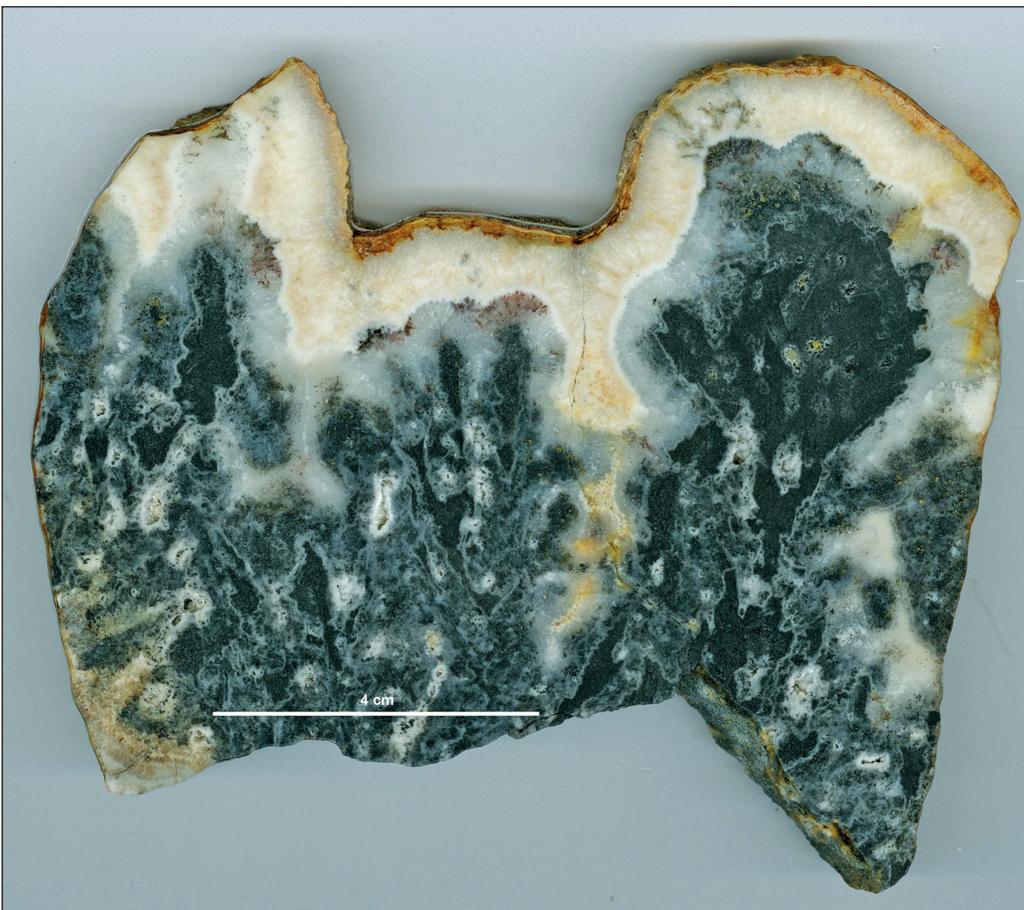# Selenium

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

Professional Paper 1802–Q

Periodic Table of Elements

1A																	8A
1 **H** hydrogen 1.008	2A											3A	4A	5A	6A	7A	2 **He** helium 4.003
3 **Li** lithium 6.94	4 **Be** beryllium 9.012											5 **B** boron 10.81	6 **C** carbon 12.01	7 **N** nitrogen 14.01	8 **O** oxygen 16.00	9 **F** fluorine 19.00	10 **Ne** neon 20.18
11 **Na** sodium 22.99	12 **Mg** magnesium 24.31	3B	4B	5B	6B	7B		8B		11B	12B	13 **Al** aluminum 26.98	14 **Si** silicon 28.09	15 **P** phosphorus 30.97	16 **S** sulfur 32.06	17 **Cl** chlorine 35.45	18 **Ar** argon 39.95
19 **K** potassium 39.10	20 **Ca** calcium 40.08	21 **Sc** scandium 44.96	22 **Ti** titanium 47.88	23 **V** vanadium 50.94	24 **Cr** chromium 52.00	25 **Mn** manganese 54.94	26 **Fe** iron 55.85	27 **Co** cobalt 58.93	28 **Ni** nickel 58.69	29 **Cu** copper 63.55	30 **Zn** zinc 65.39	31 **Ga** gallium 69.72	32 **Ge** germanium 72.64	33 **As** arsenic 74.92	34 **Se** selenium 78.96	35 **Br** bromine 79.90	36 **Kr** krypton 83.79
37 **Rb** rubidium 85.47	38 **Sr** strontium 87.62	39 **Y** yttrium 88.91	40 **Zr** zirconium 91.22	41 **Nb** niobium 92.91	42 **Mo** molybdenum 95.96	43 **Tc** technetium (98)	44 **Ru** ruthenium 101.1	45 **Rh** rhodium 102.9	46 **Pd** palladium 106.4	47 **Ag** silver 107.9	48 **Cd** cadmium 112.4	49 **In** indium 114.8	50 **Sn** tin 118.7	51 **Sb** antimony 121.8	52 **Te** tellurium 127.6	53 **I** iodine 126.9	54 **Xe** xenon 131.3
55 **Cs** cesium 132.9	56 **Ba** barium 137.3	*	72 **Hf** hafnium 178.5	73 **Ta** tantalum 180.9	74 **W** tungsten 183.9	75 **Re** rhenium 186.2	76 **Os** osmium 190.2	77 **Ir** iridium 192.2	78 **Pt** platinum 195.1	79 **Au** gold 197.0	80 **Hg** mercury 200.5	81 **Tl** thallium 204.4	82 **Pb** lead 207.2	83 **Bi** bismuth 209.0	84 **Po** polonium (209)	85 **At** astatine (210)	86 **Rn** radon (222)
87 **Fr** francium (223)	88 **Ra** radium (226)	**	104 **Rf** rutherfordium (265)	105 **Db** dubnium (268)	106 **Sg** seaborgium (271)	107 **Bh** bohrium (270)	108 **Hs** hassium (277)	109 **Mt** meitnerium (276)	110 **Ds** darmstadtium (281)	111 **Rg** roentgenium (280)	112 **Cn** copernicium (285)	113 **Uut** (284)	114 **Fl** flerovium (289)	115 **Uup** (288)	116 **Lv** livermorium (293)	117 **Uus** (294)	118 **Uuo** (294)

Lanthanide Series*

57 **La** lanthanum 138.9	58 **Ce** cerium 140.1	59 **Pr** praseodymium 140.9	60 **Nd** neodymium 144.2	61 **Pm** promethium (145)	62 **Sm** samarium 150.4	63 **Eu** europium 152.0	64 **Gd** gadolinium 157.2	65 **Tb** terbium 158.9	66 **Dy** dysprosium 162.5	67 **Ho** holmium 164.9	68 **Er** erbium 167.3	69 **Tm** thulium 168.9	70 **Yb** ytterbium 173.0	71 **Lu** lutetium 175.0

Actinide Series**

89 **Ac** actinium (227)	90 **Th** thorium 232	91 **Pa** protactinium 231	92 **U** uranium 238	93 **Np** neptunium (237)	94 **Pu** plutonium (244)	95 **Am** americium (243)	96 **Cm** curium (247)	97 **Bk** berkelium (247)	98 **Cf** californium (251)	99 **Es** einsteinium (252)	100 **Fm** fermium (257)	101 **Md** mendelevium (258)	102 **No** nobelium (259)	103 **Lr** lawrencium (262)

Los Alamos NATIONAL LABORATORY

CHEMISTRY

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. Dendrites, consisting primarily of naumannite (silver selenide) and lesser amounts of electrum, sphalerite, chalcopyrite, tetrahedrite, and other silver minerals (dark gray to black areas), quartz (light gray areas), and quartz and a minor amount of illite (beige to white areas). Sample is from the Buckskin National Mine, Humboldt County, Nevada. Photograph by Peter Vikre, U.S. Geological Survey.

Selenium

By Lisa L. Stillings

Chapter Q of

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

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

Professional Paper 1802–Q

U.S. Department of the Interior
RYAN K. ZINKE, Secretary

U.S. Geological Survey
William H. Werkheiser, Acting Director

U.S. Geological Survey, Reston, Virginia: 2017

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Conversion Factors

International System of Units to Inch/Pound

Multiply	By	To obtain
Length		
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)
Area		
hectare (ha)	2.471	acre
square kilometer (km^2)	247.1	acre
square meter (m^2)	10.76	square foot (ft^2)
square centimeter (cm^2)	0.1550	square inch (ft^2)
square kilometer (km^2)	0.3861	square mile (mi^2)
Volume		
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^3)	264.2	gallon (gal)
cubic centimeter (cm^3)	0.06102	cubic inch (in^3)
cubic meter (m^3)	1.308	cubic yard (yd^3)
cubic kilometer (km^3)	0.2399	cubic mile (mi^3)
Mass		
microgram (µg)	0.00000003527	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]
Deposit grade		
gram per metric ton (g/t)	0.0291667	ounce per short ton (2,000 lb) (oz/T)
Pressure		
megapascal (MPa)	10	bar
gigapascal (GPa)	10,000	bar
Density		
gram per cubic centimeter (g/cm^3)	62.4220	pound per cubic foot (lb/ft^3)
milligram per cubic meter (mg/m^3)	0.00000006243	pound per cubic foot (lb/ft^3)
Energy		
joule (J)	0.0000002	kilowatthour (kWh)
joule (J)	6.241×10^{18}	electronvolt (eV)
joule (J)	0.2388	calorie (cal)
kilojoule (kJ)	0.0002388	kilocalorie (kcal)

International System of Units to Inch/Pound

Multiply	By	To obtain
Radioactivity		
becquerel (Bq)	0.00002703	microcurie (µCi)
kilobecquerel (kBq)	0.02703	microcurie (µCi)
Electrical resistivity		
ohm meter (Ω-m)	39.37	ohm inch (Ω-in.)
ohm-centimeter (Ω-cm)	0.3937	ohm inch (Ω-in.)
Thermal conductivity		
watt per centimeter per degree Celsius (watt/cm °C)	693.1798	International British thermal unit inch per hour per square foot per degree Fahrenheit (Btu in/h ft^2 °F)
watt per meter kelvin (W/m-K)	6.9318	International British thermal unit inch per hour per square foot per degree Fahrenheit (Btu in/h ft^2 °F)

Inch/Pound to International System of Units

Multiply	By	To obtain
Length		
mil	25.4	micrometer (µm) [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)
Volume		
ounce, fluid (fl. oz)	29.57	milliliter (mL)
ounce, fluid (fl. oz)	0.02957	liter (L)
Mass		
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)
Deposit grade		
ounce per short ton (2,000 lb) (oz/T)	34.285714	gram per metric ton (g/t)
Energy		
kilowatthour (kWh)	3,600,000	joule (J)
electronvolt (eV)	1.602×10^{-19}	joule (J)
Radioactivity		
microcurie (µCi)	37,000	becquerel (Bq)
microcurie (µCi)	37	kilobecquerel (kBq)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:
$$°F = (1.8 \times °C) + 32$$

Temperature in degrees Celsius (°C) may be converted to kelvin (K) as follows:
$$K = °C + 273.15$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:
$$°C = (°F - 32) / 1.8$$

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 (µS/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 (µg/L), nanogams 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 (µg/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 (µCi/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).

Concentration unit	Equals
milligram per kilogram (mg/kg)	part per million
microgram per gram (µg/g)	part per million
microgram per kilogram (µg/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=0.0000000001 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- (µ-)	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

°C	degree Celsius
µg/d	microgram per day
AC	alternating current
AIDS	acquired immunodeficiency syndrome
CIGS	copper-indium-gallium-selenide
cm	centimeter
DC	direct current
EMPA	electron microprobe analysis
EPA	U.S. Environmental Protection Agency
g/d	gram per day
GWh	gigawatt-hour
HIV	human immunodeficiency virus
IMA	International Mineralogical Association
IOCG	iron oxide-copper-gold
kg	kilogram
kg/t	kilogram per metric ton
km	kilometer
lb	pound
MDEQ	Michigan Department of Environmental Quality
mg/d	milligram per day
ng/L	nanogram per liter
org-Se(-II)	organo-selenide
pm	picometer
ppb	part per billion
ppm	part per million
RDA	recommended daily allowance
Se(II)	selenide
Se(IV)	selenite
Se(VI)	selenate
USGS	U.S. Geological Survey
VMS	volcanogenic massive sulfide
WHO	World Health Organization

Selenium

By Lisa L. Stillings

Abstract

Selenium (Se) was discovered in 1817 in pyrite from copper mines in Sweden. It is a trace element in Earth's crust, with an abundance of three to seven orders of magnitude less than the major rock-forming elements. Commercial use of selenium began in the United States in 1910, when it was used as a pigment for paints, ceramic glazes, and red glass. Since that time, it has had many other economic uses—notably, in the 1930s and 1940s, when it was used in rectifiers (which change alternating current to direct current), and in the 1960s, when it began to be used in the liner of photocopier drums. In the 21st century, other compounds have replaced selenium in these older products; modern uses for selenium include energy-efficient windows that limit heat transfer and thin-film photovoltaic cells that convert solar energy into electricity.

In Earth's crust, selenium is found as selenide minerals, selenate and selenite salts, and as substitution for sulfur in sulfide minerals. It is the sulfide minerals, most commonly those in porphyry copper deposits, that provide the bulk of the selenium produced for the international commodity market. Selenium is obtained as a byproduct of copper refining and recovered from the anode slimes generated in electrolytic production of copper. Because of this, the countries that have the largest resources and (or) reserves of copper also have the largest resources and (or) reserves of selenium.

Because selenium occurs naturally in Earth's crust, its presence in air, water, and soil results from both geologic reactions and human activity. Selenium is found concentrated naturally in soils that overlie bedrock with high selenium concentrations. Selenium mining, processing, use in industrial and agricultural applications, and disposal may all contribute selenium to the environment. A well-known case of selenium contamination from agricultural practices was discovered in 1983 in the Kesterson National Wildlife Refuge in California. There, waters draining from agricultural fields created wetlands with high concentrations of dissolved selenium in the water. The selenium was taken up by aquatic wildlife and caused massive numbers of embryonic deformities and deaths.

Regulatory agencies have since worked to safeguard ecological and human health by creating environmental exposure guidelines based upon selenium concentrations in water and in fish tissue. Any attempt to regulate selenium concentrations requires a delicate balance because selenium occurs naturally and is also a vital nutrient for the health of wildlife, domestic stock, and humans. Selenium is commonly added as a vitamin to animal feed, and in some regions of the United States and the world, it is added as an amendment to soils for uptake by agricultural crops.

The important role of selenium in economic products, energy supply, agriculture, and health will continue for well into the future. The challenge to society is to balance the benefits of selenium use with the environmental consequences of its extraction. Increased understanding of the elemental cycle of selenium in the earth may lead to new (or unconventional) sources of selenium, the discovery of new methods of extraction, and new technologies for minimizing the transfer of selenium from rock to biota, so to protect environmental and human health.

Introduction

Selenium (Se) was discovered in 1817 (and named in 1818) by the Swedish chemist Jöns Jacob Berzelius, who became interested in the sludge left over after the processing of pyrite from the copper mines at Falun, Sweden. The sludge was red in color and developed the unpleasant smell of rotten radishes when it was heated. Berzelius had first thought that the sludge contained tellurium but determined that the material, though having close affinities with tellurium, was a previously unknown element. Because of its affinity with tellurium (from Latin *tellus*, meaning Earth), the element was named selenium after the Greek word *selene*, meaning Moon, or satellite of Earth (Sindeeva, 1964; Lakin and Davidson, 1973; Boyd, 2011).

In the past, selenium has been described as a somewhat mysterious element, one that can be "a metal or nonmetal, a conductor or nonconductor, amorphous or crystalline, colorant or deodorant, [or] a hydrogenator or dehydrogenator" (Sargent, 1954, p. 1). It can be either red or black (Sargent, 1954) and, when ingested, either a necessary nutrient or a poison (Trelease and Beath, 1949). It is fair to say that today, almost 200 years after the discovery of selenium, scientific

understanding has reconciled these seemingly contradictory descriptions. The complexity of selenium chemistry in economic, environmental, and geologic contexts is better understood yet remains a topic of research.

Selenium is a trace element in Earth's crust with an average crustal abundance of 0.05 part per million (ppm). Its abundance is three to seven orders of magnitude less than that of the major rock-forming elements (fig. Q1), and it is one-half to three orders of magnitude less abundant than the rare-earth elements. It is, however, more abundant (by one to four orders of magnitude) than the rarest metals, such as platinum, palladium, and gold.

Selenium is photovoltaic, meaning that it converts light into electricity. It is also photoconductive, meaning that its electrical conductivity increases with increasing light. These are the properties that make selenium useful in photovoltaic cells and solar panels, and are among the reasons why selenium has been classified as an energy-critical element (American Physical Society Panel on Public Affairs and the Materials Research Society, 2011). This chapter provides an overview of the geochemical cycle of selenium at Earth's surface and includes sections on selenium's occurrence in mineral deposits, its production and consumption, its presence in the environment, and its role in both human and environmental health.

Uses and Applications

Before World War I, according to Sargent (1954, p. 8), "selenium was regarded as the abomination of the smelterman and was discarded." Today, in comparison, selenium is considered an "energy critical element" that is important for renewable energy technologies (American Physical Society Panel on Public Affairs and the Materials Research Society, 2011), and it is also known to be an essential nutrient for humans and livestock.

Commercial use of selenium in the United States began in 1910; at that time, selenium was used as a pigment for paints, ceramic glazes, and red glass. The first large-scale commercial use of selenium began in 1915, when selenium was substituted for manganese in glassmaking. Manganese, which was used to neutralize the green tint in glass caused by iron impurities, had previously been obtained from Russia, but the supply of manganese was disrupted during World War I. Selenium, in concentrations of 0.04 to 0.14 kilogram per metric ton (kg/t) in glass, was found to be a good substitute for manganese. In addition, greater concentrations of selenium were found to provide a pink tint to glass, and at concentrations of 0.45 to 2.3 kg/t, could produce a desirable ruby red glass for use in tableware, automobile taillights, and traffic signals. The modern sheet-glass industry uses selenium in energy-efficient
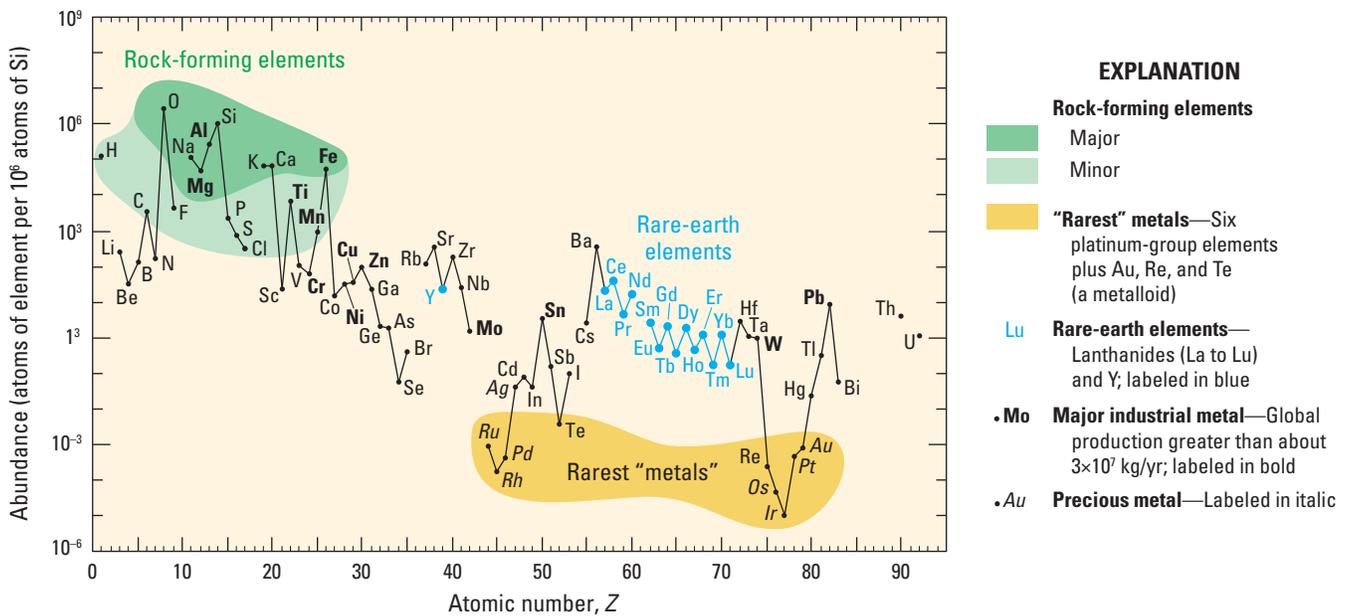
Figure Q1.   Graph showing relative abundance of the chemical elements in Earth's upper crust (from Haxel and others, 2002). Selenium (Se) is a trace element with an estimated concentration of approximately 0.05 part per million in Earth's crust (Greenwood and Earnshaw, 1997). See the periodic table at the front of this publication for definitions of element abbreviations. kg/yr, kilogram per year

windows to help limit the heat transfer from sunlight (Sargent, 1954; Butterman and Brown, 2004).

After glassmaking, the next largest commercial use for selenium was the selenium rectifier. Rectifiers, which change alternating current (AC) to direct current (DC), had been known about since 1884, but they were not extensively used until inventors improved the devices in 1930 (Sargent, 1954). After this time, rectifiers began to be used in arc lamps, battery chargers, DC motors, electroplating, magnet coils, and welding. The military used selenium rectifiers in World War II for aircraft controls, ground starters for aircraft, guided missiles, radar equipment, and numerous other applications. In 1947, miniature rectifiers were developed that could be used in radio and television circuits. This miniaturization was a tremendous improvement because the new technology could deliver 200 to 500 volts of DC from a 117-volt AC source, thus eliminating the need for the older heavy and bulky transformers and rectifier tubes, and saving greater than 0.23 kilogram (kg) of copper and 3.4 kg of steel per television set (Sargent, 1954).

Soon after World War II, many other uses for selenium were developed. Selenium became important in the rubber industry where it acted as an accelerator and vulcanizing agent, and it was also used to improve the resilience of rubber by increasing its resistance to heat, oxidation, and abrasion. Selenium was used as a pigment to produce orange, red, and maroon colors in the post-World War II plastics industry and in ceramics, dyes, inks, leather, paints, paper, rubber, soap, and other products. It was used to either hydrogenate or dehydrogenate organic compounds, crude oil, and coal, and it assisted in the production of edible fats, plastics, soaps, and waxes. It provided antioxidant properties to inks and oils, as well as nondrying properties to linseed, oiticica, and tung oils. Selenium began to be used in personal care products, such as dandruff and dermatitis shampoos and soaps, and in deodorants. It was also included in fungicides, herbicides, and insecticides. Finally, selenium came to be used in the steel industry to improve the machinability of stainless steel. Forging steels contained 0.18 to 0.22 percent selenium, and machining-grade steel contained 0.30 to 0.35 percent. A small amount of selenium (0.01 to 0.05 percent) assured a fine-grained and bubble-free texture in cast steel. Selenium was also added to copper and copper alloys to improve machinability and tensile strength (Sargent, 1954; Butterman and Brown, 2004).

The 1960s saw yet another expansion in the industrial use of selenium—as a coating on photocopier drums. Xerography, which was the forerunner to modern-day photocopying machines, was invented in 1938 and patented in 1942. It gained commercial popularity in the late 1950s when an automated process was developed using a cylindrical drum coated with selenium. Even today, in the 21st century, the majority of paper documents are produced xerographically, either on photocopiers or laser printers, which employ a similar process but use materials other than selenium as the photoreceptor (Owen, 2004).

By 1973, 40 percent of the selenium consumed in the United States was a high-purity grade used for electrostatic printing (xerography), rectifiers, exposure meters, photoelectric cells, and optical lenses. Thirty percent went toward the manufacturing of glass. Fourteen percent was used for inorganic pigments, mainly in the form cadmium sulfoselenide, which have good light stability and heat resistance and were used in enamels, inks, paints, plastics, and rubber. In the 1990s, amorphous silicon and organic compounds started to replace selenium in xerographic drums, and the use of selenium in the photocopier industry began to decline (fig. Q2; Lakin and Davidson, 1973).
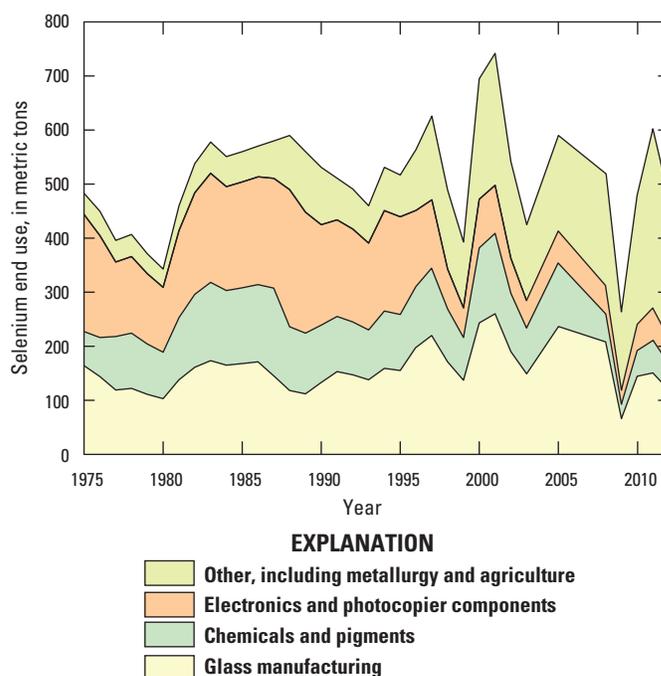
Figure Q2.   Graph showing end uses for selenium in the United States from 1975 to 2012. Data are unavailable for the years 2004, 2006, and 2007; hence, these data are interpolated. End use amounts for the years 2008 through 2012 are calculated as domestic apparent consumption of selenium multiplied by the fraction of world consumption attributed to each type of use. Data are from U.S. Geological Survey (2006–13, 2010–14, 2014b).

In the 21st century, potentially large-scale demand for selenium could result from the manufacture of thin-film photovoltaic cells that employ a copper-indium-gallium-selenide (CIGS) alloy for converting solar energy into electricity. As of 2010, silicon-based photovoltaic cells still dominated the solar energy market and accounted for greater than 90 percent of all photovoltaic cells in use. These photovoltaic cells are comparatively inefficient, however, and convert only about 15 percent of adsorbed light to electricity in actual outdoor use (Bleiwas, 2010). Recent research on the second-generation

photovoltaic thin-film cells that use CIGS technology is showing increased efficiencies of 20 to 40 percent and leading to lower production costs. Selenium is a critical element in the CIGS technology and contributes to the higher levels of light absorption and conversion to electricity demonstrated by these second-generation thin-film cells.

Bleiwas (2010) described the quantities of selenium and other metals required to produce thin-film CIGS photovoltaic cells with enough capacity (1 gigawatt) to produce 8,760 gigawatt-hours (GWh) of electricity (enough to supply 800,000 average U.S. households) annually. He calculated that 180 metric tons of selenium would be needed to produce this quantity of CIGS photovoltaic cells, which is 7.6 percent of the estimated 2013 world refinery production of selenium. The required quantities of gallium and indium necessary for this technology are 30 and 90 metric tons, or 7 percent and 11 percent of the 2014 worldwide production of these metals, respectively (Bleiwas, 2010).

Demand and Availability of Supply

Sargent (1954) provided a picture of selenium as a critical element in the post-World War II years. As noted above, 1947 was a critical year because of the development of a miniature selenium rectifier. For much of the 1940s and 1950s, selenium consumption outpaced primary refinery production, and the difference was made up from imports and releases from industry stockpiles (fig. Q3).

To safeguard the supply of selenium, the Federal Government had begun holding selenium in a strategic stockpile in the 1940s, although data on the size of the stockpile were confidential (Clark, 1950). Increased concerns regarding possible shortages became apparent when, in February 1952, the National Production Authority placed both imported and domestically produced selenium under a "complete allocation" in order to meet essential defense requirements with respect to steelmaking and rectifiers. This allocation was discontinued in early 1953, although consumption continued to be higher than domestic production through 1960 (with the exception of 1957, fig. Q3; Sargent, 1954; Massachusetts Institute of Technology, 2010; American Physical Society Panel on Public Affairs and the Materials Research Society, 2011). Ingerson (1964) noted that, throughout the 1950s and early 1960s, production and consumption of selenium was "nip and tuck," and that there was not a sufficient stockpile of selenium to last more than a few months. The situation was so "precarious" that selenium was constantly listed in Group I (that is, one of the most important) in the national stockpile list of strategic and critical materials. In 1961, the U.S. Bureau of Mines reported that the Federal stockpile held 254,000 pounds (lb) (115 metric tons) of selenium (U.S. Bureau of Mines, 1963), and, in 1964, the Office of Emergency Planning increased the stockpile objective for selenium to 475,000 lb (215 metric tons) (U.S. Bureau of Mines, 1965).

By 1970, the balance between supply and demand had shifted—selenium consumption became consistently less than the total available supply (primary refinery production plus imports plus release from stockpiles) and the excess selenium was available for export (fig. Q3; Lakin and Davidson, 1973). In August 1971, Congress authorized the disposal of the national stockpile, and the last lot was sold on May 26, 1976 (U.S. Bureau of Mines, 1973, 1978). Despite the sufficient domestic supply of selenium, however, there was some concern in 1973 of an impending shortage of selenium owing to (a) the increased use of in situ leaching for copper production from its ores, which did not allow for recovery of associated selenium, and (b) the discovery that selenium was necessary for animal nutrition. It was learned that selenium deficiency in commercial feed could result in death and disease for poultry and livestock; this happened in a number of countries and led to heavy economic losses. The deficiency could be reversed, however, by adding selenium to fertilizer for agricultural lands. Lakin and Davidson (1973) estimated that 5.7 million kilograms per year of selenium would be required to treat the most severely deficient agricultural lands in the United States.

Jensen (1985) tracked the supply of and demand for selenium from 1973 to 1983 by comparing selenium production from U.S. mines to total U.S. supply, including available stockpiles. During this period, U.S. primary refinery production peaked at 360 metric tons in 1973, dropped to a low of 140 metric tons in 1980, and recovered to 350 metric tons (revised) in 1983 (U.S. Bureau of Mines, 1989). The total U.S. supply was always higher than mine production during this period, with a high of 831 metric tons in 1974 and a low of 581 metric tons in 1977. (Jensen's calculations include the entire quantity of selenium held in stockpiles, and not the change in stockpile mass, as indicated in fig Q3.) The difference between mine production and total supply was owing to the refineries' use of U.S. Government selenium stockpiles, selenium imports, and industry stockpiles. The largest releases from the U.S. Government stockpile took place in 1973 and 1974 (150 and 55 metric tons, respectively) (U.S. Bureau of Mines, 1980). The last shipment took place in 1976, and since then, refineries have relied on an increased supply of selenium from imports (fig. Q3).

George (2013) tracked the price of selenium from 1970 to 2010 (fig. Q4). As with any commodity, the price reflects supply and demand. By using yearly prices in 1992 constant dollars, George showed that the price of selenium in the 1970s was higher than it was in 2010. Prices spiked far above 2010 prices during 1974–76 because of the elimination of the U.S. Government selenium stockpile, low commercial inventories, reduced domestic inventories, and increased demand for plain-paper copiers. Prices remained relatively steady from 1981 to 2003, at approximately $4 to $12 per pound (in 1992 dollars), because there was sufficient worldwide supply, because selenium substitutes were available for many industrial applications, and because there were no new large-scale uses for selenium. The price rise and volatility for
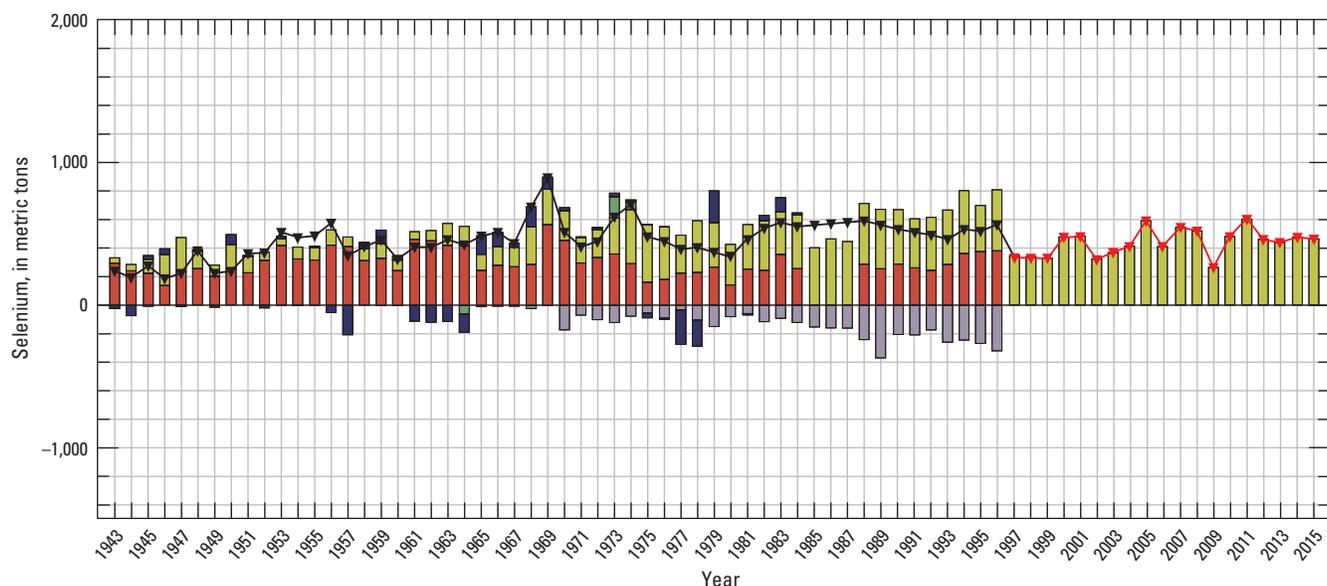
Figure Q3.   Graph illustrating a mass balance for selenium in the United States from 1943 to 2015. The supply of selenium to the United States is estimated from primary refinery production plus imports for consumption (meaning that material is added to the supply for that year), minus exports from the United States (removal of selenium from the supply for that year—shown as a negative quantity), plus or minus changes in Government and industry stockpiles (releases are shown as positive quantities and additions are shown as negative quantities), to calculate domestic apparent consumption.

