrli and Stumm, 1989; Wright et al., 2014). Additionally, in the sulfate-reduction zone of the aquifer, V(IV) may be further reduced to V(III) and sequestered as a V(III) oxide/hydroxide such as montroseite (Wanty and Goldhaber, 1992). The groundwaters of the Carrizo Sand aquifer are saturated with respect to iron oxides and therefore may also coprecipitate V(III) (Wanty and Goldhaber, 1992; Wright et al., 2014). Consequently, the mobility of V is expected to be much lower in the more

638 reducing waters of the Carrizo Sand aquifer as compared to the oxic waters of the Oasis Valley-
639 Beatty Wash, which is consistent with our measured V concentrations of groundwaters from both
640 aquifers. Specifically, the decrease in the measured Eh values along the flow path in the Carrizo
641 Sand aquifer is accompanied by a decrease in total V concentrations and dramatic increase in the
642 proportion of V(IV) relative to V(V) (Table, 3, Fig. 4c, 7b). The results of the sediment
643 digestions also suggest that decreases in V concentrations along the flow path in the Carrizo
644 Sand aquifer are likely the result of V adsorption onto Fe(III)/Mn(IV) oxides/hydroxides.
645 Vanadate may adsorb to Fe(III)/Mn(IV) oxides/hydroxides via inner-sphere surface
646 complexation at low to neutral pH, and vanadyl can adsorb onto positively charged mineral
647 surface sites despite electrostatic repulsion because of its affinity for oxygen atoms (Wehrli and
648 Stumm, 1988; Wehrli and Stumm, 1989; Peacock and Sherman, 2004).

649 Complexation with organic matter may also affect V concentration and speciation in
650 natural waters, including groundwaters (Wehrli and Stumm, 1989; Breit and Wanty, 1991).
651 Humic substances, which are generally considered unable to readily complex anions like
652 vanadate, are capable of first reducing the metavanadate anion, VO_3^- to VO^{2+} and subsequently
653 adsorbing the resulting cation (Szalay and Szilágyi, 1967). Moreover, vanadyl's affinity for
654 oxygen donor atoms not only attracts the cation to iron oxides but also to organic ligands
655 (McBride, 1978; Wehrli and Stumm, 1989; Lu et al., 1998). In shallow groundwaters from
656 western France, Pourret et al. (2012) observed higher V concentrations in DOC-rich waters than
657 in DOC-depleted waters, suggesting that vanadyl complexation to natural organic matter can
658 stabilize this oxycation in natural waters. Complexation of V by dissolved organic matter also
659 appears to be important in tidal flat porewaters where V concentrations exhibit seasonal and
660 depth changes concurrent with changes in DOC (Beck et al., 2008). The geochemical modeling

presented here for Carrizo Sand aquifer groundwaters predicts that all of the vanadyl in solution ought to be complexed with DOC (Table 6). Our geochemical modeling for Carrizo Sand aquifer groundwaters is thus consistent with the previous studies by Beck et al. (2008) and Pourret et al. (2012) by further supporting the notion that complexation with DOC stabilizes vanadyl in solution by reducing the free oxyanion concentration that would be available for further reaction (e.g., adsorption to mineral surfaces).

We note that, although V concentrations in Carrizo Sand groundwaters are likely buffered by complexation to organic matter, the V concentrations are more than 2 orders of magnitude lower than those observed by Pourret et al. (2012) (Table 5). We posit that the low concentrations of V in Carrizo Sand groundwaters mimic the lower concentrations of DOC as compared to the higher DOC concentrations of Western France (DOC averages 0.41 mg kg^{-1} in the Carrizo Sands groundwater versus an average of 25.48 mg L^{-1} reported in Pourret et al., 2012). More specifically, the low DOC concentrations of Carrizo Sand aquifer groundwater can only complex a comparatively low amount of vanadyl before all available binding sites become saturated with vanadyl, and/or other cations. Vanadyl in Carrizo Sand groundwater that is not complexed with DOC is subsequently lost from solution by adsorption onto mineral surfaces or further reduction in the sulfate-reducing regions of the aquifer to an insoluble V(III) species (Wanty and Goldhaber, 1992; Wright et al., 2014). Therefore, reduced groundwaters with higher DOC concentrations than Carrizo Sand groundwaters are expected to exhibit higher vanadyl concentrations.

V. 3. Comparison of Vanadium with Other Oxyanion-forming Elements in the Oasis Valley and Beatty Wash Groundwaters and the Carrizo Sands Groundwaters

Although V concentrations in the Oasis Valley-Beatty Wash groundwaters behave less conservatively than previously studied oxyanions, similar geochemical processes contribute oxyanion-forming trace elements to aqueous solution. In particular, geochemical modeling suggests that dissolution of volcanic glass and desorption from mineral surfaces govern the concentrations of oxyanion-forming trace elements (e.g., As, Sb, W, Se) in the Oasis Valley-Beatty Wash groundwater flow system (Johannesson and Tang, 2009). Vanadium concentrations in the Oasis Valley-Beatty Wash groundwaters above simple mixing predictions likely occur as a result of dissolution of undersaturated mafic minerals. Furthermore, if we exclude Fran's and Bailey's sites, which are hypothesized to be more enriched in As over V owing to elevated As concentrations from hydrothermal input or oxidation of As-bearing sulfide minerals associated with ore mineralization in the Bullfrog Hills, a significant relationship exists between V and As concentrations in the Oasis Valley-Beatty Wash groundwaters ($R^2=0.58$, $p<0.05$). Correlation between V and As is also reported for groundwaters in Argentina, which have a similar major ion chemistry to the groundwaters of the Oasis Valley-Beatty Wash system (e.g., Nicolli et al., 1989; Fiorentino et al., 2007; Farnfield et al., 2012; Nicolli et al., 2012). More specifically, the aquifer sediments of both the Oasis Valley-Beatty Wash and Argentina are silica rich and derived, in part, from rhyolitic volcanic glass (Broxton et al., 1989; Nicolli et al., 1989). Additionally, mafic minerals in the Salí River Basin in Argentina are dominated by pyroxene and hornblende (Nicolli et al., 1989; Nicolli et al., 2012).

