Vanadium: Global (bio)geochemistry

Jen-How Huang, Fang Huang, Les Evans, Susan Glasauer

School of Environmental Sciences, University of Guelph, Guelph, ON N1G 2W1, Canada
CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, USTC, Hefei, Anhui 230026, China
Environmental Geosciences, University of Basel, CH4056 Basel, Switzerland

ABSTRACT

Redox-sensitive transition group elements are involved in almost all fundamental geochemical processes. Of these elements, vanadium (V) contributes a particularly powerful tool to decipher the Earth’s history and its link to extraterrestrial bodies. A comprehensive view of V includes the formation and interaction between the Earth’s interior layers, the evolution of the Earth’s surface to a habitable zone, biogeochemical cycling, and anthropogenic impacts on the environment. Tracing the geochemical behavior of V through the Earth’s compartments reveals critical connections between almost all disciplines of Earth sciences. Vanadium has a history of application as a redox tracer to address the early accretion history of the Earth, to identify connections between the mantle and crust by subduction and melting, and to interpret past surface environments. The geochemical cycling of V from the deep Earth to the surface occurs through magmatism, weathering and digenesis, reflecting variations of fO2 and V species in different Earth compartments. Minerals form a link between deep Earth reservoirs of vanadium and surface environments, and the study of V in minerals has increased the understanding of V cycling. Finally, the exploitation of V has been increasing since the Industrial Revolution, and significant amounts of V have been released as a consequence into natural systems. Environmental concerns are promoting new areas of research to focus on V cycling between water, air, soil and sediment compartments. An increased understanding of V in all compartments, and knowledge of the processes that connect the compartments, is vital to tracing the fate of this intriguing element in natural systems.

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019

Contents

1. Introduction .................................................. 69
2. Vanadium geochemistry in terrestrial earth and planetary systems ........................................... 69
   2.1. Vanadium distribution in the Earth and in extraterrestrial materials ........................................ 69
      2.1.1. Meteorite, bulk earth, and moon .................................................. 69
      2.1.2. Mantle and crust .................................................. 69
   2.2. Partitioning of vanadium during magmatism .................................................. 71
      2.2.1. Valences and coordination of vanadium in melts and minerals ........................................ 71
      2.2.2. Partitioning of vanadium between metallic and silicate melts ........................................ 72
      2.2.3. Partitioning of vanadium between minerals and silicate melts ........................................ 72
   2.3. Temporal and spatial variation of mantle fO2 constrained by vanadium .................................... 72
   2.4. Vanadium isotopes .................................................. 73
3. Occurrence of vanadium in minerals .................................................. 73
   3.1. Vanadium associated with primary rocks and minerals .................................................. 73
   3.2. Weathering and diagenesis of secondary vanadium in minerals and fossil fuels ............................. 73
4. Cycling and transport of vanadium in surface environments .................................................. 75
   4.1. Aqueous speciation chemistry of vanadium .................................................. 75
      4.1.1. 4.1.2. The role of complexation in V mobilization .................................................. 75
      4.1.2. Vanadium redox transformation in surface environments .................................................. 76
   4.2. Microbial controls on V geochemistry: redox, complexation, and sorption reactions ............................ 77

* Corresponding author.
E-mail address: jen-how.huang@unibas.ch (J.-H. Huang).

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1. Introduction

Vanadium is increasingly applied to studies of almost all fundamental geochemistry disciplines. Research on V geochemistry has, however, lagged behind that for other transition metals. This is the first comprehensive review that addresses the geochemical behavior of V under dramatically different conditions, from the terrestrial Earth to other rocky planets, from magmatic to environmental studies, and from partitioning at high temperature to speciation in hydrous systems. Such a holistic approach is vital to link chemical reservoirs to the evolution of the bulk Earth. Vanadium is widely distributed in igneous and sedimentary rocks and minerals as a mildly incompatible, refractory, lithophilic element. The average crustal abundance of V is similar to that of Zn and Ni (Reimann and Caritat, 1998) although it is more dispersed in the mantle. The average crustal abundance of V is similar to that of Zn and Ni (Reimann and Caritat, 1998) although it is more dispersed in the mantle. The average crustal abundance of V is similar to that of Zn and Ni (Reimann and Caritat, 1998) although it is more dispersed in the mantle.

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2. Vanadium geochemistry in terrestrial earth and planetary systems

2.1. Vanadium distribution in the Earth and in extraterrestrial materials

Knowing the V composition of the major geochemical reservoirs is critical for understanding the geochemical behavior of V in terrestrial magmatism, and for applying V to constrain fundamental processes of the Earth. Such processes include, but are not limited to, core segregation, mantle and atmospheric evolution, and the development of ore deposits.

2.1.1. Meteorite, bulk earth, and moon

The starting point for V on Earth is accretion and core formation. A comparison of the V content between CI chondrites and the Earth provides important constraints on both processes. CI chondrites are considered to represent the primitive undifferentiated materials in the solar system and are likely the most important building blocks from which the Earth was formed (McDonough and Sun, 1995; Palme and O’Neill, 2003; Sun and McDonough, 1989). The average V contents of CI chondrites estimated in a few studies are quite consistent, ranging from 55 to 56.5 mg kg\(^{-1}\) (Anders and Grevesse, 1989; McDonough and Sun, 1995; Palme, 1988; Wasson and Kallemeyn, 1988). These values are lower than the average V contents of the silicate earth (82 mg kg\(^{-1}\)) estimated in McDonough and Sun (1995) because V is more depleted in Ca-Al-rich inclusions than are Al and rare earth elements. The bulk V in the CI chondrite is consequently diluted.

The bulk Earth has a V content of 95 mg kg\(^{-1}\), lower than that in the metallic core (120 mg kg\(^{-1}\)) (McDonough and Sun, 1995). The ratio of the V content between silicate Earth (or primitive mantle) and CI chondrite normalized to Mg content is 0.62 (McDonough and Sun, 1995), showing a terrestrial depletion. Numerous studies have demonstrated that V depletion is best explained by the preferential partitioning of V into the metallic core at high pressure and low O\(_2\) during the “deep magma ocean” process (Gessmann and Rubie, 1998; McDonough and Sun, 1995; Palme and O’Neill, 2003; Ringwood et al., 1996; Wänke and Dreibus, 1986). Simple mass-balance calculations show that the core could contain half of the total V budget of the bulk earth (McDonough, 2003). The Moon mantle is depleted in V, as well as in Cr and Mn, similar to the Earth’s mantle (Ringwood, 1966; Ringwood et al., 1991). This implies that the Moon was most likely derived from the mantle of the Earth or from an impactor larger than Mars that experienced V depletion due to core forming processes (Drake et al., 1989; Gessmann and Rubie, 2000; Ringwood et al., 1991).

2.1.2. Mantle and crust

Post-accretion processes have led to distinct signatures of V in the mantle and crust. Vanadium contents in peridotites range from a few mg kg\(^{-1}\) to around 100 mg kg\(^{-1}\), substantially lower than the concentration in mid-ocean ridge basalts (MORB), ocean island basalts (OIB), and island arc basalts (IAB) (Fig. 2). This indicates that V is mildly incompatible during mantle partial melting. Clinopyroxene, garnet, and spinel are the main hosts for V in mantle peridotite (Johnson et al., 1990). Because the valence of V is sensitive to O\(_2\), peridotites from different tectonic settings show variable V contents and correlations with other major trace elements, providing an important tool to constrain O\(_2\) of the mantle through the Earth’s history (Canil, 2002; Canil, 2004). A summary of 6590 basalts samples from spreading centers shows large variations, from less than 100 mg kg\(^{-1}\) to 800 mg kg\(^{-1}\), and gives an average V composition of ~275 mg kg\(^{-1}\) (data from http://www.petdb.org/). Similar ranges are also observed in OIB and IAB (see Mallmann and O’Neill, 2009) for a recent summary) and reflect the effect of source composition, melting degree, and melting style.

Trace element compositions for continental crust can be estimated via weighted averages of a large number of representative rock units.
exposed in the crustal surface, or measured on fine-grained sediments or sedimentary rocks such as shale, loess, and tillite (Clarke, 1889; Condie, 1993; Gao et al., 1998a; Gao et al., 1998b; Rudnick and Gao, 2003; Taylor and McLennan, 1995). As summarized in Rudnick and Gao (2003), V contents in the bulk continental crust estimated in previous works vary substantially from 96 to 230 mg kg\(^{-1}\) (Condie, 1993; Gao et al., 1998b; Rudnick and Gao, 2003; Taylor and McLennan, 1981; Taylor and McLennan, 1995). Such discrepancy could reflect regional chemical heterogeneity in the continental crust, inaccuracy of the estimating methods involving data quality and unrepresentative samples, or proportions of mafic lower crust versus felsic upper crust applied to calculate the bulk value. Nonetheless, it is generally agreed that the lower crust (196 mg kg\(^{-1}\)) has a V content within the range of mantle-derived basalts, but substantially higher than the primitive mantle (82 mg kg\(^{-1}\)), the middle crust (107 mg kg\(^{-1}\)) and the upper crust (97 mg kg\(^{-1}\)) (McDonough and Sun, 1995; Rudnick and Gao, 2003) (Fig. 2). If the upper continental crust was essentially formed by extracting felsic melt from mafic sources (lower continental crust or subducted oceanic crust), or by intra-crustal differentiation, then V as well as Sc and Cr are compatible during the igneous processes forming the upper crust.

Average V content of the juvenile upper continental crust was estimated by the map model by which the proportions of rocks were determined by geological maps and stratigraphic successions (Condie, 1993). It increases with time from 70 to 73 mg kg\(^{-1}\) (pre-Archean) to 91–106 mg kg\(^{-1}\) (post-Archean), and shows negative correlations...
with Cr and Gd/Yb (Fig. 3). In contrast to V, the MgO, Cr, and Ni contents decrease dramatically from Archean upper continental crust to the Phanerozoic crust. Such variations may reflect the fundamental change with time in growth mechanism of the felsic upper continental crust. It has been proposed that the subducted hot oceanic crust (MORB composition) could be partially melted because of the larger geothermal gradient of the Earth during the Archean (2.5–3.8 Ga) (Boehler, 2000). The melts could interact with the mantle wedge, producing tonalite–trondhjemite–granodiorite (TTG) suites with high Mg and Cr contents; in contrast, post-Archean juvenile upper continental crust grew mainly via intra-crustal differentiation of basaltic and andesitic rocks, followed by extraction of granitic melts without significant interaction with the upper mantle (e.g. (Taylor and McLennan, 1981; Taylor and McLennan, 1985; Taylor and McLennan, 1995)). Because fO2 is not well constrained during crustal differentiation, it is not clear whether variations of residual mineral phases in magma played a dominant role in producing the higher V content in the post-Archean upper crust. In essence, the question remains: is the temporal increase in V content a consequence of increasing fO2 during magma evolution? Or does it reveal changes in temperature-pressure conditions for continental growth from Archean to Phanerozoic?

2.2. Partitioning of vanadium during magmatism

A fO2-sensitive element can be exploited to estimate the oxidation states in magmatic processes such as partial melting, magma differentiation, and core formation. Vanadium is an important element for this application because it has more valence states in natural materials than many other multi-valence elements. In the following, the chemical partitioning of V during deep processes is summarized. The mineralogy of V is further discussed in Section 3.

