

Manganese

Chapter L of

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



Professional Paper 1802–L

**U.S. Department of the Interior
U.S. Geological Survey**

Periodic Table of Elements

1A 1 H hydrogen 1.008																	2 He helium 4.003
3 Li lithium 6.94	2A 4 Be beryllium 9.012											3A 5 B boron 10.81	4A 6 C carbon 12.01	5A 7 N nitrogen 14.01	6A 8 O oxygen 16.00	7A 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 (261)	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 Flerovium (289)	115 Uup (288)	116 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 (288)	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. Photograph of the Mamatwan open pit mine in South Africa. The black manganese layer is about 45 meters thick and consists of a 20-meter-thick ore bed and two lower grade subeconomic beds. The slightly folded layering is shown by the shapes of the various mine benches. Lighter material in the background is waste that must be stripped to expose the ore bed; this waste material is used as backfill in mined areas (foreground). Photograph by William F. Cannon.

Manganese

By William F. Cannon, Bryn E. Kimball, and Lisa A. Corathers

Chapter L 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–L

U.S. Department of the Interior
U.S. Geological Survey

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

For more information on the USGS—the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment—visit <https://www.usgs.gov> or call 1–888–ASK–USGS.

For an overview of USGS information products, including maps, imagery, and publications, visit <https://store.usgs.gov/>.

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Although this information product, for the most part, is in the public domain, it also may contain copyrighted materials as noted in the text. Permission to reproduce copyrighted items must be secured from the copyright owner.

Suggested citation:

Cannon, W.F., Kimball, B.E., and Corathers, L.A., 2017, Manganese, chap. L of Schulz, K.J., DeYoung, J.H., Jr., Seal, R.R., II, and Bradley, D.C., eds., Critical mineral resources of the United States—Economic and environmental geology and prospects for future supply: U.S. Geological Survey Professional Paper 1802, p. L1–L28, <https://doi.org/10.3133/pp1802L>.

ISSN 2330-7102 (online)

Contents

Abstract.....	L1
Introduction.....	L2
Uses, Applications, and Consumption.....	L2
Strategic and Critical Resource Issues	L2
Manganese Commodities.....	L2
Geology.....	L4
Geochemistry.....	L4
Mineralogy.....	L5
Deposit Types	L6
Land-Based Deposits	L6
Manganese Deposits in Marine Sedimentary Rocks	L6
Manganese Deposits Without Iron Enrichments	L6
Iron-Related Manganiferous Sedimentary Deposits	L9
Secondary Enrichment (Supergene) Deposits	L9
Seabed Deposits	L9
Ferromanganese Nodules	L10
Ferromanganese Crusts	L11
Resources and Production.....	L12
Manganese Reserves	L12
Other Identified Resources	L12
Land-Based Resources	L12
Seabed Resources	L14
Ferromanganese Nodules	L15
Ferromanganese Crusts	L15
Resources in the United States	L16
Land-Based Resources	L16
Aroostook County, Maine	L16
Cuyuna Range, Minnesota	L17
Seabed Resources	L17
Undiscovered Resources	L17
Exploration for New Deposits.....	L18
Environmental Considerations.....	L18
Sources and Fate in the Environment	L18
Mine Waste Characteristics	L21
Human Health Concerns.....	L21
Ecological Health Concerns.....	L22
Carbon Footprint.....	L22
Mine Closure.....	L23
Problems and Future Research.....	L23
References Cited.....	L24

Figures

L1.	Charts showing world production, apparent consumption, and distribution of production of manganese ore from 2007 to 2011	L3
L2.	Pie charts showing the sources and the annual average amounts of gross weight of U.S. imports of manganese ore, ferromanganese, and silicomanganese for the period 2008–11	L3
L3.	World map showing the location, relative size, and type of the major terrestrial manganese deposits listed in table L2 as well as subeconomic deposits in the United States	L7
L4.	Photographs showing examples of contrasting types of manganese ore	L8
L5.	Schematic diagram of the oceanic conditions necessary to form sedimentary manganese deposits that are not enriched in iron	L8
L6.	Photograph showing a dense carpet of ferromanganese nodules on the seabed off Johnston Island within the United States Exclusive Economic Zone near Hawaii.....	L10
L7.	Photograph showing ferromanganese crust on carbonate rock from the Blake Plateau off the southeastern coast of the United States.....	L11
L8.	Photograph of the Mamatwan open pit mine in South Africa	L13
L9.	Graphs showing the cumulative frequency of tonnages and grades of 39 marine sedimentary manganese deposits	L14

Tables

L1.	Estimated world manganese ore reserves in 2012.....	L3
L2.	Identified resources estimated for major land-based manganese deposits of the world	L13
L3.	Grade, tonnage, and quantity of contained manganese for eight manganese deposits and districts in the United States.....	L16
L4.	Background and above-background concentrations of manganese in rocks, soils, waters, and air	L19

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 (in 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)	0.0000003527	ounce, avoirdupois (oz)
milligram (mg)	0.00003527	ounce, avoirdupois (oz)
gram (g)	0.03527	ounce, avoirdupois (oz)
gram (g)	0.03215075	ounce, troy
kilogram (kg)	32.15075	ounce, troy
kilogram (kg)	2.205	pound avoirdupois (lb)
ton, metric (t)	1.102	ton, short [2,000 lb]
ton, metric (t)	0.9842	ton, long [2,240 lb]
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)	0.0000006243	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—Continued

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

Inch/Pound to International System of Units

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

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

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

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

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

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

Datum

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

Supplemental Information

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

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

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

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

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

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

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

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

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

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

Equivalencies

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

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

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

Metric system prefixes

tera- (T-)	10^{12}	1 trillion
giga- (G-)	10^9	1 billion
mega- (M-)	10^6	1 million
kilo- (k-)	10^3	1 thousand
hecto- (h-)	10^2	1 hundred
deka- (da-)	10	1 ten
deci- (d-)	10^{-1}	1 tenth
centi- (c-)	10^{-2}	1 hundredth
milli- (m-)	10^{-3}	1 thousandth
micro- (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

$\mu\text{g/L}$	microgram per liter
μm	micrometer
ATSDR	Agency for Toxic Substances and Disease Registry
CCZ	Clarion-Clipperton zone
cm	centimeter
EEZ	Exclusive Economic Zone
Eh	oxidation potential
EIS	environmental impact statement
EPA	U.S. Environmental Protection Agency
ISA	International Seabed Authority
ISMI	International Strategic Minerals Inventory
km	kilometer
km^2	square kilometer
LC_{50}	lethal concentration 50 (concentration that kills 50 percent of test population within a given timeframe)
m	meter
mg/d	milligram per day
mg/kg	milligram per kilogram
mg/L	milligram per liter
mg/m^3	milligram per cubic meter
Mkg/yr	million kilograms per year
mm	millimeter
ng/m^3	nanogram per cubic meter
OSHA	Occupational Safety and Health Administration
REE	rare-earth element
SAF	submerged-arc furnace
SiO_2	silicon dioxide (silica)
USGS	U.S. Geological Survey
WHO	World Health Organization

Manganese

By William F. Cannon, Bryn E. Kimball, and Lisa A. Corathers

Abstract

Manganese is an essential element for modern industrial societies. Its principal use is in steelmaking, where it serves as a purifying agent in iron-ore refining and as an alloy that converts iron into steel. Although the amount of manganese consumed to make a ton of steel is small, ranging from 6 to 9 kilograms, it is an irreplaceable component in the production of this fundamental material. The United States has been totally reliant on imports of manganese for many decades and will continue to be so for at least the near future. There are no domestic reserves, and although some large low-grade resources are known, they are far inferior to manganese ores readily available on the international market. World reserves of manganese are about 630 million metric tons, and annual global consumption is about 16 million metric tons. Current reserves are adequate to meet global demand for several decades. Global resources in traditional land-based deposits, including both reserves and rocks sufficiently enriched in manganese to be ores in the future, are much larger, at about 17 billion metric tons. Manganese resources in seabed deposits of ferromanganese nodules and crusts are larger than those on land and have not been fully quantified. No production from seabed deposits has yet been done, but current research and development activities are substantial and may bring parts of these seabed resources into production in the future. The advent of economically successful seabed mining could substantially alter the current scenario of manganese supply by providing a large new source of manganese in addition to traditional land-based deposits.

From a purely geologic perspective, there is no global shortage of proven ores and potential new ores that could be developed from the vast tonnage of identified resources. Reserves and resources are very unevenly distributed, however. The Kalahari manganese district in South Africa contains 70 percent of the world's identified resources and about 25 percent of its reserves. South Africa, Brazil, and Ukraine together accounted for nearly 65 percent of reserves in 2013. The combination of total import reliance for manganese, the mineral commodity's essential uses in our industrialized society, and the potential for supply disruptions because

of the limited sources of the ore makes manganese among the most critical minerals for the United States.

Manganese is the 12th most abundant element in Earth's crust. Its concentration varies among common types of rocks, mostly in the range of from 0.1 to 0.2 percent. The highest quality manganese ores contain from 40 to 45 percent manganese. The formation of these ores requires specialized geologic conditions that concentrate manganese at several hundred times its average crustal abundance. The dominant processes in forming the world's principal deposits take place in the oceans. As a result, most important manganese deposits occur in ancient marine sedimentary rocks that are now exposed on continents as a result of subsequent tectonic uplift and erosion. In many cases, other processes have further enriched these manganeseiferous sedimentary rocks to form some of today's highest grade ores. Modern seabed resources of ferromanganese nodules cover vast areas of the present ocean floor and are still forming by complex interactions of marine microorganisms, manganese dissolved in seawater, and chemical processes on the seabed.

Manganese is ubiquitous in soil, water, and air. It occurs most often in solid form but can become soluble under acidic conditions. Manganese mining, like any activity that disturbs large areas of Earth's surface, has the potential to produce increases in manganese concentrations that could be harmful to humans or the environment if not properly controlled. Although manganese is an essential nutrient for humans and most other organisms, overexposure can lead to neurotoxicity in humans. Workers at manganese mining and processing facilities have the greatest potential to inhale manganese-rich dust. Without proper protective equipment, these workers may develop a permanent neurological disorder known as manganism. Each manganese mine is unique and presents its own suite of potential hazards and preventative measures. Likewise, various nations have their own sets of standards to ensure safe mining, isolation of mine waste, treatment of mine waters, and mine closure and restoration. Interest in mining trace metals contained in ferromanganese nodules and crusts on the seabed has increased rapidly in the past decade. Prime areas for future research include overcoming the technological challenges presented by mining as deep as 6,500 meters below sea level and understanding and mitigating the potential impacts of seabed mining on marine ecosystems.

Introduction

Manganese, which is a ferrous metal, is an irreplaceable element in modern industrial economies, and it is consumed in large quantities by all industrialized nations. Manganese is important because of its desulfurizing, deoxidizing, and alloying properties, as well as its other chemical properties. An abundant and stable long-term supply of manganese is critical to the United States and other industrialized nations, as well as to developing countries. The United States has no manganese production or reserves of manganese ore and is totally reliant on imports of this mineral commodity.

Uses, Applications, and Consumption

In metallurgical applications, manganese is used predominantly as an alloying addition in steel. It is used as well in refining iron ore to metallic iron prior to the steelmaking process. Manganese has no known substitutes in the overall conversion of iron ore to steel, so steel cannot be produced without manganese. Steel and cast iron production together provide the largest market for manganese (historically accounting for 77 to 90 percent of manganese consumption in the United States), although manganese is also used as an alloy with nonferrous metals, such as aluminum and copper.

Nonmetallurgical applications of manganese include battery cathode production (mainly synthetic manganese dioxide); soft ferrites (manganese-zinc ferrites) used in electronics; micronutrient additives in fertilizers and animal feed (manganese sulfate and manganous oxide); water treatment chemicals (potassium permanganate and manganese dioxide); and other chemicals (manganese dioxide), such as those used as a colorant for automobile undercoat paints, bricks, frits, glass, textiles, and tiles. The product “manganese violet” is used for coloration in cosmetics, glazes used by artists, plastics, and powder coatings.

In the United States, manganese is imported in the following three principal forms: ore (minimally processed natural manganese concentrations), and the alloys ferromanganese and silicomanganese (both of which are products of the refining of natural ores). Because the United States imports nearly all the manganese that it consumes and because U.S. manufacturers typically do not maintain large stocks of manganese, the consumption of both ore and alloys can be estimated from the imports. For the period 2007 to 2011, the U.S. average apparent consumption of manganese from manganese dioxide, ferromanganese, and manganese metal was 739,000 metric tons of contained manganese. Steelmaking accounted for 78 percent of U.S. consumption; batteries, another 7 percent; and other uses, including chemicals, nonferrous alloys, and cast iron, the remaining 15 percent (Corathers, 2013a).

Strategic and Critical Resource Issues

The U.S. Department of Defense rates manganese as one of the most critical mineral commodities for the United States because it is both essential for industry and has no substitutes, and because of the potential for and the likely effects of supply disruptions (fig. L1; National Research Council, 2008). Geopolitical concerns have led to a long-term goal of identifying and ensuring supplies that are not susceptible to disruption.

On a global scale, manganese reserves—that is, material that can be mined economically under present-day conditions—are more than adequate to supply the world’s industries with manganese for many decades, but those materials are unequally distributed geographically. Only a relatively few nations produce large amounts of manganese (three countries account for 60 percent of production in 2011). The United States is 100 percent reliant on imports. Many industrialized nations, including many countries in Europe, as well as Canada and Japan, are also largely reliant on imports for their supply of manganese.

Identified manganese resources include identified economic deposits (reserves) as well as a substantially larger amount of naturally occurring manganese-rich rocks that are not proven to be economically minable today but that could become economically viable in the future. Some types of deposits (including volcanogenic deposits, hydrothermal vein, and karst-related deposits), mines, and ore-forming processes have local importance but are only of minor significance from a national and global perspective.

Manganese Commodities

Most manganese materials in the United States are used in metallurgical processes. The major manganese commodities for this purpose are manganese ore and manganese alloys.

Manganese ore is the primary source of manganese used in the manufacture of manganese ferroalloys. Virtually all manganese ores are subjected to some form of beneficiation to achieve a concentrated product that has greater manganese content and fewer undesirable impurities. The manganese content of the more commonly used and traded ores, concentrates, nodules, and sinter for metallurgical purposes is in the approximate range of 38 to 55 percent. A manganese content of 48 percent is considered standard as a pricing basis.

From 2007 to 2011, global manganese ore production averaged 13.2 million metric tons of contained manganese, and production was led by, in order of percent of global production, South Africa, Australia, and China (table L1; fig. L1B). From 2008 to 2011, the United States imported a total of 1.9 million metric tons of manganese ore on a gross-weight basis. The leading sources of these imports were, in order of the quantity supplied, Gabon, Australia, South Africa, and Brazil (fig. L2A). Between 2008 and 2012, the average

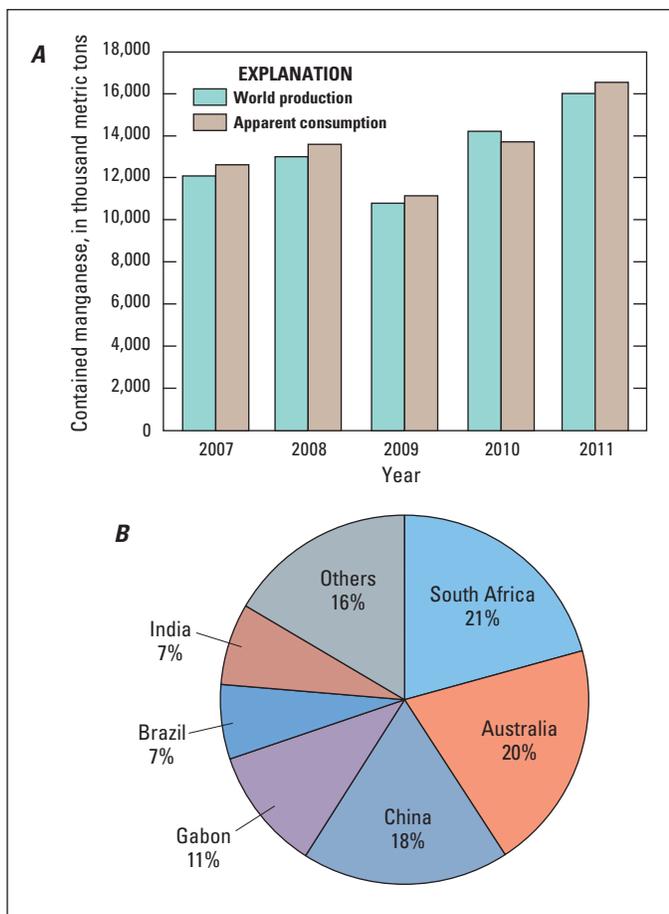


Figure L1. A, Bar chart showing world production of manganese ore (contained manganese) from 2007 to 2011 compared with world apparent consumption. Average annual production for the period was 13.2 million metric tons. B, Pie chart showing distribution of manganese ore (contained manganese) production, by country and percent of world total, for the same period (Corathers, 2013a; International Manganese Institute, 2012).