Under the reducing conditions of the Carrizo Sand aquifer, V does not correlate with the previously studied oxyanions, As ($R^2=0.08$) and W ($R^2=0.04$) (Haque and Johannesson, 2006; Johannesson et al., 2013). In the Carrizo Sand Aquifer, the trend in V concentrations along the flow path most closely corresponds to that of U. Uranium-hosting deposits within the Carrizo

Sand, which may contain V (e.g., Evans and Garrels, 1958; Wanty and Goldhaber, 1992), are also reported in the neighboring county (Karnes County) to the west of our field site in Atascosa County (Cowart and Osmond, 1977). Uranium concentrations in groundwater samples studied by Cowart and Osmond (1977) are highest in the outcrop region (up to 14.83 nmol kg⁻¹), and drop 1 to 3 orders of magnitude with depths below about 100 m. In the portion of the aquifer sampled in this study, U concentrations, like V concentrations, are near the detection limit for most samples (Table 3). Nonetheless, V and U are strongly positively correlated ($R^2=0.85$; $p<0.005$), and concentrations decrease with decreasing redox potential along the flow path. Under reducing conditions, both U and V are predicted to form relatively insoluble species (Wehrli and Stumm, 1989; Lovley et al., 1991; Tribovillard et al., 2006; Cinti et al., 2015). Additionally, in aqueous solution, both are predominantly complexed with DOC in Carrizo Sand groundwaters (Table 6). In the solid phase, both constituents are more concentrated in the iron oxide phase than in the organic matter phase, suggesting the majority of available U and V in the sediments are associated with Fe(III)/Mn(IV) oxides/oxyhydroxides in the solid phase and likely to be strongly removed to the aquifer sediments (Table 4).

VI. Summary and Conclusions

- Absolute concentrations of V in the Oasis Valley-Beatty Wash system are substantially greater than those of the Carrizo Sand aquifer (Mann-Whitney U-test, $p<0.005$) due to both higher concentrations of vanadium in local aquifer materials and more favorable redox conditions for vanadium mobility in the Oasis Valley-Beatty Wash aquifer.

- 729 • Geochemical modeling predicts that V occurs in the groundwaters of the Oasis Valley-
730 Beatty Wash system as the soluble vanadate oxyanion (H_2VO_4^- and HVO_4^{2-}) the most
731 common species under oxic, near-neutral pH conditions, whereas both V(IV) and V(V)
732 are predicted to occur in the Carrizo Sand groundwater. The predominance of V(IV) that
733 is predicted to characterize the most reducing groundwaters within the Carrizo Sand
734 aquifer (i.e., sulfate reduction zone) likely accounts for the low overall V concentrations as
735 the vanadyl ion is more mineral surface reactive in high pH groundwaters (e.g., $\text{pH} > 7.5$)
736 than the vanadate oxyanion.
- 737 • Geochemical modeling also predicts that the vanadyl ion is largely bound to colloidal
738 DOC in Carrizo Sand groundwater, which appears to buffer its concentration at around 0.2
739 nmol kg^{-1} along the majority of the flow path.
- 740 • The pH is generally more alkaline in the groundwaters of the Oasis Valley-Beatty Wash
741 aquifer than in those of the Carrizo Sand aquifer (8.21 ± 0.14 versus 7.00 ± 1.06).
742 Although, the pH of the Carrizo Sand groundwaters increases by the end of the flow path,
743 V in this reducing portion of the flow path likely exists as V(IV) and may be readsorbed.
744 Digestions of Carrizo Sand aquifer sediments also indicate that adsorption to iron oxides is
745 an important process limiting V solubility in this aquifer.
- 746 • Although oxyanion-forming trace elements can behave similarly in oxic and alkaline
747 natural waters, in circumneutral reducing water, their geochemical behavior depends more
748 strongly on source material, adsorption/desorption reactions with mineral surfaces, and
749 complexation with other aqueous species.

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References

- Auger, Y., Bodineau, L., Leclercq, S., Wartel, M., 1999. Some aspects of vanadium and chromium chemistry in the English Channel. *Continental Shelf Research*, 19(15-16): 2003-2018.
- Back, W., 1960. Origin of hydrochemical facies of ground water in the Atlantic Coastal Plain. *International Geological Congress*, 21: 87-95.
- Barwise, A.J.G., 1990. Role of nickel and vanadium in petroleum classification. *Energy & Fuels*, 4(6): 647-652.

774 Basu, R., Haque, S.E., Tang, J., Ji, J., Johannesson, K.H., 2007. Evolution of selenium
 775 concentrations and speciation in groundwater flow systems: Upper Floridan (Florida) and
 776 Carrizo Sand (Texas) aquifers. *Chemical Geology*, 246(3-4): 147-169.

777 Bebout, D. G., Gavenda, V. J., Gregory, A. R., 1978. Geothermal resources, Wilcox Group,
 778 Texas Gulf Coast. University of Texas at Austin, Bureau of Economic Geology, 82 p.

779 Beck, M., Dellwig, L., Schnetger, B., Brumsack, H.J., 2008. Cycling of trace metals (Mn, Fe,
 780 Mo, U, V, Cr) in deep pore waters of intertidal flat sediments. *Geochimica Et*
 781 *Cosmochimica Acta*, 72(12): 2822-2840.

782 Berner, R.A., 1981. A new geochemical classification of sedimentary environments. *Journal of*
 783 *Sedimentary Petrology*, 51(2): 359-365.

784 Bethke, C., 2008. *Geochemical and biogeochemical reaction modeling*. Cambridge: Cambridge
 785 University Press.

786 Breit, G.N., Wanty, R.B., 1991. Vanadium accumulation in carbonaceous rocks—a review of
 787 geochemical controls during deposition and diagenesis. *Chemical Geology*, 91(2): 83-97.

788 Broxton, D.E., Bish, D.L., Warren, R.G., 1987. Distribution and chemistry of diagenetic
 789 minerals at Yucca Mountain, Nye County, Nevada. *Clays and Clay Minerals*, 35(2): 89-
 790 110.

791 Broxton, D.E., Warren, R.G., Byers, F.M., Scott, R.B., 1989. Chemical and mineralogic trends
 792 within the Timber Mountain Oasis Valley caldera complex, Nevada—evidence for
 793 multiple cycles of chemical evolution in a long-lived silicic magma. *Journal of*
 794 *Geophysical Research-Solid Earth and Planets*, 94(B5): 5961-5985.

795 Burdige, D. J., Gardner, K. G., 1998. Molecular weight distribution of dissolved organic carbon
 796 in marine sediment pore waters. *Marine Chemistry*. 62: 45-64.