2.2.1. Valences and coordination of vanadium in melts and minerals

In oxides, silicate minerals, and melts, V exists as +2, +3, +4, and +5 (Shearer et al., 2006a; Sutton et al., 2005), and a large amount of V enters the metallic core as V⁰ (McDonough, 2003; McDonough and Sun, 1995). Using V K-edge X-ray absorption near edge spectroscopy (XANES), Sutton et al. (2005) determined the valence of V in natural and synthetic basalt glasses and developed a microscale oxybarometer to study the variation of fO2 in the melting and evolution of the Earth and its moon, and Mars. Application of this method revealed that fO2 varies from log IW -1.6 in lunar glasses to log IW + 4.0 in terrestrial glasses by at least 6 log units (Karner, 2006; Sutton et al., 2005).

Fig. 2. Correlations of V contents with SiO₂ and Sc in geochemical endmembers. PM, primitive mantle; UCC, upper continental crust; MCC, middle continental crust; LCC, lower continental crust; BCC, bulk continental crust; N-MORB, normal mid-ocean ridge basalts. Data source: crust, data Rudnick and Gao (2003); PM, Sun and McDonough (1989); N-MORB, http://www.petdb.org/.

Fig. 3. Variations of V, Cr, and Gd/Yb of continental crust with time showing decreasing contribution of mantle materials to the continental crust. Data are from Condie (1993).
Vanadium is dominantly V(IV) in terrestrial melts, V(III) in lunar melts, and a mixture of V(III) and V(IV) in Martian melts; glasses synthesized in air contain V(V) (Karner, 2006). In minerals, V also exists as a mixture of all valence states with their proportions varying as a function of fO2. For instance, a XANES study on natural titanomagnetite from a layered mafic intrusion show that V in magnetite is mostly V(III) with minor V(IV) occupying octahedral sites in the spinel structure (Balan et al., 2006).

2.2.2. Partitioning of vanadium between metallic and silicate melts

In order to more effectively use V to constrain redox variation in high-temperature planetary processes, it is critical to understand the partitioning of V between different phases at varying fO2. Several experimental studies have been performed to study the partitioning of V between silicate melt and metallic melt (Metallic/silicate D) to constrain the fO2 variation in the mantle during core formation (Drake et al., 1989; Frost et al., 2008; Mann et al., 2009; Wade and Wood, 2005; Wood, 2008; Wood et al., 2008). Metallic/silicate D and Metallic/silicate Dc may not be sensitive to silicate melt composition, but decrease dramatically with increasing fO2 and Si content in the metallic melt (Tuff et al., 2011; Wood, 2008). Wade and Wood (2005) estimated that core/mantle Dc ranges from 1.5–2.2, similar to the values reported in McDonough (2003). To reconcile the depletion of V in the silicate earth mentioned earlier with the lithophile tendency of V, high temperature with a fixed fO2 (and iron oxide in the mantle) or a continuously increasing fO2 is required during core segregation (Frost et al., 2008; Wade and Wood, 2005; Wood, 2008), while a recent experiment study in the effect of oxygen content in the core on core/mantle Dc also suggests accretion of the core under oxidizing conditions (Frost et al., 2008; Wade and Wood, 2005). The model of high temperature with a fixed fO2 can be excluded because the temperature required for an appropriate metallic/silicate Dc is too high, and is unrealistic for the base of a magma ocean (Frost et al., 2008; Wade and Wood, 2005). However, it is still an open question whether the terrestrial accretion occurred under reducing conditions, where fO2 in the silicate materials was coupled with iron oxide content due to oxidation in the late stage of the accretion process (Frost et al., 2008; Tuff et al., 2011; Wade and Wood, 2005; Wood, 2008), or under oxidizing conditions where the core has higher oxygen content than previously believed (Siebert et al., 2013).

2.2.3. Partitioning of vanadium between minerals and silicate melts

Mineral/melt Dc has been intensively investigated, with a special focus on the role of fO2 in changing the valence and thereby the partitioning of V at high temperature. Numerous experimental studies clearly show that Mineral/melt Dc is dominantly controlled by fO2. Oxygen fugacity controls valence states, coordination numbers, and incorporation mechanism of V in both melts and minerals (Karner et al., 2006; Mallmann and O’Neill, 2009; Righter et al., 2006; Righter et al., 2011; Shearer et al., 2006a; Shearer et al., 2006b). Furthermore, the addition of other high valence cations (such as Fe3+ and Ti4+) into the silicate melt can also change the coordination environment of V, and thus its partitioning between minerals and melt (Giuli et al., 2004). There is still, however, a lack of studies that quantify the effect of Fe2+, Ti4+, and H2O on mineral/melt Dc and on other single valent elements (such as Sc and Ga). This may add uncertainty to interpreting the similarity of V/Sc and V/Ga among the arc lavas, OIB, and MORB. Under the P-T-fO2 conditions of the upper mantle, mineral/melt Dc generally decreases in the order of spinel, amphibole, clinopyroxene, garnet, orthopyroxene, and olivine (Adam and Green, 2006; Canil, 1999; Canil, 2004; Karner et al., 2006; Karner et al., 2008; Mallmann and O’Neill, 2009; Righter et al., 2006; Righter et al., 2011). Olivine/melt Dc and orthopyroxene/melt Dc decrease dramatically from > 1 to < 0.01 with increasing valence state from +2 to +5, while V(III) is more compatible than V(II) and V(V) in clinopyroxene (Karner et al., 2008; Mallmann and O’Neill, 2009). Because most minerals are solid solutions with significant variation in chemical composition, crystal chemistry could play an important role in controlling the valence state and thus the partition coefficients of V. Experimental studies on Martian basalt systems show that augite/melt Dc is greater than pigeonite/melt Dc at the same fO2 because the higher Al and Na content in augite facilitate the coupled substitution of V(III) and V(IV) into the augite structure (Karner et al., 2008). Nonetheless, it is increasingly accepted that V is compatible during mantle melting only in extremely reduced environments (Δlog fO2(FMQ)–3), while it is incompatible or lithophilic (rock-loving) during magmatism at the crustal conditions, consistent with the lower V content in mantle peridotites than in basalts (e.g., (Canil, 1999; Canil, 2002; Lee, 2005; Mallmann and O’Neill, 2009). It is notable that V is compatible during generation of the felsic melt, assuming a mafic derivative of the upper continental crust as discussed earlier. This could be a sequence of V partitioning between the dominant residual phases (including garnet, clinopyroxene, and amphibole) and highly polymerized melt.

2.3. Temporal and spatial variation of mantle fO2 constrained by vanadium

Temporal variation of the mantle fO2 from Archean to Cenozoic provides important constraints on Earth’s evolution and interactions among the mantle, crust, hydrosphere, and atmosphere. The V content of peridotites is commonly correlated with major elements such as MgO and Al2O3, likely reflecting the influence of partial melting (Canil, 2002; Canil, 2004). The content of V in igneous rocks is generally correlated with magma differentiation indicators. Vanadium may be affected by the fractional crystallization of mafic minerals because it is compatible in clinopyroxene with fO2 near the fayalite-magnetite-quartz buffer (Canil, 2004; Karner et al., 2006). The ratios of V to single valent elements (such as Sc, Y, Ga, and Ti) are, however, less sensitive to magmatic differentiation or to the source heterogeneity of basalts. Such ratios could, therefore, be used to filter out the effect of differentiation and source to address the fO2 of the mantle source of mid-ocean ridge basalts (MORBs), ocean island basalts (OIBs), and island arc basalts (IABs) (Canil, 2002; Lee, 2005; Li and Lee, 2004; Mallmann and O’Neill, 2009). A careful examination of different trends between V and Al2O3 in peridotites from variable tectonic settings reveals that abyssal peridotites were formed under a similar fO2 to the MORB, but slightly lower than that of the spinel-facies Archean cratonic lithosphere (Canil, 2002). Furthermore, Canil (2002) argued that the Archean mantle may have had similar fO2 to the modern mantle, and thus gradual oxygenation of the Earth’s atmosphere does not hinge on mantle melting. The lack of temporal variation in fO2 for the mantle since the Archean is also supported by the similar V/Sc between Archean basalts (up to 3.5 Ga) and modern MORB (6.34 ± 0.62 vs. 6.74 ± 1.11, 1σ) (Li and Lee, 2004).

Comparing V/Sc between mantle sources from different tectonic settings also provides a tool to address spatial variation of the mantle fO2 (Lee, 2005; Li and Lee, 2004; Mallmann and O’Neill, 2009). Based on the observation that arc basalts have V/Sc that is indistinguishable from MORB (Lee, 2005; Li and Lee, 2004), some authors suggest that the fO2 of the mantle wedge is at the same level as the MORB source (~FMQ). This conclusion seems to contradict the observation that the primitive basalts and spinel peridotites from variable arcs have slightly higher Fe3+/Fe2+ and thus higher fO2 than MORB and its mantle sources, respectively (Ballhaus, 1993; Kelley and Cottrell, 2009; Macdonald et al., 2000; Parkinson et al., 2007). Studies on the V/Sc in the ophiolite peridotites from Alaska, Yukon and British Columbia also suggest a narrow fO2 range between NNO and NNO-1 during melting, slightly higher than the MORB mantle (Canil et al., 2006). More complications are brought by almost identical Zn/Fe between MORB and primitive arc lavas (Lee et al., 2010), and slightly lower 56Fe in arc lavas than in MORB (Dauphas et al., 2009); this does not support the higher fO2 in the source of arc lavas relative to the MORB source if both have similar initial Zn/Fe and 56Fe. Reconciling such discrepancies is challenging.
Nonetheless, future experimental studies on the partitioning of V between mantle minerals and hydrous melt under variable O₂ and P-T conditions similar to the arc systems would be helpful to address the implications of V and other elemental data in MORB and arc lavas.

2.4. Vanadium isotopes

\(^{50}\text{V}\) and \(^{51}\text{V}\) are the two most common stable isotopes of vanadium, with atomic abundances of 0.25% and 99.75%, respectively. Pioneering studies on vanadium isotopic composition in meteorites and Earth samples, using an Atlas CH-4 mass spectrometer, indicate that meteoritic and terrestrial materials have similar \(^{50}\text{V}/^{51}\text{V}\), with an error of 1%; this suggests that there is no significant difference in irradiation histories during early accretion and evolution of the solar system (Balsiger et al., 1969; Balsiger et al., 1976; Pelly et al., 1970). Such an error does not allow V isotopes to be regularly applied in geochemical studies. The main obstacles to measuring V isotopes are the weak signal of \(^{50}\text{V}\) relative to \(^{51}\text{V}\) in geological samples, and chemical separation of V from matrix elements such as Cr and Ti. The use of multi-collector inductively coupled plasma-mass spectrometry and optimized chemical separation procedure dramatically improved the external precision of V isotope analysis of terrestrial samples by two orders of magnitude, i.e., 0.10% (Nielsen et al., 2011; Prytulak et al., 2011). Taking VISSOX (Vanadium Isotope Standard Solution Oxford) as the international V isotope standard, the Oxford Group observed substantial iso- tope fractionation in meteorites and in terrestrial materials. For example, \(^{50}\text{V}\) of the Allende chondrite is 1.78%, whereas USGS whole rock standards range from 0.55 (AGV-2) to 1.04% (BHVO-2) (Nielsen et al., 2011; Prytulak et al., 2011). Further studies revealed V isotope fractionation in more terrestrial and meteorite samples (Nielsen et al., 2011; Prytulak et al., 2011). Recently, first-principles calculations predicted that V isotopes can be substantially fractionated among V species with different valences in aqueous systems and during adsorption of V(V) to goethite (Wu et al., 2015). These studies indicate a promising future for the application of V isotopes to a variety of fundamental questions, from high temperature magmatism to low temperature environmental sciences.

