

# Vanadium

Chapter U of

**Critical Mineral Resources of the United States—Economic and Environmental Geology and Prospects for Future Supply**



Professional Paper 1802–U

# Periodic Table of Elements

1A 1 <b>H</b> hydrogen 1.008																	8A 2 <b>He</b> helium 4.003		
3 <b>Li</b> lithium 6.94	2A 4 <b>Be</b> beryllium 9.012											3A 5 <b>B</b> boron 10.81	4A 6 <b>C</b> carbon 12.01	5A 7 <b>N</b> nitrogen 14.01	6A 8 <b>O</b> oxygen 16.00	7A 9 <b>F</b> fluorine 19.00	10 <b>Ne</b> neon 20.18		
11 <b>Na</b> sodium 22.99	12 <b>Mg</b> magnesium 24.31											13 <b>Al</b> aluminum 26.98	14 <b>Si</b> silicon 28.09	15 <b>P</b> phosphorus 30.97	16 <b>S</b> sulfur 32.06	17 <b>Cl</b> chlorine 35.45	18 <b>Ar</b> argon 39.95		
19 <b>K</b> potassium 39.10	20 <b>Ca</b> calcium 40.08	3B 21 <b>Sc</b> scandium 44.96	4B 22 <b>Ti</b> titanium 47.88	5B 23 <b>V</b> vanadium 50.94	6B 24 <b>Cr</b> chromium 52.00	7B 25 <b>Mn</b> manganese 54.94	8B 26 <b>Fe</b> iron 55.85			27 <b>Co</b> cobalt 58.93	28 <b>Ni</b> nickel 58.69	11B 29 <b>Cu</b> copper 63.55	12B 30 <b>Zn</b> zinc 65.39	31 <b>Ga</b> gallium 69.72	32 <b>Ge</b> germanium 72.64	33 <b>As</b> arsenic 74.92	34 <b>Se</b> selenium 78.96	35 <b>Br</b> bromine 79.90	36 <b>Kr</b> krypton 83.79
37 <b>Rb</b> rubidium 85.47	38 <b>Sr</b> strontium 87.62	39 <b>Y</b> yttrium 88.91	40 <b>Zr</b> zirconium 91.22	41 <b>Nb</b> niobium 92.91	42 <b>Mo</b> molybdenum 95.96	43 <b>Tc</b> technetium (98)	44 <b>Ru</b> ruthenium 101.1	45 <b>Rh</b> rhodium 102.9	46 <b>Pd</b> palladium 106.4	47 <b>Ag</b> silver 107.9	48 <b>Cd</b> cadmium 112.4	49 <b>In</b> indium 114.8	50 <b>Sn</b> tin 118.7	51 <b>Sb</b> antimony 121.8	52 <b>Te</b> tellurium 127.6	53 <b>I</b> iodine 126.9	54 <b>Xe</b> xenon 131.3		
55 <b>Cs</b> cesium 132.9	56 <b>Ba</b> barium 137.3	*	72 <b>Hf</b> hafnium 178.5	73 <b>Ta</b> tantalum 180.9	74 <b>W</b> tungsten 183.9	75 <b>Re</b> rhenium 186.2	76 <b>Os</b> osmium 190.2	77 <b>Ir</b> iridium 192.2	78 <b>Pt</b> platinum 195.1	79 <b>Au</b> gold 197.0	80 <b>Hg</b> mercury 200.5	81 <b>Tl</b> thallium 204.4	82 <b>Pb</b> lead 207.2	83 <b>Bi</b> bismuth 209.0	84 <b>Po</b> polonium (209)	85 <b>At</b> astatine (210)	86 <b>Rn</b> radon (222)		
87 <b>Fr</b> francium (223)	88 <b>Ra</b> radium (226)	**	104 <b>Rf</b> rutherfordium (261)	105 <b>Db</b> dubnium (268)	106 <b>Sg</b> seaborgium (271)	107 <b>Bh</b> bohrium (270)	108 <b>Hs</b> hassium (277)	109 <b>Mt</b> meitnerium (276)	110 <b>Ds</b> darmstadtium (281)	111 <b>Rg</b> roentgenium (280)	112 <b>Cn</b> copernicium (285)	113 <b>Uut</b> (284)	114 <b>Fl</b> flerovium (289)	115 <b>Uup</b> (288)	116 <b>Lv</b> livermorium (293)	117 <b>Uus</b> (294)	118 <b>Uuo</b> (294)		
Lanthanide Series*		57 <b>La</b> lanthanum 138.9	58 <b>Ce</b> cerium 140.1	59 <b>Pr</b> praseodymium 140.9	60 <b>Nd</b> neodymium 144.2	61 <b>Pm</b> promethium (145)	62 <b>Sm</b> samarium 150.4	63 <b>Eu</b> europium 152.0	64 <b>Gd</b> gadolinium 157.2	65 <b>Tb</b> terbium 158.9	66 <b>Dy</b> dysprosium 162.5	67 <b>Ho</b> holmium 164.9	68 <b>Er</b> erbium 167.3	69 <b>Tm</b> thulium 168.9	70 <b>Yb</b> ytterbium 173.0	71 <b>Lu</b> lutetium 175.0			
Actinide Series**		89 <b>Ac</b> actinium (227)	90 <b>Th</b> thorium 232	91 <b>Pa</b> protactinium 231	92 <b>U</b> uranium 238	93 <b>Np</b> neptunium (237)	94 <b>Pu</b> plutonium (244)	95 <b>Am</b> americium (243)	96 <b>Cm</b> curium (247)	97 <b>Bk</b> berkelium (247)	98 <b>Cf</b> californium (251)	99 <b>Es</b> einsteinium (252)	100 <b>Fm</b> fermium (257)	101 <b>Md</b> mendelevium (258)	102 <b>No</b> nobelium (259)	103 <b>Lr</b> lawrencium (262)			




element names in **blue** are liquids at room temperature  
 element names in **red** are gases at room temperature  
 element names in black are solids at room temperature

Modified from Los Alamos National Laboratory Chemistry Division; available at <http://periodic.lanl.gov/images/periodictable.pdf>.

**Cover.** Photographs depicting four examples of sources and uses of vanadium. Upper left, vanadiferous magnetite-rich layer from South Africa. Photograph courtesy of Kevin Walsh/CC BY 2.0 (<https://creativecommons.org/licenses/by/2.0/>). Upper right, natural vanadinite, which is a main source of vanadium from vanadate deposits. Photograph courtesy of Juergen Kummer, Jumk.de Web Projects/CC BY 3.0 (<http://images-of-elements.com/vanadium.php>). Lower left, vanadium metal crystals made by electrolysis (the largest crystal is 2 centimeters in length). Photograph courtesy of Juergen Kummer, Jumk.de Web Projects/CC BY 3.0 (<http://images-of-elements.com/vanadium.php>). Lower right, common hand wrench made with vanadium alloy steel. Photograph courtesy of MrX/CC-BY-SA-3.0 ([https://commons.wikimedia.org/wiki/File:Chrome\\_Vanadium\\_Adjustable\\_Wrench.jpg](https://commons.wikimedia.org/wiki/File:Chrome_Vanadium_Adjustable_Wrench.jpg)).

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By Karen D. Kelley, Clinton T. Scott, Désirée E. Polyak, and Bryn E. Kimball

Chapter U of

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Edited by Klaus J. Schulz, John H. DeYoung, Jr., Robert R. Seal II, and Dwight C. Bradley

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# Conversion Factors

International System of Units to Inch/Pound

<b>Multiply</b>	<b>By</b>	<b>To obtain</b>
<b>Length</b>		
angstrom (Å) (0.1 nanometer)	0.003937	microinch
angstrom (Å) (0.1 nanometer)	0.000003937	mil
micrometer (µm) [or micron]	0.03937	mil
millimeter (mm)	0.03937	inch (in.)
centimeter (cm)	0.3937	inch (in.)
meter (m)	3.281	foot (ft)
meter (m)	1.094	yard (yd)
kilometer (km)	0.6214	mile (mi)
<b>Area</b>		
hectare (ha)	2.471	acre
square kilometer (km <sup>2</sup> )	247.1	acre
square meter (m <sup>2</sup> )	10.76	square foot (ft <sup>2</sup> )
square centimeter (cm <sup>2</sup> )	0.1550	square inch (in <sup>2</sup> )
square kilometer (km <sup>2</sup> )	0.3861	square mile (mi <sup>2</sup> )
<b>Volume</b>		
milliliter (mL)	0.03381	ounce, fluid (fl. oz)
liter (L)	33.81402	ounce, fluid (fl. oz)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
cubic meter (m <sup>3</sup> )	264.2	gallon (gal)
cubic centimeter (cm <sup>3</sup> )	0.06102	cubic inch (in <sup>3</sup> )
cubic meter (m <sup>3</sup> )	1.308	cubic yard (yd <sup>3</sup> )
cubic kilometer (km <sup>3</sup> )	0.2399	cubic mile (mi <sup>3</sup> )
<b>Mass</b>		
microgram (µg)	0.0000003527	ounce, avoirdupois (oz)
milligram (mg)	0.00003527	ounce, avoirdupois (oz)
gram (g)	0.03527	ounce, avoirdupois (oz)
gram (g)	0.03215075	ounce, troy
kilogram (kg)	32.15075	ounce, troy
kilogram (kg)	2.205	pound avoirdupois (lb)
ton, metric (t)	1.102	ton, short [2,000 lb]
ton, metric (t)	0.9842	ton, long [2,240 lb]
<b>Deposit grade</b>		
gram per metric ton (g/t)	0.0291667	ounce per short ton (2,000 lb) (oz/T)
<b>Pressure</b>		
megapascal (MPa)	10	bar
gigapascal (GPa)	10,000	bar
<b>Density</b>		
gram per cubic centimeter (g/cm <sup>3</sup> )	62.4220	pound per cubic foot (lb/ft <sup>3</sup> )
milligram per cubic meter (mg/m <sup>3</sup> )	0.0000006243	pound per cubic foot (lb/ft <sup>3</sup> )
<b>Energy</b>		
joule (J)	0.0000002	kilowatthour (kWh)
joule (J)	$6.241 \times 10^{18}$	electronvolt (eV)
joule (J)	0.2388	calorie (cal)
kilojoule (kJ)	0.0002388	kilocalorie (kcal)

## International System of Units to Inch/Pound—Continued

<b>Multiply</b>	<b>By</b>	<b>To obtain</b>
<b>Radioactivity</b>		
becquerel (Bq)	0.00002703	microcurie ( $\mu\text{Ci}$ )
kilobecquerel (kBq)	0.02703	microcurie ( $\mu\text{Ci}$ )
<b>Electrical resistivity</b>		
ohm meter ( $\Omega\text{-m}$ )	39.37	ohm inch ( $\Omega\text{-in.}$ )
ohm-centimeter ( $\Omega\text{-cm}$ )	0.3937	ohm inch ( $\Omega\text{-in.}$ )
<b>Thermal conductivity</b>		
watt per centimeter per degree Celsius ( $\text{watt/cm } ^\circ\text{C}$ )	693.1798	International British thermal unit inch per hour per square foot per degree Fahrenheit ( $\text{Btu in/h ft}^2 \text{ } ^\circ\text{F}$ )
watt per meter kelvin ( $\text{W/m-K}$ )	6.9318	International British thermal unit inch per hour per square foot per degree Fahrenheit ( $\text{Btu in/h ft}^2 \text{ } ^\circ\text{F}$ )

## Inch/Pound to International System of Units

<b>Length</b>		
mil	25.4	micrometer ( $\mu\text{m}$ ) [or micron]
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
<b>Volume</b>		
ounce, fluid (fl. oz)	29.57	milliliter (mL)
ounce, fluid (fl. oz)	0.02957	liter (L)
<b>Mass</b>		
ounce, avoirdupois (oz)	28,350,000	microgram
ounce, avoirdupois (oz)	28,350	milligram
ounce, avoirdupois (oz)	28.35	gram (g)
ounce, troy	31.10 348	gram (g)
ounce, troy	0.03110348	kilogram (kg)
pound, avoirdupois (lb)	0.4536	kilogram (kg)
ton, short (2,000 lb)	0.9072	ton, metric (t)
ton, long (2,240 lb)	1.016	ton, metric (t)
<b>Deposit grade</b>		
ounce per short ton (2,000 lb) (oz/T)	34.285714	gram per metric ton (g/t)
<b>Energy</b>		
kilowatthour (kWh)	3,600,000	joule (J)
electronvolt (eV)	$1.602 \times 10^{-19}$	joule (J)
<b>Radioactivity</b>		
microcurie ( $\mu\text{Ci}$ )	37,000	becquerel (Bq)
microcurie ( $\mu\text{Ci}$ )	37	kilobecquerel (kBq)

Temperature in degrees Celsius ( $^\circ\text{C}$ ) may be converted to degrees Fahrenheit ( $^\circ\text{F}$ ) as follows:

$$^\circ\text{F} = (1.8 \times ^\circ\text{C}) + 32$$

Temperature in degrees Celsius ( $^\circ\text{C}$ ) may be converted to kelvin (K) as follows:

$$\text{K} = ^\circ\text{C} + 273.15$$

Temperature in degrees Fahrenheit ( $^\circ\text{F}$ ) may be converted to degrees Celsius ( $^\circ\text{C}$ ) as follows:

$$^\circ\text{C} = (^\circ\text{F} - 32) / 1.8$$

## Datum

Unless otherwise stated, vertical and horizontal coordinate information is referenced to the World Geodetic System of 1984 (WGS 84). Altitude, as used in this report, refers to distance above the vertical datum.

## Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ( $\mu\text{S}/\text{cm}$  at 25 °C).

Concentrations of chemical constituents in soils and (or) sediment are given in milligrams per kilogram (mg/kg), parts per million (ppm), or parts per billion (ppb).

Concentrations of chemical constituents in water are given in milligrams per liter (mg/L), micrograms per liter ( $\mu\text{g}/\text{L}$ ), nanograms per liter (ng/L), nanomoles per kilogram (nmol/kg), parts per million (ppm), parts per billion (ppb), or parts per trillion (ppt).

Concentrations of suspended particulates in water are given in micrograms per gram ( $\mu\text{g}/\text{g}$ ), milligrams per kilogram (mg/kg), or femtograms per gram (fg/g).

Concentrations of chemicals in air are given in units of the mass of the chemical (milligrams, micrograms, nanograms, or picograms) per volume of air (cubic meter).

Activities for radioactive constituents in air are given in microcuries per milliliter ( $\mu\text{Ci}/\text{mL}$ ).

Deposit grades are commonly given in percent, grams per metric ton (g/t)—which is equivalent to parts per million (ppm)—or troy ounces per short ton (oz/T).

Geologic ages are expressed in mega-annum (Ma, million years before present, or  $10^6$  years ago) or giga-annum (Ga, billion years before present, or  $10^9$  years ago).

For ranges of years, “to” and (or) the en dash (“–”) mean “up to and including.”

Concentration unit	Equals
milligram per kilogram (mg/kg)	part per million
microgram per gram ( $\mu\text{g}/\text{g}$ )	part per million
microgram per kilogram ( $\mu\text{g}/\text{kg}$ )	part per billion ( $10^9$ )

### Equivalencies

part per million (ppm): 1 ppm = 1,000 ppb = 1,000,000 ppt = 0.0001 percent

part per billion (ppb): 0.001 ppm = 1 ppb = 1,000 ppt = 0.0000001 percent

part per trillion (ppt): 0.000001 ppm = 0.001 ppb = 1 ppt = 0.000000001 percent

### Metric system prefixes

tera- (T-)	$10^{12}$	1 trillion
giga- (G-)	$10^9$	1 billion
mega- (M-)	$10^6$	1 million
kilo- (k-)	$10^3$	1 thousand
hecto- (h-)	$10^2$	1 hundred
deka- (da-)	10	1 ten
deci- (d-)	$10^{-1}$	1 tenth
centi- (c-)	$10^{-2}$	1 hundredth
milli- (m-)	$10^{-3}$	1 thousandth
micro- ( $\mu$ -)	$10^{-6}$	1 millionth
nano- (n-)	$10^{-9}$	1 billionth
pico- (p-)	$10^{-12}$	1 trillionth
femto- (f-)	$10^{-15}$	1 quadrillionth
atto- (a-)	$10^{-18}$	1 quintillionth

## Abbreviations and Symbols

$\mu\text{g/L}$	microgram per liter
$\mu\text{g V/L}$	microgram of vanadium per liter
AMD	acid mine drainage
Ga	giga-annum
HSLA	high-strength, low-alloy
km	kilometer
$\text{km}^2$	square kilometer
$\text{LC}_{50}$	lethal concentration 50 (concentration that kills 50 percent of test population within a given timeframe)
LIP	large igneous province
m	meter
Ma	mega-annum
mg/kg	milligram per kilogram
mg/L	milligram per liter
$\text{mg/m}^3$	milligram per cubic meter
MVT	Mississippi Valley-type
$\text{ng/m}^3$	nanogram per cubic meter
nm	nanometer
PGE	platinum-group element
ppb	part per billion
ppm	part per million
SSV	sandstone-hosted vanadium
VRB	vanadium redox-flow battery
VTM	vanadiferous titanomagnetite

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## Abstract

Vanadium is used primarily in the production of steel alloys; as a catalyst for the chemical industry; in the making of ceramics, glasses, and pigments; and in vanadium redox-flow batteries (VRBs) for large-scale storage of electricity. World vanadium resources in 2012 were estimated to be 63 million metric tons, which include about 14 million metric tons of reserves. The majority of the vanadium produced in 2012 was from China, Russia, and South Africa.

