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## V

1

2 **Vanadium**

[Au1]

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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: <sup>50</sup>V and <sup>51</sup>V, 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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