Table L1. Estimated world manganese ore reserves in 2012, in thousand metric tons of contained manganese.

[Data are from Corathers (2013b); NA, not available]

Country	Reserves
United States	None
Australia	97,000
Brazil	110,000
Burma	NA
China	44,000
Gabon	27,000
India	49,000
Kazakhstan	5,000
Malaysia	NA
Mexico	5,000
South Africa	150,000
Ukraine	140,000
Other countries	Small
World total	630,000

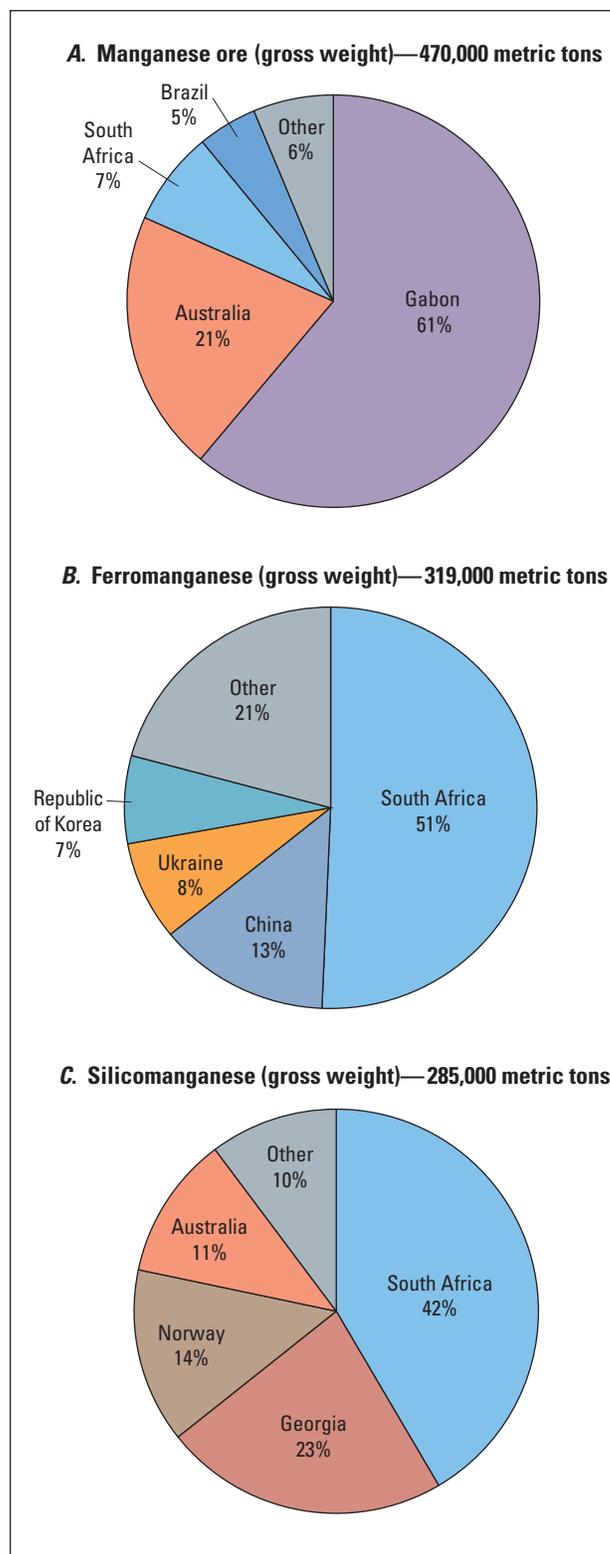


Figure L2. Pie charts showing the sources (by country) and the annual average amounts (by percentage of the total supplied) of gross weight of U.S. imports of A, manganese ore; B, ferromanganese; and C, silicomanganese for the period 2008–11. The tonnage numbers shown are the average annual gross weight of the imports. Data are from Corathers (2011–16).

L4 Critical Mineral Resources of the United States—Manganese

annual amount of manganese ore that was reported to the U.S. Geological Survey (USGS) as having been consumed domestically was 480,000 metric tons (gross weight).

The key manganese ferroalloys are ferromanganese, which is subdivided into standard (high-carbon), medium-carbon, and low-carbon grades, and silicomanganese. High-carbon ferromanganese is smelted directly in either a blast furnace or an electric submerged-arc furnace (SAF), and silicomanganese is smelted in an SAF. Silicomanganese is the manganese ferroalloy that is used predominantly throughout the world, including in the United States. Silicomanganese is smelted in a similar manner to that of high-carbon ferromanganese, except that a more siliceous charge, usually in the form of quartz, quartzite, or an ore having high silica content, is used. When an SAF is used, high-carbon ferromanganese and silicomanganese can be produced interchangeably. Production of refined grades of manganese ferroalloys, such as medium- and low-carbon ferromanganese, involves two additional stages using such equipment as a converter or a direct arc furnace. From 2006 to 2010, global ferromanganese and silicomanganese production (by gross weight) averaged 5.4 million metric tons per year and 9.2 million metric tons per year, respectively.

As of 2013, there were two producers of manganese alloys in the United States—Eramet Marietta, Inc. and Felman Productions Inc. Eramet Marietta generally produces silicomanganese and all grades of ferromanganese at its plant in Marietta, Ohio. Felman Productions produces silicomanganese at its plant in Letart, West Virginia. Even with this domestic production, the United States imported a total of 1.3 million metric tons of ferromanganese and 1.1 million metric tons of silicomanganese (gross-weight basis) from 2008 to 2011. The leading sources of these imports, by country, are shown in figure L2 (B and C).

The information and discussion presented in this chapter are based entirely on published scientific and technical literature and contain no new conclusions or interpretations. Rather, this chapter presents a summary of the vast literature on the geology and resources of manganese that are the result of more than a century of research on this important mineral commodity.

Geology

Geochemistry

Manganese is the 12th most abundant element in Earth's crust and is thus considered to be a relatively abundant metal. Average crustal rocks contain about 0.1 percent manganese, but manganese concentration varies according to rock type. Mafic rocks, such as basalt, typically contain about 0.16 percent manganese, whereas granitic rocks contain about 0.06 percent. Manganese ores contain a minimum of 15 percent manganese, but most ores are considerably higher grade, ranging up to about 50 percent manganese. The formation of manganese ore, therefore, requires a geochemical system that concentrates manganese by at least 150 times its

average crustal abundance and by as much as 500 times for the higher grade ores. An additional specialized set of conditions is required to produce strong manganese enrichment without concentrating iron, with which manganese shares many chemical similarities and is commonly compositionally correlated. Manganese ores have a much higher manganese-to-iron ratio than do typical crustal rocks. Virtually all manganese ores have formed as a result of the transport of manganese in water solutions, at least for short distances, and precipitation of manganese minerals out of those solutions in sufficiently high concentrations and volumes to form minable orebodies. Understanding the factors that control manganese solubility in water and the behavior of manganese-bearing water at scales from meters to that of ocean basins is the key to understanding manganese metallogenesis.

Manganese is a potentially mobile element and occurs in three oxidation states in nature (+2, +3, +4). The solubility and mobility of manganese in various solutions is strongly controlled by the acidity (pH) and oxidation potential (Eh) of manganese-bearing solutions, which include surface water, ocean water, and high-temperature fluids in various subsurface environments. In general, manganese solubility is highest in more acidic (lower pH) conditions and less oxidizing (lower Eh) conditions in which dissolved manganese exists primarily in the most soluble +2 oxidation state. The transport of large quantities of manganese to sites of ore formation, therefore, generally requires the existence of oxygen-poor (low Eh) ocean water or surface water. This is in contrast to the typical state of modern surface and ocean water, in which the oxidation potential is sufficiently high to make manganese essentially insoluble. The variability in chemical behavior of manganese under differing pH and Eh conditions results in many situations in which manganese can be concentrated to potentially economic concentrations. A full review of the geochemistry of manganese as it relates to manganese ore formation is beyond the scope of this summary report; for greater detail and specificity than is provided here, see for example, Roy (1988), Varentsov (1996), Nicholson and others (1997), and Maynard (2003, 2010).

The vast majority of manganese ores have formed at the ambient conditions of Earth's surface, both subaerial and submarine, and the discussion below concentrates on the geochemical behavior of manganese in these settings. Many manganese deposits are a direct result of deposition of manganese-rich sediment layers on the seabed, both in present-day oceans and oceans of the geologic past. In addition, secondary enrichment of manganese-rich marine sedimentary rocks by later continental weathering (supergene ores) has produced many high-grade manganese ore deposits. In both cases, large-scale transport of dissolved manganese in seawater and deposition of manganese from seawater are crucial components of manganese metallogeny. The most significant sources of dissolved manganese in seawater are (a) dissolved manganese in rivers entering the oceans, (b) manganese released from marine sediments by post-depositional alteration, and (c) manganese from deep-sea hydrothermal vents.

On continents, most manganese occurs in trace amounts in reduced (+2) form in silicate and carbonate minerals. It can be released by continental weathering where some of it is dissolved in surface water and eventually transported by rivers to the world's oceans. Because surface waters are generally well oxidized, the solubility of manganese is very low. The Mississippi River, for instance, shows manganese solubility that varies seasonally but averages only a few micrograms per liter (Shiller, 1997). Although this is a low concentration, it is still much higher than manganese in open oceans. Substantially more manganese is delivered by rivers to the oceans as fine-grained suspended sediments, which either contain manganese within minerals or have manganese adsorbed to their surface. Although this manganese does not immediately affect the dissolved manganese pool of the oceans, it is an important flux of manganese to seabed sediments from which it is later mobilized by reducing reactions in the upper layers of the sedimentary sequence.

Seabed hydrothermal vents are also a significant source of manganese. The character of these fluids is summarized by Tivey (2007). Vent fluids commonly have manganese concentrations measured in thousands of micrograms per liter, which is several orders of magnitude greater than typical river waters. Such vents are arrayed along active spreading centers in all the world oceans.

The formation of marine sedimentary manganese deposits, in which the contained manganese is delivered to the site of sedimentation by seawater, generally requires that such seawater be less oxidized than typical seawater in order to sustain an elevated solubility of manganese. Such seawater can exist both as layers of reduced oxygen (oxygen minimum zones) in open oceans and as highly reduced sulfidic seawater that can form in the deepwater mass in stratified oceans in restricted basins. Recent reviews of manganese mineralization (Maynard, 2003, 2010) provide further discussion of these conditions, as does the discussion below regarding deposit types.

Mineralogy

Manganese occurs as a trace element in many minerals, but the ore minerals are limited to a suite of manganese oxides, hydroxides, carbonates, and silicates. Manganese ores are commonly fine-grained or microscopic mixtures of several different manganese minerals whose accurate characterization has long been a problem. They can seldom be accurately identified solely by visual examination. Modern analytical techniques have led to revisions of older data on the composition and mineral structure of many manganese minerals. This has led, in turn, to revised descriptions in more recent literature of the mineralogy of many manganese deposits.

A full list of manganese ore minerals classified by deposit type is given in Dorr and others (1973), and details of chemical composition, crystal structure, and relative abundance are provided by Maynard (2003). In spite of

the complexity of manganese minerals and their variable occurrence in individual ore deposits, a few generalizations allow characterization of many aspects of the ore mineralogy. The most common manganese minerals within ore deposits are manganese oxides, followed by manganese carbonates. Manganese carbonates, however, are the most voluminous manganese minerals when all manganese-enriched rocks—many of which are sub-ore grade—are considered. Among oxides, pyrolusite (a simple manganese oxide) and cryptomelane (a potassium-bearing oxide) are the most widely reported, although not necessarily the most voluminous. The carbonate minerals are rhodochrosite (a manganese carbonate) and kutnahorite (a calcium-manganese carbonate). Rhodochrosite is by far the most widely recognized manganese carbonate, but kutnahorite is abundant in the vast Kalahari manganese ores of South Africa. In addition, the manganese hydroxide manganite is a very widely occurring ore mineral, as is the manganese silicate mineral braunite. Descriptions of some of the characteristics of these most abundant of the manganese minerals are given below.

Rhodochrosite.—The carbonate mineral rhodochrosite (MnCO_3) is the most widely reported manganese mineral in known deposits, including currently subeconomic deposits. It is the principal ore mineral at Molango, Mexico, and at many deposits in China. Production of a usable manganese product from rhodochrosite requires processing to convert manganese carbonate to manganese oxides. Rhodochrosite deposits are also important as protore (lower grade precursors for higher grade supergene deposits) in which oxidation and leaching at Earth's surface has converted the original carbonate mineral to manganese oxides and hydroxides and commonly increased the manganese concentration to ore grade.

Braunite.—Braunite ($\text{Mn}^{2+}\text{Mn}^{3+}_6(\text{SiO}_4)_8\text{O}_8$) is generally classified as a silicate mineral, although it contains less than 10 weight percent silicon dioxide, or silica (SiO_2). It is a major ore mineral in the Kalahari manganese district in South Africa; in Groote Eylandt, Australia; and in several districts in India. It is also a major mineral in volcanogenic manganese deposits, which are not discussed in detail in this chapter.

Cryptomelane.—Cryptomelane ($\text{K}(\text{Mn}^{4+},\text{Mn}^{2+})_8\text{O}_{16}$), a potassium-bearing manganese mineral, is a highly oxidized ore mineral in several major manganese-producing regions, including in Brazil, Gabon, and South Africa.

Manganite.—Manganite ($\text{MnO}(\text{OH})$) is a manganese hydroxide that forms commonly by oxidation at or near Earth's surface as a result of circulating groundwater. It is a significant mineral in major supergene deposits, such as those in Gabon and Ghana, as well as in parts of the Kalahari district in South Africa.

Pyrolusite.—Pyrolusite (MnO_2) is a compositionally simple manganese oxide. It forms in a variety of oxidizing conditions, especially in cases of higher acidity (lower pH). It is a major ore mineral in many significant mining districts, including in Brazil, Gabon, Ghana, the Republic of Georgia, and South Africa.

Deposit Types

Over the years, many classifications of manganese deposits have been proposed, typically based on details of mineralogy, type of associated rocks, and the geometric form of the deposits. For this summary, we use a simple classification of (a) land-based deposits consisting mostly of ancient marine sediments and zones of secondary enrichment developed within them that can be further subdivided based on the geologic environment in which they formed and the processes responsible for manganese concentrations, and (b) modern seabed deposits, which are found widely on the modern ocean floor. This discussion excludes several deposit types, such as volcanogenic, karst, and hydrothermal vein deposits, which are widespread but generally small. Although they may be important locally, their total manganese production potential is small relative to the three major deposit types (marine sedimentary, secondary enrichment, and seabed) and has only a small effect on national and global supply and demand. The global distribution of the major manganese deposits, their size, and deposit type are shown in figure L3.

Land-Based Deposits

Manganese Deposits in Marine Sedimentary Rocks

The vast majority of land-based manganese resources occur as extensive layers of manganese-rich sedimentary rocks, some of which formed as long as 2.5 billion years ago. These rocks formed on ancient seabeds (fig. L4) and have since become part of continents through tectonic processes of uplift and continental accretion. They may be of sufficiently high manganese content to constitute ores themselves, or they may be protores in which additional natural concentrating mechanisms increased the manganese content enough to form commercial ores. A recent compilation of the chemical composition of sedimentary manganese deposits of the world indicates that average manganese grade is about 24 percent and iron content is 4.3 percent (Maynard, 2010). These figures indicate that average sedimentary manganese deposits are low-grade ore, at best. Most ores currently being mined are the higher grade portion of these deposits or zones of secondary enrichment developed within them. These averages also illustrate an essential feature of sedimentary manganese deposits—the extremely efficient separation of iron from manganese during deposit formation. Whereas manganese is concentrated, on average, roughly 250 times its average crustal abundance in marine sedimentary deposits, iron occurs at concentrations near its average abundance.