Vanadium is extracted from several different types of mineral deposits and from fossil fuels. These deposits include vanadiferous titanomagnetite (VTM) deposits, sandstone-hosted vanadium (with or without uranium) deposits (SSV deposits), and vanadium-rich black shales. VTM deposits are the principal source of vanadium and consist of magmatic accumulations of ilmenite and magnetite containing 0.2 to 1 weight percent vanadium pentoxide ( $V_2O_5$ ). SSV deposits are another important source; these deposits have average ore grades that range from 0.1 to greater than 1 weight percent  $V_2O_5$ . The United States has been and is currently the main producer of vanadium from SSV deposits, particularly those on the Colorado Plateau. Vanadium-rich black shales occur in marine successions that were deposited in epeiric (inland) seas and on continental margins. Concentrations in these shales regularly exceed 0.18 weight percent  $V_2O_5$  and can be as high as 1.7 weight percent  $V_2O_5$ . Small amounts of vanadium have been produced from the Alum Shale in Sweden and from ferrophosphorus slag generated during the reduction of phosphate to elemental phosphorus in ore from shales of the Phosphoria Formation in Idaho and Wyoming. Because vanadium enrichment occurs in beds that are typically only a few meters thick, most of the vanadiferous black shales are not currently economic, although they may become an important resource in the future. Significant amounts of vanadium are recovered as byproducts of petroleum refining, and processing of coal, tar sands, and oil shales may be important future sources.

Vanadium occurs in one of four oxidation states in nature: +2, +3, +4, and +5. The  $V^{3+}$  ion has an octahedral radius that is almost identical to that of  $Fe^{3+}$  and  $Al^{3+}$  and, therefore, it substitutes in ferromagnesian minerals. During weathering, much of the vanadium may partition into newly formed clay minerals, and it either remains in the +3 valence state or oxidizes to the +4 valence state, both of which are relatively insoluble. If erosion is insignificant but chemical leaching is intense, the residual material may be enriched in vanadium, as are some bauxites and laterites. During the weathering of igneous, residual, or sedimentary rocks, some vanadium oxidizes to the +5 valence state, especially in the intensive oxidizing conditions that are characteristic of arid climates.

The average contents of vanadium in the environment are as follows: soils (10 to 500 parts per million [ppm]); streams and rivers (0.2 to 2.9 parts per billion [ppb]); and coastal seawater (0.3 to 2.8 ppb). Concentrations of vanadium in soils (548 to 7,160 ppm) collected near vanadium mines in China, the Czech Republic, and South Africa are many times greater than natural concentrations in soils. Additionally, if deposits contain sulfide minerals such as chalcocite, pyrite, and sphalerite, high levels of acidity may be present if sulfide dissolution is not balanced by the presence of acid-neutralizing carbonate minerals. Some of the vanadium-bearing deposit types, particularly some SSV and black shale deposits, contain appreciable amounts of carbonate minerals, which lowers the acid-generation potential.

Vanadium is a micronutrient with a postulated requirement for humans of less than 10 micrograms per day, which can be met through dietary intake. Primary and secondary drinking water regulations for vanadium are not currently in place in the United States. Vanadium toxicity is thought to result from an intake of more than 10 to 20 milligrams per day. Vanadium is essential for some biological processes and organisms. For example, some nitrogen-fixing bacteria require vanadium for producing enzymes necessary to convert nitrogen from the atmosphere into ammonia, which is a more biologically accessible form of nitrogen.

## Introduction

Vanadium (V) is a strategic metal that is used principally in the production of metal alloys, such as high-strength steel and alloys for use in the aerospace industry. Secondary uses are as catalysts for the chemical industry, and in ceramics, glasses, and pigments. In its native state, vanadium is a hard, silvery gray, ductile, and malleable transition metal. Vanadium consumption trends are heavily influenced by trends in steel production.

The emerging need for large-scale electricity storage makes vanadium redox-flow batteries (VRBs) a major potential future use of vanadium. Because of their large-scale storage capacity, development of VRBs could prompt increases in the use of wind, solar, and other renewable, intermittent power sources. Lithium-vanadium-phosphate batteries produce high voltages and high energy-to-weight ratios, which make them ideal for use in electric cars. Vanadium use in lithium batteries is expected to increase to 1,700 metric tons in 2017 from 200 metric tons in 2012 (Perles, 2013).

Vanadium is the 22d most abundant element in Earth's crust, and it is an essential constituent of many minerals. A total of 156 minerals contain vanadium as a major (>10 weight percent) constituent. Several diverse mineral deposit types contain vanadium-bearing minerals, and vanadium is a common component of petroleum and other fossil fuels. Vanadium deposits are globally distributed (fig. U1) and comprise four principal deposit types: vanadiferous titanomagnetite (VTM), sandstone-hosted vanadium (SSV), shale-hosted vanadium, and vanadate deposits (table U1). Additionally, significant amounts of vanadium are available for commercial use as a byproduct of petroleum refining, and processing of coal, tar sands, and oil shales may be important future sources. World vanadium resources in 2012 were estimated to be 63 million metric tons of vanadium. Reserves were estimated to be 14 million metric tons. The majority of vanadium production in 2012 was from China (37 percent), South Africa (35 percent), and Russia (25 percent) (fig. U2; Polyak, 2013).

## Uses and Applications

The vanadium market closely follows that of the steel industry, which in turn follows economic trends. Metallurgical applications in steel continued to dominate United States vanadium usage in 2011 (fig. U3), accounting for 93 percent of reported consumption (Polyak, 2013). Vanadium is used in steel to impart strength, toughness, and wear resistance. The formation of vanadium-rich carbides and nitrides imparts the strength to steel; the addition of only a few kilograms of vanadium per ton of steel increases the strength of the steel by as much as 25 percent. Apart from its strengthening characteristic, vanadium also inhibits corrosion and oxidation.

There are many sources of vanadium, and it is used in a number of common products (fig. U4). Commercial products

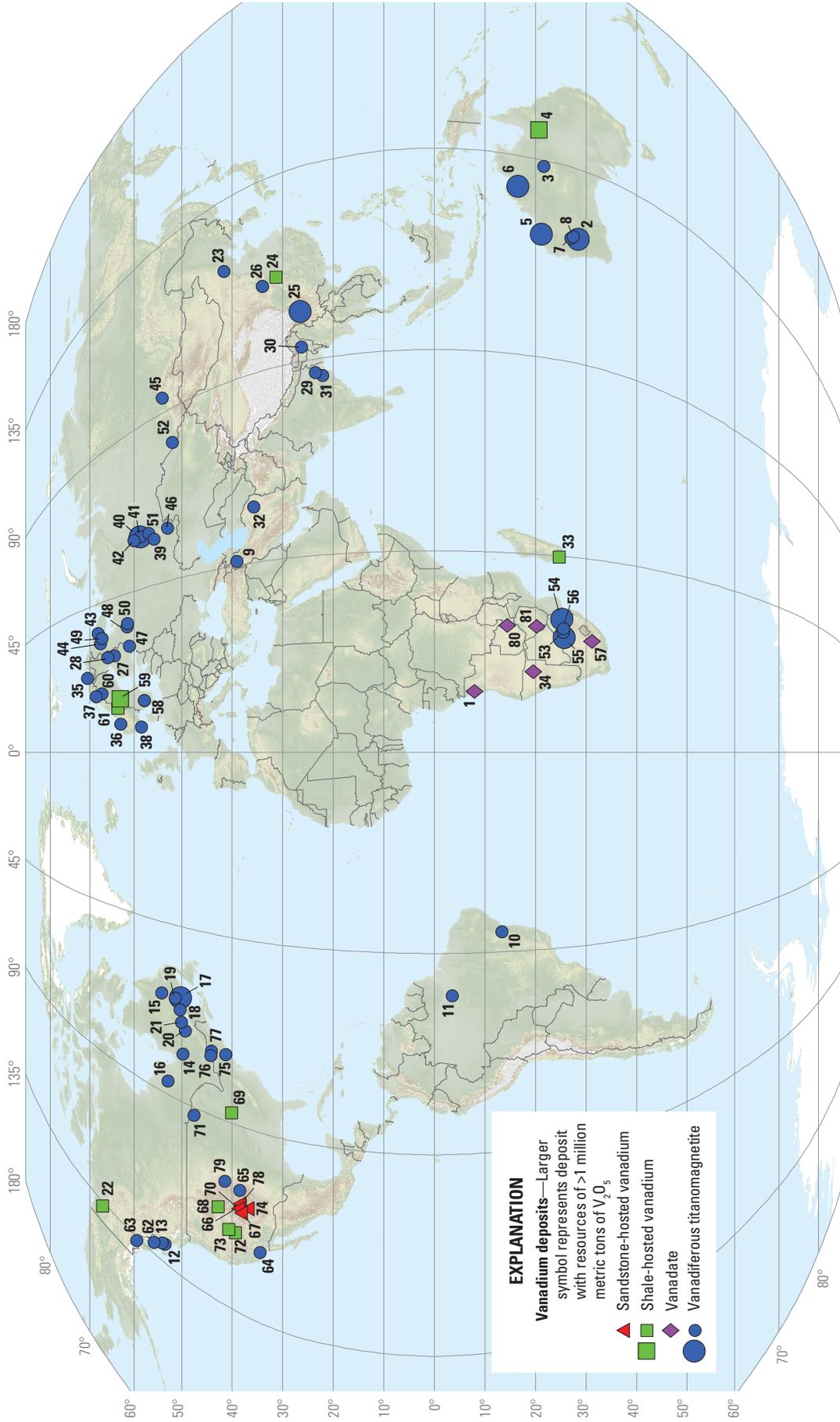
developed through the processing of vanadium ores are mainly ferrovanadium (FeV), which is an iron-vanadium alloy, and vanadium pentoxide ( $V_2O_5$ ). Most vanadium is added to steel as ferrovanadium. Ferrovanadium is available in compositions containing 45 to 50 percent vanadium and 80 percent vanadium. The 45- to 50-percent grade is produced from slag and other vanadium-bearing residues; the 80-percent grade is produced by the reduction of  $V_2O_5$ .

The high-strength, low-alloy (HSLA) steels containing vanadium are widely used for the construction of auto parts, buildings, bridges, cranes, pipelines, rail cars, ships, and truck bodies, including armor plating for military vehicles (Polyak, 2012). Such HSLA steels are increasingly being used in the oil and gas industry to meet demand for pipelines with higher strength and higher low-temperature toughness (Roskill Information Services, Ltd., 2010, p. 150). Vanadium is used in tool steels in various combinations with chromium, niobium (columbium), manganese, molybdenum, titanium, and tungsten. Only a limited degree of substitution is possible among these metals, however. Replacement of vanadium with other mineral commodities requires significant technical adjustments to the steel production process to ensure that product specifications and quality are not compromised. For example, use of vanadium generally requires less energy consumption during production than does niobium to give equivalent steel properties. Therefore, substitution for vanadium is normally not considered for short-term changes in market conditions because of the considerable effort involved in implementing the change.

Vanadium is irreplaceable for its role in aerospace applications because vanadium-titanium alloys have the best strength-to-weight ratio of any engineered material yet discovered. Vanadium, when combined with titanium, produces a stronger and more stable alloy, and when combined with aluminum produces a material suitable for jet engines and high-speed airframes. No acceptable substitutes exist for vanadium in aerospace titanium alloys.

Nonmetallurgical applications of vanadium include catalysts, ceramics, electronics, and vanadium chemicals. For catalytic uses, platinum and nickel can replace vanadium compounds in some chemical processes. Vanadium dioxide is used in the production of glass coatings that block infrared radiation.

Vanadium is becoming more widely used in green technology applications, especially in battery technology. One battery technology that continues to show promise in stabilizing energy distribution in renewable systems is the VRB, which consists of an assembly of power cells in which two vanadium-based electrolytes are separated by a proton exchange membrane. The main advantages of the VRBs are (a) their nearly unlimited capacity, which is made possible simply by using sequentially larger storage tanks; (b) their ability to be left completely discharged for long periods of time with no detrimental effects; (c) the ease of recharging them by replacing the electrolyte if no power source is available to charge it; and (d) their ability to withstand permanent damage if the electrolytes are accidentally mixed (Polyak, 2012).



Base from U.S. Geological Survey Global 3D arc-second elevation data (1996) and from Natural Earth (2014); Robinson projection; World Geodetic System 1984 datum

**Figure U1.** World map showing locations of major vanadium deposits of the world, by deposit type. Numbers refer to the identifier number in table U1, which contains additional information about the vanadium resources in these deposits.

## U4 Critical Mineral Resources of the United States—Vanadium

**Table U1.** Location, grade, tonnage, and other data for selected vanadium deposits of the world.

[ID, identifier, shown in figs. U1 and U5; WGS 84, World Geodetic System of 1984; negative values for latitude indicate that the deposit is in the Southern Hemisphere; negative values for longitude indicate that the deposit is in the Western Hemisphere; %, percent; V<sub>2</sub>O<sub>5</sub>, vanadium oxide; VTM, vanadiferous titanomagnetite; n.d., no data available; NA, not available; t, metric ton; SSV, sandstone-hosted vanadium]

ID	Deposit	Country	District, region, or State/Province	Deposit type	Latitude	Longitude	Resource tonnage (million metric tons)	Grade (% V <sub>2</sub> O <sub>5</sub> )	V <sub>2</sub> O <sub>5</sub> content (million metric tons)	Production, resources, or reserves	Source of data
					(decimal degrees, WGS 84)						
1	Lueca Mine	Angola	NA	Vanadate	-7.92	13.65	n.d.	n.d.	n.d.	n.d.	Fischer (1975a)
2	Windimurra	Australia	Mount Magnet	VTM	-28.36	118.84	242.6	0.48	1.16	Resources	Britt and others (2014)
3	Mount Peake	Australia	Northern Territory	VTM	-21.66	133.66	160	0.3	0.48	Resources	TNG Ltd. (2015)
4	Julia Creek	Australia	Queensland	Shale-hosted	-20.65	141.73	411	0.44	1.1	Resources	Lewis and others (2010)
5	Balla Balla	Australia	Western Australia	VTM	-21.14	118.06	456	0.64	2.91	Resources	Britt and others (2014)
6	Speewah	Australia	Western Australia	VTM	-16.47	128.20	4,712	0.3	14.1	Resources	Britt and others (2014)
7	Gabanimtha	Australia	Western Australia	VTM	-27.00	118.60	125.8	0.7	0.88	Resources	Britt and others (2014)
8	Barrambie	Australia	Western Australia	VTM	-27.42	119.11	47.2	0.63	0.3	Resources	Britt and others (2014)
9	Svorantskoe	Azerbaijan	Chelyabinskaya Oblast	VTM	39.00	46.00	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
10	Maracas	Brazil	Bahia	VTM	-13.41	-40.43	24.6	1.11	0.27	Resources	Fischer (1975b)
11	Tapajos	Brazil	Pará	VTM	-3.61	-54.49	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
12	Banks Island	Canada	British Columbia	VTM	53.47	-130.13	3	0.6	0.018	Resources	Fischer (1975b)
13	Porcher Island	Canada	British Columbia	VTM	54.00	-130.25	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
14	Lac Doré	Canada	Matagami, Quebec	VTM	49.76	-77.62	100	0.49	0.49	Resources	Fischer (1975b)
15	Lake Michikamau	Canada	Newfoundland and Labrador	VTM	54.12	-63.98	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
16	Ring of Fire	Canada	Ontario	VTM	52.80	-86.50	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
17	Lac Tio (Al-lard Lake)	Canada	Quebec	VTM	50.56	63.41	350	0.3	1.05	Resources	Fischer (1975b)
18	Sept Îles	Canada	Quebec	VTM	50.34	-66.51	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
19	Magpie Mountain	Canada	Quebec	VTM	51.38	-64.07	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
20	Lac St. Jean	Canada	Quebec	VTM	49.33	-71.50	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)

**Table U1.** Location, grade, tonnage, and other data for selected vanadium deposits of the world.—Continued

[ID, identifier, shown in figs. U1 and U5; WGS 84, World Geodetic System of 1984; negative values for latitude indicate that the deposit is in the Southern Hemisphere; negative values for longitude indicate that the deposit is in the Western Hemisphere; %, percent; V<sub>2</sub>O<sub>5</sub>, vanadium oxide; VTM, vanadiferous titanomagnetite; n.d., no data available; NA, not available; t, metric ton; SSV, sandstone-hosted vanadium]