797 Byers, F.M., Jr., Carr, W.J., Orkild, P.P., Quinlivan, W.D., Sargent, K.A., 1976. Volcanic
 798 suites and related caldrons of Timber Mountain–Oasis Valley caldera complex.
 799 US Geol. Surv. Prof. Paper 919, 70p.

800 Castro, M.C., Goblet, P., 2003. Calibration of regional groundwater flow models: Working
 801 toward a better understanding of site-specific systems. *Water Resources Research*, 39(6).
 802 1172.

803 Castro, M.C., Stute, M., Schlosser, P., 2000. Comparison of ^4He and ^{14}C ages in simple aquifer
 804 systems: implications for groundwater flow and chronologies. *Applied Geochemistry*, 15:
 805 1137–1167.

806 Champ, D.R., Gulens, J., Jackson, R.E., 1979. Oxidation-reduction sequences in groundwater
 807 flow systems. *Canadian Journal of Earth Science*, 16: 12-23.

808 Christiansen, R.L., Lipman, P.W., Carr, W.J., Byers, Jr., F.M., Orkild, P.P., Sargent, K.A., 1977.
 809 Timber Mountain-Oasis Valley caldera complex of Southern Nevada. *Geological Society*
 810 *of America Bulletin*, 88(7): 943-959.

811 Cinti, D., Poncia, P.P., Brusca, L., Tassi, F., Quattrocchi, F., Vaselli, O., 2015. Spatial
 812 distribution of arsenic, uranium and vanadium in the volcanic-sedimentary aquifers of the
 813 Vicano-Cimino Volcanic District (Central Italy). *Journal of Geochemical Exploration*, 152:
 814 123-133.

815 Clark, T.A., Deniset, J.F., Heyliger, C.E., Pierce, G.N., 2014. Alternative therapies for diabetes
 816 and its cardiac complications: role of vanadium. *Heart Failure Reviews*, 19(1): 123-132.

817 Collier, R.W., 1984. Particulate and dissolved vanadium in the North Pacific-Ocean. *Nature*,
818 309(5967): 441-444.

819 Cotton, F. A., Wilkinson, G., Murillo, C. A., Bochmann, M., 1999. *Advanced Inorganic*
820 *Chemistry*, 6th edition. John Wiley and Sons, New York.

821 Cowart, J.R., Osmond, J.K., 1977. Uranium isotopes in groundwater: their use in prospecting for
822 sandstone-type uranium deposits. *Journal of Geochemical Exploration*, 8:365–379

823 Davisson, M.L., Smith, D.K., Kenneally, J., Rose, T.P., 1999. Isotope hydrology of
824 southern Nevada groundwater: stable isotopes and radiocarbon. *Water Resources*
825 *Research*, 35: 279–294.

826 Deer, W. A., Howie, R. A., Zussman J., 1983. *An Introduction to the Rock-Forming Minerals*.
827 Longman Group Ltd, Harlow, UK, 528 p.

828 Delany, J. M., Lundeen, S. R., 1990. The LLNL thermochemical database. Lawrence Livermore
829 National Laboratory Report UCRL-21658. Lawrence Livermore National Laboratory.

830 Duce, R.A., Hoffman, G.L., 1976. Atmospheric vanadium transport to ocean. *Atmospheric*
831 *Environment*, 10(11): 989-996.

832 Dzombak D. A. and Morel F. M. M., 1990. *Surface Complexation Modeling: Hydrous Ferric*
833 *Oxide*. John Wiley and Sons, New York.

834 Eaton, A.D., Clesceri, L.S., Greenberg, A.E., 1995a. IRON (3500-Fe)/Phenanthroline Method.
835 Standard Methods for the Examination of Water and Waste Water, 19th ed. American
836 Public Health Association, Washington, DC, pp. 3–68 – 3–70.

837 Eaton, A.D., Clesceri, L.S., Greenberg, A.E., 1995b. SULFIDE (4500-
838 S2–)/Methylene Blue Method. Standard Methods for the Examination of Water and

839 WasteWater, 19th ed. American Public Health Association, Washington, DC, pp. 4–122 –
840 4–123.

841 Edmunds, W.M., Cook, J.M., Darling, W.G., Kinniburgh, D.G., Miles, D.L., Bath, A.H.,
842 Morgan-Jones, M., Andrews, J.N., 1987. Baseline geochemical conditions in the Chalk
843 aquifer, Berkshire, U.K.: a basis for groundwater quality management. *Applied*
844 *Geochemistry*, 2: 251-274.

845 Edmunds, W.M., Guendouz, A.H., Mamou, A., Moulla, A., Shand, P., Zouari, K., 2003.
846 Groundwater evolution in the Continental Intercalaire aquifer of southern Algeria and
847 Tunisia: trace element and isotopic indicators. *Applied Geochemistry*, 18: 805-822.

848 Evans, Jr., H.T., Garrels, R.M., 1958. Thermodynamic equilibria of vanadium in aqueous
849 systems as applied to the interpretation of the Colorado Plateau ore deposits. *Geochimica*
850 *et Cosmochimica Acta*, 15(1-2): 131-149.

851 Farnfield, H.R., Marcilla, A.L., Ward, N.I., 2012. Arsenic speciation and trace element analysis
852 of the volcanic rio Agrio and the geothermal waters of Copahue, Argentina. *Science of the*
853 *Total Environment*, 433: 371-378.

854 Farnham, I.M., 2001. Characterization of ground water using trace element
855 chemistry and multivariate statistical analysis. Ph.D. Thesis, University of
856 Nevada, Reno, NV, 160p.

857 Farnham, I.M., Johannesson, K.H., Singh, A.K., Hodge, V.F., Stetzenbach, K.J., 2003. Factor
858 analytical approaches for evaluating groundwater trace element chemistry data. *Analytica*
859 *Chimica Acta*, 490(1-2): 123-138.

860 Farnham, I.M., Stetzenbach, K.J., Singh, A.K., Johannesson, K.H., 2000. Deciphering
861 groundwater flow systems in Oasis Valley, Nevada, using trace element chemistry,

862 multivariate statistics, and geographical information system. *Mathematical Geology*, 32(8):
863 943-968.

864 Fiorentino, C.E., Paoloni, J.D., Sequeira, M.E., Arosteguy, P., 2007. The presence of vanadium
865 in groundwater of southeastern extreme the pampean region Argentina: Relationship with
866 other chemical elements. *Journal of Contaminant Hydrology*, 93(1-4): 122-129.