Data from 1943 to 2014 are from U.S. Geological Survey (2014c), and data for 2015 are from U.S. Geological Survey (2017). Primary refinery production numbers are not available for 1985 to 1987, and from 1997 to 2015, they are withheld because they are proprietary; hence, no primary refinery production data are plotted for these years. For the years 1985 to 1987, apparent consumption data have been estimated by linear interpolation. For 1997 to 2015, domestic apparent consumption data are withheld to avoid disclosing company proprietary data, and imports for consumption are used as a proxy for apparent consumption (U.S. Geological Survey, 2014c, 2017). The Federal Government held selenium in a strategic stockpile in the 1940s, but data on the size of the stockpile were confidential (Clark, 1950, p. 1342). The U.S. Bureau of Mines reported the quantity of selenium held in the national stockpile in 1961 (U.S. Bureau of Mines, 1966, p. 1071) and continued to report the size of the stockpile until the last of the selenium was sold on May 26, 1976 (U.S. Bureau of Mines, 1978, p. 1467), and there has been no stockpile since 1976. The USGS reported numbers for the industry-held stockpile from 1944 through 1984, but these values have been withheld since 1985 to avoid disclosing company proprietary data (U.S. Geological Survey, 2014c). Domestic secondary production of selenium (selenium recovered from recycled rectifiers, catalysts, and photocopier drums) was never a large percentage of domestic supply and was inconsistently reported during the period 1943–2016 and thus is not included in this compilation.

selenium since 2003 is attributed mainly to increased demand for selenium from manganese producers in China. Manganese, which is an alloying element in steel production, is produced by an electrolytic process. Substitution of selenium dioxide ($SeO_{2(g)}$) for sulfur dioxide ($SO_{2(g)}$) lowers the energy requirements of the electrolytic cells, allowing manganese to be produced more cheaply.

Supply

The period from 1945 to 1960 was a period when selenium demand (apparent consumption) outpaced supply from primary refinery production (1957 was an exception). During this time, U.S. primary refinery production averaged 290 metric tons per year; U.S. producers were American Smelting & Refining Co., U.S. Metals Refining Co., and International Smelting & Refining Co. (fig. Q3). During 1961–64, the total supply of selenium was greater than consumption, and the extra supply was stored in industry and Government stockpiles (fig. Q3). Primary refinery production decreased in 1965–68, and selenium was released from stockpiles to meet demand. Beginning in 1969, the total supply of selenium has been sufficient to meet demand, and excess supply has been exported.
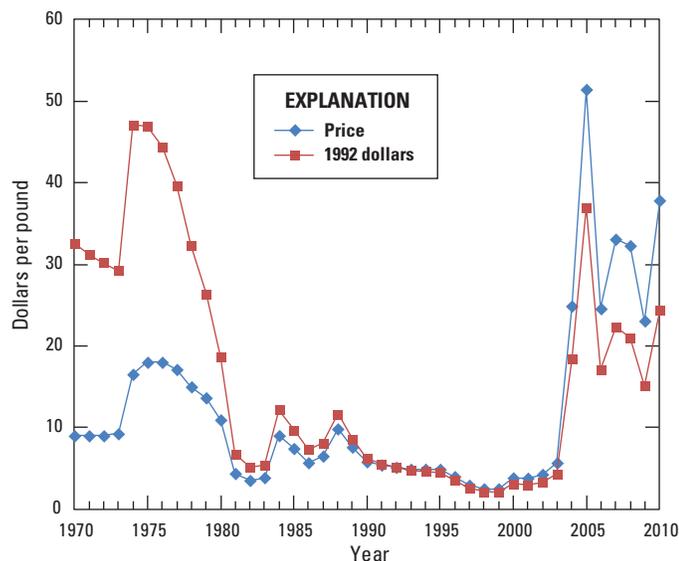
Domestic production from 1947 to 1953, which was the beginning of selenium consumption for modern technologies, contrasts markedly with production nearly 50 years later. The latest available report of domestic selenium production was for 1996, when 379,000 kg (379 metric tons) of selenium was produced as a primary product. Production figures were not published after 1996 to avoid disclosing proprietary data from the one or two known domestic refineries, and because selenium-containing residues and anode slimes from other domestic copper refiners were exported for processing.

Just as U.S. domestic production of selenium increased in the years following 1947, so did global production. Sargent (1954) reported that during 1926–31, the Soviet Union produced between 2.3 and 2.7 metric tons per year of selenium. In 1946, Canada produced 237 metric tons, although this production level could not be sustained owing to a reduction in output of selenium-rich high-grade ores from the Horne Mine at Noranda, Quebec, Canada; by 1950, Canada's production fell to less than 160 metric tons. In 1951, Sweden produced 41 metric tons; Belgium, 10 metric tons; and West Germany, 7.3 metric tons. In 1952, Belgium increased its production to 17 metric tons, and Africa produced 14 metric tons. Belgium increased production again in 1953 to about 27 metric tons, and production in the Soviet Union in that year was estimated to have increased to 45 metric tons.

Total global production in 1996 (the last year for which domestic production numbers were reported) was 2,250 metric tons, and the United States accounted for almost 17 percent of global production, or about 380 metric tons. U.S. production ranked third behind Canada (694 metric tons) and Japan (588 metric tons). During the years 1997 to 2015, Japan was the leading international producer of selenium, although it briefly slipped into second place in 2005. Germany was the second-ranked international producer in 2015. China and the United States produced selenium during this time period as well, but their production numbers are not available (U.S. Geological Survey, 1997–2014).

Demand

From 1943 to 2015, U.S. consumption of selenium was between 184 (1946) and 896 (1969) metric tons per year (fig. Q3) and was affected by increased substitution

Significant events affecting selenium prices since 1970

1974–76 Government stocks liquidated by 1974; low commercial inventories; reduced domestic production from recession and copper industry strike; increased import dependence; continued growth in plain-paper copiers

1976–80 Stock buildup and reduced demand following 1973–75 recession; production level established at about one-half of 1969 peak

1981–83 Demand surged; stocks remained high; plain-paper copiers and glass manufacturing dominate demand

1984–89 World stocks declined as demand outstrips production; speculation encouraged price fluctuations; domestic demand averaged 1.3 million pounds

1990–91 World production rose; demand slackened owing to recession; stock decline was reversed

1990–99 Organic photoreceptor compounds replaced selenium compounds for plain-paper copiers

2003–10 Increased but fluctuating demand from manganese producers in China; global financial crisis in 2008 reduced demand but supplies remained tight, and prices remained relatively high

Figure Q4.   Graph showing average annual prices of commercial-grade selenium from 1970 to 2010. Both the nominal (unadjusted) prices and real prices (in 1992 constant dollars) are shown. Graph is from George (2013).

of other materials for selenium and changes in technology that made many selenium products obsolete. As examples, high-purity silicon replaced, or has become a major substitute for, selenium in rectifiers; silicon can substitute for selenium in photovoltaic cells; and amorphous silicon and organic photoreceptors have replaced selenium in photocopier drums. Organic pigments can substitute for cadmium sulfoselenide pigments; cerium oxide (CeO) can substitute for selenium in glass; tellurium can substitute for selenium in pigments and rubber compounding; bismuth, lead, and tellurium can substitute for selenium in metal alloys; and tellurium can substitute for selenium in lead-free brass. Even with a potential increased use of selenium in CIGS photovoltaic solar cells, the demand for selenium will likely remain steady for the near future.

Recycling

Traditionally, selenium has been used in U.S. manufacturing for glass decolorizers, pigments, fertilizers, animal feeds, and metal alloys. These have been termed "dissipative" uses because of the small amounts of selenium involved, the sheer number of these products, and the difficulty in recovering selenium from them because of the disposal or recycling practices for the products. Even when selenium-containing glass and metal alloys are recycled, they are not segregated from other forms of scrap, and the selenium content is probably volatilized during melting. Major nondissipative uses for selenium have been as photoreceptors in photocopier drums and as rectifiers; however, manufacturers began to replace selenium with organic photoreceptor compounds in the 1980s; consequently, there is no longer a substantial supply of photocopier drums containing selenium for recycling, and large selenium rectifiers have been replaced with ones that use silicon. Even the use of selenium in AC current rectifiers has ended, as silicon-based rectifiers have been developed that are cheaper and more reliable. As a result of this lack of supply, no selenium recycling facilities remain in operation in the United States. This may change in the future as selenium is increasingly used in the manufacture of thin-film CIGS photovoltaic cells for solar panels (George and Wagner, 2009).

Geology

The distribution of selenium in Earth's crust is closely associated with that of sulfur (S), and because of their similar ionic radii—198 picometers (pm) for Se(-II) versus 184 pm for S(-II)—selenium readily substitutes for sulfur in structures of sulfide minerals. Selenium is less commonly found in sulfate deposits. Selenium is brought to Earth's surface by way of magmatic intrusions, where it is found in sulfide minerals, and by way of volcanic emissions, where it is vented as the gases selenium dioxide (SeO_2) and hydrogen selenide (H_2Se).

Crustal Abundance

The crustal abundance of selenium has been estimated in different ways. Sindeeva (1964) estimated 0.14 ppm selenium for rocks in the Soviet Union; Brunfelt and Steinnes (1967) estimated 0.04 ppm based on standard rock samples provided by the U.S. Geological Survey (USGS), and Wells (1967) reported an average of 0.6 ppm selenium in volcanic ash samples from New Zealand and 0.4 ppm in New Zealand lava flows (Lakin and Davidson, 1973, and references therein).

An indirect method for estimating selenium abundance was suggested by Goldschmidt and Strock (1935) based upon an estimated sulfur-to-selenium ratio of 6,000:1 in sulfide minerals. Starting with the crustal abundance for sulfur of 520 ppm, they divided this number by the sulfur-to-selenium ratio and arrived at an estimate of 0.09 ppm selenium in Earth's crust. Turekian and Wedepohl (1961) revised the crustal abundance of sulfur to 300 ppm, and by using the same sulfur-to-selenium ratio of 6,000:1, they estimated 0.05 ppm selenium in Earth's crust. This figure of 0.05 ppm remains the accepted estimate of the crustal abundance of selenium today (fig. Q1; Greenwood and Earnshaw, 1997).

Mineralogy

Selenium forms selenide minerals and selenite and selenate salts with chalcophile elements (for example, bismuth, copper, lead, mercury, and silver). Some of the natural selenides, such as berzelianite (Cu_2Se), clausthalite ($PbSe$), guanajuatite (Bi_2Se_3), krutaite ($CuSe_2$), tiemannite ($HgSe$), and umangite (Cu_3Se_2) form from selenium-rich hydrothermal fluids (Pirri, 2002) in deposits that "span the magmatic-hydrothermal spectrum" (Ciobanu and others, 2006, p. 163)—from 65 to 300 degrees Celsius (°C), as determined from fluid inclusion and isotopic studies, up to 800 °C in laboratory synthesis studies. Other selenium-bearing minerals, such as aguilarite (Ag_4SeS), contain selenium and sulfur in isomorphic substitution, and some systems show a continuous solid solution between selenium and sulfur end members. Selenium forms only one oxide mineral: downeyite (SeO_2). The selenium minerals recognized by the International Mineralogical Association (IMA) are listed in table Q1 at the back of this chapter. In a literature survey of selenium concentrations reported in worldwide sulfide and selenide deposits, selenium concentrations in selenides can be as high as 70.23 weight percent, such as in trogtalite ($CoSe_2$), which is found in the Musonoi Mine in the Democratic Republic of the Congo (Congo [Kinshasa]), and up to 4,617 ppm in sulfides, such as in bornite (Cu_5FeS_4) in the Glava Mine (in Sweden) and the Grusen, Moberg, Tinnsjå, and Tjøstølflaten Mines (all in Norway) (table Q2 at back of chapter).

In the Dana classification system for minerals (Gaines and others, 1997), selenium minerals are included in Classes 02 and 03 with sulfides and sulfosalts, respectively. This hierarchical

system emphasizes the similarity between sulfides and selenides with respect to their chemistry, atomic characteristics, and crystal structure. In selenium-bearing hydrothermal systems, selenium may commonly substitute into sulfides, such as bornite, chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$), digenite (Cu_9S_5), galena (PbS), molybdenite (MoS_2), pyrite (FeS_2), and vaesite (NiS_2) (Simon and others, 1997).

Significant selenium concentrations can be found in sulfide minerals, and numerous studies have been conducted to determine whether the selenium-sulfur content represents a continuous solid solution between end members, whether a compositional gap exists in an apparent solid-solution series, or whether the presence of selenium in a sulfide mineral is merely an opportunistic isomorphic substitution.

Phases in the silver-gold-sulfur-selenium system show ready substitution of selenium for sulfur and, in some cases, continuous solid solution exists; for example, from αAg_2Se to αAg_3AuSe_2 (α indicates the high temperature structural modification of these phases—naumannite [Ag_2Se] to fischesserite [Ag_3AuSe_2]) (Simon and Essene, 1996). Many mineral phases in this system are found in the Broken Hills deposit of the Hauraki goldfield in New Zealand. Using electron microprobe analysis (EMPA), Cocker and others (2013) observed phases with morphologies and compositions similar to the known minerals aguilarite and fischesserite, and uytenbogaardtite (Ag_3AuS_2) and petrovskaite (AuAg(S,Se)), but with atomic sulfur-to-(sulfur+selenium) ratios falling between the known members. For example, they observed substitution of selenium into uytenbogaardtite, with a sulfur-to-(sulfur+selenium) ratio that ranges from 0.55 to almost 1. They noted, however, that uytenbogaardtite and fischesserite cannot be end members of a solid solution series because the two minerals possess different crystal structures (tetragonal and isometric [cubic], respectively).

Likewise, solid solution would not be expected between the phases acanthite (Ag_2S) and aguilarite (Ag_4SeS) because they belong to different crystal systems. Whereas chemical analyses have shown significant substitution of sulfur and selenium between these two phases, this may be an analytical error owing to their occurrence as fine intergrowths with one another. It is unclear whether the chemical analyses come from chemically homogenous grains or whether the size of the analytical spot size produces a composite analysis. Many of the phases in the Broken Hills deposit showed compositions that do not match known minerals and may form a continuum between approximately $(Ag,Au)_8S_3$ and $(Ag,Au)_8Se_3$ (Cocker and others, 2013).

Sometimes a solid solution may be present in only one polymorph of a mineral composition. For example, solid solution may exist between the low-temperature orthorhombic mineral structures of naumannite, and aguilarite at temperatures from below 120 to 135 °C. At higher temperatures, they invert to their cubic polymorphs (Petruk and others, 1974). EMPA analyses of Cocker and others (2013) show a compositional gap between these low-temperature orthorhombic phases, but data from Izawa and others (1990) suggest

that these phases may show solid solution between atomic selenium-to-(selenium+sulfur) ratios of 0.57 to 0.88.

Other systems with solid solution compositions include lead-sulfur-selenium systems, where solid solution has been observed between clausthalite (PbSe) and galena (PbS) (Simon and Essene, 1996). Examples are found in various uranium-vanadium deposits of the Colorado Plateau (Coleman, 1959) and in the Niederschlema-Alberoda uranium-selenium-polymetallic deposit in Erzgebirge, Germany, where Förster (2005) documented the entire clausthalite to galena solid solution covering the range of $PbS_{1.00}$ to $Pb(S_{0.04}Se_{0.96})$.

Complete solid solution can also be found between cinnabar (HgS) and tiemannite (HgSe); sphalerite (ZnS) and stilleite (ZnSe); and native selenium (Se^0) and native tellurium (Te^0). Quaternary systems show extensive or complete solid solution at higher temperatures (Simon and Essene, 1996). At 800 °C, Drabek (1995) observed a complete solid solution between molybdenite (MoS_2) and molybdenum diselenide ($MoSe_2$) under dry laboratory conditions with a high fugacity of selenium to sulfur (f_{Se2}/f_{S2}) ratio.

Selenium-bearing sulfides may form as a replacement texture in ore deposits. Paniagua (1995) suggested that selenium-rich vaesite ($Ni(S,Se)_2$) and selenium-rich villamaninite (($(Cu,Ni,Co,Fe)(S,Se)_2$) of the Providencia Mine in Leon, Spain, are breakdown products of copper-nickel disulfides and that these phases show incremental substitution of sulfur by selenium with increasing copper+nickel contents because of increasing bonding distances within the structure. Many studies point to the formation of selenium-bearing sulfides during late stages of ore mineralization. For example, in epithermal gold-silver deposits in western Nevada, selenium enrichment is observed in late-stage stibnite (Sb_2S_3) and sphalerite, and in arsenian rims on earlier formed pyrite and marcasite (FeS_2; John and others, 2003). John and others (2003) conclude that selenides are common in late-stage ores found in veins and breccias that fill open-spaces, and form from the reaction of late-stage selenium-rich ore fluid (formed after substantial boiling and loss of hydrogen sulfide [H_2S] to vapor) with the initial alteration sulfide assembly.

Because of the close association between selenium and sulfur, Simon and Essene (1996) made a systematic thermodynamic study of the stability of selenide minerals relative to sulfides, oxides, and native elements. Their conclusions were that (a) the stability fields of selenides, in general, are more restricted than sulfide minerals, given similar fugacity values of $S_{2(g)}$ and $Se_{2(g)}$ (represented by $f Se_{2(g)}$ and $f S_{2(g)}$, respectively); (b) in hydrothermal fluids, most oxide minerals are unstable relative to their corresponding selenide mineral; and (c) for a given selenide, the larger the stability field, the more commonly it is found in ore deposits; for example, clausthalite.

In a companion paper to the above, Simon and others (1997) discussed the thermodynamic conditions that favor deposition of selenide minerals instead of selenium-substituted sulfide minerals. They conclude that an oxidizing environment is needed to form most selenide minerals. High oxygen

fugacity values (fO$_{2(g)}$) enhance separation of selenium from sulfur, leading to high fSe$_{2(g)}$/fS$_{2(g)}$, which enables deposition of selenide minerals and limits the formation of sulfide minerals. In contrast, mineralizing systems characterized by low oxygen fugacity and the presence of sulfide minerals can deposit only silver selenides and selenium-substituted sulfide minerals.

Although some selenium is produced from gold and silver selenide deposits that have anomalously high concentrations of selenium (table Q2), most of the world's production of selenium metal is from copper, copper-nickel, and some lead and zinc sulfide deposits where selenium is found in isomorphous substitution with sulfur (Bleiwas, 2010). Table Q2 illustrates the range of selenium concentrations found in sulfur and selenium minerals worldwide.

Deposit Types

The compilation of selenium deposits provided by Sindeeva (1964) remains one of the most exhaustive in today's literature. Because the information is well organized and informative in its original form, the reader is referred to table 7 (p. 174) in "Mineralogy and Types of Deposits of Selenium and Tellurium" (modified as table Q3 in this report). Here, the author noted that selenium can be found in several genetic deposit types—magmatic, volcanic, hydrothermal, and exogenic (that is, produced by chemical and mechanical weathering at Earth's surface; Jackson, 1997). In Sindeeva's table, examples from hydrothermal deposits outnumber the rest combined. In the majority of the examples, selenium is found substituted into sulfide minerals, such as chalcopyrite, cinnabar, cobaltite (CoAsS), galena, molybdenite, pentlandite ((Fe,Ni,Co)$_9$S$_8$), pyrite, pyrrhotite (Fe$_{1-x}$S), sphalerite, and stibnite. Selenide minerals are less common than selenium-bearing sulfides, but such phases as clausthalite (PbSe), guanajuatite (Bi$_2$Se$_3$), naumannite (Ag$_2$Se), and penroseite (blockite) ((Ni,Co,Cu)Se$_2$), are found in veins and stockworks of hydrothermal deposits. The compilation includes some deposits where selenium can be found as selenites, selenates, and native selenium (for example, volcanic tuffs in Shoshone and Riverton, Wyoming).

As a result of a thorough investigation into selenium content of ore deposits and its mineral associations, Sindeeva (1964) concluded the following:

- Deposits containing independent selenium minerals are rare; instead, selenium usually occurs as an isomorphous substitution for sulfur in sulfide minerals.

- The largest resources of selenium are connected with ultrabasic and basic rocks and found in magmatic and hydrothermal chalcopyrite-pentlandite-pyrrhotite deposits, especially in sulfide veins that occur during late stages of formation.

- Pyrite deposits contain large resources of selenium, which seem to accompany late stages of mineralization.

- Copper and molybdenum deposits contain selenium, where the enrichment occurred in late-stage molybdenites.

- Polymetallic lead-zinc deposits can contain selenium.

- Gold deposits can contain selenium. Selenium will form independent minerals in these deposits if the ore contains very little sulfur; otherwise, it will be dispersed in sulfide minerals.

- Quartz-wolframite ((Fe,Mn)WO$_4$)-bismuth and cassiterite (SnO$_2$)-quartz-sulfide deposits are sometimes accompanied by selenium.

- Cobaltite-selenide-telluride resources that contain selenium are not frequently observed, but selenium can be associated with chloritization in this assemblage.

- Uranium deposits carry selenium but the co-occurrence of these elements could use more study.

- Cinnabar-stibnite deposits might contain appreciable selenium and could use more study.

Magmatic and Associated Hydrothermal Deposits

Aside from selenium minerals, selenium-bearing sulfide deposits represent the greatest known concentration of selenium in Earth's crust. The reported average selenium concentration in magmatic sulfides is 0.02 percent (Sargent, 1954). In intrusive rocks, selenium will substitute for sulfur in sulfide minerals because of their similar ionic radii. High-temperature sulfides, such as pentlandite and pyrrhotite, have a sulfur-to-selenium ratio of 7,000:1, and Goldschmidt (1954) estimated hydrothermal pyrite to have a sulfur-to-selenium ratio of between 10,000 and 20,000:1. In the Falun mining area of Sweden, selenium is present in the following sulfide minerals, in decreasing order of concentration: galena, chalcopyrite, arsenopyrite, sphalerite, pyrite, and pyrrhotite (Sindeeva, 1964).

Attempts have been made to standardize the estimate of selenium in sulfide ore minerals and the most commonly used number for the average selenium content in magmatic and associated hydrothermal sulfides is 0.02 percent. Other ratios exist; for example, in porphyry copper ore with 0.5 percent copper, the selenium content is 2.5 ppm, or a copper-to-selenium ratio of 2,000:1 (Sargent, 1954; Lakin and Davidson, 1973). The U.S. Geological Survey and the former U.S. Bureau of Mines have long based their selenium production estimates on copper production figures using a factor of 0.0215 percent. Because copper ore from Canada has a higher selenium content, however, a factor of 0.064 percent is used to estimate selenium produced from its ores (for example, selenium in ore from mines located in the Sudbury basin of Ontario, Canada (table Q4; Jensen, 1985; George and Wagner, 2009).

Table Q3.   Selenium concentrations in sulfide minerals and other phases, in various deposit types.

[Data are from Sindeeva, 1964. Do., do., ditto; wt. %, weight percent; n.r., not reported, although the deposit was described as containing selenium and (or) selenide minerals; b.d.l., below detection limit; Hg, mercury; S, sulfur; Se, selenium]

Deposit type	Deposit name, Location	Mineral phase	Selenium concentration (weight percent unless otherwise indicated)
Hydrothermal			
Chalcopyrite-molybdenite	Agarak deposit, Armenia	Chalcopyrite	0.004
Do.	do.	Molybdenite	0.0131 to 0.0134
Do.	do.	Pyrite	0.006
Do.	Dastakert deposit, Armenia	Bornite	0.0066
Do.	do.	Chalcopyrite-pyrite	0.003
Do.	do.	Galena	0.0057
Do.	do.	Molybdenite	0.0016
Do.	do.	Pyrite	0.0036
Do.	do.	Sphalerite	n.r.
Do.	Dzhindara deposit, Armenia	Molybdenite	0.04
Do.	Kadzharan deposit, Armenia	Chalcopyrite	0.0052
Do.	do.	Molybdenite	0.028 to 0.0513
Do.	do.	Pyrite	0.0015 to 0.0063
Do.	Miskhana deposit, Armenia	Molybdenite	0.0056
Do.	do.	Pyrite	0.008
Cinnabar-stibnite	Almaden, Idria, Spain	Mercury ores may contain Hg,Se-tiemannite, sometimes in an isomorphous series with metacinnabar	n.r.
Do.	San Onofrio, Mexico	Onofrite, Hg(S,Se)	1:3.9 S:Se ratio
Cobaltite-selenide-telluride	Upper Seymchanskoye deposit, Verina River basin, Russia	Selenide ore	0.0001 to 0.002
Gold-selenium	Eisenberg, near Korbach, Germany	Clausthalite (common)	n.r.
Gold-silver-quartz-adularia	Comstock and Goldfield, Nevada, United States	n.r.	n.r.
Do.	El Oro, Mexico	n.r.	n.r.
Do.	Redzhang Lebong deposit, Sumatra, Indonesia	n.r.	0.02
Pyritic	Uchaley deposit, Russia	Pyrite with chalcopyrite and sphalerite	0.0004 to >0.01
Quartz-gold ore	Kirovskoye deposit, Russia	Arsenopyrite	0.0006 to 0.019
Do.	do.	Bismuthinite	0.2800 to 0.3275
Do.	do.	Chalcopyrite	0.0008 to 0.003
Do.	do.	Jamesonite	≤0.003
Do.	do.	Pyrite	≤0.003

Table Q3. Selenium concentrations in sulfide minerals and other phases, in various deposit types.—Continued

[Data are from Sindeeva, 1964. Do., do., ditto; wt. %, weight percent; n.r., not reported, although the deposit was described as containing selenium and (or) selenide minerals; b.d.l., below detection limit; Hg, mercury; S, sulfur; Se, selenium]

Deposit type	Deposit name, Location	Mineral phase	Selenium concentration (weight percent unless otherwise indicated)
Hydrothermal—Continued			
Quartz-wolframite-bismuth	Bukuka deposit, Russia	Bismuthinite	0.016
Do.	do.	Chalcopyrite	0.0012
Do.	do.	Galena	0.0116
Do.	do.	Molybdenite	0.006
Do.	do.	Pyrite	0.0175
Do.	do.	Pyrrhotite	0.0013
Do.	do.	Sphalerite	0.0017
Do.	do.	Wolframite	b.d.l.
Selenide	Pacajake deposit, Bolivia	Blockite (penroseite) is main ore mineral, also naumannite; mined for gold in World War II	n.r.
Uranite-selenide	Katanga deposit, Democratic Republic of the Congo (Congo [Kinshasa])	Reported to contain selenides	n.r.
Do.	Shinkolobse deposit, Democratic Republic of the Congo (Congo [Kinshasa])	Selenide minerals in 114th horizon	19
Magmatic			
Magmatic	Noril'sk, Siberia, Russia	Bornite	0.01 to 0.015
Do.	do.	Chalcopyrite	0.005 to 0.020
Do.	do.	Magnetite	Trace
Do.	do.	Millerite	0.001
Do.	do.	Pentlandite	0.0067
Do.	do.	Pyrite	Trace
Do.	do.	Pyrrhotite	0.0036 to 0.014
Volcanic			
Andesite tuffs	Shoshone, Jasper, and Riverton deposits, Wyoming, United States	n.r.	0.003 to 0.012
Native sulfur	Hawaiian Islands	n.r.	5.18
Do.	Kurile Islands, additional Kamchatka locations, Russia	n.r.	0.0005 to 0.19
Do.	Lipari Islands , Italy	n.r.	1.13
Do.	Mendeleev Volcano, Kunashir Island, Russia	n.r.	0.12
Do.	Mutnovskii Volcano, Kamchatka, Russia	n.r.	0.08
Do.	New Zealand	n.r.	0.3 and 0.19
Do.	Paramushir Island, Russia	n.r.	0.19

Exceptions can always be found to these general estimates; for example, selenium can be present in concentrations of hundreds of parts per million in tuffaceous rocks, and concentrations of several percent can be found in sulfides that host mercury and antimony deposits (Lakin and Davidson, 1973).

In magmatic sulfide deposits associated with mafic rocks, selenium may be found substituted for sulfur in sulfide veins. Sindeeva (1964) estimated the selenium content in such deposits to vary between 0.002 and 0.01 percent, although concentrations of as high as 0.017 percent and as low as 0.0003 percent have been found. The Permian-to-Triassic-age Noril'sk group of sulfide deposits, which are located in Siberia, Russia, inside the Arctic Circle, are representative of this type of mineralization (table Q3), as are the sulfide deposits from the Sudbury basin in Ontario, Canada (table Q4).

At Noril'sk, the selenium of economic interest is contained in sulfide minerals, where it occurs from isomorphous substitution for sulfur in concentrations of 2 to 74 ppm. Massive vein deposits at Noril'sk display greater concentrations of selenium than its disseminated ores, with a range of 0.0036 to 0.015 percent selenium in massive vein deposits owing to the greater proportion of copper sulfides in the vein deposits; however, no correlation has been found between selenium and any of the elements copper, lead, nickel, sulfur, or tellurium. Distribution of selenium depends upon the composition of the ore as well as the location of the sample within the orebody and with respect to the structural setting (table Q3). The rocks surrounding the ore deposits (andesites, diabases, and gabbros) contain merely 0.00001 percent (0.1 ppm) selenium (Sindeeva, 1964).

In addition to magmatic sulfide ores, Sindeeva (1964) considered the volcanic deposits of native sulfur and tuffs. She observed selenium concentrations of 0.0005 to 5.18 percent in sulfur deposits and 0.003 to 0.012 percent selenium in andesite tuffs that had partially transformed to bentonite in the Oligocene-age Jasper, Riverton, and Shoshone deposits in Wyoming (table Q3).

The porphyry copper deposits that host much of the selenium produced worldwide are large breccia and vein-hosted deposits found genetically related to granitoid porphyry intrusions. They form at convergent plate margins, and most are of Cenozoic or Mesozoic age, although they can range from Archean to Quaternary (John and others, 2010). John and others (2010) argued that porphyry copper mineralization forms from magmatic fluids released during emplacement of porphyritic stocks. Selenium in sulfides of porphyry copper deposits is originally transported in hypogene fluids but may also be remobilized during hydrothermal alteration of the porphyry copper system.

Many workers have attempted to employ the selenium-to-sulfur ratio in the ore minerals to ascertain whether external sulfur was involved in the genesis of mineralization. Selenium-to-sulfur ratios ranging from 0.00023:1 to 0.00035:1

have been assigned to mantle-derived rocks (Eckstrand and Hulbert, 1987), and ratios lower than this are found when sulfur is contributed from external fluids and (or) host rocks (for example, Ripley, 1990). Fitzpatrick (2008) measured selenium-to-sulfur ratios in minerals from three deposits: a volcanogenic massive sulfide (VMS) deposit in Flin Flon, Canada; a high-sulfidation epithermal deposit in Pierina, Peru; and an iron oxide-copper-gold (IOCG) deposit in Mantoverde, Chile. By combining the selenium-to-sulfur ratios with $\delta^{34}S$ values, Fitzpatrick demonstrated that the VMS and epithermal deposits displayed high selenium-to-sulfur ratios and low $\delta^{34}S$ values, which is typical of magmatic fluids; the IOCG deposit, however, showed the opposite signal, suggesting dilution of a magmatic fluid with a seawater-derived basinal fluid. He concluded that selenium-to-sulfur ratios can help identify the fluid source(s) for mineralization, and that the addition of $\delta^{34}S$ values extended the usefulness of this tracer.

Other studies have employed selenium as an exploration 'vector' to discriminate among mineralization signatures found proximal or distal to a fluid source. Bornite and chalcocite show some potential for this work (Cook and others, 2011). Zonation of selenium concentration has also been observed in marine systems, and high selenium concentrations have been observed in black smoker deposits and iron-copper massive sulfides associated with the East Pacific Rise. Here, high selenium values occur in high-temperature mineral assemblages of the inner part of the deposit, which are in equilibrium with pure, unmixed hydrothermal fluids. The lowest selenium values are found in the outer part of the deposit, where mineralization is influenced by mixing of hydrothermal fluids and seawater (Auclair and others, 1987).

