



Vanadium: Global (bio)geochemistry



Jen-How Huang^{a,*}, Fang Huang^b, Les Evans^c, Susan Glasauer^c

^a Environmental Geosciences, University of Basel, CH4056 Basel, Switzerland

^b CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, USTC, Hefei, Anhui 230026, China

^c School of Environmental Sciences, University of Guelph, Guelph, ON N1G 2W1, Canada

ARTICLE INFO

Article history:

Received 18 May 2015

Received in revised form 22 September 2015

Accepted 23 September 2015

Available online 28 September 2015

Keywords:

Vanadium

Geochemistry

Biogeochemical cycling

Microorganism

Isotope

Mineralogy

Soil

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 diagenesis, reflecting variations of fO_2 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.

© 2015 Elsevier B.V. All rights reserved.

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 fO_2 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	76
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).

4.3.	Vanadium in surface environments: water, soil, and sediment	79
4.3.1.	Freshwater environments	79
4.3.2.	Marine environments	79
4.3.3.	Soils and sediments	81
4.3.4.	Adsorption to metal oxide minerals	82
4.4.	Vanadium in the atmosphere	84
4.5.	Anthropogenic sources	84
5.	Conclusions and outlook	85
	Acknowledgements	85
	References	85

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 crust than either element; concentrated mineral deposits are consequently rare. Much of the historical interest in V has derived from the occurrence of the common redox states in Earth surface environments (+3, +4, +5) as a consequence of V's geochemical evolution. The chemical speciation and the solubility of V species are strong functions of pH and Eh conditions (Taylor and Van Staden, 1994), making it a key redox indicator. More recently, interest in V partitioning during high temperature – high pressure magma differentiation processes has increased, and new possibilities to exploit V stable isotope chemistry are being explored (Nielsen et al., 2011; Nielsen et al., 2014; Prytulak et al., 2011; Prytulak et al., 2013). Studies on the partitioning of V among the possible reservoirs in the Earth's crust have provided critical insights into the evolution of these reservoirs (Fig. 1).

The lithophilic nature of V explains its predominance in Earth surface environments, where it plays a role in a wide range of biological processes. The function of V in biology likely evolved with the chemical differentiation of the Earth's surface environments. This leads to the intriguing possibility that V played a major role in biological electron transfer early in Earth's history (Rehder, 2008a; Rehder, 2008b).

The complex redox chemistry of V and its particular application to renewable energy technologies will likely add to the demand for this element in the future. The demand for V used in construction materials, by far the greatest consumer of mined V, can be expected to further increase the volume of this element that is cycled through terrestrial, aquatic and atmospheric systems.

In the following, we explore the chemical behavior of V in the Earth's major compartments, including magma, rocks, sediments and organisms as well as in extraterrestrial matter.

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 fO₂ during the “deep magma ocean” process (Gessmann and Rubie, 1998; McDonough and Sun, 1995; Palme and O'Neill, 2003; Ringwood et al., 1991; 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 fO₂, peridotites from different tectonic settings show variable V contents and correlations with other major trace elements, providing an important tool to constrain fO₂ of the mantle through the Earth's history (Canil, 2002; Canil, 2004). A summary of 6590 basalt 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

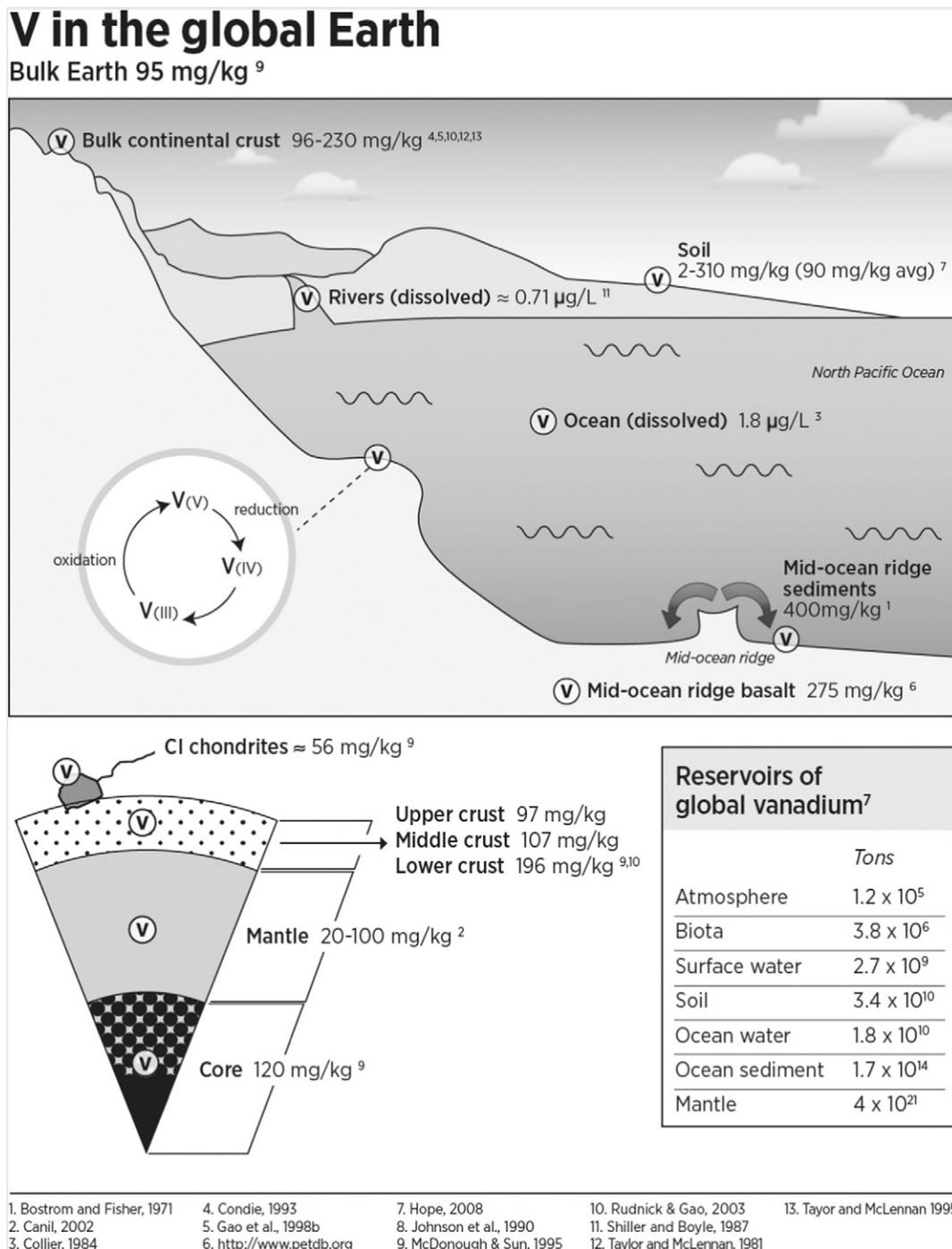


Fig. 1. Vanadium storage on earth.

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, 1985; 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 $91\text{--}106 \text{ mg kg}^{-1}$ (post-Archean), and shows negative correlations

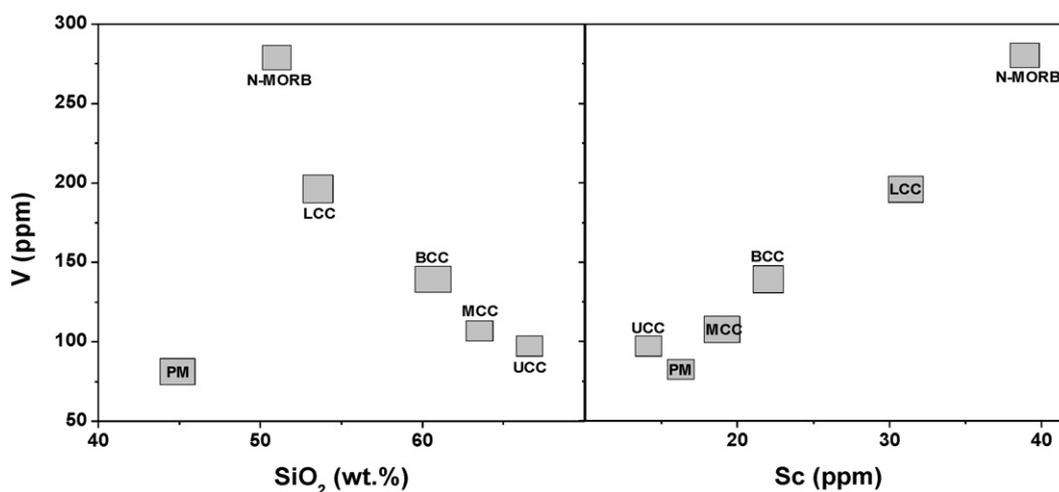


Fig. 2. Correlations of V contents with SiO₂ and Sc in geochemical endmembers. PM, primitive mantle; UCC, upper continental crust; MCC, middle continental crust; LCC, lower continental crust; BCC, bulk continental crust; N-MORB, normal mid-ocean ridge basalts. Data source: crust, data Rudnick and Gao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

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 f_{O_2} 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 f_{O_2} 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 f_{O_2} -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 in 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 f_{O_2} in the melting and evolution of the Earth and its moon, and Mars. Application of this method revealed that f_{O_2} 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).

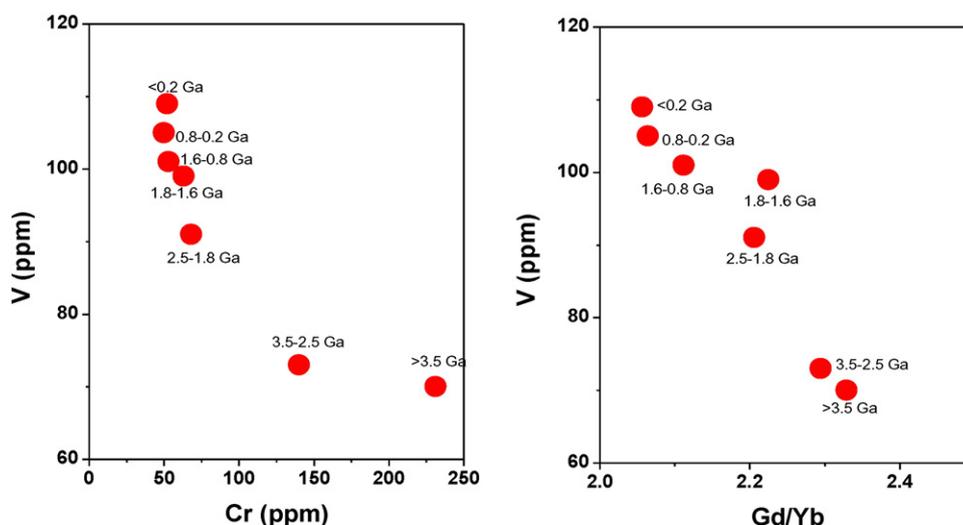


Fig. 3. Variations of V, Cr, and Gd/Yb of continental crust with time showing decreasing contribution of mantle materials to the continental crust. Data are from Condie (1993).

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 fO_2 . 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 fO_2 . Several experimental studies have been performed to study the partitioning of V between silicate melt and metallic melt ($D_{V}^{Metallic/silicate}$) to constrain the fO_2 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). $D_{V}^{Metallic/silicate}$ and $D_{Cr}^{Metallic/silicate}$ may not be sensitive to silicate melt composition, but decrease dramatically with increasing fO_2 and Si content in the metallic melt (Tuff et al., 2011; Wood, 2008). Wade and Wood (2005) estimated that $D_{V}^{core/mantle}$ 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 fO_2 (and iron oxide in the mantle) or a continuously increasing fO_2 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 $D_{V}^{core/mantle}$ 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 fO_2 can be excluded because the temperature required for an appropriate $D_{V}^{metallic/silicate}$ 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 fO_2 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

$D_{V}^{Mineral/melt}$ has been intensively investigated, with a special focus on the role of fO_2 in changing the valence and thereby the partitioning of V at high temperature. Numerous experimental studies clearly show that $D_{V}^{Mineral/melt}$ are dominantly controlled by fO_2 . 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 Fe^{3+} and Ti^{4+}) 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 Fe^{3+} , Ti^{4+} , and H_2O on $D_{V}^{mineral/melt}$ 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- fO_2 conditions of the upper mantle, $D_{V}^{mineral/melt}$ 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). $D_{V}^{Olivine/melt}$ and $D_{V}^{orthopyroxene/melt}$ 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 $D_{V}^{augite/melt}$ is greater than $D_{V}^{pigeonite/melt}$ at the same fO_2 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 ($\Delta \log fO_2$ (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 fO_2 constrained by vanadium

Temporal variation of the mantle fO_2 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 Al_2O_3 , 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 fO_2 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 fO_2 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 Al_2O_3 in peridotites from variable tectonic settings reveals that abyssal peridotites were formed under a similar fO_2 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 fO_2 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 fO_2 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 fO_2 (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 fO_2 of the mantle wedge is at the same level as the MORB source (\sim FMQ). This conclusion seems to contradict the observation that the primitive basalts and spinel peridotites from variable arcs have slightly higher Fe^{3+}/Fe^{2+} and thus higher fO_2 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 fO_2 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 $\delta^{56}Fe$ in arc lavas than in MORB (Dauphas et al., 2009); this does not support the higher fO_2 in the source of arc lavas relative to the MORB source if both have similar initial Zn/Fe and $\delta^{56}Fe$. Reconciling such discrepancies is challenging.

Nonetheless, future experimental studies on the partitioning of V between mantle minerals and hydrous melt under variable fO_2 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}V and ^{51}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}V relative to ^{51}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. $\sim 0.10\%$ (2σ) (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 isotope fractionation in meteorites and in terrestrial materials. For example, $\delta^{51}\text{V}$ 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., 2014; Prytulak et al., 2011; Prytulak et al., 2013). 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 titanomagnetite 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 $[\text{VO}(\text{OH})]$ 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 $[\text{V}(\text{V})]$ ore minerals are associated with low temperature, non-sulfidic mineralization in parts of southern Africa, including Namibia (Boni 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 (Boni et al., 2007). Minerals include mottramite $[\text{PbCu}(\text{VO}_4)(\text{OH})]$, desclozite $[(\text{Pb}, \text{Zn})_2\text{VO}_4(\text{OH})]$ and vanadinite $[\text{Pb}_5(\text{VO}_4)_3\text{Cl}]$. 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 (Boni et al., 2007). The deposits, now mined out, once contained several million tons of extractable V ore.

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

Weathering, transport, sedimentation, and diagenesis 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 $(\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O})$ and related carnotite group minerals such as tyuyamunite (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 $[\text{VO}(\text{OH})_2]$ and simplotite $[\text{Ca}(\text{VO})_2(\text{VO}_4)_2 \cdot 5\text{H}_2\text{O}]$ resulted (Roach and Thompson, 1959). More intensive weathering that leads to higher acidity and oxidizing conditions resulted in minerals such as carnotite and hewettite $[\text{Ca}(\text{V}_6\text{O}_{16}) \cdot 6\text{H}_2\text{O}]$ (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 diagenesis, metamorphism, and

Table 1
Speciation of vanadium in different compartments of the surface environment.