867 Foster, M.D., 1950. The origin of high sodium bicarbonate waters in the Atlantic and Gulf
868 Coastal Plains. *Geochimica et Cosmochimica Acta*, 1: 33-48.

869 Glenn, S.M., Lester, L.J., 2010. An analysis of the relationship between land use and arsenic,
870 vanadium, nitrate and boron contamination in the Gulf Coast aquifer of Texas. *Journal of*
871 *Hydrology*, 389(1-2): 214-226.

872 Goldberg, S., 2002. Competitive adsorption of arsenate and arsenite on oxides and clay minerals.
873 *Soil Science Society of America Journal*, 66(2), 413-421.

874 Goldberg, S., Forster, H. S., Godfrey, C. L., 1996. Molybdenum adsorption on oxides, clay
875 minerals, and soils. *Soil Science Society of America Journal*, 60(2), 425-432.

876 Goldschmidt, V.M., 1954. *Geochemistry*. Clarendon Press, Oxford.

877 Gustafsson, J. P., 2003. Modelling molybdate and tungstate adsorption to ferrihydrite. *Chemical*
878 *Geology*, 200(1), 105-115.

879 Hamlin, S.H., 1988. Depositional and ground-water flow systems of the
880 Carrizo-upper Wilcox, South Texas. Report of Investigations—Texas,
881 University, Bureau of Economic Geology, Rept, vol. 175. 61 p.

882 Haque, S., Johannesson, K.H., 2006. Arsenic concentrations and speciation along a groundwater
883 flow path: The Carrizo Sand aquifer, Texas, USA. *Chemical Geology*, 228(1-3): 57-71.

884 Hillebrand, W. F., 1898. Distribution and quantitative occurrence of vanadium and molybdenum
885 in rocks of the United States. *American Journal of Science*, 4(6): 209-216.

886 Hope, B.K., 1997. An assessment of the global impact of anthropogenic vanadium.
887 *Biogeochemistry*, 37(1): 1-13.

888 Hope, B.K., 2008. A dynamic model for the global cycling of anthropogenic vanadium. *Global*
889 *Biogeochemical Cycles*, 22(4).

890 Hu, Z., Gao, S., 2008. Upper crustal abundances of trace elements: A revision and update.
891 *Chemical Geology*, 253(3-4): 205-221.

892 Jeandel, C., Caisso, M., Minster, J.F., 1987. Vanadium behavior in the global ocean and in the
893 Mediterranean Sea. *Marine Chemistry*, 21(1): 51-74.

894 Johannesson, K.H., Dave, H.B., Mohajerin, T.J., Datta, S., 2013. Controls on tungsten
895 concentrations in groundwater flow systems: The role of adsorption, aquifer sediment
896 Fe(III) oxide/oxyhydroxide content, and thiotungstate formation. *Chemical Geology*, 351:
897 76-94.

898 Johannesson, K.H., Neumann, K., 2013. Geochemical cycling of mercury in a deep, confined
899 aquifer: Insights from biogeochemical reactive transport modeling. *Geochimica Et*
900 *Cosmochimica Acta*, 106: 25-43.

901 Johannesson, K.H., Tang, J.W., 2009. Conservative behavior of arsenic and other oxyanion-
902 forming trace elements in an oxic groundwater flow system. *Journal of Hydrology*, 378(1-
903 2): 13-28.

904 Johannesson, K.H., Tang, J.W., Daniels, J.M., Bounds, W.J., Burdige, D.J., 2004. Rare earth
 905 element concentrations and speciation in organic-rich blackwaters of the Great Dismal
 906 Swamp, Virginia, USA. *Chemical Geology*, 209(3-4): 271-294.

907 Koonce, J.E., Yu, Z., Farnham, I.M., Stetzenbach, K.J., 2006. Geochemical interpretation of
 908 groundwater flow in the southern Great Basin. *Geosphere*, 2(2): 88-101.

909 Langmuir, D., 1997. *Aqueous environmental geochemistry*. Upper Saddle River, N.J: Prentice
 910 Hall.

911 Lovley, D.R., Roden, E.E., Phillips, E.J.P., Woodward, J.C., 1993. Enzymatic iron and uranium
 912 reduction by sulfate-reducing bacteria. *Marine Geology*, 113(1-2): 41-53.

913 Lu, X.Q., Johnson, W.D., Hook, J., 1998. Reaction of vanadate with aquatic humic substances:
 914 An ESR and V-51 NMR study. *Environmental Science and Technology*, 32(15): 2257-
 915 2263.

916 Mamane, Y., Pirrone, N., 1998. Vanadium in the atmosphere. *Advances in Environmental*
 917 *Science and Technology*-New York, 30: 37-72.

918 Manohar, D.M., Noeline, B.F., Anirudhan, T.S., 2005. Removal of vanadium(IV) from aqueous
 919 solutions by adsorption process with aluminum-pillared bentonite. *Industrial &*
 920 *Engineering Chemistry Research*, 44(17): 6676-6684.

921 McBride, M.B., 1978. Transition metal bonding in humic acid: ESR study. *Soil Science*, 126(4):
 922 200-209.

923 McBride, M.B., 1979. Mobility and reactions of VO^{2+} on hydrated smectite surfaces. *Clays and*
 924 *Clay Minerals*, 27(2): 91-96.

- 925 Middelburg, J.J., Hoede, D., Van der Sloot, H.A., Van der Weijden, C.H., Wijkstra, J., 1988.
926 Arsenic, antimony and vanadium in the North Atlantic Ocean. *Geochimica et*
927 *Cosmochimica Acta*, 52: 2871-2878.
- 928 Minelli, L., Veschetti, E., Giammanco, S., Mancini, G., Ottaviani, M., 2000. Vanadium in Italian
929 waters: monitoring and speciation of V(IV) and V(V). *Microchemical Journal*, 67(1-3):
930 83-90.
- 931 Miyashiro, A., Shido, F., 1975. Tholeiitic and calc-alkalic series in relation to the behaviors of
932 titanium, vanadium, chromium, and nickel. *American Journal of Science*, 275(3): 265-277.
- 933 Mohajerin, T.J., Neal, A.W., Telfeyan, K., Sasidharan, S.M., Ford, S., Yang, N., Chevis, D.A.,
934 Grimm, D.A., Datta, S., White, C.D., Johannesson, K.H., 2014. Geochemistry of
935 Tungsten and Arsenic in Aquifer Systems: A Comparative Study of Groundwaters from
936 West Bengal, India, and Nevada, USA. *Water Air and Soil Pollution*, 225(1).
- 937 Nicolli, H.B., Garcia, J.W., Falcon, C.M., Smedley, P.L., 2012. Mobilization of arsenic and other
938 trace elements of health concern in groundwater from the Salí River Basin, Tucumán
939 Province, Argentina. *Environmental Geochemistry and Health*, 34(2): 251-262.
- 940 Nicolli, H.B., Suriano, J.M., Peral, M.A.G., Ferpozzi, L.H., Baleani, O.A., 1989. Groundwater
941 contamination with arsenic and other trace elements in an area of the Pampa, Córdoba,
942 Argentina. *Environmental Geology and Water Sciences*, 14(1): 3-16.
- 943 Nriagu, J. O., 1998. History, occurrence, and uses of vanadium. *Advances in Environmental*
944 *Science and Technology*: New York, 30: 1-24.