Two types of sedimentary manganese deposits can be distinguished based on the nature of rocks with which they are interlayered and, by inference, the character of ocean water from which they were precipitated: (a) manganiferous sediments that occur independent of iron concentrations; and (b) manganiferous sediments interlayered with ferruginous strata, including the vast Kalahari deposits of South Africa that

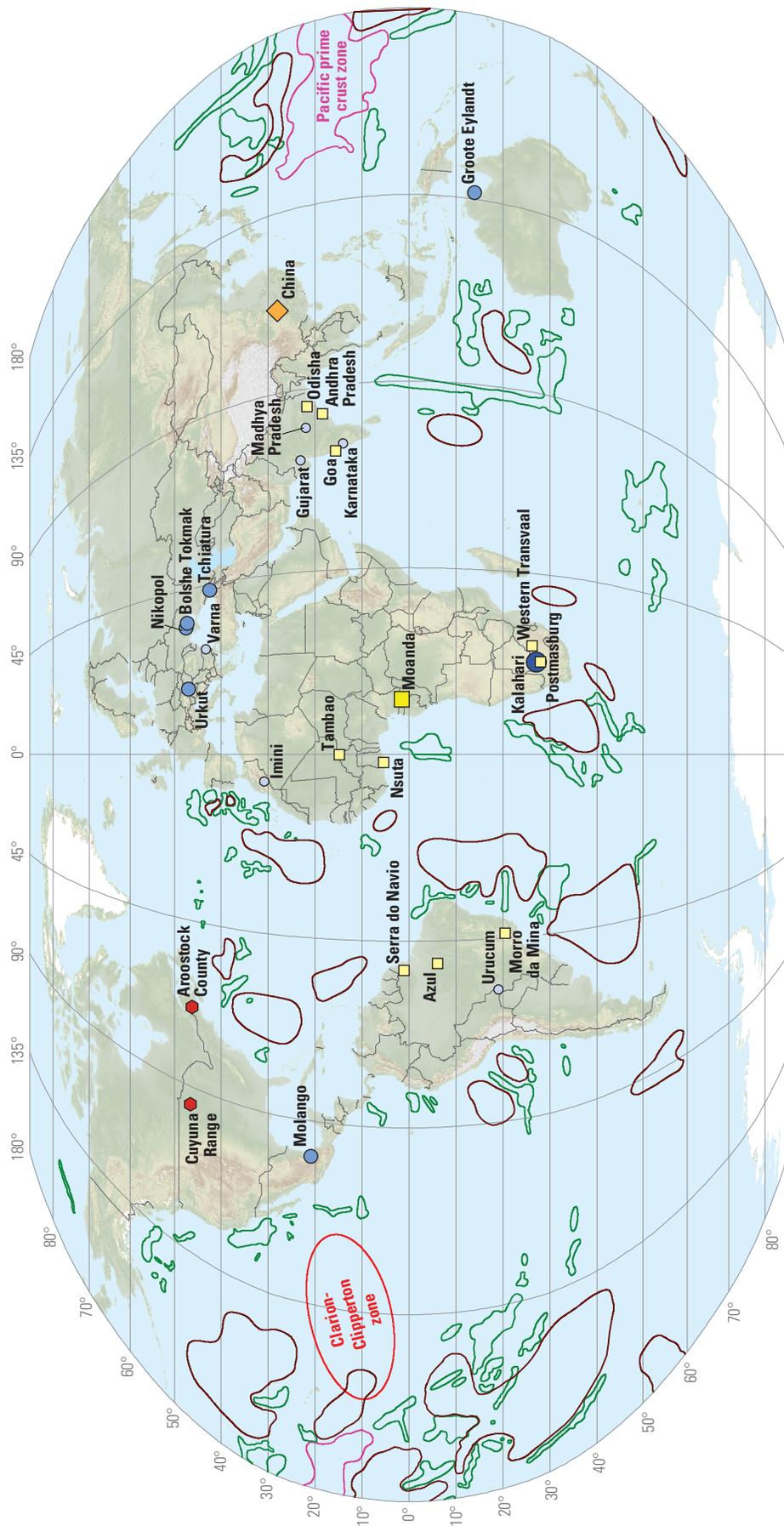
occur as interlayers in a banded iron formation. The essential difference between the two is the degree of oxygen depletion in ocean waters that varies from anoxic or suboxic (in which the solubility of both manganese and iron are enhanced—for instance, the Kalahari manganese district in South Africa), to euxinic and sulfidic (in which manganese solubility is enhanced but iron solubility is depressed—for instance, Groote Eylandt in Australia).

Manganese Deposits Without Iron Enrichments

Many sedimentary manganese deposits of the world occur in sedimentary sequences that are devoid of iron enrichments and that are themselves not enriched in iron compared with the average crustal abundance of manganese. The larger of such deposits include Molango in Mexico, Groote Eylandt in Australia, the deposits of the Black Sea region, and many deposits in China. These relatively low-iron deposits are thought to have formed in shallow marine settings adjacent to stratified oceans that contained a low oxygen deepwater mass, as illustrated in figure L5. In such water masses, dissolved hydrogen sulfide is locally present (euxinic conditions), which causes iron to be precipitated as sulfide minerals in black shale and leaves very low concentrations of dissolved iron in the seawater. Because there is no comparable manganese sulfide phase under these conditions, dissolved manganese concentrations (Mn^{2+}) remain high (Cannon and Force, 1983; Force and Cannon, 1988). This type of ocean water is a reservoir from which manganese deposits can be formed by precipitation of the dissolved manganese caused by the mixing of the manganese-rich deep ocean water with the more oxidized surface waters. Because of the increased Eh conditions, the water becomes saturated in dissolved manganese, and manganese-rich sediments can be precipitated.

These conditions occur most often in nearshore shallow water on continental shelves (fig. L5). Consequently, manganese beds are interlayered with other sediments typical of those settings. The character of these types of manganese deposits is quite variable, depending on local conditions at the eventual deposition sites. For instance, the variety in the types of manganese ores described for the Groote Eylandt deposit are related to local variations in the seabed topography and distance from the coastline (Frakes and Bolton, 1992).

A modern analog for the creation of manganese deposits without iron enrichment is the Black Sea (Cannon and Force, 1983; Force and Cannon, 1988). Deep euxinic waters of the Black Sea contain concentrations of manganese greater than 300 micrograms per liter ($\mu g/L$), whereas oxidized surface water contains less than 1 $\mu g/L$. The concentration of iron in the euxinic water is less than 5 $\mu g/L$ (Maynard, 2010). Thus, these deep waters are poised to precipitate manganese-rich sediments devoid of iron enrichments when oxidized. Circulation of water in the Black Sea produces upwelling of deep waters onto a shallower shelf to the north where manganese-rich sediments are being precipitated on the present seabed.



Base from U.S. Geological Survey Global 30 arc-second elevation data (1996) and from Natural Earth (2014); Robinson projection; World Geodetic System 1984 datum

EXPLANATION

Seabed deposits		Land-based deposits	
	Permissive areas for ferromanganese nodules		Large subeconomic deposits in the United States
	Permissive areas for ferromanganese crusts		Many small to moderate size sedimentary deposits—Total resource not quantified
	Clarton-Clipperton zone		Secondary enrichment, in thousand metric tons
	Pacific prime crust zone		<100,000
			100,000 to 10,000,000
			>10,000,000

Figure L3. World map showing the location, relative size, and type of the major terrestrial manganese deposits listed in table L2 as well as subeconomic deposits in the United States. Deposits in China have been grouped together. Areas of greatest potential for seabed mining of ferromanganese nodules and crusts are shown by colored outlines. Seabed data are from Hein and others (2013).



Figure L4. Photographs showing examples of contrasting types of manganese ore. *A*, Thinly layered ore from Molango, Mexico. The manganese mineral is rhodochrosite, which is a manganese carbonate. The delicate laminations are the result of deposition in relatively deep, quiet seawater below the zone of surface wave agitation. *B*, Pisolitic ore from Groote Eylandt, Australia. The approximately spherical masses (pisolites) are mostly pyrolusite, which is a manganese oxide. The spheres were likely formed in shallow water by progressive growth of new outer layers as the masses were rolled on the seabed by wave agitation. Photographs by William F. Cannon, U.S. Geological Survey.

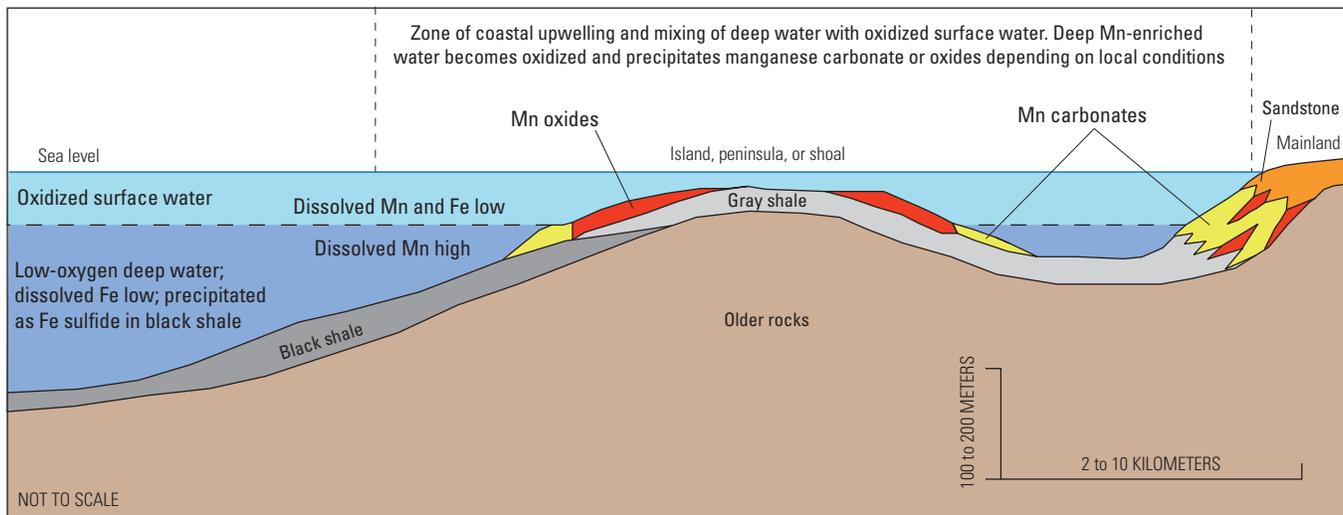


Figure L5. Schematic diagram of the oceanic conditions necessary to form sedimentary manganese deposits that are not enriched in iron. Deep seawater that is very depleted in oxygen and hydrogen sulfide reacts with iron and precipitates iron sulfides, which results in low concentrations of dissolved iron, whereas the dissolved manganese is enriched. Upwelling and mixing of this deep water with oxidized surface water causes precipitation of manganese oxide and carbonate minerals, depending on the local conditions. Diagram is modified from Cannon and Force (1983). In a variant of this model, deep water that is more oxidized and does not contain hydrogen sulfide results in high concentrations of both dissolved manganese and iron and in the precipitation of ferruginous manganese. Fe, iron; Mn, manganese

Iron-Related Manganiferous Sedimentary Deposits

Many occurrences of manganiferous sedimentary deposits occur interlayered with iron-rich strata, commonly in banded iron formations that are found widely in Precambrian sequences in many parts of the world. These include the vast manganese deposits of the Kalahari district in South Africa and the Urucum mining district in Brazil, and many deposits in India. There is voluminous literature on the Kalahari manganese deposits. Relatively recent summaries and the references therein contain the essential facts and interpretations of the occurrence and origin of these remarkable deposits (Tsikos and Moore, 1997; Tsikos and others, 2003). In the Kalahari, three manganese layers are within the banded iron formation known as the Hotazel iron formation. The lower of the three is the principal source of ore and varies from 15 to 45 meters (m) thick. The hallmark of such deposits is the interlayering of iron- and manganese-rich layers, which indicate that the deposit formed from an ocean in which both iron and manganese were enriched, but that the two metals were differentiated from each other at the site of deposition, perhaps by subtle changes in the oxidation state or acidity of the ocean water. In the Kalahari, for instance, the manganese layers have iron contents that are near the average crustal abundance but are enriched in manganese from 200 to nearly 400 times the average crustal abundance (Beukes and Gutzmer, 1996). The iron-rich layers, on the other hand, are enriched above the average crustal abundance by as much as fivefold in iron and from twofold to twentyfold in manganese.

The mutual enrichment of both iron and manganese, although in varying proportions between iron and manganese layers, seems inconsistent with the sulfidic ocean model in which manganese is enriched to the near exclusion of iron. Rather, a stratified ocean in which deeper waters are suboxic to anoxic, but not sulfidic, is more consistent with the origin of these deposits. In anoxic water, the solubility of both manganese and iron is enhanced, and such waters are capable of delivering those metals to sites of deposition by such processes as coastal upwelling onto continental margins, which is the mode of deposition favored by nearly all recent interpretations of these deposits. In the Kalahari, although the primary sedimentary accumulations of manganese are, in part, ore-grade material, secondary enrichment by later hydrothermal processes has increased manganese grades in some areas to form especially desirable ores (Tsikos and others, 2003).

The Urucum deposit in Brazil may have a somewhat different origin. The manganese beds are interlayered with hematitic jasper, similar to the Kalahari and other deposits, but the enclosing rocks bear strong evidence of glacial conditions when this deposit formed. Floating glacial ice or a persistent ice pack has been proposed, which cut off the atmospheric oxygen supply to the ocean water. The decay of organic matter consumed available oxygen and resulted in the anoxic conditions, which, in turn, allowed high solubility of manganese and iron that resulted in the formation of banded iron and

manganese deposits (Urban and others, 1992). Manganese grades range from about 27 to 45 percent, and associated iron ranges from 13 to 30 percent, which indicates that both iron and manganese were enriched in seawater during manganese deposition.

Secondary Enrichment (Supergene) Deposits

Many of the currently mined manganese ores have been enriched in manganese by processes at the present land surface, although they commonly formed in rocks that were already manganese rich. These secondary enrichment types of deposits, or supergene deposits, form where chemical reactions taking place within tens of meters of the surface redistribute manganese at a local scale and also leach out nonmanganese components, which results in residual enrichment of the manganese. Details of many of these deposits and their origin are presented in Varentsov (1996). Significant occurrences of these types of deposits are the Moanda deposit in Gabon, the Azul and the Serra do Navio deposits in Brazil, and numerous deposits in India. By their nature, the resources of these deposits are smaller than are those of the major sedimentary-type deposits, but the deposits are still substantial in terms of both their resources and current production. These deposits include some of the highest grade ores presently being mined. The process of supergene manganese enrichment is described in general terms by Lelong and others (1976), and details of the supergene enrichment at the Moanda deposit, which is the largest known deposit of this type, is outlined by Nahon and Parc (1990).

Supergene deposits are most abundant and commonly of the highest grade in tropical regions where humid conditions and abundant vegetation are key factors in forming deep tropical soils. Supergene manganese ores can be thought of as a specialized product of such tropical soil formation. The generation of humic acids by decomposition of abundant organic matter results in the dissolution of manganese-bearing minerals and transportation of manganese downward in the soil profile. It is then reprecipitated where soil water encounters less acidic conditions. The same acidic soil solutions dissolve and remove other components as well, resulting in a residual enrichment of manganese minerals. Supergene manganese deposits tend to have developed most frequently in areas of low topographic relief, commonly on plateaus, where slow erosion allows time for these ore-forming processes to take place.

Seabed Deposits

The world's ocean floors include tens of millions of square kilometers (km²) covered with manganese-rich deposits of ferromanganese nodules and crusts. No manganese or other metals have been produced from any of these deposits in spite of several decades of research and exploration. Numerous exploration and development programs are underway that could bring part of this vast resource online in the near future.

If this possibility materializes, seabed deposits could have a significant effect on the global production and supply of manganese and lead to a diversification of supply and a reduction in U.S. import reliance for manganese. The areas of greatest interest and potential for mining of seabed deposits are shown in figure L3.