ID	Deposit	Country	District, region, or State/Province	Deposit type	Latitude	Longitude	Resource tonnage (million metric tons)	Grade (% V <sub>2</sub> O <sub>5</sub> )	V <sub>2</sub> O <sub>5</sub> content (million metric tons)	Production, resources, or reserves	Source of data
					(decimal degrees, WGS 84)						
21	LaBlache-Hervieux-Shmoo Lakes	Canada	Quebec	VTM	50.06	-69.63	101.7	0.18	0.18	Resources	Fischer (1975b)
22	Nick	Canada	Yukon	Shale-hosted	68.65	-135.25	n.d.	n.d.	n.d.	n.d.	Hulbert and others (1992)
23	Luanping	China	Hubei Province	VTM	41.50	117.50	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
24	Maocaoping, Baig-uoyuan	China	Hubei Province	Shale-hosted	31.27	111.08	n.d.	n.d.	n.d.	n.d.	Coveney and Nansheng (1991)
25	Nalaqing, Gongshan, Damakan, Lanjian	China	Panzhihua region, Sichuan Province	VTM	26.65	102.00	3,460	0.3	10.4	Resources <sup>1</sup>	Zhou and others (2005)
26	Shanyang	China	Shaanxi Province	VTM	33.87	109.94	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
27	Otanmaki	Finland	Kajaani, Kainuu Region	VTM	64.13	27.10	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
28	Mustavaara	Finland	Oulu, North Ostrobothnia Region	VTM	65.78	27.99	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
29	Singhbhum-Mayurbhanj	India	Bihar and Odisha	VTM	22.00	86.00	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
30	Ganjang	India	Karbi-Anglong District	VTM	26.16	93.33	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
31	Shaltora	India	West Bengal	VTM	23.42	86.92	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
32	Rivash	Iran	Razavi Khorasan Province	VTM	35.64	58.33	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
33	Green giant	Madagascar	Tulear Region	Shale-hosted (meta)	-24.69	44.75	49.9	0.693	0.35	Resources	Energizer Resources, Inc. (2013)
34	Berg Aukas, Abenad, Tsumeb	Namibia	Otavi Mountainland	Vana-date	-19.51	18.25	3.2	0.75	0.024	Resources	Fischer (1975a); Boni and others (2007)
35	Stjernoy-Seiland	Norway	Finnmark County	VTM	70.50	23.00	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)

**U6 Critical Mineral Resources of the United States—Vanadium**
**Table U1.** Location, grade, tonnage, and other data for selected vanadium deposits of the world.—Continued

[ID, identifier, shown in figs. U1 and U5; WGS 84, World Geodetic System of 1984; negative values for latitude indicate that the deposit is in the Southern Hemisphere; negative values for longitude indicate that the deposit is in the Western Hemisphere; %, percent; V<sub>2</sub>O<sub>5</sub>, vanadium oxide; VTM, vanadiferous titanomagnetite; n.d., no data available; NA, not available; t, metric ton; SSV, sandstone-hosted vanadium]

ID	Deposit	Country	District, region, or State/Province	Deposit type	Latitude	Longitude	Resource tonnage (million metric tons)	Grade (% V <sub>2</sub> O <sub>5</sub> )	V <sub>2</sub> O <sub>5</sub> content (million metric tons)	Production, resources, or reserves	Source of data
					(decimal degrees, WGS 84)						
36	Rodsand	Norway	Møre og Romsdal County	VTM	62.85	8.12	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
37	Selvag	Norway	Nordland County	VTM	68.66	15.00	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
38	Tellnes	Norway	Rogaland County	VTM	58.33	6.42	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
39	Kusinskoe	Russia	Chelyabinskaya Oblast	VTM	55.75	57.35	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
40	Gusevogorsk	Russia	Kachkanar, Sverdlovskaya Oblast	VTM	58.70	59.49	16,200	0.084	13.6	Resources	Augé and others (2005); Laznicka (2010)
41	Guseva Gora	Russia	Kachkanar, Sverdlovskaya Oblast	VTM	58.70	59.49	n.d.	n.d.	n.d.	n.d.	Augé and others (2005); Laznicka (2010)
42	Yubryahinskoe	Russia	Kachkanar, Sverdlovskaya Oblast	VTM	59.93	59.17	n.d.	n.d.	n.d.	n.d.	Augé and others (2005); Laznicka (2010)
43	Tsagin	Russia	Murmanskaya Oblast	VTM	68.00	36.00	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
44	Afrikanda	Russia	Murmanskaya Oblast	VTM	67.42	32.68	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
45	Lysanovskoe	Russia	NA	VTM	54.00	94.00	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
46	Visean	Russia	NA	VTM	53.00	59.00	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
47	Koykara Koyarsk	Russia	NA	VTM	61.00	30.00	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
48	Pudozhgorsk	Russia	Republic of Kareliya	VTM	61.62	36.24	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
49	Yelet' ozero	Russia	Republic of Kareliya	VTM	67.07	34.21	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
50	Pudozhgorskoe	Russia	Republic of Kareliya	VTM	61.37	36.48	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
51	Pervouralsk	Russia	Sverdlovskaya Oblast	VTM	56.90	59.53	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
52	Kharlovskoe	Russia	Sverdlovskaya Oblast	VTM	52.00	81.00	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)

**Table U1.** Location, grade, tonnage, and other data for selected vanadium deposits of the world.—Continued

[ID, identifier, shown in figs. U1 and U5; WGS 84, World Geodetic System of 1984; negative values for latitude indicate that the deposit is in the Southern Hemisphere; negative values for longitude indicate that the deposit is in the Western Hemisphere; %, percent; V<sub>2</sub>O<sub>5</sub>, vanadium oxide; VTM, vanadiferous titanomagnetite; n.d., no data available; NA, not available; t, metric ton; SSV, sandstone-hosted vanadium]

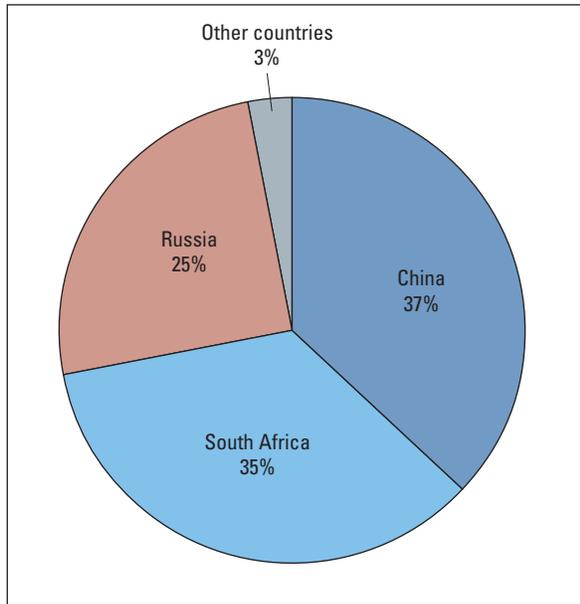
ID	Deposit	Country	District, region, or State/Province	Deposit type	Latitude	Longitude	Resource tonnage (million metric tons)	Grade (% V <sub>2</sub> O <sub>5</sub> )	V <sub>2</sub> O <sub>5</sub> content (million metric tons)	Production, resources, or reserves	Source of data
					(decimal degrees, WGS 84)						
53	Vantra	South Africa	Brits, North West Province	VTM	-25.63	27.78	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
54	Mapochs Mine	South Africa	Bushveld Igneous Complex, Limpopo Province	VTM	-25.22	29.92	100	1.5	1.5	Resources + re-serves	Reynolds (1985); Rohrmann (1985)
55	Rhovan Mine	South Africa	Bushveld Igneous Complex, Limpopo Province	VTM	-25.57	27.57	203	0.52	1.06	Resources	Reynolds (1985); Rohrmann (1985)
56	Krokodilkraal Mine	South Africa	Bushveld Igneous Complex, North West Province	VTM	-25.60	28.18	n.d.	n.d.	n.d.	n.d.	Reynolds (1985); Rohrmann (1985)
57	Kafferskrall Farm	South Africa	North West Province	Vanadate	-31.15	25.85	n.d.	n.d.	n.d.	n.d.	Fischer (1975a)
58	Taberg	Sweden	Jönköping County	VTM	57.75	14.17	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
59	Viken	Sweden	Myrviken, Jämtland County	Shale-hosted	63.12	14.36	685	0.29	1.98	Resources	Aura Energy (2012)
60	Ruoutevare	Sweden	Norrbotnen County	VTM	67.08	17.50	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
61	Häggån	Sweden	Storsjön, Jämtland County	Shale-hosted	63.50	12.73	n.d.	n.d.	n.d.	n.d.	Aura Energy (2012)
62	Union Bay	United States	Alaska	VTM	55.77	-132.10	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
63	Klukwan Fan	United States	Alaska	VTM	59.42	-135.88	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
64	San Gabriel Mountains	United States	California	VTM	34.37	-118.30	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
65	McClure Mountain	United States	Colorado	VTM	38.34	-105.42	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
66	Buckmaster Draw	United States	Green River, Utah	SSV	38.68	-110.03	0.67	0.19	0.0012	n.d.	Fischer (1968)
67	Tony M, Frank M	United States	Henry Mtns., Utah	SSV	38.11	-110.81	n.d.	n.d.	n.d.	n.d.	Johnson (1959)

**U8 Critical Mineral Resources of the United States—Vanadium**
**Table U1.** Location, grade, tonnage, and other data for selected vanadium deposits of the world.—Continued

[ID, identifier, shown in figs. U1 and U5; WGS 84, World Geodetic System of 1984; negative values for latitude indicate that the deposit is in the Southern Hemisphere; negative values for longitude indicate that the deposit is in the Western Hemisphere; %, percent; V<sub>2</sub>O<sub>5</sub>, vanadium oxide; VTM, vanadiferous titanomagnetite; n.d., no data available; NA, not available; t, metric ton; SSV, sandstone-hosted vanadium]

ID	Deposit	Country	District, region, or State/Province	Deposit type	Latitude	Longitude	Resource tonnage (million metric tons)	Grade (% V <sub>2</sub> O <sub>5</sub> )	V <sub>2</sub> O <sub>5</sub> content (million metric tons)	Production, resources, or reserves	Source of data
					(decimal degrees, WGS 84)						
68	Phosphoria	United States	Idaho	Shale-hosted	42.70	-111.83	n.d.	n.d.	n.d.	n.d.	Love and others (2003); Jasinski (2004)
69	Mecca Quarry shale	United States	Illinois and Indiana	Shale-hosted	40.02	-87.53	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
70	Mike, Pandora Mine	United States	La Sal district, Utah	SSV	38.31	-109.25	0.989	1.46	0.0144	Production	Fischer (1968); Shawe (2011)
71	TiTac	United States	Minnesota	VTM	47.58	-92.07	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
72	Gibellini	United States	Nevada	Shale-hosted	39.21	-116.09	0.082	0.29	0.00017	Resources	American Vanadium Corp. (2012)
73	Carlin Vanadium	United States	Nevada	Shale-hosted	40.61	-116.12	25.4	0.51	0.13	Resources	Scandium International Mining Corp. (2010)
74	King Tut, Carrizo, Lukachukai Mountains	United States	New Mexico and Arizona	SSV	36.74	-109.01	0.846	1.15	0.01	Production	McLemore and Chenoweth (1997)
75	Ossining	United States	New York	VTM	41.17	-73.83	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
76	Diana	United States	New York	VTM	44.15	-75.25	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
77	Tahawus Mine, MacIntyre stone pit	United States	Sanford Lake, New York	VTM	44.00	-74.08	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
78	Slick Rock Mill, Uravan	United States	Uravan Mineral Belt, Colorado	SSV	38.37	-108.74	13.99	1.29	0.18	Production	Fischer (1968); Shawe (2011)
79	Iron Mountain	United States	Wyoming	VTM	41.38	-104.83	n.d.	n.d.	n.d.	n.d.	Fischer (1975b)
80	Broken Hill	Zambia	Kabwe, Central Province	Vana-date	-14.42	28.55	n.d.	n.d.	n.d.	n.d.	Fischer (1975a)
81	Bulawayo	Zimbabwe	Bulawayo	Vana-date	-20.17	28.58	n.d.	n.d.	n.d.	n.d.	Fischer (1975a)

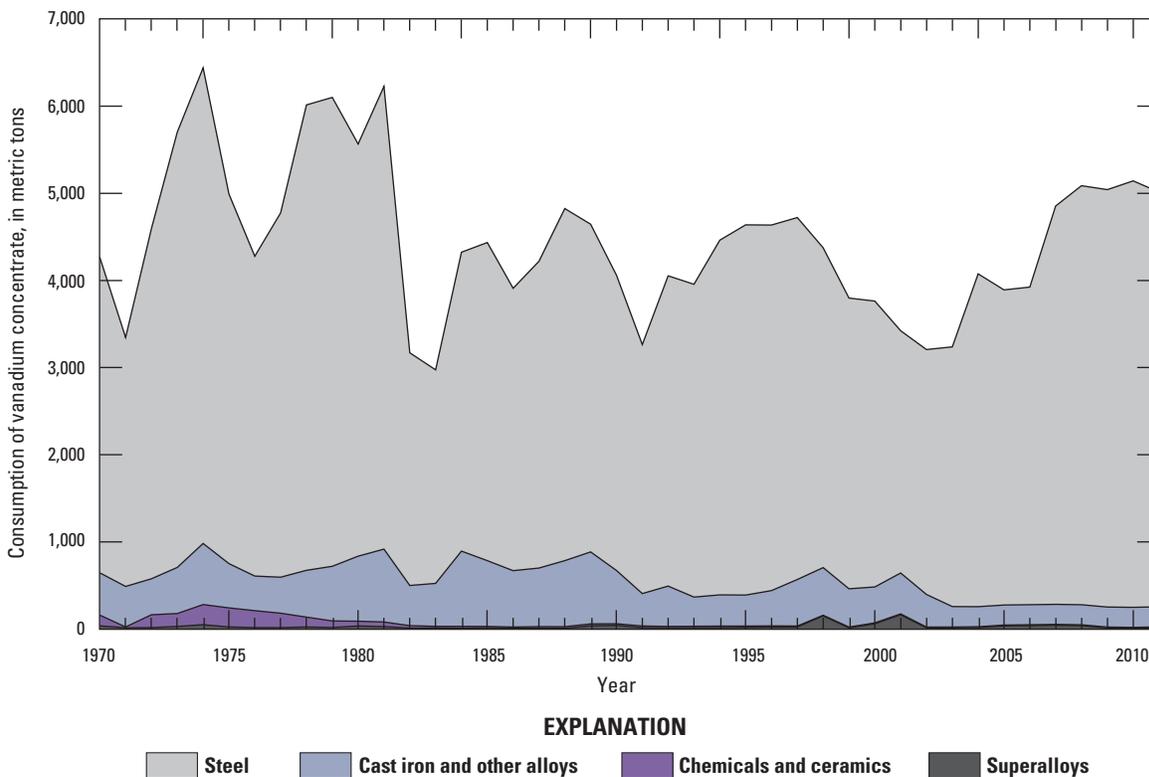
<sup>1</sup>Also includes some production and reserves.



**Figure U2.** Pie chart showing percentage of world vanadium production in 2012, by country. Compiled using data from Polyak (2013, table 7).

### Demand and Availability of Supply

World vanadium resources in 2012 were estimated to total more than 63 million metric tons of vanadium. Reserves were estimated to be 14 million metric tons of vanadium. Because vanadium is usually recovered as a byproduct or coproduct, the identified world resources of this mineral commodity are understated and therefore not fully indicative of available supply. Although domestic resources and secondary recovery are adequate to supply a large portion of domestic needs, a substantial part of U.S. demand is currently met by foreign material (Polyak, 2013). Future demand is expected to increase primarily because such countries as China and Japan are increasing the amount of vanadium used in steelmaking to match the quality of steel produced from other countries, as well as in anticipation of the probable increase in alternative renewable sources of energy that require the use of VRBs (Roskill Information Services, Ltd., 2013).



**Figure U3.** Graph showing major end uses of vanadium in the United States from 1970 to 2011. The layers of the graph are placed one above the other, forming a cumulative total. Compiled using data from U.S. Bureau of Mines (1972–76, 1992–96) and U.S. Geological Survey (1997–2013, 2014).

## Geology

### Geochemistry

Vanadium is a trace element that is widely distributed in nature. The average abundance of vanadium in the upper continental crust is approximately 60 parts per million (ppm) (Taylor and McLennan, 1995). Vanadium is produced from the combustion of fossil fuels, the mining of ores, and high-temperature industrial activities, including steel refining and the processing of phosphate ores.

The natural oxidation states of vanadium are +2, +3, +4, and +5. The trivalent ion  $V^{3+}$  has an octahedral radius (0.061 nanometers [nm]) that is almost identical with that of ferric iron ( $Fe^{3+}$ , 0.063 nm). As a consequence, vanadium substitutes in iron-rich minerals, such as amphibole, biotite, magnetite, and pyroxene, and for aluminum ( $Al^{3+}$ , 0.054 nm) in iron and ferromagnesian minerals (Fischer, 1973). Vanadium is present in large amounts in mafic igneous rocks (about 250 ppm), is less abundant in ultramafic and intermediate-composition rocks (about 50 ppm), and is present in only small amounts in felsic rocks (about 20 ppm). Vanadium is concentrated in magmatic magnetite deposits, especially those that are titaniferous; the vanadium concentrations in these deposits commonly range from 1,000 to 5,000 ppm.

Vanadium is also closely associated with organic-rich sediments. The average concentrations in shale are about 130 to 205 ppm, but some carbonaceous shales may have up to 5,000 ppm vanadium (for example, shales in eastern Kentucky; Robl and others, 1983). The addition of vanadium to sediments rich in organic carbon is owing to reduction, adsorption, and complexation. Dissolved vanadate species ( $5^+$ ) in oxic seawater are reduced to vanadyl ions ( $4^+$ ) by organic compounds or hydrogen sulfide ( $H_2S$ ) and are readily adsorbed to particle surfaces as they settle during sedimentation. Vanadium $^{3+}$  may also substitute for aluminum in the octahedral sites of clays (Breit and Wanty, 1991).