3. Occurrence of vanadium in minerals

Minerals link V circulating in the Earth’s interior to weathering and biogeochemical processes at the surface. Vanadium typically occurs as an accessory component of minerals. This can be attributed to the relatively low concentration of V in the Earth’s crust, and the tendency of V to disperse due to its sensitive response to acidity and oxygen. The size and charge of V species enable it to substitute for common transition elements, e.g., Fe and Al in primary and secondary minerals. Vanadium mineral classes, encompassing primary and secondary minerals, include oxides and hydroxides, silicates, and relatively rare sulfides; the coordination of V in minerals can be tetrahedral, pyramidal, or octahedral. There is relatively little information available on the diverse V minerals, which likely reflects their rarity, in spite of the ubiquitous presence of V in geological materials. The review by Evans and White (1987) gives an excellent introduction to “the colorful vanadium minerals”. In the following section, we focus on minerals that contain V as a significant constituent, including important primary and secondary ore minerals.

3.1. Vanadium associated with primary rocks and minerals

Because V readily substitutes for Fe in minerals, it is more abundant in mafic than in felsic rocks. Trivalent cationic V is a common lattice component of primary minerals (Hurlbut and Klein, 1977). Typical concentrations in basalts and gabbros range from 200 to 300 mg kg⁻¹, compared to concentrations in granites from 5 to 80 mg kg⁻¹ (Nriagu, 1998). Titaniferous magnetite is the principle source of mined V, which is produced primarily as a byproduct of iron and titanium mining. As mentioned, V occurs in magnetite mostly as V(III), with minor V(IV) occupying octahedral sites (Balan et al., 2006). Titaniferous magnetite is commonly associated with layered mafic intrusions such as the Bushveld Igneous Complex in South Africa, one of the largest mafic intrusions in the world. The Panzhihua vanadium-titanium-iron ore deposit in Southwest China is hosted as layers or lenses in a gabbroic layered intrusion in the Emeishan Large Igneous Province (Zhong and Zhu, 2006; Zhou, 2005), and large deposits of V occur in the titaniferous magnetite deposits of Quebec (Kish, 1972). There is still debate about the formation of the ore deposits associated with mafic intrusions. It is unclear whether the V-rich magnetite was formed from immiscible Fe-Ti oxide liquid at the late-stage of tholeiitic magma differentiation (e.g., Reynolds, 1985; Ripley et al., 1998; Zhou, 2005) or whether the titanio-magnetite accumulation was formed via crystallization as a liquidus phase (Pang et al., 2008). The predominance of V(III) in vanadiferous titanomagnetite, with up to 10% V(IV), has been established using X-ray absorption spectroscopy (XANES) (Table 1). Montroseite [VO(OH)] is a primary V(III) ore mineral first observed in the western U.S. (Weeks et al., 1950), where it is the likely source of V for associated oxidized minerals (Evans and Garrels, 1958; Weeks, 1961), discussed in the next section.

Vanadate [V(V)] ore minerals are associated with low-temperature, non-sulfidic mineralization in parts of southern Africa, including Namibia (Bonì et al., 2007), Zambia (Pelletier, 1930) and Angola (Millman, 1960). The vanadate ore deposits located in the Otavi Mountainland, Namibia occur in fractures within host dolomite and were formed by precipitation from vanadate-bearing solutions circulating through karst bodies (Bonì et al., 2007). Minerals include mottramite [PbCu(VO₄)(OH)], desclozite [(Pb, Zn)₂VO₄(OH)] and vanadinite [Pb₅(VO₄)₃Cl]. These relatively rare minerals are thought to have formed during the mid-Miocene, when the climate became drier and chemical weathering was subsequently limited in southern Africa (Bonì et al., 2007). The deposits, now mined out, once contained several million tons of extractable V ore.

3.2. Weathering and diageneis of secondary vanadium in minerals and fossil fuels

Weathering, transport, sedimentation, and diageneis processes mobilize V from high temperature magmatic and metamorphic rocks to form low temperature sedimentary rocks. The diverse mineralogy and wide range of environments where V-bearing secondary minerals occur reflect the complexity of V chemistry (Clark, 1993; Fleischer, 1987). The redox weathering of primary reduced V and U minerals (e.g., montroseite, uraninite) has led to extensive tabular and roll front deposits of uranyl vanadate minerals such as carnotite (K₂(VO₂)₂(VO₄)₂·3H₂O) and related carnotite group minerals such as tvuyumunite (Ca-variant) in the Colorado Plateau (Weeks, 1961). Cycles of reduction and oxidation fueled by organic matter likely transformed the source minerals over time into the diverse mineral assemblages that currently exist (Hansley and Spirakis, 1992; Spirakis, 1996). Minerals in the Colorado Plateau encompass V in +3, +4 and +5 valence states and reflect a wide range of reduction potentials and pH values during formation (Evans and Garrels, 1958). Where oxygen exposure was low and the pH was neutral, partly oxidized minerals such as duttonite [VO(OH)₂] and simplotite [Ca(V₃O₈)(VO₄)·5H₂O] resulted (Roach and Thompson, 1959). More intensive weathering that leads to higher acidity and oxidizing conditions resulted in minerals such as carnotite and hewettite [Ca₅(V₂O₈)₃·6H₂O] (Elston and Botinelly, 1959; Roach and Thompson, 1959). The role of microorganisms in forming these V mineral deposits is discussed in Section 4.2.

Vanadium incorporates in the structure of secondary minerals such as clays (micas, smectites, illite, kaolinite, and chlorite), Fe-Mn hydrous oxides, and organic rich facies during diageneis, metamorphism, and
hydrous thermal processes (Algeo and Maynard, 2008; Brumsack, 2006; Condie, 1993; Morford et al., 2005). In clay minerals, V(IV) substitutes for Al(III) in the octahedral sheet as \( \text{VO}_2^+ \) (Gehring et al., 1993). Structural similarities between Fe and V oxides have suggested the substitution of V(III) for Fe(III) in Fe-oxides (Taylor and Giles, 1970), and it was subsequently shown that V can replace octahedrally coordinated Fe(III) in the diaspore structure of goethite (Schwertmann and Pfaff, 1994; Schwertmann and Pfab, 1996). The incorporation of reduced V species (III, IV) in clays and other secondary minerals provides a useful redox indicator for past anoxic conditions (Gehring et al., 1994; Gehring et al., 1999; Lebedel et al., 2013).

Crude oil can contain high concentrations of V due to the sorption or uptake of V by algae, plankton and plants and incorporation into porphyrin groups (e.g., chlorophyll). The organic matter settles in basins where degradation takes place, causing anoxic conditions to develop. Decomposition of organic matter and diagenetic processes tend to concentrate trace elements in these materials, leading to an enrichment of V that can be diagnostic for the depositional environment and facilitates identification of the source rock (Barwise, 1990).

In oil, V tends to concentrate in the heavy crude fractions, an association that is enhanced in the presence of reduced sulfur species (Punanova, 2014). Vanadium is commonly one of the most abundant metal elements in crude oil deposits (up to around 1200 mg L\(^{-1}\)) (López and Lo Mónaco, 2004). Asphaltenes in crude oil contain up to 5000 mg L\(^{-1}\) V (López et al., 1995). Barwise (1990) developed a classification scheme which relates the Ni/V ratio to the depositional environment; Ni is also an abundant metal in petroleum. The environments identified by Barwise (1990) for organic matter accumulation leading to oil genesis are marine (Ni/V < 0.5) and lacustrine or terrestrial (Ni/V > 10); however, the typically poor preservation of the organic groups that contain Ni and V in terrestrial deposits generally excludes these materials from the classification (Barwise, 1990). Classification by Ni/V ratios has been used widely to distinguish sources of crude oil (Jia et al., 2012; Shafer et al., 2012); however, the typically poor preservation of the organic groups that contain Ni and V in terrestrial deposits generally excludes these materials from the classification (Barwise, 1990).

Vanadium in coal is generally considered a trace element, due to concentrations that are typically less than 100 mg kg\(^{-1}\) (Sia and Abdullah, 2011). Coal may contain up to 70% (by volume) of non-carbonaceous materials, which are often aluminosilicate minerals such as clays, or carbonates. Vanadium appears to be located preferentially as clays, or carbonates. Vanadium appears to be located preferentially as clays, or carbonates. Vanadium appears to be located preferentially in association with clay minerals (Chen et al., 2011; Huggins et al., 2009; Sia and Abdullah, 2011; Wang et al., 2008). For example, in one study of coal (Illinois #6), the estimated V content of associated illite was 420 mg kg\(^{-1}\), whereas the organic fraction contained around 20 mg kg\(^{-1}\) V (Huggins et al., 2009).

Shales containing high amounts of organic matter, known as black or carbonaceous shales, are typically enriched in V relative to "average"
shale as well as containing relatively high total sulfur (Lipinski et al., 2003). Carbonaceous shales can contain up to 16,000 mg kg$^{-1}$ (Michibata et al., 1991; Vine and Tourtelo, 1970) compared to non-carbonaceous shales that average 130 mg kg$^{-1}$ (Turekian and Wedepohl, 1961). As observed for coal, V in shale associates preferentially with the clay minerals (e.g., Peacor et al. (2000) and Lipinski et al. (2003)). In one recent study, soils developed on V-enriched black shale were shown to retain the signature of high V concentration, and V in the soil was distributed more homogeneously than in the parent rock; the fresh shale had V concentrations ranging from 225 to 5162 mg kg$^{-1}$, and the soils from 187 to 442 mg kg$^{-1}$ (Xu et al., 2013). The difference between the unweathered and weathered material was attributed to a two-stage differentiation process: 1) chemical differentiation, largely by leaching of more mobile chemical components, and 2) chemical homogenization, which includes hydrolysis of resistant silicate minerals as well as continued preferential leaching of some elements (Xu et al., 2013).

4. Cycling and transport of vanadium in surface environments

Although many minerals can be enriched in V, the processes that control the release and mobilization of V in weathering environments have been much less studied as compared to other trace element e.g. As and Hg (Huang, 2014; Selin, 2009; Smedley and Kinniburgh, 2002). The diverse pools of V found in Earth surface environments reflect conditions of redox, pH, concentration and complexation that shed light on geochemical and biogeochemical processes that link the reservoirs of V (Fig. 4, Table 1). The following sections address V chemistry and biochemistry in the context of Earth surface environments.