Ferromanganese Nodules

The widespread occurrence of seabed nodules composed mostly of manganese and iron oxide and hydroxide minerals has been known since the research expedition of the H.M.S. *Challenger* in the 1870s; these nodules have come to be referred to as ferromanganese nodules. The locations of these nodules are shown in figure L3. In the area of prime economic interest in the Pacific Ocean, nodules range in size from 1 to 12 centimeters (cm) and median dimensions are 8 cm, 6 cm, and 4 cm for the maximum, intermediate, and minimum dimensions, respectively (fig. L6; Morgan, 2000). The abundance of nodules within known nodule fields ranges from sparse to a nearly continuous blanket covering the seabed. These nodules also contain substantial amounts of other valuable metals, such as nickel, copper, and cobalt, and potentially valuable concentrations of rare-earth elements (REEs). The amount of manganese in known nodule fields dwarfs that

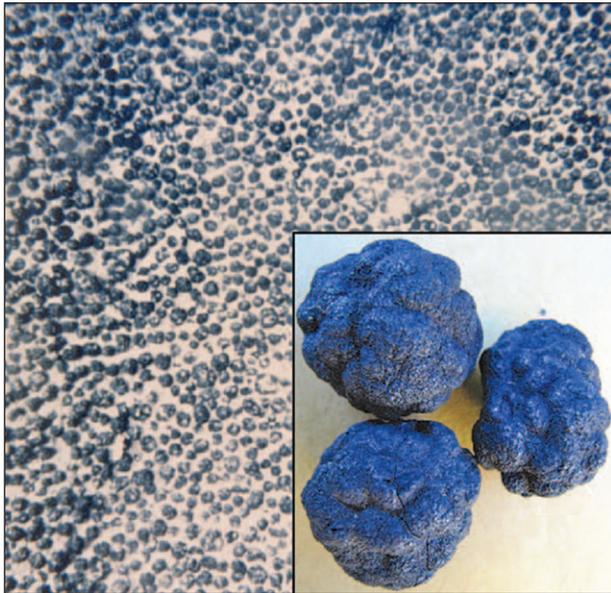


Figure L6. Photograph showing a dense carpet of ferromanganese nodules on the seabed off Johnston Island within the United States Exclusive Economic Zone near Hawaii. The field of view is about 4 meters square. The inset shows individual nodules, each of which is about 3 centimeters in diameter, from the equatorial Pacific Ocean. Photographs by James Hein, U.S. Geological Survey.

found in traditional continental deposits, but its availability as a source of ore is uncertain in the near term. Considerable technological issues of mining at abyssal depths in the oceans, the economic competitiveness of seabed mining versus traditional mining, and legal issues of ownership and control of resources in international waters are still being addressed.

Recent summaries of the origin, distribution, and potential value of manganese nodules are provided by Hein (2012), and the International Seabed Authority (ISA) (2010), both of which form the basis of the following discussion. Manganese nodules occur widely in global oceans and their distribution has commonly been mapped, for both scientific and potential commercial purposes. Vast areas of ocean floor contain blankets of nodules in varying abundance at the sediment surface, and an equal amount of nodules is believed to be buried within the uppermost meter or two of underlying sediment. Nodule fields range in depth below the ocean surface of from 3,500 to 6,500 m. The nodule fields of the greatest current commercial interest are those located in the northern equatorial Pacific Ocean and the central Indian Ocean.

Ferromanganese nodules are geologically young features and many continue to grow today. They form on the seabed at the sediment-water interface, mostly by precipitation of metals that are mobilized by redox reactions in the underlying sediments. An expert panel convened by the ISA (an organization established by the 1982 United Nations Convention on the Law of the Sea) developed a biogeochemical model for nodule formation in the northern equatorial Pacific Ocean, generally referred to as the Clarion-Clipperton zone (CCZ), and subsequently used the model to make resource estimates. According to the ISA model, the principal source of copper, manganese, and nickel is believed to be continental runoff from North America; volcanogenic sources from the East Pacific rise, including submarine hydrothermal vents; and atmospheric dust. The metals from continental sources occur in dissolved form and are also adsorbed onto fine-grained sediment particles that are carried westward by the North Pacific current. Some metals can be delivered to the sea floor through slow settling of these particles, but biological activity is also an essential part of the deposition. In the near-surface photic zone, metals are scavenged by planktonic organisms and can then be delivered to the sea floor by settling of those organisms after their death and also by incorporating metals into fecal pellets, which likewise settle to the sea floor. Thus, areas of highest metal enrichment on the sea floor correspond to areas of high surface biological productivity, such as the CCZ.

Once deposited in sea-floor sediments, metals are available to be metabolized by benthic organisms and mobilized into dissolved form by reducing reactions within the upper meter of sediments. Metal-rich pore waters so produced are the source fluids for most components of nodules. Metals dissolved

in seawater may add additional components. As pore waters migrate to the sediment surface, they reenter oxidizing conditions where manganese is precipitated as oxide and hydroxide minerals that effectively scavenge other metals, such as nickel and copper. The precipitated minerals commonly nucleate around small solid particles and sequentially add growth layers to form the present nodules.

Ferromanganese Crusts

Ferromanganese crusts are layers of manganese and iron oxides and hydroxides, ranging from a thin veneer to 260 millimeters (mm) thick, that have precipitated on hard rock substrates on the seabed. The geology and resource status of ferromanganese crusts are outlined by Hein and others (2009, 2010, 2013). The principal commercial interest in ferromanganese crusts has been their concentrations of cobalt (0.3 to 0.67 percent) and nickel (0.23 to 0.46 percent). Elevated concentrations of REEs might also add to their potential economic value. Manganese grades range from

20 to 25 percent in Pacific Ocean and Indian Ocean crusts and are somewhat lower elsewhere. A detailed summary of the chemical composition of ferromanganese crusts from the world's oceans was compiled by Manheim and Lane-Bostwick (1988) and provides much more detail than this chapter. The locations of these crusts are shown in figure L3, and an example of such crustal material is shown in figure L7.

Ferromanganese crusts are less extensive than nodule fields and are restricted to seabed topographic highs, such as volcanic edifices, seamounts, and ridges. Crusts are found at depths of 400 to 7,000 m; the thickest and most metal-rich crusts are found at depths of between 800 and 2,500 m. Ferromanganese crusts form in areas that were kept sediment-free for millions of years, principally by bottom currents with sufficient velocity to sweep the seabed free of sediment accumulations. Crusts grow extremely slowly by precipitating manganese and other elements that occur in low concentrations in seawater. It is this very slow growth that allows the ferromanganese minerals to scavenge economically interesting concentrations of metals.



Figure L7. Photograph showing ferromanganese crust (black material above) on carbonate rock from the Blake Plateau off the southeastern coast of the United States. The surface below the black material was the seabed on which the manganese minerals were precipitated. Photograph by William F. Cannon, U.S. Geological Survey.

Resources and Production

Manganese resources are very large relative to current and anticipated demand on a global scale, but they are unevenly distributed. Many industrialized countries, including the United States, are largely or wholly reliant on imports for their manganese supply. The United States has relatively large tonnages of resources in several districts, but the larger deposits are low grade and well below economic viability in current economic and technological scenarios.

The nature of manganese deposits presents problems for precise quantitative resource estimates. Many deposits occur as laterally extensive manganese-rich layers that do not have sharp lateral boundaries, but rather, grade gradually from higher to lower grades, in some cases over long distances. Very different resource estimates can be made for the same deposit based on what criteria are used for acceptable manganese content to be classed as a resource, as well as assumptions of how grades change in poorly explored areas. Additional variability in published resource values is introduced by a variety of resource classification schemes and definitions of resource categories used by various Governments around the world. There is no simple way to convert resource estimates between such diverse classifications into a uniform resource compilation. Global resources of manganese were estimated by the USGS and published in 1973 (Dorr and others, 1973). A more-detailed study was conducted by a panel of industry, Government, and academic experts through the U.S. National Materials Advisory Board (1981). The following year, a summary of global manganese resources was conducted through the International Strategic Minerals Inventory (ISMI), a cooperative effort of Federal geological and resource agencies from the United States, Australia, Canada, the Germany, South Africa, and the United Kingdom (DeYoung and others, 1984). Estimated resources by country and district differ substantially between the two older reports, in large part because of somewhat different definitions of resource and reserve categories used in them, as well as the criteria used to calculate resource figures. The ISMI study produced consensus estimates based both on older reports and resource values compiled by the participating Government agencies. For this summary, we have not revised older resource estimates although we recognize that depletion of resources through continued mining and addition to resources through continued exploration has modified older resource estimates to some degree. The discussion below is based on the ISMI resource values, although the same general picture of global resources could be formed from any of the three cited studies.

Manganese Reserves

The United States possesses no reserves of manganese ore containing 35 percent or more manganese or from which concentrates of such grade could be commercially produced.

As a result, manganese ore is not mined in the United States, with the exception of ultra-low-grade manganese schists that contain less than 5 percent manganese at two mines in South Carolina—the Grover and the Martin Mines. Manganese recovered from these mines is used as a brick colorant. The estimated manganese content of world manganese ore reserves in 2012 totaled 630 million metric tons (table L1). The countries with the most manganese ore reserves are, in descending order of reserves, South Africa, Ukraine, and Brazil.

Other Identified Resources

Manganese resources can be divided into (a) land-based deposits and districts, which are the traditional sources of manganese ore, and (b) seabed resources, which are deposits on the ocean floor that have been identified and characterized to varying degrees of detail. Seabed resources are enormous and dwarf traditional resources, but their technological and economic availability is unproven.

Land-Based Resources

The locations of identified manganese resources in conventional land-based deposits and mining districts are shown in figure L3. Some details of the resource amounts are in table L2.

Total global identified resources are in excess of 17 billion metric tons of manganiferous material. Global resources are dominated by the Kalahari manganese district of South Africa, which contains more than 70 percent of global resources (fig. L3). Kalahari ores are among the highest grade, typically about 40 percent manganese, and are widely used in industrial processes in many parts of the world. The Kalahari district clearly has the potential to provide international markets with high-quality manganese ore for a very long time. One of the larger mines in the Kalahari district, the Mamatwan Mine, is shown in figure L8. The second-ranked district in terms of total resources is the Molango district in Mexico, which has about 9 percent of the world's total resources. The resource consists of an extensive layer of manganese carbonate, with grades of approximately 28 percent manganese. Although this resource is large, economic extraction is impaired by the steep mountainous terrain of the district, which requires that most, or all, of the mining be conducted from underground operations rather than more efficient surface mines. The carbonate character of the ore also is a detriment in that it requires an additional processing step to convert the carbonate minerals to manganese oxide. Molango is an important source of manganese in Mexico, but its future significance in global manganese supply is uncertain. The third largest resource is in the Bolshe Tokmak mining district in Ukraine, which constitutes about 6 percent of global resources. The Bolshe Tokmak ore is low grade by global standards, averaging about

Table L2. Identified resources estimated for major land-based manganese deposits of the world.

[Data are from DeYoung and others (1984). WGS 84, World Geodetic System of 1984; negative values for latitude indicate that the deposit is in the Southern Hemisphere; negative values for longitude indicate that the deposit is in the Western Hemisphere. Deposits are shown on the map in figure L3. Resource values are the sum of all manganese resource categories. —, not applicable]

Country	Deposit (fig. L3)	Latitude	Longitude	Type	Resource (thousand metric tons)
		Decimal degrees WGS 84			
Australia	Groote Eylandt	-14.00	136.50	Marine sedimentary	436,000
Brazil	Azul	-6.13	-50.35	Secondary enrichment	65,000
Brazil	Morro da Mina	-20.58	-43.83	Secondary enrichment	4,500
Brazil	Serra do Navio	1.00	-52.00	Secondary enrichment	21,000
Brazil	Urucum	-19.13	-57.55	Marine sedimentary	59,000
Bulgaria	Varna	43.22	27.92	Marine sedimentary	28,000
Burkina Faso	Tambao	14.78	-0.07	Secondary enrichment	17,000
China	Hsiang-tan	27.83	112.92	Marine sedimentary	>10,000
China	Leiping	23.33	109.50	Marine sedimentary	>10,000
China	Tsun-i	27.50	106.50	Marine sedimentary	>10,000
China	Wafangtzu	39.58	122.00	Marine sedimentary	4,000
Gabon	Moanda	1.57	13.28	Secondary enrichment	220,000
Georgia	Tchiatura	42.32	43.30	Marine sedimentary	155,000
Ghana	Nsuta	5.28	-1.95	Secondary enrichment	20,000
Hungary	Urkut	47.08	17.67	Marine sedimentary	215,000
India	Andhra Pradesh	18.37	83.45	Secondary enrichment	1,700
India	Goa	15.50	73.92	Secondary enrichment	8,550
India	Gujarat	23.00	72.50	Marine sedimentary	2,900
India	Karnataka	13.93	75.52	Marine sedimentary	15,000
India	Madhya Pradesh	21.83	80.30	Marine sedimentary	49,000
India	Odisha	21.63	85.67	Secondary enrichment	43,600
Mexico	Molango	20.83	98.73	Marine sedimentary	1,526,000
Morocco	Imini	30.73	6.90	Marine sedimentary	1,500
South Africa	Kalahari	-27.18	22.95	Marine sedimentary	12,565,800
South Africa	Postmasburg	-28.05	23.05	Secondary enrichment	15,000
South Africa	Western Transvaal	-26.25	27.02	Secondary enrichment	15,000
Ukraine	Bolshe Tokmak	47.25	35.70	Marine sedimentary	1,100,000
Ukraine	Nikopol	47.57	34.42	Marine sedimentary	655,000
World total	—	—	—	—	>17,273,000



Figure L8. Photograph of the Mamatwan open pit mine in South Africa. The black manganese layer is about 45 meters thick and consists of a 20-meter-thick ore bed and two lower grade subeconomic beds. The slightly folded layering is shown by the shapes of the various mine benches. Lighter material in the background is waste that must be stripped to expose the ore bed; this waste material is used as backfill in mined areas (foreground). Photograph by William F. Cannon, U.S. Geological Survey.

18 percent manganese. The mines at Bolshe Tokmak were significant sources of manganese to the Soviet Union, but their importance in market economies is impaired by their low grade. The Obrochishte deposit in the Varna district in Bulgaria, the Nikopol mining district in Ukraine, and the Tchiatura (also known as Chiat'ura) district in Georgia are similar to the Bolshe Tokmak district and together constitute an additional large but low-grade resource. All the deposits in these districts are of the marine sedimentary type.

A compilation of tonnage and grade for sedimentary-type deposits (Mosier, 1986) shows that their median tonnage is 7.3 million metric tons and that the largest 10 percent of the deposits (made up of three deposits) have a median tonnage of greater than 280 million metric tons (fig. L9A). The median grade is 31 percent Mn and the grade of the richest 10 percent of deposits is greater than 49 percent Mn (fig. L9B).

Although they constitute a relatively small percentage of total global manganese resources, other types of deposits are also important sources of high-grade manganese ore to the United States and other countries. An example is Moanda in Gabon, which was formed from secondary enrichment.

China has become a major manganese ore producer in recent decades. In 2011, it was the second-ranked producer in the world in terms of gross weight of ore and the third-ranked producer in terms of contained manganese. China's reserves are also large, consisting of about 44 million metric tons of

manganese ore distributed over many deposits, according to figures compiled by the USGS (Corathers, 2013b). Most Chinese deposits consist of sedimentary accumulations of manganese carbonate that average about 20 percent contained manganese and thus are of relatively low grade compared with many other deposits globally. Most ores are upgraded, many by magnetic separation of manganese-rich material from waste material, before use in manufacturing (International Manganese Institute, 2012). The total manganese resource in China is poorly known. The ISMI summary prepared by DeYoung and others (1984) lists China's proven resource at greater than 34 million metric tons, but the total resource, although not quantified, is likely much larger.

Seabed Resources

A vast resource of manganese lies on the seabed, mostly in international waters and at great depths. A strong interest in exploitation of these deposits in the late 1970s and early 1980s, with hopes of developing mines by the late 1980s, vanished in a morass of technological, economic (low metal prices), and legal issues. More recently, with the establishment of a legal framework for exploring and mining in international waters, and a rebound in metal prices, a strong interest in exploiting these deposits has reemerged. Nevertheless, the technological and economic viability of doing so had yet

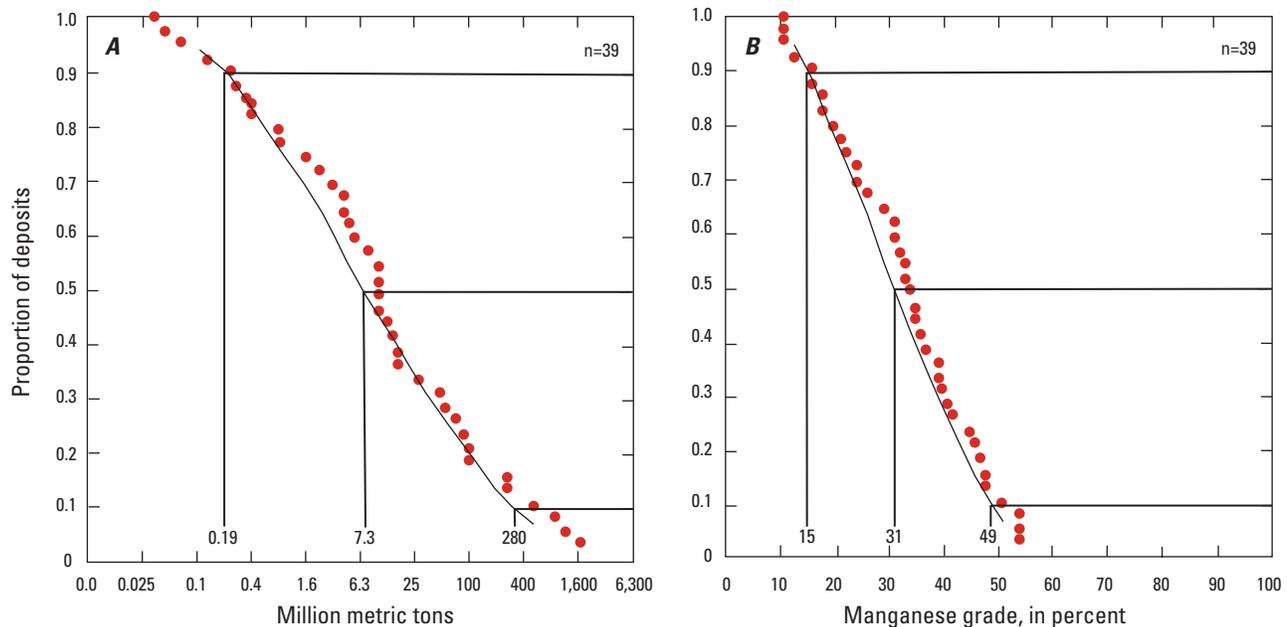


Figure L9. Graphs showing the cumulative frequency of tonnages and grades of 39 marine sedimentary manganese deposits. *A*, The median tonnage of the deposits is 7.3 million metric tons, and the largest 10 percent of the deposits has a tonnage of greater than 280 million metric tons. *B*, The median grade is 31 percent manganese, and the richest 10 percent of the deposits has a grade of greater than 49 percent manganese (Mosier, 1986).

to be proven in 2013. Importantly, the economic interest in ferromanganese nodules is driven by such metals as, in order of economic importance, nickel, copper, and cobalt, rather than by manganese. Manganese would, at best, be a byproduct of seabed mining, and perhaps not a metal that would be economically recovered at all in some scenarios. Consequently, the availability of manganese from seabed deposits will be closely tied to the demand for those other metals. Two types of deposits of current interest—ferromanganese nodules and ferromanganese crusts—are similar in that they are composed largely of manganese and iron oxides and hydroxides, but they differ substantially in their mode of origin, chemical composition, location on the seabed, and economic potential. They are discussed separately below.