Because most vanadium in primary minerals is in the weakly soluble +3 valence state, very little vanadium is transported by hydrothermal fluids; therefore, most hydrothermal ore deposits contain low concentrations (10 to 100 ppm) of vanadium. Some hydrothermal deposits related to alkaline igneous rocks contain high concentrations of vanadium, however. Altered titanium-rich syenite intrusions at Potash Sulphur Springs in Garland County, Arkansas, contain high concentrations of vanadium (McCormick, 1978) as do some gold-quartz veins associated with alkaline igneous rocks, especially those with gold-telluride minerals (for example, Spry and Scherbarth, 2006).

During weathering in humid climates, much of the vanadium contained in ferromagnesian minerals apparently partitions into newly formed clay minerals, but it remains in the +3 valence state or oxidizes to the +4 valence state, both of which are relatively insoluble. If erosion is insignificant but chemical leaching is intense, the residual material may be enriched in vanadium, as are some bauxites and laterites

(Patterson, Kurtz, and others, 1986). During the weathering of igneous, residual, or sedimentary rocks, some vanadium oxidizes to the +5 valence state (vanadate), especially in the intensive oxidizing conditions that are characteristic of arid climates. In this oxidized valence state and under relatively alkaline conditions, vanadium is enriched in surface waters or groundwaters and remains in solution (Wright and Belitz, 2010). It can be precipitated from solution and locally concentrated in rocks by the following processes (Fischer, 1973, p. 682):

(a) Coprecipitation and adsorption with hydroxides of aluminum or ferric iron. This process forms or enriches the vanadium concentration in some bauxites and in residual or sedimentary iron ores;

(b) Reaction with cations of heavy metals, such as copper, lead, uranium, and zinc. This process forms epigenetic vanadate minerals in the oxidized zones of base-metal deposits; and

(c) Reduction in the presence of organic material or biologically generated  $H_2S$ . Interactions of vanadium-bearing solutions with wall rocks during fluid flow may produce epigenetic ore deposits, such as those occurring in sandstones of the Colorado Plateau province in the United States. On the other hand, if the vanadium is carried to the oceans by surface waters, it may concentrate syngenetically in carbonaceous phosphorites, marls, and shales. Furthermore, if the organic materials in these shales are converted to liquid hydrocarbons, the vanadium may be moved with the petroleum in vanadium-organic compounds and in fine inorganic particulates; some crude oils contain as much as several hundred parts per million vanadium. Vanadium accumulates in the ashes of these oils and also in the residues resulting from their natural or industrial distillation. These ashes and residues have been used as commercial sources of vanadium (Fischer, 1973, p. 682; Breit, 1992).

### Mineralogy

Vanadium occurs in nature in a wide variety of minerals (table U2). The following four principal types of mineral deposits are recognized: vanadiferous titanomagnetite (VTM) deposits, sandstone-hosted vanadium (SSV) deposits, shale-hosted deposits, and vanadate deposits. Magnetite ( $Fe_3O_4$ ) and ilmenite ( $FeTiO_3$ ) are the principal vanadium-bearing ore minerals in VTM deposits (fig. U4A), but hematite ( $Fe_2O_3$ ), perovskite ( $CaTiO_3$ ), and rutile ( $TiO_2$ ) are present in some deposits (Fischer, 1975b). These minerals occur in medium- to fine-grained intergrowths and in exsolution and solid-solution relations; ulvospinel and titanomagnetite are two mineral names commonly applied to some of these exsolution and solid-solution forms. Small blebs and exsolution blades of coulsonite ( $FeV_2O_4$ ) in magnetite have been recognized in a few VTM deposits (Balsley, 1943).

Ore minerals below the zone of oxidation in SSV deposits are low-valence oxides and silicates of uranium and vanadium. Coffinite, montroseite, paramontroseite, uraninite, and

**Table U2.** Selected vanadium-bearing minerals, by deposit type.

Mineral name	Chemical formula or description	Mineral name	Chemical formula or description
Vanadiferous titanomagnetite (VTM) deposits		Vanadate deposits	
Coulsonite	$(\text{Fe}, \text{V})_3\text{O}_4$	Brachebuschite	$\text{Pb}_2(\text{Mn}, \text{Fe})(\text{VO}_4)_2 \cdot \text{H}_2\text{O}$
Hematite	$\text{Fe}_2\text{O}_3$	Calciovolborthite	$\text{CaCuVO}_4(\text{OH})$
Ilmenite <sup>1</sup>	$\text{FeTiO}_3$	Chervetite	$\text{Pb}_2\text{V}_2\text{O}_7$
Magnetite <sup>1</sup>	$\text{Fe}_3\text{O}_4$	Curienite	$\text{Pb}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 5\text{H}_2\text{O}$
Perovskite	$\text{CaTiO}_3$	Descloizite <sup>1</sup>	$\text{PbZn}(\text{VO}_4)(\text{OH})$
Rutile	$\text{TiO}_2$	Francevillite	$(\text{Ba}, \text{Pb})(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 5\text{H}_2\text{O}$
Sandstone-hosted vanadium (SSV) deposits		Heyite	$\text{Pb}_3\text{Fe}_2(\text{VO}_4)_2\text{O}_4$
Carnotite	$\text{K}_2(\text{UO}_2)_2(\text{VO}_8) \cdot 1-3\text{H}_2\text{O}$	Mottramite <sup>1</sup>	$\text{PbCu}(\text{VO}_4)(\text{OH})$
Coffinite	$\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$	Mounanaite	$\text{PbFe}_2(\text{VO}_4)_2(\text{OH})$
Corvusite	$(\text{Na}, \text{Ca}, \text{K})\text{V}_8\text{O}_2 \cdot 4\text{H}_2\text{O}$	Pyrobelonite	$\text{PbMnVO}_4(\text{OH})$
Doloresite	$\text{H}_8\text{V}_6\text{O}_{16}$	Sengierite	$\text{Cu}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 8 \text{ or } 10\text{H}_2\text{O}$
Hewettite	$\text{CaV}_6^{5+}\text{O}_{16} \cdot 9\text{H}_2\text{O}$	Turanite	$\text{Cu}_5(\text{VO}_4)_2(\text{OH})_4$
Montroseite	$(\text{V}^{3+}\text{Fe}^{3+}\text{V}^{4+})\text{O}(\text{OH})$	Vanadinite <sup>1</sup>	$\text{Pb}_5(\text{VO}_4)_3\text{Cl}$
Paramontroseite	$\text{VO}_2$	Volborthite	$\text{Cu}_3(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$
Pascoite	$\text{Ca}_3(\text{V}_{10}\text{O}_{28}) \cdot 17\text{H}_2\text{O}$	Epithermal/porphyry/magmatic deposits	
Roscoelite	$\text{K}(\text{V}^{3+}, \text{Al}, \text{Mg})[(\text{Si}, \text{Al})_4\text{O}_{10}](\text{OH})_2$	Duttonite	$\text{V}^{4+}\text{O}(\text{OH})_2$
Tyuyamunite	$\text{Ca}(\text{UO}_2)_2\text{V}_2\text{O}_8 \cdot 5-8\text{H}_2\text{O}$	Fervanite	$\text{Fe}_4^{3+}(\text{VO}_4)_4 \cdot 5\text{H}_2\text{O}$
Uraninite	$\text{UO}_2$ (with Pb, Th, V, Zr)	Hewettite	$\text{CaV}_6^{5+}\text{O}_{16} \cdot 9\text{H}_2\text{O}$
Vanadium clays	Vanadium-bearing hydrous mica	Karelianite <sup>4</sup>	$\text{V}_2\text{O}_3$
Vanadian chlorite	Vanadium-bearing chlorite	Metatyuyamunite <sup>6</sup>	$\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 5-7\text{H}_2\text{O}$
Volborthite	$\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$	Montroseite	$(\text{V}^{3+}\text{Fe}^{3+}\text{V}^{4+})\text{O}(\text{OH})$
Shale-hosted vanadium deposits		Nolanite <sup>4</sup>	$(\text{V}, \text{Fe}, \text{Al})_{10}\text{O}_{14}(\text{OH})_2$
Illite-smectite <sup>3</sup>	$\text{K}_{0.8}(\text{Al}_{2.8}\text{Mg}_{0.5}\text{Fe}_{0.4}\text{V}_{0.3})(\text{Si}_{7.2}\text{Al}_{0.8})\text{O}_{20}(\text{OH})_4$	Roscoelite	$\text{K}(\text{V}^{3+}, \text{Al}, \text{Mg})[(\text{Si}, \text{Al})_4\text{O}_{10}](\text{OH})_2$
Metaheawettite	$\text{CaV}_6\text{O}_{16} \cdot \text{H}_2\text{O}$	Rutile, brookite	$\text{TiO}_2$
Quisqueite <sup>2</sup>	Vanadium-bearing organic matter	Schreyerite <sup>4</sup>	$\text{VSiO}_3(\text{OH})$
Patronite <sup>2</sup>	$\text{V}^{4+}(\text{S}_2^{2-})_2$	Vanadium andradite <sup>5</sup>	$\text{Ca}^3(\text{Fe}^{3+}, \text{V}^{3+})_2(\text{SiO}_4)_3$
		Vanadium muscovite <sup>4</sup>	Vanadium-bearing muscovite
		Vanadium silicates <sup>4</sup>	$\text{Si}_3\text{O}_9\text{V}_2$
		Vanadium- and titanium-bearing mixed layer clay <sup>7</sup>	$(\text{Ca}_{0.08}\text{K}_{0.02}\text{Na}_{0.03})_{0.13}(\text{Al}_{0.11}\text{V}_{0.90}\text{Ti}_{0.19}\text{Fe}_{0.64}\text{Mg}_{0.14})_{1.98}(\text{Si}_{3.79}\text{Al}_{0.21})_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$

<sup>1</sup> Most common.

<sup>2</sup> Mina Ragra, Peru (Fischer, 1973).

<sup>3</sup> Mecca Quarry Shale, Illinois and Indiana (Peacor and others, 2000).

<sup>4</sup> Tuvatu deposit, Fiji (Spry and Scherbarth, 2006).

<sup>5</sup> Potash Sulphur Springs or Wilson Springs, Arkansas (Howard and Owens, 1995).

<sup>6</sup> Weeks and others, 1959.

<sup>7</sup> Potash Sulphur Springs or Wilson Springs, Arkansas (McCormick, 1978).



**Figure U4.** Photographs showing four examples of vanadium. *A*, Magnetite layer (dark) from the Bushveld Complex, South Africa. It is these layers that commonly host vanadium. *B*, Natural vanadinite, which is a main source of vanadium from vanadate deposits. *C*, Vanadium metal crystals made by electrolysis (the largest crystal is 2 centimeters in length). *D*, Common hand wrench made with vanadium alloy steel. Photograph *A* courtesy of Kevin Walsh/CC BY 2.0 (<https://creativecommons.org/licenses/by/2.0/>). Photographs *B* and *C* courtesy of Juergen Kummer, Jumk.de Web Projects/CC BY 3.0 (<http://images-of-elements.com/vanadium.php>). Photograph *D* courtesy of MrX/CC-BY-SA-3.0 ([https://commons.wikimedia.org/wiki/File:Chrome\\_Vanadium\\_Adjustable\\_Wrench.jpg](https://commons.wikimedia.org/wiki/File:Chrome_Vanadium_Adjustable_Wrench.jpg)).

vanadium-rich clay or mica (roscoelite), vanadian chlorite, and vanadium-rich clay minerals are the most common (table U2). Chalcopyrite, clausthalite, ferroselite, galena, naumannite, pyrite, sphalerite, and other sulfides and selenides are common trace minerals (Shawe, 2011). Copper sulfides are widespread in sparse amounts but are abundant enough in a few deposits to constitute ore minerals (Fischer, 1968). Partially oxidized orebodies (for example, those immediately above the water table) contain minerals similar to those of deposits below the zone of oxidation, but with the addition of corvusite-group minerals and hewettite (Shawe, 2011). Oxidized deposits contain carnotite and tyuyamunite, together with vanadium clays and chlorite. The most common authigenic gangue minerals in SSV deposits are barite, carbonates (mostly calcite), and quartz (Breit and Goldhaber, 1996). Ore minerals are typically disseminated in the sandstone or form radiating

acicular aggregates that fill open pore spaces (Wanty and others, 1990). The ore minerals are typically concentrated near carbonaceous material (Fischer, 1968; Shawe, 2011).

Vanadate deposits contain a wide variety of vanadium-bearing minerals (table U2). Vanadate minerals are formally described as containing an oxoanion of vanadium generally in its highest oxidation state of +5. Most vanadate minerals are compounds of copper, iron, or lead because these deposits form within the oxidized zones of base-metal deposits in areas of arid climate and deep oxidation (Fischer, 1975a). Descloizite, mottramite, and vanadinite (fig. U4B) are the most common vanadium minerals, although numerous others are known (table U2). Wulfenite ( $\text{PbMoO}_4$ ), which is a molybdate of lead, is also common in vanadate deposits (Fischer, 1975a). Where paragenetic relations are reported, the vanadium-bearing minerals are late in the sequence. For example, the association

of vanadinite and descloizite is paragenetically late in the Berg Aukas and Abenab deposits in the Otavi Mountainland, Namibia (Boni and others, 2007). Fischer (1975a) suggests that vanadate minerals typically coat and partly replace supergene base-metal minerals in deposits in Arizona, but in most cases, the vanadates overlap or precede the last stage of supergene mineral formation (Boni and others, 2007). Once formed, vanadate minerals are stable in the environment of the oxidized zone; these minerals persist from the surface to the bottom of the oxidized zone, and leaching and corrosion of them are rarely reported (Fischer, 1975a). In the Kabwe district (formerly known as Broken Hill), Zambia, the vanadate minerals are persistent to depths of 350 meters (m) below the surface, which defines the lowest depth of oxidation.

Some hydrothermal deposits contain vanadium-bearing minerals, particularly deposits genetically and (or) spatially associated with alkaline igneous rocks. In epithermal gold deposits, roscoelite is the most common mineral, but vanadium-bearing rutile or brookite, karelianite, nolanite, shreyerite, and vanadium-rich muscovite and silicate minerals have also been identified (Spry and Scherbarth, 2006).

## Deposit Types

Vanadium is present in economic concentrations in four main types of mineral deposits and as a minor constituent in several other types. Fossil fuels are another important source of vanadium.

### Vanadiferous Titanomagnetite Deposits

Vanadiferous titanomagnetite (VTM) deposits (Fischer, 1975b) are found throughout the world and are the principal source of vanadium (fig. U1). The most economically significant VTM deposits or regions, both in the past and currently, include the Bushveld Complex in South Africa (Reynolds, 1985); the Panzhihua layered intrusion in Sichuan Province, China (Zhou and others, 2005); the Kachkanar massif in the Ural Mountains in Russia; the Windimurra Complex in Western Australia (Ivanic and others, 2010); and the Bell River Complex (Matagami deposit) and the Lac Doré Complex in Quebec, Canada (fig. U1; Taner and others, 1998).

The VTM deposits consist of magmatic accumulations of magnetite and ilmenite, defined arbitrarily as having grades of more than about 1 percent rutile (Fischer, 1975b). They commonly contain 0.2 to 1 percent  $V_2O_5$ , but some zones (for example, the Bushveld Complex) contain greater than 1.5 percent  $V_2O_5$  (Reynolds, 1985). Most exposed VTM deposits are Archean or Proterozoic in age, having formed in intraplate continental tectonic settings; a few deposits (for example, the Panzhihua region in Sichuan Province, China) are younger (table U1; fig. U1). Most deposits are associated with large igneous province (LIP) magmatism; some layered intrusive complexes are linked to mantle plumes and hotspot tracks (Hatton, 1995; Ernst and others, 2005).

VTM deposits are hosted mainly within mafic and ultramafic igneous rocks, most commonly anorthosite and gabbro. Lithologies within the igneous complexes that contain the vanadium-rich ores vary considerably, however. For example, in the Bushveld Complex, lithologies range from dunite and pyroxenite to anorthosite and pure oxide layers (Eales and Cawthorn, 1996). Some vanadiferous deposits are hosted in zoned mafic to ultramafic complexes with high levels of chromium and platinum-group elements (PGEs); these complexes are sometimes referred to as Alaska-type PGE deposits; and examples include the Union Bay deposit in Alaska (United States), and the Kachkanar complex in Sverdlovsk Oblast, Russia. A few deposits are associated with alkalic igneous rocks (for example, syenodiorite is genetically related to layered gabbro in the Panzhihua district of Sichuan Province, China [Shellnut and Jahn, 2010] and in the Ganjang deposit in Assam, northeastern India [Saha and others, 2010]). The mafic to ultramafic igneous host rocks are typically of deep-seated origin, and they occur in stratiform tabular bodies, such as sills and laccoliths that are thick and laterally extensive. For example, the Mesoarchean gabbroic Windimurra Complex in the Yilgarn craton (Western Australia, Australia) covers an area of about 2,500 square kilometers ( $km^2$ ) and contains layers of gabbroic and ultramafic rocks with cumulative thicknesses of 13 kilometers (km) (Ivanic and others, 2010). The Paleoproterozoic Bushveld Complex (dated at 2.06 giga-annum [Ga]) in the Transvaal basin in South Africa contains layers with cumulative thicknesses (about 9 km) that are comparable to those of the Windimurra Complex, and it has an areal extent of about 65,000  $km^2$  (Eales and Cawthorn, 1996).

In contrast to laterally extensive and thick tabular bodies, some titaniferous magnetite deposits are hosted in relatively complex intrusive or lens-shaped bodies (Fischer, 1975b). Such deposits are variable in size and shape. In the Panzhihua region of China, the maximum size of the lens-shaped ore bodies is 160 m long and 30 m wide (Zhou and others, 2005). Vanadium-bearing titanomagnetite previously mined in the Sanford Lake District of New York and the Taberg deposit in Jönköping County, Sweden, was contained in small (550 m by 180 m) bodies of gabbro and anorthosite (Balsley, 1943; Gross, 1968; Fischer, 1973, 1975b).