Compartment	Vanadium speciation	Remarks	References
Coastal waters, USA	V(IV): up to 0.56 $\mu\text{g L}^{-1}$; V(V): up to 1.68 $\mu\text{g L}^{-1}$,	High V(IV) and V(V) concentrations in summer; low in spring	Wang and Sañudo Wilhelmy (2009b)
Lake Sediment, Venezuela	V(IV): 0.4–25.8 mg kg^{-1} ; V(V): 1.4–9.2 mg kg^{-1} ,	Separation with Chelex 100 resin	Colina et al. (2005)
Fish muscle	V(IV): 0.92 mg kg^{-1}	Oil production with 10,000 platforms	
Mussel	V(IV): 1.52 mg kg^{-1}	Speciation with LC-ICP-MS	
Coal, Kentucky, USA	V(III) and V(IV) in oxygen coordination	Speciation by EXAFS	Maylotte et al. (1981)
Red mud leachate, Hungary	V(V) detected	Speciation by EXAFS	Burke et al. (2012)
Vanadiferous titanomagnetite	V(III) predominance with up to 10% of V(IV)	Speciation by XANES	Balan et al. (2006)
Magnetite, South Africa	V(III) predominance with up to 9–16% of V(IV)	Speciation by HERFD-XAS	Bordage et al. (2011)
Hematite, India	V(III) and V(IV) (41–72%)		
Soil extracts, Belgium, Denmark, Sweden	V(IV): 0.06–0.14 mg L^{-1} ; V(V): 0.6–3.0 mg L^{-1} (n = 3)	Extraction with 10 mM CaCl_2	Baken et al. (2012)
Oil shale	Prophyrin associated V(IV)	Speciation by HPLC-ICP-MS	
Sedimentary limestone,	9% and 19% of V as prophyrin associated V(IV) (n = 2)	Determined by XRD	Ekstrom et al. (1983)
Coke waters;	V(IV): 48–1090 $\mu\text{g L}^{-1}$; V(V): 926–5137 $\mu\text{g L}^{-1}$ (n = 2)	Determined by ESR	Premović et al. (1986)
Peat pond; Alberta, Canada	V(IV): 105 $\mu\text{g L}^{-1}$; V(V): 30 $\mu\text{g L}^{-1}$ (n = 1)	Speciation by HPLC-ICP-MS	Li et al. (2007)
Mineral water,	V(IV): <DL–3.19 $\mu\text{g L}^{-1}$; V(V): 5.07–45 $\mu\text{g L}^{-1}$ (n = 10)	Speciation by HPLC-ICP-MS	Aureli et al. (2008)
Lake water, Yangzhou, China	V(IV): undetectable; V(V) 4.36 $\mu\text{g L}^{-1}$ (n = 1)	Speciation by GFASS after ion-exchange resin separation	Zhao et al. (2006)
Soils	V(IV), 46.8 $\mu\text{g g}^{-1}$; V(V) 26 mg kg^{-1} (Pintung, Taiwan)	Speciation by HPLC-ICP-MS	Kuo et al. (2007)
	V(IV), 49.2 mg kg^{-1} ; V(V) 51.8 mg kg^{-1} (SRM 2709)		
Oil refining leachate, Taiwan	V(IV): 12.2 mg L^{-1} ; V(V), 16.5 mg L^{-1} (n = 1)	UV detection after LC separation	Jen and Yang (1994)
Lake water, Wuhan, China	V(IV): <DL; V(V): 2.53 $\mu\text{g L}^{-1}$ (n = 1)	Speciation by FETV-ICP-OES	Wu et al. (2005)
Soils, South Africa	V(IV): 520–7120 mg kg^{-1} ; V(V): 11–42 mg kg^{-1} (n = 4)	AAS determination after NaCO_3 extraction	Mandiwana and Panichev (2004)
Sea water	V(IV): 0.61–0.90 $\mu\text{g L}^{-1}$; V(V) 0.50–0.86 $\mu\text{g L}^{-1}$ (NASS-4 and CASS-3) (n = 2)	Speciation by HPLC-ICP-MS	Wann and Jiang (1997)
River water	V(IV): 0.38 $\mu\text{g L}^{-1}$; V(V): <DL (SLRS-3) (n = 1)		
Mineral water	V(IV): 0.38 $\mu\text{g L}^{-1}$; V(V): 0.60 $\mu\text{g L}^{-1}$ (n = 1)	ICP-MS detection after anion-exchange membrane separation	Jia et al. (2012)
Lake water, Ji Lin, China	V(IV): 0.25 $\mu\text{g L}^{-1}$; V(V): 1.0 $\mu\text{g L}^{-1}$ (n = 1)		
Particulates from diesel engine	V(IV): 10.2–20.1 ng mile^{-1} ; V(V): 2.3–109 ng mile^{-1} (n = 4)	Acetate soluble fraction	Shafer et al. (2012)
Urban aerosols, USA	V(II), V(III), V(IV) and V(V) identified with XANES	Acetate soluble fraction	
	V(IV): ca. 0.15–4.5 mg kg^{-1} ; V(V): ca. 0.4–7.7 mg kg^{-1} (n = 10)	ICP-MS detection after Chelex resin separation and XANES	
Seawater, Galician, Spain	V(IV): <DL; V(V): up to 0.25 $\mu\text{g L}^{-1}$	AAS determination after Chelex 100 resin separation	Alcalde-Isorna et al. (2011)
Seawater, China	V(IV): 0.5–1.6 $\mu\text{g L}^{-1}$; V(V): 0.5–1.8 $\mu\text{g L}^{-1}$ (n = 3)	ICP-OES determination after CTAB- modified alkyl silica micro-column	Xiong et al. (2010)
River water,	V(IV): 1.0 $\mu\text{g L}^{-1}$; V(V): 1.2 $\mu\text{g L}^{-1}$ (n = 1)		
Lakewater,	V(IV): 1.7–3.4 $\mu\text{g L}^{-1}$; V(V): 1.2–1.3 $\mu\text{g L}^{-1}$ (n = 2)		
Well water,	V(IV): 0.4–11.7 $\mu\text{g L}^{-1}$; V(V): 1.4–4.2 $\mu\text{g L}^{-1}$ (n = 2)		
Rain water,	V(IV): 0.2–0.4 $\mu\text{g L}^{-1}$; V(V): 1.5–1.6 $\mu\text{g L}^{-1}$ (n = 2)		

N: number of samples measured; <DL: below detection limit.

Average dissolved ocean V = 1.8–2.3 $\mu\text{g L}^{-1}$ (reviewed in (Emerson and Husted, 1991)).

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 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 shown subsequently that V can replace octahedrally coordinated Fe(III) in the diaspore structure of goethite (Schwertmann and Pfab, 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). Asphaltene in crude oil contains 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 1–10); 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 between marine and terrestrial environments, most recently in crude deposits in Nigeria, Russia, Venezuela and South Africa (Akinlua et al., 2015; Lopez et al., 2015; Ogunlaja et al., 2014; Yasnygina et al., 2015).

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 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 V (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 Sañudo Wilhelmly, 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, VO₂⁺, vanadic acid, H₃VO₄⁰ and its three conjugate bases, H₂VO₄⁻, HVO₄²⁻ and VO₄³⁻ (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_nVO₄ⁿ⁻³ (Wanty and Goldhaber, 1992; Wehrli and Stumm, 1989). The species VO₂⁺ dominates under acidic conditions, and VO₄³⁻ occurs in extremely alkaline conditions (Fig. 5).

Vanadic acid, H₃VO₄⁰, 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 (Wanty and Goldhaber, 1992). Polynuclear species have enhanced stability, as shown using reaction enthalpy for V₄ and V₅ 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

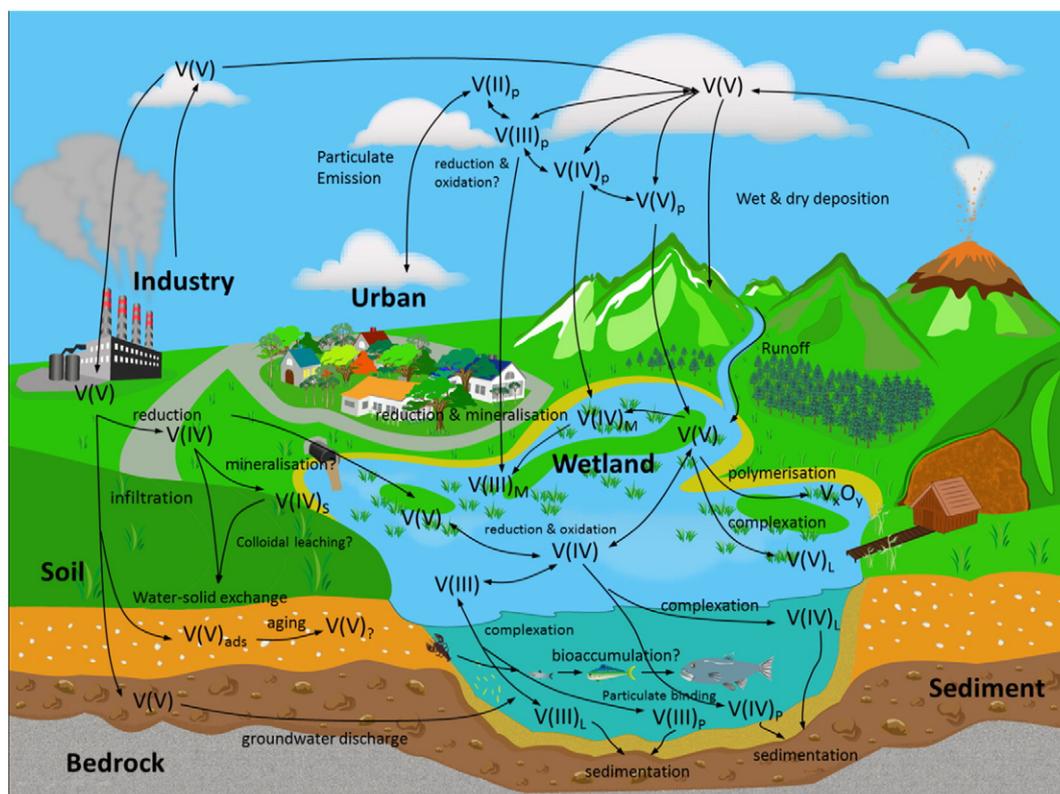


Fig. 4. Schematic presentation of vanadium biogeochemical cycling in the surface environment.

Table 2

Dissociation constants, log K, for mono-nuclear vanadium(V) species (calculated from the Gibb's energy values given in Wanty and Goldhaber (1992), 25 °C, 1 atm. Pressure, zero ionic strength (I).

	log K		log K
$\text{VO}_2^+ + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{VO}_4^+ + \text{H}^+$	-3.67	$\text{H}_2\text{VO}_4^- \rightleftharpoons \text{HVO}_4^{2-} + \text{H}^+$	-8.06
$\text{H}_3\text{VO}_4^+ \rightleftharpoons \text{H}_2\text{VO}_4^- + \text{H}^+$	-3.40	$\text{HVO}_4^{2-} \rightleftharpoons \text{VO}_4^{3-} + \text{H}^+$	-13.28

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) occurs as the vanadyl cation, VO^{2+} or $\text{VO}(\text{OH})^+$ (Table 4, see also Fig. 7). The aqueous chemistry of V(IV) is strongly influenced by its associated complexes with inorganic and organic 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 VOH^{2+} , $\text{V}(\text{OH})_2^+$ and $\text{V}_2(\text{OH})_4^{2+}$ (Pajdowski, 1966; Pajdowski and Jeżowska-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; Wällstedt et al., 2010; Wang and Sañudo Wilhelmy, 2009b) (Table 1).

4.1.1. 4.1.2. The role of complexation in V mobilization

The complexation of vanadium by organic and inorganic ligands can elevate its mobility at solid-water interfaces (Wanty and Goldhaber, 1992). Vanadium(IV) forms complexes more readily than does V(V) and with a wider range of organic and inorganic ligands. Common complexes formed by V with inorganic ligands include $\text{H}_4\text{VO}_4(\text{C}_2\text{O}_4)_2^{3-}$ and $\text{H}_4\text{VO}_4\text{C}_2\text{O}_4^-$ for V(V); VOCl^+ , VOF^+ , VOF_2 , VOF_3^- , VOF_4^{2-} , VOSO_4 , $\text{VO}(\text{C}_2\text{O}_4)_2^{2-}$, $\text{VO}(\text{OH})\text{C}_2\text{O}_4^-$, $\text{VO}(\text{CH}_3\text{COO})_2$, $\text{VO}(\text{CH}_3\text{COO})$, VOCO_3 , $\text{VO}(\text{OH})\text{CO}_3^-$ for V(IV); and VSO_4^- for V(III) (Wanty and Goldhaber, 1992).

A large number of organic compounds can complex V, including fulvic and humic acids, via oxygen groups (Cheshire et al., 1977; Wehrli, 1987). Table 5 provides an overview of some studies that have investigated the complexation of V(IV) and V(V) by natural organic matter. It is known that vanadate oxyanions form relatively weak complexes with organic compounds, as compared to the V(IV) oxyanion VO_2^{2+} (Wehrli, 1987). Nevertheless, V(V)-organic complexes have

Table 3

Poly-nuclear soluble vanadium(V) species.

$\text{H}_2\text{V}_2\text{O}_7^{2-}$	$\text{V}_3\text{O}_{10}^{3-}$	$\text{V}_4\text{O}_{12}^{4-}$	$\text{V}_5\text{O}_{15}^{5-}$	$\text{V}_6\text{O}_{18}^{6-}$	$\text{H}_3\text{V}_{10}\text{O}_{28}^{3-}$
$\text{HV}_2\text{O}_7^{3-}$		$\text{HV}_4\text{O}_{13}^{3-}$			$\text{H}_2\text{V}_{10}\text{O}_{28}^{2-}$
$\text{HV}_2\text{O}_7^{4-}$		$\text{V}_4\text{O}_{13}^{6-}$			$\text{HV}_{10}\text{O}_{28}^{5-}$
					$\text{V}_{10}\text{O}_{28}^{6-}$

been suggested as the essential intermediates for the reduction of V(V) (Kustin et al., 1974; Wells and Kuritsyn, 1970), and V is known to be stabilized against reduction by binding to humic substance at circumneutral pH values (Lu et al., 1998). The strong tendency of V(IV) to form stable complexes helps explain the presence of V(IV) in natural waters under toxic conditions (Wehrli, 1987). Aluminum and titanium oxide surfaces have been shown to catalyze V(IV) oxidation (Wang and Sañudo Wilhelmy, 2009b; Wehrli and Stumm, 1988; Wehrli and Stumm, 1989), and complexation with organic molecules may serve to inhibit oxidation.

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; Bredberg 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^0 , are given in Table 6.

It is apparent that V(V) 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 VO_2^+ concentrations in solution decreased with increasing pH from 2 to 6 because of the formation of $(\text{VOOH})_2^{2+}$ and $\text{VO}(\text{OH})_2$ species. The increased pH may, however, cause condensation of VO_2^+ to $\text{V}_{10}\text{O}_{28}^{6-}$, which is not directly involved in the reduction reaction (Lu et al., 1998). The vanadyl ion, VO^{2+} , and its hydrolyzed species, VOOH^+ , 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(V) species.

The oxyhydroxide of V(IV), $\text{VO}(\text{OH})_{2(s)}$ and the hydroxide of V(III), $\text{V}(\text{OH})_{3(s)}$, can form at relatively low concentrations at 25 °C (Fig. 8). The oxidation–reduction reactions for V which include solids is shown in Table 7. The precipitation of V in soils and sediments is discussed in Section 4.3.3.