Ferromanganese Nodules

The possible commercial recovery of ferromanganese nodules, which were of little economic interest for several decades after initial investigations and conditions showed them unfavorable, has received significantly increased activity in recent years because of higher metal prices and the establishment of a legal framework for exploiting resources on the international seabed through the ISA. By 2013, 13 organizations or Governments had signed contracts with the ISA to explore and potentially mine ferromanganese nodules, mostly in the CCZ. One of the companies that signed a contract with the ISA is a U.S. company, Lockheed Martin Corp., through its British subsidiary Lockheed Martin UK, which is evaluating the feasibility of nodule mining in two areas within the CCZ (Schrope, 2013).

The ISA assessed mineral resources within the CCZ using a biogeochemical model for nodule formation and several statistical methods (International Seabed Authority, 2010, 2012). The various methods produced somewhat different results that ranged from 20 to 30 billion metric tons of nodules containing from 6 to 8.7 billion metric tons of manganese at a median grade of about 30 percent manganese. The resource covers an area of seabed of roughly 4 million km². The central Indian Ocean, which is a 150,000-km² area in which exclusive exploration rights are held by India, is estimated to contain a nodule resource of 700 million metric tons containing 20 to 30 percent manganese (Banakar, 2010). No comparable estimates have been done for other nodule fields, but it is reasonable to assume that their combined resource would be several times that of the CCZ and the central Indian Ocean.

As previously mentioned, an important factor in the potential of ferromanganese nodules as a manganese source is that most economic interest in nodules is driven by metals other than manganese, including cobalt, copper, nickel, possibly REEs, and other metals needed for high-technology applications. (See discussion in Hein and others [2013].) Without the value provided by the presence of these metals,

it is unlikely that nodules would be an economically viable source of manganese based solely on their contained manganese value. It is not clear to what extent future seabed mining and processing would recover manganese rather than dispose of it as a component of limited economic value if manganese prices remain relatively low. In any case, the processing of manganese nodules would at least result in an inventory of manganese-rich material at processing facilities that could be accessed when economically or strategically appropriate.

Ferromanganese Crusts

The area of greatest interest for ferromanganese crusts in the north Pacific was outlined by Hein and others (2009) and is referred to as the Pacific prime crust zone (fig. L3). This large area contains 155 volcanic features that could host a ferromanganese crust resource. In 2013, three nations (China, Japan, and Russia) had contracts with the ISA to explore tracts totaling 9,000 km². A model based on geologic parameters (and not on economic considerations) predicted that about eighteen 100-km² blocks of seabed might be included in an initial mining program under the auspices of the ISA (Hein and others, 2009).

An additional area in the northeast Atlantic Ocean that lies partly within the Portuguese Exclusive Economic Zone (EEZ) has been described by Muiños and others (2013). Crusts with resources of cobalt, copper, nickel, and other trace elements that may be comparable to those in the central Pacific region have been identified on 10 seamounts. The crusts average about 15 percent manganese, so manganese would be a byproduct, at best, of mining of these deposits.

Many other areas with potential for ferromanganese crusts are known and many lie within the EEZs of various nations rather than in international waters (fig. L3). Areas within the United States EEZ lie off both the Atlantic and Pacific Coasts. The area of greatest previous economic interest is the Blake Plateau off the southeastern coast of the United States. Geologic knowledge of this area is summarized by Manheim and others (1982). Median manganese grades are about 20 percent. Median cobalt and nickel grades are roughly 0.5 percent and 0.4 percent, respectively. An estimate of the total tonnage of crusts in the area has not been made.

The future of mining of seabed ferromanganese crusts is more uncertain than for nodules. Whereas nodules are discrete masses lying unattached to the seabed, ready for the taking, crusts are firmly attached to bedrock substrate. Successful mining requires development of methods and equipment that can effectively break crusts free from their substrate with minimal incorporation of substrate into the recovered material to minimize dilution. As with nodules, the metals of principal economic interest do not include manganese, but, rather, are cobalt and nickel. Thus, future production of crusts will be driven by consumption needs and prices for those metals rather than by demand for manganese.

Resources in the United States

Land-Based Resources

Manganese ore was last produced in the United States in 1973. Significant past production has been limited to times of war or Government subsidies and purchases for strategic stockpiles. Several deposits and districts in the United States have traditionally been included in identified resources, although all are well below manganese grades of material readily available on international markets. All would require substantial beneficiation to make usable manganese products or discovery of higher grade zones within them, which would likely be small relative to national consumption. Table L3 lists these domestic resources and some of their characteristics based on a manganese availability study conducted by the U.S. Bureau of Mines (Kilgore and Thomas, 1982). In that study, economic and technological parameters were applied to each deposit, and cost estimates were made for producing a usable manganese product. All deposits were shown to be far short of economic viability. Of these identified resources, those of Aroostook County, Maine (Maple Mountain-Hovey Mountain area and North Aroostook district) and the Cuyuna Range in Minnesota (fig. L3) are the only two that are of sufficient tonnage to be significant on a national scale of manganese demand. Others may be capable of providing some smaller amount of manganese or specialized manganese products, but the discussion below is limited to these two largest resources.

Aroostook County, Maine

The manganese deposits of Aroostook County lie in a discontinuous north-south belt about 50 kilometers (km) long. The bulk of the manganese resource lies in the middle part of this belt in the Maple Mountain-Hovey Mountain area. These

deposits and their geologic setting were comprehensively studied in the early 1960s (Pavlidis, 1962). The manganese-rich rocks occur in three beds of Silurian age and are of two lithologic types: (a) hematitic shale and slate and hematitic ironstone, and (b) siliceous carbonate rocks. These iron-rich layers contain manganese in both braunite and rhodochrosite. Manganese grade varies between beds and ranges from 7 to 11 percent. Iron grades range from 13 to 24 percent in the same beds. The grades are relatively uniform within individual beds. Individual manganese beds are as much as about 20 m thick. The deposits, although now folded and recrystallized, formed as discontinuous marine sedimentary layers in shallow, nearshore settings. The bulk of the resource as estimated by Pavlidis (1962) is the hematitic variety that contains about 300 million metric tons of material averaging 7 percent manganese and 17 percent iron. The carbonate variety is much smaller and contains only 3 million metric tons of material. These figures were revised downward by a more recent study (Kilgore and Thomas, 1982), and are shown in table L3. Deposits farther north in the North Aroostook district are similar to those of the Maple Mountain-Hovey Mountain area but are significantly smaller. Together, those northern deposits contain an additional 60 million metric tons.

Although the deposits in Aroostook County contain sufficient manganese to satisfy U.S. consumption for several decades, the production of a manganese product that would be viable in current markets would require substantial beneficiation of these low-grade resources. An economic analysis of the cost of mining, beneficiation, and transport showed that these deposits are far from being economically viable (Kilgore and Thomas, 1982). Although that analysis was done 30 years ago, more recent developments have not substantially increased the economic value of these deposits. Thus, they remain a relatively large but subeconomic resource that can

Table L3. Grade, tonnage, and quantity of contained manganese for eight manganese deposits and districts in the United States.

[Data are as reported in Kilgore and Thomas (1982). Numbers for contained manganese (Mn) have been rounded to three significant figures. %, percent; —, not applicable]

Deposit/district	State	Grade (% Mn)	Resource (metric tons)	Contained Mn (thousand metric tons)
Hardshell Mine	Arizona	15.0	5,895,500	884
Maggie Mine	Arizona	8.75	8,441,000	739
Sunnyside Mine	Colorado	10.0	24,909,000	2,490
Maple Mountain-Hovey Mountain	Maine	8.87	260,000,000	23,100
North Aroostook district	Maine	9.54	63,100,000	6,110
Cuyuna Range (southwest portion)	Minnesota	7.84	48,960,000	3,840
Butte district (Emma Mine)	Montana	18.0	1,232,000	222
Three Kids Mine	Nevada	13.2	7,230,000	954
Total	—	—	419,767,500	38,300

become a significant manganese supplier for the United States only with major advancements in processing and beneficiation technology or long-term disruption of international manganese trade.

Cuyuna Range, Minnesota

The Cuyuna Range is one of several iron ranges of the Lake Superior region that have supplied a large proportion of the iron needed to meet U.S. iron consumption. The deposits include Precambrian banded iron formations and secondary iron concentrations within them. The Cuyuna Range, which is now inactive as an iron producer, is distinct from other ranges in its relatively high content of manganese. The range produced substantial quantities of manganiferous iron ores, as distinct from manganese ore, for more than 70 years. Production ceased in 1984, at which time more than 100 million metric tons of ore had been produced, largely from open pit operations. The produced ores averaged between 13 percent and 14 percent manganese. A relatively recent summary of the geology and manganese resources of the range was provided by Morey (1990) from which most of the following summary is extracted.

The Cuyuna Range ores are supergene concentrations of iron and manganese that formed in Precambrian strata that are themselves enriched in both iron and manganese. The original strata contain 20 to 35 percent iron and from less than 1 percent to 16 percent manganese. The supergene enrichments that constitute the manganiferous iron ores range from 30 to 40 percent iron and 5 to 15 percent manganese. Several estimates of manganese resources have been made and summarized by Morey (1990). An estimate of measured resources at 39 existing (abandoned) mines is 5.5 million metric tons that average about 11.7 percent manganese (Beltrame and others, 1981). A much larger tonnage of manganiferous material has been estimated within the ferruginous strata of the district. A resource of 80 million metric tons averaging about 10.5 percent manganese and within 120 m of the surface was estimated by Beltrame and others (1981). The same authors estimated that an additional inferred resource of 90 million metric tons within 120 m of the surface exists within less well characterized parts of the district. In 1982, a summary of U.S. resources (Kilgore and Thomas, 1982) estimated a resource of about 49 million metric tons with a grade of 7.84 percent manganese. These are included in table L3.

The production of a commercial manganese product from Cuyuna Range manganiferous iron ores requires either physical processing and concentration of manganese minerals or hydrometallurgical concentration. Because a great majority of the manganese minerals are fine-grained and intergrown with other minerals, physical separation and beneficiation would be difficult. Some renewed interest in manganese production is indicated by pilot-scale testing of an innovative hydraulic mining method in which high-pressure jets

of water are used to mobilize these physically soft ores into slurry within large-diameter drill holes (Crow Wing Power, 2013). The economic feasibility of this method was still being evaluated in 2013.

Seabed Resources

A large but incompletely characterized and quantified manganese resource lies within the vast area of the United States EEZ. Extensive areas of both ferromanganese crusts and, to a lesser extent, nodules, are known offshore of both the Atlantic Coast and the Pacific Coast of the U.S. mainland, including Alaska, as well as the Hawaiian Islands, and other island possessions. Most economic interest and exploration for seabed deposits has been focused on the prime nodule zone of the CCZ in international water where seabed mining of nodules is most likely to take place first. The United States EEZ, however, holds some promise to provide manganese and related metals in the future if the technology and economics of seabed mining lead to viable mining operations in the areas of current highest interest. Because most deposits within the EEZ are crusts, which are considerably more challenging to mine than nodules, the potential mining of these deposits may lag development of nodule mining operations. So, although the EEZ undoubtedly contains a very large tonnage of manganese resources, it is unlikely to have an effect on domestic and global manganese production and consumption in the short term.

Undiscovered Resources

Marine sedimentary manganese deposits of economic significance are large geologic features. They generally have been found by accidental discovery in surface rock exposures rather than by purposeful exploration or exploration for subsurface deposits. It has been many decades since the last such major discovery in spite of an increasing pace of geologic studies and mineral exploration. Currently, exploration for new deposits is mostly confined to known districts rather than exploration intended to find wholly new districts. With time, the likelihood of new discoveries of major deposits is diminished. That said, there is still some possibility of important new discoveries, especially in light of the rather unremarkable outward appearance of some manganiferous sediments, especially manganese carbonate deposits. In some cases, the manganiferous character of these rocks was realized only after discovery of supergene deposits formed from them.

Supergene deposits offer a greater potential for undiscovered deposits because of their smaller size and propensity to occur in tropical regions with poor bedrock exposure, limited access, and incomplete geologic studies. Exploration focused in suitable areas with known manganiferous sediments is likely to result in new discoveries.

Exploration for New Deposits

There are currently 10 new land-based manganese mines under development in various parts of the world that are scheduled for completion by the end of 2014. The total annual production capacity of new production will be nearly 5.42 million metric tons of ore, more than one-half of which will be from the Kalahari manganese district in South Africa (Corathers, 2013a). These new mines attest to the continued need for manganese exploration throughout the world. Most, if not all, of these new mines are in areas of previously known manganese mineralization and do not represent newly discovered manganese districts.

The exact methods of exploration and discovery are not known for all of these deposits, but likely included surface geologic studies and exploration drilling. In some cases, geophysical methods, particularly electromagnetic surveys, aided in defining targets for drilling.

It is reasonable to assume that, for the near future, land-based exploration will continue to focus on areas where there are known manganese rocks and will be designed to outline areas of sufficiently high grade and tonnage to constitute an economic orebody. More-wide-ranging exploration aimed at discovery of new frontier districts or new manganese sedimentary units may also take place in areas where geologic conditions suggest favorable settings for manganese deposits to have formed. Significant sedimentary manganese deposits cover large areas and are at least partly exposed at the surface. As such, they represent large exploration targets. Remote sensing methods, including satellite imagery, airborne geophysical surveys, and hyperspectral mapping, may be effective exploration tools. Satellite imagery may help identify and refine favorable exploration tracts and outcropping manganese rocks. Airborne geophysical surveys, especially electromagnetic surveys, may be useful in mapping shallowly buried layers rich in manganese because of the electrically conductive nature of manganese oxides. Hyperspectral mapping has the potential to specifically identify manganese oxide minerals because they have a low reflectance signature relative to other common minerals. Once a manganese deposit has been identified by these methods, more-detailed ground surveys are needed to refine the size and grade of deposits to evaluate their economic viability fully. Early stages of such exploration are commonly conducted at least partly confidentially by exploration and mining companies so that the degree to which such exploration might currently be taking place is not well known.

Exploration of the seabed is also active; 13 individual entities were exploring for ferromanganese nodules in 2013. Identification of nodule-rich seabed regions is relatively simple and can be done by remote visual examination to identify areas with the greatest abundance of nodules. Physical sampling of nodules is also required, followed by chemical assays to map the distribution of nodules with the most favorable grades of manganese and other economically important metals, such as cobalt, copper, and nickel. Exploration for

ferromanganese crusts is much less advanced, although in 2013, the ISA received two plans for exploration in the western Pacific Ocean.