The textures and mineralogy of VTM ores are remarkably similar among the largest known deposits, including the Panzhihua deposit and the Bushveld and Windimurra deposits (Fischer, 1975b; Reynolds, 1985; Rohrmann, 1985; Zhou and others, 2005; Ivanic and others, 2010). Ores typically form discrete layers that are concordant with the igneous layering, which varies between 0.1 and 10 m in thickness, although some oxide layers in deposits in the Panzhihua region of southwestern China attain thicknesses of 60 m (Zhou and others, 2005). Similar to the silicate rocks that host them, the oxide layers are laterally extensive, and they can be traced for hundreds of kilometers in the case of the Bushveld Complex (Rohrmann, 1985; Reynolds, 1985). Most oxide layers have sharp lower boundaries that host silicate rocks and have

gradational tops; some oxide layers contain thin intercalations of gabbro (Eales and Cawthorn, 1996; Zhou and others, 2005). Most of the vanadium in titaniferous magnetite deposits is concentrated as a solid solution in magnetite-ulvospinel, where  $V^{3+}$  has replaced  $Fe^{3+}$  (Fischer, 1975b); the vanadium-rich spinel mineral coulsonite ( $FeV_2O_4$ ) was reported as small blebs and exsolution blades in magnetite in a few deposits (Balsley, 1943; Fischer, 1975b). Ilmenite, hematite, rutile, and perovskite commonly accompany magnetite (Fischer, 1975b). Where exposed to weathering, the magnetite may oxidize to vanadomagemite ( $(FeTi)_2O_3$ ) and small concentrations of hematite without any change in the texture of the ore (Rohrman, 1985).

Ores may be either massive or disseminated. Massive ores typically consist of closely packed, nearly equant grains of more than 80 percent titanomagnetite and contain variable amounts of clinopyroxene, olivine, and plagioclase. If silicate minerals are present, they are completely surrounded by oxides (Zhou and others, 2005). Disseminated ores are generally coarse grained and are composed of about 50 percent titanomagnetite, about 20 percent clinopyroxene, about 20 percent plagioclase, about 10 percent ilmenite, and small amounts of olivine (Rohrman, 1985; Eales and Cawthorn, 1996; Zhou and others, 2005).

The mechanisms by which millions of tons of vanadium become concentrated in massive iron-titanium oxide deposits remain poorly understood, but most researchers agree that partial melting of mantle rocks and extensive fractionation of the derivative magma are critical early-stage processes. Large-scale, in situ crystallization of plagioclase and other anhydrous phases (olivine, pyroxene) in the basal parts of magma chambers results in an increase in total iron and water contents of the residual magma with eventual formation of immiscible oxide melts (Reynolds, 1985; Eales and Cawthorn, 1996; Ivanic and others, 2010; Shellnut and Jahn, 2010). Such oxide ore melts are denser than silicate melts and therefore settle to the bottom of the magma chamber, where the oxide melts accumulate (Eales and Cawthorn, 1996; Zhou and others, 2005). Many layered intrusions show evidence of multiple magma injections (Eales and Cawthorn, 1996), suggesting that magma mixing may have played a role in the development of some titaniferous magnetite deposits (Von Gruenwaldt, 1993). Other factors involved in forming immiscible oxide melts from silicate magmas are abrupt changes in oxygen fugacity, and (or) an introduction of fluids (Reynolds, 1985; Zhou and others, 2005). The presence of minor disseminated sulfides and apatite (for example, the Panzihua deposits) suggests that sulfur and phosphorus may have acted as fluxing agents that promoted the concentration of immiscible liquids that led to formation of the Panzihua deposits (Zhou and others, 2005).

*Associated metals.*—The igneous rocks that host significant vanadium resources are commonly temporally and spatially associated with magmatic chromium, copper, nickel, and PGE deposits (Cawthorn and others, 2002; Naldrett, 2010; Zientek, 2012). At least minor amounts of copper-nickel-PGE

enrichment occurs in igneous complexes adjacent to the vanadiferous zones in the Windimurra region of Australia (Ivanic and others, 2010), the Panzihua region of China (Zhou and others, 2005), and Kachkanar in the Urals region of Russia (Augé and others, 2005). The largest resources of PGEs and chromium in the world are contained within the Bushveld Complex of South Africa in layers that lie below the vanadiferous zones (Eales and Cawthorn, 1996; Naldrett and others, 2009). Additionally, high contents of scandium (up to 500 grams per metric ton of scandium oxide [ $Sc_2O_3$ ]) occur in some of the VTM deposits in Russia (Bykhovskiy and Tiginov, 2008).

## Sandstone-Hosted Vanadium Deposits

Sandstone-hosted uranium deposits have been identified on all continents, and many are known to have enrichments of vanadium (Dahlkamp, 2010). These deposits of vanadium- and uranium-bearing sandstone (known as sandstone-hosted vanadium [SSV] deposits) have average resource and ore grades that range from 0.1 to 1 weight percent vanadium (George Breit, U.S. Geological Survey [retired], written commun., 2013). On a global scale, the United States has been and is currently the main producer of vanadium from SSV deposits, particularly from those on the Colorado Plateau. Additionally, these SSV deposits are the chief domestic source of vanadium in the United States (Fischer, 1968, 1973; Polyak, 2012, 2013). Most deposits are located in western Colorado and eastern Utah, although some are also located in northern Arizona and New Mexico (fig. U1). Vanadium enrichments in sandstones elsewhere in the world include the Bigrlyi deposit in Northern Territory, Australia, which has a grade of 0.13 weight percent vanadium (McKay and Mieztis, 2001); deposits in the Tonco-Amblyo district in Argentina, which have grades of 0.1 to 0.3 weight percent vanadium (Dahlkamp, 2010); and a deposit in the Karamurun district of Almaty Oblasy, Kazakhstan (Dahlkamp, 2009).

The Colorado Plateau province covers an area of 337,000 km<sup>2</sup> and was developed through a series of geologic and tectonic events. Important processes in this region that promoted the formation of SSV deposits include deposition of evaporitic-sapropelic strata from which brine fluids were derived; deposition of fluvial, fine-grained, locally carbonaceous sandstone that served as host rocks for the deposits; and magma generation and emplacement of laccoliths during the Tertiary that may have heated and driven brine fluids upwards along favorable structures (Shawe, 2011).

The SSV deposits occur in fluvial sandstone lenses of the Chinle Formation (Upper Triassic) and the Jurassic Morrison and aeolian Entrada Formations. The most economically significant vanadium deposits occur within the Salt Wash Member, which is the basal unit of the Morrison Formation (Northrop and others, 1990; McLemore and Chenoweth, 1997; Shawe, 2011). The Salt Wash Member is 30 to 150 m thick and contains laterally continuous fluvial sandstone and interbedded mudstone. This member was deposited by a west-to-east aggrading alluvial system (Shawe, 2011).

The SSV deposits form subhorizontal lenses or tabular bodies that are variable in thickness but are typically less than a few meters thick (Northrop and others, 1990; McLemore and Chenoweth, 1997) and up to 150 m long (Shawe, 2011). Some elongate mineralized zones are parallel to paleostream channels in the fluvial sandstone (McLemore and Chenoweth, 1997; Shawe, 2011). Deposits are typically concordant with bedding, although discordant lenses of uranium-vanadium minerals cut bedding planes locally. Most commonly, the orebodies are entirely within sandstone, although some occur at the interface between sandstone and less permeable shale or siltstone (Northrop and others, 1990; McLemore and Chenoweth, 1997). Tabular bodies display sharp to gradational transitions into unmineralized sandstone, and generally terminate abruptly against mudstone or claystone seams (Shawe, 2011). The SSV deposits are typically found in areas with local accumulations of detrital carbonaceous material. Pyrite is common within all forms of carbonized plant material (Shawe, 2011). Northrop and others (1990) reported that pyrite from mineralized intervals has distinctly lower sulfur isotope compositions (−4.8 to −2 per mil) than pyrite in unmineralized rocks (which average 12.1 per mil). Some tabular deposits have been reworked over time by groundwater, resulting in the formation of redistributed orebodies (Shawe, 2011).

Vanadium concentrations in SSV ores (expressed as  $V_2O_5$ ) are commonly 1 percent or greater, and some deposits in southwestern Colorado have grades of more than 2.5 percent (Shawe, 2011). Vanadium-to-uranium weight ratios in deposits within the Morrison Formation vary from 2:1 to 6:1 among most areas of production, and therefore, are considered vanadium deposits with accessory uranium (Northrop and others, 1990; Shawe, 2011). Deposits with high vanadium-to-uranium weight ratios are located in southeastern Utah and southwestern Colorado; those in east-central Utah and west-central Colorado are characterized by lower vanadium-to-uranium weight ratios (George Breit, U.S. Geological Survey [retired], written commun., 2013). Many deposits have multiple ore zones, consisting of two (or more) closely spaced intervals enriched in vanadium and uranium, separated by an interval (or intervals) containing no uranium but enriched in vanadium (Northrop and others, 1990). The uranium-vanadium minerals form the matrix of the mineralized sandstones and locally replace detrital quartz and feldspar grains (Kovschak and Nylund, 1981; McLemore and Chenoweth, 1997). Vanadium, as +2, +3, +4, or +5, occurs as oxide phases or is combined with other elements, forming more than 40 different minerals in SSV ores (Weeks and others, 1959). Primary SSV ores are characterized by a consistent black-mineral suite composed of coffinite, montroseite, uraninite, and vanadium aluminosilicates (that is, low-valence  $V^{3+}$  minerals). These primary minerals are modified by progressive secondary oxidation above the water table to form an oxidized mineral assemblage dominated by carnotite, corvusite, and tyuyamunite (Weeks and others, 1959). Tabular vanadium-uranium deposits in the Salt Wash Member are unusual in that one of the major ore phases is typically roscoelite (a vanadium-bearing mica)

accompanied by chlorite, mixed layer “chloritemontmorillonite” (chlorite-smectite), mixed-layer illite-montmorillonite, and “vanadium-hydromicas” (vanadium-bearing illite) (Northrop and others, 1990; Wanty and others, 1990). Gangue minerals that have been introduced or redistributed during formation of the deposits are anatase, barite, carbonates (mostly calcite and dolomite), and quartz (mostly calcite and dolomite) containing appreciable amounts of iron and (or) magnesium (Breit and Goldhaber, 1996).

Most proposed models for the formation of SSV deposits suggest that deposition occurred at an interface between two fluids of different chemical compositions and (or) states of oxidation-reduction (Fischer, 1968; Northrop and others, 1990; Shawe, 2011). Deposition involving two fluids was proposed many years ago during the early stages of exploration and production, and subsequent models, such as the brine-interface model, have refined or incorporated portions of these early theories. Although details differ, most models suggest that these deposits form by multistage processes: (1) shallow burial and diagenesis (<400 m), and reduction of dissolved uranium and vanadium by organic matter and bacteriogenic hydrogen sulfide that create local ore-grade accumulations; (2) progressive burial of the sandstone, creating changes in pore-water composition, pressure, and temperature and recrystallization of ore phases; and (3) migration of brines that move upward along faults and outward into permeable sandstone, mix with dilute meteoric water, and result in alteration of existing uranium and vanadium deposits (Breit and Goldhaber, 1996). The source of the vanadium is not well constrained, but is likely from the dissolution of iron-titanium-oxide minerals (ilmenite and magnetite) in volcanic detritus and sandstones within the Morrison Formation, or from unspecified source rocks that could be either younger or older than the host formation (Thamm and others, 1981; Northrop and others, 1990). Critical to the development of brines and the location of the SSV deposits in the Salt Wash Member was the deposition of evaporitic-sapropelic sedimentary units of Middle and Late Pennsylvanian age beneath the Morrison Formation (Shawe, 2011). Determinations of the age of formation of the deposits varies greatly; some estimates are that primary ores formed close to the time of deposition of the host rock (about 130 mega-annum [Ma]), whereas others suggest a much later time (about 30 Ma or latest Oligocene) (Shawe, 2011).

*Associated metals.*—Uranium occurs with vanadium in all SSV deposits, although the uranium-to-vanadium ratio varies greatly. Most deposits in the southwestern part of the United States (New Mexico and Arizona) have high uranium-to-vanadium ratios that decrease to the north (because of the increasing contents of vanadium). After initial mining for uranium, these deposits were sought as a source of radium. In the 1930s and 1940s, the deposits were of interest mainly for vanadium. Most mines were closed for nearly a decade, but mining resumed again in 1949 (until about 1983) for major production of uranium, with vanadium as a byproduct (Shawe, 2011). Copper accompanies uranium or vanadium in many of the deposits (Shawe, 2011).

## Shale-Hosted Vanadium Deposits

Vanadium-rich metalliferous black shales occur primarily in late Proterozoic and Phanerozoic marine successions. The term shale is used here broadly to include a range of carbonaceous rocks that include marls and mudstones. These fine-grained sedimentary rocks were deposited in epeiric (inland) seas and on continental margins. They typically contain high concentrations of organic matter (greater than 5 percent) and reduced sulfur (greater than 1 percent; mainly as pyrite), as well as a suite of metals, such as copper, molybdenum, nickel, PGEs, silver, uranium, vanadium, and zinc (Desborough and others, 1979; Coveney and Martin, 1983; Coveney and others, 1992; Hatch and Leventhal, 1992; Piper, 1999). Concentrations regularly exceed 0.18 percent  $V_2O_5$  and can be as high as 1.7 percent  $V_2O_5$ . Vanadiferous black shales are commonly found with phosphorite deposits and marine oil shales and, in North America, are marine equivalents of coal-bearing cyclothems. Well-characterized vanadiferous black shales include the Woodruff Formation in Nevada (Desborough and others, 1979), the Meade Peak Phosphatic Shale Member of the Phosphoria Formation in Idaho and Wyoming (McKelvey and others, 1986; Love and others, 2003), the Mecca Quarry Shale Member of Illinois and Indiana (Coveney and others, 1987), the Doushantuo Formation in Hubei Province in southern China (Fan and others, 1992), and portions of the Toolebuc Formation in Queensland, Australia (Lewis and others, 2010). Although these black shales have long been recognized as potential sources of vanadium, they are not currently exploited. Project development is underway at the Gibellini vanadium prospect in Nevada (Woodruff Formation), and if production begins, it will be the first primary shale-hosted producer of vanadium in the United States. The Julia Creek deposit (Toolebuc Formation) is also in the planning stages. The Green Giant deposit in southern Madagascar (Energizer Resources, Inc., 2013) consists of metamorphosed vanadiferous shale that extends for at least 21 km along strike and is reported to contain about 350,000 metric tons of  $V_2O_5$  (table U1; fig. U1).

The ultimate source of vanadium in metalliferous black shales is dissolved vanadium in seawater (Breit and Wanty, 1991; Piper, 1994). Whereas the specific mechanisms of enrichment are disputed, all require the reduction of dissolved  $V^{5+}$  (Breit and Wanty, 1991), which is the predominant redox state in the oceans (Collier, 1984). Vanadium is used by various phytoplankton species (Robson and others, 1986; Moore and others, 1996), and sedimentation of phytoplankton debris likely acts as a minor source of vanadium in black shales (Piper, 1994). In oxygen-deficient bottom waters and pore waters, dissolved vanadium is reduced to particle-reactive  $V^{4+}$  and is incorporated into the sedimentary fraction (Wehrli and Stumm, 1989). Further reduction to  $V^{3+}$  requires the presence of dissolved aqueous sulfide ( $H_2S$ ) and promotes the incorporation of vanadium into sedimentary organic matter and authigenic clays (Lewan and Maynard, 1982; Lewan, 1984; Breit and Wanty, 1991).

Vanadium concentrations correlate with organic carbon in black shales, suggesting that vanadium is incorporated into organic matter upon burial (Breit and Wanty, 1991). Black shales that have been buried to depths sufficient to pass through the oil window typically produce petroleum that has high vanadium concentrations (Lewan and Maynard, 1982; Lewan, 1984). Conversely, vanadium can become incorporated into illite upon burial (Peacor and others, 2000). Because no modern analogues for vanadiferous black shales are known, the processes of vanadium enrichment are not well understood.

Vanadium-rich black shales of North America occur in Devonian to Permian marine successions. Black shale of the Upper Devonian Woodruff Formation (Nevada) contains 0.5 to 1.2 percent  $V_2O_5$  in unaltered rocks containing high concentrations of organic matter (greater than 10 percent) (Desborough and others, 1979, 1981). Oxidized zones of the Woodruff Formation contain 1.1 to 1.4 percent  $V_2O_5$ , reflecting secondary enrichment of vanadium during oxidation; the principal vanadium mineral in the oxidized shales is metahewettite ( $CaV_6O_{162} \cdot H_2O$ ).

Vanadiferous black shales are also found with Pennsylvanian cyclothems of North America (Coveney and Martin, 1983; Coveney and others, 1987; Coveney and Glascock, 1989; Hatch and Leventhal, 1992). These typically thin, metalliferous black shales occur throughout the midcontinent region. The Mecca Quarry Shale of Illinois and Indiana is conspicuously rich in various metals, including vanadium, with concentrations of up to 10,000 ppm (Coveney and Martin, 1983). These concentrations of vanadium exceed that of many VTM deposits; however, because the Mecca Quarry Shale is only a few tens of centimeters thick, it is not considered an economically viable vanadium resource (Coveney and Martin, 1983). Vanadium enrichments in the Mecca Quarry Shale could be related to the action of basinal brines, similar to processes that concentrate lead-zinc in Mississippi Valley-type (MVT) deposits (Coveney and Glascock, 1989), although direct evidence for this mineralizing process is lacking.