4.1. Aqueous speciation chemistry of vanadium

The chemical behavior of V in water controls the biogeochemical cycling of V in surface environments. Vanadium speciation is a complex function of pH, Eh, concentration, solution chemistry and, in many surface environments, biology. Vanadium exists in the +3, +4 and +5 oxidation states in natural waters. Vanadate species [V(V)] are thermodynamically stable in oxic conditions, while V(IV) is stable under suboxic conditions, and V(III) is found in anoxic environments (Sadiq, 1988); redox chemistry is discussed in more detail in Section 4.4.3. Aqueous V species in natural systems occur mainly as V(V) and V(IV), as shown using different chemical and spectroscopic speciation methods (Table 1; Alcalde-Isorna et al., 2011; Aureli et al., 2008; Colina et al., 2005; Jia et al., 2012; Li et al., 2007; Wang and Sanudo Wilhelmy, 2009b; Wann and Jiang, 1997; Wu et al., 2005; Xiong et al., 2010; Zhao et al., 2006).

Vanadium speciation is a strong function of concentration and pH. Five V(V) species have been reported: the pervanadyl ion, VO$_2^+$, vanadic acid, H$_3$VO$_4$ and its three conjugate bases, H$_2$VO$_4^−$, HVO$_4^{2−}$ and VO$_4^{3−}$ (Table 2). Unless otherwise indicated, all the thermodynamic data used in the following Tables are derived from the NIST data base (Martell and Smith, 2004) and recalculated, if necessary, to zero ionic strength (Verweij, 2013). The mass action and mass balance equations used to generate the Figures from these Tables were solved using the computer program MICROQl (Westall, 1979), rewritten in Visual Basic Version 6.1 by one of the authors (L.E.).

In dilute solutions at neutral pH, the dominant species of V(V) are the phosphate-like mononuclear vanadate oxyanions H$_n$VO$_4^{n−}$ (Wanty and Goldhaber, 1992; Wehrli and Stumm, 1989). The species VO$_2^+$ dominates under acidic conditions, and VO$_4^{3−}$ occurs in extremely alkaline conditions (Fig. 5). Vanadic acid, H$_3$VO$_4$, is a minor constituent within the pH range 2–5. Vanadium has a notable tendency to polymerize, forming species containing up to 10 atoms of V (Wanyt and Goldhaber, 1992; Wehrli and Stumm, 1989). The species VO$_2^+$ dominates under acidic conditions, and VO$_4^{3−}$ occurs in extremely alkaline conditions (Fig. 5).

Vanadyl ion, H$_2$VO$_2^+$, is a minor constituent within the pH range 2–5. Vanadium has a notable tendency to polymerize, forming species containing up to 10 atoms of V (Wanyt and Goldhaber, 1992). Polynuclear species have enhanced stability, as shown using reaction enthalpy for V$_4^-$ and V$_7$ cyclic species (McCann et al., 2013). Eleven soluble poly-nuclear species have been reported by Petterson et al. (1983) and fourteen are listed in Martell and Smith (2004) containing 2, 3, 4, 5, 6 or 10 atoms of vanadium (Table 2). The speciation of V(V) at 0.5 mM concentration
is illustrated using the formation constants given in Elvingson et al. (1996) (Table 3, Fig. 6).

Vanadium(IV) is prevalent in reduced groundwater (Bosque-Sendra et al., 1998; Hirayama et al., 1992; Nakano et al., 1990) and in water influenced by volcanic (Minelli et al., 2000) and industrial activities (Banerjee et al., 2003). Under moderately reducing and acidic conditions, V(IV) is strongly influenced by its associated complexes with organic and inorganic cations (Wanty and Goldhaber, 1992) (Table 4), which is further discussed in Section 4.1.2.

Vanadium(III) is thermodynamically stable over a wide range of pH values in anoxic environments (Wright and Belitz, 2010). It hydrolyzes rapidly in aqueous solution as VOH₂⁺, V(OH)₂⁺ (Pajdowski, 1966; Pajdowski and Ježowska-Trzebiatowska, 1966) and readily precipitates as insoluble V(III) oxyhydroxides (Wanty and Goldhaber, 1992). Because of its sensitivity to oxygen, V(III) species are relatively rare in surface and near-surface waters (Aureli et al., 2008; Wållstedt et al., 2010; Wang and Sañudo Wilhelmy, 2009b) (Table 1).

4.1.2. Vanadium redox transformation in surface environments

V(IV) and V(III) are generated via biotic and abiotic reduction of V(V) (Bautista and Alexandre, 1972; Fredberg et al., 2004; Carpentier et al., 2003; Li et al., 2009; Wanty and Goldhaber, 1992). Microbial reduction is discussed in the next section.

An Eh–pH diagram illustrates the distribution of vanadium’s three common oxidation states, V(III), V(IV) and V(V), constructed using the thermodynamic data given in Wanty and Goldhaber (1992) (Fig. 7). The oxidation–reduction reactions and the calculated standard electrode potential, E°, are given in Table 6.

It is apparent that V(IV) species predominate in oxic environments at low pH values, and in both oxic and anoxic environments at pH values greater than about 8 (Fig. 7). Francavilla and Chasteen (1975) observed that VO₂²⁻ concentrations in solution decreased with increasing pH from 2 to 6 because of the formation of VOOH²⁻ and VO(OH)⁻ species. The increased pH may, however, cause condensation of VO₂²⁻ to V₈O₁₈⁴⁻, which is not directly involved in the reduction reaction (Lu et al., 1998). The vanadyl ion, VO₂⁺, and its hydrolyzed species, VO(OH)⁺, do not exist at pH values above about 7 if not complexed with inorganic and organic ligands; they are stable below this value in environments that are oxic to anoxic. Vanadium(III) species in solution exist only under anoxic conditions and at pH values up to about 10, where they become unstable relative to V(IV) species.

The oxyhydroxide of V(IV), VO(OH)₃(OH)⁻, and the hydroxide of V(III), V(OH)₃O⁻, can form at relatively low concentrations at 25 °C (Fig. 8). The oxidation–reduction reactions for which included solids is shown in Table 7. The precipitation of V in soils and sediments is discussed in Section 4.3.3.
Organic compounds such as humic, fulvic, and ascorbic acids can reduce V(IV) to V(III), and dissolved sulfide will reduce V(IV) to V(III) under conditions of pH and ionic strength common in natural systems (Table 8).

Because V solubility depends strongly on oxygen presence, the redox potential can control V mobility in surface environments (Fig. 7), which has been demonstrated in studies of soil, saturated sediments and rock diagenesis (Breit and Wanty, 1991; Francois, 1988; Yang et al., 2014). The V(IV) and V(III) species generated by low reduction potential will associate rapidly with the particulate fraction via complexation or adsorption, formation of insoluble hydroxides, and incorporation into minerals (Francois, 1988; Szalay and Szilágyi, 1967). By extension, the oxidation of V(III) and V(IV) to V(V) during weathering of V-containing minerals is a major cause of V mobilization in soil and sediment (Yang et al., 2014). There is evidence that reduced V is subsequently complexed by naturally occurring organic substances (Ferrer and Baran, 2001); this will decrease V solubility if the organic matter is insoluble. For example, complexation of V(IV) by high molecular weight fulvic acids can lead to aggregation (Templeton and Chasteen, 1980), and the reduction of V(V) by humic substances with consequent complexation by organic matter is a probable source of V associated with fossil plant detritus and bioliths (Szalay and Szilágyi, 1967). Reduced V(IV) and V(III) can hydrolyze and form insoluble hydroxides (Carpentier et al., 2003; Li et al., 2007; Ortiz-Bernad et al., 2004), which could also contribute to V that is preserved in solids. Reduced sediments are generally considered sinks for V. Suboxic conditions may, however, result in the release of V into the solution phase due to the reductive dissolution of adsorbing phases, e.g. Mn and Fe (hydr)oxides (Fox and Doner, 2003). For example, the mobilization of V associated with saline sediments in evaporation ponds was interpreted as a complex function of the redox dissolution of Mn and V oxides in the presence of organic matter (Amrhein et al., 1993).

4.2. Microbial controls on V geochemistry: redox, complexation, and sorption reactions

The flexible redox chemistry of V and its role as an essential trace element suggest that it may have once played a larger role in the chemistry of life (Rehder, 2008a; Rehder, 2008b). Some microorganisms can respire using V(V) and even V(IV) as electron acceptors (Carpentier et al., 2003; Li et al., 2009; Li et al., 2007; Lyalikova and Yurkova, 1992; Ortiz-Bernad et al., 2004; Zhang et al., 2014). The relatively low toxicity of vanadium and the high reduction potential for the V(V)/V(IV) redox couple suggests that V will be used in preference to other electron acceptors, such as Fe(III). The association of V with microbes via sorption and uptake processes may cause vanadium to concentrate in sediments, which is speculated to be a major source of this element in association with fossil fuels (Breit, 1988; Lewan, 1984). In the following, we highlight several studies to provide background on V-microbe interactions. For excellent discussions of V bioinorganic chemistry, see Chasteen (1983) and Rehder (2008a).

Many microorganisms are highly resistant to V. For example, Pseudomonas and Thiobacilli were shown to tolerate V(V) at 5000 mg L\(^{-1}\) (Lyalikova and Yurkova, 1992). A high tolerance to V is surprising given the several common valence states of V, which could be expected to disrupt redox reactions (Bell et al., 2004). Soils that have been exposed to crude oil and refined oil products harbor microorganisms that are particularly tolerant to vanadium, which is perhaps not surprising given reported concentrations of around 1200 mg kg\(^{-1}\) V in crude oil (Crans et al., 1998). For example, bacteria isolated from soils at an oil refinery tolerant ranged from 510 mg kg\(^{-1}\) vanadyl sulfate, and accumulated around 35,200 mg kg\(^{-1}\) V (bacterial dry weight) (Hernández et al., 1998). A similar high tolerance was observed for bacteria isolated from soils contaminated with crude oil in Russia and Saudi Arabia (Bell et al., 2004). Tolerance to V can be widespread in a microbial community. For example, bacteria present in a water sample taken from a South African mine containing around 420 mg L\(^{-1}\) V(V) at pH 3 encompassed 17 phylogenetic orders (Kamika and Momba, 2014); one isolate was found to tolerate up to around 700 mg L\(^{-1}\) V at pH 7; tolerance was slightly lower at pH 3.