Table Q4.   Selenium concentrations in copper-nickel ores in the Sudbury basin, Ontario, Canada.

Mine name	Ore type[1]	Selenium concentration[2] (parts per million)
Murray	Massive sulfide	32 to 64
	Gabbro peridotite inclusion sulfide	82
Creighton	Interstitial sulfide	26
	Ragged disseminated sulfide	20
	Gabbro peridotite inclusion sulfide	42
	Massive sulfide	65
Garson	Contorted schist inclusion sulfide	22
Levack	Interstitial sulfide in sublayer norite	25
Frood	Disseminated sulfide in quartz diorite	28
	Interstitial sulfide	36
	Ragged disseminated sulfide	20

[1]Ore type classification is from Schwarcz (1973).

[2]Selenium analysis is from Nriagu and Wong (1983).

Selenide-Bearing Deposits

In contrast to Sindeeva (1964), who discussed all selenium-bearing deposits whether they contained selenium-bearing sulfides, selenides, selenates, selenites, or native selenium, Simon and others (1997) discussed deposits that contained selenide minerals only. Their purpose was to "determine the conditions that favor deposition of selenide minerals over substitution of selenium in sulfide minerals" (Simon and others, 1997, p. 468). Deposits were grouped into the following four types: (a) telethermal selenide vein-type, (b) unconformity-related uranium deposits, (c) sandstone-hosted uranium deposits (roll-front type), and (d) gold-silver epithermal volcanic-hosted deposits. The following brief descriptions of these four deposit types are taken mostly from Simon and others (1997):

a. *Telethermal selenide vein-type deposits* include selenide-bearing deposits like those of the Tilkerode-Zorge-Lerbach deposit in the Harz Mountains of Germany, the Pacajake and El Dragon deposits in Bolivia, the Hope's Nose deposit in the United Kingdom, and the Sierra de Umango and Sierra de Cacheuta deposits in Argentina. In these deposits, selenide minerals occur in veins or veinlets with carbonate minerals, gold, hematite (Fe_2O_3), platinum-group elements, and rare sulfides, and are commonly hosted in sedimentary rocks. Some of these deposits were classified as the "selenide-type" by Sindeeva (1964). Conditions for formation of these deposits include $fO_{2(g)}$ above the hematite-magnetite buffer (that is, in the hematite stability field) and a ratio of selenium-to-sulfur fugacities that is greater than one ($fSe_{2(g)}/fS_{2(g)} > 1$). Simon and others (1997) argue that the high fO_2 value helps to separate selenium from sulfur, thus preventing the incorporation of selenium into sulfides and allowing the system to form selenide minerals.

b. *Selenide minerals in unconformity-related uranium deposits* are found in vein deposits in the Bohemian Massif of the Czech Republic, the Massif Central of France, and the Athabasca area of northern Saskatchewan, Canada. Cobalt, copper, and nickel selenides in these deposits are associated with carbonates; cobalt, copper, and nickel sulfides and arsenides; hematite; and uraninite minerals. As with the vein-type deposits above, the conditions for selenide formation include $fO_{2(g)}$ values within the hematite stability field and a ratio of selenium-to-sulfur fugacities that is greater than one ($fSe_{2(g)}/fS_{2(g)} > 1$).

c. *Selenium-bearing sandstone-hosted uranium deposits (roll-front-type)* include the uranium and vanadium sandstone deposits of the Colorado Plateau, and similar deposits in Oklahoma, Wyoming, and Texas (Davidson, 1963; Howard, 1977). Davidson (1963) surveyed uranium deposits in oxidized sandstones ranging from Paleozoic to Cenozoic age in several States across the United States and found selenium concentrations that ranged from 3 to 4,500 ppm. In a survey by Coleman and Delevaux (1957), selenium concentrations up to 3 weight percent were measured in uranium deposits of the Colorado Plateau.

In the roll-front uranium deposits, selenium is commonly found in isomorphic substitution for sulfur in chalcocite, galena, marcasite, and pyrite. It is also found as the selenide minerals ferroselite ($FeSe_2$), clausthalite, and native selenium. Howard (1977) provided a good description of the location of selenium mineralization with respect to the redox interface of a roll-front-type uranium orebody. He described the uranium ore deposits as forming in gently dipping permeable sandstone units, sandwiched between units of lower permeability. Mineralization occurred as oxidizing meteoric solutions moved through the host sandstone and dissolved pyrite and other redox-active minerals. At the front of the plume of meteoric water, the solution lost its oxidizing potential and deposited iron, selenium, and uranium at the interface between oxidizing and reducing environments. In this model, selenium is commonly found as native selenium in the sandstone on the oxidized side of the redox boundary, as ferroselite in both goethite ($FeO(OH)$)-hematite and pyrite-marcasite associations on either side of the redox interface, and as ferroselite and native selenium within the uraninite-coffinite ($U(SiO_4)_{1-x}(OH)_{4x}$) assemblages of the orebody. In the unaltered reduced rock, selenium will be found as ferroselite or in isomorphous substitution with sulfur in pyrite. It is the continued cycle of oxidative dissolution (of reduced minerals in the unaltered rock) and redeposition (at the redox interface at the front of the groundwater plume) that serves to concentrate selenium, iron, and the uranium-ore minerals of these deposits (Howard, 1977).

d. *Selenide-bearing gold-silver epithermal volcanic-hosted deposits* are found at Hishikari, Japan; the western Great Basin, Nevada; the Great Barrier Island, New Zealand; Salida and Redzhang Lobong, Indonesia; Guanajuato, Mexico; and Prasolovskoye, Kunashir Island, Russia. Selenium in these deposits is primarily found in silver selenides and, less commonly, in bismuth, copper, and lead selenides, all associated with sulfides, sulfosalts, and native elements. John (2001) observed that the silver selenides aguilarite and naumannite are found in almost all low-sulfidation epithermal gold-silver deposits associated with Miocene bimodal magmatism in the Great Basin, Nevada. Selenium-bearing stibnite and sphalerite

are found among the ore-stage minerals, and selenium can be enriched in the gold-bearing arsenian rims found on pyrite and marcasite. It is thought that these deposits formed from hydrothermal fluids with $fO_{2(g)}$ below the hematite-magnetite buffer and have a ratio of selenium-to-sulfur fugacities that is less than one ($fSe_{2(g)}/fS_{2(g)} < 1$) (Simon and others, 1997). These conditions lead to a greater abundance of sulfides than selenides.

Sedimentary Rocks

The substitution of selenium for sulfur in biological processes leads to the presence of selenium in pyrite contained in black shales and coal, yet compared with magmatic rocks, the sulfur-to-selenium ratio in diagenetic pyrite is estimated to be 200,000:1 or higher (Goldschmidt, 1954). Selenium in detrital organic matter may be enriched many times above its crustal abundance. Highly organic shales may contain up to 1,500 ppm selenium. Marine phosphorites may contain as much as 300 ppm selenium. Coals of the United States have a geometric mean concentration of 1.7 ppm (Coleman and others, 1993).

Selenium concentrations in coal have been a topic of interest for many decades owing to the release of trace elements to the atmosphere during coal combustion. Coal contains 5 to 300 times the amount of selenium as average sedimentary and igneous rocks, and it is enriched 82 times above the average selenium concentration in Earth's crust (table Q5; Coleman and others, 1993). The study by Coleman and others (1993) analyzed almost 9,000 coal samples from across the United States (fig. Q5) and found that the highest selenium values (with a geometric mean of 4.9 ppm) are found in coals from Texas. Coal found in the Atlantic Coast region (Virginia and North Carolina) and coal in Alaska have the lowest geometric means, at 0.2 and 0.42 ppm selenium, respectively. The highest concentration in an individual sample (75 ppm) was observed in coals from northern Appalachia. Because of the close association of selenium with sulfur, it might be expected that selenium concentrations would correlate with concentrations of pyritic sulfur or organic sulfur, but this was not generally observed throughout the dataset. Coleman and others (1993) speculated that the lack of correlation may be owing to multiple sources of selenium, including detrital particles, plant matter, volcanic ash, surface water and groundwater, and epigenetic mineralization. They note, in addition, that selenium concentrations can be modified by diagenetic processes. Whereas selenium is shown to be closely associated with the organic fraction in coal, it is also found in selenium-bearing pyrite and galena, and as clausthalite. Selenium is also found in water-soluble and ion exchangeable forms.

Much of the Western United States is underlain by seleniferous sedimentary rocks whose ages range from Permian (for example, the Phosphoria Formation, which has phosphate rock members containing 1 to 1,200 ppm selenium),

to Cretaceous (for example, the Niobrara Formation and the Pierre Formation, which have selenium concentrations of 0 to 113 ppm, and 0 to 103 ppm, respectively) to Upper Cretaceous-Paleogene (for example, the Moreno Formation and the Kreyenhagen Formation of the California Coast Ranges, which have selenium concentrations that together range from 0.6 to 45 ppm) (table Q5; figs. Q6*A*–*C*; Presser and others, 1990). Trelease and Beath (1949) extensively mapped and documented the widespread extent of seleniferous bedrock in the Western United States as part of their study of the source of selenium in livestock food and forage (figs. Q6*A*–*B*). Seiler and others (2003) extended this survey in their work to identify the source of selenium contamination to irrigation waters in the Western United States (fig. Q6*C*). Presser and others (2004) attributed the high selenium concentration in these sedimentary bedrock units to its depositional origin in marine basins with high primary biological productivity. Selenium is cycled from ocean waters into bacteria, algae, fungi, and plants with the production of selenium-containing amino acids. Deposition of these species as organic detritus on the sea floor, and subsequent loss of organic matter from diagenesis resulted in accumulation and concentration of selenium and other trace elements in the sediments. This is the general model for trace-element enrichment in the Permian Phosphoria Formation (Piper, 1994, 2001) as well as in the Cretaceous and Paleogene marine formations of the Western United States (Presser and others, 2004). Preservation of selenium and other trace elements in these rocks is attributed to their high initial concentrations, retention by the sediments (often in an organic fraction), and extremely low accumulation of other diluting phases.

Resources and Reserves

More than 80 percent of global production of selenium is obtained as a byproduct of copper refining; it is recovered from anode slimes generated in electrolytic production of copper (Brown, 2002). The blister copper (that is, the partly refined copper formed during smelting) that serves as the anode in an electrolytic cell contains an average of 0.05 percent selenium (0.5 kg of selenium per metric ton of copper), but recovery ranges from 0.02 percent to 0.038 percent (0.2 to 0.38 kg of selenium per metric ton of copper; Lakin and Davidson, 1973). Other methods of refining copper, such as in situ leaching or the ISASMELT™ technology, do not recover selenium; hence, the global production of selenium is dependent on the method of copper refining. Because selenium production is mainly a byproduct of copper refining, countries with selenium resources and (or) reserves are those with resources and (or) reserves of copper, and they include Canada, Chile, China, Congo (Kinshasa), Mexico, Peru, the Philippines, Russia, the United States, and Zambia (Jensen, 1985; John and others, 2010). Minor amounts of selenium have also been recovered from lead, nickel, and zinc ores.
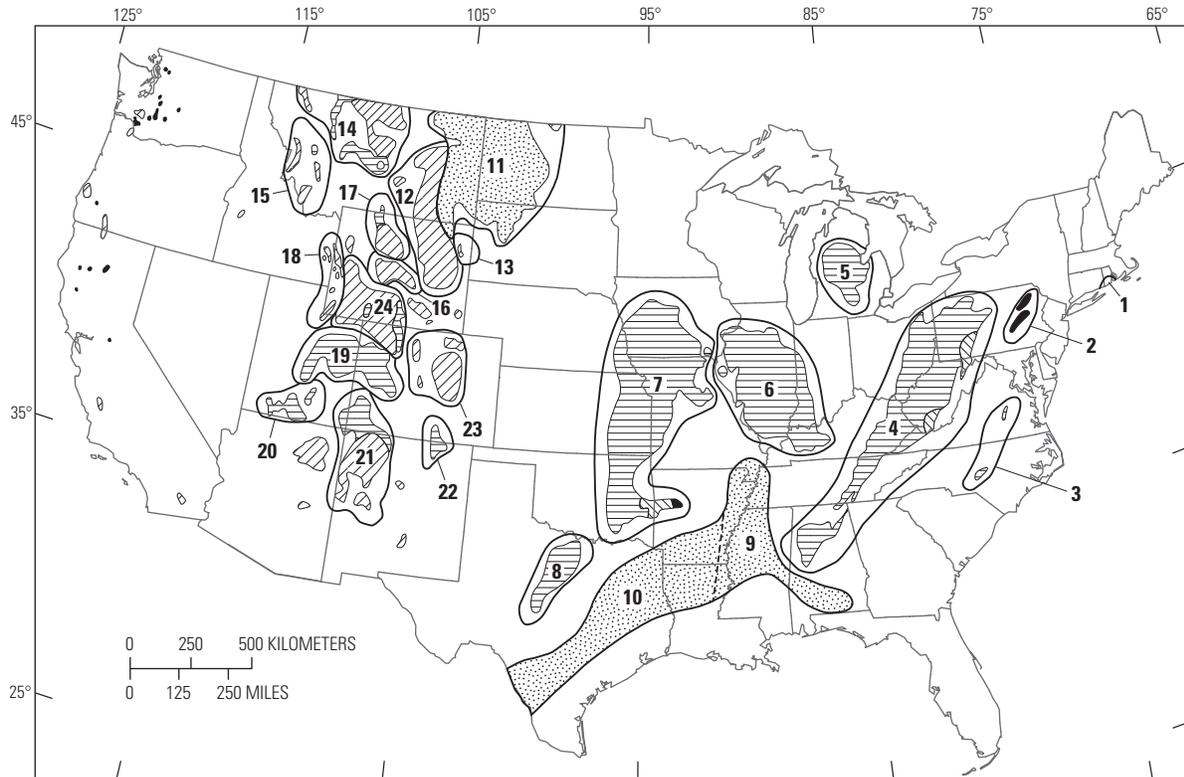
Region number and name	Selenium concentration, in ppm		Region number and name	Selenium concentration, in ppm
1 Rhode Island Meta-anthracite	—		13 Black Hills	—
2 Pennsylvania Anthracite	2.6		14 North Central	1.4
3 Atlantic Coast	—		15 Tertiary Lake Beds	—
4 Appalachian	2.7		16 Bighorn Basin	—
5 Northern Interior	2.3		17 Wind River	1.6
6 Eastern Interior	2.3		18 Hams Fork	1.1
7 Western Interior	2.4		19 Uinta	1.3
8 Southwestern Interior	—		20 Southwestern Utah	1.1
9 Mississippi	4.4		21 San Juan River	1.9
10 Texas	4.9		22 Raton Mesa	2.3
11 Fort Union	0.7		23 Denver	1.5
12 Powder River	0.8		24 Green River	1.1

EXPLANATION

Types of coal in fields
- Anthracite
- Low-volatile bituminous
- Medium- and high-volatile bituminous
- Subbituminous
- Lignite

Figure Q5.   Map showing selenium concentrations (in parts per million) in coal samples, by region of the United States. Selenium concentrations were analyzed in almost 9,000 U.S. coal samples. Data are plotted as the geometric means of samples from 24 regions. The map shows the highest selenium values (with a geometric mean of 4.9 ppm) are found in coals from Texas. Coal found in the Atlantic Coast region (Virginia and North Carolina) and coal in Alaska (not shown on the map) have the lowest geometric means, at 0.2 and 0.42 ppm selenium, respectively. The highest concentration in an individual sample (75 ppm) was observed in coals from the northern portion of the Appalachian region. Map is from Coleman and others (1993).

Table Q5.   Selenium concentrations in selected Earth and lunar materials.

[Biologic samples are dry weight unless otherwise noted. Abbreviations: ppm, part per million; ppb, part per billion; ng/L, nanogram per liter; nmol/kg, nanomole per kilogram]

Material	Source of material	Selenium concentration (and additional explanation)	Unit	Reference(s)
Rocks				
Earth's crust	Continental crust	0.05	ppm	Taylor (1964, p. 1280)
Earth's crust	Granite	0.01 to 0.05	ppm	Kabata-Pendias and Pendias (1984, p. 186)
Earth's crust	Limestone	0.03 to 0.10	ppm	Kabata-Pendias and Pendias (1984, p. 186)
Earth's crust	Phosphate rock	1 to 300	ppm	McNeal and Balistrieri (1989, and references therein)
Earth's crust	Sandstone	0.05 to 0.08	ppm	Kabata-Pendias and Pendias (1984, p. 186)
Earth's crust	Shale	0.6 (average)	ppm	Adriano (1986, p. 392)
Coal	World	3	ppm	Minkin and others (1984)
Coal	China	3.65	ppm	Zhang and others (1999)
Coal	United States	0.46 to 10.65	ppm	Pillay and others (1969, p. 480)
Coal	United States	1.7 (geometric mean)	ppm	Coleman and others (1993)
Marine shale	Kreyenhagen Formation	8.7 (median)	ppm	Presser (1994, p. 145)
Marine shale	Mancos Formation	0.1 to 5.46	ppm	Tuttle and others (2007, appendix tables)
Marine shale	Mead Peak Member, Phosphoria Formation	1 to 1,200; 182 (average)	ppm	Presser and others (2004)
Marine shale	Moreno Formation	6.5 (median)	ppm	Presser (1994, p. 145)
Marine shale	Niobrara Formation	0 to 30	ppm	Moxon and others (1938, p. 797–799)
Marine shale	Pierre Formation	0 to 103	ppm	Moxon and others (1938, p. 799–802)
Moon rocks	Apollo 11	0.12 to 1.6	ppm	Leutwein (1972, p. 34-C-3)
Moon rocks	Apollo 16	0.40 to 314	ppb	Krähenbühl and others (1973, p. 1328)
Soils and dusts				
Soil	Worldwide, seleniferous, upper limit	1,200	ppm	Winkel and others (2012, p. 572)
Soil	Worldwide, selenium-deficient, lower limit	<0.01	ppm	Winkel and others (2012, p. 572)
Soil	England and Wales	<0.01 to 4.7	ppm	Thornton and others (1983; as cited in McNeal and Balistrieri, 1989)
Soil	Finland, near a Cu-S orebody	0.1 to 5.5	ppm	Koljonen (1976, p. 263)
Soil	Ireland, seleniferous	≤1,200	ppm	Fleming (1962, p. 30)
Soil	Italy, volcanic	0.12 to 2.25	ppm	Floor and others (2011, p. 238)

Table Q5.   Selenium concentrations in selected Earth and lunar materials.—Continued

[Biologic samples are dry weight unless otherwise noted. Abbreviations: ppm, part per million; ppb, part per billion; ng/L, nanogram per liter; nmol/kg, nanomole per kilogram]

Material	Source of material	Selenium concentration (and additional explanation)	Unit	Reference(s)
Soils and dusts—Continued				
Soil	Sweden, agricultural	0.065 to 1.7	ppm	Johnsson (1992, section 4.1)
Soil	Sweden, background, not affected by agriculture	<0.45	ppm	Johnsson (1992, section 4.1)
Soil	United States	<0.1 to 4.3	ppm	Shacklette and Boerngen (1984, p. 4); Tidball (1984, p. H6)
Soil	United States	<0.2 to 8.3	ppm	Smith and others (2014, p. 197–202)
Soil	United States, seleniferous	2.7 to 90	ppm	Trelease and Beath (1949, p. 111–112)
Soil	United States, Hawaii, volcanic	1 to 20	ppm	Floor and Román-Ross (2012, p. 521)
Atmospheric dust	Major U.S. cities, 1941	0.05 to 10	ppm	Lakin and Byers (1941, p. 20)
Biologic samples				
Algae	Freshwater	<2.0	ppm	Jenkins (1980; as cited in McNeal and Balistrieri, 1989)
Animal tissue	Domestic stock	0.44 to 4.0	ppm	Frost (1972, p. 471)
Whole fish	Freshwater	0.05 to 2.87 (wet weight)	ppm	May and McKinney (1981, p. 35)
Whole fish	Marine	0.1 to 20	ppm	Hall and others (1978, p. 94–98)
Water				
Seawater	Pacific Ocean, 18° N., 108° W.	0.95 to 2.44	nmol/kg	Cutter and Bruland (1984, p. 1183)
River water	Amazon River	0.00021	ppm	Kharkar and others (1968, p. 290)
River water	Colorado River, United States	0.01 to 0.4	ppm	Scott and Voegeli (1961; as cited in McNeal and Balistrieri, 1989)
River water	Finland, stream sediments	0.26	ppm	Wang (1994; as cited in Parkman and Hultberg, 2002)
River water	Mississippi River, United States	0.000114	ppm	Kharkar and others (1968, p. 290)
Lake water	Finland, lakes affected by agriculture	76.8	ng/L	Wang (1994; as cited in Parkman and Hultberg, 2002)
Lake water	Finland, lakes, background, not affected by agriculture runoff	56 to 62	ng/L	Wang (1994; as cited in Parkman and Hultberg, 2002)
Lake water	Sweden	43 to 209	ng/L	Parkman and Hultberg (2002)
Lake water	United States, Lake Michigan	0.083	ppb	Robberecht and Van Grieken (1982, p. 839)
Lake water	Finland, lake sediment	0.27 to 3.64	ppm	Wang (1994; as cited in Parkman and Hultberg, 2002)

In 1973, the USGS estimated the world's identified resources of selenium to be almost 13 million metric tons (28.6 billion pounds) based upon the selenium content of identified resources of coal, copper, lead, and pyrite. Estimates from copper resources were made using a ratio of 0.325 kg of selenium recovered per metric ton of copper produced. Selenium from lead ores was estimated based upon an average of 10 ppm selenium in galena and the estimate of identified lead resources. Estimates for selenium in pyrite were made assuming 10 ppm selenium in pyrite and estimates of the

sulfur resources in pyrite. Selenium resources in coal were estimated using estimates for coal resources and an average of 1.5 ppm Se in coal. Lakin and Davidson (1973) noted that although the estimated resource of selenium in coal was two orders of magnitude greater than that in copper resources, it could not be easily recovered. As of 2016, the recovery of selenium from coal is technically feasible but not economical.

In contrast, modern estimates of selenium reserves in table Q6 are based only on copper reserves and do not include selenium found in other copper resources or in lead,
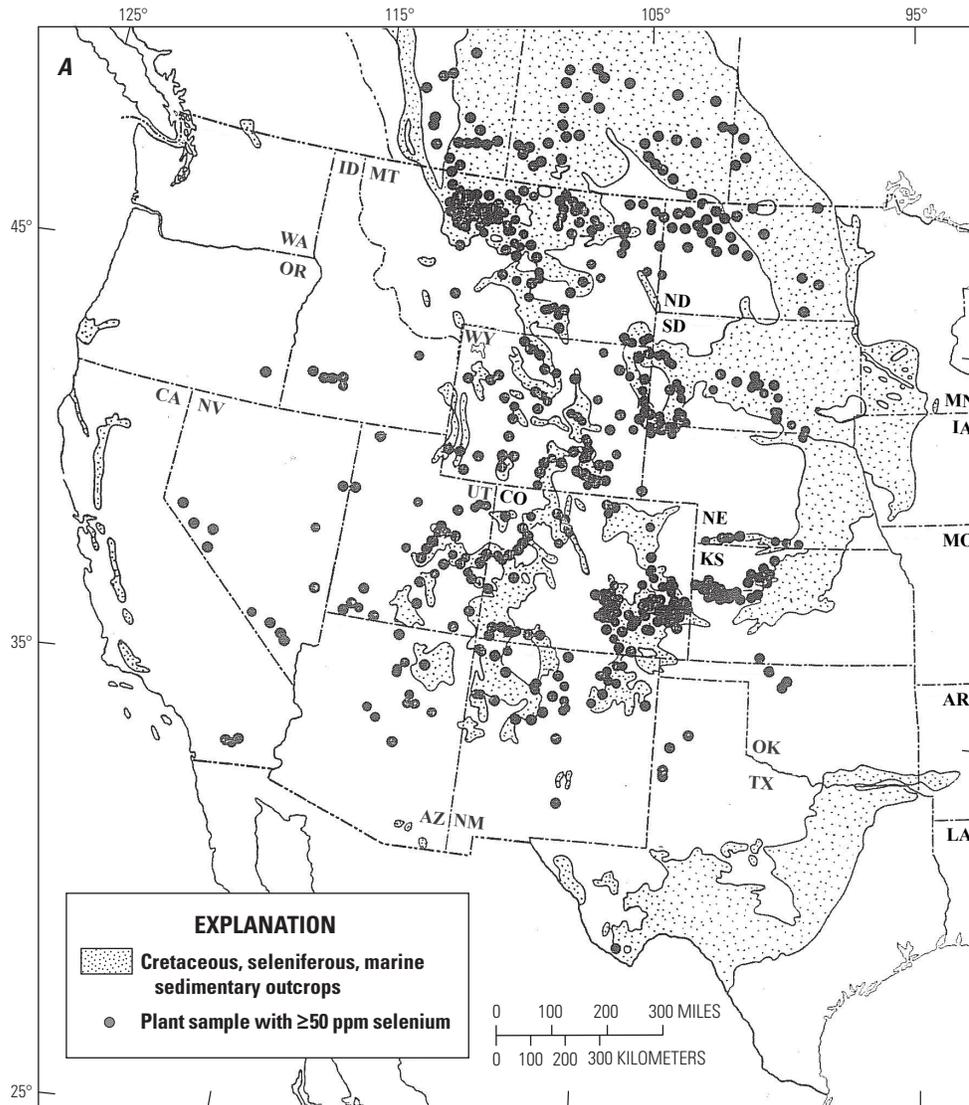
Figure Q6. Maps showing locations of seleniferous sedimentary outcrops and deposits and plant samples with significant selenium content. This map, *A*, shows the spatial relation among locations of Cretaceous, seleniferous, marine sedimentary outcrops and plant samples with greater than or equal to 50 parts per million (ppm) selenium. Map *A* is from Trelease and Beath (1949) and, with map *B*, shows the widespread extent of seleniferous bedrock across the Western United States and its correlation with selenium in plant samples.

pyrite, and coal resources. The fraction of copper reserves expected to be recovered by leaching and electrowinning is subtracted from the total because these processes do not recover selenium. The estimates are derived, as mentioned previously, by using a recovery factor of 0.215 kg of selenium per metric ton of primary recoverable electrolytic copper (0.0215 percent). In Canada, where the selenium content of copper ore is higher, a factor of 0.64 kg of selenium per metric ton of copper (0.064 percent) is employed (Butterman and Brown, 2004; George and Wagner, 2009). Global supplies of selenium have steadily increased over the past few years owing to an increase in copper production.

Identified Resources

No deposits in the world are mined for selenium alone. Instead, as discussed above, selenium is produced mostly as a byproduct of copper refining. Whereas Japan and Germany (in order of output) were the leading producers of selenium in the world in 2015 (U.S. Geological Survey, 1997–2014), the selenium was sourced from copper concentrates and residues supplied from mining operations in Africa, Asia, Australia, and South America (Bleiwas, 2010). Of the global reserves of 120,000 metric tons of selenium, almost 60 percent is located in Chile, China, and Russia combined, whereas
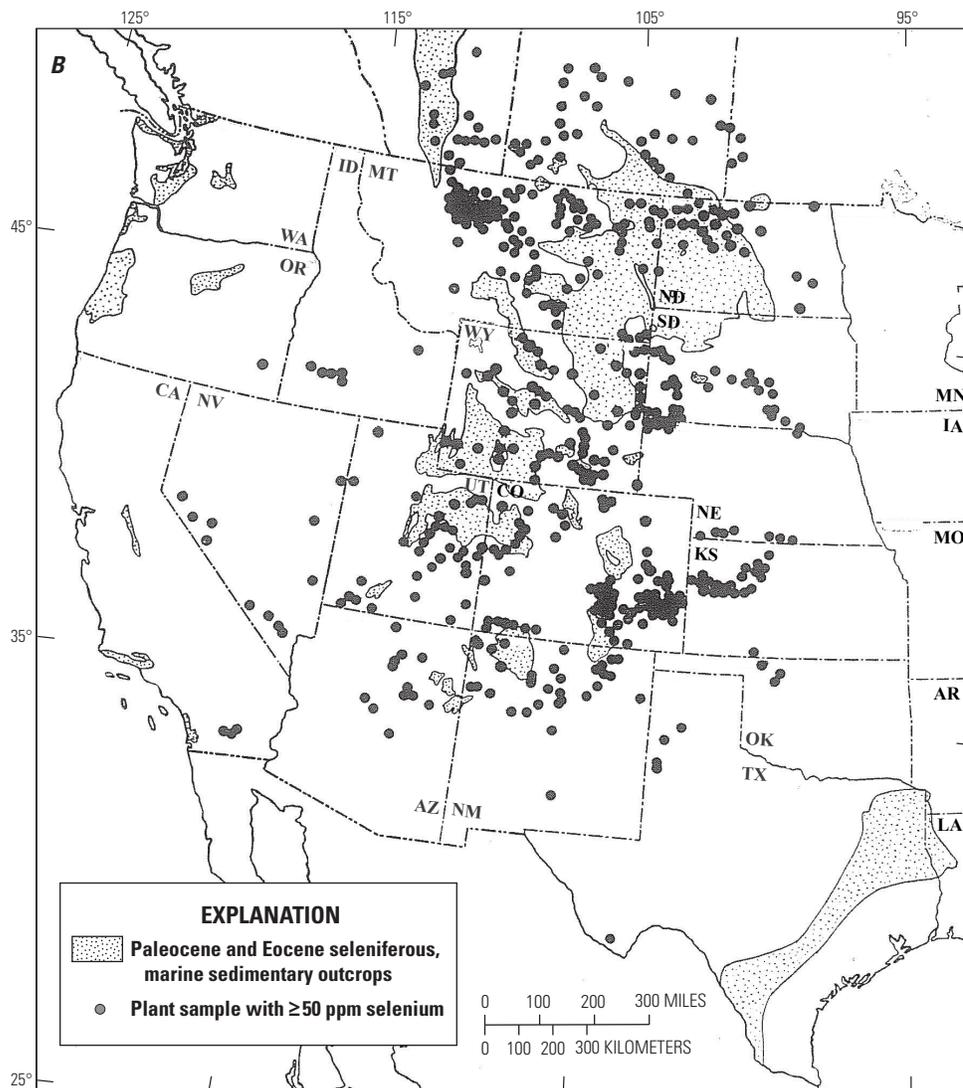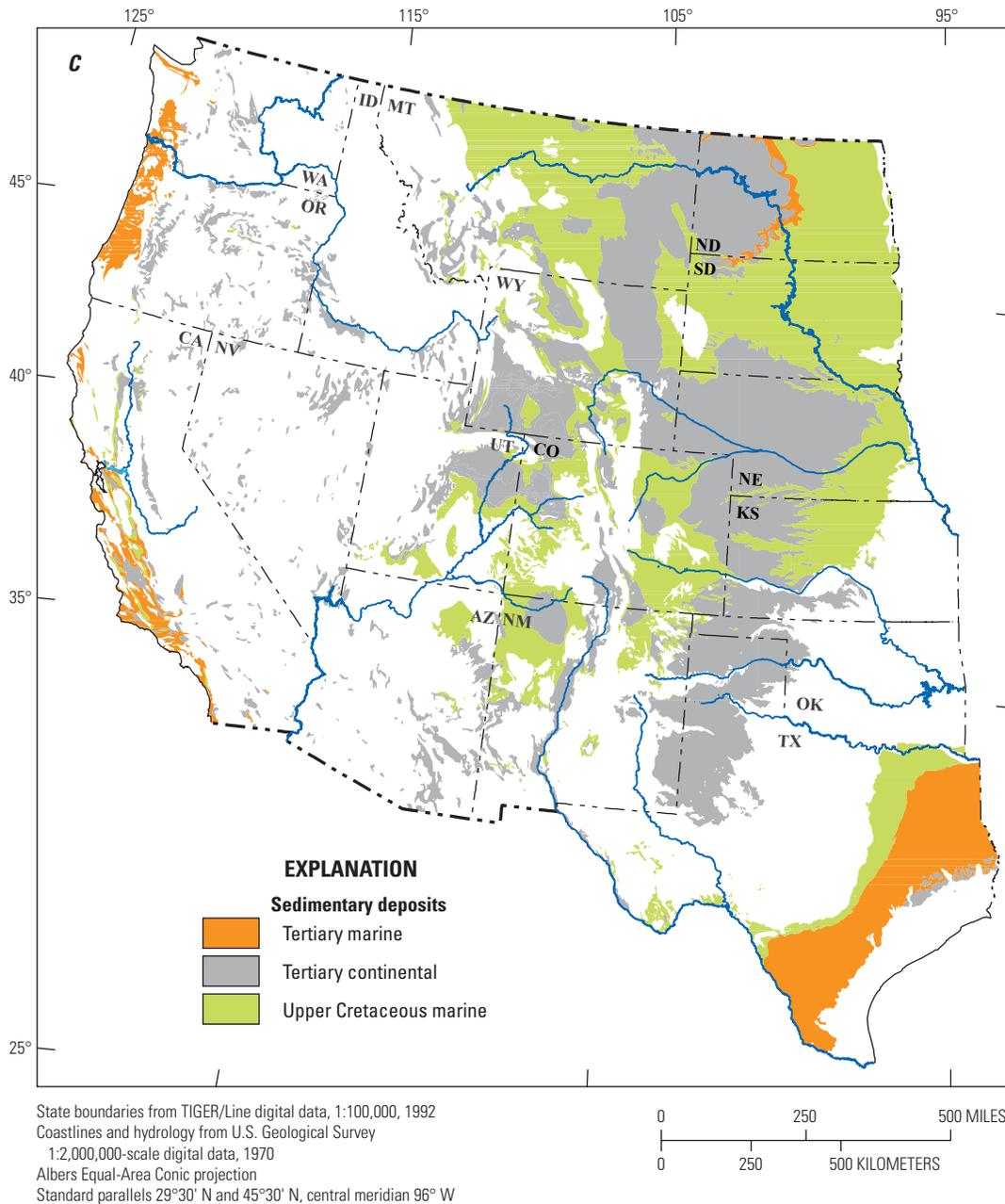

Figure Q6.—Continued Maps showing locations of seleniferous sedimentary outcrops and deposits and plant samples with significant selenium content. This map, *B*, shows the spatial relation among locations of Paleocene and Eocene, seleniferous, marine sedimentary outcrops and plant samples with greater than or equal to 50 ppm selenium. Map *B* is from Trelease and Beath (1949) and, with map *A*, shows the widespread extent of seleniferous bedrock across the Western United States and its correlation with selenium in plant samples.