The Permian Phosphoria Formation in Idaho and Wyoming contains a world-class phosphate deposit that also includes vanadium-rich strata (McKelvey and others, 1986; Piper, 1999). The black-shale interval within the Meade Peak Phosphatic Shale Member contains an average of 1.2 percent  $V_2O_5$  (Piper, 1999) and, since the early 1940s, has been considered a potential economic source of vanadium (Love and others, 2003). In the 1960s, vanadium and uranium were produced from ferrophosphorus, a byproduct of an elemental phosphorus plant in southeastern Idaho (McKelvey and others, 1986). The occurrence of vanadium-rich shale with black-shale-hosted phosphorite deposits is common worldwide and suggests that steep and (or) fluctuating redox gradients existed within bottom waters and pore waters of the sedimentary basin (Piper, 1994).

The Julia Creek deposit in the Cretaceous Toolebuc Formation in Queensland, Australia, is an example of a vanadium-rich oil shale (Riley and Saxby, 1982; Patterson, Ramsden, and others, 1986). The oil shale was deposited in a shallow, epicontinental sea under reducing bottom water

conditions that promoted the enrichment of vanadium. Concentrations range from 0.1 to 1.0 percent  $V_2O_5$ . Other known vanadium-rich (greater than 0.17 percent  $V_2O_5$ ) oil shales include the Mississippian Heath Formation in Montana (Desborough and others, 1981; Derkey and others, 1985) and the Cretaceous La Luna Formation, which is a major petroleum source rock in Colombia and Venezuela (Alberdi-Genolet and Tocco, 1999).

*Associated metals.*—Vanadium-rich black shales commonly contain high contents of other metals, such as silver, barium, cobalt, copper, molybdenum, nickel, phosphorus, PGEs, uranium, and zinc. Well-characterized deposits include the following (metals associated with vanadium are in parentheses): Julia Creek (molybdenum) in Queensland, Australia (Lewis and others, 2010); Nick (nickel, PGEs, and zinc) in Yukon Territory, Canada (Hulbert and others, 1992); and Viken (molybdenum, nickel, phosphorus, and uranium) and Häggån (uranium, molybdenum, and nickel) in Sweden (Hallberg, 2012; Aura Energy, 2012). As reported by Coveney and others (1992), carbonaceous and phosphatic black shales of Cambrian age in China, which have reported values exceeding 4 percent  $V_2O_5$ , contain exceptionally high grades of nickel (from 2 to 4 percent) and molybdenum (>2 percent), and high concentrations of PGEs (20 to 80 parts per billion for platinum and palladium combined). Although vanadium has not been recovered from these strata, molybdenum and nickel have been mined on a small scale in China since about 1985. Metamorphosed sulfide- and phosphate-rich black shale in southwestern Catalonia, Spain, contains unusually high concentrations of vanadium and chromium (as silicates and oxides) together with palladium and platinum minerals (Canet and others, 2003). The Talvivaara deposit in Finland has elevated contents of vanadium (averages 600 ppm) (Loukola-Ruskeeniemi and Heino, 1996; Loukola-Ruskeeniemi and Lahtinen, 2013), and until recently, was mined for cobalt, copper, nickel, and zinc, all of which were extracted using a bioheapleach mineral processing method (Jowitt and Keays, 2011; Saari and Riekkola-Vanhanen, 2012; Loukola-Ruskeeniemi and Lahtinen, 2013). Vanadium is not currently recovered by this process, however.

## Vanadate Deposits

Vanadates of lead, zinc, and copper (vanadinite and minerals of the descloizite-mottramite series) form in the oxidized zones of base-metal deposits, especially in areas of arid climate and deep oxidation (Fischer, 1975a). The copper-lead-zinc vanadate ores in the Otavi Mountainland of northern Namibia were once considered to be among the largest vanadium deposits in the world, with an estimated resource of several million metric tons (Boni and others, 2007). Other areas with known vanadate deposits include Angola, South Africa, Zambia (Broken Hill district, now known as the Kabwe Mine), and Zimbabwe (fig. U1). Small deposits occur in Argentina, Mexico, and the United States (Arizona, California, Nevada, and New Mexico), but are unlikely ever to be economically significant resources.

Vanadates as a supply of vanadium essentially ceased in 1978 when the last producing vanadium mine at Berg Aukas (Otavi Mountainland) in Namibia was closed.

Vanadate minerals and wulfenite (a lead molybdate mineral) within these deposits form crusts on open cavities or are intergrown with residual clays (Fischer, 1975a). The vanadate ores in the Otavi Mountainland occur in collapse breccias and solution cavities related to karst development in Neoproterozoic carbonate rocks of the Otavi Supergroup and are spatially associated with primary sulfide orebodies within the carbonate strata (Boni and others, 2007). Mottramite and copper descloizite are particularly abundant around copper sulfide deposits (Tsumeb type), whereas descloizite occurs in areas surrounding primary sphalerite-willemite (a zinc silicate mineral) orebodies (Berg Aukas type).

Vanadate deposits are secondary accumulations that form during supergene processes. The vanadate ores of the Otavi Supergroup are interpreted to have formed during several stages, preferentially within a karstic network. The vanadate ores, formed by low-temperature fluids related to weathering, are clearly distinct in age from that of the associated primary sulfide concentrations (Boni and others, 2007). The source of vanadium in such deposits is most likely the surrounding country rocks, especially shales (Fischer, 1975a), or in the case of the Otavi Mountainland deposits, mafic rocks of the older Paleoproterozoic basement (Boni and others, 2007).

## Other Magmatic-Hydrothermal Vanadium Resources

Some magmatic-hydrothermal niobium-titanium deposits contain elevated concentrations of vanadium. Deposits at Potash Sulphur Springs (also called Wilson Springs) in Arkansas were the most important sources of vanadium in North America in the 1970s and 1980s, and nearly 4.3 million metric tons of 1.2 percent  $V_2O_5$  was produced. By 1990, all the mines at Wilson Springs were closed (Howard and Owens, 1995). The deposits are located within secondary enrichment zones and fenite that formed during and after intrusion of syenite and mafic alkalic igneous rocks (McCormick, 1978). The Wilson Springs deposits host a variety of vanadium-bearing minerals (Howard and Owens, 1995), including several minerals specific to these deposits (table U2). Adjacent carbonatite and alkaline igneous complexes at the Christy deposit within the Magnet Cove complex in Arkansas have high concentrations of vanadium together with titanium, niobium, and (or) rare-earth elements (Verplanck and Van Gosen, 2011; Flohr, 1994), and carbonatites and related rocks in Kenya are enriched in vanadium (Barber, 1974). Typical vanadium concentrations in such deposits are about 1 percent and are contained in magnetite and titanium minerals. At Magnet Cove and Wilson Springs, sodic pyroxene and magnetite contain up to 3.19 and 1.43 weight percent  $V_2O_3$ , respectively, and high concentrations occur in goethite (Flohr, 1994; Howard and Owens, 1995).

Several other deposit types contain vanadium concentrations that are noteworthy, but all are presently uneconomic and

are unlikely to be considered vanadium resources in the future. For example, heavy-mineral-concentrate samples from iron ores (Kiruna-type apatite-magnetite deposits) in Sweden and Chile have reported high concentrations (1,000 to 2,000 ppm) of vanadium (Nyström and Henriquez, 1994) and iron oxide mineral separates (magnetite and hematite) from such deposits contain up to 0.479 weight percent vanadium (Dupuis and Beaudoin, 2011). Vanadium concentrations of a few tenths of a percent are also common in titanium-bearing minerals, such as rutile and brookite (table U2) in some epithermal gold-silver and porphyry copper deposits (Fischer, 1973). For example, porphyry deposits in Australia contain rutile with vanadium contents of 0.2 and 1.3 weight percent (Scott, 2005), and rutile from the Pebble porphyry deposit in Alaska has vanadium concentrations that average 6.3 weight percent (Kelley and others, 2011). Even iron-rich minerals that do not contain titanium, such as magnetite and hematite, in some porphyry deposits contain elevated concentrations (up to 0.619 weight percent) of vanadium (Dupuis and Beaudoin, 2011).

In some gold-quartz veins, especially those containing gold-telluride minerals, roscoelite and other vanadium-bearing minerals are common as fine-grained intergrowths with quartz and other gangue minerals (Richards, 1995). In the Tuvatu gold-telluride deposit in Viti Levu, Fiji, vanadium occurs in roscoelite together with karelianite, vanadian muscovite, titanium-free nolanite, vanadian rutile, schreyerite, and an unnamed vanadium silicate mineral (Spry and Scherbarth, 2006). Rutile in the Tuvatu deposit contains up to 5.2 weight percent  $V_2O_5$ ; roscoelite contains 32.71 weight percent  $V_2O_5$ , which is among the highest reported vanadium value for roscoelite from an epithermal gold-tellurium deposit (Spry and Scherbarth, 2006). The source of the vanadium is probably magnetite-bearing mafic alkalic igneous rocks that are spatially associated with the gold ores (Spry and Scherbarth, 2006).

## Fossil Fuels

Vanadium closely correlates with organic carbon and, therefore, is enriched in many oil shales. It follows that significant amounts of vanadium are available for commercial use as a byproduct of petroleum, and minor amounts are produced as byproducts of coal and tar sands (Breit, 1992; Polyak, 2012, 2013). At least 10 percent of the world's supply of vanadium comes from coal, crude oil, and petroleum (Polyak, 2012, 2013). The highest concentrations of vanadium are in heavy crude oils (Breit, 1992). Most of the world's heavy oil and vanadiferous petroleum resources are located in Venezuela. These oilfields contain consistently high (up to 1,400 ppm) concentrations of vanadium (Kapo, 1978). Other oils with greater than 50 ppm vanadium are produced in Iran and Japan, and from several fields within the United States, including Alaska, Arkansas, California, Louisiana, Mississippi, Oklahoma, Texas, and Wyoming. Vanadium is recovered from oil by processing ash generated in thermoelectric powerplants,

petroleum coke residues generated during refining of heavy oils, and residues plated onto catalysts (Breit, 1992).

Vanadium abundances in ashes formed by burning coals generally range from 0.01 to 0.3 weight percent, with some as high as 8 percent (Reynolds, 1948). The lowest values are contained in coals formed from subaerial plant material; the highest concentrations are in marine sapropelic coals (Breit, 1992). Although China is the only producer of vanadium from coal, coal deposits in Venezuela contain high vanadium contents. The average vanadium content of coal in the United States is 20 ppm (Swanson and others, 1976).

Tar sands are large deposits of bitumen or extremely heavy crude oil. The sands were originally named for those in the Athabasca region in northeastern Alberta, Canada, and tar sand deposits in this region are the best known examples in the world. Other documented occurrences are in Alabama, Alaska, California, Kansas, Kentucky, Oklahoma, Missouri, New Mexico, Texas, and Utah in the United States (Wever and Kustin, 1990), and in other countries, such as Jordan (Breit, 1992; Dill and others, 2009). The oil sands consist of a mixture of crude bitumen (a semisolid form of crude oil), silica sand, clay minerals, and water. Production of refinery-grade oil from the tar sand deposits generates a substantial amount of petroleum coke fly ash that may contain appreciable amounts of valuable metals, such as nickel, titanium, and vanadium. The amount and form of vanadium varies, depending on the nature of the sands. Tar sands in the Athabasca region average several hundred ppm vanadium, whereas other localities contain lower concentrations (Wever and Kustin, 1990; Breit, 1992).

## Resources and Production

### Identified Resources (United States and World)

A majority of the world's supply of vanadium (approximately 80 to 85 percent) is derived from mined ore that comes either directly from deposits or from steelmaking slags produced by processing the ores mined from VTM deposits. The remaining 15 to 20 percent of the world's supply of vanadium comes from (a) spent catalysts that collected vanadium during the refining of crude oils; (b) residues from the production of alumina, uranium, and some hydrocarbons; and (c) ash derived from burning high-vanadium-content coal or petroleum. Although the leading vanadium-producing countries in 2012 (fig. U2) were China (37 percent), South Africa (35 percent), and Russia (25 percent), Australia is poised to become a major world producer of vanadium in the future (Moskalyk and Alfantazi, 2003). World vanadium resources in 2012 were estimated to be 63 million metric tons of vanadium, and world reserves were estimated to be 14 million metric tons (Polyak, 2013). Because vanadium is usually recovered as a byproduct or coproduct, the demonstrated world resources of this mineral commodity are

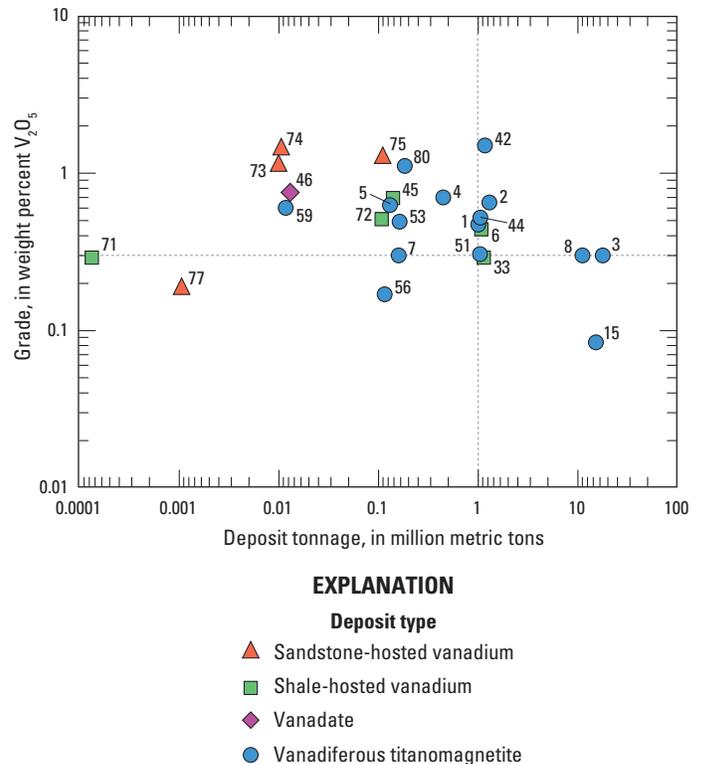
understated and, therefore, not fully indicative of available supply. Although domestic resources and secondary recovery are adequate to supply a large portion of domestic needs, a substantial part of U.S. demand is currently met by foreign material (Polyak, 2013).

Among the vanadium-rich ore deposits currently being mined, VTM deposits contain the largest tonnages of ore (table U1; fig. U5) and are the reason that China, South Africa, and Russia lead the world in vanadium production. Sandstone-hosted deposits commonly have the highest grades of vanadium, but most are small; that is, they have less than 1 million metric tons of ore (table U1; fig. U5). Among the three deposit types, however, the leading producers of vanadium in the United States have been SSV deposits. In 2010, production from a mill facility in Utah that recovered vanadium from SSV ores was sufficient to meet 20 percent of the vanadium demand for the United States, which amounted to nearly 2 percent of global vanadium production (Polyak, 2011).

Some carbonaceous and phosphatic shale-hosted deposits (Julia Creek, Australia; Viken, Sweden; and Green Giant, Madagascar) have reported high tonnages of vanadium, but these deposits are not currently in production. Technology to recover vanadium profitably in current markets is still being developed. Small amounts of vanadium were produced during World War II from the organic-rich Alum Shale in southern and central Sweden (Dyni, 2006). Also, until 1999, approximately 2,000 metric tons of  $V_2O_5$  was produced annually from the ferrophosphorus slag generated during the reduction of phosphate to elemental phosphorus in ore from the Phosphoria Formation in Idaho and Wyoming (Jasinski, 2004).

Bauxite is another source of vanadium. The vanadium content depends on the origin and nature of the bauxite, but average  $V_2O_5$  contents typically range from 0.05 to 0.25 percent. France, Germany, and India host important occurrences of vanadium-rich bauxite (Patterson, Kurtz, and others, 1986). During the processing of bauxite and the production of alumina, vanadium accumulates in residual sludge (red mud) and other byproducts that contain as much as 10 to 18 percent  $V_2O_5$ .

Vanadium is present in crude oil or the residues (bitumen or asphalts) of crude oils remaining in petroleum source rocks. Japan and the United States have recovered significant quantities of vanadium from petroleum residues. Asphaltine or bitumen in the Mina Ragra deposit in the Pasco Region of Peru, was extensively exploited for vanadium from 1907 until 1955. It was the principal source of vanadium in the world in the early 1900s (Fischer, 1973). Unoxidized ore at Mina Ragra consists of quisqueite (a vanadium hydrocarbon) and patronite (vanadium sulfide) (table U2). Vanadates and vanadium oxide minerals form the near-surface oxidized ore, some of which is extremely rich and contains as much as 40 percent  $V_2O_5$  (Fischer, 1973). Bitumen and asphaltine that contain vanadium-rich minerals occur in fractures and as disseminations in the host shale, forming a lens-shaped body (Fischer, 1973).