The relatively low toxicity of vanadium and its favorable redox chemistry make it a predictable electron acceptor for bacterial respiration. A number of microorganisms, including Pseudomonas vanadium-reductans T-1, Pseudomonas isachsenkii A-1, Geobacter metallireducens, Enterobacter cloacea and species of Shewanella have demonstrated respiration of soluble V(V) to produce V(IV) in pH-neutral conditions (Carpentier et al., 2003; Li et al., 2007; Lyalikova and Yurkova, 1992; Ortiz-Bernad et al., 2004; van Marwijk et al., 2009; Zhang et al., 2014). Vanadium(III) has been detected during the dissimilatory reduction of V(V) by Shewanella putrefaciens CN-32, indicating highly anoxic conditions (Li et al., 2009; Li et al., 2007). Because of the relationship between V oxidation state and solubility, dissimilatory V respiration has been suggested as a strategy to remove V from contaminated water (Carpentier et al., 2003; Ortiz-Bernad et al., 2004). For example, acetate injected into an aquifer contaminated with U and V enhanced the growth and activity of Geobacteraceae, and V was effectively removed from the groundwater (Ortiz-Bernad et al., 2004). Removal of V(V) from groundwater by bioreduction was suggested in another study, which demonstrated stimulation of bacteria that reduced V(V) in columns of aquifer sediment that were exposed to V-containing water (Yelton et al., 2013). These studies were focused on bacteria, but archaea were recently shown to also be capable of V reduction. Two methanogenic archaea, one mesophilic and one thermophilic, reduced V(V) to V(IV) under growth conditions only, at concentrations up to 10 mM. Vanadium reduction occurred at the expense of methanogenesis and resulted in extracellular precipitates of V(IV) (Zhang et al., 2014).
summary, V reduction has been demonstrated for a wide phylogenetic range of microorganisms, typically results in extracellular precipitates of V(IV), and may or may not require growth conditions. Although the bioreduction of V appears to lead to V immobilization, the activity of microorganisms may also mobilize V from solid phases. Sulfur oxidizing Thiobacillus sp. facilitated the leaching of V from soils and minerals via oxidation of sulfide minerals (Briand et al., 1999; Gomez and Bosecker, 1999). Neutrophilic bacteria, including species of Pseudomonas and its relative Shewanella, mobilized V from shale at a former uranium mine, which was attributed to the production of chelating agents (Kalinsky et al., 2004). Shewanella putrefaciens CN-32 exposed to carnotite under reducing conditions resired mineral-bound V(V) in preference to U(VI), resulting in higher solution concentrations of V (Glaser, 2015; Li et al., 2009). It is an interesting speculation that the dissimilatory reduction of V and U by microbes may have contributed to forming the roll front and tabular ore-grade deposits, as suggested by several researchers (Evans and Garrels, 1958; Hansley and Spirakis, 1992; Hostetler and Garrels, 1958; Spirakis, 1996).

The positive correlation between organic matter and V in fossil fuels is likely due in part to the strong interaction of V with microbial surfaces. An investigation of V(V) biosorption by Halomonas sp. GT-83 showed an uptake capacity of 52,700 mg kg⁻¹ V(V) (Chazvini and Mashkani, 2009). The biosorption efficiency is likely highest at pH 3 (relative to more alkaline values tested) because most V(V) exists in cationic form at low pH (Fig. 8). Electrostatic attraction was important for the adsorption of V(V) to Halomonas GT-83, as indicated by an observed decrease in adsorption with increasing salinity. Temperature appears to have little impact on V(V) biosorption, whereas increasing microbial cell density may reduce V(V) adsorption capacity due to cell aggregation (Chazvini and Mashkani, 2009).

Sorption/desorption, reduction-oxidation, complexation and precipitation reactions all play important roles in the geochemical cycling of V in surface and near-surface environments (Fig. 9). As discussed, the

<table>
<thead>
<tr>
<th>Organic Substance</th>
<th>Vanadium Species</th>
<th>Interaction</th>
<th>Comments</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC</td>
<td>V(V)</td>
<td>Humic substance-V(V) complexes less than 1% of total V</td>
<td>DOC: &gt;10 mg L⁻¹, pH: 8, Wabamun Lake, Canada</td>
<td>Canada (2010)</td>
</tr>
<tr>
<td>DOM</td>
<td>V(V)</td>
<td>V complexion with DOM is not important</td>
<td>V: 2.0–2.5 μg kg⁻¹; pH: 7.72</td>
<td>Shiller and Boyle (1987)</td>
</tr>
<tr>
<td>Humic substance</td>
<td>V(V)</td>
<td>V(V) monomer complexation with humic substance at pH 7.2 with formation equilibrium constant of 108 M⁻¹</td>
<td>V(V): 12.8–166 mg L⁻¹, Humic substance: 0.025–0.58 mM, 25 °C</td>
<td>Lu et al. (1998)</td>
</tr>
<tr>
<td>Fulvic acid</td>
<td>V(IV)</td>
<td>V(IV) bound to carboxylic groups of humic substance</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Peat humic acid</td>
<td>V(IV)</td>
<td>Partially complexed at pH 2, predominantly complexed at pH 4 and 6</td>
<td>V: 0.51 g L⁻¹</td>
<td>Wilson and Weber (1979)</td>
</tr>
<tr>
<td>Soil fulvic acid</td>
<td>V(IV)</td>
<td>Complexed by oxygen or mixed oxygen-nitrogen donor groups in the humic acid</td>
<td>-</td>
<td>Goodman and Cheshire (1975)</td>
</tr>
<tr>
<td>Soil organic matter</td>
<td>V(IV)</td>
<td>Association as (VO)₂(heavier fractioned fluvic acid)₆</td>
<td>V:12.8–28 μg L⁻¹; pH 5; fulvic acid: 2.5 × 10⁻³ M</td>
<td>Templeton and Chasteen (1980)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Soil obtained from Scotland</td>
<td>Cheshire et al. (1977)</td>
</tr>
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</table>

- no information
4.3. Vanadium in surface environments: water, soil, and sediment

4.3.1. Freshwater environments

As discussed in previous sections, the presence of soluble V is a complex function of the solution chemistry, the presence of sorbing colloids, and the source material. The relationship between V in solution and environmental factors can vary as a function of the environmental setting; for example, a strong association with colloidal or particulate Fe explained low dissolved V content in streams (Wällstedt et al., 2010), whereas the concentration of dissolved V in major rivers was related more strongly to weathering and source rock than to the association with colloids or organic matter (Shiller and Boyle, 1987). At sites where V is detected in water at elevated concentrations, commonly in association with mining activities, dissolved V concentrations may reach several hundred mg L$^{-1}$, e.g., 30–220 mg L$^{-1}$ in Wyoming River, U.S.A. (Schroeder, 1970; Shiller and Boyle, 1987). A study of groundwater in California showed a similar correlation between V and the source rock, in particular basaltic and andesitic rocks (Schroeder, 1970; Wright and Belitz, 2010). The concentrations of V in that study were highest in theoxic and alkaline groundwater, while V is present as dissolved V(V).

Vanadium concentrations in water can be seasonally dependent. Higher concentrations of dissolved V during warm (summer) conditions have been documented in freshwater and marine systems, e.g., in Long Island Sound (Wang and Sañudo Wilhelmy, 2009a), Toyko Bay and Shimizu Port, Biwa Lake (Sato and Okabe, 1978; Sato and Okabe, 1982) and Florida Bay (Caccia and Millero, 2003). Elevated concentrations of V were observed during the seasonal transition from winter to spring for water draining from a wetland (Pourret et al., 2012). Several factors can contribute to seasonal V mobility. The association of V with particulates in water is a strong function of pH and Eh conditions, which can fluctuate seasonally. Light can be a contributing factor; in one study, diel variations in V concentrations that were observed in an acidic stream could be attributed to photoreduction (Kay et al., 2011).

4.3.2. Marine environments

In seawater, V is one of the two most abundant trace elements (molybdenum is the other) due to rock weathering. Concentrations of dissolved V in the open ocean average 35–45 nmol L$^{-1}$ (as reviewed in Emerson and Huested (1991)) and higher concentrations occur locally (Table 1). V in the ocean exhibits conservative behavior, although non-conservative behavior is common in coastal waters where concentrations are typically lower (reviewed in Wang and Sañudo Wilhelmy (2009b)). Most V in open ocean seawater is dissolved rather than particulate (>0.45 μm), as shown by studies in the North Atlantic (Hoffman et al., 1974; Riley and Taylor, 1972; Riley and Saxby, 1982). These studies concur with the much higher reservoir of dissolved V (2.7 × 10$^{13}$ g) as compared to suspended particulate V (1.8 × 10$^{18}$ g) estimated for the global ocean (Hope, 2008). Ocean sediment contains, however, the largest reservoir of V (1.7 × 10$^{20}$ g) on the Earth’s surface (Hope, 2008), mainly in marine shale and carbonaceous sediments (Ekström et al., 1983). This reflects that the ocean floor is the ultimate sink of V in the global circulation (Bengtsson and Tyler, 1976; Miramand and Fowler, 1998). Submarine volcanoes are important sources of V in marine sediments; V concentrations in active ridge sediments may reach >400 mg kg$^{-1}$ (Boström and Fisher, 1971). Atmospheric deposition is another important source of V input to global oceans and is discussed in Section 4.4.

The abundance of V in seawater, its occurrence in several oxidation states that control solubility, and its role as an essential trace element to life have made it a valuable proxy for establishing paleoredox and paleoproductivity conditions (reviewed in Tribovillard et al. (2006)). In oxic seawater, the main species of V(V) are HVO$_4^-$ and H$_2$VO$_4^-$, while V(IV) species are VO$_2^+$, VO$_2$H$^+$, and insoluble VO(OH)$_2$. Common V(IV) species are VO$_2^+$, VO$_2$H$^+$, and insoluble VO(OH)$_2$. (Rehder, 2008a; Rehder, 2008b). Vanadyl species can be further reduced under anoxic conditions to V(II), which readily forms solid oxides of V$_2$O$_3$ and V(OH)$_3$ that can accumulate in sediments. The relative accumulation rates of V, as well as those of other redox sensitive elements such as Mo and U, increase dramatically with decreasing fO$_2$ in the ocean (Shaw et al., 1990; Tribovillard et al., 2006; Wanta and Goldhaber, 1992). The distinct chemical signatures of V and other multivalent elements that are preserved in sedimentary marine rocks can be excellent paleo-oxygen barometers, an indice for paleo fO$_2$ variation, for recording the history of fO$_2$ variation in the atmosphere (Algeo and Maynard, 2004; Algeo and Maynard, 2008; Anbar and Rouxel, 2007; Tribovillard et al., 2006). Vanadium supplied to oceans from weathered detrital inputs from the continental crust has been used with other redox tracers to track oceanic evolution from oxic-suboxic to anoxic (non-sulfidic, anoxicogenic) and euxinic (sulfidic, oxygenic) conditions. Precipitation with organic carbon occurs at redox boundary zones, producing a strong correlation between organic carbon and V, as well as other trace elements (Tribovillard et al., 2006). In euxinic environments, V is mainly hosted in authigenic phases and is les associated with organic carbon. For example, there is a weak correlation between V total organic carbon content in oceanic black shale, which distinguishes V from other transition metals with strong euxinic affinity (Algeo and Maynard, 2004; Algeo and Maynard, 2008). To relate trace element signatures in sediments and sedimentary rock, concentrations are typically normalized to aluminum content; aluminum represents the aluminosilicate fraction, which has low mobility during diagene- sis, in contrast to carbonate and opal mineral fractions (reviewed in Tribovillard et al. (2006)). The reference shales may not, however accurately represent the sediments being studied (Van der Weijden, 2002).

Concentrations of V in shales span a wide range globally and can vary widely across local geographic areas (see Xu et al. (2013) and Section 3.2).
New approaches to apply trace metal data to paleoceanographic systems extend conventional approaches based on differences in trace metal accumulation between oxygenated and non-oxygenated environments. Algeo and Rowe (2012) present a method which applies trace-metal/TOC ratios to assess watermass restriction and deepwater renewal times in restricted anoxic marine systems. This can be effective because the onset of ocean anoxia results in the drawdown of trace metals. Although their investigation uses Mo as the example, V may also be suitable given its similar redox properties, as described above.

