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► **To cite this version:**

Olivier Pourret, Aline Dia. Vanadium. Bill White; William Casey; Steve Goldstein; Hiliary Harnett; Bernard Marty; Hisayoshi Yurimoto. Encyclopedia of Geochemistry, Springer, pp.1474-1476, 2018, 978-3-319-39311-7. 10.1007/978-3-319-39312-4_272 . insu-01346032

HAL Id: insu-01346032

<https://insu.hal.science/insu-01346032>

Submitted on 18 Jul 2016

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2 **Vanadium**

[Au1]

3 Olivier Pourret¹ and Aline Dia²4 ¹Institut Polytechnique, LaSalle Beauvais, Beauvais, France5 ²Géosciences Rennes, Rennes, France6 **Element Data**7 *Atomic Symbol: V*8 *Atomic Number: 23*9 *Atomic Weight: 50.9415 g/mol*10 *Isotopes and Abundances: ⁵⁰V 0.25 %, ⁵¹V 99.75 %*11 *1 Atm Melting Point: 1910 °C*12 *1 Atm Boiling Point: 3407 °C*13 *Common Valences: 5+, 4+, 3+, 2+*14 *Ionic Radii: 64 pm (in 3+, 6-fold coordination)*15 *Pauling Electronegativity: 1.63*16 *First Ionization Energy: 6.74 eV*17 *Chondritic (CI) Abundance: 54.6 ppm^a*18 *Silicate Earth Abundance: 86 ppm^a*19 *Crustal Abundance: 138 ppm^b*20 *Seawater Abundance: ~30–37 nmol/kg^c*21 *Core Abundance: ~150 ppm^d*22 ^a*Palme et al. (2014)*23 ^b*Rudnick and Gao (2014)*24 ^c*Bruland et al. (2014)*25 ^d*McDonough (2014)*26 **Properties**

27 Vanadium (chemical symbol, V) is a d-block transition metal,
 28 silver in color, appearing in the first long period of the peri-
 29 odic table between titanium and chromium. Vanadium has
 30 two stable isotopes: ⁵⁰V and ⁵¹V, with atomic abundance of

0.25 % and 99.75 %, respectively. Vanadium has several 31
 oxidation forms (between 2+ and 5+). In the lithosphere, 32
 V occurs as reducing V(III) form, whereas in oxidizing con- 33
 ditions V prevails under V(IV) form. Vanadium(II) is partic- 34
 ularly unstable in the environment. Vanadium(III) is more 35
 stable than V(II), but it is also gradually oxidized by the air 36
 or dissolved oxygen. Vanadium(V) is expected to be the 37
 prevailing form in waters exposed to atmospheric oxygen, 38
 whereas V(IV) may be present in reducing environments. 39
 Depending upon geometry and environment, V ionic radii 40
 vary between 36 pm and 79 pm. Vanadium has a high melting 41
 point of 1910 °C and is a mildly incompatible, refractory, 42
 lithophile (siderophile in the iron core and chondrites) ele- 43
 ment. Vanadium has an electronegativity of 1.63 on the Pau- 44
 ling scale and displays a first ionization potential of 45
 6.74 eV. More details can be found in Richards (2006) and 46
 Haynes (2015). 47

48 **History and Use**

49 Vanadium was first discovered by del Rio in 1801 and was
 50 incorrectly considered as impure chromium. Vanadium was
 51 rediscovered and named by Sefström in 1830 after the Scan-
 52 dinavian goddess Vanadis. In 1867, Roscoe isolated V in
 53 nearly pure form by reducing V chloride with hydrogen.
 54 Vanadium of high purity (99.3–99.8 %) was not produced
 55 until 1927. The V redox chemistry and its specific application
 56 to renewable energy technologies (e.g., vanadium redox bat-
 57 tery; a type of rechargeable flow battery using V in different
 58 oxidation states to store chemical potential energy) have
 59 already add to the demand for this element and will definitely
 60 continue to increase in the near future. Vanadium demand for
 61 construction materials is the greatest consumer of mined V -
 62 (Moskalyk and Alfantazi, 2003). Indeed, vanadium is the
 63 most widely used alloying element for strengthening steels
 64 employed in buildings and bridges. Vanadium volume that is
 65 cycled through terrestrial and aquatic reservoirs can thus be

66 expected to further growth. It results in uncontrolled
67 V releases in the environment, and environmental issues
68 appear in developing and developed countries (Imtiaz et al.,
69 2015).

70 Geochemical Behavior

71 Widely and sparsely distributed, V is not found as the free
72 metal in nature. It originates from primary sources such as
73 ores (i.e., iron oxides deposits), metallurgical slags (i.e.,
74 processing of U and Ti ores), and petroleum residues. Other
75 sources include vanadiferous sandstones, bauxite, coals, or oil
76 shales.

77 Vanadium is widely distributed in igneous and sedimentary
78 rocks and minerals. Among more than fifty minerals,
79 carnotite $[K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O]$, roscoelite $[KV^{3+}_2(Si_3Al$
80 $O_{10}(OH)_2]$, vanadinite $[Pb_5(VO_4)_3Cl]$, mottramite $[PbCu$
81 $(VO_4)(OH)]$, and patrónite (VS_4) are the most important
82 V-carriers. It is also present in some crude oils as organic
83 complexes. Its average content in the Earth's crust is approx-
84 imately 138 ppm and is similar to that of Zn and Ni. It is,
85 however, more dispersed in the crust than either of those
86 elements, and concentrated mineral deposits are consequently
87 rare. The average V contents of CI chondrites range from
88 54.6 ppm to 56.5 ppm. The silicate Earth has a V content of
89 86 ppm, the bulk Earth of 105 ppm, whereas its content in the
90 metallic core is slightly higher (150 ppm). Vanadium contents
91 in the bulk continental crust vary significantly from 96 ppm to
92 230 ppm. These aspects have been further reviewed by
93 McDonough (2014), Palme et al. (2014), and Rudnick and
94 Gao (2014).