Figure Q6.—Continued   Maps showing locations of seleniferous sedimentary outcrops and deposits and plant samples with significant selenium content. This map, *C,* shows locations of potentially seleniferous marine and continental sedimentary deposits in the Western United States. Map *C* is from Seiler and others (2003, p. 51, fig. 20) and shows additional areas with potentially seleniferous bedrock not identified by Trelease and Beath (1949).

the United States has an estimated 10,000 metric tons of world selenium reserves, or about 8 percent. As of 2012, the leading copper-producing mines in the United States were located in Arizona, Nevada, New Mexico, and Utah and accounted for all U.S. domestic selenium reserves (Brininstool, 2015).

Globally, the countries with the largest mine production of copper in 2012 were Australia, Canada, Chile, China, Congo (Kinshasa), Indonesia, Kazakhstan, Mexico, Peru, Poland, Russia, the United States, and Zambia (Brininstool, 2015). Copper mines from these countries account for the global reserves of selenium and are the sources of concentrates and residues for the leading selenium producers.

Undiscovered Resources

Although selenium is produced currently from copper ores—mostly from porphyry copper deposits—it also occurs in many other types of mineral deposits and earth materials (tables Q2 through Q5). The highest concentrations of selenium are likely to occur in deposits that host selenide minerals, such as the selenide vein-type deposits described by Simon and others (1997). Although the selenium grade is high in selenide deposits, the overall tonnage is low. Deposits of native sulfur may also contain high concentrations of selenium (table Q3), yet the tonnage of these deposits compared with that of porphyry copper deposits is also low.

The close association of selenium with sulfur is the reason that copper ores are a resource for selenium. One approach to identifying new selenium resources would be to investigate this selenium-to-sulfur relationship in other rock types. Rocks enriched in organic carbon are likely to have high selenium concentrations, where selenium has substituted for sulfur in diagenetic sulfide minerals. These resources might be coal (where selenium recovery is technically feasible but not currently economic), marine phosphate deposits, or oil shales. Presser and others (2004) have mapped a global distribution of selenium-rich rocks found in sedimentary basins enriched in organic carbon (fig. Q7). Although the purpose of their mapping was to identify selenium source rocks that might create environmental concerns, their analysis might also be useful in identifying new selenium resources.

Environmental Considerations

Selenium is both a necessary nutrient and a potential hazard to Earth ecosystems, and it is present in the environment both naturally and as a result of human activity. Selenium mining, processing, use, and disposal may all potentially release selenium to the environment. Environmental considerations are integral to decisions regarding extraction and use of selenium.

Table Q6.   Estimated world selenium reserves in 2014, in metric tons.

[Reserves are defined as the amount of selenium that could be economically extracted at the time the estimate was made (see U.S. Geological Survey, 2014a, appendix C, for more information). Selenium reserves, including those in China, are based upon the selenium content of identified copper deposits and do not include lead ores and coal. Other countries with reserves may include Australia, India, Kazakhstan, the United Kingdom, and Zimbabwe. Data have been rounded to no more than two significant digits. Data are from George (2014).]

Country	Reserves (metric tons)
United States	10,000
Canada	6,000
Chile	25,000
China	26,000
Peru	13,000
Poland	3,000
Russia	20,000
Other countries	21,000
World total	**120,000**

Sources and Fate in the Environment

The geochemical processes that control the presence and distribution of selenium in mineral deposits also operate, more broadly, in Earth's surface environment. The processes of oxidation and reduction, adsorption at mineral surfaces, and isomorphic substitution of selenium for sulfur also govern selenium distribution and fate, including its uptake in biological organisms.

Natural and Anthropogenic Sources in Air, Water, and Soil

Volcanoes are the primary source of selenium in Earth's upper crust and atmosphere. The selenium species H_2Se and SeO_2 are volatile and found along with sulfur gases in volcanic emissions. Lakin and Davidson (1973) estimated that 1 kilogram per square meter (reported as 2 pounds per square yard) of selenium has been deposited on Earth's surface from volcanic emissions over geologic time.

Selenium is produced in volcanic emissions when magmatic selenium is volatilized while in the volcanic plumbing system, and tens of kilograms of selenium can be released daily from a single volcano (Greenland and Aruscavage, 1986; Floor and others, 2011). Regardless of how selenium is emitted into the atmosphere, once there, it can be

deposited onto surfaces by dry deposition or incorporated into water droplets and removed by wet deposition.

After selenium has been introduced to the upper crust, it cycles among the atmosphere, biosphere, and hydrosphere. Natural biologic emissions that cycle selenium between the biosphere and atmosphere account for approximately one-half to two-thirds of atmospheric selenium (Mosher and others, 1987); these emissions are composed mostly of dimethyl selenide gas from marine biogenic sources and account for 70 percent of natural biologic emissions of selenium. Other natural sources of atmospheric selenium are the continental biosphere (20 percent), volcanoes (8 percent), sea salt (2 percent), and crustal weathering (less than 1 percent) (Cahill and Eldred, 1998).

Anthropogenic selenium emissions to the atmosphere are derived mostly from coal and oil combustion (50 percent and 10 percent, respectively), and base-metal production of copper, zinc, and lead (20 percent, 4 percent, and 4 percent, respectively) using roasters and autoclaves (Cahill and Eldred, 1998; Winkel and others, 2012). It has been known for some time that coal combustion is a major source of selenium to the environment and that coal can contain 5 to 300 times the amount of selenium as other rocks (table Q5). Emission controls on coal-fired powerplants are limited in their ability to remove volatile selenium species (Ranville and others, 2010); hence, selenium

escapes into the atmosphere. Coal combustion also generates fly ash that can concentrate selenium 10 to 25 times beyond its original concentration in the coal (Lemly, 1985). Other than coal, the remaining anthropogenic selenium emissions come from other forms of combustion and from ceramic and glass manufacturing (Cahill and Eldred, 1998).

One important natural source of selenium to surface and groundwaters is weathering of marine shales. A significant portion of the bedrock in the Western United States is composed of marine shales (most notably of Cretaceous age but with a range of Permian to Paleogene ages). These shales are noted for their high selenium content (table Q5) derived from the volcanic eruptions that were especially extensive during the Cretaceous Period. Selenium became incorporated into marine sediments, often substituting for sulfur in pyrite, and then mobilized as sediments were uplifted and weathered. Selenium-rich soils in the northern Great Plains of the United States owe their selenium content to the underlying shales of the Pierre Formation and the Niobrara Formation (Trelease and Beath, 1949; Mayland, 1985). Moxon and others (1938) hypothesized that the selenium content of the Pierre Formation and the Niobrara Formation was inversely related to the rate of sediment deposition because they observed that thin stratigraphic sections (which were produced from low deposition rates) had high concentrations of selenium, whereas thicker
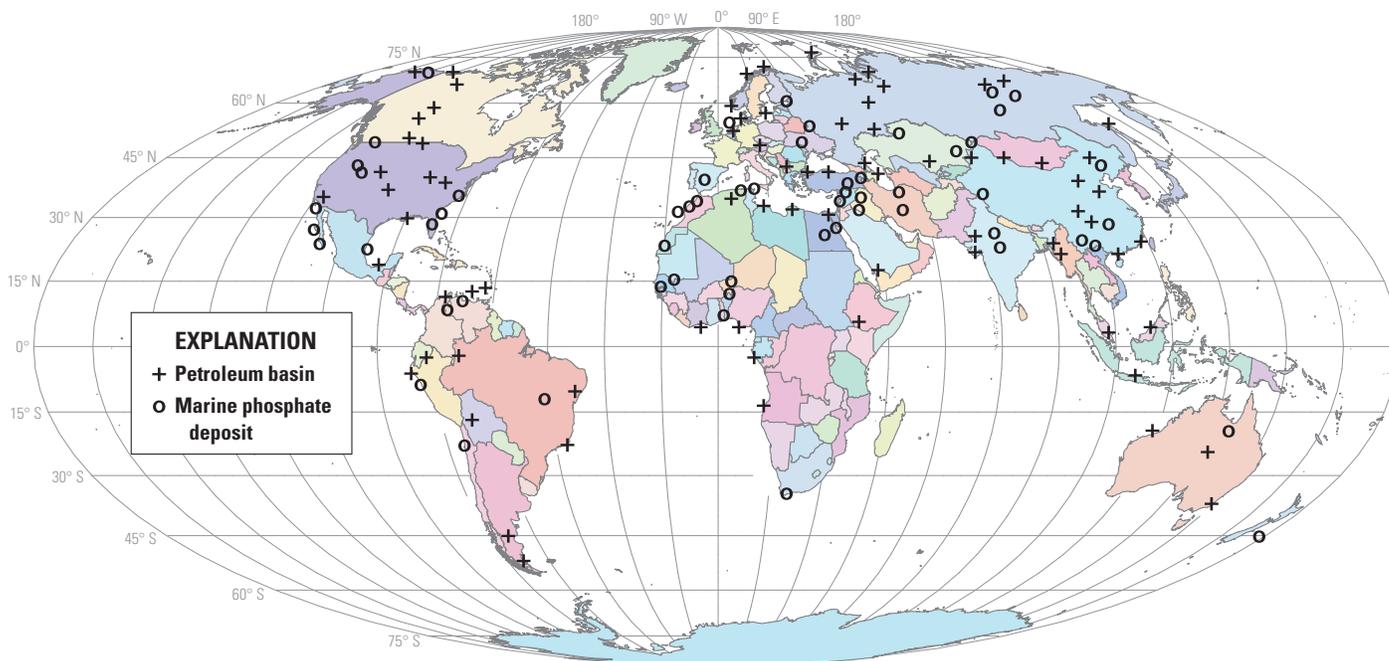
Figure Q7.   A predictive map of selenium source rocks associated with organic-rich depositional marine basins. This map is useful both for identifying selenium source rocks that could be of potential environmental concern and for identifying potential new selenium resources. Modified from Presser and others (2004, p. 313).

sections (representing fast deposition rates) had low selenium concentrations. Other marine shales, such as the Meade Peak member of the Permian Phosphoria Formation in southeastern Idaho and western Wyoming (Stillings and Amacher, 2004; Presser and others, 2004), the Cretaceous-Paleocene Moreno Formation, and the Eocene-Oligocene Kreyenhagen Formation in the California Coast Range (Presser, 1994) are sources of selenium to groundwater, surface water, and soil. Additionally, coal and other organic-rich sediments release selenium through weathering (McNeal and Balistrieri, 1989).

In other regions of the United States where the soils are selenium-deficient, and in other countries, selenium is added to soils by way of selenium-containing fertilizers, lime, and manure. It is widely recognized that selenium is a necessary dietary nutrient for humans, as well as for other animals, and in the United Kingdom, selenium fertilizers are used in pastures and forage areas to increase the human intake of selenium through meat and dairy products. In Finland, a national-scale use of selenium fertilizers began in 1984 and has resulted in a fourfold increase in the intake of dietary selenium in the human study population (Winkel and others, 2012, and references therein). Because crops take up only 5 to 20 percent of the selenium applied in fertilizers, the rest of the selenium is either immobilized in the soil through chemical reduction or leached from the soil and added to surface runoff waters. The Finnish study calculated that application of selenium fertilizers was expected to have increased selenium in soils by 20 percent, but because no increase in the soil was observed, selenium must have been leached from the soils. In Tennessee, the use of selenium in fertilizers has caused selenium runoff in surface waters, resulting in an accumulation in aquatic biota (Winkel and others, 2012, and references therein).

Average Ambient Concentrations in Air, Streams, Groundwater, and Soil

Ambient concentrations of selenium in the environment are dependent upon selenium concentrations in the underlying bedrock. Soils in the United States that overlie pre-Cretaceous-age sedimentary rocks, volcanic ash, or granitic rock tend to be low in selenium because most of these bedrock materials are also low in selenium (McNeal and Balistrieri, 1989).

Recent data on soil chemistry in the conterminous United States show selenium concentrations to range from less than 0.2 to 8.3 ppm (figs. Q8A–C; Smith and others, 2014). The data were collected from three soil sections—0 to 5 centimeters (cm) depth, the A horizon, and the C horizon. Although the spatial distribution of selenium varied among the three soil sections (figs. 8A–C), the concentration range and histogram of selenium concentrations were fairly consistent among them—from less than 0.2 to 6.9 ppm for the 0-to-5-cm-depth section; from less than 0.2 to 8.3 ppm for the A horizon section; and from less than 0.2 to 7.5 ppm for the C horizon section. Many of the general trends in selenium concentration in the Western United States, as mapped by Trelease and

Beath (1949), were confirmed by current maps, as illustrated in figs. Q8A and Q8B. A striking feature in the recent maps, however, is the trend of high concentrations of selenium in the Dakotas, and eastward through the mid-continent and into the Appalachian and New England regions. Future scientific studies may debate the authigenic versus anthropogenic origin of this selenium.

Scandinavia is another region with low selenium content in the bedrock. In Sweden, 89 percent of the mineral soils have less than 0.45 ppm selenium, which is comparable to the blue-to-light-orange regions of the United States shown in figs. Q8A–C, and is the minimum concentration needed for forage to provide the necessary selenium for stock animals (Parkman and Hultberg, 2002, and references therein). In contrast, selenium-amended agricultural soils show increased selenium of 0.065 to 1.7 ppm. Lake waters in Sweden—both those affected by and those not affected by selenium effluent—show between 43 and 209 nanograms per liter (ng/L) of total selenium (total = particulate + dissolved), and this concentration is independent of the trophic status of the lake (Parkman and Hultberg, 2002, and references therein).

In Finland, background concentrations of dissolved selenium in lake waters are estimated to be 56 to 62 ng/L, and although no seasonal variations were observed, researchers did find spatial variations caused by human activities. As a comparison, in lakes affected by agricultural runoff, the selenium concentration was 76.8 ng/L. In these lakes, the total selenium concentration was distributed among (1) selenium in organic materials, such as humic acids, which was greater than or equal to 50 percent of the total; (2) particulate selenium that was approximately 10 percent of the total selenium concentration; (3) dissolved selenite and selenate, which accounted for 8 to 9 percent of the total selenium concentration; and (4) selenium associated with neutral humic acids, which made up approximately 5 percent (Parkman and Hultberg, 2002). Sediments in these lakes show an increase in selenium concentration during the 20th century, most likely because of selenium-containing fertilizers. In 1992, concentrations in nine lakes ranged between 0.27 and 3.64 ppm, and concentrations were higher in oligotrophic lakes than in mesotropic or eutrophic lakes. In stream sediments in Finland, the mean concentration of selenium was 0.26 ppm (Parkman and Hultberg, 2002, and references therein).

Above-Background Concentrations of Selenium in the Environment Near Major Deposits and Enriched Bedrock

Soils can have highly variable selenium concentrations, ranging from less than 0.01 ppm in deficient soils to up to 1,200 ppm in selenium-rich soils (Winkel and others, 2012, and references therein). Seleniferous soils can be found overlying selenium-rich rocks, such as black shales, carbonaceous limestones, carbonaceous cherts, mudstones, and seleniferous coal (Winkel and others, 2012).
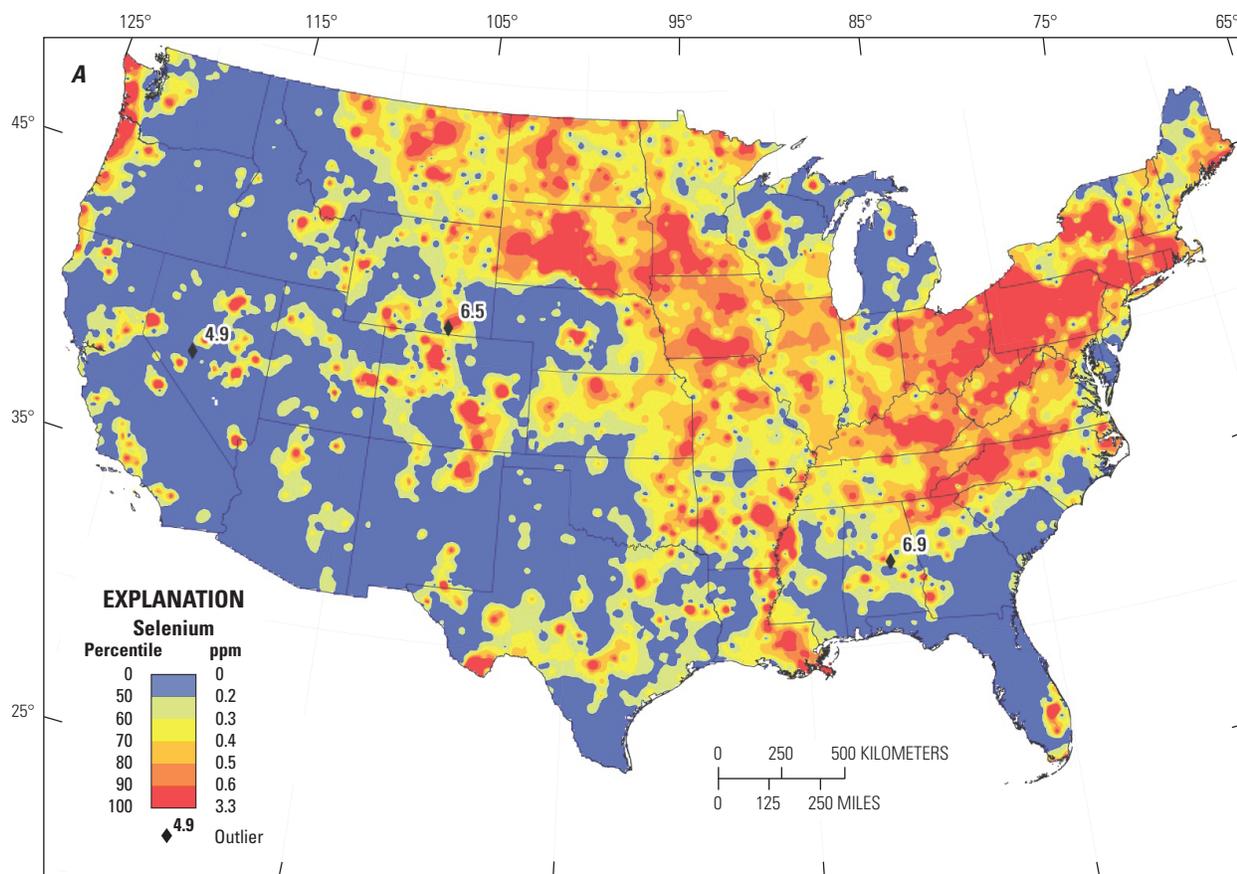
Base from U.S. Geological Survey digital files, Lambert Conformal Conic projection
Standard parallels 33° N. and 45° N., central meridian 96° W.
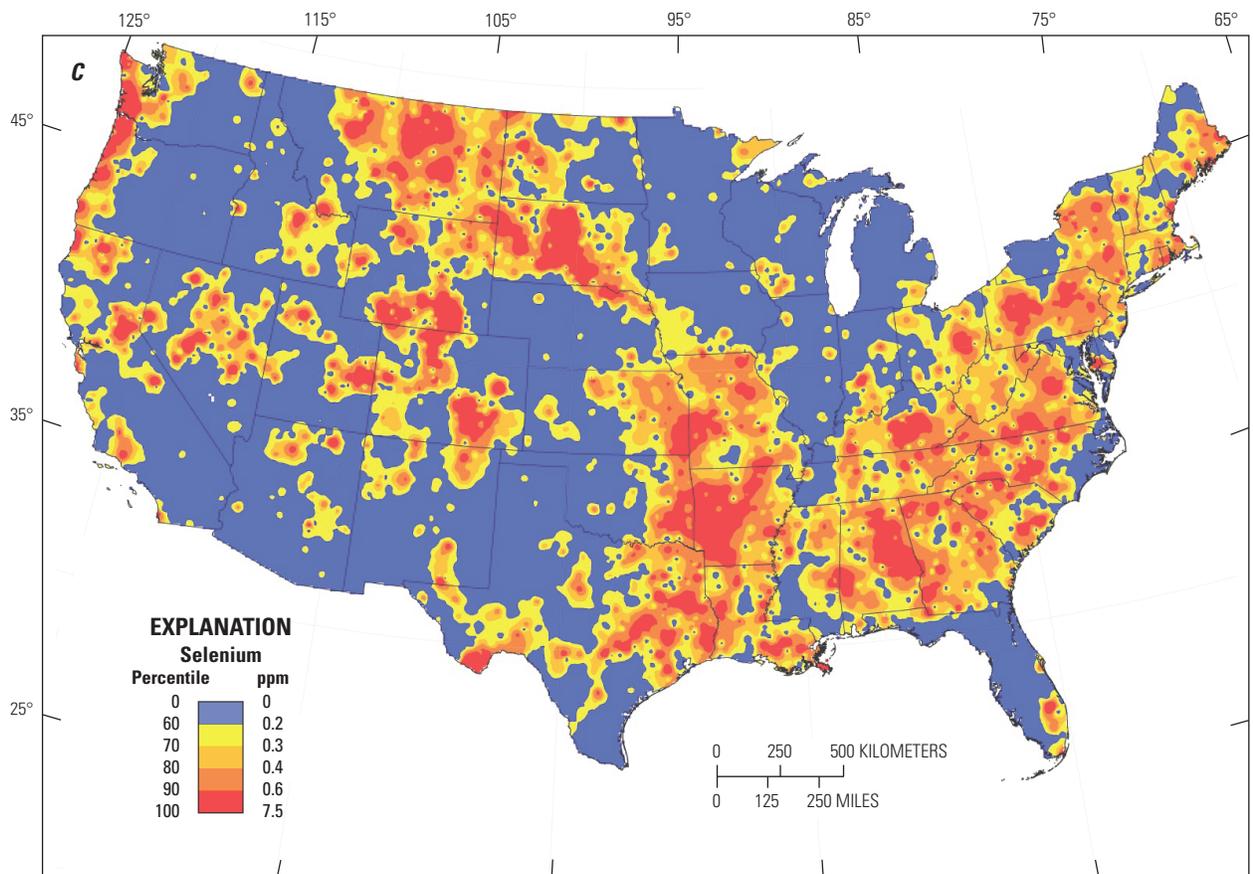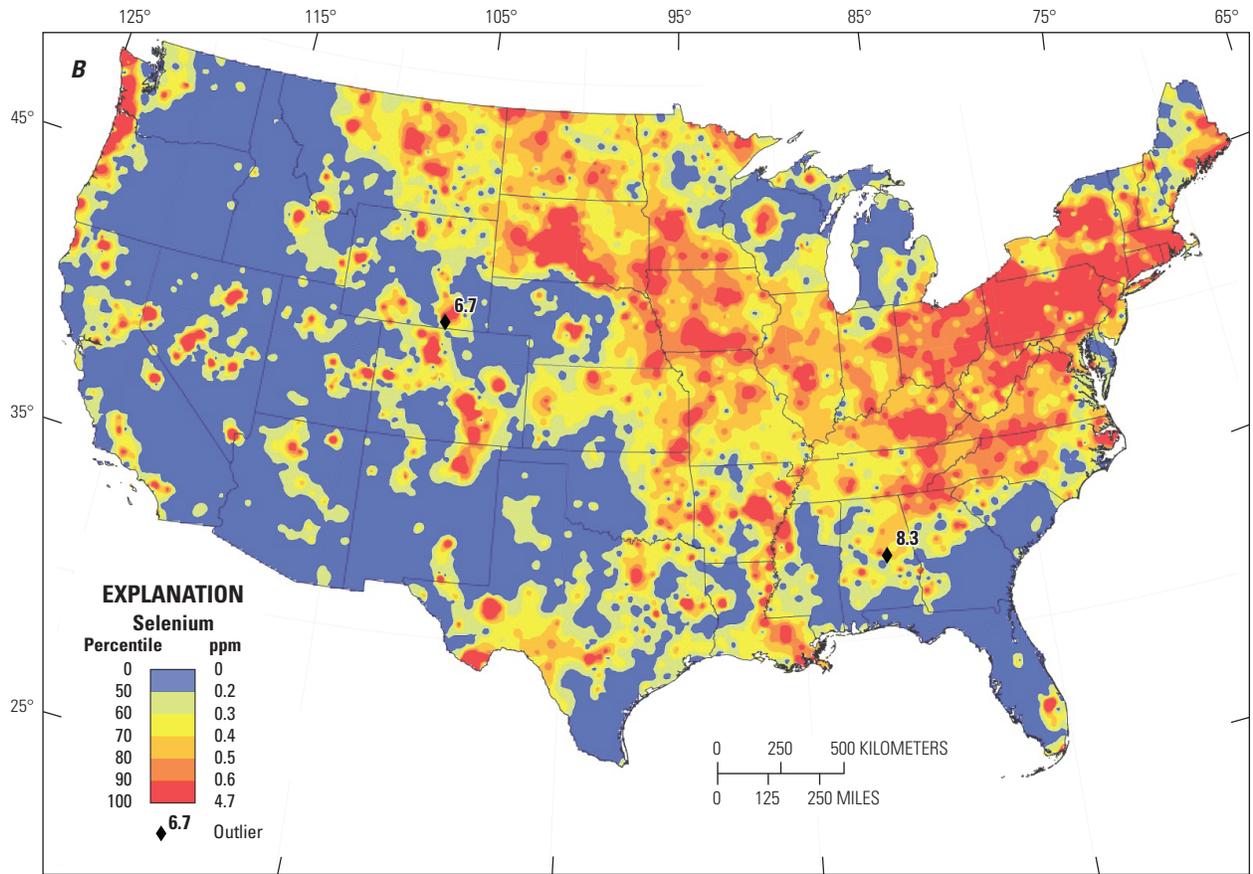Datum is North American Datum of 1983

Figure Q8 (pages Q24 and Q25).   Maps showing selenium concentrations in soils of the conterminous United States. The selenium concentrations shown are in *A*, the top 0 to 5 centimeters of surface soils, *B*, the A horizon of surface soils, and *C*, the C horizon of surface soils. A visual comparison of the soils maps with the bedrock and plant maps in fig. Q6 shows many correlations in the Western United States. Maps are from Smith and others (2014, p. 197–202, figs. 95, 96, and 97). ppm, parts per million

Some examples of seleniferous soils are those that develop over seleniferous marine shales in the United States. Presser (1994) found that salinized soils of alluvial fans in the San Joaquin Valley, California, could contain as much as 4.5 ppm of selenium, with a median of 1.8 ppm. These soils developed from weathering of the Upper Cretaceous-Paleocene Moreno Formation and the Eocene-Oligocene Kreyenhagen Formation, which themselves contained concentrations of selenium up to 45 ppm, with median concentrations of 6.5 and 8.7 ppm, respectively (table Q5). Even higher concentrations have been recorded in shales of the Cretaceous Pierre Formation and the Niobrara Formation in the Western United States (maximums of 103 and 113 ppm, respectively) (table Q5; Moxon and others, 1938; Trelease and Beath, 1949; Presser, 1999).

High concentrations of selenium can develop in irrigation drainage waters and wetland environments when these waters interact with seleniferous soils. The wetlands of the Kesterson National Wildlife Refuge in San Joaquin Valley, Calif., were the site of an ecological crisis beginning in 1983,

when it was discovered that high concentrations of dissolved selenium caused massive numbers of embryonic deformities and deaths of aquatic wildlife (Garone, 1999; Ohlendorf, 2002). The wetlands developed at the terminus of irrigation drainage within the San Joaquin Valley, and the drainage waters held high concentrations of selenium (in the range of 106 to 452 parts per billion (ppb), with an average concentration of 300 ppb) leached from seleniferous, salinized soils that developed over high-selenium-content marine shales. The link between high selenium concentrations and selenium toxicity is discussed in the sections of this chapter on human and ecological health.

Soils in the vicinity of sulfide orebodies may show naturally high concentrations of selenium, and this association has been cited in models for exploration geochemistry (Koljonen, 1976). The Luikonlahti copper orebody in eastern Finland displays elevated selenium concentrations in soils and glacial deposits immediately adjacent to sulfide-rich rocks (0.1 to 0.4 ppm selenium), in colloid- and organic-rich river and lake sediments downstream from the orebody

EXPLANATION

Selenium

Percentile	ppm
0	0
50	0.2
60	0.3
70	0.4
80	0.5
90	0.6
100	4.7

◆ 6.7   Outlier

EXPLANATION

Selenium

Percentile	ppm
0	0
60	0.2
70	0.3
80	0.4
90	0.6
100	7.5

(0.2 to 1.1 ppm selenium), in forest mull humus atop the orebody (2.3 to 5.5 ppm selenium), and in sulfate- and iron-oxide-rich gossans developed above the orebody (2.9 to 13.0 ppm selenium). In contrast, similar soils and sediments from nonmineralized regions in Finland showed background selenium concentrations of 0.0 to 0.2 ppm selenium, with iron-rich lake and bog ores containing 0.4 ppm selenium (Koljonen, 1976).

Groundwaters near an undisturbed porphyry copper deposit in the Atacama Desert of Chile also display above-average concentrations of selenium. Leybourne and Cameron (2008) measured naturally occurring concentrations of up to 800 ppb selenium within 2 kilometers (km) downstream of the deposit. They attribute these high concentrations to Eh-pH conditions and pH, which put the waters at the boundary between Fe(III) and Fe(II) speciation. Limited quantities of solid iron oxyhydroxides are present in environments with these values of Eh-pH; therefore, adsorption reactions with iron oxyhydroxides did not reduce dissolved concentrations of selenium.

In contrast, sorption reactions may be an important control on selenium mobility in volcanic soils (Floor and Román-Ross, 2012). High concentrations of selenium have been recorded in volcanic soils owing to weathering of seleniferous parent materials and deposition of atmospheric selenium. Floor and Román-Ross (2012) reported 1,200 ppm of selenium in volcanic soils from Ireland, and 1 to 20 ppm of selenium in soils from Hawaii. Floor and others (2011) reported a range of 0.12 to 2.25 ppm selenium in soils from the Mount Etna volcano in Italy, with a median of 0.39 ppm selenium. Despite these high soil concentrations, selenium is not readily leached from soils. Strong sorption of selenium with soil compounds, such as ferrihydrite, poorly crystalline aluminosilicates, and organic matter, has been cited in volcanic soils from Hawaii, Mount Etna in Italy, and New Zealand (Floor and Román-Ross, 2012).

The strong sorption between selenium and volcanic soils may be site specific, as sorption is highly dependent upon soil chemistry and mineralogy. Whereas groundwater in volcanic aquifers can have low concentrations—often less than 0.1 ppb selenium (Floor and Román-Ross, 2012)—some sites show distinctly higher concentrations. Aiuppa and others (2000) sampled groundwaters near Mount Etna and found a range of 0.6 to 66.8 ppb selenium, with an average of 2.9 ppb selenium. At Mount Vesuvius, Italy, Aiuppa and others (2005) demonstrated that selenium can be one of the most mobile elements during rock weathering.

Plants show elevated concentrations of selenium when grown in soils with high selenium concentration, although the accumulation can vary by more than two orders of magnitude for a given selenium concentration in the soil (Winkel and others 2012, and references therein). Selenium accumulator plants include *Astragalus* L., as well as *Oonopsis* (Nutt.) Greene, *Oryzopsis* Michx., *Xylorhiza* Nutt., *Mentzelia* L.,

and *Stanleya* Nutt. (Moxon and others, 1938; Trelease and Beath, 1949; Cannon, 1957; Presser, 1999). Cannon (1957) reported that members of *Astragalus* can display selenium concentrations of several hundreds to a thousand parts per million when grown in soils that contain only 2 ppm selenium. In addition to soil selenium, other factors that affect the plant's selenium content include the age of the plant, the stage of growth, and the part of the plant analyzed—seed, leaf, or stem (Moxon and others, 1938).

Mobility in Water and Soils

The chemical form of selenium (its speciation) determines its behavior and fate in the environment. Selenium is a metalloid that commonly takes an anionic form in oxic to suboxic conditions when dissolved, and its primary species in water are selenate (Se(VI) or SeO_4^{2-}), selenite (Se(IV) or SeO_3^{2-}), and organo-selenide (org-Se(-II), such as selenomethionine) (Luoma and Presser, 2009). Speciation will also determine whether selenium can be taken up by algae or microbes, or whether it can transform to particulate matter in seawater (seston) or in sediments.