945 Nriagu, J. O., Pirrone, N., 1998. Emission of vanadium into the atmosphere. *Advances in*
946 *Environmental Science and Technology*: New York, 30: 25-36.

947 Payne, J. N., 1975. Geohydrologic significance of lithofacies of the Carrizo Sand of Arkansas,
948 Louisiana, and Texas and the Meridian Sand of Mississippi: US Geological Survey
949 Professional Paper 569-C.

950 Peacock, C.L., Sherman, D.M., 2004. Vanadium(V) adsorption onto goethite (α -FeOOH) at
951 pH 1.5 to 12: A surface complexation model based on ab initio molecular geometries and
952 EXAFS spectroscopy. *Geochimica Et Cosmochimica Acta*, 68(8): 1723-1733.

953 Pearson, F. J., White, D. E., 1967. Carbon 14 ages and flow rates of water in Carrizo Sand,
954 Atascosa County, Texas. *Water Resources Research*, 3(1): 251-261.

955 Peccerillo, A., Taylor, S. R., 1976. Geochemistry of Eocene calc-alkaline volcanic rocks from
956 the Kastamonu area, northern Turkey. *Contributions to mineralogy and petrology*, 58(1):
957 63-81.

958 Pourret, O., Dia, A., Gruau, G., Davranche, M., Bouhnik-Le Coz, M., 2012. Assessment of
959 vanadium distribution in shallow groundwaters. *Chemical Geology*, 294-295: 89-102.

960 Reeves, R. D., Brooks, R. R., 1978. *Trace element analysis of geologic materials*. John Wiley
961 and Sons, New York.

962 Sawyer, D.A., Fleck, R.J., Lanphere, M.A., Warren, R.G., Broxton, D.E., Hudson, M.R., 1994.
963 Episodic caldera volcanism in the Miocene southwestern Nevada volcanic field –
964 revised stratigraphic framework, AR-40 AR-39 geochronology, and implications for
965 magmatism and extension. *Geological Society of America Bulletin*, 106(10): 1304-
966 1318.

967 Shiller, A.M., Boyle, E.A., 1987. Dissolved vanadium in rivers and estuaries. *Earth and*
968 *Planetary Science Letters*, 86(2-4): 214-224.

969 Shiller, A.M., Mao, L.J., 2000. Dissolved vanadium in rivers: effects of silicate weathering.
970 *Chemical Geology*, 165(1-2): 13-22.

971 Soveid, M., Dehghani, G.A., Omrani, G.R., 2013. Long- term Efficacy and Safety of Vanadium
972 in the Treatment of Type 1 Diabetes. *Archives of Iranian Medicine*, 16(7): 408-411.

973 Sracek, O., Mihaljevič, M., Křibek, B., Majer, V., Filip, J., Vaněk, A., Penížek, V., Ettler, V.,
974 Mapani, B., 2014. Geochemistry and mineralogy of vanadium in mine tailings at Berg
975 Aukus, northeastern Namibia. *Journal of African Earth Sciences*, 96: 180-189.

976 Stollenwerk, K. G., 1995. Modeling the effects of variable groundwater chemistry on adsorption
977 of molybdate. *Water Resources Research*, 31(2), 347-357.

978 Strady, E., Blanc, G., Schafer, J., Coynel, A., Dabrin, A., 2009. Dissolved uranium, vanadium
979 and molybdenum behaviours during contrasting freshwater discharges in the Gironde
980 Estuary (SW France). *Estuarine Coastal and Shelf Science*, 83(4): 550-560.

981 Stumm, W., and J. Morgan. 1996. *Aquatic chemistry: Chemical equilibria and rates in natural*
982 *waters*, 3rd ed. New York: John Wiley & Sons.

983 Stute, M., Schlosser, P., Clark, J.F., Broecker, W.S., 1992. Paleotemperatures in the
984 Southwestern United States derived from noble gases in groundwater. *Science*, 256(5059):
985 1000-1003.

986 Szalay, A., Szilágyi, M., 1967. The association of vanadium with humic acids. *Geochimica et*
987 *Cosmochimica Acta*, 31: 1–6.

988 Tang, J.W., Johannesson, K.H., 2005. Rare earth element concentrations, speciation, and

989 fractionation along groundwater flow paths: the Carrizo Sand (Texas) and upper Floridan
 990 aquifers. In: Johannesson, K.H. (Ed.), *Rare Earth Elements in Groundwater Flow*
 991 *Systems*. Springer, Dordrecht, pp. 223–251.

992 Tang, J.W., Johannesson, K.H., 2006. Controls on the geochemistry of rare earth elements along
 993 a groundwater flow path in the Carrizo Sand aquifer, Texas, USA. *Chemical Geology*,
 994 225(1-2): 156-171.

995 Tang, J.W., Whittecar, G.R., Johannesson, K.H., Daniels, W.L., 2004. Potential contaminants at
 996 a dredged spoil placement site, Charles City County, Virginia, as revealed by
 997 sequential extraction. *Geochemical Transactions*, 5(4): 49-60.

998 Tang, L.Y., Su, Y., He, J., Chen, W., Su, F., Wu, B., Lin, Y., Ren, Z., 2012. Urinary Titanium
 999 and Vanadium and Breast Cancer: A Case-Control Study. *Nutrition and Cancer-an*
 1000 *International Journal*, 64(3): 368-376.

1001 Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the
 1002 speciation of particulate trace-metals. *Analytical Chemistry*, 51(7): 844-851.