As for Mo, the uptake of V in anoxic marine environments depends on both the concentration of V and on the concentration of the sedimentary organic matter which hosts the element. Vanadium isotope fractionation was presented in Section 2.4. The feasibility of applying V isotopes \(^{50}\text{V}(0.24\%)\) and \(^{51}\text{V}(99.76\%)\) as a new paleoredox proxy for ocean sediments is promising (Wu et al., 2015). The proposed approach is based on the balance of V fluxes into and out of the ocean at steady state, with rivers as the sole input and marine sediments and hydrothermal deposits as the outputs. The

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\text{Redox reaction} \quad \text{Redox couple/reagents} \quad \text{Comments} \quad \text{Reference}
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<table>
<thead>
<tr>
<th>Redox reaction</th>
<th>Redox couple/reagents</th>
<th>Comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(IV) to V(III)</td>
<td>(\text{H}_2\text{S})</td>
<td>Slow reduction kinetics; V: 0.5–12.2 mg L(^{-1}); pH 3.6–6.8, (\text{H}_2\text{S}: 8.1 \times 10^{-4}) to 0.471 atm; ionic strength 0.05–0.1</td>
<td>Wanty and Goldhaber (1992)</td>
</tr>
<tr>
<td>V(V) to V(IV)</td>
<td>Humic substance</td>
<td>pH &lt; 6; V(V): 25.5 mg L(^{-1})</td>
<td>Lu et al. (1998)</td>
</tr>
<tr>
<td>V(V) to V(IV)</td>
<td>Fulvic acid</td>
<td>Higher reduction rate at pH 2 than pH 6</td>
<td>Wilson and Weber (1979)</td>
</tr>
<tr>
<td>V(V) to V(IV)</td>
<td>benzene-1,4-diol (Quinol)</td>
<td>Reduction rates increase with increasing acidity via formation of VO(_2),QH(_2) and VO(OH)(_2)(_2) : V: 25.5 and 51 mg L(^{-1}); quinol: 27–324 g L(^{-1}); HClO(_4): 503–503 g L(^{-1}); at 16, 25, 32 and 40 °C</td>
<td>Wells and Kuritsyn (1970)</td>
</tr>
<tr>
<td>V(V) to V(IV)</td>
<td>Insoluble peat humic acid</td>
<td>pH: 7.2, 1.17 g L(^{-1}), 1 g humic acid.</td>
<td>Szalay and Szilágyi (1967)</td>
</tr>
<tr>
<td>V(V) to V(IV)</td>
<td>Hydroxylamine</td>
<td>Via formation of VO(_2)\cdot\text{NH}_3\text{OH}^+ and V(OH)(_2)(_2)\cdot\text{NH}_3\text{OH}^+ V: 51 mg L(^{-1}); Hydroxylamine: 0.33–6.6 g L(^{-1}); 25–60 °C; HClO(_4): 100–503 g L(^{-1}).</td>
<td>Nazer and Wells (1980)</td>
</tr>
<tr>
<td>V(V) to V(IV)</td>
<td>Benzene-1,2-diol (catechol) and its derivatives</td>
<td>Formation of V(V)-reductant complex as intermediate</td>
<td>Kustin et al. (1974)</td>
</tr>
<tr>
<td>V(V) to V(IV)</td>
<td>L-ascorbic acid</td>
<td>Formation of VO(_2^+) complexes with the derivatives of ascorbic acid</td>
<td>Ferrer and Baran (2001)</td>
</tr>
<tr>
<td>V(IV) to V(V)</td>
<td>(\text{O}_2)</td>
<td>Three order of magnitude faster oxidation kinetics for V(IV) adsorbed to (\text{Al}_2\text{O}_3) and (\text{TiO}_2) than solution V(IV) V: (&gt;0.51) mg L(^{-1}), pH: 4–9</td>
<td>Wehrli and Stumm (1988), Wehrli and Stumm (1989)</td>
</tr>
<tr>
<td>V(III) to V(IV)</td>
<td>(\text{O}_2)</td>
<td>-</td>
<td>Fallab (1967)</td>
</tr>
</tbody>
</table>

\[-: \text{no information}\]

Fig. 9. Vanadium mobilization and immobilization processes at the water-soil/sediment interface.
model remains to be tested; there are currently no V isotope measurement for seawater or ocean sediments (Wu et al., 2015).

4.3.3. Soils and sediments

Vanadium in soils may originate from source rock, atmospheric deposition and anthropogenic sources. Vanadium in soils and sediments appears to be generally immobile as sorbed and precipitated phases. Its mobilization is often decoupled from other metals and metalloids, and is governed by weathering and redox processes (Shiller and Mao, 2000; Yang et al., 2014). The speciation of V in soils is strongly impacted by the formation of complexes with anions present in the soil solution. This is demonstrated for V(IV) in a simulated soil solution (Fig. 10).

Because sulfate ions are stronger complexant ligands for VO²⁺ than chloride ions, the VOSO₄ complex is much more important than the VOCl⁺ complex, even though the SO₄²⁻ ion concentration is lower than Cl⁻ (Fig. 10).

The aqueous chemistry of V(III) is similar to Fe(III) in that the vanadic, V⁵⁺, ions hydrolyzes in water to form the VOH²⁺ and V(OH)₃⁻ ions (Table 9). By analogy with the Fe(III) system, the V³⁺ ion can be expected to form relatively weak complexes with the Cl⁻ ion, and strong complexes with SO₄²⁻ ions although the VOSO₄ complex is not the major species. A formation constant, log β, of 3.28 has been calculated for the VSO₄²⁻ ion (Wanyt and Goldhaber, 1992). This compares with values of 3.89, 3.81 and 2.25 for Al³⁺, Cr⁶⁺ and Fe⁷⁺ respectively.

A dinuclear, tetravalent species, V₂(OH)⁶⁴⁺, is only likely to be found at relatively high V⁶⁺ concentrations. Complexation with sulfate, at a typical soil sulfate concentration, occurs at very acidic pH values, which are not expected for the majority of soils (Fig. 11).

Vanadium forms oxide minerals at elevated concentrations. These include vanadium pentoxide, V₂O₅(s), vanadium oxyhydroxide, VO(OH)₂(s), vanadium tetroxide, V₂O₄(s), vanadium trioxide, V₂O₃(s) and vanadium hydroxide, V(OH)₃(s) (Table 10). The oxides V₂O₅(s), V₂O₄(s), and V₂O₃(s) are generally prepared at high temperatures (>300 °C) (Cook, 1947), conditions unlikely to occur in soils or sediments and are therefore unlikely to precipitate under ambient conditions. However, VO(OH)₂(s) and V(OH)₃(s) can form at 25 °C (Garrels, 1953) and so are possible vanadium oxide precipitates in soils and sediments.

Vanadium pentaoxide, V₂O₅(s), is the most important synthesized V compound, and is used in a number of industrial processes. It may enter soils through atmospheric deposition or the disposal of wastes in the vicinity of industrial establishments. It is, however, relatively soluble in water, with a minimum solubility at about pH 4 (Fig. 5). The solubilities of VO(OH)₂(s), and V(OH)₃(s), on the other hand, both decrease as pH increases (Fig. 12), supporting the strong tendency toward decreased solubility as a function of valence.

Another likely means to immobilize V is through association with soil organic matter and retention by clay minerals and Fe oxides (Mikkonen and Tummavuori, 1994). The interaction of V with soil minerals has not, however, been well studied to date, and can be difficult to predict because of the complexities of soil mineralogy, the chemical complexity of the soil solution, and the diverse chemistry of V. As a consequence, estimates of the mobility and bioavailability of V in soils are contradictory. This is also due in part to the methods that are commonly used to assess mobility. Selective sequential extraction (SSE) techniques are widely used to characterize the reactivity of V and other elements associated with different soil components. The quality of the results obtained by SSE depends on the assurance that a given treatment or reagent can selectively and specifically extract the intended phases (Hass and Fine, 2010). A lack of standardization in SSE protocols can complicate the comparison of results between studies (Hass and Fine, 2010). We present a few examples of results from studies that applied SSE techniques to assess V frations in soil in order to illustrate the wide range of outcomes.

Sequential leaching of V in a variety of agricultural and industrial soils from Poland indicated the predominance of V in the soluble fraction (Poledniok and Buhl, 2003). An investigation of Egyptian and Greek soils differing in origin and properties showed that the bicarbonate-DTPA extractable V (related to soluble V) was positively correlated with total soil V, soil pH, clay, silt and cation exchange capacity, but negatively with organic matter (Tsadilas and Shaheen, 2010). An investigation of German soils highlighted a large range in V extractability for different soils: EDTA extraction recovered 0.2–35% of V soluble in aqua regia, which is considered to represent total V (Gäbler et al., 2009). Other studies have documented the majority of V in the soil residual fraction, which may comprise up to 93% of total V in some soils (Cappuyns and Swennen, 2014; Ovari et al., 2001; Teng et al., 2011). In general, most V in soils appears to have low mobility except under strongly acidic conditions (Cappuyns and Swennen, 2014). The mobile V in soils occurs mainly as V(V) and only

| Table 9 Formation constants, log β, for vanadium(III) with some inorganic ligands (calculated from the Gibb’s energy values given in Wanyt and Goldhaber (1992), 25 °C, 1 atm. Pressure, zero ionic strength (I)). |
|-----------------|-----------------|-----------------|
| Vanadium(III)   | log β           |                  |
| V³⁺ + H₂O ⇌ VOH²⁺ + H⁺ | −2.30 2V³⁺ + 2H₂O ⇌ V₂(OH)₄²⁺ + H⁺ | −3.79 |
| V³⁺ + 2H₂O ⇌ V(OH)₃²⁻ + 2 H⁺ | −6.33 V³⁺ + SO₄²⁻ ⇌ VSO₄²⁻ | 3.28 |

Fig. 10. Speciation of vanadium(IV) in a simulated soil solution using the thermodynamic data given in Table 4.

Fig. 11. Speciation of V(III) in the presence of SO₄²⁻ ions.
Vanadium is also the most available form for plants (Tian et al., 2015). Although red mud, the fine sediment byproduct of bauxite processing, is not soil, a recent study provides insight into V mobilization from mineral solids. This study was motivated by the failure of a red mud dam at Ajka, Hungary, which released sediment with elevated concentrations of potentially toxic elements, including V (Burke et al., 2012). All of the V was present in the red mud as V(V) at pH 13, determined using X-ray absorption spectroscopy (XANES), and was relatively immobile. Neutralization of the sediment to circumneutral pH values resulted in immobilization of Cr and As, but mobilized V. It was surmised that dissolution of V-bearing minerals during neutralization, anion exchange processes, and the formation of polymeric V species could have contributed to enhancing V mobility at lower pH (Burke et al., 2012). In comparison, pH was shown to influence V mobility indirectly in floodplain and paddy soils, and redox status controls V mobility (Frohne et al., 2015; Shaheen et al., 2014a; Shaheen et al., 2014b). These microcosm experiments with controlled redox variations further highlighted that the length of the redox period changes substantially with the concentration of V in porewater (Shaheen et al., 2014b). Higher porewater V concentrations were detected in the experiment with short-term overflooding, probably due to kinetic limitation of anoxic V immobilization.