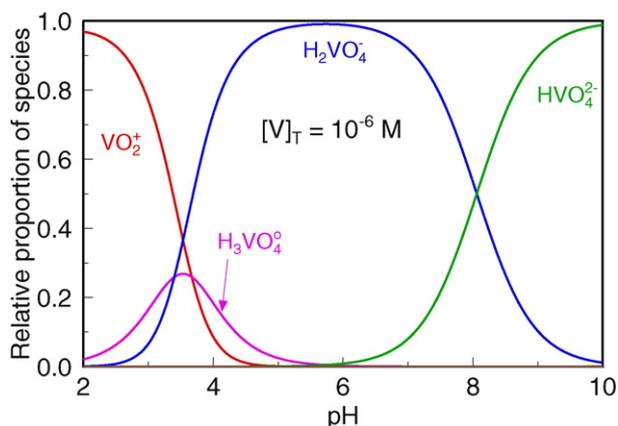


Fig. 5. Speciation of vanadium(V) at low concentrations using the thermodynamic data given in Table 2.

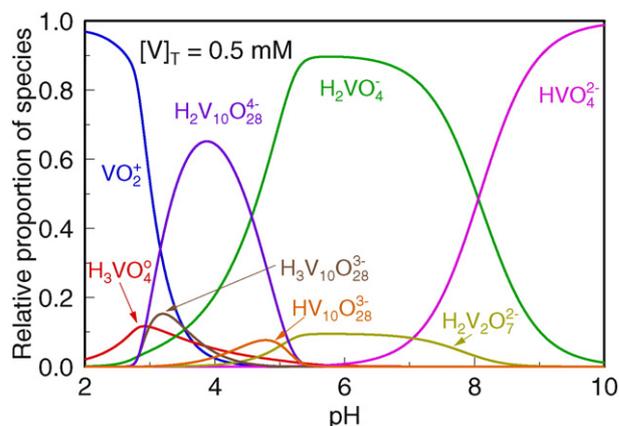


Fig. 6. Speciation of vanadium(V) at 0.5 mM concentration (thermodynamic constants are from Elvingson et al. (1996), 25 °C, 1 atm. Pressure, I = 0.15 M NaCl).

Table 4

Formation constants, $\log \beta$, for vanadium(IV) with some inorganic ligands (calculated from the Gibb's energy values provided in Wanty and Goldhaber (1992), 25 °C, 1 atm. Pressure, zero ionic strength (I)).

Vanadium(IV)	$\log \beta$		$\log \beta$
$\text{VO}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{VO}(\text{OH})^+ + \text{H}^+$	-5.7	$\text{VO}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{VOSO}_4^0$	2.46
$2\text{VO}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons (\text{VO}(\text{OH}))_2^{2+} + 2\text{H}^+$	-6.7	$\text{VO}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{VOCO}_3^0$	3.47
$\text{VO}^{2+} + \text{Cl}^- \rightleftharpoons \text{VOCl}^+$	-0.1	$\text{VO}^{2+} + \text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{VO}(\text{OH})\text{CO}_3^- + \text{H}^+$	1.52

Organic compounds such as humic, fulvic, and ascorbic acids can reduce V(V) to V(IV), 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 fossils. 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 reductive 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

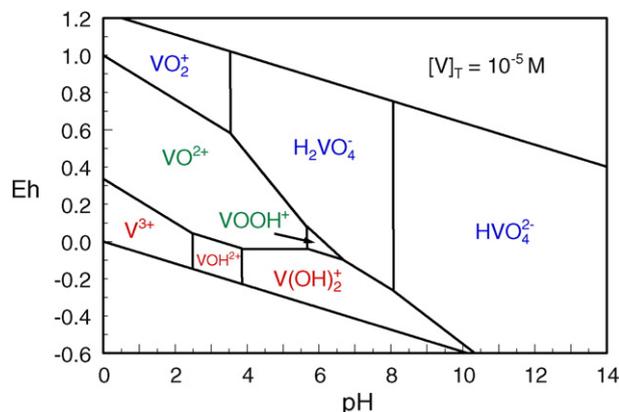


Fig. 7. Eh–pH predominance diagram for soluble species of vanadium.

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 tolerated up to 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(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 isachenkovii* A-1, *Geobacter metallireducens*, *Enterobacter cloacae* 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). In

Table 5
Vanadium complexation with natural organic matter.

Organic Substance	Vanadium Species	Interaction	Comments	References
DOC	V(V)	Humic substance-V(V) complexes less than 1% of total V	DOC: >10 mg L ⁻¹ , pH: 8, Wabamun Lake, Canada DOC: >10 mg L ⁻¹ , pH: 7, Allard river, Canada DOC: >10 mg L ⁻¹ , pH: 6.5, Colombiere river, Canada DOC: <1 mg L ⁻¹ , pH: 8, St. Lawrence Gulf, Canada	Canada (2010)
DOM	V(V)	V complexation with DOM is not important	V: 2.0–2.5 μg kg ⁻¹ ; pH: 7.72 Mississippi river, USA	Shiller and Boyle (1987)
Humic substance	V(V)	V(V) monomer complexation with humic substance at pH 7.2 with formation equilibrium constant of 108 M ⁻¹ .	V(V): 12.8–166 mg L ⁻¹ , Humic substance: 0.025–0.58 mM, 25 °C	Lu et al. (1998)
Fulvic acid	V(IV)	V(IV) bound to carboxylic groups of humic substance	-	Wilson and Weber (1979)
Peat humic acid	V(IV)	Partially complexed at pH 2, predominantly complexed at pH 4 and 6	-	Goodman and Cheshire (1975)
Soil fulvic acid	V(IV)	Complexed by oxygen or mixed oxygen-nitrogen donor groups in the humic acid.	V: 0.51 g L ⁻¹	Goodman and Cheshire (1975)
Soil organic matter	V(IV)	Complexation Aggregation as (VO) ₂ (heavier fractioned fulvic acid) ₆ Association of 4.2% of total soil V with humic and fulvic acids	V: 12.8–28 μg L ⁻¹ ; pH 5; fulvic acid: 2.5 × 10 ⁻³ M Soil obtained from Scotland	Templeton and Chasteen (1980) Cheshire et al. (1977)

–: no information

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 (Kalinowski et al., 2004). *Shewanella putrefaciens* CN-32 exposed to carnotite under reducing conditions respired mineral-bound V(V) in preference to U(VI), resulting in higher solution concentrations of V (Glasauer, 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 of carnotite and associated minerals in the Colorado Plateau. The mobility of co-occurring V and U is highest under weakly reducing conditions as V(IV) and U(VI). Fully oxidized V and U will co-precipitate as carnotite minerals, whereas reduced species will precipitate in separate mineral phases. Organic matter in association with V and U species may have created cycles of oxidizing and reducing conditions that eventually formed the deposits, as suggested by several researchers (Evans and Garrels, 1958; Hansley and Spirakis, 1992; Hostetler and Garrels, 1962; Spirakis, 1996).

In addition to the control on V geochemistry that microbes exert through redox reactions, adsorption to microbial surfaces can also play a role in V cycling. The microbial surface contains different organic functional groups that contribute negative and positive charges, e.g. carboxyl, phosphoryl, hydroxyl and amide groups. Although the net surface charge

is negative at pH values where most life exists, both anionic and cationic metal and metalloid species will be retained within the cell envelope (French et al., 2013a; French et al., 2013b). In addition, the generally high surface-to-volume ratio of microbial cells facilitates contact between the surface and sorbates, which enables sorption and uptake. Because of the high density of functional groups in the microbial cell wall that can react with cations and anions, it is feasible that strong metal binding will impact the structural integrity of the wall. This was observed for cultures of *Shewanella putrefaciens* CN-32 exposed to V(IV). Under oxic conditions, V(IV) stabilized membrane fluidity, which is controlled by lipid packing (French et al., 2013a; French et al., 2013b). Exposure to V(IV) did not, however, impact membrane fluidity under anoxic conditions although more V (as VO²⁺) was associated with the cell wall, which could not be explained definitively and reflects the complex biological chemistry of V.

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 dry weight at pH 3 (Ghazvini 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 (Ghazvini 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 6
Oxidation–reduction reactions for the oxidation states of vanadium (calculated from the Gibb's energy values given in Wanty and Goldhaber (1992), 25 °C, 1 atm. Pressure, zero ionic strength (I).

Vanadium(V)–Vanadium(IV)	E°	Vanadium(IV)–Vanadium(III)	E°
VO ₂ ⁺ + 2 H ⁺ + e ⁻ ⇌ VO ²⁺ + H ₂ O	1.000	VO ²⁺ + 2 H ⁺ + e ⁻ ⇌ V ³⁺ + H ₂ O	
H ₂ VO ₄ ⁻ + 4 H ⁺ + e ⁻ ⇌ VO ²⁺ + 3H ₂ O	1.419	VO ²⁺ + H ⁺ + e ⁻ ⇌ VOH ²⁺	0.191
H ₂ VO ₄ ⁻ + 3 H ⁺ + e ⁻ ⇌ VOOH ⁺ + 2H ₂ O	1.084	VO ²⁺ + H ₂ O + e ⁻ ⇌ V(OH) ₂ ⁺	-0.038
Vanadium(IV)–Vanadium(III)	E°	VOOH ⁺ + H ⁺ + e ⁻ ⇌ V(OH) ₂ ⁺	0.297
H ₂ VO ₄ ⁻ + 4 H ⁺ + 2e ⁻ ⇌ V(OH) ₂ ⁺ + 2H ₂ O	0.691		
HVO ₄ ²⁻ + 5 H ⁺ + 2e ⁻ ⇌ V(OH) ₂ ⁺ + 2H ₂ O	0.029		

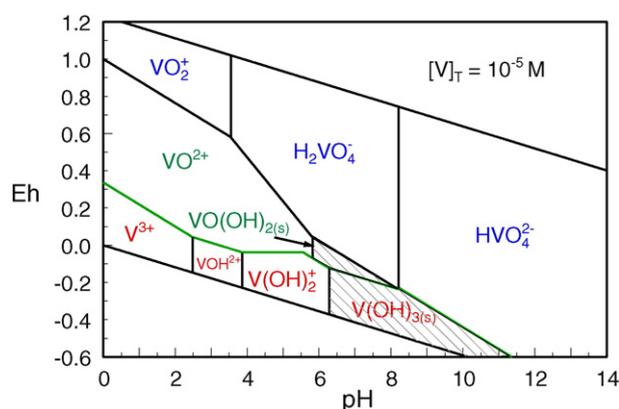


Fig. 8. Eh–pH predominance diagram for soluble and solid species of vanadium.

cycling of V between major V-containing minerals by weathering processes and processes controlled by microorganisms, including complexation and redox-driven reactions, are key to V's mobility. In the following sections, we expand the discussion of these processes by focusing on particular environments for which vanadium research has been active.

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 oxic and alkaline groundwater, where 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 (Pouret 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 Husteded (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 ($>0.45 \mu\text{m}$), 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 ($2.7 \times 10^{15} \text{ g}$) as compared to suspended particulate V ($1.8 \times 10^{10} \text{ g}$) estimated for the global ocean (Hope, 2008). Ocean sediment contains, however, the largest reservoir of V ($1.7 \times 10^{20} \text{ g}$) on the Earth's surface (Hope, 2008), mainly in marine shale and carbonaceous sediments (Ekstrom 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 $>400 \text{ mg kg}^{-1}$ (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 ocean seawater, the main species of V(V) are HVO_4^{2-} and H_2VO_4^- . Common V(IV) species are VO^{2+} , VOOH^+ , and insoluble $\text{VO}(\text{OH})_2$ (Rehder, 2008a; Rehder, 2008b). Vanadyl species can be further reduced under anoxic conditions to V(III), which readily forms solid oxides of V_2O_3 and $\text{V}(\text{OH})_3$ 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 $f\text{O}_2$ in the ocean (Shaw et al., 1990; Tribovillard et al., 2006; Wanty 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 $f\text{O}_2$ variation, for recording the history of $f\text{O}_2$ 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, anoxygenic) 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 less associated with organic carbon. For example, there is a weak correlation between V and 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 diagenesis, 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).

Table 7

Oxidation–reduction reactions for vanadium which include solid species for V(IV) and V(III). (calculated from the Gibb's energy values given in Wanty and Goldhaber (1992), 25 °C, 1 atm. Pressure, zero ionic strength (I)).

Reduction reaction	E°
$\text{H}_2\text{VO}_4^- + 2 \text{H}^+ + \text{e}^- \rightleftharpoons \text{VO}(\text{OH})_{2(\text{s})} + \text{H}_2\text{O}$	1.057
$\text{HVO}_4^{2-} + 4 \text{H}^+ + 2\text{e}^- \rightleftharpoons \text{V}(\text{OH})_{3(\text{s})} + \text{H}_2\text{O}$	0.892
$\text{VO}(\text{OH})_{2(\text{s})} + 2 \text{H}^+ + \text{e}^- \rightleftharpoons \text{V}(\text{OH})_2^+ + \text{H}_2\text{O}$	0.324
$\text{VO}(\text{OH})_{2(\text{s})} + \text{H}^+ + \text{e}^- \rightleftharpoons \text{V}(\text{OH})_{3(\text{s})}$	0.248

Table 8
Potential pathways of vanadium redox transformation in the surface environment.