1003 Thomas, J.M., Benedict, F.C., Jr., Rose, T.P., Hershey, R.L., Paces, J.B., Peterman, Z.E.,
 1004 Farnham, I.M., Johannesson, K.H., Singh, A.K., Stetzenbach, K.J., Hudson, G.B.,
 1005 Kenneally, J.M., Eaton, G.F., Smith, D.K., 2002. Geochemical and isotopic
 1006 interpretations of groundwater flow in the Oasis Valley flow system, southern Nevada,
 1007 Desert Research Institute Publication, No. 45190.

1008 Thurman, E. M., 1985. Ed. *Organic geochemistry of natural waters*. Vol. 2. Springer.

1009 Tipping, E., 1998. Humic ion-binding model VI: An improved description of the interactions of
 1010 protons and metal ions with humic substances. *Aquatic Geochemistry*, 4(1): 3-48.

1011 Tipping, E., Lofts, S., Sonke, J.E., 2011. Humic Ion-Binding Model VII: a revised
 1012 parameterisation of cation-binding by humic substances. *Environmental Chemistry*, 8(3):
 1013 225-235.

1014 Tribouvillard, N., Algeo, T.J., Lyons, T., Riboulleau, A., 2006. Trace metals as paleoredox and
 1015 paleoproductivity proxies: An update. *Chemical Geology*, 232(1-2): 12-32.

1016 Turner, H. W., 1899. Some rock-forming biotites and amphiboles. *American Journal of Science*,
 1017 4(7): 294-298

1018 U.S. Environmental Protection Agency. 2009. Candidate Contaminant List 3.
 1019 <http://www2.epa.gov/ccl/contaminant-candidate-list-3-ccl-3#chemical-list> (accessed
 1020 January 14, 2014).

1021 Veschetti, E., Maresca, D., Lucentini, L., Ferretti, E., Citti, G., Ottaviani, M., 2007. Monitoring
 1022 of V(IV) and V(V) in Etnean drinking-water distribution systems by solid phase
 1023 extraction and electrothermal atomic absorption spectrometry. *Microchemical Journal*,
 1024 85(1): 80-87.

1025 Vine, J. D., Tourtelot, E. B., 1970. Geochemistry of Black Shale Deposits—A Summary Report.
 1026 *Economic Geology and the bulletin of the Society of Economic Geologists*, 65: 253-272.

1027 Wang, D., Sañudo Wilhelmy, S.A., 2008. Development of an analytical protocol for the
 1028 determination of V (IV) and V (V) in seawater: Application to coastal environments.
 1029 *Marine Chemistry*, 112(1-2): 72-80.

1030 Wang, D., Sañudo Wilhelmy, S.A., 2009. Vanadium speciation and cycling in coastal waters.
 1031 *Marine Chemistry*, 117(1-4): 52-58.

- 1032 Wanty, R.B., Goldhaber, M.B., 1992. Thermodynamics and kinetics of reactions involving
1033 vanadium in natural systems – accumulation of vanadium in sedimentary rocks.
1034 *Geochimica Et Cosmochimica Acta*, 56(4): 1471-1483.
- 1035 Wehrli, B., Stumm, W., 1988. Oxygenation of vanadyl(IV) – effect of coordinated surface
1036 hydroxyl-groups and OH. *Langmuir*, 4(3): 753-758.
- 1037 Wehrli, B., Stumm, W., 1989. Vanadyl in natural waters – adsorption and hydrolysis promote
1038 oxygenation. *Geochimica Et Cosmochimica Acta*, 53(1): 69-77.
- 1039 Weisel, C.P., Duce, R.A., Fasching, J.L., 1984. Determination of aluminum, lead, and vanadium
1040 in north-Atlantic seawater after coprecipitation with ferric hydroxide. *Analytical*
1041 *Chemistry*, 56(6): 1050-1052.
- 1042 Welch, K. A., Lyons, W. B., Graham, E., Neumann, K., Thomas, J., Mikeselml, D., 1996.
1043 Determination of major element chemistry in terrestrial waters from Antarctica by ion
1044 chromatography. *Journal of Chromatography A*, 739: 257-263.
- 1045 Western Regional Climate Center, 2008. Desert Research Institute. [http://www.wrcc.dri.edu/cgi-](http://www.wrcc.dri.edu/cgi-bin/cliMAIN.pl?nvbeat)
1046 [bin/cliMAIN.pl?nvbeat](http://www.wrcc.dri.edu/cgi-bin/cliMAIN.pl?nvbeat) (accessed November 13, 2008).
- 1047 White, A.F., 1979. Geochemistry of ground water associated with tuffaceous rocks, Oasis
1048 Valley, Nevada: U.S. Geological Survey Professional Paper 712-E, 25 p.
- 1049 White, A. F., Chuma, N. J., 1987. Carbon and Isotopic Mass Balance Models of Oasis-Valley-
1050 Fortymile Canyon Groundwater Basin, Southern Nevada. *Water Resources Research*,
1051 23(4): 571-582.
- 1052 Willis, S.S., Haque, S.E., Johannesson, K.H., 2011. Arsenic and Antimony in Groundwater Flow
1053 Systems: A Comparative Study. *Aquatic Geochemistry*, 17(6): 775-807.

1054 Winograd, I.J., Robertson, F.N., 1982. Deep oxygenated groundwater-anomaly or common
 1055 occurrence. *Science*, 216(4551): 1227-1230.

1056 Winograd, I.J., Thordarson, W., 1975. Hydrogeologic and hydrochemical framework, south-
 1057 central Great Basin, Nevada-California, with special reference to the Nevada Test Site, US
 1058 Geol. Surv. Prof. Paper 712-C.

1059 Wright, M.T., Belitz, K., 2010. Factors Controlling the Regional Distribution of Vanadium in
 1060 Groundwater. *Ground Water*, 48(4): 515-525.

1061 Wright, M.T., Stollenwerk, K.G., Belitz, K., 2014. Assessing the solubility controls on
 1062 vanadium in groundwater, northeastern San Joaquin Valley, CA. *Applied Geochemistry*,
 1063 48: 41-52.

1064 Zwolak, I., 2014. Vanadium carcinogenic, immunotoxic and neurotoxic effects: a review of in
 1065 vitro studies. *Toxicology Mechanisms and Methods*, 24(1): 1-12.

a)

b)

Fig 1. a) Map of sample sites in the Oasis Valley-Beatty Wash aquifer. Samples in Blue are along the Oasis Valley flow path, and samples in orange are along the Beatty Wash flow path. The two flowlines converge in the vicinity of the EROV4a well. Figure modified from Johannesson and Tang (2009) from a Google™ Earth Image. b) Location of Carrizo aquifer sample sites in Atascosa and McMullen counties, TX. Figure modified from Johannesson and Neumann (2013) from a Google™ Earth Image.