Other environmental factors may also impact V mobility. In one study, aging caused V(V) added to soil to become less soluble, bioavailable and toxic (Burke et al., 2012). Vanadium(IV) appears to predominate in soils over other valence states (Kuo et al., 2007; Mandiwana and Panichev, 2004) (Table 1), possibly reflecting the incorporation of VO\(^{2+}\) into the lattice of soil minerals (Gehring et al., 1993) as well as favorable conditions for dissimilatory reduction by microorganisms. Drought and rewetting greatly increase the leaching of V, as observed in soil column studies (Yang et al., 2014). The observation that the leaching behavior of V did not correlate with its sorption affinity suggests that weathering and oxidation of V-containing minerals is responsible for an increase in mobile V during the drought period, which was flushed during rewetting.

Atmospheric deposition is an important input of V to soils located far from a point source, such as peat bogs (Cloy et al., 2011). Because the matrix in peat bogs is almost exclusively organic, the migration of V is likely retarded by the formation of organic complexes. Vanadium in wetland soils is found mainly in the acid-digestible fraction (>70%) (Fox and Doner, 2003). Lead is well known to be immobile in organic soils; the general similarity between the vertical distribution of V and Pb suggests that V is similarly immobile in peat bogs (Cloy et al., 2011). Seasonal effects can also play a role (Pouret et al., 2012).

Few countries have established standards for V contamination in soil. In Russia, a maximum of 150 mg kg\(^{-1}\) is allowed in agricultural soils (GOST-17.4.4.02-84, 1985). The general soil quality guideline for V in Canada is 130 mg kg\(^{-1}\) (Canadian_Environmental_Quality_Guidelines, 1999).

### 4.3.4. Adsorption to metal oxide minerals

The water-soil partitioning of V in soils and sediments reveals the generally low mobility of soil V, with adsorption coefficients of up to 750 000 L kg\(^{-1}\) (Table 1). Most research on the sorption of V by minerals has focused on sorption to metal oxides. In addition to the surface chemistry of the sorbent, V adsorption and desorption depend strongly on the concentration, chemical valence and chemical species (Table 11) (Peacock and Sherman, 2004; Wehrli and Stumm, 1988; Wehrli and Stumm, 1989).

Adsorption of both V(IV) and V(V) onto metal oxide minerals has been interpreted in terms of the formation of inner-sphere bidentate complexes and monodentate complexes.

#### Table 10

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log (K_{so})</th>
<th>Reaction</th>
<th>log (K_{so})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium(V)</td>
<td></td>
<td>Vanadium(V)</td>
<td></td>
</tr>
<tr>
<td>(V_2O_5(s) + 2H^+ \rightleftharpoons 2VO^2+ + H_2O)</td>
<td>-1.36</td>
<td>(VO(OH)_{2(s)} + 2H^+ \rightleftharpoons VO^{2+} + 2H_2O)</td>
<td>6.11</td>
</tr>
<tr>
<td>Vanadium(III)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(V(OH)_{3(s)} + 3H^+ \rightleftharpoons V^3+ + 3H_2O)</td>
<td>7.59</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 12. Solubility of some vanadium oxides as a function of pH.](image-url)
complexes for the vanadyl ion, VO$^{2+}$, and mono-dentate complexes for vanadate ions, H$_2$VO$_{3-}$ (Motschi and Rudin, 1984; Peacock and Sherman, 2004; Wehrli and Stumm, 1989). Recent work on the adsorption of V(V) ions onto goethite (Peacock and Sherman, 2004) has demonstrated the formation of two bidentate complexes, $\equiv$Fe$_2$OVO(OH)$_4$ and $\equiv$Fe$_2$OVO$_2$OH$^{-}$; their intrinsic formation constants were determined by batch adsorption experiments (Table 12). The calculated adsorption of V(V) ions onto goethite as a function of pH using the Diffuse Layer Model and the constants given in Peacock and Sherman (2004) shows very high affinity across environmentally relevant pH values (Fig. 13). Using EXAFS, the two complexes were shown to be inner-sphere bidentate corner-sharing complexes with the edges hydroxyls of goethite.

The solution pH can be expected to control V sorption, given the strong dependence of V speciation on pH. Adsorption involving ligand exchange can, however, offer exceptions to what might be expected based on simple electrostatic repulsion. For example, adsorption of V(V) at low pH to positively charged iron oxide mineral surfaces can be expected to occur via VO$_2^{+}$ cations (Figs. 6, 7). At higher pH, V(V) occurs as conjugate acids of VO$_4^{3-}$ that can be expected to adsorb to positively charged oxide mineral surfaces by ligand exchange, analogous to the sorption behavior of phosphate. Charge dependence for V sorption has been observed in several studies. For example, the adsorption of vanadate to α-FeOOH and i-Al$_2$O$_3$ was suppressed below pH values ~<3 and ~<8, and was suppressed at pH ~>8 for Fe(III)/Cr(III) hydroxide at 2.5 mg L$^{-1}$; sorption decreased around pH 9 for TiO$_2$ at the same concentration. Adsorption of vanadyl cations to TiO$_2$ and Al$_2$O$_3$ was suppressed below pH ~3 and ~4, respectively (Wehrli, 1987). The adsorption behavior was explained by the predominance of VO$^{2+}$ at pH values ~<3, resulting in repulsion by the positively charged TiO$_2$ and Al$_2$O$_3$ surface (Wehrli and Stumm, 1989).

The adsorption of V to mineral surfaces depends on concentration. Concentration is particularly important to consider for V(V) because of the formation of polymeric V(V) i.e., metavanadate (e.g. V$_2$O$_5^{3-}$), species, which can result in decreased sorption (Fig. 6); for example, less V(V) was sorbed to goethite between pH 6 and 9 at 25 mg L$^{-1}$ V than at 2.5 mg L$^{-1}$ V in one study (Peacock and Sherman, 2004). Competition with other ions also impacts sorption. Vanadate competes with other oxyanions such as phosphate, arsenate, selenate and molybdate for sites on positively charged mineral surfaces (Blackmore et al., 1996; Brinza et al., 2008; Wang et al., 2003). Prathap and Namisivayam (2010) proposed an order of adsorption among common oxyanions and chloride to positively charged metal oxide surfaces of: vanadate > phosphate > selenate > molybdate; sulfate, nitrate and chloride showed no effect on V(V) adsorption. In another study, vanadate outcompeted

![Fig. 13. Adsorption of vanadium(V) onto goethite.](image)

Table 11
Solid-solution partition coefficients (K$_{d}$) calculated from experimental data for a range of metal oxides, clays and environmental materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Components</th>
<th>K$_{d}$ (L kg$^{-1}$)</th>
<th>pH</th>
<th>Comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agricultural soil, China</td>
<td>Not specified</td>
<td>1’400–10’950</td>
<td>4.3</td>
<td>H$_2$O leaching</td>
<td>Yang et al. (2014)</td>
</tr>
<tr>
<td>Mine tailing</td>
<td>V(V)</td>
<td>5’170–70’530</td>
<td>8.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soils, South Africa</td>
<td>V(V)</td>
<td>9.37–526</td>
<td>–</td>
<td>H$_2$O extraction</td>
<td>Mandiwana et al. (2005)</td>
</tr>
<tr>
<td>Dust</td>
<td></td>
<td>23.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Marine sediment, (MESS-3)</td>
<td>V(V)</td>
<td>48.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay soil, USA</td>
<td>V(V)</td>
<td>-150</td>
<td>5.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sandy soil</td>
<td></td>
<td>-1.71</td>
<td>5.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Floodplain soils, Belgian</td>
<td>V(V)</td>
<td>-21’800–35’500</td>
<td>–</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferricyanide</td>
<td>Not specified</td>
<td>-90’000</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferricarbonate</td>
<td>Not specified</td>
<td>-60’000</td>
<td>9</td>
<td>I = 0.01</td>
<td></td>
</tr>
<tr>
<td>Sandy soils,</td>
<td>Not specified</td>
<td>247–34’100</td>
<td>4.2</td>
<td>Ca(NO$_3$)$_2$ extraction</td>
<td>Gäßler et al. (2009)</td>
</tr>
<tr>
<td>Silty soils</td>
<td>7’560–323’600</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Loamy soils</td>
<td>4’200–75’500</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay soils</td>
<td>4’540–489’167</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>River suspended particulate matter</td>
<td>Not specified</td>
<td>29.600</td>
<td>–</td>
<td>–</td>
<td>Gobei et al. (2005)</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>V(V)$^b$</td>
<td>-2500–225’000</td>
<td>1–3.3</td>
<td>C = 10–50 mg L$^{-1}$</td>
<td>Wehrli (1987)</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>V(V)</td>
<td>-1’500–9’500</td>
<td>2.75–4</td>
<td>C = 41–128 mg L$^{-1}$, I = 0.1</td>
<td>Prathap and Namisivayam (2010)</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>V(V)</td>
<td>-5000–49’500</td>
<td>0.5–11.5</td>
<td>C = 2.55 mg L$^{-1}$, I = 0.1</td>
<td>Trefry and Metz (1989)</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>-2500–47’500</td>
<td>1–10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Insoluble peat humic acid</td>
<td>V(V)</td>
<td>-6–60</td>
<td>2.1</td>
<td>–</td>
<td>Szalay and Szilágyi (1967)</td>
</tr>
</tbody>
</table>

$^a$ no information.  
$^b$ calculation infeasible at pH 4–7.

Table 12
Surface reactions and intrinsic complexation constants for V(V) onto goethite calculated using the Diffuse Layer Model (Specific surface = 37.2 m$^2$ g$^{-1}$; [SOH]$_0$ = 6.02 sites nm$^{-2}$; log K$_{HF}$ = 6.78; log K$_{HCl}$ = –10.10).

<table>
<thead>
<tr>
<th>Adsorption reaction</th>
<th>log K$^{11}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Fe$^{3+}$ + V$^{5+}$ + 4 H$^+$ ↔ Fe$_2$OVO(OH)$_4^{2-}$ + 2H$_2$O</td>
<td>42.67</td>
</tr>
<tr>
<td>2 Fe$^{3+}$ + V$^{5+}$ + 3 H$^+$ ↔ Fe$_2$OVO$_2$OH$^-$_2 + 2H$_2$O</td>
<td>41.26</td>
</tr>
</tbody>
</table>

arsenite for adsorption to Fe₂O₃, but had an equal affinity for Al₂O₃ (Jeong et al., 2007). The adsorption of negatively charged V oxyanion species will increase the adsorption of cationic metals to positively charged surfaces due to charge screening, formation of cation-anion complexes at the surface and surface precipitation (Zhao et al., 2004).

4.4. Vanadium in the atmosphere

Atmospheric V is a key component of the V cycle. The major natural sources of atmospheric V globally are marine aerosols produced when bubbles burst at the sea surface, continental dust from crustal weathering, and volcanic debris (Zoller et al., 1973). Volcanic activity contributes V associated with tephra and ashes, and in hydrothermal springs (Bortnikova et al., 2009; Mizuno et al., 2008; Smichowski et al., 2003). The total V added to the atmosphere from natural sources has been estimated at 37 x 10⁹ g yr⁻¹ and is comparable in magnitude to V contributed by anthropogenic sources (Duce and Hoffman, 1976). Duce and Hoffman (1976) estimated that around 10% of anthropogenic atmospheric V is deposited in the global oceans.