Environmental Considerations

Manganese is ubiquitous on Earth's surface. Humans and virtually all other life forms interact with it every day. Manganese is an essential nutrient for most life, including humans, but it can produce a variety of toxic effects at anomalously high concentrations. As such, the potential for manganese mining and processing to produce such elevated concentrations must be addressed throughout the life cycle of manganese production and use. Manganese deposits and the types of operations that mine them are very diverse around the globe. Some examples of possible concerns regarding increased environmental manganese around mines and processing plants are discussed below, along with some general aspects of manganese geochemistry that could make it possible to predict potential environmental and health impacts of manganese mining.

Sources and Fate in the Environment

Examples of natural concentrations of manganese in rocks, soil, water, and air are given in table L4. Manganese contents in soils range from 7 to 9,200 milligrams per kilogram (mg/kg) (or parts per million), with higher manganese concentrations commonly occurring in soils developed from mafic rocks, soils rich in iron and (or) organic matter, and soils developed in arid or semiarid regions (Kabata-Pendias and Mukherjee, 2007). Dissolved manganese concentrations in large rivers around the world range from 0.4 to 113 $\mu\text{g/L}$ (or parts per billion) (Gaillardet and others, 2003, and references therein), whereas the average concentration of manganese in the suspended sediment of world rivers has been reported as 1,679 mg/kg (Viers and others, 2009). Occasionally, dissolved manganese concentrations can be comparable to particulate manganese concentrations. For example, during flood events in Magela Creek in the Northern Territory, Australia, dissolved (<0.02 micrometer [μm]-size) manganese concentrations (0.8 to 9.6 $\mu\text{g/L}$) are similar to particulate (>0.02 μm -size) manganese concentrations (0.3 to 7.9 $\mu\text{g/L}$); the relatively high dissolved manganese concentrations are attributed to the acidic soils, which create favorable conditions for manganese dissolution from minerals (Hart and others, 1992). Manganese occurs naturally in the atmosphere as part of mineral dust particles. Nriagu (1989) estimated manganese emission to the atmosphere from natural sources to be 317 million kilograms per year (Mkg/yr). Air manganese concentrations in remote regions range from 0.004 to 0.02 nanograms per cubic meter (ng/m^3) over the South Pole and from 2.8 to 4.5 ng/m^3 over Greenland (Kabata-Pendias and Pendias, 2001).

Table L4. Background and above-background concentrations of manganese in rocks, soils, waters, and air.

[DOE, U.S. Department of Energy; EPA, U.S. Environmental Protection Agency. Units of measure: cm, centimeter; mg/kg, milligram per kilogram (or part per million); mg/L, milligram per liter; mg/m³, milligram per cubic meter; ng/m³, nanogram per cubic meter; µg/L, microgram per liter; µg/m³, microgram per cubic meter; µm, micrometer]

Environment and (or) location	Manganese concentration	Unit	Notes	Reference(s)
Rocks				
Upper continental crust	600	mg/kg	Average	Taylor and McLennan (1995)
Bulk continental crust	1,400	mg/kg	Average	Taylor and McLennan (1995)
Lower continental crust	1,700	mg/kg	Average	Taylor and McLennan (1995)
Soils				
Western United States	380	mg/kg	Mean for 20 cm depth	Shacklette and Boerngen (1984)
Eastern United States	260	mg/kg	Mean for 20 cm depth	Shacklette and Boerngen (1984)
Central Pennsylvania, United States	900 to 14,400	mg/kg	Surface soil in an undisturbed watershed	Herndon and others (2011)
Central Pennsylvania, United States	340 to 1,300	mg/kg	Surface soil proximal to historic steel manufacturing site	Herndon and others (2011)
Poland	143±5	mg/kg	Agricultural soil; nonpolluted	Poędniok and others (2012)
Poland	658±7	mg/kg	Agricultural soil; nonpolluted	Poędniok and others (2012)
Poland	130±4	mg/kg	Agricultural soil; nonpolluted	Poędniok and others (2012)
Poland	292 to 571	mg/kg	Proximal to mining and industrial sources	Poędniok and others (2012)
Sweden	76 to 206	mg/kg	Range of profile developed on quartzite and gneiss	Tyler (2004)
Proposed DOE benchmark (recommended upper limit in soil)	500	mg/kg	Contaminant screening benchmark for terrestrial plants	Efroymsen and others (1997)
Waters				
Bathurst Harbour, Australia	0.6 to 2	µg/L	Dissolved and colloidal (<0.45 µm); nonpolluted	Mackey and others (1996)
Macquarie Harbour, Australia	1 to 10	µg/L	Dissolved and colloidal (<0.45 µm); polluted	Mackey and others (1996)
African rivers	0.4 to 30	µg/L	Dissolved load (<0.2 µm); nonpolluted	Gaillardet and others (2003) and references therein
Asian rivers	0.5 to 1	µg/L	Dissolved load (<0.2 µm); nonpolluted	Gaillardet and others (2003) and references therein
European rivers	3.8 to 48	µg/L	Dissolved load (<0.2 µm); nonpolluted	Gaillardet and others (2003) and references therein
North American rivers	0.4 to 15	µg/L	Dissolved load (<0.2 µm); nonpolluted	Gaillardet and others (2003) and references therein
South American rivers	0.46 to 113	µg/L	Dissolved load (<0.2 µm); nonpolluted	Gaillardet and others (2003) and references therein
River water, Republic of Georgia	0.52 to 6.65	mg/L	Dissolved and colloidal (<0.45 µm); near Mn mining operation	Caruso and others (2012)
Magela Creek, Australia	0.8 to 9.6	µg/L	Dissolved (<0.02 µm); wet season flooding	Hart and others (1992)
Magela Creek, Australia	0.6 to 7.9	µg/L	Particulate (>0.02 µm); wet season flooding	Hart and others (1992)
Tap water, southern Quebec, Canada	98	µg/L	Mean; range is 1 to 2,700 µg/L	Bouchard and others (2011)

L20 Critical Mineral Resources of the United States—Manganese

Table L4. Background and above-background concentrations of manganese in rocks, soils, waters, and air.—Continued

[DOE, U.S. Department of Energy; EPA, U.S. Environmental Protection Agency. Units of measure: cm, centimeter; mg/kg, milligram per kilogram (or part per million); mg/L, milligram per liter; mg/m³, milligram per cubic meter; ng/m³, nanogram per cubic meter; µg/L, microgram per liter; µg/m³, microgram per cubic meter; µm, micrometer]

Environment and (or) location	Manganese concentration	Unit	Notes	Reference(s)
Waters—Continued				
Sediment, world rivers	1,679	mg/kg	Average suspended sediment	Viers and others (2009)
Proposed EPA benchmark	2,300	µg/L	Tier II secondary acute value for aquatic life	Suter and Tsao (1996)
Proposed EPA benchmark	120	µg/L	Tier II secondary chronic value for aquatic life	Suter and Tsao (1996)
United States recommended upper limit in secondary drinking water	50	µg/L	None	U.S. Environmental Protection Agency (2013)
Air				
Greenland	2.8 to 4.5	ng/m ³	None	Kabata-Pendias and Pendias (2001)
Molango mining district, Mexico	420	ng/m ³	Mean; range is 3 to 5,860 ng/m ³	Rodriguez-Agudelo and others (2006)
South Pole	0.004 to 0.02	ng/m ³	None	Kabata-Pendias and Pendias (2001)
Urban/industrial	50 to 900	ng/m ³	None	Kabata-Pendias and Pendias (2001)
Minimum risk level chronic inhalation	0.3	µg/m ³	Chronic duration greater than or equal to 1 year	Agency for Toxic Substances and Disease Registry (2012)
Workplace limit	5	mg/m ³	Not-to-exceed limit over an 8-hour workday	Occupational Safety and Health Administration (2013)

In weathering environments at Earth's surface, manganese commonly occurs in three active oxidation states. Manganese(II) occurs as dissolved Mn²⁺ in solution, especially under acidic pH values, as insoluble carbonate minerals, and as a minor component in other minerals. Manganese(III) is thermodynamically unstable and tends to be a temporary phase during redox reactions or a minor component in manganese-bearing minerals. Manganese(IV) tends to form insoluble oxide and hydroxide minerals. The manganese(III) and manganese(IV) phases are some of the strongest oxidants in the environment, so the reactivity of manganese is dominated by its tendency to participate in redox reactions (Tebo and others, 2004). In surface water, manganese tends to attach to particulate matter that is either transported downstream or deposited as sediment.

Mining and industrial activities can lead to above-background concentrations of manganese in the environment (table L4). For example, manganese concentrations in soils near mining and industrial sources in Poland range from 292 to 571 mg/kg (Połedniok and others, 2012). Comparable

manganese concentrations in surface soils collected in central Pennsylvania from both an undisturbed watershed site and a nearby historic steel plant site (table L4) led Herndon and others (2011) to a comprehensive analysis that showed that more than one-half of the soils surveyed in North America and Europe are enriched in manganese as a result of atmospheric deposition from industrial sources. Indeed, the atmospheric concentrations of manganese in urban and industrial areas (50 to 900 ng/m³) are far greater than those measured at the poles (0.004 to 4.5 ng/m³). Likewise, the dissolved and colloidal (<0.45 µm-sized) fraction of manganese in river water near a manganese mining site in the Republic of Georgia contains 0.5 to 6.7 milligrams per liter (mg/L) (Caruso and others, 2012), which is roughly an order of magnitude greater than dissolved manganese concentrations in some world rivers (table L4). Mackey and others (1996) measured dissolved and colloidal manganese concentrations of seawater in nonpolluted and polluted harbors of Tasmania and found ranges of 0.6 to 2 µg/L and 1 to 10 µg/L, respectively.

The primary anthropogenic inputs of manganese to the atmosphere are from mining and ore processing, as well as from iron and steel production. The median anthropogenic emission of manganese to the atmosphere in 1983 was estimated to be 38.3 Mkg/yr (Nriagu and Pacyna, 1988), and the median manganese concentration reported for “polluted air” is 90 ng/m³ (Reimann and de Caritat, 1998, and references therein).

Because manganese is so critical to steel manufacturing, society’s need for manganese continues to increase. Unlike many metals, manganese recycling is relatively efficient. The recycled content (that is, the proportion of scrap) used in manganese production is between 25 and 50 percent, and the fraction of manganese in discarded products that get recycled is greater than 50 percent (Graedel and others, 2011). The factors that contribute to the economic and technologic feasibility of manganese recycling are that (a) manganese is used in large quantities, and (b) it occurs in alloys in relatively pure form, making it easier to remelt and recover (Reck and Graedel, 2012).

Mine Waste Characteristics

Manganese deposits are mined by open pit and underground methods. The mine waste generated is generally considered to be the material that originates and accumulates at a mine site that has no current economic value (Lottermoser, 2010), and includes both solid and liquid waste. Because sedimentary manganese deposits tend to be laterally extensive, the expanse of land disrupted during mining is potentially great. The largest deposits on land include the Kalahari manganese field, which covers approximately 400 km² (Jupiter Mines Ltd., 2013), and the Molango mining district, which covers 180 km² (Rivera-Becerril and others, 2013). Although many mines in sedimentary manganese deposits can be viewed from satellite imagery, values for the volume or tonnage of solid mine waste generated during mining are difficult to obtain. Supergene manganese deposits tend to be smaller and higher grade, so the amount of solid mine waste generated is expected to be less.

Solid mine waste includes overburden (the waste rock that overlies an orebody, which must be removed during mining) and gangue (the economically valueless material that surrounds or is mixed with the ore). The mineralogy of overburden varies depending upon the deposit, whereas the mineralogy of gangue from manganese mining can be similar among deposits. In general, gangue minerals in sedimentary manganese deposits include biogenic silica, carbonates, chert, clays, glauconite, pyrite, and quartz (Force and others, 1995). Gangue minerals in the Groote Eylandt supergene manganese deposit include gibbsite, goethite, kaolinite, and quartz, and the trace metals associated with these minerals include As, Ce, Cr, Gd, P, Pb, Sc, Th, Ti, and Zr (Pracejus and Bolton, 1992). Clarke and others (2010) have characterized mine tailings in the Kalahari manganese field as being predominantly

sand-sized and containing the minerals birnessite, bixbyite, braunite, calcite, hausmannite, hematite, manganite, and todorokite. Trace metals detected in these tailings include (in milligrams per kilogram): Ag (<0.8), As (20), Be (0.9), Cd (0.6), Cr (42), Cu (41), Hg (0.1), Mo (5.9), Pb (110), Se (<0.2), and Th (<0.1). Most of these trace metals are expected to be immobile given the tailings pore water pH of 8.8.

The enrichment of trace metals (for example, Co, Cu, Mo, Ni, and REEs) in manganese oxide minerals is why manganese nodules and crusts on the seabed have become an attractive metal resource. In weathering environments, trace metals contained in manganese oxides are expected to remain immobile under oxidic, near-neutral pH conditions (5 < pH < 8), especially in the presence of iron-rich solids (Smith and Huyck, 1999). Under anoxic and (or) acidic conditions, however, both manganese oxides and associated trace metals are expected to be mobile. In some manganese deposits, generation of acidity is possible if pyrite dissolution is not balanced by the acid-neutralizing capacity of carbonate minerals, but this scenario is expected to be rare. Dissolution of manganese oxides and associated trace elements is more likely to occur in soil environments, where organic acids can be highly concentrated in pore water, creating acidic conditions. Manganese oxide minerals are also expected to be less stable under anoxic conditions, which can develop upon burial. In anoxic subsurface environments, manganese-reducing microorganisms are known to catalyze manganese oxide dissolution, thereby contributing to increased dissolved manganese and trace metal concentrations in groundwater (Myers and Nealson, 1988; Lovley, 1991).

Human Health Concerns

A wealth of information exists on the effects of manganese on human health because it is both an essential nutrient and a potential neurotoxin in cases of overexposure. The Agency for Toxic Substances and Disease Registry (ATSDR) provides a useful summary of the human toxicology of manganese (Agency for Toxic Substances and Disease Registry, 2012). The general public is exposed to manganese through consumption of food and water; inhalation of air; and skin contact with air, water, soil, and consumer products that contain manganese. The U.S. Recommended Dietary Allowance of manganese is 2 to 5 milligrams per day (mg/d) (National Research Council, 1989). Extended oral exposure above these levels can lead to adverse neurological effects. Workers at manganese mining and processing facilities are most likely to inhale manganese-rich dust. Inhaled manganese can lead to a permanent neurological disorder called manganism, which causes such symptoms as tremors, difficulty walking, and facial muscle spasms. Additionally, occupational exposure to manganese dust can lead to lung inflammation and impaired lung function. The mean air concentration within the Molango mining district in Mexico is 420 micrograms of manganese per cubic meter; in this region,

surveyed adults exhibited decreased motor abilities with increasing air manganese concentrations (Rodríguez-Agudelo and others, 2006).

Children exposed to high levels of manganese show neurodevelopmental effects, including changes in behavior, memory, and learning ability. For example, surveyed school-age children in the Molango mining district contained significantly higher manganese levels in blood and hair relative to children in a control site; children also showed decreased intellectual function with increased manganese content in hair (Riojas-Rodríguez and others, 2010). In a similar study of school-aged children exposed to relatively high manganese levels (mean=98 micrograms of manganese per liter) in drinking water supplied by groundwater, higher manganese concentrations in hair were significantly correlated with higher manganese concentrations in drinking water and with decreased IQ scores (Bouchard and others, 2011).

The U.S. national secondary drinking water regulation for manganese, which is a nonenforceable guideline, is 50 µg/L (U.S. Environmental Protection Agency, 2013). The World Health Organization's (WHO) "Guidelines for Drinking Water Quality" included manganese at 400 µg/L until 2011, at which point the inclusion of manganese was discontinued on the grounds that the recommended value was well above normal concentrations of manganese in drinking water (World Health Organization, 2011). Frisbie and others (2012) argue that a substantial number of surveyed countries have drinking water manganese concentrations greater than 400 µg/L, and that given the possible negative human health effects of manganese, the earlier WHO guideline was probably too high to protect human health.

Manganese levels in soils are not regulated because of the ubiquity of manganese in soil and groundwater. The U.S. Environmental Protection Agency (EPA) does, however, require the reporting of manganese concentrations in waste streams from factories that use or produce manganese. The chronic duration (equal to or greater than 1 year) minimal risk level of 0.3 microgram per cubic meter (µg/m³) Mn has been set for manganese inhalation by the U.S. Department of Health and Human Services (Agency for Toxic Substances and Disease Registry, 2012). Likewise, the U.S. Occupational Safety and Health Administration (OSHA) has set a limit of 5 milligrams per cubic meter (mg/m³) for the average allowable manganese concentration in workplace air over an 8-hour workday (Occupational Safety and Health Administration, 2013).