Fig 2. Field parameter data for the Oasis Valley-Beatty Wash groundwater (a-c) and the Carrizo Sand groundwater (d-f) as a function of distance along flow path. Shown are conductivity (a,d), pH (b,e), and dissolved oxygen (c,f).

a)

b)

Fig 3. a) Piper diagrams for Oasis Valley-Beatty Wash groundwaters. b) Piper diagram for Carrizo groundwaters with blue arrow showing the evolution to alkali bicarbonate dominated waters. RF-2 and G-1 are not included due to a lack of major ion data for these sites.

Fig 4. Geochemical data for the Carrizo Sand aquifer samples as a function of distance along flow path. a) Dissolved sulfide ($\mu\text{mol kg}^{-1}$); b) dissolved Fe (II) and Fe (III) ($\mu\text{mol kg}^{-1}$) are the average values of the most recent and previous sampling campaigns (e.g. Haque and Johannesson, 2006; Tang et al., 2006; Basu et al., 2007; Table 3); and c) dissolved V concentrations (nmol kg^{-1}) are from the most recent sampling campaign (March 2013). Sulfide reduction begins at 14.5 km but Fe(II) concentrations are high enough to buffer sulfide concentrations and precipitate Fe sulfide minerals. Towards the end of the flow path, Fe(II) production is outpaced by sulfate reduction, and sulfide concentrations increase (Johannesson and Neumann, 2013). The bar along the bottom shows the redox transition zones with the corresponding distance along flow path.

Fig 5. Vanadium concentrations along the Oasis and Beatty Wash groundwater flow paths.

Fig 6. a) Eh-pH diagram for Oasis Valley-Beatty Wash groundwaters using average V activity (log activity = -7.6) and measured Eh and pH values. b) Predicted V species as a percent of total V concentration calculated using Geochemist's Workbench® SpecE8. Only major species (>1% total V) are shown.

a)

b)

Figure 7. a) Eh-pH diagram for the Carrizo Sand aquifer wells. The average V activity for the Carrizo samples (log activity=-9.6) determines the redox boundaries, and average measured Eh (i.e., platinum electrode) were used to calculate sample Eh values. b) Predicted V species as a percent of total V concentration calculated using Geochemist's Workbench® Spec8. Only major species (>1% total V) are shown.

Fig 8. Vanadium concentrations versus chloride concentrations for the Oasis Valley-Beatty Wash groundwater.

Fig 9. Saturation Indices of selected minerals calculated using Spec8 program of Geochemist's Workbench®

	EROV1	EROV2	EROV3a3	EROV3a	Goss	EROV4a	Bailey's	Fran's	Coffer's	EROV3c
Distance (km)	0.00	5.71	10.02	10.02	10.99	16.02	13.2	17.51	1.66	5.25
Depth (m)	55	61	40.5	76.5	ND	46	ND	ND	ND	165
pH	8.30	8.21	8.26	8.17	8.20	8.38	7.86	8.25	8.25	8.29
Temp. (°C)	25.4	18.9	21.2	17.5	18.8	23.7	34.7	28.2	20.6	22.2
Cond. (µS/cm)	666	725	625	618	627	512	823	510	397	434
<i>mg kg⁻¹</i>										
DOC	0.20	0.10	0.20	ND	0.085 ± 0.021	0.10	0.20	ND	0.10	0.30
<i>mmol kg⁻¹</i>										
Alk. as HCO₃⁻	3.16	3.70	2.69	2.97	2.88	2.62	4.21	2.64	3.03	2.62
Cl	1.30	1.44	1.27	1.22	1.23	0.802	1.19	0.728	0.218	0.494
SO₄²⁻	0.870	0.917	0.845	0.792	0.793	0.624	1.21	0.684	0.321	0.452
Ca	0.156	0.357	0.332	0.354	0.409	0.216	0.387	0.176	0.478	0.376
Na	6.08	6.22	5.24	5.13	4.65	4.30	6.52	4.35	3.09	3.47
Mg	0.0030	0.025	0.045	0.042	0.048	0.0040	0.027	0.0040	0.008	0.016
K	0.176	0.147	0.171	0.132	0.128	0.200	0.192	0.067	0.026	0.032
Si	1.17	0.955	0.917	0.910	0.885	1.15	1.08	0.862	0.669	0.714
NO₃⁻	0.034	0.030	0.041	0.039	0.034	0.030	0.0090	0.010	0.044	0.022
DO	0.153	0.150	0.200	0.197	0.231	0.166	0.100	0.044	0.038	0.15
<i>nmol kg⁻¹</i>										
Al	1600 ± 300	140 ± 160	360 ± 370	350 ± 280	75 ± 41	250 ± 140	210 ± 150	140 ± 160	190 ± 170	220 ± 170
Mn	9.10	18.0	13.0	14.0	1.40	4.60	3.60	5.50	149	9.10
Fe	64.0	61.0	81.0	47.0	131	47.0	47.0	43.0	3460	41.0
V	34.8	30.2	53.0	58.0	45.5	73.3	41.2	35.5	21.8	50.2
As	85.8	69.7	106	117	98.2	195	246	316	112	133
U	36.7	77.6	35.9	34.8	39.3	11.6	41.3	24.6	23.9	17.2
W	4.76	3.48	3.97	8.40	2.83	9.33	15.0	8.70	8.05	9.85

Table 2. Field and ICP-MS measurements from Oasis Valley-Beatty Wash wells. Data are from Johannesson and Tang (2009) and Thomas et al. (2002).
ND = not determined