The abundance of V transported in the atmosphere from continental pollution sources may make it a useful tracer for atmospheric pollutant transport (Duce and Hoffman, 1976). For example, the accumulation of anthropogenic V, as determined for a peat bog core in Scotland, could be correlated with industrial activities begun in the late 19th century (Cloy et al., 2011). Deposition rates peaked (~1.3 to 2.0 mg m⁻² yr⁻¹) in the mid-20th century before decreasing to 0.1–0.3 mg m⁻² yr⁻¹ in the early years of the 21st century. This was attributed to more stringent emission standards in the United Kingdom (Cloy et al., 2011). Studies on a Swiss peat bog revealed an increased deposition of anthropogenic V since 1936, reflecting the growing impact of industrialization on atmospheric inputs (Krachler et al., 2003). Although fossil fuel combustion has increased since some early studies on V atmospheric deposition (e.g., (Duce and Hoffman, 1976; Zoller et al., 1973)) and controls on emissions in some countries have reduced the inputs of V to the atmosphere, which is reflected by lower rates of land deposition (Cloy et al., 2011; Harmens et al., 2007). Elevated concentrations of V in Sphagnum moss collected from rain-fed peat bogs near the Athabasca oil sands in Alberta, Canada support, however, that emissions from mining and processing bitumen do still contribute to increased land deposition of V locally (Shotyk et al., 2014).

Climate cycles have a strong impact on the atmospheric deposition of V, which is true in general for many trace metals. For example, V accumulation in the Swiss peat bog discussed above was highest during the Younger Dryas cold climate event (centered at 10,590 ± 14 C yr. B.P.), with corresponding atmospheric fluxes of approximately 14 mg m⁻² yr⁻¹; this value is ~40 times background (Krachler et al., 2003). Vanadium concentrations in sections of the 3623 m Vostok deep Antarctic ice core, dated from 4600 to 410,000 years BP, were low during interglacial periods and warm interstadials, and much higher during the coldest periods of the last four ice ages (Gabrielli et al., 2005). Higher historical V concentrations preserved in peat have been attributed to increased atmospheric soil dust, which is a consequence of climate as well as changes in land use, e.g., forest clearing for agriculture (Gabrielli et al., 2005; Krachler et al., 2003). Because particulates, especially geologically-derived dusts, are a major contributor to atmospheric V (Sakata and Asakura, 2011; Song and Gao, 2009; Theodosi et al., 2010), changes in climate that increase dust loads in the atmosphere should increase the transport of V.

Vanadium is found within a range of particle sizes in atmospheric compartments. The speciation of V by size fraction in Japanese rainwater showed that 45–100% of V was present as labile forms with molecular weight <1000 Da (Kawakubo et al., 1997). Non-labile V was mainly found in the higher molecular weight (≥10,000 Da) or insoluble fractions. Another study in Japan found that ~50% of suspended atmospheric V occurred in particles smaller than 2 μm in size (Adachi et al., 1997). The association of V with mineral dusts can be expected to mirror the association of V with soil minerals, although this has been given little attention. In one study, V in dry atmospheric deposition was strongly correlated with Al, indicating clay mineral association (Adachi et al., 1997; Sakata and Asakura, 2011).

Vanadium that reaches the atmosphere from volcanic emission and fossil fuel combustion is generally expected to occur as V(V) due to the ubiquity of oxygen (Challenge, 2010). A recent study detected mainly V(IV) species in diesel vehicle emissions, with higher emissions of V(V) from vehicles equipped with exhaust after-treatment; V(V) was the major component in the finest size fraction (Table 1) (Shafer et al., 2012). In another study, V was detected in association with organic carbon and sulfate in air-borne emission plumes released from ships in port. It was speculated that V(V) may catalyze the oxidation of reduced sulfur species to form sulfate and sulfuric acid. This supports that V redox chemistry, likely driven by SO₂ and photochemistry, may occur in atmospheric particles and is a health concern because of synergistic effects of V particulates and sulfates (Ault et al., 2010).

4.5. Anthropogenic sources

Around 85% of global V produced is used as ferrovanadium in the steel industry, while another 10% is used in the aerospace industry in the form of V-Al-Ti alloys (Moskalyk and Alfantazi, 2003). Although the other industrial applications of V (including catalysts, glass coating and rechargeable batteries; Table 13) have less impact, some uses in

---

**Table 13**

<table>
<thead>
<tr>
<th>Chemical forms</th>
<th>Application</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrovanadium (FeV)</td>
<td>Vanadium high-carbon steel alloys, high speed tool steels (surgical instruments and tools)</td>
<td>Moskalyk and Alfantazi (2003)</td>
</tr>
<tr>
<td>Chrome-vanadium steels</td>
<td>Springs and transmission gears are fabricated from</td>
<td>Moskalyk and Alfantazi (2003)</td>
</tr>
<tr>
<td>V-Al-Ti alloys</td>
<td>Jet engines, high-speed airframes and dental implants, missile cases, nuclear reactor components, jet engine housings and associated airframes</td>
<td>Moskalyk and Alfantazi (2003)</td>
</tr>
<tr>
<td>Vanadium foil</td>
<td>Cladding titanium to steel</td>
<td>Lositskii et al. (1966)</td>
</tr>
<tr>
<td>Vanadium pentoxide (V₂O₅)</td>
<td>Manufacturing sulfuric acid, maleic anhydride production, ceramics production</td>
<td>Abon and Volta (1997)</td>
</tr>
<tr>
<td>Vanadium dioxide (VO₂)</td>
<td>Glass coatings</td>
<td>Manning et al. (2004)</td>
</tr>
<tr>
<td>Vanada</td>
<td>Electrochemical conversion coating</td>
<td>Guan and Buchheit (2004)</td>
</tr>
<tr>
<td>Vanadium redox couple</td>
<td>Rechargeable batteries</td>
<td>Jorissen et al. (2004)</td>
</tr>
<tr>
<td>V₂O₅-WO₃ (MoO₃)/TiO₂</td>
<td>Vehicle exhaust catalyst</td>
<td>Liu et al. (2012), Shafer et al. (2012)</td>
</tr>
<tr>
<td>Vanadium and V alloys</td>
<td>Superconductor</td>
<td>Ponyatovski et al. (2009)</td>
</tr>
<tr>
<td>Other applications</td>
<td>Color modifiers in mercury-vapor lamp, photographic developer, drying agent in various paints and varnishes, and reducing agent, production of pesticides, and the black dyes (e.g., mordants), inks, and pigments, (Vanadium Production, 2003).</td>
<td>Moskalyk and Alfantazi (2003)</td>
</tr>
</tbody>
</table>
particular those related to energy generation and storage, are likely to increase in the future.

The waste V generated by the ferrous metallurgy industry is mainly in liquid and particulate form (WHO, 1988). The recovery of V from these wastes is around 60–70%; the remaining 30–40% of V is discharged into the environment via gas emission, dust, waste water and slag (Hope, 1997; Jiao and Teng, 2008). Liquid waste and wash water from plants may contain up to several hundred mg L⁻¹ of V. Other industries that generate V-containing wastes include the chemical and polymer industry, where V is an important component in a wide array of chemical syntheses and oxidation reactions, and the mining industry, where the processing of U and Ti ores produces V-containing effluents and leachates (Nriagu, 1998). Additional V is released to surface environments by fossil fuel processing and burning, mining activity, and the application of phosphorus fertilizers (Aide, 2005; Nakano et al., 1990; Shotyk et al., 2014). The combustion of V-enriched fossil fuels in particular, primarily in the form of residual crude oil, is a significant source of anthropogenic V emissions to the atmosphere (Duce and Hoffman, 1976; Hope, 1997).

5. Conclusions and outlook

Interest in V geochemistry spans the deep Earth, the crust, aquatic and terrestrial sediments and extraterrestrial materials. The unique chemical characteristics of V make it well suited for a range of applications, both industrial and scientific. New knowledge of V partitioning in the deep Earth and crust supports exploration for V ores. Recent progress on high precision V isotope analysis has opened a new door for studying the geochemical behavior of V and its application to a number of fundamental processes. The abundance and active redox chemistry of V can make it an important electron acceptor in natural environments, and forms the basis for vanadium’s application as an environmental tracer. Recent improvement in speciation methods will allow improved analysis of V species in environmentally relevant sample, leading to a better understanding of V biogeochemistry.

Two open areas for investigation are the mobility of V in soils and sediments, and the roles of microorganisms in V biogeochemical cycles. It appears that the release kinetics of soil and sediment V is largely determined by the rate at which V is transferred from immobile to mobile pools. Quantifying the binding states of soil and sediment V is critical to predict V mobility at soil and sediment interfaces with water. Studies that include X-ray absorption spectroscopy, i.e., XANES, would compliment column separation techniques and can offer important information on V chemical states at nm-scales. These techniques can also be used to articulate the role of soil and sediment microorganisms in controlling the biogeochemical cycling of V, in particular the biological reduction of V followed by incorporation of reduced V species into secondary minerals.

Vanadium isotope chemistry is another developing research area that we anticipate will lead to breakthroughs in understanding V cycling, in both deep Earth and in surface environments. Because V occurs naturally in many valence states, V isotopes can be fractionated in a variety of processes from high temperature to low temperature as sensitive markers of redox conditions. Vanadium isotopes can be useful tracers to help understand fundamental processes involving the partitioning of different valence states of V between minerals, melts, and vapors. Such processes include formation of the Earth and moon, segregation of the core, evolution of the mantle and crust, magmatism, and ore deposit formation. It is also promising to apply V isotopes to low temperature geochemistry studies. Because V is a reserve element in the ocean, V content and isotopic composition should be homogenous in open oceans. The concentration of V in ocean sediment is controlled by redox reaction and absorption to clay and oxide minerals, which could also substantially fractionate V isotopes. Given that Cr and Mo isotopes have been used to study redox conditions of the paleo-ocean, V isotopes should be similarly sensitive to O₂ variation in paleo-environments. The V isotope geochemistry of black shales would be especially interesting for such a purpose. Furthermore, because of the enrichment of V in some organisms, such as marine algae and plankton, V isotopes can provide an additional tool to study V cycling among water, soils, and life.

As the global demand for V increases, its occurrence will receive more attention; at the same time, its presence will likely become a more urgent environmental issue. Attention is currently focused on V with respect to exploitation and disposal. New mining activity for V is increasing, as evidenced by developing mines in North America and Asia. There is large scale V pollution in many regions worldwide, which is largely attributable to mining activities and fossil fuel consumption. The challenge of defining the problem of V in the environment is confounded by the limited understanding of V biogeochemistry relative to other 3d transition elements. Vanadium has been suggested to be a potentially dangerous pollutant in the same class as mercury, lead and arsenic (Moskalyk and Alfantazi, 2003); the United Nations Environment Program has advised categorizing V in the priority list of environmental risk elements (Naem et al., 2007). A more detailed understanding of the biogeochemical behavior of V may help to assess the risk to the environment and to human health, and to facilitate the design of new remediation technologies.

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