**Figure U5.** Plot of grade and tonnage of vanadium deposits for which data were available. Each symbol represents an individual deposit. Numbers next to the symbol correspond to the deposit numbers given in table U1 and figure U1. The deposits with the highest grades (greater than or equal to 0.3 percent vanadium oxide [ $V_2O_5$ ]) and tonnages (greater than 1 million metric tons of  $V_2O_5$ ) are located in Africa, Australia, Canada, and China.

## Undiscovered Resources

Given that most of the present-day vanadium comes from VTM deposits and steelmaking slags produced from these deposits, it is likely that additional vanadium resources will come predominantly from VTM deposits and districts. VTM deposits in Australia, Brazil, Canada, Chile, India, and Malaysia have been identified only recently, and the full extent of the resources has not yet been evaluated fully. Among the largest regions with potential for widespread VTM resources is the 5,000-km<sup>2</sup> region known as the “Ring of Fire” in northern Ontario (fig. U1). Results from early exploration programs indicate that vanadium grades for deposits within mafic and ultramafic complexes in this region (for example, 0.64 percent  $V_2O_5$  at the Butler Lake area, Ontario, Canada; MacDonald Mines Exploration Ltd., 2013) are comparable to economic deposits elsewhere in the world.

Some uranium SSV ores in southwestern South Dakota and northeastern Wyoming are part of the Wyoming basin’s uranium province and have recently been distinguished from

deposits elsewhere in the province by their substantially higher vanadium contents (George Breit, U.S. Geological Survey [retired], written commun., 2013). These are possible deposits for future vanadium production in the United States.

The amount of vanadium recovered from processing crude oils, coals, and tar sands will undoubtedly increase with future technological advances. Oil from large fields in the Caribbean Basin, the Middle East, and Russia are known to contain anomalously high vanadium contents (Mukhametshin and Punanova, 2011). Tar sands in North America may become an important resource of vanadium in the future. The effectiveness of recovery of vanadium is dependent on the silica and alumina contents of the fly ash; high silica and alumina contents tie up metal values in a silica-alumina matrix (Gomez-Bueno and others, 1981). Results of experimental work show that such matrixes can be broken down by application of a saline water roast of the carbon-free fly ash (Gomez-Bueno and others, 1981). Additional research on development of processing techniques of fly ash may lead to further enhanced recoveries of vanadium (Holloway and Etsell, 2006).

Iron sands are another potential source of vanadium. Iron sands are placer deposits that contain abundant concentrations of iron-bearing heavy minerals, including vanadium-rich magnetite. These iron sands are distributed extensively on the west coast of New Zealand's North Island (Sweatman and others, 2012), but other placer occurrences most likely are present on the east coast of the conterminous United States and the coasts of Africa and Brazil, as well as fluvial iron-titanium-vanadium placer deposits (for example, interior Iran; Razmara and Asadi, 2010). Vanadium concentrations in the New Zealand sands are as high as 0.5 percent. Although vanadium is currently not produced as a byproduct, research that is focused on methods to optimize its recovery is reportedly underway (Sweatman and others, 2012).

Most known occurrences of vanadium in shale are currently uneconomic but are estimated to contain large resources (table U1). Targets may become more viable in the future with advances in extraction technology. For example, development of a method to extract vanadium from the Gibellini vanadium deposit in central Nevada (American Vanadium Corp., 2012) is underway. Similar efforts to produce vanadium from metashales are reported for the Green Giant deposit in Madagascar (Energizer Resources, Inc., 2013). Graphitic deposits in Alabama and China (Liu Mao Mine) contain mica and garnet with elevated vanadium concentrations (up to 0.2 percent  $V_2O_5$ ) that may be similar to the Green Giant deposit (Pallister and Thoenen, 1948; this volume, chap. J). Other vanadiferous shales include the low-to medium-grade Okcheon metamorphic belt in Korea (Jowitt and Keys, 2011), where metalliferous black shales were used locally as fuel, and contain up to 2.04 percent vanadium, together with high concentrations of gold, molybdenum, nickel, PGEs, and uranium (Jeong, 2006). The Alum Shale in Sweden is an organic-rich marine sequence that is 15 to 60 m thick and contains up to 3,100 ppm vanadium and high

concentrations of molybdenum, nickel, uranium, and zinc (Dyini, 2006). Although small amounts of vanadium have already been produced from the Alum Shale, new technologies may allow industrial-scale extraction from this laterally extensive unit (Dyini, 2006; Aura Energy, 2012; Hallberg, 2012). Black shales in Russia that occur within the Mongolia/Ural and Pacific gold belts have local concentrations of vanadium and uranium and therefore are also potential resources for these metals (Karpuzov and others, 2008). Although it lies at great depths (about 2,000 m below the surface), the oil-bearing Bazhenov Formation in the West Siberian Basin is another potential source of byproduct metals (Laznicka, 2010), with reported average concentrations of 105 ppm uranium, 285 ppm molybdenum, and 1,015 ppm vanadium in a laterally extensive interval that is at least 15 to 20 m thick.

## Exploration for New Deposits

Exploration methods for vanadium-rich ores vary with deposit type. An understanding of how each type of deposit forms is essential for predicting the potential for undiscovered deposits.

### Exploring for Vanadiferous Titanomagnetite Deposits

Most vanadiferous titanomagnetite (VTM) deposits that formed on cratons of Archean to Proterozoic age are closely associated with LIPs; consequently, exploration for this deposit type is focused on LIPs. Mafic to ultramafic complexes that host VTM deposits are generally apparent as aeromagnetic anomalies, even if not exposed at the surface. Most commonly, airborne geophysical surveys that show coincident magnetic and electromagnetic anomalies are further investigated with followup ground geophysical surveys, including gravity, induced polarization, resistivity, and electromagnetic methods. Modeling of aeromagnetic and gravity data can indicate the extent, thickness, and form of intrusions (Cawthorn and Webb, 2001; Ivanic and others, 2010), which can help delineate intrusive bodies having the potential to host vanadium-rich magnetite layers. Paleomagnetic investigations of the Bushveld Complex have shown that different mineralized zones have different paleomagnetic signatures (that is, ages), allowing for regional correlation and delineation of the lateral extent of selected zones (Eales and others, 1993).

An important frontier issue in the exploration for VTM deposits is development of better exploration models that integrate the characteristics of these deposits with an improved understanding of LIP plumbing systems (Ernst and others, 2005). LIPs can have direct links to ore deposits (as hosts or heat engines) or indirect links, and can be used as guides for determining Precambrian paleocontinental reconstructions and related tracing of metallogenic belts between formerly adjacent tectonic blocks (Ernst and Peck, 2010).

Moreover, the compositions of igneous rocks in LIPs can be used to assess fertility and ore potential. For example, specific element ratios can be used to identify whether particular igneous rocks are permissive for hosting vanadium mineralization (Ernst and Peck, 2010). Litho-geochemistry, therefore, provides a guide for selecting the most prospective LIPs and LIP segments for exploration for VTM deposits, or for associated chromium, copper-nickel, or PGE deposits (Augé and others, 2005; Ivanic and others, 2010).

Major known ore-bearing magmatic intrusions are widespread within, or can be traced to the edge of, host continental blocks, suggesting that the intrusions likely continued into a formerly adjacent block. Examples include intrusions such as the Bushveld Complex (Kaalvaal craton), and the Great Dyke of Zimbabwe (Zimbabwe craton). From an exploration standpoint, robust Precambrian reconstructions aid in tracking well-documented metallogenic belts from heavily explored to frontier regions. New methods that use comprehensive data for LIPs can make such Precambrian reconstructions much more efficient (Ernst and Peck, 2010).

## Exploring for Sandstone-Hosted Vanadium Deposits

All sandstone-hosted vanadium (SSV) deposits in the Colorado Plateau province contain uranium; therefore, methods used to explore for uranium deposits of this type are applicable to the search for vanadium. The recognition and documentation of meander bends and possible bifurcating paleochannels in the sandstone host rocks are important broad characteristics. Features that may be used as guides to ore include sandstone-mudstone facies, trunk channel systems, stratigraphic pinchouts, individual channels, thick sandstone lenses, and carbonaceous material (Kovschak and Nylund, 1981). Models for the formation of SSV deposits suggest that bacteriogenic hydrogen sulfide acted as a reducing agent for ore formation (Northrop and others, 1990; Wanty and others, 1990). In addition, pyrite in mineralized zones typically has lower sulfur isotope values than pyrite above or below the zone (Northrop and others, 1990), indicating that isotopically light pyrite is an indicator of mineralizing processes in an area.

Some deposits have readily recognizable alteration zones, whereas others show only subtle differences between unmineralized, altered, and mineralized zones. Principal criteria used to distinguish the alteration zones are color, pyrite morphology, kaolinization of feldspar, and low gamma-ray counts commonly accompanied by gamma-ray anomalies at the upper and lower margins of the altered zone (Rackley and others, 1968). The presence of limonite stains, green and blue secondary copper minerals, gray-green alteration of brown or reddish mudstone seams or lenses, and iron and (or) copper sulfide minerals were used as guides to ore in the 1950s (Johnson, 1959).

Geophysical methods assist in determining regional subsurface geology as it may relate to SSV deposits. Conspicuous gravity lows may indicate evaporite units that

typically underlie the deposits, although many units may be too thin for detection. Magnetic anomalies highlight depths to basement, major faults that serve as conduits for ore fluids, and the presence of laccolithic intrusions that are interpreted as a possible source of metals in some deposits (Case and Joesting, 1972). More refined geophysical methods are needed to resolve the shape and position of channel sands. Airborne electromagnetic techniques have recently been applied in Nebraska to map the three-dimensional configuration of aquifers and paleochannels (Abraham and Cannia, 2011) and may be useful for delineating channels that are SSV ore hosts.

## Exploring for Shale-Hosted Vanadium Deposits

High vanadium concentrations in shales are closely correlated with elevated contents (greater than 5 percent) of organic carbon. Many vanadiferous shales with more than 20 percent organic carbon are considered oil shales (for example, Julia Creek deposit, Queensland, Australia). Deposits of oil shale occur worldwide, and include major deposits in the United States (INTEK, Inc., 2011). Some of these oil shales are known to have high vanadium contents (for example, Heath Formation in Montana; La Luna Formation in Venezuela), but many others likely have not been analyzed for trace metals. Existing and new geochemical data for vanadium and other trace elements in shales would need to be examined to locate potential shale-hosted vanadium deposits.

A good understanding of how vanadiferous shales form is critical for exploration. It is generally accepted that the source of vanadium is seawater, but the enrichment mechanism is uncertain. The close occurrence of vanadium-rich shales with black-shale-hosted phosphate deposits suggests control by fluctuating redox gradients within a sedimentary basin (Piper, 1994). If this suggestion is correct, then exploration will likely be focused in marine successions that were deposited along continental margins or inland seas, where redox gradients are likely to have occurred. Furthermore, because shales can be laterally extensive but have variable grades, understanding the distribution of metal enrichments may help target areas of interest.

National-scale geochemical datasets also may be useful in highlighting regions with black shales that are permissive for hosting vanadium deposits. Preliminary soil and sediment maps of the United States (Smith and others, 2015) show arcuate highs for a range of elements, including cobalt, molybdenum, nickel, and vanadium in central Kentucky—an area that is underlain by the New Albany Shale (Ripley and others, 1990) and stratigraphically equivalent shales that are known to contain high concentrations of these metals. Although less pronounced, similar high concentrations are evident in east-central Nevada and could be related to shales of the metal-rich Woodruff Formation.

Geophysical methods may prove valuable for delineating the distribution of black shales, although many of these shales may not contain significant concentrations of vanadium.

Shales are good conductors, particularly if graphite is present, and therefore, electromagnetic and resistivity surveys may prove useful in delineating the extent of shale units under shallow cover. Recent studies show that combined seismic and electromagnetic methods are effective in highlighting zones of high gas potential in shale reservoirs (Kumar and Hoversten, 2012); such methods could be tested for use in the search for high-organic intervals in shales. Because many vanadium-rich carbonaceous shales also contain high uranium concentrations, downhole geophysical techniques (gamma logs) may be useful in identifying the position of metalliferous shales. Aerial radiometric surveys may also resolve the outcrop position of uranium-rich (and, by association, other metal-rich) shales (Pirkle and others, 1982). The arcuate trend of metals in surficial materials described above for Kentucky is readily mapped in an aeroradiometric survey (Hill and others, 2009).

## Environmental Considerations

### Sources and Fate in the Environment

Vanadium commonly occurs in one of three oxidation states in weathering environments: +3, +4, and +5. Vanadium +3 and +4 are relatively insoluble ions because they tend to form solid (oxy)hydroxides (for example  $V(OH)_3$  and  $VO(OH)$ ), respectively, but the  $V^{5+}$  state is generally dissolved in solution as various oxyanions (for example  $VO_4^{3-}$ ,  $HVO_4^{2-}$ , and  $H_2VO_4^-$ ). Under a wide pH range, these high-valence vanadium oxyanions may sorb to iron and aluminum (oxyhydr)oxide minerals. Most dissolved vanadium in rivers and streams derives from the weathering of silicate minerals (Shiller and Mao, 2000). Dissolved  $V^{4+}$  and  $V^{3+}$  are known to form strong complexes with organic compounds, many of which originated as  $V^{5+}$ -organic complexes that were reduced. The formation of strong vanadium-organic compound complexes is one of the mechanisms by which fossil fuels and black shales may become enriched in vanadium.

Examples of natural concentrations of vanadium in rocks, soils, water, and air are given in table U3. Vanadium contents in soils away from known vanadium deposits, mines, or smelters range from 13 to 227 ppm (Shacklette and Boerngen, 1984; Tyler, 2004), whereas streams and rivers contain vanadium concentrations that range from 0.23 to 3.7 micrograms per liter ( $\mu\text{g/L}$ ) or ppb (Shiller and Mao, 2000; Gaillardet and others, 2003). The concentration of vanadium in suspended particulates in world rivers averages 129 mg/kg (Viers and others, 2009). Dissolved vanadium in coastal seawater ranges from 0.31 to 2.8  $\mu\text{g/L}$  (Shiller and Mao, 1999; Wang and Sañudo-Wilhelmy, 2008; Strady and others, 2009). In North Pacific seawater, dissolved vanadium concentrations generally increase with depth with a total range of 1.5 to 1.9  $\mu\text{g/L}$  (Collier, 1984). In contrast, concentrations in particulate matter (with diameters greater than 53 micrometers) decrease in the upper 100 to 200 m of seawater, then remain relatively constant over a range of 0.0001 to 0.0004  $\mu\text{g/L}$  (Collier, 1984).

Among nearly 9,000 samples of filtered and unfiltered groundwaters collected in California, 90 percent contained vanadium concentrations ranging from 3 to 24  $\mu\text{g/L}$  (Wright and Belitz, 2010). Vanadium occurs naturally in the atmosphere as part of mineral dust particles, and ranges in concentration from 0.0006 to 0.002 nanogram per cubic meter ( $\text{ng/m}^3$ ) over the South Pole and from 0.8 to 1.4  $\text{ng/m}^3$  over Greenland (Kabata-Pendias and Pendias, 2001).

Mining and industrial activities can lead to above-background concentrations of vanadium in the environment (table U3). For example, the concentration of vanadium in soils (548 to 7,160 ppm) collected near a vanadium mine in the North West Province of South Africa (Mandiwana and Panichev, 2004) is roughly an order of magnitude greater than natural concentrations in soils. In the Panzhihua region, China, soil vanadium concentrations depend upon the predominant land use and decrease in the following order: smelting (208 to 938 ppm), mining (112 to 591 ppm), agricultural (86 to 227 ppm), and urban use (94 to 184 ppm) (Teng and others, 2011). The Bilina River in the Czech Republic receives drainage from municipal and industrial areas; vanadium concentrations range from 2.5 to 85.6  $\mu\text{g/L}$ , with the highest concentrations observed in the industrial region (Kohušová and others, 2011). Primary inputs of vanadium to the atmosphere result from mining, ore processing, and combustion of fuel oils and coal. Vanadium concentrations in air in urban and industrial areas range from 5 to 200  $\text{ng/m}^3$  (Kabata-Pendias and Pendias, 2001).

### Mine Waste Characteristics

Mine waste is generally considered to be the material that originates and accumulates at a mine site but has no current economic value (Lottermoser, 2010), and it includes both solid and liquid waste. Because vanadium can be recovered as a byproduct of the mining of bauxite, carnotite, phosphate, and titanomagnetite ores, the character of the mine waste will vary according to the methods used to extract the primary ore. Vanadium mining of black shales and copper-lead-zinc vanadate deposits, as well as recovery of vanadium from fly ash, generates additional types of mine and processing waste. Mining of vanadium from VTM deposits in Australia is projected to generate 12 million cubic meters of waste rock at the Windimurra deposit (Environmental Protection Authority, 2008) and 59 million metric tons of tailings at the Balla Balla deposit (Environmental Protection Authority, 2009). American Vanadium Corp. is planning to mine vanadium from the Gibellini vanadium deposit in Nevada. Production is to involve open pit mining and processing on site by heap leaching; the total amount of ore and waste to be extracted is projected to be 24 million metric tons (Hanson and others, 2011). Plans to mine vanadium at the metashale-hosted Green Giant deposit in Madagascar includes a well-known process called alkaline press leaching, which is expected to produce a battery-grade form of  $V_2O_5$  that has a purity of greater than 99.5 percent.