	RF-2	BCW-5	KS-1	N-3	G-1	Poteet	PCW-1	Peeler	AC74R-1	SMA74R-2
Distance (km)	0.500	4.29	7.40	9.37	12.8	14.5	26.1	41.1	59.0	65.8
Depth (m)	61	160	122	183	ND	290	488	655	1317	1420
pH	7.09	6.10	6.15	5.99	6.11	6.15	7.17	8.22	8.59	8.44
Temp. (°C)	24.00	24.19	23.54	25.68	25.79	27.94	33.98	26.99	42.01	41.82
Cond. (µS/cm)	755.0	326.9	323.2	340.4	283.9	393.3	596.4	579.5	943.7	1097.0
Eh (mV)	-26	145	187	116	76	94	-56	-172	-195	-194
<i>mg kg⁻¹</i>										
DOC	0.35 ^a	0.43 ^a	0.17	0.31	ND	0.82	0.26	0.19	0.65	0.28
<i>mmol kg⁻¹</i>										
Alk. as HCO₃⁻	2.72	0.22	0.86	0.54	0.78	0.68	3.14	3.52	4.64	5.48
Cl	ND	2.11	1.43	1.06	ND	1.44	0.87	0.37	1.23	1.78
SO₄²⁻	ND	0.72	0.27	0.22	ND	0.36	0.37	0.35	0.79	0.71
Ca	ND	1.35	0.63	0.38	ND	0.76	2.01	0.45	0.06	0.08
Na	ND	1.42	1.12	0.71	ND	1.16	1.15	3.96	8.74	10.2
Mg	ND	0.34	0.20	0.12	ND	0.23	0.33	0.36	0.010	0.010
K	ND	0.19	0.13	0.13	ND	0.20	0.14	0.15	0.050	0.060
Si	ND	ND	ND	0.29	ND	ND	0.23	ND	ND	ND
<i>µmol kg⁻¹</i>										
DO	8.75 ^a	8.13 ^a	11.30	123.00	4.69	8.75	16.4	6.25	5.63	4.06
Mn	0.800	1.02	0.200	0.750	0.590	1.70	3.83	2.90	0.450	1.00
Fe(II)	9.66	4.30	0.72	11.6	18.3	12.7	9.67	1.73	0.540	0.900
Fe(III)^b	1.43	0.720	0.180	0.900	1.79	2.33	1.43	4.72	0.360	0.00
Fe_T	11.1	5.02	0.900	12.5	20.1	15.0	11.1	6.45	0.900	0.900
S(-II)	0.18 ^c	0.62 ^c	0.18 ^c	0.62 ^c	0.62 ^c	0.09	0.62 ^c	0.34	7.6	62
<i>nmol kg⁻¹</i>										
V	2.00	0.761	0.305	0.244	0.209	0.235	0.194	0.188	0.242	0.193
As	2.19 ^a	2.08 ^a	0.970	2.44	2.47	2.33	0.370	0.910	0.410	1.92
U	1.12	0.03	0.32	0.012 ^c	0.02	0.012 ^c	0.02	0.012 ^c	0.012 ^c	0.012 ^c
<i>pmol kg⁻¹</i>										
W	78.7 ^a	9.46	3.64	16.3	18.1	1.9	27.4	246	780	1297

Table 3. Field and ICP-MS measurements for Carrizo wells. pH, temperature, Eh conductivity, alkalinity, iron, sulfide, uranium and vanadium measurements are from the most recent sampling campaign (March 2013).

Other major cation and DOC data are from Tang and Johannesson (2005), and dissolved oxygen, reported as DO, as well as As concentrations are from Haque and Johannesson, (2006). Tungsten concentrations are from Johannesson et al. (2013)

^a Data from adjacent wells

^b Determined by difference (Fe_T – Fe(II))

^c For samples measured below the detection limit the value is reported as $\frac{\text{detection limit}}{\sqrt{2}}$

ND = not determined

Fraction	V (mg kg⁻¹)	stdev (mg kg⁻¹)	U (mg kg⁻¹)	stdev (mg kg⁻¹)
Reducible (Bound to Fe oxides or sulphides)	4.19	0.37	0.64	0.09
Oxidizable (Bound to organic matter)	0.49	0.09	0.10	0.004
Total	4.02	0.19	1.98	0.08

Table 4. Results from sediment digestions. U concentrations are presented for comparison.

Reservoir	Concentration	Reference
Shallow groundwaters, Western France	$81 \pm 64 \text{ nmol kg}^{-1}$	Pourret et al., 2012
Italian groundwaters proximal to Mt. Etna	$726 \pm 533 \text{ nmol kg}^{-1}$	Minelli et al., 2000
SW of Buenos Aires Province, Argentina	$10760 \pm 6805 \text{ nmol kg}^{-1}$	Fiorentino et al., 2007
Salí River Basin, NW Argentina	$589\text{-}5889 \text{ nmol kg}^{-1}$	Nicolli et al., 2012
Average California groundwaters, USA	98 nmol kg^{-1}	Wright and Belitz, 2010
Median San Joaquín Valley, CA, USA	412 nmol kg^{-1}	Wright et al., 2014
Average Texas Gulf Coast groundwaters, USA	347 nmol kg^{-1}	Glenn and Lester, 2010
Average Oasis Valley, Nevada, USA	$44.4 \pm 15.0 \text{ nmol kg}^{-1}$	This study; Thomas et al., 2002
Average Carrizo, Texas, USA	$0.458 \pm 0.541 \text{ nmol kg}^{-1}$	This study
Concentration of Oasis Valley rocks	$18.1 \pm 13.5 \text{ mg kg}^{-1}$	Broxton et al., 1989
Concentration of Carrizo Sands sediment	$4.02 \pm 0.19 \text{ mg kg}^{-1}$	This study

Table 5. Comparison of V concentrations from previous investigations. Standard deviations are provided where full datasets are available

	RF-2	BCW-5	N-3	Poteet	PCW-1	Peeler	AC74R-1	SMA74R-2
Fraction bound to colloidal HA : VO	0.37	0.22	0.21	0.23	0.23	0.22	0.23	0.12
Fraction bound to colloidal HA: U(IV)	0.02	0.01	0.01	0.02	0.02	0.01	0.02	-
Fraction bound to colloidal FA : VO	0.63	0.78	0.79	0.77	0.77	0.78	0.77	0.88
Fraction bound to colloidal FA: U(IV)	0.98	0.99	0.99	0.98	0.98	0.98	0.98	100
Total organic-bound V(IV) (%)	100	100	100	100	100	100	100	100
Total organic-bound U(IV) (%)	100	100	100	100	100	99	100	100
Predicted V(IV) (nmol kg⁻¹)	1.2	0.080	0.011	0.0075	0.055	0.12	0.17	0.16

Table 6. Results from WHAM VII calculations showing the fraction of V bound to humic and fulvic acids. G-1 lacks DOC data and the calculated concentration of V(IV) for KS-1 is negligible. Speciation modeling of the thermodynamically stable U species predicts all U exists as U(IV). Therefore, U(IV) is used in WHAM VII calculations.