Redox reaction	Redox couple/reagents	Comments	Reference
V(IV) to V(III)	H ₂ S	Slow reduction kinetics; V: 0.5–12.2 mg L ⁻¹ , pH 3.6–6.8, H ₂ S: 8.1 × 10 ⁻⁴ to 0.471 atm; ionic strength 0.05–0.1	Wanty and Goldhaber (1992)
V(V) to V(IV)	Humic substance	pH < 6; V(V): 25.5 mg L ⁻¹	Lu et al. (1998)
V(V) to V(IV)	Fulvic acid	Higher reduction rate at pH 2 than pH 6 Semiquinone radical was not involved	Wilson and Weber (1979)
V(V) to V(IV)	benzene-1,4-diol (Quinol)	Reduction rates increase with increasing acidity via formation of VO ₂ QH ₂ ⁺ and VO(OH)QH ₂ ⁺ : 25.5 and 51 mg L ⁻¹ ; quinol: 27–324 g L ⁻¹ ; HClO ₄ : 5.03–503 g L ⁻¹ ; at 16, 25, 32 and 40 °C	Wells and Kuritsyn (1970)
V(V) to V(IV)	Insoluble peat humic acid	pH: 7.2, 1.17 g L ⁻¹ , 1 g humic acid. No V(III) was identified	Szalay and Szilágyi (1967)
V(V) to V(IV)	Hydroxylamine	Via formation of VO ₂ ⁺ ·NH ₃ OH ⁺ and V(OH) ₃ ³⁺ ·NH ₃ OH ⁺ : 51 mg L ⁻¹ ; Hydroxylamine: 0.33–6.6 g L ⁻¹ ; 25–60 °C, HClO ₄ : 100–503 g L ⁻¹ .	Nazer and Wells (1980)
V(V) to V(IV)	Benzene-1,2-diol (catechol) and its derivatives	Formation of V(V)-reductant complex as intermediate	Kustin et al. (1974)
V(V) to V(IV)	L-ascorbic acid	HClO ₄ : 20.1–100 g L ⁻¹ ; 25 °C, Formation of VO ₂ ⁺ complexes with the derivatives of ascorbic acid	Ferrer and Baran (2001)
V(IV) to V(V)	O ₂	Three order of magnitude faster oxidation kinetics for V(IV) adsorbed to Al ₂ O ₃ and TiO ₂ than solution V(IV)	Wehrli and Stumm (1988), Wehrli and Stumm (1989)
V(III) to V(IV)	O ₂	V: > 0.51 mg L ⁻¹ , pH: 4–9	Fallab (1967)

–: no information

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 – ⁵⁰V (0.24%) and ⁵¹V (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

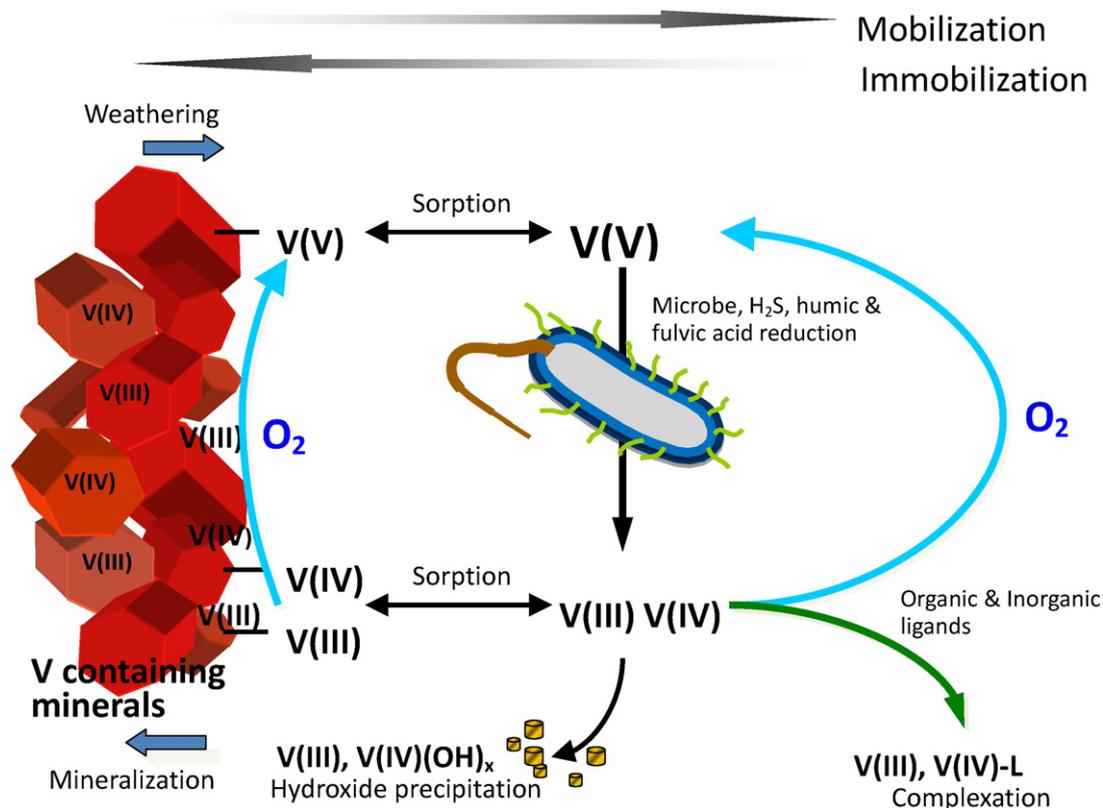


Fig. 9. Vanadium mobilization and immobilization processes at the water-soil/sediment interface.

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 VO^{2+} than chloride ions, the VOSO_4^0 complex is much more important than the VOCl^+ complex, even though the SO_4^{2-} ion concentration is lower than Cl^- (Fig. 10).

The aqueous chemistry of V(III) is similar to Fe(III) in that the vanadic, V^{3+} , ion hydrolyzes in water to form the VOH^{2+} and $\text{V}(\text{OH})_2^+$ ions (Table 9). By analogy with the Fe(III) system, the V^{3+} ion can be expected to form relatively weak complexes with the Cl^- ion, and strong complexes with SO_4^{2-} ions although the VOSO_4^0 complex is not the major species. A formation constant, $\log \beta$, of 3.28 has been calculated for the VSO_4^+ ion (Wanty and Goldhaber, 1992). This compares with values of 3.89, 3.81 and 2.25 for Al^{3+} , Cr^{3+} and Fe^{3+} respectively.

A dinuclear, tetravalent species, $\text{V}_2(\text{OH})_2^{4+}$, is only important at relatively high V^{3+} 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, $\text{V}_2\text{O}_5(\text{s})$, vanadium oxyhydroxide, $\text{VO}(\text{OH})_2(\text{s})$, vanadium tetroxide, $\text{V}_2\text{O}_4(\text{s})$, vanadium trioxide, $\text{V}_2\text{O}_3(\text{s})$ and vanadium hydroxide, $\text{V}(\text{OH})_3(\text{s})$ (Table 10). The oxides $\text{V}_2\text{O}_5(\text{s})$, $\text{V}_2\text{O}_4(\text{s})$ and $\text{V}_2\text{O}_3(\text{s})$ 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, $\text{VO}(\text{OH})_2(\text{s})$ and $\text{V}(\text{OH})_3(\text{s})$ can form at 25 °C (Garrels, 1953) and so are possible vanadium oxide precipitates in soils and sediments.

Vanadium pentoxide, $\text{V}_2\text{O}_5(\text{s})$, 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 $\text{VO}(\text{OH})_2(\text{s})$ and $\text{V}(\text{OH})_3(\text{s})$, on the other hand, both decrease

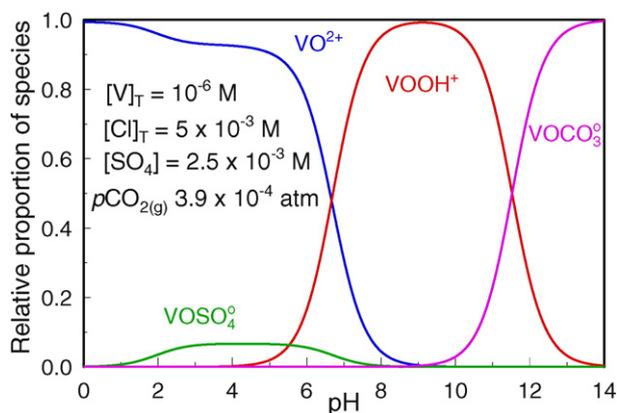


Fig. 10. Speciation of vanadium(IV) in a simulated soil solution using the thermodynamic data given in Table 4.

Table 9

Formation constants, $\log \beta$, for vanadium(III) with some inorganic ligands (calculated from the Gibb's energy values given in Wanty and Goldhaber (1992), 25 °C, 1 atm. Pressure, zero ionic strength (I)).

Vanadium(III)	$\log \beta$	$\log \beta$	
$\text{V}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{VOH}^{2+} + \text{H}^+$	-2.30	$2\text{V}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{V}_2(\text{OH})_2^{4+} + \text{H}^+$	-3.79
$\text{V}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{V}(\text{OH})_2^+ + 2\text{H}^+$	-6.33	$\text{V}^{3+} + \text{SO}_4^{2-} \rightleftharpoons \text{VSO}_4^+$	3.28

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 fractions 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

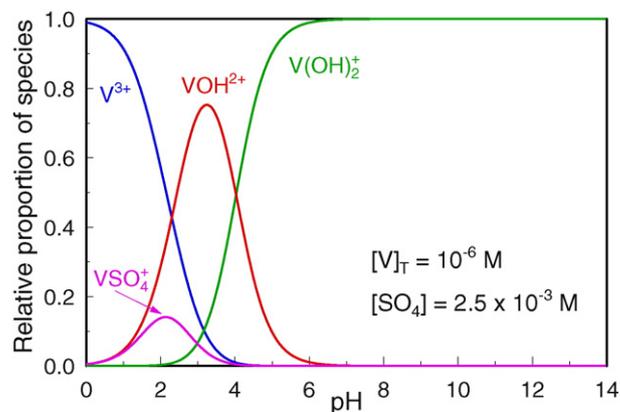


Fig. 11. Speciation of V(III) in the presence of SO_4^{2-} ions.

Table 10
Some oxide, oxyhydroxide and hydroxide precipitates of vanadium.

Reaction	log K_{so}	Reaction	log K_{so}
Vanadium(V)			
$V_2O_5(s) + 2H^+ \rightleftharpoons 2VO_2^+ + H_2O$	-1.36	Vanadium(IV)	
		$VO(OH)_{2(s)} + 2H^+ \rightleftharpoons VO^{2+} + 2H_2O$	6.11
Vanadium(III)			
$V(OH)_{3(s)} + 3H^+ \rightleftharpoons V^{3+} + 3H_2O$	7.59		

minor amounts are present as V(IV) (Baken et al., 2012; Burke et al., 2012). Vanadate 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 highlight 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 overflowing, 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 $750,000 \text{ L kg}^{-1}$ (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

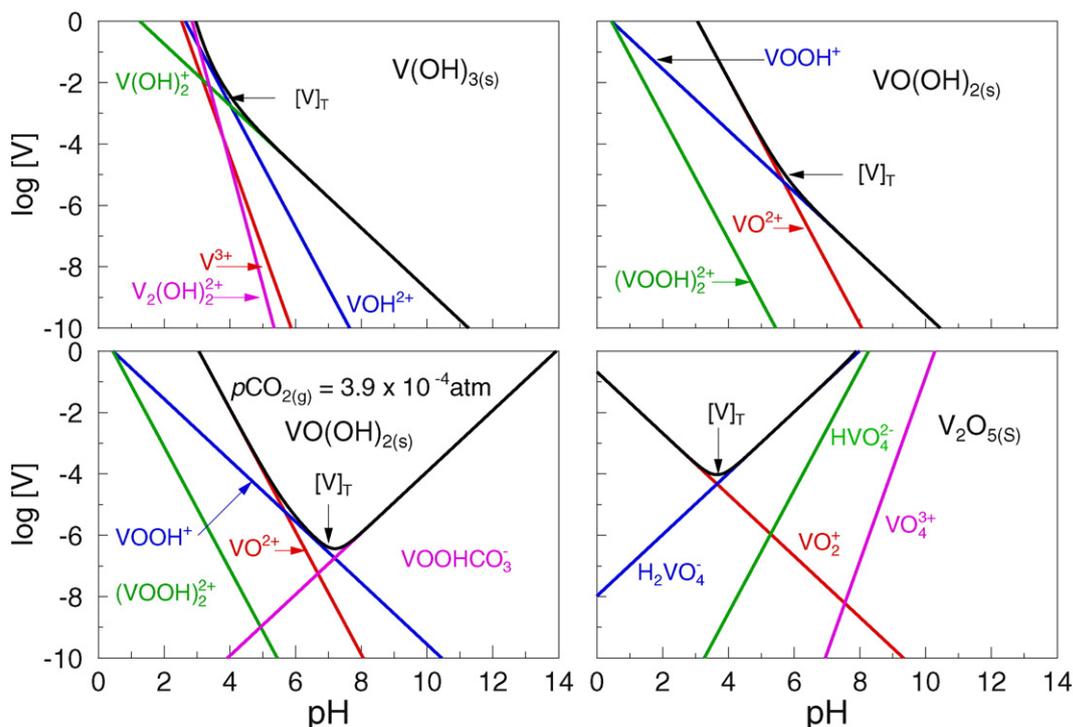


Fig. 12. Solubility of some vanadium oxides as a function of pH.

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

Material	Components	K_d (L kg ⁻¹)	pH	Comments	Reference
Agricultural soil, China	Not specified	1'400–10'950	4.3	H ₂ O leaching	Yang et al. (2014)
Mine tailing		5'170–70'530	8.1		
Soils, South Africa	V(V)	9.37–526	–	H ₂ O extraction	Mandiwana et al. (2005)
Dust		23.4			
Marine sediment, (MESS-3)		48.6			
Clay soil, USA	V(V)	~150	5.6	$c = 5\text{--}100 \text{ mg L}^{-1}$	Wang et al. (2003)
Sandy soil		~1.71	5.9		
Floodplain soils, Belgian	Not specified	~21'800–35'500	–	10 mM CaCl ₂ extraction	Cappuyens and Salbbinck (2012)
Ferrihydrite ^a	Not specified	~90'000	8	$c = 5.1 \text{ mg V L}^{-1}$	Brinza et al. (2008)
		~60'000	9	$I = 0.01$	
Ferrihydrite	Not specified	~2'000	8	$c = 10.2 \text{ mg V L}^{-1}$ $I = 0.7$	Trefry and Metz (1989)
Sandy soils,	Not specified	247–34'100	4.2–7.3	Ca(NO ₃) ₂ extraction	Gäbler et al. (2009)
Silty soils,		7'560–323'600			
Loamy soils,		4'200–755'000			
Clay soils,		4'540–489'167			
River suspended particulate matter	Not specified	29,600	–	–	Gobeil et al. (2005)
Fe(III)/Cr(III) hydroxide	V(V)	~170–270	7.9–8.2	32 °C	Prathap and Namasivayam (2010)
		~220–530		40 °C	
		~260–430		50 °C	
		~280–900		60 °C	
				$c = 10\text{--}50 \text{ mg L}^{-1}$	
TiO ₂	V(IV) ^b	~2500–225'000	1–.8–3.5	$c = 0.41\text{--}12.8 \text{ mg L}^{-1}, I = 0.1$	Wehrli (1987)
Al ₂ O ₃		~1'500–9'500	2.75–4	$c = 2.55 \text{ mg L}^{-1}, I = 0.1$	
TiO ₂	V(V)	~5000–49,500	0.5–11.5		
Al ₂ O ₃		~2500–47,500	1–10		
Insoluble peat humic acid	V(IV)	~6–60	2.1	–	Szalay and Szilágyi (1967)

–: no information.

^a calculation infeasible at pH 4–7.^b K_d from pH 3.5–5 can not be estimated, however, higher values are expected.

complexes for the vanadyl ion, VO²⁺, and mono-dentate complexes for vanadate ions, H_nVO₄^{3–n} (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, ≡Fe₂OVO(OH)₄⁺ and ≡Fe₂OVO₂OH⁰; 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.

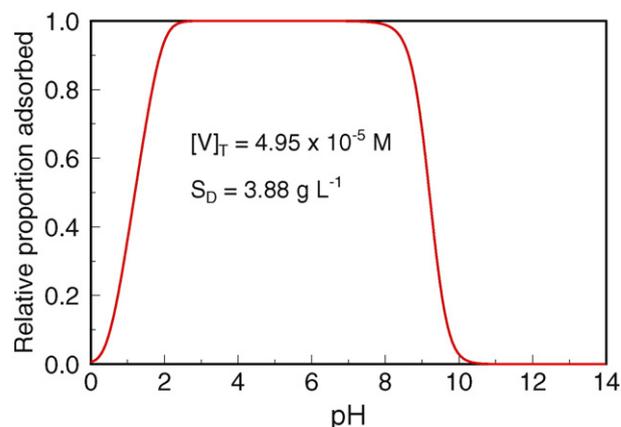
The solution pH can be expected to control V sorption, given the strong dependence of V speciation on pH. Adsorption involving ligand exchange can, however, offer exceptions to what might be expected based on simple electrostatic repulsion. For example, adsorption of V(V) at low pH to positively charged iron oxide mineral surfaces can be expected to occur via VO₂⁺ cations (Figs. 6, 7). At higher pH, V(V) occurs as conjugate acids of VO₄^{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 δ-Al₂O₃ 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 TiO₂ at the same concentration. Adsorption of vanadyl cations to TiO₂ and

Al₂O₃ was suppressed below pH ~3 and ~4, respectively (Wehrli, 1987). The adsorption behavior was explained by the predominance of VO²⁺ at pH values <~3, resulting in repulsion by the positively charged TiO₂ and Al₂O₃ 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 polynuclear V(V), i.e., metavanadate (e.g. V₃O₉^{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 Namasivayam (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

Table 12
Surface reactions and intrinsic complexation constants for V(V) onto goethite calculated using the Diffuse Layer Model (Specific surface = 37.2 m² g⁻¹; [SOH]_T = 6.02 sites nm⁻²; log K_{H1} = 6.78; log K_{H2} = – 10.10).