In the sections above, the sources of selenium in the environment have been identified as emissions from volcanoes, biogenic processes, manufacturing and power generation, weathering of marine shale bedrock and overlying soils, and selenium leachate from fly ash and other solid waste materials. Mobilization of selenium from these sources to aquatic environments and pore waters occurs under oxidizing, slightly alkaline weathering conditions and produces soluble selenate and selenite (McNeal and Balistrieri, 1989; Presser and Swain, 1990; Piper and others, 2000).

Once selenium has transformed to aqueous selenate and selenite, it is readily mobile and bioavailable (meaning that it can be taken up by organisms). Selenate predominates in well-aerated surface waters, especially at alkaline pH. Selenite predominates in slow-moving waters, such as lakes and reservoirs. Chemical parameters, such as pH and redox, and microbial respiration, can convert selenate to selenite and organo-selenium. Dissolved selenium can sometimes be predominately organo-selenium, and this species may be seasonally important (Skorupa and others, 2004). The presence of organic carbon, ferric oxyhydroxides, and clays in soils affect the partitioning of these selenium species among water and soil and (or) sediments.

Selenate (Se (VI)) does not form strong adsorption complexes on mineral surfaces. It can be easily desorbed by a change in solution chemistry (for example pH, or ionic strength), and it exchanges readily with SO_4. Ready desorption and exchange are among the reasons for the high solubility of Se(VI), which enhances its mobility (Fukushi and Sverjensky, 2007). In solutions of alkaline pH with high Eh values, Se(VI) is mobile and bioavailable to plants (Winkel and others, 2012). In contrast, selenite (Se(IV)) is stable in solutions of moderate

to low Eh values, and it is more likely to adsorb irreversibly to iron oxyhydroxides, clay minerals, and organic matter than to selenate. When selenite is tightly held by mineral surfaces and organic matter, it is less mobile and less available for plant uptake (Winkel and others, 2012, and references therein).

In a system where mineral surfaces and organic matter are not present in sufficient concentrations, however, Se(IV) and organo-selenide may be more readily incorporated into biota. When selenium is taken up at the base of the food web by plants and microbes, it is converted to organo-selenide, regardless of whether it was initially present as Se(IV) or Se(VI) (Presser and others, 1994). Organo-selenide is rereleased to water as these cells die or are consumed, and it can be reoxidized to Se(IV). Slow reaction kinetics restrict reoxidation to Se(VI). This means that biologically productive systems will evolve to see a decrease in soluble Se(VI) and an increase in Se(IV) and organo-Se(-II). For example, in streams in the upper part of California's San Joaquin River watershed, dissolved selenium is almost 100 percent Se(VI), but lower in the watershed and downstream of the delta of the San Joaquin River, Se(VI), Se(IV), and organo-Se(-II) are equal in abundance (Cutter and Cutter, 2004).

Elemental (native) selenium is not soluble in water and is considered unavailable to plants. Some estimates suggest that elemental selenium may account for 30 to 60 percent of the total selenium in sediments (Zhang and others, 2004). It is often found as nanometer-sized spherical particles that are produced from microbially mediated reduction of Se(VI) and Se (IV). The extremely small size of these particles enables them to remain in colloidal suspension for weeks, and they may be able to enter cells directly, making the particles more bioavailable. A high surface-to-volume ratio makes them highly reactive, meaning that they may reoxidize to selenite and selenate. Finally, an organic polymer layer of protein that has been observed on the surface of these spherical particles may alter their surface properties and affect the distribution of elemental selenium in the environment (Winkel and others, 2012).

It was noted earlier that selenium exchanges readily with sulfur; this is because selenium and sulfur are both members of Group 6b of the periodic table; hence, they exhibit similar chemical behavior because they have similar ionic radii and can have the same valence. The S(VI) competition with Se(VI) for adsorption sites on mineral surfaces and in biological uptake is a primary mechanism for Se(VI) mobilization. For example, in soils developed on the flanks of Mount Etna, it was observed that selenium is mobilized during rainwater-soil interaction. It was found that aluminum oxides and soil organic matter were the active phases to sequester selenate in soil through adsorption and complexation reactions. When sulfate was introduced from rainwater, however, sulfate exchanged with adsorbed and complexed selenate, transforming it to a soluble and therefore mobile selenium species. Yet when redox conditions allowed for selenium

transformation to Se⁰, selenium would not be remobilized by acidic water (Floor and others, 2011).

Mine Waste Characteristics

Coal deposits and associated mine waste rock are common geologic sources for environmental selenium (fig. Q5). In the Appalachian region, coal mining companies often practice mountaintop mining to access underlying coal seams, and the waste rock is commonly placed in streams and valleys. According to the U.S. Environmental Protection Agency (EPA), an estimated 724 stream miles (1,165 stream kilometers), or 1.2 percent of streams, were covered by more than 6,800 valley fill waste piles from 1985 to 2001 in the States of Kentucky, Tennessee, Virginia, and West Virginia (U.S. Environmental Protection Agency, 2005, p. 4–5). This waste disposal practice serves to increase selenium input into aquatic systems because fresh faces on newly broken rock provide increased surface area for water-rock reaction and selenium transfer into surface waters. Bryant and others (2003) observed that the selenium concentration in Appalachian streams associated with valley fills (<0.3 to 37 ppb selenium) was greater than background concentration (<0.3 ppb selenium), and that the selenium concentrations in holding ponds at the base of valley fills ranged from 24 to 42 ppb selenium. Surface and groundwater pH greatly affect selenium solubility. Unlike other trace elements associated with coal (for example, cadmium, copper, and lead), the oxic forms of selenium are soluble in waters with neutral-to-alkaline pH. This behavior is explained by the difference in adsorption potential among base cations (for example, cadmium, copper, and lead), which adsorb strongly to oxide surfaces at higher pH values, and oxyanion forms of selenate and selenite, which adsorb more strongly at lower pH values (Stumm, 1992; Elzinga and others, 2009).

Although selenium can occur naturally in soils associated with unmined coal seams, mining is known to enhance its solubility in reclaimed and revegetated mine lands, which can potentially result in aquifer contamination and elevation of selenium in plant materials. Sharmasarkar and Vance (1997) analyzed 40 soil samples (ranging in depth from 0 to 200 cm) from native, reclaimed, and abandoned coal mine environments in Wyoming, and observed selenium concentrations of 0.26 to 26.13 ppm selenium, with a mean concentration of 1.73 ppm.

Another source of selenium to natural waters is ash and other waste products produced from coal-fired powerplants. The case study for this selenium pathway was Belews Lake in North Carolina. From 1974 to 1985, lake water was withdrawn and mixed with ash generated by a nearby coal-fired electricity-generating plant. Presser (1999) noted that fly ash may contain even higher levels of soluble selenium than the initial, seleniferous coal; that is, 50 to 500 ppm versus 2 to 20 ppm. Solids were allowed to settle from the slurry before the wastewater,

which contained 150 to 200 ppb selenium, was returned to the lake, creating lake water selenium concentrations of 20 ppb. Once this disposal practice was ended, lake water selenium concentrations fell to less than 1 ppb (Lemly, 1997).

High ash content in bone coals (coal with a high ash content) creates another source of environmental selenium. In Pingli County, Shaanxi Province, China, the Badao bone coal contains 41 to 75 ppm of selenium, with a mean concentration of 57.5 ppm. After combustion, the coal ash fraction was found to contain 28 ppm of selenium, indicating that the difference (approximately 30 ppm) is volatilized to the atmosphere. Selenium is also released to the environment through the use of bone coal ash as an agricultural soil amendment. The local environment in Pingli County was found to contain soil with a mean concentration of 7.1 ppm selenium, surface water with concentrations of 0.3 to 1.1 ppm selenium, and agricultural crops with concentrations of 0.57 to 2.75 ppm selenium (Fang and others, 2003).

As discussed previously, selenium is associated with phosphate deposits, and, quite notably, in the United States, with the Meade Peak member of the Permian Phosphoria Formation in Idaho, Montana, Nevada, Utah, and Wyoming. Features of the mined environment include lakes that form in open pit mines after mining has ended, waste rock contoured into hills or emplaced as cross-valley fills, wetlands that form at the base of waste dumps, and vegetation that is reseeded onto the surface of the dumps.

A selenium mass-balance study was conducted for the wetland that formed at the base of the Wooley Valley Unit 4 waste dump in southeastern Idaho (Stillings and Amacher, 2004; Stillings and others, 2007). The waste dump was created in the 1970s from overburden and waste shale that remained after the mining of the upper and lower phosphate zones of the Meade Peak member, and the wetland developed soon thereafter. In 2002, inlet and outlet flow volumes and chemistry were measured continuously from May through September. The calculated influx of selenium was high at the beginning of May (approximately 90 grams per day [g/d] of selenium), but dropped rapidly throughout the month and became zero when the seep dried up at the end of June. The outflow of selenium ranged from approximately 0.05 to 2.0 g/d during the entire season. The mass balance created for this time period showed that although 685 grams (g) of selenium was delivered to the wetland, only 84 g of selenium left the wetland, meaning that 601 g, or 88 percent of the influx, was retained within the wetland. Further work determined that selenium was scavenged from wetland surface waters by adsorption and co-precipitation with iron oxyhydroxides that precipitated on the surface of wetland soils (Stillings and Amacher, 2004; Stillings and others, 2007).

In a related study, selenium concentrations were measured in plants grown on the waste rock dumps at Wooley Valley Units 1, 3, and 4 and compared with concentrations of plants growing on undisturbed areas of the Phosphoria Formation. Vegetation growing in highly disturbed soils, including those on the surface of waste dumps, had the highest tissue selenium concentrations. The mean concentration for legumes was 80 ppm; trees, 52 ppm; grasses, 18 ppm; shrubs, 6 ppm; and forbs, 3 ppm. The grasses collected from the wetland described in the previous paragraph showed a mean selenium concentration of 53 ppm. This second study was used to argue for the removal of legumes from seed mixtures used to revegetate the surfaces of the cross-valley waste dumps, thus decreasing selenium in browse vegetation for herbivores (Mackowiak and others, 2004).

Roll-front uranium deposits in the Western United States are another deposit type known to contain selenium; hence, selenium is likely to be present in these mine wastes as well. When uranium is mined with in situ methods (which are commonly used with roll-front deposits), the overlying rock is not disturbed and thus not exposed to oxidizing conditions at Earth's surface; however, the in situ mining methods used rely on injections of lixiviant (an oxidizing agent—either oxygen or hydrogen peroxide) into the uranium deposit to oxidize and extract the uranium ore. This fluid can leach selenium into the surrounding groundwater by oxidizing organic matter that contains selenium, and by converting insoluble organic selenides to soluble selenate and selenite. Selenium concentrations can exceed 1,000 ppm in areas that have been mined for uranium (Naftz and Rice, 1989, and references therein).

Both groundwater and surface water in areas near copper mines and processing facilities may show elevated selenium concentrations because of selenium's association with sulfide minerals. Elevated selenium concentrations (>10 ppm) have been found in groundwater under the copper smelter and refinery facility near the Great Salt Lake, Utah. The facility is located within 1.5 km of the southern shore of the lake, and there is some concern that a portion of this plume could discharge into the lake (Naftz and others, 2009, p. 35, and references therein). In 2001, the facility was selected for an EPA selenium treatment/demonstration project, which field-tested three technologies for removing selenium from the Garfield Wetlands-Kessler Springs site. At the start of this project (in May 1999), the Garfield Wetlands-Kessler Springs water contained approximately 2,000 ppm selenium (MSE Technology Applications, Inc., 2001, p. 1).

Soils near a lead-zinc smelter in Kabwe, Zambia, show contamination from atmospheric dust fallout from smelting activities. Křibek and others (2010) sampled contaminated topsoil and a reference (background) subsoil horizon at 80 to 90 cm depth. The topsoil had a maximum selenium concentration of 0.01 percent (100 ppm), which was significantly higher than the concentrations of trace metals in the subsurface soil.

There are limited reports of selenium in leachate from mine waste associated with banded iron formations in the Upper Peninsula of Michigan. In 2008, the Michigan Department of Environmental Quality (MDEQ) began to assess selenium concentrations and water quality impacts in the vicinity of the Empire Mine and the Tilden Mine in the Marquette Iron Range near Palmer, Michigan. Results of the MDEQ

assessment showed that selenium concentration in water at many lakes near the mine sites were less than 5 ppb, which is the chronic selenium water quality standard for Michigan. Two streams that flowed through mine waste facilities carried mean values of 9.3 and 11 ppb selenium, however, and a popular fishing site, Goose Lake, exhibited 8.8 to 10 ppb selenium. Small streams and springs buried by waste rock piles showed selenium concentrations that ranged from 15 to 68 ppb. Sediments from streams and lakes ranged from less than 5 ppm to between 27 and 39 ppm selenium in Goose Lake (Selenium Monitoring Work Group, 2009, p. ii). Biological samples from Goose Lake Outlet showed a mean value of 8.0 to 17.35 ppm selenium in brook trout (*Salvelinus fontinalis* [Mitchill, 1814]), white suckers (*Catostomus commersonii* [Lacepède, 1803]), fathead minnows (*Pimephales promelas* [Rafinesque, 1820]), and creek chubs (*Semotilus* [Rafinesque, 1820]) and 22.3 ppm selenium (composite sample of northern caddisfly [*Limnephilidae* (Kolenati, 1848)] tissue). Selenium was present in lower levels in benthic macroinvertebrates, such as leeches, snails, mayflies, and odonates (Selenium Monitoring Work Group, 2009, p. 7–8).

Human Health Concerns

Dietary selenium plays a critical role in human health owing to its importance to thyroid hormone metabolism, anti-oxidant defense mechanisms, and immune functions (Rayman, 2000). Insufficient selenium is associated with growth retarda-tion, impaired bone metabolism, and abnormalities in thyroid function (Stone, 2009). Human populations with insufficient selenium in their diet can be found living in geographic areas with low selenium contents in local bedrock and soils. One example is a northeast-southwest-trending belt in China and an area of southeastern Siberia where populations are at risk for Keshan disease (which causes cardiomyopathy) and Kashin Beck disease (a chronic degenerative osteoarthritis); both are caused by a deficiency of selenium.

Keshan disease was described in Chinese medical literature 100 years ago, but it was not until the mid-1970s that selenium deficiency was identified as its primary cause. After a widespread outbreak in 1935, it was determined to be endemic in children aged 2 to 10 years and in women of child-bearing age. Symptoms are fatigue after light exercise, cardiac arrhythmia and palpitations, loss of appetite, cardiac insufficiency, cardiomegaly, and congestive heart failure (World Health Organization and Food and Agricultural Orga-nization of the United Nations, 2004). Kashin Beck disease was also detected in Chinese children aged 5 to 13 years and in southeastern Siberia. The disease causes joint necrosis in the form of degeneration of the arm and leg joints, which results in structural shortening of bones and leads to growth retardation and stunting (World Health Organization and Food and Agricultural Organization of the United Nations, 2004).

In Finland, blood serum levels of less than 45 ppb selenium were believed to increase the risk of cardiovascular disease and cancer. Because of this, sodium selenate has been added to agricultural fertilizers since 1985 in order to increase the dietary intake. This practice has caused selenium dietary intake to increase from a base of 30 to 40 micrograms per day (µg/d) to greater than 100 µg/d by the early 1990s, and the daily intake is now considered safe and adequate (Varo and others, 1994). It should be noted, however, that some research recommends lower levels of dietary intake, and finds that doses of selenium greater than 75 µg/d, can be mildly toxic and related to an increased risk of diabetes (Winkel and others, 2012, and references therein)

Somewhat analogously, human populations living in geographic areas with high levels of selenium in local foods may suffer from selenium toxicity. This has been observed in humans and animals in the Hubei and Shaanxi Provinces in China, and in Punjab, India, where selenium levels in local foods are high and dietary intake per person is between 750 and 4,990 µg/d. In Punjab, the high dietary selenium values are the result of agricultural irrigation practices and high evaporation rates, which serve to concentrate selenium into irrigated soils and food crops. At doses of greater than 400 µg/d, selenium is acutely toxic and may lead to acute respiratory distress, cardiac failure, facial flushing, hair loss, kidney failure, light headedness, muscle tenderness, myocardial infarction, severe gastrointestinal and neurological symptoms, tremors, and, in rare cases, death (National Institutes of Health, 2013, and references therein). Chronic exposure to subacute levels leads to brittle hair and nails, skin lesions, and neurological disturbances (Winkel and others, 2012, and references therein).

One outcome of modern research into selenium and human health is a better understanding of its role in the immune system. It has been found that the cardiac lesions of Keshan disease are not the result solely of selenium deficiency, but are also related to infection by the coxsackie virus, which is initially nonvirulent, but which becomes virulent and myopathogenic in individuals with selenium deficiency. This process is not unique to the coxsackie virus. It has been determined that the early preclinical stages of human immu-nodeficiency virus (HIV) infection are marked by a significant decrease in blood plasma selenium concentrations, and that the magnitude of this decrease is linked to the rates of develop-ment of acquired immunodeficiency syndrome (AIDS) and to mortality rates associated with AIDS (World Health Organiza-tion and Food and Agricultural Organization of the United Nations, 2004). Finally, selenium deficiency has been linked to an increase in mercury toxicity (Berry and Ralston, 2008). Because of the high binding affinity between mercury and selenium, it is thought that selenium can function to chelate mercury and reduce its toxicity; if the molar ratio of mercury to selenium is high, however (that is, greater than 1:1), then the concentration of selenium is insufficient to provide this protective effect.

Pathways for Selenium Ingestion in Humans

Plant foods are the main dietary sources of selenium in most countries, followed by meats and seafood (National Institutes of Health, 2013). In all cases, the selenium content of food is derived from soils and the feed for livestock (World Health Organization, 2011). Although soil selenium is the source of selenium, it is important to note that total selenium concentration is not what controls selenium levels in food crops; rather, it is the concentration of bioavailable selenium that controls the levels. For example, the classical definition of selenium-deficient soils is when concentrations are less than 0.1 ppm selenium, whereas selenium-rich soils have greater than 0.5 ppm selenium. These concentrations refer to total selenium. Soils in areas of China where Keshan disease has occurred have an average concentration of 0.15 ppm selenium, which would not be classified as selenium deficient; however, these soils are selenium deficient because the bioavailable selenium is low. High content of organic matter is the cause of the low bioavailable selenium concentration because it immobilizes selenium by adsorption and biochemical reduction, making it unavailable for uptake by food crops.

The dietary intake of selenium varies somewhat across the United States and Canada because of differences in local soils and food; however, most Americans consume adequate amounts of selenium. The average daily selenium intake in Americans over 2 years in age is 108.5 micrograms from food alone, and if supplements are included, this value increases to 120.8 µg/d (National Institutes of Health, 2013).

Related Diseases, Cancers, and Human Health Effects From Industrial Exposures

Little has been reported regarding selenium health effects from human industrial exposures, and it is selenium deficiency from an inadequate diet that is the greatest human health concern. Selenium concentrations in gas emissions from coal combustion could be one potential cause of industrial exposure, as could exposure in industries with a significant occupational metals exposure risk, such as metals recovery (Fairweather-Tait and others, 2011). The manufacturing process for modern products, such as solar panels, might represent a potential risk if selenium is present in a bioavailable form. Manufactured nanomaterials may also pose health effects, because selenium is a key component in CdSe and PbSe quantum dots, which are nano-sized semiconductors used in light-emitting diodes and photovoltaics. Emergent properties of these materials could elicit toxic responses that may be different from those current selenium sources (Young and others, 2010).

Human Health Guidelines

Although water is not usually a major source of selenium to the human population (Fairweather-Tait and others, 2011),

the World Health Organization (WHO) has set a provisional guideline value for selenium in drinking water. The WHO recommendation is that when selenium intake from dietary sources is unknown, then 40 ppb should be the upper limit of selenium in drinking water (World Health Organization, 2011). In Canada, the Government has set this level at 10 ppb, although the Canadian Government is revisiting the criterion and proposing a new maximum acceptable concentration for human consumption of 50 ppb in response to a review of current scientific studies and an understanding of chronic selenosis (Health Canada, 2013). In the United States, the EPA has set the maximum contaminant level for selenium in drinking water at 50 ppb (U.S. Environmental Protection Agency 2014a).

Because there is a narrow concentration range between dietary deficiency (< 40 µg/d) and highly toxic levels (> 400 µg/d) (Winkel and others, 2012), the WHO recommends dietary intakes of 15 µg/d for infants from birth to 6 months, 30 µg/d for children aged 4 to 8 years, and 55 µg/d for older children and adults (World Health Organization, 2011). Older recommendations were 0.05 to 2 milligrams per day (mg/d) for adults, with lower ranges for children (Health Canada, 1992). In the United States, the National Institutes of Health has published recommended daily allowances (RDAs) for humans; these RDAs are similar to those recommended by the WHO, and range from an adequate intake of 15 µg/d for infants from birth to 6 months, to 55 µg/d for older children and adults (table Q7). Pregnant and breast-feeding women have RDAs of 60 and 79 µg/d, respectively (table Q7; National Institutes of Health, 2013).

Ecological Health Concerns

Research on selenium in the environment began in the 1930s when livestock in the Great Plains and Western United States were found with the symptoms of "alkali disease," including emaciation, loss of hair, deformation and shedding of hooves, loss of vitality, and erosion of joints in long bones (Science Dictionary, 2015). It became recognized that livestock poisoning was occurring because the livestock were browsing on selenium accumulator plants of the genus *Astragalus*; these plants grow in saline soils derived from marine Cretaceous sedimentary rocks exposed in more than 830,000 square kilometers of the Western United States (Trelease and Beath, 1949).

Once the cause of selenium poisoning was recognized, efforts were made to prevent and control the exposure of livestock to seleniferous plants using range management techniques. In 1957, however, it was learned that selenium is an essential trace element (or micronutrient) in mammals. It is an essential component of bacterial and mammalian enzyme systems, and that without it, selenium deficiency disorders, such as white muscle disease (in sheep) and mulberry heart disease (in pigs), could occur (Young and others, 2010, and references therein).

In 1976, the sudden disappearance of popular game fish from Belews Lake, North Carolina, was attributed to selenium poisoning. It was learned that the manmade reservoir was fed by water from a coal-ash settling basin that had created lake waters with selenium concentrations of 20 ppb. This level of selenium caused chronic selenium poisoning in the Belews Lake fish populations, where the most serious symptom was reproductive failure and post-hatch mortality. As a result of the selenium toxicity, 19 of 20 species of fish in Belews Lake were eradicated (Lemly, 2002).

Soon after this, in 1983, another extinction of fish populations was discovered. This time it was at the Kesterson Reservoir in San Joaquin Valley, Calif., which is a wetland area fed by agricultural drainage from the San Joaquin Valley. Massive numbers of dead and deformed bird embryos and chicks were found to accompany the fish extinction, and the cause was determined to be selenium poisoning from bioaccumulation in the food chain (Ohlendorf, 2002). After this discovery, deformities of aquatic birds from selenium toxicosis began to be observed in similar environments; that is, wetland basins that received waters draining seleniferous soils, such as the Tulare Lake Bed Area, Calif.; the Middle Green River Basin, Utah; the Kendrick Reclamation Project Area, Wyoming; the Sun River Basin, Montana; and the Stillwater Wildlife Management Area, Nevada. Most of these study areas had climate, geology, and hydrology similar to that of the San Joaquin Valley. Results indicated that bioaccumulation of selenium was occurring in most of the wetland areas, and these data marked the initial elucidation of a biogeochemical pathway for selenium from geologic source to aquatic wildlife (Presser and others, 1994).

Pathways for Selenium Ingestion in Aquatic and Terrestrial Organisms

Just as in human health, the main pathway for selenium entry into aquatic and terrestrial organisms is through diet, and speciation is an important factor in determining the amount of selenium that enters the food chain. The primary step by which selenium accumulates in aquatic systems is found at the base of the food chain where algae and other microorganisms (trophic level 1) accumulate selenium from water by factors of up to 1 million times the aqueous concentration. Selenate (Se(VI)) is slow to be taken up by these organisms, especially in the presence of sulfate, which is more competitive. Selenite (Se(IV)) and organo-selenides are taken up more quickly. Once selenium has been accumulated by an organism, the selenium is reduced to selenide (Se(-II)) and ultimately incorporated into amino acids, primarily selenomethionine, which is the organo-selenide that bioaccumulates in food webs and produces toxicity (Luoma and Presser, 2009).

The algae and microbes, together with abiotic particle-sorbed selenium, constitute the particulate selenium fraction in the water column. Particulate matter is ingested by aquatic primary consumers, such as zooplankton, insect larvae, larval fish, and bivalves (trophic level 2), thus transferring

Table Q7. National Institutes of Health recommended dietary reference intakes (DRIs) for selenium.

[Data are from the Food and Nutrition Board of the Institute of Medicine, National Academy of Sciences, and published by the National Institutes of Health (2013). Recommendations are for men and for women who are not pregnant or nursing. µg/d, microgram per day]

Age (years)	Recommended daily allowance (µg/d)	Tolerable upper intake level (µg/d)
0 to 0.5	[1]15	45
0.5 to 1	20	60
1 to 3	20	90
4 to 8	30	150
9 to 13	40	280
14 to 18	55	400
19 to 50	55	400
51+	55	400

[1]This level is called the adequate intake (AI) level because evidence is insufficient to develop a recommended daily allowance.

selenomethionine (a naturally occurring amino acid) up the food chain. Abiotic selenium, which may be ingested with particulate matter, is transformed to selenomethionine by the primary consumers, which may, in turn, be consumed by predators, such as fish and birds (trophic level 3 and above). In this manner, selenium continues to accumulate, and its concentrations magnify as it is transferred to higher trophic levels. The accumulated concentration determines whether toxicity is manifested (Luoma and Presser, 2009; Young and others, 2010; U.S. Environmental Protection Agency, 2014b).

Recycling of selenium in the aquatic environment occurs when organo-selenide, mostly in the form of selenomethionine, is returned to the water upon the death and decay of aquatic organisms. Some organo-selenide may be oxidized to Se(IV), but neither organo-selenide nor Se(IV) will be converted to Se(VI) because the reaction is very slow, with a half-life of hundreds of years. The net outcome of recycling in a watershed is an evolution of selenium from Se(VI), which is the primary form of selenium from natural and anthropogenic sources, to Se(IV) and organo-selenide (Se-II), which are the more bioavailable species (Young and others, 2010).

Selenium enters terrestrial organisms by a similar pathway. Accumulator plants take up selenium from soil water, usually as Se(VI) or Se(IV), and transform it primarily into the amino acid selenomethionine. These accumulators are able to incorporate large amounts of selenium—some as high as 15,000 ppm (Trelease and Beath, 1949). Livestock grazing on these plants accumulate selenomethionine, with potentially fatal results.

Aquatic Toxicity and Aquatic Ecosystem Health Guidelines

Selenium is bioaccumulative, meaning that fish and other aquatic life can contain concentrations greater than the surrounding water. The primary source of selenium to aquatic life is dietary, and toxicity primarily occurs through transfer to eggs and subsequent reproductive effects. Because selenium bioaccumulation rates may vary among aquatic environments, the EPA has proposed a four-part freshwater criterion that includes elements for (1) fish eggs and ovaries, set at 15.2 ppm selenium dry weight; (2) whole fish body tissue not to exceed 8.1 ppm dry weight, or muscle tissue not to exceed 11.8 ppm dry weight; (3) a 30-day average selenium concentration not to exceed 4.8 ppb selenium in lotic (flowing) waters or 1.3 ppb selenium in lentic (standing) waters, more than 1 time in 3 years, on average; and (4) repeated short-term exposures where the intermittent water quality concentration for both lentic and lotic waters is calculated from the 30-day concentration; the background selenium concentration; and the fraction of time (over the 30-day period) during which elevated selenium concentrations occur. The purpose of this criterion with two fish-tissue-based and two water-based elements is to protect against adverse reproductive effects of selenium on aquatic life, and the criterion apply to total selenium concentrations; that is, the sum of all forms of selenium (selenate, selenite, organic selenium, and any other forms) (U.S. Environmental Protection Agency, 2014a).

Previous to this four-part criterion, the EPA freshwater criterion for protection of aquatic life was 5 ppb selenium with a lower criterion of 2 ppb selenium for some wetland environments in California (Luoma and Presser, 2009). In marine waters, the maximum allowable concentration is 290 ppb selenium, whereas the continuous concentration is 71 ppb selenium (U.S. Environmental Protection Agency, 2014c). It should be noted that there is no international agreement on these guidelines. In Canada, the marine and freshwater guidelines are 2 ppb selenium, and in Europe, selenium is not considered an ecological threat and is not subject to environmental quality standards (Luoma and Presser, 2009; European Commission Joint Research Centre Institute for Health and Consumer Protection, 2011).

Problems and Future Research

There is no "free lunch." Selenium extraction from mineral resources has led to technological development and has greatly benefited our society. At the same time, there are environmental consequences of mining that must be recognized and evaluated for every mining project. This chapter provides an overview of the selenium life cycle. Although the main focus is selenium as a mineral resource and commodity, these selenium topics cannot be presented without acknowledging the environmental concerns that accompany the presence of selenium in the environment.

Challenges abound for new research on selenium in the 21st century. Extraction of selenium from the waste products (anode slimes) of copper ore processing has been a proven technology for many decades, but changes in processing technology will affect selenium recovery. Will it be possible to recover selenium from other sources economically? Coal and other organic carbon sources come immediately to mind; these technologies exist but are not economically favorable at present. High-grade but low-tonnage deposits with selenide minerals may be another source for selenium extraction, contingent upon available technology and favorable economics.

Other research directions would contribute to the scientific understanding of the selenium elemental cycle in Earth's crust. A very basic question concerns the amount of selenium in the crust. The current estimate of 0.05 ppm selenium in the continental crust dates to 1961. Could this estimate be updated and revised, given our current knowledge of selenium concentrations in various crustal reservoirs? Next, can selenium concentrations and isotopic composition be used as an exploration tool for the discovery of concealed deposits? Finally, to thoroughly understand the elemental cycle of selenium in the earth, it would be useful to compare and contrast the magmatic selenium pathway from volcanoes to enriched ore deposits, to the sedimentary selenium pathway that involves selenium uptake by algae and bacteria in productive marine basins and deposition in organic-rich sediments. Are there connections between these two pathways and does selenium cycle between them?

Research opportunities exist under the topic of selenium environmental concerns as well. Some of the most pressing topics involve the bioavailability of selenium and its incorporation into the food web and whether the understanding of this cycle can translate into ecosystem and human health guidelines. The newly proposed tissue-based criterion for selenium in aquatic systems is a direct result of years of focused scientific study. Other research might target methods to redirect or disrupt the process that transfers selenium from rock to biota. Studies that amend selenium-rich soil with sulfur, or plant non-selenium-accumulating plants on mine waste, are creative attempts to break the rock-biota selenium connection. Studies to limit selenium solubility from nanoparticles would aid in keeping new technologies environmentally safe. Regardless of the focus, research into the elemental cycle of selenium, including the manufacture and disposal of selenium-containing commodities, will continue to increase understanding of Earth processes.

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References Cited

Note: All Web links listed were active as of the access date but may no longer be available.

Adriano, D.C., 1986, Trace elements in the terrestrial environment: New York, N.Y., Springer-Verlag, 533 p.

Aiuppa, Alessandro, Allard, Patrick, D'Alessandro, Walter, Michel, Agnes, Parello, Francesco, Treuil, Michel, and Valenza, Mariano, 2000, Mobility and fluxes of major, minor and trace metals during basalt weathering and groundwater transport at Mt. Etna volcano (Sicily): Geochimica et Cosmochimica Acta, v. 64, no. 11, p. 1827–1841. [Also available at http://dx.doi.org/10.1016/S0016-7037(00)00345-8.]

Aiuppa, Alessandro, Federico, Cinzia, Allard, Patrick, Gurrieri, Sergio, and Valenza, Mariano, 2005, Trace metal modeling of groundwater-gas-rock interactions in a volcanic aquifer—Mount Vesuvius, southern Italy: Chemical Geology, v. 216, nos. 3–4, p. 289–311. [Also available at http://dx.doi.org/10.1016/j.chemgeo.2004.11.017.]

American Physical Society Panel on Public Affairs and the Materials Research Society, 2011, Energy critical elements—Securing materials for emerging technologies: Washington, D.C., American Physical Society, 19 p. plus 2 appendixes, accessed May 13, 2016, at http://www.aps.org/policy/reports/popa-reports/upload/elementsreport.pdf.

Auclair, Gilles, Fouquet, Yves, and Bohn, Marcel, 1987, Distribution of selenium in high-temperature hydrothermal sulfide deposits at 13° north, East Pacific Rise: The Canadian Mineralogist, v. 25, no. 4, p. 577–587. [Also available at http://canmin.geoscienceworld.org/content/25/4/577.full.pdf+html.]

Baker, L., Gustafson, J., Wood, S., and Geist, D., 2000, Selenium chemistry in the Red Dog Mine ore, mill and tailings pond: Geological Society of America, Abstracts with Programs, v. 32, no. 7, p. 191.

Berry, M.J., and Ralston, N.V., 2008, Mercury toxicity and the mitigating role of selenium: EcoHealth, v. 5, no. 4, p. 456–459. [Also available at http://dx.doi.org/10.1007/s10393-008-0204-y.]