95 Historically, geochemists' interest in vanadium has
96 derived from the occurrence of variable redox states in Earth
97 surface environments, +3, +4, +5, and as a consequence its
98 application as a redox indicator (Huang et al., 2015). Indeed,
99 V chemical speciation and solubility are strong functions of
100 pH and Eh conditions. Incorporation of reduced V species
101 (III, IV) in clays and other secondary minerals provides a
102 useful redox indicator for past anoxic conditions. Moreover,
103 V behaves as an incompatible element because V(III) is
104 preferentially incorporated into crystals: V-bearing minerals
105 which crystallized in equilibrium with a low fO_2 magma have
106 a higher V content than crystals from the same magma with
107 high fO_2 (Mallmann and O'Neill, 2009). It results in an
108 increasing interest in V partitioning during high
109 temperature – high pressure magma differentiation processes.
110 Studies on V partitioning among Earth's crustal reservoirs
111 have provided critical insights into the interaction and evolu-
112 tion of these reservoirs. Vanadium depletion in the silicate
113 Earth is explained by its preferential partitioning into the
114 metallic core during "deep magma ocean" process (at high
115 pressure and low fO_2 ; Wood et al., 2006). The core could

116 contain half of the total V budget of the bulk Earth
117 (McDonough, 2014). Perspectives to exploit V stable isotope
118 chemistry are considered: Wu et al. (2015) proposed first-
119 principles calculations that predict V isotopes fractionation
120 among V species with different valences in aqueous systems
121 and during sorption of V(V) to goethite.

122 Vanadium is also a naturally occurring element in air, soil,
123 plants, and water. The concentration of dissolved V in natural
124 freshwater and seawater is generally several mg/L or lower
125 (Bruland et al., 2014; Gaillardet et al., 2014). Vanadium
126 concentrations in marine and nonmarine sediments are gener-
127 ally below 100 ppm, reflecting a net accumulation from the
128 aqueous phase. Vanadium in trace amounts represents an
129 essential element for normal cell growth, but it may cause
130 adverse effects when its concentration is much greater than a
131 few tenths of $\mu\text{g/L}$ (Chatterjee, 2009). Most data on the
132 release of V into the environment have been related to indus-
133 trial activities, especially from oil refineries and power plants
134 using V-rich fuel oil, and coal crude oil is enriched in V with
135 respect to many other trace elements, with concentrations
136 occasionally exceeding 1 mg/L. Thus, the fraction of
137 dissolved V in surface waters might be an environmental
138 indicator of oil combustion or pollution (Hope, 2008). Such
139 pollution sources may be responsible for appreciable amounts
140 of V into the environment, well above the natural background
141 levels associated with rock weathering and sediment
142 leaching. Fluvial dissolved V concentrations might also be
143 indicative of the types of rocks being weathered or of the
144 nature of the involved weathering processes. Weathering rate
145 and source rock type, rather than solution chemistry or anthro-
146 pogenic influences, appeared to be the important controlling
147 factors on fluvial dissolved V concentrations (Hope, 2008).

148 The oxidation rate of V(IV) to V(V) and the equilibrium
149 between these two species in aqueous solution will regulate
150 V prevalence in water (Pourret et al., 2012). It further depends
151 on several factors, such as pH, V concentration, redox poten-
152 tial, ionic strength of the aqueous system, and biological
153 activity. In water, V(IV) is commonly present as a vanadyl
154 cation $[VO^{2+}, VO(OH)^+]$, whereas V(V) exists as a vanadate
155 oxyanion $(H_2VO_4^-, HVO_4^{2-})$. VO^{2+} is strongly adsorbed
156 onto solid phases, including organic and oxyhydroxide
157 phases. Adsorption of anionic V $(H_2VO_4^-, HVO_4^{2-})$ is
158 much lower than the cations; however, VO^{2+} solubility may
159 be greatly increased through complexation with organic mat-
160 ter. Whereas V(IV) is not thermodynamically stable at
161 $pH > 7$, complexation by various organic and inorganic spe-
162 cies may considerably increase its stability. Eventually, V
163 (V) oxidation state ion is more toxic than V(IV) ion one.

164 **Biological Utilization and Toxicity**

165 Whereas low concentrations of V are required for plants to
 166 positively influence chlorophyll synthesis, K consumption, or
 167 N assimilation, higher V concentrations are toxic as they
 168 cause chlorosis and limit growth. At trace amounts V is essen-
 169 tial for normal cell growth, whereas possibly toxic at high
 170 concentrations, especially when occurring as pentoxide
 171 Chronic exposure may result in inflammation of bronchi and
 172 trachea, eyes and skin irritation, pulmonary edema, and sys-
 173 temic poisoning

174 **Summary**

175 Vanadium's occurrence receives more attention as the global
 176 demand for V increases. However, its prevalence in environ-
 177 ment becomes a new critical issue. Vanadium has been
 178 suggested to be a potentially dangerous pollutant, and the
 179 United States Environmental Protection Agency classifies
 180 V in the priority list of environmental risk elements. Fixing
 181 the environmental issue of V is constrained by the limited
 182 understanding of V biogeochemistry relative to other d-block
 183 transition metals. A better understanding of
 184 V biogeochemical behavior may support to assess the risk to
 185 the environment and to human health and to assist in devel-
 186 oping new remediation tools.

187 **Cross-References**

- 188 ► [Complexation](#)
- 189 ► [Lithophile Elements](#)
- 190 ► [Oxidation-Reduction](#)
- 191 ► [Transition Elements](#)

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