Adsorption reaction	log K ^{int}
2 ≡ Fe–OH ⁰ + VO ₄ ^{3–} + 4 H ⁺ ≡ Fe ₂ –OVO(OH) ₄ ⁺ + 2 H ₂ O	42.87
2 ≡ Fe–OH ⁰ + VO ₄ ^{3–} + 3 H ⁺ ≡ Fe ₂ –OVO ₂ OH ⁰ + 2 H ₂ O	41.26

**Fig. 13.** Adsorption of vanadium(V) onto goethite.

arsenate for adsorption to Fe_2O_3 , but had an equal affinity for Al_2O_3 (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 $37 \times 10^9 \text{ g yr}^{-1}$ 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 mid-to-late 19th century (Cloy et al., 2011). Deposition rates peaked (~ 1.3 to $2.0 \text{ mg m}^{-2} \text{ yr}^{-1}$) in the mid-20th century before decreasing to 0.1 – $0.3 \text{ mg m}^{-2} \text{ y}^{-1}$ 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 $10,590 \text{ }^{14}\text{C yr. B.P.}$), 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 $< 1000 \text{ Da}$ (Kawakubo et al., 1997). Non-labile V was mainly found in the higher molecular weight ($\leq 10,000 \text{ Da}$) or insoluble fractions. Another study in Japan found that $\sim 50\%$ of suspended atmospheric V occurred in particles smaller than $2 \mu\text{m}$ 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-born 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 SO_2 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
Industrial uses of vanadium.

Chemical forms	Application	References
Ferrovanadium (FeV)	Vanadium high-carbon steel alloys, high speed tool steels (surgical instruments and tools)	Moskalyk and Alfantazi (2003)
Chrome-vanadium steels	Springs and transmission gears are fabricated from	Moskalyk and Alfantazi (2003)
V–Al–Ti alloys	Jet engines, high-speed airframes and dental implants, missile cases, nuclear reactor components, jet engine housings and associated airframes	Moskalyk and Alfantazi (2003)
Vanadium foil	Cladding titanium to steel	Lositskii et al. (1966)
Vanadium pentoxide (V_2O_5)	Manufacturing sulfuric acid maleic anhydride production ceramics production	Abon and Volta (1997)
Vanadium dioxide (VO_2)	Glass coatings	Manning et al. (2004)
Vanadate	Electrochemical conversion coating	Guan and Buchheit (2004)
Vanadium redox couple	Rechargeable batteries	Joerissen et al. (2004)
V_2O_5 – WO_3 (MoO_3)/ TiO_2	Vehicle exhaust catalyst	Liu et al. (2012), Shafer et al. (2012)
Vanadium and V alloys	Superconductor	Ponyatovskii et al. (2009)
Other applications	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).	Moskalyk and Alfantazi (2003)

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 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 phosphorous fertilizers (Aide, 2005; Nakano et al., 1990; Shoty 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 fO₂ 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.

Acknowledgements

This work is financially supported by the Natural Science Foundation of China (41101484 and 41173031), the Swiss National Science Foundation (PZ00P2_122212 and PZ00P2_142232). S. Glasauer thanks R. Kretzschmar and the ETH Zurich for providing support during a sabbatical leave stay at the ETH Zurich.

References

- Abon, M., Volta, J.C., 1997. Vanadium phosphorus oxides for n-butane oxidation to maleic anhydride. *Appl. Catal.* A 157 (1–2), 173–193.
- Adachi, A., Ogawa, K., Tsushi, Y., Nagao, N., Kobayashi, T., 1997. Determination of vanadium in environmental samples by atomic absorption spectrophotometry. *Water Res.* 31 (5), 1247–1250.
- Adam, J., Green, T., 2006. Trace element partitioning between mica- and amphibole-bearing garnet lherzolite and hydrous basanitic melt: 1. Experimental results and the investigation of controls on partitioning behaviour. *Contrib. Mineral. Petrol.* 152, 1–17.
- Aide, M., 2005. Geochemical assessment of iron and vanadium relationships in oxic soil environments. *Soil Sediment Contam.* 14 (5), 403–416.
- Akinlua, A., Siedle, A., Buthelezi, T., Fadipe, O.A., 2015. Trace element geochemistry of crude oils and condensates from South African basins. *Mar. Pet. Geol.* 59, 286–293.
- Alcalde-Isorna, L., Barciela-Alonso, M.C., Bermejo-Barrera, P., 2011. Selective determination of V(IV) and V(V) in seawater by solid phase extraction and electrothermal atomic absorption spectrometry. *At. Spectrosc.* 32 (6), 234–239.
- Algeo, T.J., Maynard, J.B., 2004. Trace-element behavior and redox facies in core shales of upper pennsylvanian Kansas-type cyclothems. *Chem. Geol.* 206, 289–318.
- Algeo, T.J., Maynard, J.B., 2008. Trace-metal covariation as a guide to water-mass conditions in ancient anoxic marine environments. *Geosphere* 4 (5), 872.
- Algeo, T.J., Rowe, H., 2012. Paleocyanographic applications of trace-metal concentration data. *Chem. Geol.* 324, 6–18.
- Amrhein, C., Mosher, P., Brown, A., 1993. The effects of redox on Mo, U, B, V, and as solubility in evaporation pond soils. *Soil Sci.* 155 (4), 249.
- Anbar, A.D., Rouxel, O., 2007. Metal stable isotopes in paleoceanography. *Annu. Rev. Earth Planet. Sci.* 35, 717–746.
- Anders, E., Grevesse, N., 1989. Abundances of the elements: meteoritic and solar. *Geochim. Cosmochim. Acta* 53, 197–214.
- Ault, A.P., et al., 2010. Characterization of the single particle mixing state of individual ship plume events measured at the port of Los angeles. *Environ. Sci. Technol.* 44 (6), 1954–1961.
- Aureli, F., Ciardullo, S., Pagano, M., Raggi, A., Cubadda, F., 2008. Speciation of vanadium (IV) and (V) in mineral water by anion exchange liquid chromatography-inductively coupled plasma mass spectrometry after EDTA complexation. *J. Anal. At. Spectrom.* 23 (7), 1009.
- Baken, S., Larsson, M.A., Gustafsson, J.P., Cubadda, F., Smolders, E., 2012. Ageing of vanadium in soils and consequences for bioavailability. *Eur. J. Soil Sci.* 63 (6), 839–847.
- Balan, E., et al., 2006. The oxidation state of vanadium in titanomagnetite from layered basic intrusions. *Am. Mineral.* 91 (5–6), 953–956.
- Ballhaus, C., 1993. Redox states of lithospheric and asthenospheric upper mantle. *Contrib. Mineral. Petrol.* 114, 331–348.
- Balsiger, H., Geiss, J., Lipschutz, M.E., 1969. Vanadium isotopic composition in meteoritic and terrestrial matter. *Earth Planet. Sci. Lett.* 6 (2), 117–122.

- Balsiger, H., Mendia, M.D., Pelly, I.Z., Lipschutz, M.E., 1976. Vanadium isotopic composition and contents in gas-rich meteorites. *Earth Planet. Sci. Lett.* 28 (3), 379–384.
- Banerjee, D., Mondal, B.C., Das, D., Das, A.K., 2003. Use of imidazole 4, 5-dicarboxylic acid resin in vanadium speciation. *Microchim. Acta* 141 (3), 107–113.
- Barwise, A.J.G., 1990. Role of nickel and vanadium in petroleum classification. *Energy Fuel* 4 (6), 647–652.
- Bautista, E.M., Alexandre, M., 1972. Reduction of inorganic compounds by soil microorganisms. *Soil Sci. Soc. Am. J.* 36 (6), 918–920.
- Bell, J.M.L., et al., 2004. Methods evaluating vanadium tolerance in bacteria isolated from crude oil contaminated land. *J. Microbiol. Methods* 58 (1), 87–100.
- Bengtsson, S., Tyler, G., 1976. Vanadium in the environment MARC Report No. 2. University of London Monitoring and Assessment Research Centre, London.
- Blackmore, D.P.T., Ellis, J., Riley, P.J., 1996. Treatment of a vanadium-containing effluent by adsorption/coprecipitation with iron oxyhydroxide. *Water Res.* 30 (10), 2512–2516.
- Boehler, R., 2000. High-pressure experiments and the phase diagram of lower mantle and core materials. *Rev. Geophys.* 38 (2), 221–245.
- Boni, M., et al., 2007. Genesis of vanadium ores in the otavi mountainland, Namibia. *Econ. Geol.* 102 (3), 441–469.
- Bordage, A., et al., 2011. V oxidation state in Fe-Ti oxides by high-energy resolution fluorescence-detected X-ray absorption spectroscopy. *Phys. Chem. Miner.* 38 (6), 449–458.
- Bortnikova, S.B., Gavrilenko, G.M., Bessonova, E.P., Lapukhov, A.S., 2009. The hydrogeochemistry of thermal springs on mutnovskii volcano, southern Kamchatka. *J. Volcanol. Seismol.* 3 (6), 388–404.
- Bosque-Sendra, J.M., Valencia, M.C., Boudra, S., 1998. Speciation of vanadium (IV) and vanadium (V) with eriochrome cyanine R in natural waters by solid phase spectrophotometry. *Fresenius J. Anal. Chem.* 360 (1), 31–37.
- Boström, K., Fisher, D.E., 1971. Volcanogenic uranium, vanadium and iron in Indian ocean sediments. *Earth Planet. Sci. Lett.* 11 (2), 95–98.
- Bredberg, K., Karlsson, H.T., Holst, O., 2004. Reduction of vanadium(V) with *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*. *Bioresour. Technol.* 92 (1), 93–96.
- Breit, G., 1988. Vanadium: resources in fossil fuels. U. S. Geological Survey. Bulletin 1877 (Denver).
- Breit, G.N., Warty, R.B., 1991. Vanadium accumulation in carbonaceous rocks – a review of geochemical controls during deposition and diagenesis. *Chem. Geol.* 91 (2), 83–97.
- Briand, L., Thomas, H., De la Vega Alonso, A., Donati, E., 1999. Vanadium recovery from solid catalysts by means of *Thiobacilli* action. *Process Metall.* 9, 263–271.
- Brinza, L., Benning, L.G., Satham, P.J., 2008. Adsorption studies of Mo and V onto ferrihydrite. *Mineral. Mag.* 72 (1), 385–388.
- Brumsack, H.-J., 2006. The trace metal content of recent organic carbon-rich sediments: implications for cretaceous black shale formation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 232, 344–361.
- Burke, I.T., et al., 2012. Speciation of arsenic, chromium, and vanadium in red mud samples from the ajka spill site, Hungary. *Environ. Sci. Technol.* 46 (6), 3085–3092.
- Caccia, V.G., Millero, F.J., 2003. The distribution and seasonal variation of dissolved trace metals in Florida bay and adjacent waters. *Aquat. Geochem.* 9 (2), 111–144.
- Canada, E.C.H., 2010. Screening Assessment for the Challenge Vanadium Oxide (Vanadium Pentoxide) Chemical Abstracts Service Registry Number 1314–62–1. Government Canada.
- Canadian Environmental Quality Guidelines, 1999. Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health: Vanadium. Canadian environmental quality guidelines. Canadian Council of Ministers of the Environment, Winnipeg.
- Canil, D., 1999. Vanadium partitioning between orthopyroxene, spinel and silicate melt and the redox states of mantle source regions for primary magmas. *Geochim. Cosmochim. Acta* 63 (3–4), 557–572.
- Canil, D., 2002. Vanadium in peridotites, mantle redox and tectonic environments: archean to present. *Earth Planet. Sci. Lett.* 195 (1–2), 75–90.
- Canil, D., 2004. Mildly incompatible elements in peridotites and the origins of mantle lithosphere. *Lithos* 77 (1–4), 375–393.
- Canil, D., Johnston, S.T., Mihalynuk, M., 2006. Mantle redox in cordilleran ophiolites as a record of oxygen fugacity during partial melting and the lifetime of mantle lithosphere. *Earth Planet. Sci. Lett.* 248 (1–2), 106–117.
- Cappuyens, V., Salbinck, E., 2012. Occurrence of vanadium in Belgian and european alluvial soils. *Appl. Environ. Soil Sci.* 2012, 1–12.
- Cappuyens, V., Swennen, R., 2014. Release of vanadium from oxidized sediments: insights from different extraction and leaching procedures. *Environ. Sci. Pollut. Res.* 21 (3), 2272–2282.
- Carpentier, W., et al., 2003. Microbial reduction and precipitation of vanadium by *Shewanella oneidensis*. *Appl. Environ. Microbiol.* 69 (6), 3636–3639.
- Challenge, S.A.F.T., 2010. Chemical Abstracts Service Registry Number 1314–62–1: Vanadium Oxide. Environment Canada Health, Canada.
- Chasteen, N.D., 1983. The biochemistry of vanadium. *Struct. Bond.* 53, 105–138.
- Chen, J., et al., 2011. Geochemistry of environmentally sensitive trace elements in permian coals from the huainan coalfield, Anhui, China. *Int. J. Coal Geol.* 88 (1), 41–54.
- Cheshire, M.V., Berrow, M.L., Goodman, B.A., Mundie, C.M., 1977. Metal distribution and nature of some Cu, Mn and V complexes in humic and fulvic-acid fractions of soil organic-matter. *Geochim. Cosmochim. Acta* 41 (8), 1131–1138.
- Clark, A.M., 1993. Hey's Mineral Index. Chapman and Hall, London (848 pp).
- Clarke, F.W., 1889. The relative abundance of the chemical elements. *Philological Society Washington Bull XI pp.* 131–142.
- Cloy, J.M., Farmer, J.G., Graham, M.C., MacKenzie, A.B., 2011. Scottish peat bog records of atmospheric vanadium deposition over the past 150 years: comparison with other records and emission trends. *J. Environ. Monit.* 13 (1), 58–65.
- Colina, M., Gardiner, P.H.E., Rivas, Z., Troncone, F., 2005. Determination of vanadium species in sediment, mussel and fish muscle tissue samples by liquid chromatography-inductively coupled plasma-mass spectrometry. *Anal. Chim. Acta* 538 (1–2), 107–115.
- Condie, K.C., 1993. Chemical composition and evolution of the upper continental crust: contrasting results from surface samples and shales. *Chem. Geol.* 104 (1–4), 1–37.
- Cook, O.A., 1947. High-temperature heat contents of V_2O_3 , V_2O_4 and V_2O_5 . *J. Am. Chem. Soc.* 69 (2), 331–333.
- Crans, D.C., Amin, S.S., Keramidis, A.D., 1998. Chemistry of relevance to vanadium in the environment. In: Nriagu, J.O. (Ed.), *Vanadium in the Environment: Part 1. Chemistry and Biochemistry*. Wiley, Canada, pp. 73–96.
- Dauphas, N., et al., 2009. Iron isotopes may reveal the redox conditions of mantle melting from archean to present. *Earth Planet. Sci. Lett.* 288, 255–267.
- Drake, M.J., Newsom, H.E., Capobianco, C.J., 1989. V, Cr, and Mn in the earth, moon, EPB, and SPB and the origin of the moon: experimental studies. *Geochim. Cosmochim. Acta* 53 (8), 2101–2111.
- Duce, R.A., Hoffman, G.L., 1976. Atmospheric vanadium transport to the ocean. *Atmos. Environ.* 10 (11), 989–996.
- Ekstrom, A., et al., 1983. Determination of the crystal structure of a petroporphyrin isolated from oil shale. *Nature* 306, 173–174.
- Elston, D.P., Botinelly, T., 1959. Geology and mineralogy of the J. J. mine, montrose county, Colorado. U. S. Geol. Surv. Prof. Pap. 320, 203–212.
- Elvington, K., Baro, A.G., Pettersson, L., 1996. Speciation in vanadium bioinorganic systems. 2. An NMR, ESR, and potentiometric study of the aqueous $H + -$ vanadate-maltol system. *Inorg. Chem.* 35 (11), 3388–3393.
- Emerson, S.R., Husteded, S.S., 1991. Ocean anoxia and the concentrations of molybdenum and vanadium in seawater. *Mar. Chem.* 34 (3–4), 177–196.
- Evans, H.T., White, J.S., 1987. The colorful vanadium minerals: a brief review and a new classification. *Mineral. Rec.* 18, 333–340.
- Evans, H.T.J., Garrels, R.M., 1958. Thermodynamic equilibria of vanadium in aqueous systems as applied to the interpretation of the Colorado plateau ore deposits. *Geochim. Cosmochim. Acta* 15 (1–2), 131–149.
- Fallab, S., 1967. Reactions with molecular oxygen. *Angew. Chem. Int. Ed.* 6 (6), 496–507.
- Ferrer, E.G., Baran, E.J., 2001. Reduction of vanadium(V) with ascorbic acid and isolation of the generated oxovanadium(IV) species. *Biol. Trace Elem. Res.* 83 (2), 111–119.
- Fleischer, M., 1987. Glossary of Mineral Species. Mineralogical Record, Inc., Tucson.
- Fox, P.M., Donner, H.E., 2003. Accumulation, release, and solubility of arsenic, molybdenum, and vanadium in wetland sediments. *J. Environ. Qual.* 32 (6), 2428–2435.
- Francavilla, J., Chasteen, N.D., 1975. Hydroxide effects on electron-paramagnetic resonance-spectrum of aqueous vanadyl(IV) ion. *Inorg. Chem.* 14 (11), 2860–2862.
- Francois, R., 1988. A study on the regulation of the concentrations of some trace-metals (Rb, Sr, Zn, Pb, Cu, V, Cr, Ni, Mn and Mo) in saanich inlet sediments, British-Columbia, Canada. *Mar. Geol.* 83 (1–4), 285–308.
- French, S., Fakra, S.C., Trevors, J.T., Glasauer, S., 2013a. Changes in *Shewanella putrefaciens* CN32 membrane stability upon growth in the presence of soluble Mn(II), V(IV), and U(VI). *Geomicrobiol J.* 30 (3), 245–254.
- French, S., Puddephatt, D., Habash, M., Glasauer, S., 2013b. The dynamic nature of bacterial surfaces: implications for metal-membrane interaction. *Crit. Rev. Microbiol.* 39 (2), 196–217.
- Frohne, T., Diaz-Bone, R.A., Laing, D., Rinklebe, G.J., 2015. Impact of systematic change of redox potential on the leaching of Ba, Cr, Sr, and V from a riverine soil into water. *J. Soils Sediments* 15 (3), 623–633.
- Frost, D.J., Mann, U., Asahara, Y., Rubie, D.C., 2008. The redox state of the mantle during and just after core formation. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* 366 (1883), 4315–4337.
- Gäbler, H.E., Glüh, K., Bahr, A., Utermann, J., 2009. Quantification of vanadium adsorption by German soils. *J. Geochem. Explor.* 103 (1), 37–44.
- Gabrielli, P., et al., 2005. Trace elements in vostok antarctic ice during the last four climatic cycles. *Earth Planet. Sci. Lett.* 234 (1–2), 249–259.
- Gao, S., et al., 1998a. Chemical composition of the continental crust as revealed by studies in east China. *Geochim. Cosmochim. Acta* 62, 1959–1975.
- Gao, S., et al., 1998b. How mafic is the lower continental crust? *Earth Planet. Sci. Lett.* 106, 101–117.
- Garrels, R.M., 1953. Some thermodynamic relations among the vanadium oxides, and their relation to the oxidation state of the uranium ores of the Colorado plateaus. *Am. Mineral.* 38 (11–1), 1251–1265.
- Gehring, A.U., Fry, I.V., Luster, J., Sposito, G., 1994. Vanadium in sepiolite – a redox-indicator for an ancient closed brine system in the Madrid basin, central Spain. *Geochim. Cosmochim. Acta* 58 (16), 3345–3351.
- Gehring, A.U., Fry, V., Luster, J., Sposito, G., 1993. The chemical form of vanadium (IV) in kaolinite. *Clay Clay Miner.* 41 (6), 662–667.
- Gehring, A.U., Schosseler, P.M., Weidler, P.G., 1999. Mineral formation and redox-sensitive trace elements in a near-surface hydrothermal alteration system. *Geochim. Cosmochim. Acta* 63 (13–14), 2061–2069.
- Gessmann, C.K., Rubie, D.C., 1998. The effect of temperature on the partitioning of nickel, cobalt, manganese, chromium, and vanadium at 9 GPa and constraints on formation of the earth's core. *Geochim. Cosmochim. Acta* 62 (5), 867–882.
- Gessmann, C.K., Rubie, D.C., 2000. The origin of the depletions of V, Cr and Mn in the mantles of the earth and moon. *Earth Planet. Sci. Lett.* 184 (1), 95–107.
- Ghazvini, P.T.M., Mashkani, S.G., 2009. Effect of salinity on vanadate biosorption by halomonas sp. GT-83: preliminary investigation on biosorption by micro-PIXE technique. *Bioresour. Technol.* 100 (8), 2361–2368.
- Giuli, G., Paris, E., Mungall, J., Romano, C., Dingwell, D., 2004. V oxidation state and coordination number in silicate glasses by XAS. *Am. Mineral.* 89 (11–12), 1640–1646.
- Glasauer, S., 2015. Personal Communication.
- Gobeil, C., Rondeau, B., Beaudin, L., 2005. Contribution of municipal effluents to metal fluxes in the St. Lawrence river. *Environ. Sci. Technol.* 39 (2), 456–464.
- Gomez, C., Bosecker, K., 1999. Leaching heavy metals from contaminated soil by using *Thiobacillus ferrooxidans* or *Thiobacillus thiooxidans*. *Geomicrobiol J.* 16 (3), 233–244.