Bindi, Luca, and Pratesi, Giovanni, 2005, Selenojalpaite, Ag$_3$CuSe$_2$, a new mineral species from the Skrikerum Cu-Ag-Tl selenide deposit, Småland, southeastern Sweden: The Canadian Mineralogist, v. 43, no. 4, p. 1373–1377. [Also available at http://dx.doi.org/10.2113/gscanmin.43.4.1373.]

Bleiwas, D.I., 2010, Byproduct mineral commodities used for the production of photovoltaic cells: U.S. Geological Survey Circular 1365, 10 p., accessed May 24, 2016, at http://pubs.er.usgs.gov/publication/cir1365.

Boyd, Russel, 2011, Selenium stories: Nature Chemistry, v. 3, p. 570. [Also available at http://www.nature.com/nchem/journal/v3/n7/full/nchem.1076.html]

Brininstool, Mark, 2015, Copper [advance release], in Metals and minerals: U.S. Geological Survey Minerals Yearbook 2012, v. I, p. 20.1–20.27, accessed May 24, 2016, at http://minerals.usgs.gov/minerals/pubs/commodity/copper/myb1-2012-coppe.pdf.

Brown, R.D., Jr., 2002, Selenium and tellurium, in Metals and minerals: U.S. Geological Survey Minerals Yearbook 2000, v. I, p. 67.1–67.7, accessed May 24, 2016, at http://minerals.usgs.gov/minerals/pubs/commodity/selenium/830400.pdf.

Brunfelt, A.O., and Steinnes, E., 1967, Determination of selenium in standard rocks by neutron activation analysis: Geochimica et Cosmochimica Acta, v. 31, no. 2, p. 283–285. [Also available at http://dx.doi.org/10.1016/S0016-7037(67)80051-6.]

Bryant, Gary, McPhilliamy, Scott, and Childers, Hope, 2003, A survey of the water quality of streams in the primary region of mountaintop/valley fill coal mining—October 1999 to January 2001—Final report, in Appendix D of Mountaintop mining/valley fills in Appalachia—Draft programmatic environmental impact statement: U.S. Environmental Protection Agency Report EPA–9–03–R–00013B, p. 661–789, accessed May 24, 2016, at http://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P100G122.txt.]

Butterman, W.C., and Brown, R.D., Jr., 2004, Mineral commodity profiles—Selenium: U.S. Geological Survey Open-File Report 03–018, 19 p. plus 1 appendix, accessed May 24, 2016, at http://pubs.usgs.gov/of/2003/of03-018/of03-018.pdf.

Cabral, A.R., Lehmann, B., Kwitko, R., and Cravo Costa, C.H., 2002, The Serra Pelada Au-Pd-Pt deposit, Carajás mineral province, northern Brazil—Reconnaissance mineralogy and chemistry of very high grade palladian gold mineralization: Economic Geology, v. 97, p. 1127–1138. [Also available at http://dx.doi.org/10.2113/gsecongeo.97.5.1127.]

Cahill, T.A., and Eldred, R.A., 1998, Particulate selenium in the atmosphere, *in* Frankenberger, W.T., Jr., and Engberg, R.A., eds., Environmental chemistry of selenium: New York, N.Y., Marcel Dekker, Inc., p. 613–632.

Cannon, H.L., 1957, Description of indicator plants and methods of botanical prospecting for uranium deposits on the Colorado Plateau: U.S. Geological Survey Bulletin 1030–M, p. 399–516. [Also available at http://pubs.usgs.gov/bul/1030m/report.pdf.]

Chouinard, Annick, Paquette, Jeanne, and Williams-Jones, A.E., 2005, Crystallographic controls on trace-element incoporation in auriferous pyrite from the Pascua epithermal high-sulfidation deposit, Chile-Argentina: The Canadian Mineralogist, v. 43, no. 3, p. 951–963. [Also available at http://dx.doi.org/10.2113/gscanmin.43.3.951.]

Ciobanu, S.L., Cook, N.J., and Spry, P.G., 2006, Preface— Special issue—Telluride and selenide minerals in gold deposits—How and why?: Mineralogy and Petrology, v. 87, no. 3, p. 163–169. [Also available at http://dx.doi.org/10.1007/s00710-006-0133-9.]

Clark, J.W., 1950, Minor metals, *in* Minerals yearbook 1948: U.S. Bureau of Mines, p. 1310–1350. [Also available at http://minerals.usgs.gov/minerals/pubs/usbmmyb.html.]

Cocker, H.A., Mauk, J.L., and Rabone, S.D.C., 2013, The origin of Ag-Au-S-Se minerals in adularia-sericite epithermal deposits—Constraints from the Broken Hills deposit, Hauraki goldfield, New Zealand: Mineralium Deposita, v. 48, no. 2, p. 249–266. [Also available at http://dx.doi.org/10.1007/s00126-012-0410-y.]

Coleman, Lynn, Bragg, L.J., and Finkelman, R.B., 1993, Distribution and mode of occurrence of selenium in US coals: Environmental Geochemistry and Health, v. 15, no. 4, p. 215–227. [Also available at http://dx.doi.org/10.1007/BF00146745.]

Coleman, R.G., 1959, The natural occurrence of galena– clausthalite solid solution series: The American Mineralogist, v. 44, January–February, p. 166–175. [Also available at http://www.minsocam.org/ammin/AM44/AM44_166.pdf.]

Coleman, R.G., and Delevaux, M.H., 1957, Occurrence of selenium in sulfides from some sedimentary rocks of the Western United States: Economic Geology, v. 52, p. 499–527. [Also available at http://dx.doi.org/10.2113/gsecongeo.52.5.499.]

Cook, N.J., Ciobanu, C.L., Danyushevsky, L.V., and Gilbert, Sarah, 2011, Minor and trace elements in bornite and associated Cu-(Fe)-sulfides—A LA–ICP–MS study: Geochimica et Cosmochimica Acta, v. 75, no. 21, p. 6473–6496. [Also available at http://dx.doi.org/10.1016/j.gca.2011.08.021.]

Cutter, G.A., and Bruland, K.W., 1984, The marine biogeochemistry of selenium—A re-evaluation: Limnology and Oceanography, v. 29, no. 6, p. 1179–1192. [Also available at http://dx.doi.org/10.4319/lo.1984.29.6.1179.]

Cutter, G.A., and Cutter, L.S., 2004, Selenium biogeochemistry in the San Francisco Bay estuary—Changes in water column behavior: Estuarine, Coastal and Shelf Science, v. 61, no. 3, p. 463–476. [Also available at http://dx.doi.org/10.1016/j.ecss.2004.06.011.]

Dare, S.A.S., Barnes, S.J., and Prichard, H.M., 2010, The distribution of platinum group elements (PGE) and other chalcophile elements among sulfides from the Creighton Ni-Cu-PGE sulfide deposit, Sudbury, Canada, and the origin of palladium in pentlandite: Mineralium Deposita, v. 45, no. 8, p. 765–793. [Also available at http://dx.doi.org/10.1007/s00126-010-0295-6.]

Davidson, D.F., 1963, Selenium in some oxidized sandstone-type uranium deposits: U.S. Geological Survey Bulletin 1162–C, p. C1–C33. [Also available at http://pubs.usgs.gov/bul/1162c/report.pdf.]

Drabek, M., 1995, The Mo-Se-S and the Mo-Te-S systems: Neues Jahrbuch für Mineralogie–Abhandlungen, v. 169, p. 255–263.

Eckstrand, O.R., and Hulbert, L.J., 1987, Selenium and the source of sulphur in magmatic nickel and platinum deposits: Geological Association of Canada and Mineralogical Association of Canada, Program with Abstracts, v. 12, p. 40.

Elzinga, E.J., Tang, Yuanzhi, McDonald, Jason, DeSisto, Stephanie, and Reeder, R.J., 2009, Macroscopic and spectroscopic characterization of selenate, selenite, and chromate adsorption at the solid-water interface of γ-Al$_2$O$_3$: Journal of Colloid and Interface Science, v. 340, no. 2, p. 153–159. [Also available at http://dx.doi.org/10.1016/j.jcis.2009.08.033.]

European Commission Joint Research Centre Institute for Health and Consumer Protection, 2011, Environmental quality standards applicable to surface water: European Commission Joint Research Centre, accessed May 24, 2016, at http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=URISERV%3Al28180.

Fairweather-Tait, S.J., Bao, Yongping, Broadley, M.R., Collings, Rachel, Ford, Dianne, Hesketh, J.E., and Hurst, Rachel, 2011, Selenium in human health and disease: Antioxidants & Redox Signaling, v. 14, no. 7, p. 1337–1383. [Also available at http://dx.doi.org/10.1089/ars.2010.3275.]

Fang, W.X., Huang, Z.Y., and Wu, P.W., 2003, Contamination of the environmental ecosystems by trace elements from mining activities of Badao bone coal mine in China: Environmental Geology, v. 44, no. 4, p. 373–378. [Also available at http://dx.doi.org/10.1007/s00254-003-0768-3.]

Filimonova, L.Ye., 1972, Selenium and tellurium in the Boshchekul' copper-molybdenum deposit: Geochemistry International, v. 9, p. 151–156. [English translation of Russian article. Originally published in Geokhimiya, no. 2, p. 241–246.]

Fitzpatrick, A.J., 2008, The measurement of the Se/S ratios in sulphide minerals and their application to ore deposits: Kingston, Ontario, Canada, Queen's University, Ph.D. dissertation, 203 p. [Also available at https://qspace.library.queensu.ca/bitstream/1974/1045/1/Fitzpatrick_Alexander_J_200802_PHD.pdf.]

Fleming, G.A., 1962, Selenium in Irish soils and plants: Soil Science, v. 94, no. 1, p. 28–35.

Floor, G.H., and Román-Ross, Gabriela, 2012, Selenium in volcanic environments—A review: Applied Geochemistry, v. 27, no. 3, p. 517–531. [Also available at http://dx.doi.org/10.1016/j.apgeochem.2011.11.010.]

Floor, G.H., Calabrese, S., Román-Ross, G., D'Alessandro, W., and Aiuppa, A., 2011, Selenium mobilization in soils due to volcanic derived acid rain—An example from Mt Etna volcano, Sicily: Chemical Geology, v. 289, nos. 3–4, p. 235–244. [Also available at http://dx.doi.org/10.1016/j.chemgeo.2011.08.004.]

Förster, H.J., 2005, Mineralogy of the U-Se-polymetallic deposit Niederschlema-Alberoda, Erzgebirge, Germany. IV—The continuous clausthalite-galena solid-solution series: Neues Jahrbuch für Mineralogy—Abhandlungen, v. 181, no. 2, April, p. 125–134. [Also available at http://dx.doi.org/10.1127/0077-7757/2005/0011.]

Frost, D.V., 1972, The two faces of selenium—Can selenophobia be cured?: CRC Critical Reviews in Toxicology, v. 1, no. 4, p. 467–514.

Fukushi, Keisuke, and Sverjensky, D.A., 2007, A surface complexation model for sulfate and selenate on iron oxides consistent with spectroscopic and theoretical molecular evidence: Geochimica et Cosmochimica Acta, v. 71, no. 1, p. 1–24. [Also available at http://dx.doi.org/10.1016/j.gca.2006.08.048.]

Gaines, R.V., Skinner, C., Foord, E.E., Mason, B., and Rosenzweig, A., 1997, Dana's new mineralogy—The system of mineralogy of James Dwight Dana and Edward Salisbury Dana (8th ed.): New York, N.Y., John Wiley & Sons, Inc., 1,872 p.

Garone, Philip, 1999, The tragedy at Kesterson Reservoir—A case study in environmental history and a lesson in ecological complexity: Environs, v. 22, no. 2, p. 107–144. [Also available at http://environs.law.ucdavis.edu/volumes/22/2/articles/garone.pdf.]

George, M.W., 2013, Selenium (Se), in Metal prices in the United States through 2010: U.S. Geological Survey Scientific Investigations Report 2012–5188, p. 158–160, accessed May 24, 2016, at http:/pubs.usgs.gov/sir/2012/5188.

George, M.W., 2014, Selenium, in Mineral commodity summaries 2014: U.S. Geological Survey, 196 p., accessed March 29, 2016, at https://minerals.usgs.gov/minerals/pubs/commodity/selenium/mcs-2014-selen.pdf .

George, M.W., and Wagner, L.A., 2009, Selenium recycling in the United States in 2004, chap. T of Sibley, S.F., ed., Flow studies for recycling metal commodities in the United States: U.S. Geological Survey Circular 1196–T, p. T1–T7, accessed May 25, 2016, at http://pubs.usgs.gov/circ/circ1196t/.

Goldschmidt, V.M., 1954, Geochemistry: Oxford, United Kingdom, Clarendon Press, 730 p.

Goldschmidt, V.M., and Strock, L.W., 1935, Zur Geochemie des Selens, II [Geochemistry of Selenium]: Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen Mathematisch-Physikalische Klasse IV [Proceedings of the Society of Sciences in Göttingen, Mathematics and Physical Class 4], v. 1, no. 11, p. 123–142.

Greenland, L.P., and Aruscavage, Philip, 1986, Volcanic emission of Se, Te, and As from Kilauea volcano, Hawaii: Journal of Volcanology and Geothermal Research, v. 27, nos. 1–2, p. 195–201. [Also available at http://dx.doi.org/10.1016/0377-0273(86)90086-7.]

Greenwood, N.N., and Earnshaw, A., 1997, Chemistry of the elements (2d ed.): Oxford, United Kingdom, Butterworth Heinemann, 1,341 p.

Gregory, M.J., Lang, J.R., Gilbert, Sarah, and Hoal, K.O., 2013, Geometallurgy of the Pebble porphyry copper-gold-molybdenum deposit, Alaska—Implications for gold distribution and paragenesis: Economic Geology, v. 108, p. 463–482. [Also available at http://dx.doi.org/10.2113/econgeo.108.3.463.]

Hall, R.A, Zook, E.G., and Meaburn, G.M., 1978, National Marine Fisheries Service survey of trace elements in the fishery resource: U.S. Department of Commerce, NOAA Technical Report NMFS SSRF–721, 313 p. [Also available at http://docs.lib.noaa.gov/noaa_documents/NMFS/special_scientific_report_fisheries/NMFS_SSRF_721.PDF.]

Hawley, J.E., and Nichol, Ian, 1959, Selenium in some Canadian sulfides: Economic Geology, v. 54, p. 608–628. [Also available at http://dx.doi.org/10.2113/gsecongeo.54.4.608.]

Haxel, G.B., Hedrick, J.B., and Orris, G.J., 2002, Rare earth elements—Critical resources for high technology: U.S. Geological Survey Fact Sheet 087–02, 4 p. [Also available at http://geopubs.wr.usgs.gov/fact-sheet/fs087-02/.]

Health Canada, 1992, Selenium, *in* Guidelines for Canadian drinking water quality [supporting document]: Ottawa, Ontario, Canada, Health Canada, Health Protection Branch, accessed May 25, 2016, at http://publications.gc.ca/collections/Collection/H48-10-1-68-1992E.pdf.

Health Canada, 2013, Selenium in drinking water: Ottawa, Ontario, Canada, Health Canada, Water, Air, and Climate Change Bureau, accessed August 1, 2015, at http://www.hc-sc.gc.ca/ewh-semt/consult/index-eng.php#water. [Available upon request from the Water, Air, and Climate Change Bureau.]

Howard, J.H., III, 1977, Geochemistry of selenium—Formation of ferroselite and selenium behavior in the vicinity of oxidizing sulfide and uranium deposits: Geochimica et Cosmochimica Acta, v. 41, no. 11, p. 1665–1678. [Also available at http://dx.doi.org/10.1016/0016-7037(77)90176-4.]

Huston, D.L., Sie, S.H., Suter, G.F., Cooke, D.R., and Both, R.A., 1995, Trace elements in sulfide minerals from eastern Australian volcanic-hosted massive sulfide deposits; Part I, Proton microprobe analyses of pyrite, chalcopyrite, and sphalerite, and Part II, Selenium levels in pyrite; comparison with delta^{34}S values and implications for the source of sulfur in volcanogenic hydrothermal systems: Economic Geology, v. 90, p. 1167–1196. [Also available at http://dx.doi.org/10.2113/gsecongeo.90.5.1167.]

Ingerson, Earl, 1964, Introduction, *in* Sindeeva, N.D., Mineralogy and types of deposits of selenium and tellurium: New York, N.Y., Wiley Interscience Publishers, p. v–vi.

International Mineralogical Association, 2014, The new IMA list of minerals—A work in progress: International Mineralogical Association, December, accessed March 29, 2016, at http://nrmima.nrm.se//IMA_Master_List_(2014-12).pdf.

Izawa, Eiji, Urashima, Yukitoshi, Ibaraki, Kenzo, Suzuki, Ryoichi, Yokohama, Takeo, Kawasaki, Kiyoshi, Koga, Akito, and Sachihiro, Taguchi, 1990, The Hishikari gold deposit—High-grade epithermal veins in Quaternary volcanics of southern Kyushu, Japan: Journal of Geochemical Exploration, v., 36, nos. 1–3, p. 1–56. [Also available at http://dx.doi.org/10.1016/0375-6742(90)90050-K.]

Jackson, J.A., ed., 1997, Glossary of geology (4th ed.): Alexandria, Va., American Geological Institute, 769 p.

Jenkins, D.W., 1980, Biological monitoring of toxic trace metals. v. 2, Toxic trace metals in plants and animals of the world. Part III: U.S. Environmental Protection Agency Report no. 600/3–80/0921, p. 1130–1148.

Jensen, N.L., 1985, Selenium, *in* Knoerr, A.W., ed., Mineral facts and problems: U.S. Bureau of Mines Bulletin 675, p. 705–711.

John, D.A., 2001, Miocene and early Pliocene epithermal gold-silver deposits in the northern Great Basin, Western United States—Characteristics, distribution, and relationship to magmatism: Economic Geology, v. 96, p. 1827–1853. [Also available at http://dx.doi.org/10.2113/gsecongeo.96.8.1827.]

John, D.A., Ayuso, R.A., Barton, M.D., Blakely, R.J., Bodnar, R.J., Dilles, J.H., Gray, Floyd, Graybeal, F.T., Mars, J.C., McPhee, D.K., Seal, R.R., Taylor, R.D., and Vikre, P.G., 2010, Porphyry copper deposit model, chap. B *of* Mineral deposit models for resource assessment: U.S. Geological Survey Scientific Investigations Report 2010–5070–B, 169 p. [Also available at http://pubs.usgs.gov/sir/2010/5070/b/.]

John, D.A., Hofstra, A.H., Fleck R.J., Brummer, J.E., and Saderholm, E.C., 2003, Geologic setting and genesis of the Mule Canyon low-sulfidation epithermal gold-silver deposit, north-central Nevada: Economic Geology, v. 98, p. 425–463.

Johnsson, Lars, 1992, Selenium in Swedish soils—Factors influencing soil content and plant uptake: Uppsala, Sweden, Swedish University of Agricultural Science, Department of Soil Sciences, Reports and Dissertations 10. [Also available at http://www.vaxteko.nu/html/sll/slu/reports_diss_markvetenskap/RDV10/RDV10.HTM.]

Kabata-Pendias, Alina, and Pendias, Henryk, 1984, Trace elements in soils and plants: Boca Raton, Fla., CRC Press, 413 p.

Kharkar, D.P., Turekian, K.K., and Bertine, K.K., 1968, Stream supply of dissolved silver, molybdenum, antimony, selenium, chromium, cobalt, rubidium, and cesium to the oceans: Geochimica et Cosmochimica Acta, v. 32, no. 3, p. 285–298. [Also available at http://dx.doi.org/10.1016/0016-7037(68)90016-1.]

Koljonen, T., 1976, Luikonlahti—Selenium in the vicinity of copper ore, *in* Kauranne, L.K., ed., Conceptual models in exploration geochemistry—Norden 1975: Journal of Geochemical Exploration, v. 5, no. 3, p. 263–265. [Also available at http://www.sciencedirect.com/science/journal/03756742/5/3.]

Kovalenker, V.A., Gladyshev, G.D., and Nosik, L.P., 1975, Isotopic composition of sulfide sulfur from deposits of Talnakh ore node in relation to their selenium content: International Geology Review, v. 17, no. 6, p. 725–734. [Also available at http://dx.doi.org/10.1080/00206817509471656.]

Krähenbühl, Urs, Ganapathy, R., Morgan, J.W., and Anders, Edward, 1973, Volatile elements in Apollo 16 samples—Implication for highland volcanism and accretion history of the moon—Lunar Science Conference, 4th, Houston, Texas, March 5–8, 1973, Proceedings, v. 2: New York, N.Y., Pergamon Press, Inc., p. 1325–1348. [Also available at http://adsabs.harvard.edu/full/1973LPSC....4.1325K.]

Křibek, B., Majer, V., Knésl, I., Mihaljevic, M., Ettler, V., and Sraček, O., 2010, Soil contamination and health risks associated with former smelting of Pb-Zn ores at Kabwe, Zambia: Geochimica et Cosmochimica Acta, v. 74, no. 12, Supplement, p. A540. [Also available at http://dx.doi.org/10.1016/j.gca.2010.04.036.]

Lakin, H.W., and Byers, H.G., 1941, Selenium occurrence in certain soils in the United States, with a discussion of related topics—Sixth report: Washington, D.C., U.S. Department of Agriculture Technical Bulletin 783, October, 27 p. [Also available at https://naldc.nal.usda.gov/download/CAT86200778/PDF.]

Lakin, H.W., and Davidson, D.F., 1973, Selenium, in Brobst, D.A., and Pratt, W.P., eds., United States mineral resources: U.S. Geological Survey Professional Paper 820, p. 573–576. [Also available at https://pubs.er.usgs.gov/publication/pp820.]

Lemly, A.D., 1985, Toxicology of selenium in a freshwater reservoir—Implications for environmental hazard evaluation and safety: Ecotoxicology and Environmental Safety, v. 10, no. 3, p. 314–338.

Lemly, A.D., 1997, Ecosystem recovery following selenium contamination in a freshwater reservoir: Ecotoxicology and Environmental Safety, v. 36, no. 3, p. 275–281.

Lemly, A.D., 2002, Symptoms and implications of selenium toxicity in fish—The Belews Lake case example: Aquatic Toxicology, v. 57, nos. 1–2, p. 39–49. [Also available at http://dx.doi.org/10.1016/S0166-445X(01)00264-8.]

Leutwein, F., 1972, Selenium 34, chaps. B through O of Wedepohl, K.H., ed., Handbook of geochemistry, v. 2, pt. 3: West Berlin, West Germany, Springer-Verlag, p. 34-B-1–34-O-1.

Leybourne, M.I., and Cameron, E.M., 2008, Source, transport, and fate of rhenium, selenium, molybdenum, arsenic, and copper in groundwater associated with porphyry-Cu deposits, Atacama Desert, Chile: Chemical Geology, v. 247, nos. 1–2, p. 208–228. [Also available at http://dx.doi.org/10.1016/j.chemgeo.2007.10.017.]

Luoma, S.N., and Presser, T.S., 2009, Emerging opportunities in management of selenium contamination: Environmental Science and Technology, v. 43, no. 22, p. 8483–8487. [Also available at http://dx.doi.org/10.1021/es900828h.]

Mackowiak, C.L., Amacher, M.C., Hall, J.O., and Herring, J.R., 2004, Uptake of selenium and other contaminant elements into plants and implications for grazing animals in southeast Idaho, chap. 19 of Hein, J.R., ed., Life cycle of the Phosphoria Formation—From deposition to the post-mining environment: Handbook of Exploration and Environmental Geochemistry, v. 8, p. 527–555. [Also available at http://dx.doi.org/10.1016/S1874-2734(04)80021-4.]

Massachusetts Institute of Technology, 2010, Critical elements for new energy technologies—An MIT Energy Initiative Workshop report: Cambridge, Mass., Massachusetts Institute of Technology, 175 p. accessed May 26, 2016, at http://mitei.mit.edu/publications/reports-studies/critical-elements-new-energy-technologies. [Also available at https://energy.mit.edu/publication/critical-elements-for-new-energy-technologies/.]

May, T.W., and McKinney, G.L., 1981, Cadmium, lead, mercury, arsenic, and selenium concentrations in freshwater fish, 1976–77—National Pesticide Monitoring Program: Pesticides Monitoring Journal, v. 15, no. 1, June, p. 14–38. [Also available at https://archive.org/details/pesticidesmonito15unit.]

Mayland, H.F., 1985, Selenium in soils and plants, in Maas, J., ed., Selenium responsive diseases in food animals—Proceedings of a symposium held at the Western States Veterinary Conference, Las Vegas, Nev., February 18, 1985: Princeton Junction, N.J., Veterinary Learning Systems Co., Inc., p. 5–10. [Also available at http://eprints.nwisrl.ars.usda.gov/764/.]

McNeal, J.M., and Balistrieri, L.S., 1989, Geochemistry and occurrence of selenium—An overview, in Jacobs, L.W., ed., Selenium in agriculture and the environment: SSSA Special Publication 23, p. 1–13. [Also available at http://dx.doi.org/10.2136/sssaspecpub23.c1.]

Mindat.org, 2015, Mindat.org online database: Hudson Institute of Mineralogy, accessed March 29, 2015, at http://www.mindat.org/.

Minkin, J.A., Finkelman, R.B., Thompson, C.L., Chao, E.C.T., Ruppert, L.F., Blank, H., and Cecil, C.B., 1984, Microcharacterization of arsenic- and selenium-bearing pyrite in Upper Freeport coal, Indiana County, Pennsylvania: Scanning Electron Microscopy, v. 4, p. 1515–1524.

Mosher, B.W., Duce, R.A., Prospero, J.M., and Savoie, D.L., 1987, Atmospheric selenium—Geographical distribution and ocean to atmosphere flux in the Pacific: Journal of Geophysical Research, v. 92, no. D11, November 20, p. 13277–13287. [Also available at http://dx.doi.org/10.1029/JD092iD11p13277.]

Moxon, A.L., Olson, O.E., Searight, W.V., and Sandals, K.M., 1938, The stratigraphic distribution of selenium in the Cretaceous formations of South Dakota and the selenium content of some associated vegetation: American Journal of Botany, v. 25, no. 10, p. 794–809. [Also available at http://www.jstor.org/stable/2436607.]

MSE Technology Applications, Inc., 2001, Selenium treatment/removal alternatives demonstration project, final report prepared for the U.S. Environmental Protection Laboratory, National Risk Management Research Laboratory, and the USDOE National Energy Technology Laboratory under Contract No. DE–AC22–96EW96405: Butte, Mont., MSE Technology Applications, Inc., EPA/600/R-01/077, June, accessed March 9, 2015, at http://www.epa.gov/nscep/index.html. [Also available at http://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P1008GVL.txt.]

Naftz, D.L., and Rice, J.A., 1989, Geochemical processes controlling selenium in ground water after mining, Powder River Basin, Wyoming, U.S.A.: Applied Geochemistry, v. 4, no. 6, November–December, p. 565–575. [Also available at http://dx.doi.org/10.1016/0883-2927(89)90067-X.]

Naftz, D.L., Johnson, W.P., Freeman, M.L., Beisner, Kimberly, Diaz, Ximena, and Cross, V.A., 2009, Estimation of selenium loads entering the south arm of Great Salt Lake, Utah, from May 2006 through March 2008: U.S. Geological Survey Scientific Investigations Report 2008–5069, 40 p. [Also available at http://pubs.usgs.gov/sir/2008/5069/.]

National Institutes of Health, 2013, Selenium—Dietary supplement fact sheet: National Institutes of Health Web page, accessed March 9, 2015, at http://ods.od.nih.gov/factsheets/Selenium-HealthProfessional/.

Nickel, E.H., 2002, An unusual occurrence of Pd, Pt, Au, Ag and Hg minerals in the Pilbara region of Western Australia: The Canadian Mineralogist, v. 40, no. 2, p. 419–433. [Also available at http://dx.doi.org/10.2113/gscanmin.40.2.419.]

Nriagu, J.O., and Wong, H.K., 1983, Selenium pollution of lakes near the smelters at Sudbury, Ontario: Nature, v. 301, p. 55–57. [Also available at http://dx.doi.org/10.1038/301055a0.]

Ohlendorf, H.M., 2002, The birds of Kesterson Reservoir—A historical perspective: Aquatic Toxicology, v. 57, nos. 1–2, p. 1–10. [Also available at http://dx.doi.org/10.1016/S0166-445X(01)00266-1.]

Owen, David, 2004, Making copies: Smithsonian Magazine, August, accessed June 22, 2014, at http://www.smithsonianmag.com/history/making-copies-2242822/.

Paniagua, A., 1995, Selenium in copper-rich disulfides of the Providencia Mine, Leon, Spain: Neues Jahrbuch für Mineralogie Abhandlungen, v. 169, no. 3, p. 291–295.

Parkman, Helena, and Hultberg, Hans, 2002, Occurrence and effects of selenium in the environment—A literature review: Stockholm, Sweden, Swedish Environmental Research Institute, IVL Report B 1486, 28 p., accessed September 1, 2013, at http://www3.ivl.se/rapporter/pdf/B1486.pdf. [Also available at http://www.ivl.se/download/18.343dc99d14e8bb0f58b7417/1445515506056/B1486.pdf.]

Petruk, W., Owens, D.R., Stewart, J.M., and Murray E.J., 1974, Observations on acanthite, aguilarite, and naumannite: The Canadian Mineralogist, v. 12, no. 6, p. 365–369.

Pillay, K.K.S., Thomas, C.C., Jr., and Kaminski, J.W., 1969, Neutron activation analysis of the selenium content of fossil fuels: Nuclear Technology, v. 7, no. 5, p. 478–483.

Pinto, A.M.M., Relvas, J.M.R.S., Carvalho, J.R.S., Pacheco, Nelson, and Liu, Yanan, 2013, Mineralogy and distribution of indium and selenium metals within zinc-rich ore types of the Neves Corvo deposit, Portugal: Mineralogical Magazine, v. 77, no. 5, p. 1973.

Piper, D.Z., 1994, Seawater as the source of minor elements in black shales, phosphorites, and other sedimentary rocks: Chemical Geology, v. 114, nos. 1–2, p. 95–114. [Also available at http://dx.doi.org/10.1016/0009-2541(94)90044-2.]

Piper, D.Z., 2001, Marine chemistry of the Permian Phosphoria Formation and basin, southeast Idaho: Economic Geology, v. 96, p. 599–620. [Also available at http://dx.doi.org/10.2113/96.3.599.]

Piper, D.Z., Skorupa, J.P., Presser, T.S., Hardy, M.A., Hamilton, S.J., Huebner, M., and Gulbrandsen, R.A., 2000, The Phosphoria Formation at the Hot Springs Mine in southeast Idaho; a source of selenium and other trace elements to surface water, ground water, vegetation, and biota: U.S. Geological Survey Open-File Report 00–50, 73 p. [Also available at http://www.cerc.usgs.gov/pubs/center/pdfDocs/91013.pdf.]

Pirard, Cassian, and Hatert, Frédéric, 2008, The sulfides and selenides of the Musconoï Mine, Kolwezi, Katanga, Democratic Republic of Congo: The Canadian Mineralogist, v. 46, no. 1, p. 219–231. [Also available at http://dx.doi.org/10.3749/canmin.46.1.219.]

Pirri, I.V., 2002, On the occurrence of selenium in sulfides of the ore deposit of Baccu Locci (Gerrei, SE Sardinia): Neues Jahrbuch für Mineralogie—Monatshefte, v. 2002, no. 5, p. 207–224. [Also available at http://dx.doi.org/10.1127/0028-3649/2002/2002-0207.]

Presser, T.S., 1994, Geologic origin and pathways of selenium from the California coast ranges to the west-central San Joaquin Valley, in Frankenberger, W.T., Jr., and Benson, Sally, eds., Selenium in the environment: New York, N.Y., Marcel Dekker, Inc., p. 139–155.

Presser, T.S., 1999, Selenium pollution, in Alexander, P.E., and Fairbridge, R.W., eds., Encyclopedia of environmental science: Berlin, Germany, Springer-Verlag, p. 554–556.

Presser, T.S., and Swain, W.C., 1990, Geochemical evidence for Se mobilization by the weathering of pyritic shale, San Joaquin Valley, California, U.S.A.: Applied Geochemisry, v. 5, nos. 5–6, p. 703–713. [Also available at http://dx.doi.org/10.1016/0883-2927(90)90066-E.]

Presser, T.S., Piper, D.Z., Bird, K.J., Skorupa, J.P., Hamilton, S.J., Detwiler, S.J., and Huebner, M.A., 2004, The Phosphoria Formation—A model for forecasting global selenium sources to the environment, chap. 11 *of* Hein, J.R., ed., Life cycle of the Phosphoria Formation—From deposition to the post-mining environment: Handbook of Exploration and Environmental Geochemistry, v. 8, p. 299–319. [Also available at http://wwwrcamnl.wr.usgs.gov/Selenium/Library_articles/chap11_global_Se-optimized.pdf.]

Presser, T.S., Swain, W.C., Tidball, R.R., and Severson, R.C., 1990, Geologic sources, mobilization, and transport of selenium from the California coast ranges to the western San Joaquin Valley—A reconnaissance study: U.S. Geological Survey Water-Resources Investigations Report 90–4070, 66 p. [Also available at https://pubs.er.usgs.gov/publication/wri904070.]