Ecological Health Concerns

Many studies focus on the ecological effects of manganese in the environment. Because fish tend to be sensitive to low concentrations of dissolved metals, they are commonly useful indicators of contamination in aquatic systems. One of several useful endpoints used in toxicity tests is the concentration that leads to 50 percent mortality (lethal concentration 50 [LC₅₀]) after exposure to a substance for a certain amount of time. Chronic toxicity tests with dissolved manganese and

developing rainbow trout (*Oncorhynchus mykiss*) revealed a mean LC₅₀ value of 2.9 mg/L after 28 days of exposure (Birge and others, 1980). Tests on the chronic toxicity of manganese to developing brown trout (*Salmo trutta Linnaeus*) showed that at 30 mg/L hardness (high dissolved mineral content), decreased survival after 62 days correlated significantly with increased manganese concentrations, which ranged from 0.5 to 15.5 mg/L (Stubblefield and others, 1997). The toxic effects of manganese on this species decreased with increasing hardness because less toxic Ca²⁺ and Mg²⁺ were able to outcompete with Mn²⁺ for biologic sites. Decreased manganese toxicity with increasing hardness was also observed for the water flea (*Ceriodaphnia dubia*) (Peters and others, 2011). Some regions of the United States have adopted secondary acute and chronic screening benchmarks for manganese concentrations of 2,300 µg/L and 120 µg/L, respectively, for aquatic freshwater life, as recommended by the Oakridge National Laboratory (Suter and Tsao, 1996).

Manganese is considered to be an essential nutrient for healthy plant growth, partially because of its role in supporting photosynthesis (Kabata-Pendias and Mukherjee, 2007). Land plants exhibit a range of 15 to 100 micrograms of manganese per gram dry weight (Misra and Mani, 1991). Plants vary in their ability to withstand high manganese concentrations, and those plants with higher manganese tolerance may accumulate manganese in roots and (or) precipitate manganese oxide within the epidermis (Kabata-Pendias and Mukherjee, 2007). A survey of plant roots growing in the Molango mining district in Mexico revealed that native ragweed growing in soil proximal to manganese mine waste was more resistant to manganese incorporation than ragweed growing directly in the mine waste; higher manganese resistance in the former specimen was attributed to a symbiotic relationship with mycorrhizal fungi in plant roots (Rivera-Becerril and others, 2013). As summarized by Nagajyoti and others (2010), plants that are sensitive to excessive manganese tend to develop diseases that affect their leaves. Some regions of the United States have adopted a soil-screening benchmark of 500 milligrams of manganese per kilogram of soil for terrestrial plants, as recommended by the Oakridge National Laboratory (Efroymsen and others, 1997).

Carbon Footprint

Use of manganese contributes to greenhouse gas emissions. During the production of ferromanganese, which is an important component in steel, manganese oxides are mixed with iron ore and carbon and then reduced in either a blast furnace or an electric arc furnace. The energy requirements for this process can be great. Additionally, when rhodochrosite (MnCO₃) is the starting manganese ore, either for ferromanganese or nonmetallurgical applications, an initial processing step involves converting MnCO₃ to pyrolusite (MnO₂) in a process known as calcination. This results in additional process-related carbon dioxide (CO₂) emissions. Using a basic emission calculation and assuming

100 percent calcination, an emission factor of 383 kilograms of carbon dioxide per kilogram of rhodochrosite results (Hanle and others, 2006). The EPA requires facilities that emit 25,000 metric tons or more of greenhouse gases and that consume at least 2,000 metric tons per year of carbonates, such as rhodochrosite, to report their process-based CO₂ emissions in addition to their energy-related greenhouse gas emissions. Certain industries, such as manganese alloy and iron and steel production, are excluded from this requirement (U.S. Environmental Protection Agency, 2011).

Mine Closure

Most recently opened and new mining operations include closure plans that address issues related to the mine footprint. A mine's footprint includes the waste left on site and locally affected soil and water, as well as ecological effects, such as habitat destruction and loss of biodiversity. The environmental impact assessment for the proposed Kalahari manganese mine in Northern Cape Province, South Africa, which is part of the Kalahari manganese field, provides examples of some mine footprint issues and possible control measures (Strategic Environmental Focus (Pty) Ltd., 2007). The manganese ore, mainly rhodochrosite, would be mined by underground methods, and both ore beneficiation and ferromanganese production would take place on site. The mine waste generated on site would include tailings (projected to be 250,000 metric tons per year) and slimes from ore treatment (projected to be 45,000 metric tons per year). The tailings pile would increase in size for about 10 years before being returned to the underground workings as backfill. Any remaining piles would be graded and covered with vegetation. Potential loss of native vegetation and disruption of faunal migrations would be addressed by a 1.5-km no-development buffer zone along the major river that flows through the proposed mine site and by revegetation of disturbed soils with native species. Surface and groundwater quality would be monitored frequently, and potential seepage from tailings and slime dams would be prevented through engineering means. The potential for dust emissions from mining and sinter operations would be mitigated through various methods, such as wet suppression and early revegetation.

Long-term plans for closed manganese mining operations will depend on the country, State, and local regulations. Potential long-term environmental impacts that could be of concern are dust generation and seepage of metal-rich water from waste material. An additional long-term issue relates to revegetation of manganese-rich waste, which applies to both closure of current mines and attempted reclamation of abandoned mines. Some plant species may contribute to soil acidification, which could lead to solubilization of manganese from minerals and transport of dissolved manganese downstream. Attention to the type of plant species used for revegetation and close monitoring of soil parameters during soil development might prevent this from happening.

Problems and Future Research

Identified global manganese resources, including currently subeconomic deposits, are essentially inexhaustible by any scenario of future consumption. Thus, there are no geologic problems related to the adequacy of manganese resources from a global perspective. Substantial increases in the price of manganese and increases in the efficiency of mining and processing will be necessary to convert much of this vast resource to economically workable deposits, however. The unequal distribution of the global manganese resources has long been recognized as a matter of concern for the United States and other industrialized countries that have inadequate domestic resources to meet their own needs. For the United States, discovery of manganese deposits of better quality than the few known large low-grade domestic deposits would be advantageous, whether they were immediately economic or could provide a more accessible source of manganese in the event of future supply disruptions.

Perhaps the most significant area available for domestic manganese exploration is the seabed within the United States EEZ. The vast size of this area alone provides incentive for research and exploration opportunities, many of which have been only superficially addressed to date. The United States EEZ contains more than 11 million km² of seabed, an area larger than all of the land areas of the Nation. There are substantial known deposits of ferromanganese crusts and nodules in the EEZ where the United States has sole authority for regulation and mining. A more definitive characterization of the EEZ's potential as a source of manganese could help to focus future research and exploration efforts on areas that have the highest possibility for development and production. An expanded information base regarding the occurrence, abundance, and metal grades of these deposits would be a significant step toward eventual metal production. Beyond geologic research, prime areas for research include mining and processing technology and advances in understanding and mitigating the potential impact of seabed mining on marine ecosystems.

With regard to seabed mineral resources, development of this resource would disturb potentially millions of square kilometers of the abyssal seabed, an unprecedentedly large area of mine disturbance that would constitute a new type of human impact on the environment. Significant new research would be needed to assess the effects on marine ecosystems and understand other environmental impacts of this completely new human activity and to minimize its adverse impacts. The ISA has developed guidelines for the environmental impact statement (EIS) that must be submitted by companies interested in applying for seabed mineral exploration licenses. In an EIS, developers must address all environmental and social issues and relevant mitigation measures that could result from the mining activity (International Seabed Authority, 2012). More information on these issues has been discussed in the various technical reports published online by the ISA (2014).

Processing of manganese nodules and crusts mined on the seabed will most likely take place on land, so the same mine waste issues mentioned for terrestrial manganese ores will also apply to seabed resources. Seabed mining in the CCZ would involve many additional issues. In addition to overcoming the technological challenges presented by mining as deep as 6,500 m below sea level, perhaps one of the most controversial issues is the potential impact on benthic, midwater, and pelagic ecosystems. Benthic ecosystems developed on the abyssal plain are the ecosystems that are the most threatened by mining in the CCZ. Understanding of abyssal, benthic ecosystems has grown rapidly in the past several decades. Even so, an international effort to evaluate the biodiversity in the CCZ revealed that “high, unanticipated, and still poorly sampled levels of species diversity for all three sediment-dwelling faunal components (foraminifera, nematodes and polychaetes) [exist] at [the] individual study sites” (International Seabed Authority, 2008). These findings led to the recommendation that “marine protected areas” be maintained throughout the CCZ in order to preserve abyssal biodiversity (International Seabed Authority, 2008). Another major environmental concern relates to wastewater being discharged from mining ships. This waste could contain crushed nodules and trace metals and has the potential to disrupt phytoplankton and, because the wastewater would be colder and denser than the surface water, to disrupt the natural circulation patterns in the water column (Markussen, 1994). As a result, current conceptual engineering designs separate nodules from waste material (such as clay, sediments, and muddy water) and return waste to the seabed at depths of nearly 5,000 m below sea level so as not to disturb the midwater and pelagic regions (for example, Agarwal and others, 2012). As interest in mining seabed resources continues, additional studies would be needed to document its impacts on ocean life.

References Cited

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

- Agarwal, B., Hu, P., Placidi, M., Santo, H., and Zhou, J.J., 2012, Feasibility study on manganese nodules recovery in the Clarion-Clipperton zone, v. 2 of Shenoi, R.A., Wilson, P.A., and Bennett, S.S., eds., Seabed exploitation—The LRET Collegium 2012 Series: Highfield, Southampton, United Kingdom, University of Southampton, 128 p. [Also available at http://www.southampton.ac.uk/engineering/research/groups/fsi/lrf/lrf_collegium_2012_book_series.page.]
- Agency for Toxic Substances and Disease Registry, 2012, Toxicological profile for manganese: Atlanta, Ga., U.S. Department of Health and Human Services, Public Health Services, September, 506 p. plus 3 appendixes, accessed February 15, 2013, at <http://www.atsdr.cdc.gov/ToxProfiles/tp151.pdf>.
- Banakar, V.K., 2010, Deep-sea ferromanganese deposits and their resource potential for India: Journal of the Indian Institute of Science, v. 90, no. 4, p. 535–541.
- Beltrame, R.J., Holtzman, R.C., and Wahl, T.E., 1981, Manganese resources of the Cuyuna Range, east-central Minnesota: Saint Paul, Minn., Minnesota Geological Survey Report of Investigations 24, 22 p.
- Beukes, N.J., and Gutzmer, J[ens], 1996, A volcanic-exhalative origin for the world’s largest (Kalahari) manganese field (Discussion): Mineralium Deposita, v. 31, no. 3, p. 242–245.
- Birge, W.J., Black, J.A., Westerman, A.G., and Hudson, J.E., 1980, Aquatic toxicity tests on inorganic elements occurring in oil shale, *in* Gale, Charles, ed., Oil shale symposium—Sampling analysis and quality assurance, March 1979, Proceedings: Cincinnati, Ohio, U.S. Environmental Protection Agency, EPA-600/9-80-022, p. 519–534. [Also available at <http://babel.hathitrust.org/cgi/pt?id=coo.31924004323303;view=1up;seq=531>.]
- Bouchard, M.F., Sauvé, Sébastien, Barbeau, Benoit, Legrand, Melissa, Brodeur, Marie-Ève, Bouffard, Thérèse, Limoges, Elyse, Bellinger, D.C., and Mergler, Donna, 2011, Intellectual impairment in school-age children exposed to manganese from drinking water: Environmental Health Perspectives, v. 119, no.1, p. 138–143. [Also available at <http://dx.doi.org/10.1289/ehp.1002321>.]
- Cannon, W.F., and Force, E.R., 1983, Potential for high-grade shallow-marine manganese deposits in North America, *in* Shanks, W.C., ed., Cameron volume on unconventional mineral deposits: New York, N.Y., American Institute of Mining, Metallurgical, and Petroleum Engineers, p. 175–189.

- Caruso, B.S., Mirtskhulava, Merab, Wireman, Michael, Schroeder, William, Kornilovich, Boris, and Griffin, Susan, 2012, Effects of manganese mining on water quality in the Caucasus Mountains, Republic of Georgia: *Mine Water and the Environment*, v. 31, no. 1, p. 16–28. [Also available at <http://dx.doi.org/10.1007/s10230-011-0163-3>.]
- Clarke, C.E., Kielar, Filip, Talbot, H.M., and Johnson, K.L., 2010, Oxidative decolorization of acid azo dyes by a Mn oxide containing waste: *Environmental Science and Technology*, v. 44, no. 3, p. 1116–1122. [Also available at <http://dx.doi.org/10.1021/es902305e>.]
- Corathers, L.A., 2011–16, Manganese, in *Metals and minerals: U.S. Geological Survey Minerals Yearbook 2009–2012*, v. I, variously paged.
- Corathers, L.A., 2013a, Manganese, in *Metals and minerals: U.S. Geological Survey Minerals Yearbook 2011*, v. I, p. 47.1–47.20. [Also available at <https://minerals.usgs.gov/minerals/pubs/commodity/manganese/myb1-2011-manga.pdf>.]
- Corathers, L.A., 2013b, Manganese: U.S. Geological Survey Mineral Commodity Summaries 2013, p. 100–101. [Also available at <https://minerals.usgs.gov/minerals/pubs/commodity/manganese/mcs-2013-manga.pdf>.]
- Crow Wing Power, 2013, Manganese deposit in Emily Minnesota... Crow Wing Power's newest business investment....: Crow Wing Power, accessed March 10, 2014, at <http://www.cwpower.com/manganese.shtml>.
- DeYoung, J.H., Jr., Sutphin, D.M., and Cannon, W.F., 1984, International Strategic Minerals Inventory summary report—Manganese: U.S. Geological Survey Circular 930–A, 22 p. [Also available at <http://pubs.er.usgs.gov/publication/cir930A/>.]
- Dorr, J.V.N., II, Crittenden, M.D., Jr., and Worl, R.G., 1973, Manganese, in Brobst, D.A., and Pratt, W.P. eds., *United States mineral resources: U.S. Geological Survey Professional Paper 820*, p. 385–399. [Also available at <http://pubs.er.usgs.gov/publication/pp820/>.]
- Efroymson, R.A., Will, M.E., Sunter, G.W., II, and Wooten, A.C., 1997, Toxicological benchmarks for screening contaminants of potential concern for effects on terrestrial plants—1997 revision, report prepared for the U.S. Department of Energy by Lockheed Martin Energy Systems, Inc.: Oak Ridge, Tenn., Oak Ridge National Laboratory, ES/ER/TM–85/R3, November, 68 p. and two appendixes, accessed March 4, 2013, at <http://www.esd.ornl.gov/programs/ecorisk/documents/tm85r3.pdf>.
- Force, E.R., and Cannon, W.F., 1988, Depositional model for shallow-marine manganese deposits around black shale basins: *Economic Geology*, v. 83, p. 93–117. [Also available at <http://dx.doi.org/10.2113/gsecongeo.83.1.93>.]
- Force, E.R., Cannon, W.F., and Klein, D.P., 1995, Sedimentary Mn deposits, chap. 33 of du Bray, E.A., ed., *Preliminary compilation of descriptive geoenvironmental mineral deposit models: U.S. Geological Survey Open-File Report 95–831*, p. 257–260. [Also available at <http://pubs.usgs.gov/of/1995/ofr-95-0831/>.]
- Frakes, Larry, and Bolton, B.R., 1992, Effects of ocean chemistry, sea level, and climate on the formation of primary sedimentary manganese ore deposits: *Economic Geology*, v. 87, p. 1207–1217. [Also available at <http://dx.doi.org/10.2113/gsecongeo.87.5.1207>.]
- Frisbie, S.H., Mitchell, E.J., Dustin, Hannah, Maynard, D.M., and Sarkar, Bibudhendra, 2012, World Health Organization discontinues its drinking-water guideline for manganese: *Environmental Health Perspectives*, v. 120, p. 775–778. [Also available at <http://dx.doi.org/10.1289/ehp.1104693>.]
- Gaillardet, J., Viers, J., and Dupré, B., 2003, Trace elements in river waters, in Drever, J.I., ed., *Surface and ground water, weathering, and soils*, v. 5 of Holland, H.D., and Turekian, K.K., eds., *Treatise on geochemistry: Oxford, United Kingdom, Elsevier-Pergamon*, p. 225–272. [Also available at <http://dx.doi.org/10.1016/B0-08-043751-6/05165-3>.]
- Graedel, T.E., Allwood, Julian, Birat, J.-Pi., Buchert, Matthias, Hagelüken, Christian, Reck, B.K., Sibley, S.F., and Sonnemann, Guido, 2011, What do we know about metal recycling rates?: *Journal of Industrial Ecology*, v. 15, no. 3, p. 355–366. [Also available at <http://dx.doi.org/10.1111/j.1530-9290.2011.00342.x>.]
- Hanle, Lisa, Maldonado, Pedro, Onuma, Eiichi, Tichy, Milos, and van Oss, H.G., 2006, Mineral industry emissions, in Eggleston, Simon, Buendia, Leandro, Miwa, Kyoko, Ngara, Todd, and Tanabe, Kouptp, eds., v. 3, *Industrial processes and product use, of 2006 IPCC guidelines for national greenhouse gas inventories: Hayama, Japan, Institute for Global Environmental Strategies*, p. 2.1–2.40. [Also available at <http://www.ipcc-nggip.iges.or.jp/public/2006gl/vol3.html>.]
- Hart, B.T., Noller, B.N., Legras, C., and Currey, N., 1992, Manganese speciation in Magela Creek, northern Australia: *Australian Journal of Marine and Freshwater Research*, v. 43, no. 2, p. 421–441. [Also available at <http://dx.doi.org/10.1071/MF9920421>.]
- Hein, J.R., 2012, Prospects for rare earth elements from marine minerals: Kingston, Jamaica, International Seabed Authority Briefing Paper 02/12, 4 p.
- Hein, J.R., Conrad, T.A., and Dunham, R.E., 2009, Seamount characteristics and mine-site model applied to exploration- and mining-lease-block selection for cobalt-rich ferromanganese crusts: *Marine Georesources and Geotechnology*, v. 27, no. 2, p. 160–176. [Also available at <http://dx.doi.org/10.1080/10641190902852485>.]
- Hein, J.R., Conrad, T.A., and Staudigel, Hubert, 2010, Seamount mineral deposits—A source of rare metals for high-technology industries: *Oceanography*, v. 23, no. 1, p. 184–189. [Also available at <http://dx.doi.org/10.5670/oceanog.2010.70>.]