- Goodman, B.A., Cheshire, M.V., 1975. The bonding of vanadium in complexes with humic acid: an electron paramagnetic resonance study. *Geochim. Cosmochim. Acta* 39 (12), 1711–1713.
- GOST-17.4.4.02-84, 1985. *Nature Protection. Soils. Methods of sampling and preparation of soil samples for chemical analysis.*, Moscow.
- Guan, H., Buchheit, R.G., 2004. Corrosion protection of aluminum alloy 2024-T3 by vanadate conversion coatings. *Corrosion* 60 (3), 284–296.
- Hansley, P.L., Spirakis, C.S., 1992. Organic-matter diagenesis as the key to a unifying theory for the genesis of tabular uranium-vanadium deposits in the morrison formation, Colorado plateau. *Econ. Geol.* 87, 352–365.
- Harmens, H., et al., 2007. Temporal trends in the concentration of arsenic, chromium, copper, iron, nickel, vanadium and zinc in mosses across Europe between 1990 and 2000. *Atmos. Environ.* 41, 6673–6687.
- Hass, A., Fine, P., 2010. Sequential selective extraction procedures for the study of heavy metals in soils, sediments and water materials – a critical review. *Crit. Rev. Environ. Sci. Technol.* 40, 365–399.
- Hernández, A., Mellado, R.P., Martínez, J.L., 1998. Metal accumulation and vanadium-induced multidrug resistance by environmental isolates of *Escherichia hermannii* and *Enterobacter cloacae*. *Appl. Environ. Microbiol.* 64 (11), 4317–4320.
- Hirayama, K., Kageyama, S., Unohara, N., 1992. Mutual separation and preconcentration of vanadium (V) and vanadium (IV) in natural waters with chelating functional group immobilized silica gels followed by determination of vanadium by inductively coupled plasma atomic emission spectrometry. *Analyst* 117 (1), 13–17.
- Hoffman, G.L., et al., 1974. Residence time of some particulate trace metals in the oceanic surface microlayer: significance of atmospheric deposition. *J. Rech. Atmosph.* 8 (3–4).
- Hope, B.K., 1997. An assessment of the global impact of anthropogenic vanadium. *Biogeochemistry* 37 (1), 1–13.
- Hope, B.K., 2008. A dynamic model for the global cycling of anthropogenic vanadium. *Glob. Biogeochem. Cycles* 22 (4), GB4021.
- Hostetler, P., Garrels, R., 1962. Transportation and precipitation of uranium and vanadium at low temperatures, with special reference to sandstone-type uranium deposits. *Econ. Geol.* 57 (2), 137–167.
- Huang, J.-H., 2014. Impact of microorganisms on arsenic biogeochemistry: a review. *Water Air Soil Pollut.* 225 (2).
- Huggins, F.E., et al., 2009. Elemental modes of occurrence in an Illinois #6 coal and fractions prepared by physical separation techniques at a coal preparation plant. *Int. J. Coal Geol.* 78 (1), 65–76.
- Hurlbut, C.S., Klein, C., 1977. *Manual of Mineralogy*. John Wiley and Sons, New York (302 pp.).
- Jen, J.F., Yang, S.M., 1994. Simultaneous speciation determination of vanadium(IV) and vanadium(V) as EDTA complexes by liquid-chromatography with UV-detection. *Anal. Chim. Acta* 289 (1), 97–104.
- Jeong, Y., Fan, M., Van Leeuwen, J., Belczyk, J.F., 2007. Effect of competing solutes on arsenic(V) adsorption using iron and aluminum oxides. *J. Environ. Sci. China* 19 (8), 910–919.
- Jia, X.Y., Gong, D.R., Han, Y., Duan, T.C., Chen, H.T., 2012. First order speciation of vanadium and chromium in water samples by on-line continuous membrane separation hyphenated to inductively coupled plasma mass spectrometry. *Anal. Methods* 4 (2), 575–580.
- Jiao, X., Teng, Y., 2008. Techniques on soil remediation and disposal of vanadium pollution. *Chin. J. Soil Sci.* 39, 448–452.
- Joerissen, L., Garche, J., Fabjan, C., Tomazic, G., 2004. Possible use of vanadium redox-flow batteries for energy storage in small grids and stand-alone photovoltaic systems. *J. Power Sources* 127 (1–2), 98–104.
- Johnson, K.T.M., Dick, H.J.B., Shimizu, N., 1990. Melting in the oceanic upper mantle: an ion microprobe study of diopsides in abyssal peridotites. *J. Geophys. Res.* 95 (B3), 2661–2678.
- Kalinowski, B.E., et al., 2004. Microbial leaching of uranium and other trace elements from shale mine tailings at ranstad. *Geoderma* 122 (2), 177–194.
- Kamika, I., Momba, M.N.B., 2014. Microbial diversity of emalaheni mine water in South Africa and tolerance ability of the predominant organism to vanadium and nickel. *PLoS One* 9 (1).
- Karner, J., Papike, J.J., Shearer, C.K., 2006. Comparative planetary mineralogy: pyroxene major- and minor-element chemistry and partitioning of vanadium between pyroxene and melt in planetary basalts. *Am. Mineral.* 91 (10), 1574–1582.
- Karner, J.M., 2006. Application of a new vanadium valence oxybarometer to basaltic glasses from the earth, moon, and mars. *Am. Mineral.* 91 (2–3), 270–277.
- Karner, J.M., et al., 2008. Valence state partitioning of V between pyroxene-melt: effects of pyroxene and melt composition, and direct determination of V valence states by XANES. Application to martian basalt QUE 94201 composition. *Meteorit. Planet. Sci.* 43 (8), 1275–1285.
- Kawakubo, S., Netsu, T., Iwatsuki, M., 1997. Speciation of vanadium in rain water by size-fractionation and catalytic spectrofluorometry. *Anal. Sci.* 13 (6), 1033–1035.
- Kay, R.T., Groschen, G.E., Cygan, G., Dupre, D.H., 2011. Diel cycles in dissolved barium, lead, iron, vanadium, and nitrate in a stream draining a former zinc smelter site near hegeler, Illinois. *Chem. Geol.* 283, 99–108.
- Kelley, K.A., Cottrell, E., 2009. Water and the oxidation state of subduction zone magmas. *Science* 325, 605–607.
- Kish, L., 1972. Vanadium in titaniferous magnetite of Quebec. *Can. Min. Metall. Bull.* 65, 117–119.
- Krachler, M., Mohl, C., Emons, H., Shoty, W., 2003. Atmospheric deposition of V, Cr, and Ni since the late glacial: effects of climatic cycles, human impacts, and comparison with crustal abundances. *Environ. Sci. Technol.* 37 (12), 2658–2667.
- Kuo, C.Y., Jiang, S.J., Sahayam, A.C., 2007. Speciation of chromium and vanadium in environmental samples using HPLC-DRC-ICP-MS. *J. Anal. At. Spectrom.* 22 (6), 636–641.
- Kustin, K., Liu, S.T., Nicolini, C., Toppen, D.L., 1974. Interaction of catechol and catechol derivatives with dioxovanadium(V). I. kinetics of complex-formation in acidic media. *J. Am. Chem. Soc.* 96 (24), 7410–7415.
- López, L., Lo Mónaco, S., 2004. Geochemical implications of trace elements and sulfur in the saturate, aromatic and resin fractions of crude oil from the Mara and Mara oeste fields, Venezuela. *Fuel* 83 (3), 365–374.
- López, L., Lo Mónaco, S., Galarraga, F., Lira, A., Cruz, C., 1995. V/Ni ratio in maltene and asphaltene fractions of crude oils from the west venezuelan basin: correlation studies. *Chem. Geol.* 119 (1–4), 255–262.
- Lebedel, V., et al., 2013. Geochemical and palaeoecological record of the cenomanian-turonian anoxic event in the carbonate platform of the preafrikan trough, morocco. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 369, 79–98.
- Lee, C.-T.A., et al., 2010. The redox state of arc mantle using Zn/Fe systematics. *Nature* 468, 681–685.
- Lee, C.T.A., 2005. Similar V/Sc systematics in MORB and arc basalts: implications for the oxygen fugacities of their mantle source regions. *J. Petrol.* 46 (11), 2313–2336.
- Lewan, M., 1984. Factors controlling the proportionality of vanadium to nickel in crude oils. *Geochim. Cosmochim. Acta* 48 (11), 2231–2238.
- Li, H., Feng, Y., Zou, X., Luo, X., 2009. Study on microbial reduction of vanadium metallurgical waste water. *Hydrometallurgy* 99 (1–2), 13–17.
- Li, X.S., Glasauer, S., Le, X.C., 2007. Speciation of vanadium in oil sand coke and bacterial culture by high performance liquid chromatography inductively coupled plasma mass spectrometry. *Anal. Chim. Acta* 602 (1), 17–22.
- Li, Z.-X.A., Lee, C.-T.A., 2004. The constancy of upper mantle fO_2 through time inferred from V/Sc ratios in basalts. *Earth Planet. Sci. Lett.* 228, 483–493.
- Lipinski, M., Warning, B., Brumsack, H.J., 2003. Trace metal signatures of jurassic/cretaceous black shales from the Norwegian shelf and the barents sea. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 190, 459–475.
- Liu, F., Shan, W., Shi, X., He, H., 2012. Vanadium-based catalysts for the selective catalytic reduction of NO_x with NH_3 . *Prog. Chem.* 24, 445–455.
- Lopez, L., Lo Monaco, S., Volkman, J.K., 2015. Evidence for mixed and biodegraded crude oils in the socororo field, eastern Venezuela basin. *Org. Geochem.* 82, 12–21.
- Lositskii, N.T., Grigor'ev, A.A., Khitrova, G.V., 1966. Welding of chemical equipment made from two-layer sheet with titanium protective layer. *Chem. Pet. Eng.* 2 (12), 854–856.
- Lu, X.Q., Johnson, W.D., Hook, J., 1998. Reaction of vanadate with aquatic humic substances: an ESR and V-51 NMR study. *Environ. Sci. Technol.* 32 (15), 2257–2263.
- Lyalikova, N., Yurkova, N., 1992. Role of microorganisms in vanadium concentration and dispersion. *Geomicrobiol. J.* 10 (1), 15–26.
- Macdonald, R., Hawkesworth, C.J., Heath, E., 2000. The lesser antilles volcanic chain: a study in arc magmatism. *Earth-Sci. Rev.* 49, 1–76.
- Mallmann, G., O'Neill, H.S.C., 2009. The crystal/melt partitioning of V during mantle melting as a function of oxygen fugacity compared with some other elements (Al, P, Ca, Sc, Ti, Cr, Fe, Ga, Y, Zr and Nb). *J. Petrol.* 50 (9), 1765–1794.
- Mandiwana, K.L., Panichev, N., 2004. Electrothermal atomic absorption spectrometric determination of vanadium(V) in soil after leaching with Na_2CO_3 . *Anal. Chim. Acta* 517 (1–2), 201–206.
- Mandiwana, K.L., Panichev, N., Molalhegi, R., 2005. The leaching of V(V) with PO_4^{3-} in the speciation analysis of soil. *Anal. Chim. Acta* 545 (2), 239–243.
- Mann, U., Frost, D.J., Rubie, D.C., 2009. Evidence for high-pressure core-mantle differentiation from the metal-silicate partitioning of lithophile and weakly-siderophile elements. *Geochim. Cosmochim. Acta* 73, 7360–7386.
- Manning, T.D., Parkin, I.P., Pemble, M.E., Sheel, D., Vernardou, D., 2004. Intelligent window coatings: atmospheric pressure chemical vapor deposition of tungsten-doped vanadium dioxide. *Chem. Mater.* 16 (4), 744–749.
- Martell, A.F., Smith, R.M., 2004. NIST critically selected stability constants of metal complexes. NIST Standard Reference Database 46, Version 8.0, Gaithsburg, MD, U.S.A.
- Maylotte, D.H., Wong, J., Stpeters, R.L., Lytle, F.W., Gregor, R.B., 1981. X-ray absorption spectroscopic investigation of trace vanadium sites in coal. *Science* 214 (4520), 554–556.
- McCann, N., Wagner, M., Hasse, H., 2013. A thermodynamic model for vanadate in aqueous solution – equilibria and reaction enthalpies. *Dalton Trans.* 42 (7), 2622–2628.
- McDonough, W.F., 2003. Compositional model for the earth's core. *Treatise Geochem.* 2, 547–568.
- McDonough, W.F., Sun, S.-S., 1995. The composition of the earth. *Chem. Geol.* 120, 223–253.
- Michibata, H., Iwata, Y., Hirata, J., 1991. Isolation of highly acidic and vanadium-containing blood cells from among several types of blood cell from ascidiidae species by density gradient centrifugation. *J. Exp. Zool.* 257 (3), 306–313.
- Mikkonen, A., Tummavuori, J., 1994. Retention of vanadium (V) by three Finnish mineral soils. *Eur. J. Soil Sci.* 45 (3), 361–368.
- Millman, A.P., 1960. The desclozite-mottramite series of vanadates from minas-do-lueta, Angola. *Am. Mineral.* 45 (7–8), 763–773.
- Minelli, L., Veschetti, E., Giammanco, S., Mancini, G., Ottaviani, M., 2000. Vanadium in Italian waters: monitoring and speciation of V(IV) and V(V). *Microchem. J.* 67 (1), 83–90.
- Miramand, P., Fowler, S., 1998. Bioaccumulation and transfer of vanadium in marine organisms. In: Nriagu, J. (Ed.), *Vanadium in the environment. Part 1: Chemistry and biochemistry*. John Wiley & Sons, New York, pp. 167–197.
- Mizuno, N., Amano, Y., Mizuno, T., Nanzyo, M., 2008. Changes in the heavy mineral content and element concentration of tarumae-a tephra with distance from the source volcano. *Soil Sci. Plant Nutr.* 54, 839–845.
- Morford, J.L., Emerson, S.R., Breckel, E.J., Kim, S.H., 2005. Diagenesis of oxyanions (V, U, Re, and Mo) in pore waters and sediments from a continental margin. *Geochim. Cosmochim. Acta* 69, 5021–5032.
- Moskalyk, R.R., Alfantazi, A.M., 2003. Processing of vanadium: a review. *Miner. Eng.* 16 (9), 793–805.
- Motschi, H., Rudin, M., 1984. Al-27 endor study of VO^{2+} adsorbed on delta-alumina: direct evidence for inner coordination with surface functional-groups. *Colloid Polym. Sci.* 262 (7), 579–583.