Presser, T.S., Sylvester, M.A., and Low, W.H., 1994, Bio-accumulation of selenium from natural geologic sources in Western States and its potential consequences: Environmental Management, v. 18, no. 3, p. 423–436. [Also available at http://dx.doi.org/10.1007/BF02393871.]

Ranville, M.A., Cutter, G.A., Buck, C.S., Landing, W.M., Cutter, L.S., Resing, J.A., and Flegal, A.R., 2010, Aeolian contamination of Se and Ag in the North Pacific from Asian fossil fuel combustion: Environmental Science and Technology, v. 44, no. 5, p. 1587–1593. [Also available at http://dx.doi.org/10.1021/es902523m.]

Rayman, M.P., 2000, The importance of selenium to human health: Lancet, v. 356, no. 9225, p. 233–241.

Reich, Martin, Palacios, Carlos, Barra, Fernando, and Chryssoulis, Stephen, 2013, "Invisible" silver in chalcopyrite and bornite from the Mantos Blancos Cu deposit, northern Chile: European Journal of Mineralogy, v. 25, no. 3, May, p. 453–460.

Ripley, E.M., 1990, Se/S ratios of the Virginia Formation and Cu-Ni sulfide mineralization in the Babbitt area, Duluth Complex, Minnesota: Economic Geology, v. 85, p. 1935–1940. [Also available at http://dx.doi.org/10.2113/gsecongeo.85.8.1935.]

Ripley, E.M., Chusi, Li, and Shin, Dongbok, 2002, Paragneiss assimilation in the genesis of magmatic Ni-Cu-Co sulfide mineralization at Voisey's Bay, Labrador—δ^{34}S, δ^{13}C, and Se/S evidence: Economic Geology, v. 97, p. 1307–1318. [Also available at http://dx.doi.org/10.2113/gsecongeo.97.6.1307.]

Robberecht, H., and Van Grieken, R., 1982, Selenium in environmental waters—Determination, speciation and concentration levels: Talanta, v. 29, no. 10, p. 823–844.

Sargent, J.D., 1954, Selenium: U.S. Bureau of Mines Information Circular 7690, 25 p. [Also available at http://babel.hathitrust.org/cgi/pt?id=mdp.39015006378528;view=1up;seq=5.]

Schwarcz, H.P., 1973, Sulfur isotope analyses of some Sudbury, Ontario, ores: Canadian Journal of Earth Sciences, v. 10, no. 9, p. 1444–1459. [Also available at http://dx.doi.org/10.1139/e73-135.]

Science Dictionary, 2015, What is Alkali disease?: Science Dictionary, accessed August 1, 2015, at http://thesciencedictionary.org/alkali-disease/.

Scott, R.C., and Voegeli, P.T., 1961, Radiochemical analyses of ground and surface water in Colorado, 1954–1961: Denver, Colo., Colorado Water Conservation Board Basic Data Report no. 7, 27 p.

Seiler, R.L., Skorupa, J.P., Naftz, D.L., and Nolan, B.T., 2003, Irrigation-induced contamination of water, sediment, and biota in the Western United States—Synthesis of data from the National Irrigation Water Quality Program: U.S. Geological Survey Professional Paper 1655, ver. 1.1, 123 p., accessed June 20, 2014, at http://pubs.usgs.gov/pp/pp1655/.

Selenium Monitoring Work Group, 2009, An assessment of environmental selenium levels around Empire and Tilden Mines, Marquette County, Michigan: Lansing, Mich., Michigan Department of Environmental Quality Report no. MI/DEQ/WB-09/038, 25 p., accessed May 24, 2016, at https://www.michigan.gov/documents/deq/wb-swas-selenium-report_287994_7.pdf.

Shacklette, H.T., and Boerngen, J.G., 1984, Element concentrations in soils and other surficial materials of the conterminous United States: U.S. Geological Survey Professional Paper 1270, 105 p. [Also available at https://pubs.er.usgs.gov/publication/pp1270.]

Sharmasarkar, S., and Vance, G.F., 1997, Extraction and distribution of soil organic and inorganic selenium in coal mine environments of Wyoming, USA: Environmental Geology, v. 29, p. 17–22. [Also available at http://dx.doi.org/10.1007/s002540050099.]

Shimizu, M., Schmidt, S.T., Stanley, C.J., and Tsunoda, K., 1995, Kawazulite and unnamed $Bi_3(Te,Se,S)_4$ in Ag-Bi-Te-Se-S mineralization from the Suttsu Mine, Hokkaido, Japan: Neues Jahrbuch für Mineralogie—Abhandlungen, v. 169, p. 305–308.

Simon, Grigore, and Essene, E.J., 1996, Phase relations among selenides, sulfides, tellurides, and oxides; I, Thermodynamic properties and calculated equilibria: Economic Geology, v. 91, p. 1183–1208. [Also available at http://dx.doi.org/10.2113/gsecongeo.91.7.1183.]

Simon, Grigore, Kesler, S.E., and Essene, E.J., 1997, Phase relations among selenides, tellurides, and oxides; II, applications to selenide-bearing ore deposits: Economic Geology, v. 92, p. 468–484. [Also available at http://dx.doi.org/10.2113/gsecongeo.92.4.468.]

Sindeeva, N.D., 1964, Mineralogy and types of deposits of selenium and tellurium: New York, N.Y., Wiley Interscience, 363 p.

Skorupa, J.P., Presser, T.S., Hamilton, S.J., Lemly, A.D., and Sample, B.E., 2004, EPA's draft tissue-based selenium criterion—A technical review—Presentation for the U.S. Environmental Protection Agency, June 16, 36 p., accessed May 26, 2016, at http://wwwrcamnl.wr.usgs.gov/Selenium/Library_articles/skorupa_et_al_2004.pdf. [Published draft.]

Smith, D.B., Cannon, W.F., Woodruff, L.G., Solano, Federico, and Ellefsen, K.J., 2014, Geochemical and mineralogical maps for soils of the conterminous United States: U.S. Geological Survey Open-File Report 2014–1082, 386 p. [Also available at http://dx.doi.org/10.3133/ofr20141082.]

Stillings, L.L., and Amacher, M.C., 2004, Selenium attenuation in a wetland formed from mine drainage in the Phosphoria Formation, southeast Idaho, chap. 17 of Hein, J.R., ed., Life cycle of the Phosphoria Formation—From deposition to the post-mining environment: Handbook of Exploration and Environmental Geochemistry, v. 8, p. 467–482.

Stillings, L.L., Willard, P.J., and Amacher, M.C., 2007, Geochemical controls on Se—A comparison of two wetlands, in Bullen, T.D., and Wang, Yanxin, eds., Water-rock interaction—International Symposium on Water-Rock Interaction, 12th, Kunming, Yunnan, China, July 31–August 5, 2007, Proceedings, v. 2: Boca Raton, Fla., CRC Press, p. 1271–1275.

Stone, R.A., 2009, A medical mystery in middle China: Science, v. 324, no. 5933, p. 1378–1381. [Also available at http://dx.doi.org/10.1126/science.324_1378.] (Article correction posted July 24, 2009.)

Stumm, Werner, 1992, Chemistry of the solid-water interface—Processes at the mineral-water and particle-water interface in natural systems: New York, N.Y., John Wiley Sons, 428 p.

Taylor, S.R., 1964, Abundance of chemical elements in the continental crust—A new table: Geochimica et Cosmochimica Acta, v. 28, no. 8, p. 1273–1285. [Also available at http://dx.doi.org/10.1016/0016-7037(64)90129-2.]

Thornton, I., Kinniburgh, D.G., Pullen, G., and Smith, C.A., 1983, Geochemical aspects of selenium in British soils and implications to animal health, in Hemphill, D.D., ed., Trace substances in environmental health, Conference on Trace Substances in Environmental Health, 17th, June 13–16, 1983, Proceedings: Columbia, Missouri, University of Missouri-Columbia, v. 17, p. 391–398.

Tidball, R.R., 1984, Geochemical survey of Missouri—Geography of soil geochemistry of Missouri agricultural soils: U.S. Geological Survey Professional Paper 954–H, 54 p. [Also available at http://pubs.usgs.gov/pp/0954h-i/report.pdf.]

Trelease, S.F., and Beath, O.A., 1949, Selenium—Its geological occurrence and its biological effects in relation to botany, chemistry, agriculture, nutrition, and medicine: New York, N.Y., published by the authors, 292 p.

Turekian, K.K., and Wedepohl, K.H., 1961, Distribution of the elements in some major units of the Earth's crust: Geological Society of America Bulletin, v. 72, no. 2, p. 175–192. [Also available at http://dx.doi.org/10.1130/0016-7606(1961)72[175:DOTEIS]2.0.CO;2.]

Tuttle, M.L.W., Fahy, Juli, Grauch, R.I., Ball, B.A., Chong, G.W., Elliott, J.G., Kosovich, J.J., Livo, K.E., and Stillings, L.L., 2007, Results of chemical analyses of soil, shale, and soil/shale extract from the Mancos Shale Formation in the Gunnison Gorge National Conservation Area, southwestern Colorado, and at Hanksville, Utah: U.S. Geological Survey Open-File Report 2007–1002D, 24 p., accessed May 26, 2016, at http://pubs.usgs.gov/of/2007/1002/D/.

U.S. Bureau of Mines, 1963, Metals and minerals (except fuels): U.S. Bureau of Mines Minerals Yearbook 1962, v. I, 1,410 p. [Also available at http://minerals.usgs.gov/minerals/pubs/usbmmyb.html.]

U.S. Bureau of Mines, 1965, Metals and minerals (except fuels): U.S. Bureau of Mines Minerals Yearbook 1964, v. I, 1,258 p. [Also available at http://minerals.usgs.gov/minerals/pubs/usbmmyb.html.]

U.S. Bureau of Mines, 1966, Minor metals and minerals, with a section on Selenium, by Arnold M. Lansche, in Division of Minerals Staff, Metals and minerals (except fuels): U.S. Bureau of Mines Minerals Yearbook 1965, v. I, p. 1059–1074. [Also available at http://minerals.usgs.gov/minerals/pubs/usbmmyb.html.]

U.S. Bureau of Mines, 1973, Metals and minerals (except fuels): U.S. Bureau of Mines Minerals Yearbook 1971, v. I, 1,303 p. [Also available at http://minerals.usgs.gov/minerals/pubs/usbmmyb.html.]

U.S. Bureau of Mines, 1978, Minor metals, with a section on Selenium, by George J. Coakley, in U.S. Bureau of Mines Staff, Metals, minerals, and fuels: U.S. Bureau of Mines Minerals Yearbook 1976, v. I, p. 1459–1474. [Also available at http://minerals.usgs.gov/minerals/pubs/usbmmyb.html.]

U.S. Bureau of Mines, 1980, Metals and minerals: U.S. Bureau of Mines Minerals Yearbook 1977, v. I, 1,066 p. [Also available at http://minerals.usgs.gov/minerals/pubs/usbmmyb.html.]

U.S. Bureau of Mines, 1989, Metals and minerals: U.S. Bureau of Mines Minerals Yearbook 1987, v. I, 990 p. [Also available at http://minerals.usgs.gov/minerals/pubs/usbmmyb.html.]

U.S. Environmental Protection Agency, 2005, Mountaintop mining/valley fills in Appalachia—Final Programmatic Environmental Impact Statement: Washington, D.C., U.S. Environmental Protection Agency, EPA 9–03–R–05002, 507 p., accessed May 26, 2016, at http://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=20005XA6.txt.

U.S. Environmental Protection Agency, 2014a, Basic information about selenium in drinking water: U.S. Environmental Protection Agency, NRC–065, accessed May 26, 2016, at http://pbadupws.nrc.gov/docs/ML1513/ML15131A122.pdf.

U.S. Environmental Protection Agency, 2014b, External peer review draft—Aquatic life ambient water quality criterion for selenium—Freshwater: U.S. Environmental Protection Agency, EPA 822–P–14–001, 637 p., accessed May 26, 2016, at http://www.nma.org/pdf/selenium/2014%20External%20Peer%20Review%20Draft%20Aquatic%20Life%20Ambient%20WQC%20for%20Se%20Freshwater.pdf.

U.S. Environmental Protection Agency, 2014c, National recommended water quality criteria—Aquatic life criteria table: U.S. Environmental Protection Agency, accessed May 26, 2016, at http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm#cmc.

U.S. Geological Survey, 1997–2014, Mineral commodity summaries 1997–2014: U.S. Geological Survey, variously paged. [Also available at http://minerals.usgs.gov/minerals/pubs/mcs/.]

U.S. Geological Survey, 2006–13, Mineral commodity summaries 2006–2013: U.S. Geological Survey, variously paged. [Also available at https://minerals.usgs.gov/minerals/pubs/mcs/.]

U.S. Geological Survey, 2010–14, Minerals yearbook 2008–2012: U.S. Geological Survey, variously paged. [Also available at http://minerals.usgs.gov/minerals/pubs/myb.html.]

U.S. Geological Survey, 2014a, Mineral commodity summaries 2014: U.S. Geological Survey, 196 p., accessed March 29, 2016, at http://minerals.usgs.gov/minerals/pubs/mcs/2014/mcs2014.pdf.

U.S. Geological Survey, 2014b, Selenium end-use statistics [through 2003; last modified September 1, 2005], in Kelly, T.D., and Matos, G.R., comps., Historical statistics for mineral and material commodities in the United States (2014 version): U.S. Geological Survey Data Series 140, 3 p., accessed November 30, 2016, at http://minerals.usgs.gov/minerals/pubs/historical-statistics/.

U.S. Geological Survey, 2014c, Selenium statistics [through 2014; last modified January 28, 2016], in Kelly, T.D., and Matos, G.R., comps., Historical statistics for mineral and material commodities in the United States (2014 version): U.S. Geological Survey Data Series 140, 3 p., accessed March 23, 2017, at https://minerals.usgs.gov/minerals/pubs/historical-statistics/.

U.S. Geological Survey, 2017, Mineral commodity summaries 2017: U.S. Geological Survey, 202 p. [Also available at https://minerals.usgs.gov/minerals/pubs/mcs/.]

Varo, Pertti, Alfthan, Georg, Huttunen, J.K., and Aro, Antti, 1994, Nationwide selenium supplementation in Finland—Effects on diet, blood and tissue levels, and health, chap. 11 of Burk, R.F., ed., Selenium in biology and human health: New York, N.Y., Springer-Verlag, p. 197–218.

Vikre, P.G., 2007, Sinter-vein correlations at Buckskin Mountain, National district, Humboldt County, Nevada: Economic Geology, v. 102, p. 193–224. [Also available at http://dx.doi.org/10.2113/gsecongeo.102.2.193.]

Wang, Dacheng, 1994, The environmental biogeochemistry of selenium in natural water ecosystems: Helsinki, Finland, National Public Health Institute, thesis, 124 p.

Wells, N., 1967, Selenium content of soil-forming rocks: New Zealand Journal of Geology and Geophysics, v. 10, no. 1, p. 198–208.

Willgallis, Alexander, Özgür, Nevzat, and Siegmann, Eveline, 1990, Se- and Te-bearing sulphides in copper ore deposits of Murgul, NE Turkey: European Journal of Mineralogy, v. 2, p. 145–148. [Also available at http://jeotermal.sdu.edu.tr/assets/uploads/sites/144/files/30-03052012.pdf.]

Winkel, L.H.E., Johnson, C.A., Lenz, Markus, Grundl, Tim, Leupin, O.X., Amini, Manouchehr, and Charlet, Laurent, 2012, Environmental selenium research—From microscopic processes to global understanding: Environmental Science and Technology, v. 46, no. 2, p. 571–579. [Also available at http://dx.doi.org/10.1021/es203434d.]

World Health Organization, 2011, Selenium in drinking-water—Background document for development of WHO Guidelines for drinking-water quality: Geneva, Switzerland, World Health Organization, WHO/HSE/WSH/10.01/14, 14 p., accessed June 19, 2014, at http://www.who.int/water_sanitation_health/dwq/chemicals/selenium.pdf.

World Health Organization and Food and Agricultural Organization of the United Nations, 2004, Selenium, chap. 10 of Vitamin and mineral requirements in human nutrition, 2d ed.: Geneva, Switzerland, World Health Organization, accessed March 8, 2016, at http://www.who.int/nutrition/publications/micronutrients/9241546123/en/.

Young, T.F., Finely, Keith, Adams, W.J., Besser, John, Hopkins, W.D., Jolley, Dianne, McNaughton, Eugenia, Presser, T.S., Shaw, D.P., and Unrine, Jason, 2010, What you need to know about selenium, *in* Chapman, P.M., Adams, W.J., Brooks, M.L., Delos, C.G., Luoma, S.N., Maher, W.A., Ohlendorf, H.M., Presser, T.S., and Shaw, D.P., eds., Ecological assessment of selenium in the aquatic environment: Boca Raton, Fla., CRC Press, p. 7–45.

Yushoko-Zakharova, O.Ye., Ivanov, V.V., Vorob'yeva, M.S., Duvakina, L.S., Razina, I.S., and Karpukhina, V.S., 1978, Geochemistry of selenium, tellurium, and bismuth in copper-zinc sulfide deposits in the Urals, and some problems of sulfide ore formation: Geochemistry International, v. 15, no. 5, p. 59–68.

Zhang, J., Ren, D., Xu, D., and Zhao, F., 1999, Advances in the studies of selenium in coal: Coal Geology and Exploration, v. 2, p. 17–19. [In Chinese with English abstract.]

Zhang, Yiqiang, Zahir, Z.A., and Frankenberter, W.T., Jr., 2004, Fate of colloidal-particulate elemental selenium in aquatic systems: Journal of Environmental Quality, v. 33, no. 2, p. 559–564. [Also available https://dl.sciencesocieties.org/publications/jeq/pdfs/33/2/559.]

Tables Q1 and Q2

Table Q1.   Selenium minerals recognized by the International Mineralogical Association.

[Data are from Mindat.org (2015) and the International Mineralogical Association (IMA) (2014). ?, uncertain according to the IMA; NA, not available]

Mineral name	Chemical formula	Date of discovery or IMA approval	Geologic setting and (or) first recorded locality
Achavalite	$(Fe,Cu)Se$	1939	Selenide deposit, Mendoza, Argentina
Aguilarite	Ag_4SeS	1891	Low-temperature hydrothermal deposits with silver and selenium but low amount of sulfur, Guanajuato, Mexico
Ahlfeldite	$(Ni,Co)SeO_{36} \cdot 2H_2O$	1935	Alteration product of nickel sulfides and selenides, Pacajake Mine, Potosí Department, Bolivia
Allochalcoselite	$Cu^+PbCu^{2+}_5(SeO_3)_2Cl_5O_2$	2004	Scoria cone, Tolbachik volcano, Far Eastern Region, Russia
Antimonselite	Sb_2Se_3	1993	Uranium deposit No. 504, Guizhou Province, China
Athabascaite	Cu_5Se_4	1970	Inclusions in and replacements of umangite, as well as stringers and veinlets in carbonate veins cutting basalt, Martin Lake Mine, Saskatchewan, Canada
Babkinite	$Pb_2Bi_2(S,Se)_3$	1994	Hydrothermal deposit in sediments, near contact with granite intrusion, Nevskoe tungsten-tin deposit, Far Eastern Region, Russia
Bambollaite	$Cu(Se,Te)$	1972	Oxidized gold-tellurium ore, Moctezuma Mine, Sonora, Mexico
Bellidoite	Cu_2Se	1975	Low-to-moderate temperature hydrothermal deposits, Habři Mine, Moravia, Czech Republic
Berzelianite	Cu_2Se	1850	Hydrothermal veins, Skrikerum Mine, Östergötland, Sweden
Bohdanowiczite	$AgBiSe_2$	1967	Fluorite and quartz veins near magnetite skarn, Kletno, Lower Silesia, Poland
Bornhardtite	$Co^{2+}Co^{3+}_2Se_4$	1955	Hydrothermal deposits, Trogtal Quarries, Lower Saxony, Germany
Brodtkorbite	Cu_2HgSe_2	1999	Telethermal selenide vein-type assemblage, Tumiñico Mine, La Rioja Province, Argentina
Bukovite	$Tl_2(Cu,Fe)_4Se_4$	1971	Calcite veins of hydrothermal origin, Bukov Mine, Moravia, Czech Republic
Burnsite	$KCdCu^{2+}_7(SeO_3)_2O_2Cl_9$	2000	Scoria cone, Tolbachik volcano, Far Eastern Region, Russia
Cadmoselite	$CdSe$	1957	Sedimentary rocks in an alkaline, reducing environment, Ust' Uyok deposit, eastern Siberia, Russia
Carlosruizite	$K_6(Na,K)_4Na_6Mg_{10}(SeO_4)_{12}(IO_3)_{12} \cdot 12H_2O$	1994	Zapiga, Tarapacá Region, Chile
Chalcomenite	$CuSeO_3 \cdot 2H_2O$	1881	Secondary mineral in copper-selenium deposits, Cerro de Cacheuta, Mendoza, Argentina
Chaméanite	$(Cu,Fe)_4As(Se,S)_4$	1980	Late-stage deposits cutting granites, Chaméane uranium deposit, Auvergne, France
Chloromenite	$Cu_9(SeO_3)_4O_2Cl_6$	1996	Novaya fumarole, Tolbachik volcano, Far Eastern Region, Russia
Chrisstanleyite	$Ag_2Pd_3Se_4$	1996	Gold-bearing veins, Hope's Nose, Devon, England
Clausthalite	$PbSe$	1832	Selenium-bearing, low-sulfur hydrothermal deposits, St. Lorenz Mine, Lower Saxony, Germany
Cobaltomenite	$CoSeO_3 \cdot 2H_2O$	1882	Cerro de Cacheuta, Mendoza, Argentina
Crerarite	$Pt_{2-x}(Bi,Pb)_{11}(S,Se)_{11}$	1994	Copper–nickel–platinum-group-element deposit, Lac Sheen, Quebec, Canada
Crookesite	$Cu_7(Tl, Ag)Se_4$	1866	Copper-silver-lead-selenium hydrothermal deposits, Skrikerum Mine, Östergötland, Sweden
Demesmaekerite	$Pb_2Cu_5(UO_2)_2(SeO_3)_6(OH)_6 \cdot 2H_2O$	1965	Copper-cobalt-manganese-uranium deposit, Musonoi Mine, Democratic Republic of the Congo (Congo [Kinshasa])
Derriksite	$Cu_4(UO_2)(SeO_3)_2(OH)_6 \cdot H_2O$	1971	Copper-cobalt-manganese-uranium deposit, Musonoi Mine, Democratic Republic of the Congo (Congo [Kinshasa])

Table Q1.   Selenium minerals recognized by the International Mineralogical Association.—Continued

[Data are from Mindat.org (2015) and the International Mineralogical Association (IMA) (2014). ?, uncertain according to the IMA; NA, not available]

Mineral name	Chemical formula	Date of discovery or IMA approval	Geologic setting and (or) first recorded locality
Downeyite	SeO_2	1971	Burning anthracite coal deposits, Pennsylvania, United States
Drysdallite	$Mo(Se,S)_2$	1973	Oxidation zone of uranium deposits, Kampijimpanga, North-Western Province, Zambia
Dzharkenite	$FeSe_2$	1995	Suluchekinskoye selenium-uranium deposit, Almaty Province, Kazakhstan
Eldragónite	$Cu_6BiSe_4(Se_2)$	2011	Hydrothermal veins with selenium > sulfur, El Dragón Mine, Potosí Department, Bolivia
Eskebornite	$CuFeSe_2$	1949	Low-temperature hydrothermal deposits, Eskaborn Adit, Saxony-Anhalt, Germany
Eucairite	$AgCuSe$	1818	Copper-silver-lead-selenium hydrothermal deposits, Skrikerum Mine, Östergötland, Sweden
Favreauite	$PbBiCu_6O_4(SeO_3)_4(OH) \cdot H_2O$	2014	Hydrothermal veins with selenium > sulfur, El Dragón Mine, Potosí Department, Bolivia
Ferroselite	$FeSe_2$	1955	Red bed deposits of Colorado plateau type, Ust' Uyok deposit, eastern Siberia, Russia
Fischesserite	Ag_3AuSe_2	1971	Carbonate vein in epithermal hydrothermal gold-uranium-selenium deposit, Předbořice, Bohemia, Czech Republic
Francisite	$Cu_3Bi(SeO_3)_2O_2Cl$	1990	Iron Mine, Iron Monarch open cut, South Australia, Australia
Freboldite	$CoSe$	1957	Dolomite veinlets, Trogtal Quarries, Lower Saxony, Germany
Geffroyite	$(Cu,Fe,Ag)_9(Se,S)_8$	1982	Late-stage veins cutting granite, Chaméane uranium deposit, Auvergne, France
Georgbokiite	$Cu_5(SeO_3)_2O_2Cl_2$	1996	Scoria cone, Great Fissure eruption, Far Eastern Region, Russia
Giraudite	$Cu_6[Cu_4(Fe,Zn)_2]As_4Se_{13}$	1982	Late-stage veins cutting granite, Chaméane uranium deposit, Auvergne, France
Guanajuatite	Bi_2Se_3	1873	Low- to moderate-temperature hydrothermal deposits, Santa Catarina Mine, Guanajuato, Mexico
Guilleminite	$Ba(UO_2)_3(SeO_3)_2(OH)_4 \cdot 3H_2O$	1965	Oxidized zone of a copper-cobalt-manganese-uranium deposit, Musonoi Mine, Democratic Republic of the Congo (Congo [Kinshasa])
Hakite	$Cu_6[Cu_4Hg_2]Sb_4Se_{13}$	1970	In epithermal calcite veins, Předbořice, Bohemia, Czech Republic
Haynesite	$(UO_2)_3(OH)_2(SeO_3)_2 \cdot 5H_2O$	1991	Oxidized uranium deposits, Repete Mine, Utah, United States
Ikunolite[1]	$Bi_4(S,Se)_3$	1959	Xenothermal veins with silver-gold-copper-lead-tin-tungsten-zinc, Ikuno Mine, Honshu Island, Japan
Ilinskite	$(Na,K)Cu_5(SeO_3)_2O_2Cl_3$	1996	Scoria cone, Tolbachik volcano, Far Eastern Region, Russia
Jacutingaite	Pt_2HgSe_3	2011	Iron-gold-palladium deposit, Cauê Mine, Minas Gerais, Brazil
Jagüéite	$Cu_2Pd_3Se_4$	2002	Teletethermal selenide vein-type deposit, El Chire prospect, La Rioja Province, Argentina
Jolliffeite	$NiAsSe$	1991	Uraninite vein, Fish Hook Bay, Saskatchewan, Canada
Junoite	$Cu_2Pb_3Bi_8(S,Se)_{16}$	1975	Gold-copper-bismuth deposit, Juno Mine, Northern Territory, Australia
Kalungaite	$PdAsSe$	2004	Gold deposit, related to a peraluminous granite, Buraco do Ouro Mine, Goiás, Brazil
Kawazulite	Bi_2Te_2Se	1970	Epithermal gold-silver-tellurium-manganese veins, Kawazu Mine, Honshu Island, Japan
Kitkaite	$NiTeSe$	1961	Low-grade uranium and selenium mineralization in carbonate-bearing veinlets, Kitka River Valley, northern Finland

Table Q1.   Selenium minerals recognized by the International Mineralogical Association.—Continued

[Data are from Mindat.org (2015) and the International Mineralogical Association (IMA) (2014). ?, uncertain according to the IMA; NA, not available]

Mineral name	Chemical formula	Date of discovery or IMA approval	Geologic setting and (or) first recorded locality
Klockmannite	$CuSe$	1928	Silver-copper-selenium deposit, Las Asperezas Mine, La Rioja Province, Argentina
Krut'aite	$CuSe_2$	1972	Uranium deposit, Petrovice, Moravia, Czech Republic
Kullerudite	$NiSe_2$	1964	Alteration of wilkmanite in low-grade uranium and selenium mineralization, Kitka River Valley, northern Finland
Kurilite	Ag_8Te_3Se	2009	Kuril islands gold deposit, Prasolovskoe gold deposit, Far Eastern Region, Russia
Laitakarite	Bi_4Se_2S	1959	Copper-gold deposit, Orijärvi, southwestern Finland
Laphamite	$As_2(Se,S)_3$	1985	Burning anthracite coal deposit, Burnside, Pennsylvania, United States
Larisaite	$Na(H_3O)(UO_2)_3(Se^{4+}O_3)O_2 \cdot 4H_2O$	2002	Uranium deposit, Repete Mine, Blanding, San Juan County, Utah, United States
Litochlebite	$Ag_2PbBi_4Se_8$	2009	Quartz-uranium-carbonate deposit, Zálesí, Moravia, Czech Republic
Luberoite	Pt_5Se_4	1992	Lubero region, Kivu, Democratic Republic of the Congo (Congo [Kinshasa])
Mäkinenite	γ-$NiSe$	1967	Low-grade uranium and selenium mineralization, Kitka River Valley, northern Finland
Mandarinoite	$Fe_3^{+2}(Se^{4+}O_3)_3 \cdot 6H_2O$	1978	Oxidation product of penroseite and pyrite, Virgen de Surumi Mine (Pacajake Mine), Potosí Department, Bolivia
Marthozite	$Cu(UO_2)_3(SeO_3)_2(OH)_2 \cdot 8H_2O$	1969	Copper-cobalt-manganese-uranium deposit, Musonoi Mine, Katanga, Democratic Republic of the Congo (Congo [Kinshasa])
Mgriite	Cu_3AsSe_3	1982	Silver-uranium deposit, Schlema-Hartenstein District, Saxony, Germany
Miessiite	$Pd_{11}Te_2Se_2$	2006	Placer deposits, Miessijoki River, Lapland Region, Finland
Milotaite	$PdSbSe$	2003	Gold-uranium-selenium deposit, Redbořice, Bohemia, Czech Republic
Molybdomenite	$PbSeO_3$	1882	Cacheuta Mine, Mendoza, Argentina
Mozgovaite	$PbBi_4(S,Se)_7$	1998	Magmatic-hydrothermal system, La Fossa crater, Vulcano Island, Sicily, Italy
Munakataite	$Pb_2Cu_2(Se^{4+}O_3)(SO_4)(OH)_4$	2007	Oxide zone of aguilarite-bearing lead-zinc-gold-silver ores, Kato Mine, Kyushu Region, Japan
Naumannite	Ag_2Se	1828	Selenium mineralization in hematite mine, Tilkerode, Saxony-Anhalt, Germany
Nestolaite	$CaSeO_3 \cdot H_2O$	2013	In sandstone host, Little Eva Mine, Utah, United States
Nevskite	$Bi(Se,S)$	1984	Nevskoe tungsten-tin deposit, Far Eastern Region, Russia
Nicksobolevite	$Cu_7(SeO_3)_2O_2Cl_6$	2013	Scoria cone, Tolbachik volcano, Far Eastern Region, Russia
Nordströmite[2]	$CuPb_3Bi_7(Se_4S_{10})$	1978	Copper-gold-silver-lead-zinc deposit, Falun Mine, Falun, Dalarna, Sweden
Olsacherite	$Pb_2(SeO_4)(SO_4)$	1969	Silver-selenium deposit, Virgen de Surumi Mine (Pacajake Mine), Potosí Department, Bolivia
Oosterboschite	$(Pd,Cu)_7Se_5$	1970	Copper-cobalt-manganese-uranium deposit, Musonoi Mine, Katanga, Democratic Republic of the Congo (Congo [Kinshasa])
Orlandiite	$Pb_{10}(SeO_4)O_7Cl_4 \cdot H_2O$	1998	Galena-arsenopyrite deposit, Baccu Locci Mine, Sardinia, Italy

Table Q1.   Selenium minerals recognized by the International Mineralogical Association.—Continued

[Data are from Mindat.org (2015) and the International Mineralogical Association (IMA) (2014). ?, uncertain according to the IMA; NA, not available]