**Table U3.** Vanadium concentrations in rocks, soils, waters, and air.

[DOE, U.S. Department of Energy; EPA, U.S. Environmental Protection Agency; V, vanadium; cm, centimeter; µg/L, microgram per liter; µm, micrometer; ng/m<sup>3</sup>, nanogram per cubic meter; ppm, part per million; %, percent]

Environment and (or) location	Vanadium concentration	Unit	Comments	Reference(s)
<b>Rocks</b>				
Upper continental crust	60	ppm	Average	Taylor and McLennan (1995)
Bulk continental crust	230	ppm	Average	Taylor and McLennan (1995)
Lower continental crust	285	ppm	Average	Taylor and McLennan (1995)
Basalt	250	ppm	Average	Levinson (1974, p. 44)
Black shale	205	ppm	Average	Ketris and Yudovich (2009)
Granite	20	ppm	Average	Levinson (1974, p. 44)
Limestone	15	ppm	Average	Levinson (1974, p. 44)
Shale	130	ppm	Average	Levinson (1974, p. 44)
<b>Soils</b>				
Western United States	70	ppm	Mean for 20 cm depth	Shacklette and Boerngen (1984)
Eastern United States	43	ppm	Mean for 20 cm depth	Shacklette and Boerngen (1984)
North West Province, South Africa	548 to 7,160	ppm	Composite of upper 20 cm; proximal to V mining	Mandiwana and Panichev (2004)
Panzhihua, China	94 to 184	ppm	Composite of upper 20 cm; urban soil	Teng and others (2011)
Panzhihua, China	86 to 227	ppm	Composite of upper 20 cm; agricultural soil	Teng and others (2011)
Panzhihua, China	112 to 591	ppm	Composite of upper 20 cm; proximal to V mining	Teng and others (2011)
Panzhihua, China	208 to 938	ppm	Composite of upper 20 cm; proximal to V smelting	Teng and others (2011)
Sweden	13 to 47	ppm	Range of profile developed on quartzite and gneiss	Tyler (2004)
Proposed DOE benchmark	2	ppm	Screening benchmark for terrestrial plants	Efroymsen and others (1997)
Soil-quality guideline	130	ppm	Canadian agricultural soil guideline	Canadian Council of Ministers of the Environment (2007)
<b>Waters</b>				
Seawater, North Pacific	1.5 to 1.9	µg/L	Dissolved	Collier (1984)
Seawater, North Pacific	0.0001 to 0.0004	µg/L	Particulate (<53 µm)	Collier (1984)
Seawater, coastal New York, United States	0.31 to 1.78	µg/L	Dissolved (<0.2 µm)	Wang and Sañudo-Wilhelmy (2008)
Seawater, Louisiana Shelf, United States	0.32 to 1.70	µg/L	Dissolved and colloidal (<0.45 µm)	Shiller and Mao (1999)
African rivers	0.59 to 0.65	µg/L	Dissolved load (< 0.2 µm); nonpolluted	Gaillardet and others (2003) and references therein
European rivers	0.4 to 2.9	µg/L	Dissolved load (< 0.2 µm); nonpolluted	Gaillardet and others (2003) and references therein
North American rivers	0.4 to 1.84	µg/L	Dissolved load (< 0.2 µm); nonpolluted	Gaillardet and others (2003) and references therein
Amazon River	0.703	µg/L	Mean dissolved load (<0.2 µm); nonpolluted	Gaillardet and others (2003) and references therein
Bilina River	2.5 to 85.6	µg/L	Receives municipal and industrial drainage	Koňušová and others (2011)

**Table U3.** Vanadium concentrations in rocks, soils, waters, and air.—Continued

[DOE, U.S. Department of Energy; EPA, U.S. Environmental Protection Agency; V, vanadium; cm, centimeter; µg/L, microgram per liter; µm, micrometer; ng/m<sup>3</sup>, nanogram per cubic meter; ppm, part per million; %, percent]

Environment and (or) location	Vanadium concentration	Unit	Comments	Reference(s)
Waters—Continued				
Mississippi River tributaries, United States	0.23 to 1.77	µg/L	Dissolved and colloidal (<0.4 µm)	Shiller and Mao (2000)
Stream water, California, United States	0.29 to 3.7	µg/L	Dissolved and colloidal (<0.4 µm)	Shiller and Mao (2000)
Gironde Estuary, France	0.89 to 2.76	µg/L	Dissolved	Strady and others (2009)
Groundwater, California	3 to 24	µg/L	Filtered and unfiltered; range is for 90% of samples	Wright and Belitz (2010)
Sediment, world river (average)	129	ppm	Suspended sediment	Viers and others (2009)
Proposed EPA benchmark	280	µg/L	Tier II Secondary acute value	Suter and Tsao (1996)
Proposed EPA benchmark	20	µg/L	Tier II Secondary chronic value	Suter and Tsao (1996)
Air				
South Pole	0.0006 to 0.002	ng/m <sup>3</sup>	None	Kabata-Pendias and Pendias (2001)
Greenland	0.8 to 1.4	ng/m <sup>3</sup>	None	Kabata-Pendias and Pendias (2001)
Urban/industrial	5 to 200	ng/m <sup>3</sup>	None	Kabata-Pendias and Pendias (2001)

The mineralogy of solid mine waste derived from vanadium mining is similar to that of the deposit from which it is extracted, but the proportion of vanadium minerals is smaller. Tailings from the VTM deposit in Panzhihua, China, contain ilmenite (15 to 18 mass percent), augite (46 mass percent), plagioclase (31 to 34 mass percent), and pyrite (2 to 3 mass percent) (Dahe, 2004). The Slick Rock SSV deposit in Colorado typically contains low contents of uranium and vanadium ore minerals, as well as anatase, barite, calcite, jordisite, pyrite, and quartz; selenium- and copper-bearing minerals are found in some deposits (Shawe, 2011). In the Gibellini vanadium deposit, vanadium is concentrated in organic material; associated phases are apatite, calcite, clay, microcline, pyrite, and sphalerite (Desborough and others, 1979). Copper-lead-zinc vanadate deposits may contain the ore minerals descloizite, mottramite, and vanadinite (table U2), which at the Otavi Mountainland deposits in Namibia host trace amounts of arsenic, cadmium, chromium, iron, manganese, molybdenum, nickel, and phosphorus (Boni and others, 2007). The most common gangue minerals in the Otavi Mountainland deposits are calcite and dolomite, which have high concentrations of iron, phosphorus, and lead and trace amounts of arsenic, barium, cadmium, copper, nickel, strontium, and vanadium (Boni and others, 2007).

In weathering environments, trace metals in vanadium deposits are expected to remain immobile under oxic, near-neutral pH conditions (5<pH<8), especially in the presence of iron-rich solids (Smith and Huyck, 1999). Under anoxic and (or) acidic conditions, however, vanadium minerals, some gangue minerals, and associated trace metals may

dissolve. In those deposits that contain sulfide minerals (for example, chalcocite, pyrite, and sphalerite), generation of acidity is possible if sulfide dissolution is not balanced by the acid-neutralizing capacity of carbonate minerals (for example calcite and dolomite). The dissolution of sulfide minerals releases metals and produces sulfuric acid, and the subsequent acidic pH values of the solutions allow higher concentrations of metals to be dissolved—potentially causing the environmental problem known as acid mine drainage (AMD). Mining of VTM, SSV, and black shale deposits that contain sulfides and lack appreciable quantities of carbonate minerals increases the potential for AMD generation. Alternatively, some of these deposit types, particularly some SSV and black shale deposits, contain appreciable amounts of carbonate minerals, thereby lowering the acid-generation potential.

Recovery of vanadium from mine tailings and other wastes is becoming an increasingly important source, particularly because the fraction of vanadium in discarded products that are recycled is less than 1 percent (Graedel and others, 2011). The main challenge of vanadium recycling is that it is often included in alloys in small amounts, making recovery technologically and economically unfeasible (Reck and Graedel, 2012).

## Human Health Concerns

The Agency for Toxic Substances and Disease Registry provides a useful summary of the human toxicology of vanadium (Agency for Toxic Substances and Disease Registry, 2012).

The general public is most likely to be exposed to vanadium through consumption of contaminated food. Occupational exposure to vanadium usually results from the inhalation of  $V_2O_5$  dust during the production of FeV and steel. Exposure to high oral doses of vanadium may lead to nausea, diarrhea, stomach cramps, decreased numbers of red blood cells, and increased blood pressure. Inhalation of  $V_2O_5$  may cause extended coughing and is suspected to cause cancer.

Vanadium is believed to be a micronutrient, with a postulated requirement for humans of less than 10 micrograms per day, which can be met through dietary intake (Anke, 2004, and references therein). Vanadium in the form of vanadyl sulfate and sodium metavanadate has been administered to diabetic patients as a dietary supplement because these compounds have been observed to mimic the actions of insulin in isolated cell systems (Anke, 2004, and references therein), but clear therapeutic benefit has yet to be established (Wiernsperger and Rapin, 2010). Primary and secondary drinking-water regulations for vanadium currently do not exist in the United States, but the Occupational Safety and Health Administration has set an exposure limit of 0.05 milligrams per cubic meter ( $mg/m^3$ ) for  $V_2O_5$  dust (Occupational Safety and Health Administration, 2013b) and 0.1  $mg/m^3$  for  $V_2O_5$  fumes (Occupational Safety and Health Administration, 2013a) in workplace air over an 8-hour workday. Vanadium toxicity is believed to result from an intake of more than 10 to 20 milligrams per day (Anke, 2004).

## Ecological Health Concerns

Vanadium is essential for some biological processes and organisms, as well as a potential toxicant. For example, some nitrogen-fixing bacteria require vanadium for producing vanadium nitrogenase, an enzyme used to convert nitrogen ( $N_2$ ) from the atmosphere into ammonia, which is a more biologically accessible form of nitrogen (Madigan and others, 2003). This process is critical to the health of the biosphere. Vanadium is also essential to certain species of algae for chlorophyll production and overall growth (Anke, 2004).

Compared with other metals and metalloids, the ecological impacts of vanadium in the environment are not well known. Because fish tend to be sensitive to low concentrations of dissolved metals, they are often indicators of contamination in aquatic systems. One of several useful endpoints used in toxicity tests is that which determines the lethal concentration that leads to 50 percent mortality ( $LC_{50}$ ) after exposure to a substance for a specified amount of time. Chronic toxicity tests (that is, lower doses over longer time periods) of dissolved vanadium in developing rainbow trout (*Oncorhynchus mykiss*) revealed a mean  $LC_{50}$  value of 0.17 milligrams per liter (mg/L) after 28 days of exposure (Birge and others, 1980). Acute toxicity tests (higher doses over shorter times) of vanadium to a fish known as the threespine stickleback (*Gasterosteus aculeatus*) revealed  $LC_{50}$  values that ranged from 2.4 to 4.1 mg/L after 4 days of exposure (Gravenmier

and others, 2005). Similar acute toxicity tests of vanadium to three species of endangered fish from the Green River, Utah, which runs through carnotite deposits, showed no difference in sensitivity among species, but  $LC_{50}$  values ranged from 5.3 to 8.8 mg/L for young specimens and 2.2 to 5.1 mg/L for older stages (Hamilton, 1995) after 4 days of exposure. These dissolved vanadium concentrations are much greater than those observed in many rivers and streams (table U3). Some regions of the United States have adopted secondary acute and chronic screening benchmarks of 280 micrograms of vanadium per liter of water ( $\mu g$  V/L) and 20  $\mu g$  V/L, respectively, for aquatic freshwater life (Suter and Tsao, 1996).

The essentiality of vanadium to higher plants is debated, but clear evidence exists for vanadium phytotoxicity. After amending soils with vanadium in the form of dissolved ammonium metavanadate ( $NH_4VO_3$ ), Wang and Liu (1999) found that soybean seedling growth was markedly stunted in flood plain soils (fluvaquents) with greater than 30 ppm of vanadium, whereas little to no stunting occurred in red earth soil (Oxisol), even at vanadium concentrations as high as 75 ppm. Likewise, in phytotoxicity tests with forb (a herbaceous flowering plant), crop, and grass species,  $LC_{50}$  values ranged from 21 to 59 ppm of  $V_2O_5$  after exposure for 4 to 5 weeks; higher  $LC_{50}$  values (90 to greater than 130 ppm of  $V_2O_5$ ) were observed under similar conditions, but with greater soil nutrient levels (Smith and others, 2013). These studies highlight how vanadium toxicity to plants varies, depending upon the prevailing soil conditions, the type of plant species, and the chemical form of vanadium, which determines its bioaccessibility. The chemical form of vanadium in ecotoxicity studies may be more bioaccessible than the chemical form of vanadium in soils. Furthermore, the amount of bioaccessible vanadium is likely to be smaller than the amount of total vanadium in soils. For example, the concentration of bioaccessible vanadium in soils of Northern Ireland was determined to be about 7.5 to 17 percent of the total soil vanadium content (Barsby and others, 2012). Some regions of the United States have adopted a soil screening benchmark of 2 ppm of vanadium for terrestrial plants (Efroymsen and others, 1997). The Canadian agricultural soil quality guideline for vanadium is 130 ppm of vanadium (Canadian Council of Ministers of the Environment, 2007).

## Mine Closure

Most recent and new mining operations include closure plans that address issues related to the mine footprint. A mine's footprint includes the waste left on site and the locally affected soil and water, as well as ecological impacts, such as habitat destruction and loss of biodiversity. Mine closure issues that could have the greatest environmental impacts depend upon the type of deposit being mined, and if applicable, the methods employed to process the ore on site. Given the variety of deposit types from which vanadium is obtained, all mine closure issues related to vanadium mining are too numerous to

describe here. Instead, the focus is on potential issues related to mining of the largest and economically most important deposit type (VTM deposits), and to the new mining operation planned in the Gibellini vanadium deposit in Nevada.

Some VTM and shale-hosted deposits contain sulfide minerals, and, therefore, the potential for AMD exists at both types of mine sites. Acidic drainage may seep from waste piles or tailings ponds. Common methods for treating AMD include active water-treatment facilities, passive limestone-lined channels, and constructed wetlands (Plumlee and Logsdon, 1999). The end result of both active and passive approaches is eventual precipitation of dissolved metals. Precipitated metals in passive wetland systems tend to be more stable under the prevailing anoxic conditions, whereas the metal-rich precipitates that result from active treatment facilities form a sludge that can cause environmental problems if not disposed of responsibly. When the potential for AMD exists at a mine site, common preventative measures include conducting water quality surveys before, during, and after mining.

The great size of VTM deposits tends to result in large mine waste piles. These waste piles have the potential to become unstable and can be a source of metal-rich dust. If using mine waste as backfill into dry mine workings is not an option, problems of mine-waste-pile stability and dust generation can often be addressed through grading and covering the piles with vegetation.

Vanadium-rich black shale at the Gibellini vanadium deposit is planned to be processed on site using acid heap leaching and solvent extraction—a recovery process that has yet to be applied to vanadium ores (Hanson and others, 2011). Acid heap leaching is commonly used on low-grade cobalt, copper, and nickel ores. In general, heap leaching involves placing crushed ores on top of impervious liners to form a slightly sloped leach pad, applying leach solutions to the pad, then collecting the leachates delivered by the impervious liners into ponds or tanks for further processing. During solvent extraction, leachates are mixed with a vanadium-optimized organic extractant (that is, a chelating agent), thereby forming vanadium-organic complexes that can be separated from other undesired metals present in the solution. At the Gibellini vanadium deposit, the resulting metal solution is planned to be recirculated back through the leaching process, while the vanadium-organic solution will undergo acidic stripping of vanadium from the organics, followed by precipitation of  $V_2O_5$  (Hanson and others, 2011). Potential seepage or spillage of leachates into local surface and groundwater can have negative impacts on the environment, however, given that leachates may contain metals, such as arsenic, cadmium, chromium, copper, mercury, lead, and zinc (U.S. Environmental Protection Agency, 1994). Best practices for this type of operation include engineering for leak prevention, ongoing seepage testing, and post-closure monitoring of mine waste discharges and downstream water quality (U.S. Environmental Protection Agency, 1994).

## Problems and Future Research

Infrastructure development and the need for steel products are the main sources of demand for vanadium worldwide. The current worldwide resources of about 63 million metric tons of vanadium appear to be adequate to meet current demand. Future demand is expected to increase because of the following factors (Roskill Information Services, Ltd., 2013):

- China is the top steel producer and consumer of vanadium in the world (the country accounted for about 34 percent of the world's vanadium consumption in 2012), and China's demand for vanadium to use in the production of steel is expected to remain strong for the next 10 to 20 years.
- China and Japan have legislated increased vanadium content in steel rebar so that the quality of their steel matches that of other major steel-producing countries; therefore, use of vanadium for steel production in China and Japan is expected to increase dramatically.
- India's steel production is projected to almost double owing to industrialization of that country.
- Development of alternate renewable sources of energy will likely require increased use of VRBs.

With the anticipated increase in demand for vanadium and the limited supply, maintaining a constant supply would likely mean that new sources of vanadium would need to be identified and the extraction of vanadium from currently defined sources would need to be optimized. Many future resources are likely contained within VTM deposits in unexplored regions. Another potential source is vanadium-rich shale because known deposits of this type have large tonnages and grades that are similar to those of presently mined VTM deposits (fig. U5). For shale-hosted deposits to be a viable resource, however, methods of profitably extracting the vanadium and producing a product that could be used in VRBs would be required, and future research would need to be designed to optimize these methods. Other sources, such as iron sands (placers) likely exist in many parts of the world; identification and quantification of these sands in terms of tonnage and vanadium content could be undertaken. Research on optimizing the recovery of vanadium from crude oil, bauxite, and tar sands also may increase global identified resources of this valuable metal.

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