- Naeem, A., Westerhoff, P., Mustafa, S., 2007. Vanadium removal by metal (hydr)oxide adsorbents. *Water Res.* 41, 1596–1602.
- Nakano, S., Kinoshita, S., Ikuta, M., Kawashima, T., 1990. Fractional determination of nanogram amounts of vanadium(IV) and vanadium(V) in natural-water by a catalytic method combined with solvent-extraction. *Anal. Sci.* 6 (3), 435–438.
- Nazer, A.F.M., Wells, C.F., 1980. Kinetics and mechanism of the oxidation of hydroxylamine by aqua-vanadium(V) ions in aqueous perchlorate-media. *J. Chem. Soc. Dalton Trans.* 9, 1532–1536.
- Nielsen, S.G., Prytulak, J., Halliday, A.N., 2011. Determination of precise and accurate 51 V/50 V isotope ratios by MC-ICP-MS, part 1: chemical separation of vanadium and mass spectrometric protocols. *Geostand. Geoanal. Res.* 35, 293–306.
- Nielsen, S.G., Prytulak, J., Wood, B.J., Halliday, A.N., 2014. Vanadium isotopic difference between the silicate earth and meteorites. *Earth Planet. Sci. Lett.* 389, 167–175.
- Nriagu, J.O., 1998. History, occurrence, and use of vanadium. In: Nriagu, J.O. (Ed.), *Vanadium in the environment. Part 1: chemistry and biochemistry*. John Wiley & Sons, New York, pp. 1–24.
- Ogunlaja, A.S., et al., 2014. The ratios of vanadium-to-nickel and phenanthrene-to-dibenzothiophene as means of identifying petroleum source and classification of Nigeria crude oils. *Pet. Sci. Technol.* 32 (19), 2283–2291.
- Ortiz-Bernad, I., Anderson, R.T., Vronis, H.A., Lovley, D.R., 2004. Vanadium respiration by *Geobacter metallireducens*: novel strategy for in situ removal of vanadium from groundwater. *Appl. Environ. Microbiol.* 70 (5), 3091–3095.
- Ovari, M., Csukas, M., Záray, G., 2001. Speciation of beryllium, nickel, and vanadium in soil samples from csepel island, Hungary. *Fresenius J. Anal. Chem.* 370 (6), 768–775.
- Pajdowski, L., 1966. A spectrophotometric study of the hydrolysis of vanadium (III) ion. *J. Inorg. Nucl. Chem.* 28 (2), 433–442.
- Pajdowski, L., Jeżowska-Trzebiatowska, B., 1966. A magnetochemical study of the hydrolysis of vanadium (III) ion. *J. Inorg. Nucl. Chem.* 28 (2), 443–446.
- Palme, H., 1988. Chemical abundances in meteorites. In: Klare, G. (Ed.), *Reviews in Modern Astronomy*. Springer, Berlin, pp. 28–51.
- Palme, H., O'Neill, H.S.C., 2003. Cosmochemical estimates of mantle composition. *Treatise Geochem.* 2, 1–38.
- Pang, K.-N., Li, C., Zhou, M.-F., Ripley, E.M., 2008. Abundant Fe–Ti oxide inclusions in olivine from the panzhihua and hongge layered intrusions, SW China: evidence for early saturation of Fe–Ti oxides in ferrobaltic magma. *Contrib. Mineral. Petrol.* 156, 307–321.
- Parkinson, I.J., Hammond, S.J., James, R.H., Rogers, N.W., 2007. High-temperature lithium isotope fractionation: insights from lithium isotope diffusion in magmatic systems. *Earth Planet. Sci. Lett.* 257, 609–621.
- Peacock, C.L., Sherman, D.M., 2004. Vanadium(V) adsorption onto goethite (α -FeOOH) at pH 1.5 to 12: a surface complexation model based on ab initio molecular geometries and EXAFS spectroscopy. *Geochim. Cosmochim. Acta* 68 (8), 1723–1733.
- Peacor, D.R., Covey, R.M., Zhao, G.M., 2000. Authigenic illite and organic matter: the principal hosts of vanadium in the mecca quarry shale at velpen, Indiana. *Clay Clay Miner.* 48 (3), 311–316.
- Pelletier, R.A., 1930. The zinc, lead and vanadium deposit of broken hill, N. Rhodesia. *S. Afr. Min. Eng.* 40, 91.
- Pelly, I.Z., Lipschutz, M.E., Balsiger, H., 1970. Vanadium isotopic composition and contents in chondrites. *Geochim. Cosmochim. Acta* 34, 1033–1036.
- Peterson, L., Hedman, B., Andersson, I., 1983. Multi component polyanions. *Chem. Scrip.* 22, 254–264.
- Poledniok, J., Buhl, F., 2003. Speciation of vanadium in soil. *Talanta* 59 (1), 1–8.
- Ponyatovskii, E.G., Bashkin, I.O., Tissen, V.G., Nefedova, M.V., 2009. Superconductivity of vanadium and vanadium-titanium alloys at high pressure. *JETP Lett.* 89 (5), 253–255.
- Pouret, O., Dia, A., Gruau, G., Davranche, M., Coz, M.B.-L., 2012. Assessment of vanadium distribution in shallow groundwaters. *Chem. Geol.* 294–295, 89–102.
- Prathap, K., Namasivayam, C., 2010. Adsorption of vanadate(V) on Fe(III)/Cr(III) hydroxide waste. *Environ. Chem. Lett.* 8 (4), 363–371.
- Premović, P.I., Pavlović, M.S., Pavlović, N.Z., 1986. Vanadium in ancient sedimentary rocks of marine origin. *Geochim. Cosmochim. Acta* 50 (9), 1923–1931.
- Prytulak, J., Nielsen, S.G., Halliday, A.N., 2011. Determination of precise and accurate 51 V/50 V isotope ratios by multi-collector ICP-MS, part 2: isotopic composition of six reference materials plus the allende chondrite and verification tests. *Geostand. Geoanal. Res.* 35, 307–318.
- Prytulak, J., et al., 2013. The stable vanadium isotope composition of the mantle and mafic lavas. *Earth Planet. Sci. Lett.* 365, 177–189.
- Punanova, S.A., 2014. Supergene transformed naphthides: peculiarities of trace-element composition. *Geochim. Int.* 52 (1), 57–67.
- Rehder, D., 2008a. *Bioinorganic Vanadium Chemistry*, 29. Wiley (224 pp.).
- Rehder, D., 2008b. Is vanadium a more versatile target in the activity of primordial life forms than hitherto anticipated? *Org. Biomol. Chem.* 6 (6), 957–964.
- Reimann, C., Caritat, P., 1998. *Chemical Elements in the Environment: Fact Sheets for the Geochimist and Environmental Scientist*. Springer-Verlag, Berlin (398 pp.).
- Reynolds, I.M., 1985. Contrasting mineralogy and textural relationships in the uppermost titaniferous magnetite layers of the bushveld complex in the bierkraal area north of rustenburg. *Econ. Geol.* 80, 1027–1048.
- Righter, K., Leeman, W., Hervig, R., 2006. Partitioning of Ni, Co and V between spinel-structured oxides and silicate melts: importance of spinel composition. *Chem. Geol.* 227 (1–2), 1–25.
- Righter, K., et al., 2011. The effect of fO_2 on the partitioning and valence of V and Cr in garnet/melt pairs and the relation to terrestrial mantle V and Cr content. *Am. Mineral.* 96 (8–9), 1278–1290.
- Riley, J., Taylor, D., 1972. The concentrations of cadmium, copper, iron, manganese, molybdenum, nickel, vanadium and zinc in part of the tropical north-east atlantic ocean. *Deep Sea Res. Oceanogr. Abstr.* 19, 307–317.
- Riley, K.W., Saxby, J.D., 1982. Association of organic matter and vanadium in oil shale from the toolebuc formation of the eromanga basin, Australia. *Chem. Geol.* 37, 265–275.
- Ringwood, A.E., 1966. The chemical composition and origin of the earth. In: Hurlley, P.M. (Ed.), *Advances in Earth Sciences*. MIT Press, Cambridge, pp. 287–356.
- Ringwood, A.E., Kato, T., Hibberson, W., Ware, N., 1991. Partitioning of Cr, V, and Mn between mantles and cores of differentiated planetesimals: implications for giant impact hypothesis of lunar origin. *Icarus* 89, 122–128.
- Ripley, E.M., Severson, M.J., Hauck, S.A., 1998. Evidence for sulfide and Fe–Ti–P-rich liquid immiscibility in the duluth complex, Minnesota. *Econ. Geol.* 93, 1052–1062.
- Roach, C.H., Thompson, M.E., 1959. Sedimentary structures and localization and oxidation of ore at the Peanut Mine, Montrose County, Colorado. *U. S. Geol. Surv. Prof. Pap.* 320, 197–202.
- Rudnick, R.L., Gao, S., 2003. In: Holland, H.D., Turekian, K.K. (Eds.), *Composition of the continental crust*. The Crust vol. 3 Treatise on Geochemistry. Elsevier-Pergamon, Oxford, pp. 1–64.
- Sadiq, M., 1988. Thermodynamic solubility relationships of inorganic vanadium in the marine environment. *Mar. Chem.* 23 (1–2), 87–96.
- Sakata, M., Asakura, K., 2011. Atmospheric dry deposition of trace elements at a site on Asian-continent side of Japan. *Atmos. Environ.* 45, 1075–1083.
- Sato, Y., Okabe, S., 1978. Vanadium in sea waters and deposits from Tokyo bay, suruga bay and harima nada. *J. Fac. Mar. Sci. Technol. Tokai Univ.* 11, 1–19.
- Sato, Y., Okabe, S., 1982. Molybdenum and vanadium in coastal water. *J. Fac. Mar. Sci. Technol. Tokai Univ.* 15, 43–55.
- Schroeder, H.A., 1970. Vanadium, air Quality Monographs 70–13. American Petroleum Institute, Washington DC (32 pp.).
- Schwertmann, U., Pfab, G., 1994. Structural vanadium in synthetic goethite. *Geochim. Cosmochim. Acta* 58 (20), 4349–4352.
- Schwertmann, U., Pfab, G., 1996. Structural vanadium and chromium in lateritic iron oxides: genetic implications. *Geochim. Cosmochim. Acta* 60 (21), 4279–4283.
- Selin, N.E., 2009. Global biogeochemical cycling of mercury: a review. *Annu. Rev. Environ. Resour.* 34, 43–63.
- Shafer, M.M., et al., 2012. Chemical speciation of vanadium in particulate matter emitted from diesel vehicles and urban atmospheric aerosols. *Environ. Sci. Technol.* 46 (1), 189–195.
- Shaheen, S.M., Rinklebe, J., Frohne, T., White, J.R., DeLaune, R.D., 2014a. Biogeochemical factors governing cobalt, nickel, selenium, and vanadium dynamics in periodically flooded egyptian north nile delta rice soils. *Soil Sci. Soc. Am. J.* 78 (3), 1065–1078.
- Shaheen, S.M., Rinklebe, J., Rupp, H., Meissner, R., 2014b. Lysimeter trials to assess the impact of different flood-dry-cycles on the dynamics of pore water concentrations of as, Cr, Mo and V in a contaminated floodplain soil. *Geoderma* 228, 5–13.
- Shaw, T.J., Gieskes, J.M., Jahnke, R.A., 1990. Early diagenesis in differing depositional environments – the response of transition-metals in pore water. *Geochim. Cosmochim. Acta* 54, 1233–1246.
- Shearer, C.K., McKay, G., Papike, J.J., Karner, J.M., 2006a. Valence state partitioning of vanadium between olivine-liquid: estimates of the oxygen fugacity of Y980459 and application to other olivine-phyric martian basalts. *Am. Mineral.* 91 (10), 1657–1663.
- Shearer, C.K., Papike, J.J., Karner, J.M., 2006b. Pyroxene europium valence oxybarometer: effects of pyroxene composition, melt composition, and crystallization kinetics. *Am. Mineral.* 91 (10), 1565–1573.
- Shiller, A.M., Boyle, E.A., 1987. Dissolved vanadium in rivers and estuaries. *Earth Planet. Sci. Lett.* 86 (2–4), 214–224.
- Shiller, A.M., Mao, L.J., 2000. Dissolved vanadium in rivers: effects of silicate weathering. *Chem. Geol.* 165 (1–2), 13–22.
- Shotyk W., et al., 2014. Sphagnum mosses from 21 ombrotrophic bogs in the athabasca bituminous sands region show no significant atmospheric contamination of “heavy metals. *Environ. Sci. Technol.* 48 (21), 12603–12611.
- Sia, S.-G., Abdullah, W.H., 2011. Concentration and association of minor and trace elements in mukah coal from Sarawak, Malaysia, with emphasis on the potentially hazardous trace elements. *Int. J. Coal Geol.* 88 (4), 179–193.
- Siebert, J., Badro, J., Antonangeli, D., Ryerson, F.J., 2013. Terrestrial accretion under oxidizing conditions. *Science* 339 (6124), 1194–1197.
- Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* 17 (5), 517–568.
- Smichowski, P., Gomez, D., Rosa, S., Polla, G., 2003. Trace elements content in size-classified volcanic ashes as determined by inductively coupled plasma-mass spectrometry. *Microchem. J.* 75 (2), 109–117.
- Song, F., Gao, Y., 2009. Chemical characteristics of precipitation at metropolitan newark in the US east coast. *Atmos. Environ.* 43, 4903–4913.
- Spirakis, C.S., 1996. The roles of organic matter in the formation of uranium deposits in sedimentary rocks. *Ore Geol. Rev.* 11 (1–3), 53–69.
- Sun, S.-S., McDonough, W.F., 1989. Chemical and isotopic systematics of oceanic basalts: implication for mantle composition and processes. *Geol. Soc. Lond., Spec. Publ.* 42, 313–345.
- Sutton, S.R., et al., 2005. Vanadium K edge XANES of synthetic and natural basaltic glasses and application to microscale oxygen barometry. *Geochim. Cosmochim. Acta* 69 (9), 2333–2348.
- Szalai, A., Szilágyi, M., 1967. The association of vanadium with humic acids. *Geochim. Cosmochim. Acta* 31 (1), 1–6.
- Taylor, M., Van Staden, J., 1994. Spectrophotometric determination of vanadium(IV) and vanadium(V) in each other's presence. *Rev. Anal.* 119 (6), 1263–1276.
- Taylor, R., Giles, J., 1970. The association of vanadium and molybdenum with iron oxides in soils. *J. Soil Sci.* 21 (2), 203–215.
- Taylor, S.R., McLennan, S.M., 1981. The composition and evolution of the continental crust: rare earth element evidence from sedimentary rocks. *Philos. Trans. R. Soc. Lond. A* 301, 381–399.