Mineral name	Chemical formula	Date of discovery or IMA approval	Geologic setting and (or) first recorded locality
Padmaite	PdBiSe	1991	Uranium-vanadium deposit, Srednyaya Padma Mine, Northern Region, Russia
Palladseite	$Pd_{17}Se_{15}$	1977	Itabira, Iron Quadrangle, Minas Gerais, Brazil
Parageorgbokiite	$Cu_5(SeO_3)_2O_2Cl_2$	2006	Scoria cone, Tolbachik volcano, Far Eastern Region, Russia
Paraguanajuatite	Bi_2Se_3	1948	Gold-sulfur deposit, Santa Catarina Mine, Guanajuato, Mexico
Pekoite[1]	$PbCuBi_{11}(S,Se)_{18}$	1975	Gold-copper-bismuth deposit, Juno Mine, Northern Territory, Australia
Penroseite	$(Ni,Co,Cu)Se_2$	1926	Silver-selenium deposit, Virgen de Surumi Mine (Pacajake Mine), Potosí Department, Bolivia
Penzhinite	$(Ag,Cu)_4Au(S,Se)_4$	1984	Sergeevskoye gold-silver occurrence, Far Eastern Region, Russia
Permingeatite	Cu_3SbSe_4	1971	Gold-uranium-selenium deposit, Předbořice, Bohemia, Czech Republic
Petrovicite	$Cu_3HgPbBiSe_5$	1976	Uranium deposit, Petrovice, Moravia, Czech Republic
Petrovskaite[1]	$AuAg(S,Se)$	1984	Maikain gold deposit, Pavlodar Province, Kazakhstan
Piretite	$Ca(UO_2)_3(SeO_3)_2(OH)_4 \cdot 4H_2O$	1996	Copper-cobalt-nickel-uranium deposit, Shinkolobwe Mine, Katanga, Democratic Republic of the Congo (Congo [Kinshasa[)
Plumboselite	$Pb_3O_2(SeO_3)$	2010	Copper-lead-zinc-silver-germanium-cadmium deposit in dolomite, Tsumeb Mine, Otjikoto Region, Namibia
Poubaite	$PbBi_2(Se,Te,S)_4$	1978	Uraninite deposit with sulfur-selenium, Oldřichov, Bohemia, Czech Republic
Prewittite	$KPb_{1.5}ZnCu_6(SeO_3)_2O_2Cl_{10}$	2002	In fumarole field, Tolbachik volcano, Far Eastern Region, Russia
Proudite	$CuPb_{7.5}Bi_{9.33}(S,Se)_{22}$	1975	Gold-copper-bismuth deposit, Juno Mine, Northern Territory, Australia
Sabatierite	Cu_6TlSe_4	1976	Uranium deposit, Bukov Mine, Moravia, Czech Republic
Sarrabusite	$Pb_5CuCl_4(SeO_3)_4$	1997	Galena-arsenopyrite deposit, Baccu Locci Mine, Sardinia, Italy
Schlemaite[3]	$(Cu,\square)_6(Pb,Bi)Se_4$	2003	Hydrothermal selenium-bearing dolomite-ankerite vein, Schlema-Hartenstein District, Saxony, Germany
Schmiederite	$Pb_2Cu_2(Se_6+O_4)(Se_4+O_3)(OH)_4$	1962	Hydrothermal veinlets in sedimentary host, selenium > sulfur, El Cóndor Mine, Los Llantenes district, La Rioja Province, Argentina
Sederholmite	ß-NiSe	1964	In calcite veins with nickel selenides associated with low-grade uranium mineralization, Kitka River Valley, northern Finland
Selenium	Se	1828?	NA
Selenojalpaite	Ag_3CuSe_2	2004	Copper-silver-lead-selenium hydrothermal deposits, Skrikerum Mine, Östergötland, Sweden
Selenopolybasite	$[(Ag,Cu)_6(Sb,As)_2(S,Se)_7][Ag_9Cu(S,Se)_2Se_2]$	2006	Silver deposit, De Lamar Mine, Idaho, United States
Selenostephanite	$Ag_5Sb(Se,S)_4$	1985	Volcanogenic silver-gold deposit, Rudnaya Sopka, Far Eastern Region, Russia
Skippenite	Bi_2TeSe_2	1987	Otish Mountains uranium deposit, Quebec, Canada
Sofiite	$Zn_2(SeO_3)Cl_2$	1989	Scoria cone, Tolbachik volcano, Far Eastern Region, Russia
Součekite	$PbCuBi(S,Se)_3$	1979	Uranium deposit with sulfur-selenium, Oldřichov, Bohemia, Czech Republic

Table Q1.   Selenium minerals recognized by the International Mineralogical Association.—Continued

[Data are from Mindat.org (2015) and the International Mineralogical Association (IMA) (2014). ?, uncertain according to the IMA; NA, not available]

Mineral name	Chemical formula	Date of discovery or IMA approval	Geologic setting and (or) first recorded locality
Stilleite	ZnSe	1956	Uranium deposit with copper, cobalt, and nickel, Shinkolobwe Mine, Katanga, Democratic Republic of the Congo (Congo [Kinshasa])
Sudovikovite	$PtSe_2$	1995	Uranium-vanadium deposit, Srednyaya Padma Mine, Northern Region, Russia
Telluronevskite	Bi_3TeSe_2	1993	Selenium and tellurium mineralization in hydrothermal veins, in argillic andesite host, Poruba pod Vihorlatom, Michalovce County, Košice Region, Slovakia
Tiemannite	HgSe	1855	Ancient lead and zinc mine, working veins of the Burgstadt vein system, St. Lorenz Mine, Lower Saxony, Germany
Tischendorfite	$Pd_8Hg_3Se_9$	2001	Selenium mineralization in hematite mine, Eskaborn Adit, Tilkerode, Saxony-Anhalt, Germany
Trogtalite	$CoSe_2$	1955	Abandoned greywacke quarries, Trogtal Quarries, Lower Saxony, Germany
Trüstedtite	Ni_3Se_4	1967	Low-grade uranium and selenium mineralization in an albite diabase, Kitka River Valley, northern Finland
Tsnigriite	$Ag_9SbTe_3(S,Se)_3$	1991	Black-shale-hosted Vysokovol'tnoye silver-gold deposit, Bel'tau Mountains, Kyzylkum Desert, Uzbekistan
Tyrrellite	$Cu(Co^{3+},Ni^{3+})_2Se_4$	1952	Ato Bay, Beaverlodge Lake, Goldfields District, Beaverlodge Region, Saskatchewan, Canada; and Eagle Claims uranium-copper-selenium occurrence, Eagle shaft area, Melville Lake, Goldfields District, Beaverlodge Region, Saskatchewan, Canada
Umangite	Cu_3Se_2	1891	Las Asperezas silver mine (Sarmiento deposit, Veta Sarmiento), Sierra de Cacho, Villa Castelli, General Lamadrid Department, La Rioja Province, Argentina; and abandoned greywacke quarries, Trogtal Quarries, Lautenthal, Harz, Lower Saxony, Germany
Verbeekite	$PdSe_2$	2001	Copper-cobalt-manganese-uranium deposit. Known for rare assemblage of uranyl selenites, Musonoi Mine, Kolwezi, Kolwezi District, Katanga Copper Crescent, Katanga (Shaba), Democratic Republic of the Congo (Congo [Kinshasa])
Vihorlatite	$Bi_{24}Se_{17}Te_4$	1988	Poruba pod Vihorlatom, Michalovce County, Košice Region, Slovakia
Watkinsonite	$Cu_2PbBi_4(Se,S,Te)_8$	1985	Otish Mountains uranium deposit, Otish Mountains, Baie-James, Nord-du-Québec, Quebec, Canada
Weibullite	$Pb_5Bi_8Se_7S_{11}$	1910	Copper mine with minor amount of gold, Falun Mine, Falun, Dalarna, Sweden
Wilkmanite	Ni_3Se_4	1964	Low-grade uranium and selenium mineralization in an albite diabase, Kitka River Valley, Kuusamo, northern Finland
Wittite	$Pb_8Bi_{10}(S,Se)_{23}$	1924	Falun Mine, Falun, Dalarna, Sweden
Zincomenite	$ZnSeO_3$	2014	Northern fumarole field, first scoria cone, Northern Breakthrough (North Breach), and Great Fissure eruption (Main Fracture), Tolbachik volcano, Far Eastern Region, Russia

[1]The IMA chemical formula does not show selenium substitution for sulfur.

[2]The IMA chemical formula is $Pb_3CuBi_7(S,Se)_{14}$.

[3]The symbol □ in the chemical formula denotes an empty atomic site that can be filled (or not), depending upon compositional variation.

Table Q2.   A summary of selenium concentrations in various selenides and sulfides from deposits around the world.

[avg, average; b.d.l., below detection limit; Do., do., ditto; IOCG, iron oxide-copper-gold; n.d., not detected; n.r., not reported; ppm, part per million; wt. %, weight percent; —, none. Abbreviations for elements: Ag, silver; As, arsenic; Au, gold; Bi, bismuth; Co, cobalt; Cu, copper; Fe, iron; Hg, mercury; Mo, molybdenum; Ni, nickel; Pb, lead; Pd, palladium; PGE, platinum-group element; Pt, platinum; S, sulfur; Se, selenium; Te, tellurium; Ti, titanium; Tl, thallium; U, uranium; Zn, zinc]

Deposit type and (or) chemistry	Mine/deposit name	Mineral phases	Selenium concentration	Notes	Reference(s)
Australia, eastern					
Volcanic-hosted massive sulfide	Agincourt deposit	Pyrite	<6 to 9 ppm	—	Huston and others (1995)
Do.	Dry River South deposit	do.	<6 to 760 ppm	—	Do.
Do.	Mount Chalmers deposit	do.	<5 to 200 ppm	—	Do.
Do.	Rosebery deposit	do.	<6 to 33 ppm	—	Do.
Do.	Waterloo deposit	do.	<6 to 180 ppm	—	Do.
Australia, southern					
Protoerozoic Olympic Dam IOCG	Olympic Dam	Bornite	18.8 ppm	—	Cook and others (2011)
Do.	do.	Chalcopyrite	8.7 ppm	—	Do.
Australia, western					
Au-Ag-PGE-Hg-Se polymetallic veins	Pilbara region, Copper Hills	Chrisstanleyite ($Ag_2Pd_2Se_4$)	38.5 wt. %	—	Nickel (2002)
Do.	do.	Cu-chrisstanleyite ($Cu_2Pd_2Se_4$)	41.33 wt. %	—	Do.
Do.	do.	Naumannite (Ag_2Se)	28.8 wt. %	—	Do.
Do.	do.	Oosterboschite ($Pd_4Cu_3Se_5$)	45 wt. %	—	Do.
Do.	do.	Umangite (Cu_3Se_2)	13.7 wt. %	—	Do.
Brazil, northern					
Au-Pd-Pt	Serra Pelada	Bulk rock of bonanza grade Au-Pd-Pt	21 to 36 ppm	Disaggregated, clayey material	Cabral and others (2002)
Do.	do.	Palladseite ($Pd_{17}Se_{15}$)	n.r.	—	Do.
Do.	do.	Sudovikovite ($PtSe_2$)	11.5 to 12.2 wt. %	Pd-Pt-Se inclusions in palladian gold aggregates	Do.
Canada, British Columbia					
Au-pyrite quartz veins	Caribooa	Pyrite	<15 ppm	Low to negligible Se content of Au-quartz deposits is attributed to Se-poor magmatic sources and (or) wall rocks.	Hawley and Nichol (1959)
Canada, Manitoba					
Massive Cu-Fe-(Zn)-S replacement	Flin Flon	Chalcopyrite	145 to 470 ppm	Major concentration of Se found in the Canadian Precambrian deposits occurs in the massive Cu, Fe S replacement types of deposits, hydrothermal in origin.	Hawley and Nichol (1959)
Do.	do.	Pyrite	<15 to 220 ppm	—	Do.
Do.	do.	Pyrrhotite	375 ppm	—	Do.
Canada, New Brunswick					
Cu-Fe-Zn-S banded ores	Heath Steele	Pyrite	20 ppm	—	Hawley and Nichol (1959)
Massive Cu-Fe-(Zn)-S replacement, banded	do.	Pyrrhotite	21 ppm	—	Do.
Canada, Newfoundland and Labrador					
Ni-Cu-Co	Nain Plutonic Suite, Voisey's Bay, Ovid ore zone	Chalcopyrite	38 to 70 ppm	—	Ripley and others (2002)
Do.	do.	Pentlandite	53 to 93 ppm	—	Do.

Table Q2.   A summary of selenium concentrations in various selenides and sulfides from deposits around the world.—Continued

[avg, average; b.d.l., below detection limit; Do., do., ditto; IOCG, iron oxide-copper-gold; n.d., not detected; n.r., not reported; ppm, part per million; wt. %, weight percent; —, none. Abbreviations for elements: Ag, silver; As, arsenic; Au, gold; Bi, bismuth; Co, cobalt; Cu, copper; Fe, iron; Hg, mercury; Mo, molybdenum; Ni, nickel; Pb, lead; Pd, palladium; PGE, platinum-group element; Pt, platinum; S, sulfur; Se, selenium; Te, tellurium; Ti, titanium; Tl, thallium; U, uranium; Zn, zinc]

Deposit type and (or) chemistry	Mine/deposit name	Mineral phases	Selenium concentration	Notes	Reference(s)
		Canada, Northwest Territories			
Au-pyrite quartz veins	Yellowknife, Discovery Mine	Pyrrhotite	26 to 30 ppm	—	Hawley and Nichol (1959)
		Canada, Ontario			
Sudbury Ni-Cu-PGE sulfide deposit	Sudbury Complex, Creighton deposit, Western Branch	Chalcopyrite	49.43 to 124.59 ppm	—	Dare and others (2010)
Do.	do.	Pentlandite	49.34 to 113.66 ppm	—	Do.
Do.	do.	Pyrite	60.56 to 151.83 ppm	—	Do.
Do.	do.	Pyrrhtotite	63.52 to 133.98 ppm	—	Do.
Do.	Creighton, Frood, Garson, Levack, Murray Mines	Cu-Ni ores, no specific minerals	20 to 82 ppm	—	Nriagu and Wong (1983)
Au-pyrite quartz veins	Cathroy-Larder, Hardrock, Howey-Hasaga (Red Lake), Renabi	Pyrite	<15 ppm	Low to negligible Se content of Au-quartz deposits is attributed to Se-poor magmatic sources and (or) wall rocks.	Hawley and Nichol (1959)
Do.	Hollinger	Chalcopyrite	23 ppm	—	Do.
Do.	do.	Pyrrhotite	26 to 30 ppm	—	Do.
Do.	McIntyre Mine	High-temperature pyrite	<15 to 83 ppm	—	Do.
Do.	do.	Low-temperature pyrite	<15 to 110 ppm	In the McIntyre Mine, the authors identified low-temperature pyrite with a higher range of Se concentrations than high-temperature pyrite.	Do.
Do.	McIntyre Mine	Pyrite	<15 to 110 ppm	—	Do.
Banded siderite-pyrite	Michipicoten Iron Formation, Rand No. 2 Mine	Pyrrhotite	<15 ppm	—	Do.
Do.	Michipicoten Iron Frm, Rand No. 2 Mine	Pyrite	<15 ppm	—	Do.
Diabase dikes	Algoma U district, Can-Met Mine	Pyrrhotite	<15 ppm	—	Do.
Magnetite (replacement)	Marmora	Pyrite	<15 ppm	Author noted that Se showed no order of preference among individual sulfide, phases, but showed a tendency for progressive concentration of Se with the order of crystallization.	Do.
Massive Cu-Fe-(Zn)-S replacement	Manitouwadge, Geco Mine,	Chalcopyrite	130 to 540 ppm	—	Do.
Do.	do.	Pyrite	44 to 310 ppm	—	Do.
Do.	do.	Pyrrhotite	<15 to 595 ppm	—	Do.
Ni-Cu-S ore	Porcupine, Alexo Mine	do.	17 ppm	—	Do.
Do.	Sudbury Complex	Chalcopyrite	11 to 165 ppm	—	Do.
Do.	do.	Pentlandite	30 to 160 ppm	—	Do.
Do.	do.	Pyrite	25 to 130 ppm	—	Do.
Do.	do.	Pyrrhotite	17 to 230 ppm	—	Do.
Pyritiferous U banded or bedded deposits	Algoma, Blind River area	Pyrite	<15 to 79 ppm	—	Do.

Table Q2. A summary of selenium concentrations in various selenides and sulfides from deposits around the world.—Continued

[avg, average; b.d.l., below detection limit; Do., do., ditto; IOCG, iron oxide-copper-gold; n.d., not detected; n.r., not reported; ppm, part per million; wt. %, weight percent; —, none. Abbreviations for elements: Ag, silver; As, arsenic; Au, gold; Bi, bismuth; Co, cobalt; Cu, copper; Fe, iron; Hg, mercury; Mo, molybdenum; Ni, nickel; Pb, lead; Pd, palladium; PGE, platinum-group element; Pt, platinum; S, sulfur; Se, selenium; Te, tellurium; Ti, titanium; Tl, thallium; U, uranium; Zn, zinc]

Deposit type and (or) chemistry	Mine/deposit name	Mineral phases	Selenium concentration	Notes	Reference(s)
Canada, Quebec					
Au-pyrite quartz veins	Granada	Pyrite	<15 ppm	Low to negligible Se content of Au-quartz deposits is attributed to Se-poor magmatic sources and (or) wall rocks.	Hawley and Nichol (1959)
Do.	Powell Rouyn	do.	23 to 24 ppm	—	Do.
Cu-Fe-Zn-S banded	Suffield	do.	<15 ppm	—	Do.
Massive Cu-Fe-(Zn)-S replacement	Aldermac	Chalcopyrite	135 ppm	—	Do.
Do.	do.	Pyrite	56 ppm	—	Do.
Do.	do.	Pyrrhotite	74 ppm	—	Do.
Do.	Campbell-Chibougamau	Chalcopyrite	25 to 94 ppm	—	Do.
Do.	do.	Pyrite	51 ppm	In pyrite, pyrrhotite, and chalcopyrite, the Se content is greatest when the mineral phase is located in a massive Cu-S replacement body.	Do.
Do.	do.	Pyrrhotite	<15 to 82 ppm	—	Do.
Do.	Noranda	Chalcopyrite	360 to 535 ppm	—	Do.
Do.	do.	Pyrite	33 to 1,000 ppm	—	Do.
Do.	do.	Pyrrhotite	36 to 555 ppm	—	Do.
Do.	Normetal	Chalcopyrite	23 to 260 ppm	—	Do.
Do.	do.	Pyrite	<15 to 320 ppm	—	Do.
Do.	do.	Pyrrhotite	15 to 235 ppm	—	Do.
Do.	Quemont	Chalcopyrite	40 to 280 ppm	—	Do.
Do.	do.	Pyrite	10 to 250 ppm	—	Do.
Do.	do.	Pyrrhotite	54 to 425 ppm	—	Do.
Do.	Waite Amulet	Chalcopyrite	395 ppm	—	Do.
Canada, Saskatchewan					
Au-pyrite quartz veins	Foudulac, Algold	Pyrite	23 to 24 ppm	—	Hawley and Nichol (1959)
Chile, northern					
High sulfidation, epithermal Au-Ag-Cu	Pascua deposit	Main stage pyrite	0.01 to 0.06 wt. %	—	Chouinard and others (2005)
Volcanic-hosted strata-bound Cu	Mantos Blancos deposit	Chalcopyrite	0.34 to 4.76 ppm	—	Reich and others (2013)
Do.	do.	Bornite	0.16 to 5.11 ppm	—	Do.
Democratic Republic of the Congo (Congo [Kinshasa])					
U-Cu-Co	Katanga Copperbelt, Musonoi Mine	Berzelianite (Cu_2Se)	28.65 to 40.40 wt. %	—	Pirard and Hatert (2008)
Do.	do.	Digenite ($Cu_{1.8}S$)	0.63 to 19.05 wt. %	—	Do.
Do.	do.	Athabascaite (Cu_5Se_4)	12.48 to 34.37 wt. %	—	Do.
Do.	do.	Trogtalite ($CoSe_2$)	69.43 to 70.23 wt. %	—	Do.

Table Q2. A summary of selenium concentrations in various selenides and sulfides from deposits around the world.—Continued

[avg, average; b.d.l., below detection limit; Do., do., ditto; IOCG, iron oxide-copper-gold; n.d., not detected; n.r., not reported; ppm, part per million; wt. %, weight percent; —, none. Abbreviations for elements: Ag, silver; As, arsenic; Au, gold; Bi, bismuth; Co, cobalt; Cu, copper; Fe, iron; Hg, mercury; Mo, molybdenum; Ni, nickel; Pb, lead; Pd, palladium; PGE, platinum-group element; Pt, platinum; S, sulfur; Se, selenium; Te, tellurium; Ti, titanium; Tl, thallium; U, uranium; Zn, zinc]

Deposit type and (or) chemistry	Mine/deposit name	Mineral phases	Selenium concentration	Notes	Reference(s)
Europe, southeastern					
Cretaceous skarn, epithermal and porphyry deposits	Baita Bihor, Chelopeck, Elasite, Ocna de Fier, Radka, Sasca Montana; Banatitic magmatic and metallogenetic belt (BMMB)	Bornite	1.5 to 1,046 ppm	—	Cook and others (2011)
Do.	Baita Bihor, Ocna de Fier; Banatitic magmatic and metallogenetic belt (BMMB)	Chalcopyrite	8.7 to 538 ppm	—	Do.
Do.	do.	$Cu_{2-x}S$ sulfides	151 to 383 ppm	—	Do.
Italy, Sardinia					
Pb-As	Baccu Locci Mine	Cupropavonite	0.26 wt. %	—	Pirri (2002)
Do.	do.	Galena	0.64 wt. %	—	Do.
Do.	do.	Greenockite	0.13 wt. %	—	Do.
Do.	do.	Se-rich galena (claust-halite?)	12.99 wt. %	—	Do.
Do.	do.	Sphalerite	0.12 wt. %	—	Do.
Do.	do.	Wittichenite	0.22 wt. %	—	Do.
Japan, Hokkaido					
Ag-Bi-Te-Se-S	Suttsu Mine	Kawazulite $(Bi_{2.01}(Te_{1.42}Se_{1.15}S_{0.42})_{2.99})$	12.9 wt. %	—	Shimizu and others (1995)
Do.	do.	Selenian bismuthinite $(Bi_{2.00}(S_2Se_{0.25})_{3.01})$	3.7 wt. %	—	Do.
Do.	do.	Selenian pavonite $(Ag_{1.00}(Bi_{2.86}Pb_{0.18})_{3.04}(S_{3.54}Se_{1.36}Te_{0.06})_{4.96})$	11.1 wt. %	—	Do.
Do.	do.	Unnamed $(Bi_3(Te, Se, S)_4)$	9.5±4 wt. %	—	Do.
Kazakhstan					
Porphyry Cu-Mo	Boshchekul' deposit	Chalcopyrite II	64 to 123.7 ppm	—	Filimonova (1972)
Do.	do.	Chalcopyrite III	111 to 225 ppm	—	Do.
Do.	do.	Chalcopyrite IV	20.6 to 44.4 ppm	—	Do.
Do.	do.	Magnetite	5 to 7 ppm	—	Do.
Do.	do.	Molybdenite I	120 to 781 ppm	—	Do.
Do.	do.	Molybdenite II	235 to 800 ppm	—	Do.
Do.	do.	Pyrite I	42 to 105 ppm	—	Do.
Do.	do.	Pyrite III	50 to 203 ppm	—	Do.
Do.	do.	Pyrite IV	16 to 100 ppm	—	Do.
Do.	do.	Sphalerite	29.5 ppm	—	Do.

Table Q2.   A summary of selenium concentrations in various selenides and sulfides from deposits around the world.—Continued

[avg, average; b.d.l., below detection limit; Do., do., ditto; IOCG, iron oxide-copper-gold; n.d., not detected; n.r., not reported; ppm, part per million; wt. %, weight percent; —, none. Abbreviations for elements: Ag, silver; As, arsenic; Au, gold; Bi, bismuth; Co, cobalt; Cu, copper; Fe, iron; Hg, mercury; Mo, molybdenum; Ni, nickel; Pb, lead; Pd, palladium; PGE, platinum-group element; Pt, platinum; S, sulfur; Se, selenium; Te, tellurium; Ti, titanium; Tl, thallium; U, uranium; Zn, zinc]

Deposit type and (or) chemistry	Mine/deposit name	Mineral phases	Selenium concentration	Notes	Reference(s)
Pacific Ocean, 13° North, East Pacific Rise					
Cu sulfides, Black smoker active chimneys	Hi-T hydrothermal sulfide deposits: axial graben	Chalcopyrite	100 to 2,000 ppm	High Se values occur in high-temperature mineral assemblages, found in the inner part of the deposit in equilibrium with pure, unmixed hydrothermal water; lowest Se values in outer part of deposit, influenced by mixing of hydrothermal waters and seawater.	Auclair and others (1987)
Fe-Cu massive sulfides, mature hydrothermal edifice	Off-axis seamounts	Chalcopyrite	0 to 2,500 ppm	—	Do.
Do.	do.	Pyrite	0 to 1,500 ppm	—	Do.
Portugal					
Cu-Zn ore	Neves Corvo deposit, Lombador orebody	Se-galena, up to 30% of clausthalite (PbSe), and junoite ($Pb_3Cu_2Bi_8[S,Se]_{16}$)	2,560 ppm (avg)	—	Pinto and others (2013)
Pb-Zn ore	Neves Corvo deposit, Zambugal orebody	do.	3,220 ppm (avg)	—	Do.
Russia, Siberia					
Cu-Ni-PGE	Noril'sk, Oktyabr deposit	Chalcopyrite	44 to 148 ppm	—	Kovalenker and others (1975)
Do.	do.	Cubanite ($CuFe_2S_3$)	92 to 94 ppm	—	Do.
Do.	do.	Millerite, NiS	496 ppm	—	Do.
Do.	do.	Moikhukite	94 ppm	—	Do.
Do.	do.	Pentlandite	56 to 213 ppm	—	Do.
Do.	do.	Pyrrhotite	50 to 98 ppm	—	Do.
Do.	do.	Troilite (FeS)	87 ppm	—	Do.
Do.	Noril'sk, Talnakh deposit	Chalcopyrite	69 to 152 ppm	—	Do.
Do.	do.	Cubanite	85 to 181 ppm	—	Do.
Do.	do.	Pentlandite	139 to 190 ppm	—	Do.
Do.	do.	Pyrrhotite	70 to 74 ppm	—	Do.
Do.	do.	Taknakhite	115 to 190 ppm	—	Do.
Russia, Ural Mountains					
Cu-S	Karabash group	Bornite	18 ppm	—	Yushoko-Zakharova and others (1978)
Do.	do.	Chalcopyrite (from Cu-sphalerite ores)	3.8 to 216 ppm	—	Do.
Do.	do.	Chalcopyrite (from late quartz-carbonate veinlets)	11 to 16 ppm	—	Do.
Do.	do.	Galena	0.5 ppm	—	Do.
Do.	do.	Pyrite	3 to 110 ppm	—	Do.
Do.	do.	Sphalerite	16 ppm	—	Do.
Do.	do.	Tetrahedrite-tennantite (from cupreous pyrite)	81 ppm	—	Do.

Table Q2.   A summary of selenium concentrations in various selenides and sulfides from deposits around the world.—Continued

[avg, average; b.d.l., below detection limit; Do., do., ditto; IOCG, iron oxide-copper-gold; n.d., not detected; n.r., not reported; ppm, part per million; wt. %, weight percent; —, none. Abbreviations for elements: Ag, silver; As, arsenic; Au, gold; Bi, bismuth; Co, cobalt; Cu, copper; Fe, iron; Hg, mercury; Mo, molybdenum; Ni, nickel; Pb, lead; Pd, palladium; PGE, platinum-group element; Pt, platinum; S, sulfur; Se, selenium; Te, tellurium; Ti, titanium; Tl, thallium; U, uranium; Zn, zinc]

Deposit type and (or) chemistry	Mine/deposit name	Mineral phases	Selenium concentration	Notes	Reference(s)
			Russia, Ural Mountains—Continued		
Cu-S	Karabash group	Tetrahedrite-tennantite (from quartz-carbonate veins and veinlets)	45 to 100 ppm	—	Yushoko-Zakharova and others (1978)
Do.	Mauk deposit	Chalcopyrite (from Cu-pyrrhotite ores)	180 to 325 ppm	—	Do.
Do.	do.	Pyrite	n.d. to 119 ppm	—	Do.
Do.	do.	Pyrrhotite	21 to 145 ppm	—	Do.
Do.	do.	Sphalerite	140 to 187 ppm	—	Do.
Cu-Zn-S	Gay deposit	Bornite	10 to 120 ppm	—	Do.
Do.	do.	Chalcopyrite (from Cu-sphalerite ores)	5 to 150 ppm	—	Do.
Do.	do.	Galena	30 ppm	—	Do.
Do.	do.	Pyrite	5 to 550 ppm	—	Do.
Do.	do.	Sphalerite	8 to 84 ppm	—	Do.
Do.	do.	Tetrahedrite-tennantite (from cupreous pyrite)	10 ppm	—	Do.
Do.	III Internatsional deposit	Bornite	Trace to 10 ppm	—	Do.
Do.	do.	Chalcocite	n.d. to 200 ppm	—	Do.
Do.	do.	Chalcopyrite (from Cu-sphalerite ores)	33 to 220 ppm	—	Do.
Do.	do.	Chalcopyrite (from late quartz-carbonate veinlets)	Trace to 30 ppm	—	Do.
Do.	do.	Pyrite	Trace to 146 ppm	—	Do.
Do.	do.	Sphalerite	2 to 16 ppm	—	Do.
Do.	do.	Tetrahedrite-tennantite (from cupreous pyrite)	9 ppm	—	Do.
Do.	Levikha XIV deposit	Chalcopyrite (from Cu-sphalerite ores)	5 to 210 ppm	—	Do.
Do.	do.	Tetrahedrite-tennantite (from quartz-carbonate veins and veinlets)	13 to 20 ppm	—	Do.
Do.	Sibay deposit	Chalcopyrite (from Cu-pyrrhotite ores)	80 to 265 ppm	—	Do.
Do.	do.	Chalcopyrite (from Cu-sphalerite ores)	10 to 130 ppm	—	Do.
Do.	do.	Pyrite	1 to 88 ppm	—	Do.
Do.	do.	Pyrrhotite	53 to 126 ppm	—	Do.
Do.	do.	Sphalerite	0.5 to 13 ppm	—	Do.
FeS$_2$	Zyuzel'skoye deposit	Chalcopyrite (from Cu-sphalerite ores)	160 ppm	—	Do.
Do.	do.	Chalcopyrite (from late quartz-carbonate veinlets)	Trace to 54 ppm	—	Do.
Do.	do.	Pyrite	Trace to 495 ppm	—	Do.

Table Q2.   A summary of selenium concentrations in various selenides and sulfides from deposits around the world.—Continued

[avg, average; b.d.l., below detection limit; Do., do., ditto; IOCG, iron oxide-copper-gold; n.d., not detected; n.r., not reported; ppm, part per million; wt. %, weight percent; —, none. Abbreviations for elements: Ag, silver; As, arsenic; Au, gold; Bi, bismuth; Co, cobalt; Cu, copper; Fe, iron; Hg, mercury; Mo, molybdenum; Ni, nickel; Pb, lead; Pd, palladium; PGE, platinum-group element; Pt, platinum; S, sulfur; Se, selenium; Te, tellurium; Ti, titanium; Tl, thallium; U, uranium; Zn, zinc]

Deposit type and (or) chemistry	Mine/deposit name	Mineral phases	Selenium concentration	Notes	Reference(s)
			Sweden and Norway		
Late Proterozoic metamorphic Cu-vein systems	Glava, Grusen, Moberg, Tinnsjå, Tjøstølflaten	Bornite	2.8 to 4,617 ppm	Se concentrations in bornite show promise as a vector for exploration and may be able to track proximal to distal zonation.	Cook and others (2011)
Do.	Tinnsjå	Chalcopyrite	20.7 ppm	—	Do.
Do.	Grusen, Moberg, Tinnsjå	$Cu_{2-x}S$ sulfides	b.d.l. to 1,291 ppm	—	Do.
			Sweden, southeastern		
Cu-Ag-Tl-Se	Skrikerum deposit, Småland	Selenojalpaite (Ag_3CuSe_2)	29.01 wt. %	—	Bindi and Pratesi (2005)
			Spain		
Carbonate-hosted epithermal gold	Providencia Mine, Leon	Villamaninite ($(Cu,Ni,Co,Fe)(S,Se,Te)_2$)	1.89 to 9.12 wt. %	—	Paniagua (1995)
			Turkey, northeastern		
Cu	Murgul deposit	Aikinite $)Pb_{0.96}Cu_{1.10}Bi_{0.98}S_{2.73}Se_{0.20}Te_{0.03})$	2.75 wt. %	—	Willgallis and others (1990)
Do.	do.	Galena ($Pb_{1.00}Ag_{0.01}Bi_{0.01}S_{0.95}Se_{0.03})$	1 wt. %	—	Do.
Do.	do.	Tennantite ($Cu_{9.66}Zn_{2.02}Fe_{0.03}As_{3.90}Bi_{0.35}Te_{0.08}S_{12.95}Se_{0.01}$ and $Cu_{9.59}Zn_{1.97}Fe_{0.03}As_{3.76}Bi_{0.44}Te_{0.11}S_{13.03}Se_{0.07})$	0.05 and 0.36 wt. %	—	Do.
Do.	do.	Tetradymite ($Bi_{1.76}Pb_{0.22}Cu_{0.06}Te_{1.72}S_{0.68}Se_{0.56})$	6.33 wt. %	—	Do.
			United States, Alaska		
Porphyry Cu-Au-Mo	Bristol Bay, Pebble deposit	Sample pyrite-4	142 ppm	—	Gregory and others (2013)
Pb-Zn	Southern Brooks Range, Red Dog	Galena and sphalerite (ore minerals), and associated pyrite	<1 ppm	Se distributed evenly among these mineral phases	Baker and others (2000)
			United States, Minnesota		
Cu-Ni-PGE	Duluth Complex, Babbitt deposit	Cubanite	6 to 157 ppm	—	Ripley (1990)
Do.	do.	Pentlandite	24 to 363 ppm	—	Do.
Do.	do.	Pyrrhotite	24 to 169 ppm	—	Do.
			United States, Nevada		
Au-Ag veins	Humboldt Coounty, National District, Buckskin Mountain	HgSeSCl phases	2.12 to 21.91 wt. %	—	Vikre (2007)
Do.	do.	Stibnite	0.10 to 3.62 wt. %	—	Do.