- Taylor, S.R., McLennan, S.M., 1985. *The Continental Crust: Its Composition and Evolution*. Blackwell Oxford (312 pp.).
- Taylor, S.R., McLennan, S.M., 1995. The geochemical evolution of the continental crust. *Rev. Geophys.* 33, 241–265.
- Templeton, G.D., Chasteen, N.D., 1980. Vanadium-fulvic acid chemistry – conformational and binding-studies by electron-spin probe techniques. *Geochim. Cosmochim. Acta* 44 (5), 741–752.
- Teng, Y., et al., 2011. Environmental vanadium distribution, mobility and bioaccumulation in different land-use districts in panzhuhua region, SW China. *Environ. Monit. Assess.* 176 (1), 605–620.
- Theodosi, C., Markaki, Z., Tselepidis, A., Mihalopoulos, N., 2010. The significance of atmospheric inputs of soluble and particulate major and trace metals to the eastern mediterranean seawater. *Mar. Chem.* 120, 154–163.
- Tian, L., Yang, J., Huang, J.-H., 2015. Uptake and speciation of vanadium in the rhizosphere soil of rape (*Brassica juncea* L.). *Environ. Sci. Pollut. Res.* in press.
- Trefry, J.H., Metz, S., 1989. Role of hydrothermal precipitates in the geochemical cycling of vanadium. *Nature* 342 (6249), 531–533.
- Tribouillard, N., Algeo, T.J., Lyons, T., Riboulleau, A., 2006. Trace metals as paleoredox and paleoproductivity proxies: an update. *Chem. Geol.* 232 (1–2), 12–32.
- Tsadilas, C.D., Shaheen, S.M., 2010. Distribution of total and ammonium bicarbonate-DTPA-extractable soil vanadium from Greece and Egypt and their correlation to soil properties. *Soil Sci.* 175 (11), 535.
- Tuff, J., Wood, B.J., Wade, J., 2011. The effect of Si on metal–silicate partitioning of siderophile elements and implications for the conditions of core formation. *Geochim. Cosmochim. Acta* 75 (2), 673–690.
- Turekian, K.K., Wedepohl, K.H., 1961. Distribution of the elements in some major units of the earth's crust. *Geol. Soc. Am. Bull.* 72 (2), 175–192.
- Van der Weijden, C.H., 2002. Pitfalls of normalization of marine geochemical data using a common divisor. *Mar. Geol.* 184 (3–4), 167–187.
- van Marwijk, J., Opperman, D.J., Piater, L.A., van Heerden, E., 2009. Reduction of vanadium (V) by *Enterobacter cloacae* EV-SA01 isolated from a South African deep gold mine. *Biotechnol. Lett.* 31 (6), 845–849.
- Verweij, W., 2013. Equilibria and constants in CHEAQS: selection criteria, sources and assumptions. Version 10. <http://www.cheaqs.eu>.
- Vine, J.D., Tourtelo, E., 1970. Geochemistry of black shale deposits—a summary report. *Econ. Geol.* 65 (3), 253–272.
- Wällstedt, T., Björkvald, L., Gustafsson, J.P., 2010. Increasing concentrations of arsenic and vanadium in (southern) Swedish streams. *Appl. Geochem.* 25 (8), 1162–1175.
- Wänke, H., Dreibus, G., 1986. Geochemical evidence for the formation of the moon by impact induced fission of the proto-earth. In: Hartmann, W.K., Phillips, R.J., Taylor, G.J. (Eds.), *Origin of the Moon*. Lunar and Planetary Institute, Houston, pp. 649–672.
- Wade, J., Wood, B.J., 2005. Core formation and the oxidation state of the earth. *Earth Planet. Sci. Lett.* 236, 78–95.
- Wang, D., Sañudo Wilhelmy, S.A., 2009a. Vanadium speciation and cycling in coastal waters. *Mar. Chem.* 117 (1), 52–58.
- Wang, D., Sañudo Wilhelmy, S.A., 2009b. Vanadium speciation and cycling in coastal waters. *Mar. Chem.* 117 (1–4), 52–58.
- Wang, J., et al., 2008. Statistical analysis of the concentrations of trace elements in a wide diversity of coals and its implications for understanding elemental modes of occurrence. *Fuel* 87 (10–11), 2211–2222.
- Wang, K., Selim, H.M., Zhu, D., 2003. Competitive adsorption and transport of vanadium and phosphorus in soils. *J. Agro-Environ. Sci.* 22, 536–540.
- Wann, C.C., Jiang, S.J., 1997. Determination of vanadium species in water samples by liquid chromatography inductively coupled plasma mass spectrometry. *Anal. Chim. Acta* 357 (3), 211–218.
- Wanty, R.B., Goldhaber, M.B., 1992. Thermodynamics and kinetics of reactions involving vanadium in natural systems: accumulation of vanadium in sedimentary rocks. *Geochim. Cosmochim. Acta* 56, 1471–1483.
- Wasson, J.T., Kallemeyn, G.W., 1988. Compositions of chondrites. *Philos. Trans. R. Soc. Lond. A* 325, 535–544.
- Weeks, A.D., 1961. Mineralogy and geochemistry of vanadium in the Colorado plateau. *J. Less-Common Met.* 3 (6), 443–450.
- Weeks, A.D., Cisney, E.A., Sherwood, A.M., 1950. Hummerite and montroseite, two new vanadium minerals from montrose county, Colorado. *Geol. Soc. America Bull.* 61, 1513.
- Wehrli, B., 1987. Vanadium in der Hydrosphäre; Oberflächenkomplexe und Oxidationskinetik. Zurich, Eidgenössische Technische Hochschule Zurich (ETH Zurich) (129 pp.).
- Wehrli, B., Stumm, W., 1988. Oxygenation of vanadyl(IV). effect of coordinated surface hydroxyl groups and hydroxide ion. *Langmuir* 4 (3), 753–758.
- Wehrli, B., Stumm, W., 1989. Vanadyl in natural waters: adsorption and hydrolysis promote oxygenation. *Geochim. Cosmochim. Acta* 53 (1), 69–77.
- Wells, C.F., Kuritsyn, L.V., 1970. Kinetics of oxidation of quinol by aquovanadium(V) ions in perchlorate media. *J. Chem. Soc. A* 8, 1372–1376.
- Westall, J.C., 1979. MICROQL: I. A chemical equilibrium program in BASIC. EAWAG CH-8600. Swiss Federal Institute of Technology, Dübendorf, Switzerland.
- WHO, 1988. Environmental health criteria 81, vanadium.
- Wilson, S.A., Weber, J.H., 1979. An EPR study of the reduction of vanadium(V) to vanadium(IV) by fulvic acid. *Chem. Geol.* 26 (3–4), 345–354.
- Wood, B.J., 2008. Accretion and core formation: constraints from metal–silicate partitioning. *Phil. Trans. A Math. Phys. Eng. Sci.* 366 (1883), 4339–4355.
- Wood, B.J., Wade, J., Kilburn, M.R., 2008. Core formation and the oxidation state of the earth: additional constraints from Nb, V and Cr partitioning. *Geochim. Cosmochim. Acta* 72 (5), 1415–1426.
- Wright, M.T., Belitz, K., 2010. Factors controlling the regional distribution of vanadium in groundwater. *Ground Water* 48 (4), 515–525.
- Wu, F., et al., 2015. First-principles investigation of vanadium isotope fractionation in solution and during adsorption. *Earth Planet. Sci. Lett.* 426, 216–224.
- Wu, Y.W., Jiang, Z.C., Hu, B., 2005. Speciation of vanadium in water with quinine modified resin micro-column separation/preconcentration and their determination by fluorination assisted electrothermal vaporization (FETV)-inductively coupled plasma optical emission spectrometry (ICP-OES). *Talanta* 67 (4), 854–861.
- Xiong, C.M., Qin, Y.C., Hu, B., 2010. On-line separation/preconcentration of V(IV)/V(V) in environmental water samples with CTAB-modified alkyl silica microcolumn and their determination by inductively coupled plasma-optical emission spectrometry. *J. Hazard. Mater.* 178 (1–3), 164–170.
- Xu, J.Z., et al., 2013. Geochemistry of soils derived from black shales in the ganziping mine area, western Hunan, China. *Environ. Earth Sci.* 70 (1), 175–190.
- Yang, J., et al., 2014. Leaching characteristics of vanadium in mine tailings and soils near a vanadium titanomagnetite mining site. *J. Hazard. Mater.* 264, 498–504.
- Yasnygina, T.A., et al., 2015. Trace elements and Sr isotopes in the crude oils from the sakhalin offshore fields. *Russ. J. Pac. Geol.* 9 (2), 109–119.
- Yelton, A.P., et al., 2013. Vanadate and acetate biostimulation of contaminated sediments decreases diversity, selects for specific taxa, and decreases aqueous V⁵⁺ concentration. *Environ. Sci. Technol.* 47 (12), 6500–6509.
- Zhang, J., Dong, H.L., Zhao, L.D., McCarrick, R., Agrawal, A., 2014. Microbial reduction and precipitation of vanadium by mesophilic and thermophilic methanogens. *Chem. Geol.* 370, 29–39.
- Zhao, L., Huang, Y., Zhu, Y., Li, J., 2004. The interactions of arsenate or vanadium with cadmium and the effects of arsenate and vanadium on the adsorption of cadmium by soils. *Environ. Chem.* 23 (4), 409–412.
- Zhao, L., Zhu, X.S., Feng, K., Wang, B.S., 2006. Speciation analysis of inorganic vanadium (V(IV)/V(V)) by graphite furnace atomic absorption spectrometry following ion-exchange separation. *Int. J. Environ. Anal. Chem.* 86 (12), 931–939.
- Zhong, H., Zhu, W.-G., 2006. Geochronology of layered mafic intrusions from the pan-xi area in the emeishan large igneous province, SW China. *Mineral. Deposita* 41 (6), 599–606.
- Zhou, M.F., 2005. Geochemistry, petrogenesis and metallogenesis of the panzhuhua gabbroic layered intrusion and associated Fe-Ti-V oxide deposits, Sichuan province, SW China. *J. Petrol.* 46 (11), 2253–2280.
- Zoller, W.H., Gordon, G.W., Gladney, E.S., Jones, A.G., 1973. The sources and distribution of vanadium in the atmosphere, trace elements in the environment. *Advances in Chemistry*. American chemical society, pp. 31–47.