- Hein, J.R., Mizell, Kira, Koschinsky, Andrea, and Conrad, T.A., 2013, Deep-ocean mineral deposits as a source of critical metals for high- and green-technology applications—Comparison with land-based resources: *Ore Geology Reviews*, v. 51, June, p. 1–14. [Also available at <http://dx.doi.org/10.1016/j.oregeorev.2012.12.001>.]
- Herndon, E.M., Jin, Lixin, and Brantley, S.L., 2011, Soils reveal widespread manganese enrichment from industrial inputs: *Environmental Science and Technology*, v. 45, no. 1, p. 241–247. [Also available at <http://dx.doi.org/10.1021/es102001w>.]
- International Manganese Institute, 2012, Annual market research report—2011: Paris, France, International Manganese Institute, 34 p.
- International Seabed Authority, 2008, Biodiversity, species ranges, and gene flow in the abyssal Pacific nodule province—Predicting and managing the impacts of deep seabed mining: Kingston, Jamaica, International Seabed Authority Technical Study no. 3, 38 p. [Also available at <http://www.isa.org.jm/files/documents/EN/Pubs/TechStudy3.pdf>.]
- International Seabed Authority, 2010, A geological model of polymetallic nodule deposits in the Clarion Clipperton fracture zone: Kingston, Jamaica, International Seabed Authority Technical Study no. 6, 211 p. [Also available at <http://www.isa.org.jm/files/documents/EN/Pubs/GeoMod-web.pdf>.]
- International Seabed Authority, 2012, Environmental management needs for exploration and exploitation of deep sea minerals: Kingston, Jamaica, International Seabed Authority Technical Study no. 10, 47 p. [Also available at <http://www.isa.org.jm/files/documents/EN/Pubs/TS10/index.html/>.]
- Jupiter Mines Ltd., 2013, Tshipi manganese project: Jupiter Mines Ltd., accessed March 17, 2013, at http://www.jupitermines.com/projects/manganese/tshipi_manganese_project.phtml.
- Kabata-Pendias, Alina, and Mukherjee, A.B., 2007, Trace elements from soil to human: Berlin, Germany, Springer-Verlag, 550 p.
- Kabata-Pendias, Alina, and Pendias, Henryk, 2001, Trace elements in soils and plants (3d ed.): Boca Raton, Fla., CRC Press, 413 p.
- Kilgore, C.C., and Thomas, P.R., 1982, Manganese availability—Domestic: U.S. Bureau of Mines Information Circular 8889, 14 p.
- Lelong, F., Tardy, Y., Grandin, G., Trescases, J.J., and Boulange, B., 1976, Pedogenesis, chemical weathering and processes of formation of some supergene ore deposits, chap. 3 of Wolf, K.H., ed., *Handbook of strata-bound and stratiform ore deposits*: Amsterdam, Netherlands, Elsevier, p. 93–173. [Also available at http://horizon.documentation.ird.fr/exl-doc/pleins_textes/pleins_textes_5/b_fdi_06-07/08437.pdf.]
- Lottermoser, B.G., 2010, Mine wastes—Characterization, treatment, and environmental impacts, 3d ed.: Berlin, Germany, Springer-Verlag, 400 p. [Also available at <http://dx.doi.org/10.1007/978-3-642-12419-8>.]
- Lovley, D.R., 1991, Dissimilatory Fe(III) and Mn(IV) reduction: *Microbiological Reviews*, v. 55, p. 259–287. [Also available at <http://www.ncbi.nlm.nih.gov/pmc/articles/PMC372814/>.]
- Mackey, D.J., Butler, E.C.V., Carpenter, P.D., Higgins, H.W., O’Sullivan, J.E., and Plaschke, R.B., 1996, Trace elements and organic matter in a pristine environment—Bathurst Harbour, southwestern Tasmania: *The Science of the Total Environment*, v. 191, p. 137–151. [Also available at [http://dx.doi.org/10.1016/0048-9697\(96\)05255-2](http://dx.doi.org/10.1016/0048-9697(96)05255-2).]
- Manheim, F.T., and Lane-Bostwick, C.M., 1988, Chemical composition of ferromanganese crusts in the world ocean—A review and comprehensive database: U.S. Geological Survey Open-File Report 89–20, 200 p. [Also available at <http://pubs.er.usgs.gov/publication/ofr8920/>.]
- Manheim, F.T., Popenoe, Peter, Siapno, William, and Lane, C., 1982, Manganese-phosphorite deposits of the Blake Plateau (western North-Atlantic Ocean), in Halbach, P., and Winter, P., eds., *Marine mineral deposits—New research results and economic prospects*; Proceedings of the Clausholer workshop: Essen, Germany, Verlag Gluckauf GmbH, p. 9–44.
- Markussen, J.M., 1994, Deep seabed mining and the environment—Consequences, perceptions, and regulations, in Bergesen, H.O., and Parmann, Georg, eds., *Green Globe yearbook of international co-operation on environment and development*: Oxford, United Kingdom, Oxford University Press, p. 31–39.
- Maynard, J.B., 2003, Manganiferous sediments, rocks, and ores, in MacKenzie, F.T., ed., *Sediments, diagenesis, and sedimentary rocks*, v. 7 of Holland, H.D., and Turekian, K.K., eds., *Treatise on geochemistry*: Oxford, United Kingdom, Elsevier-Pergamon, p. 289–308. [Also available at <http://www.sciencedirect.com/science/article/pii/B0080437516070997>.]
- Maynard, J.B., 2010, The chemistry of manganese ores through time—A signal of increasing diversity of Earth-surface environments: *Economic Geology*, v. 105, p. 535–552. [Also available at <http://dx.doi.org/10.2113/gsecongeo.105.3.535>.]
- Misra, S.G., and Mani, Dinesh, 1991, *Soil pollution*: New Delhi, India, Ashish Publishing House, 209 p.
- Morey, G.B., 1990, *Geology and manganese resources of the Cuyuna Iron Range, east-central Minnesota*: Minnesota Geological Survey Information Circular 32, 28 p.
- Morgan, C.L., 2000, Resource estimates of the Clarion-Clipperton manganese nodule deposits, chap. 6 of Cronan, D.S., ed., *Handbook of marine mineral deposits*: Boca Raton, Fla., CRC Press, p. 145–170.

- Mosier, D.L., 1986, Grade and tonnage model of sedimentary Mn, in Cox, D.P., and Singer, D.A., eds., Mineral deposit models: U.S. Geological Survey Bulletin 1693, p. 231–233. [Also available at <https://pubs.er.usgs.gov/publication/b1693>.]
- Muiños, S.B., Hein, J.R., Frank, Martin, Montiero, J.H., Gaspar, Luís, Conrad, Tracey, Periera, H.G., and Arbantes, Fátima, 2013, Deep-sea Fe-Mn crusts from the northeast Atlantic Ocean—Composition and resource considerations: Marine Georesources and Geotechnology, v. 31, no. 1, p. 40–70. [Also available at <http://dx.doi.org/10.1080/1064119X.2012.661215>.]
- Myers, C.R., and Nealson, K.H., 1988, Bacterial manganese reduction and growth with manganese oxide as the sole electron acceptor: Science, v. 240, no. 4857, p. 1319–1321. [Also available at <http://dx.doi.org/10.1126/science.240.4857.1319>.]
- Nagajyoti, P.C., Lee, K.D., and Sreekanth, T.V.M., 2010, Heavy metals, occurrence and toxicity for plants—A review: Environmental Chemistry Letters, v. 8, no. 3, p. 199–216. [Also available at <http://dx.doi.org/10.1007/s10311-010-0297-8>.]
- Nahon, Daniel, and Parc, Sylvie, 1990, Lateritic concentrations of manganese oxyhydroxides and oxides: Geologische Rundschau, v. 79, no. 2, p. 319–326. (In German.) [Also available at <http://dx.doi.org/10.1007/BF01830628>.]
- National Materials Advisory Board, 1981, Manganese reserves and resources of the world and their industrial implications: Washington D.C., The National Academies Press, 334 p.
- National Research Council, 1989, Recommended dietary allowances, 10th ed.: Washington, D.C., The National Academies Press, 285 p. [Also available at <http://www.nap.edu/catalog/1349/recommended-dietary-allowances-10th-edition>.]
- National Research Council, 2008, Minerals, critical minerals, and the U.S. economy: Washington, D.C., The National Academies Press, 245 p. [Also available at <http://www.nap.edu/catalog/12034/minerals-critical-minerals-and-the-us-economy>.]
- Natural Earth, 2014, Small scale data: Natural Earth map dataset, scale 1:110,000,000, accessed March 13, 2014, at <http://www.naturearthdata.com>.
- Nicholson, K., Hein, J.R., Bühn, B., and Dasgupta, S., eds., 1997, Manganese mineralization—Geochemistry and mineralogy of terrestrial and marine deposits: Bath, United Kingdom, Geological Society Special Publication no. 119, 370 p.
- Nriagu, J.O., 1989, A global assessment of natural sources of atmospheric trace metals: Nature, v. 338, p. 47–49. [Also available at <http://dx.doi.org/10.1038/338047a0>.]
- Nriagu, J.O., and Pacyna, J.M., 1988, Quantitative assessment of worldwide contamination of air, water and soils by trace metals: Nature, v. 333, no. 6169, p. 134–139. [Also available at <http://dx.doi.org/10.1038/333134a0>.]
- Occupational Safety and Health Administration, 2013, Manganese compounds (as Mn): Occupational Safety and Health Administration, accessed March 17, 2013, at http://www.osha.gov/dts/chemicalsampling/data/CH_250190.html.
- Pavlidis, Louis, 1962, Geology and manganese deposits of the Maple and Hovey Mountains area, Aroostook County, Maine, with a section on Lithology and mineralogy of the deposits, by Louis Pavlidis and Charles Milton: U.S. Geological Survey Professional Paper 362, 116 p. [Also available at <http://pubs.er.usgs.gov/publication/pp362/>.]
- Peters, Ada, Lofts, Stephen, Merrington, Graham, Brown, Bruce, Stubblefield, William, and Harlow, Kevin, 2011, Development of biotic ligand models for chronic manganese toxicity to fish, invertebrates, and algae: Environmental Toxicology and Chemistry, v. 30, no. 11, p. 2407–2415. [Also available at <http://dx.doi.org/10.1002/etc.643>.]
- Poledniok, Justnya, Andrzej, Kita, and Zierzucha, Piotr, 2012, Spectrophotometric and inductively coupled plasma—Optical emission spectroscopy determination of gallium in natural soils and soils polluted by industry—Relationships between elements: Communications in Soil Science and Plant Analysis, v. 43, p. 1121–1135. [Also available at <http://dx.doi.org/10.1080/00103624.2012.662561>.]
- Pracejus, Bernhard, and Bolton, B.R., 1992, Geochemistry of supergene manganese oxide deposits, Groote Eylandt, Australia: Economic Geology, v. 87, p. 1310–1335. [Also available at <http://dx.doi.org/10.2113/gsecongeo.87.5.1310>.]
- Reck, B.K., and Graedel, T.E., 2012, Challenges in metal recycling: Science, v. 337, no. 6095, p. 690–695. [Also available at <http://dx.doi.org/10.1126/science.1217501>.]
- Reimann, Clemens, and de Caritat, Patrice, 1998, Chemical elements in the environment: Berlin, Germany, Springer-Verlag, 398 p.
- Riojas-Rodríguez, Horacio, Solís-Vivanco, Rodolfo, Schilmann, Astrid, Montes, Sergio, Rodríguez, Sandra, Ríos, Camilo, and Rodríguez-Agudelo, Yaneth, 2010, Intellectual function in Mexican children living in a mining area and environmentally exposed to manganese: Environmental Health Perspectives, v. 118, p. 1465–1470. [Also available at <http://dx.doi.org/10.1289/ehp.0901229>.]
- Rivera-Becerril, Facundo, Juárez-Vázquez, L.V., Hernández-Cervantes, S.C., Acevedo-Sandoval, O.A., Vela-Correa, Gilberto, Cruz-Chávez, Enrique, Moreno-Espíndola, I.P., Esquivel-Herrera, Alfonso, and de León-González, Fernando, 2013, Impacts of manganese mining activity on the environment—Interactions among soil, plants, and arbuscular mycorrhiza: Archives of Environmental Contamination and Toxicology, v. 64, no. 2, p. 219–227. [Also available at <http://dx.doi.org/10.1007/s00244-012-9827-7>.]

- Rodríguez-Agudelo, Yaneth, Riojas-Rodríguez, Horacio, Ríos, Camilo, Rosas, Irma, Pedraza, E.S., Mirandar, Javier, Siebe, Christina, Texcalac, J.L., and Santos-Burgoa, Carlos, 2006, Motor alterations associated with exposure to manganese in the environment in Mexico: *Science of the Total Environment*, v. 368, nos. 2–3, p. 542–556. [Also available at <http://dx.doi.org/10.1016/j.scitotenv.2006.03.025>.]
- Roy, Supriya, 1988, Manganese metallogenesis—A review: *Ore Geology Reviews*, v. 4, nos. 1–2, p. 155–170.
- Schrope, Mark, 2013, UK company pursues deep-sea bonanza: *Nature*, v. 495, March 21, p. 294.
- 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 <http://pubs.er.usgs.gov/publication/pp1270/>.]
- Shiller, A.M., 1997, Dissolved trace elements in the Mississippi River—Season, interannual, and decadal variability: *Geochemica and Cosmochemica Acta*, v. 61, no. 20, p. 4321–4330. [Also available at [http://dx.doi.org/10.1016/S0016-7037\(97\)00245-7](http://dx.doi.org/10.1016/S0016-7037(97)00245-7).]
- Smith, K.S., and Huyck, L.O., 1999, An overview of the abundance, relative mobility, bioavailability, and human toxicity of metals, in Plumlee, G.S., and Logsdon, M.J., eds., *The environmental geochemistry of mineral deposits—Part A, Processes, techniques and health issues*: Littleton, Colo., Society of Economic Geologists, v. 1, p. 29–70.
- Strategic Environmental Focus (Pty) Ltd., 2007, Final environmental impact assessment for the proposed Kalahari Manganese Mine, prepared for Kalahari Resources (Pty) Ltd.: Pretoria, South Africa, Strategic Environmental Focus (Pty) Ltd., Report NC30/5/1/2/2/104MR, 348 p.
- Stubblefield, W.A., Brinkman, S.F., Davies, P.H., Garrison, T.D., Hockett, J.R., and McIntyre, M.W., 1997, Effects of water hardness on the toxicity of manganese to developing brown trout (*Salmo trutta*): *Environmental Toxicology and Chemistry*, v. 16, no. 10, p. 2082–2089. [Also available at <http://dx.doi.org/10.1002/etc.5620161014>.]
- Suter, G.W., II, and Tsao, C.L., 1996, Toxicological benchmarks for screening potential contaminants of concern for effects on aquatic biota—1996 revision: Oak Ridge, Tenn., Lockheed Martin Energy Systems Inc., ES/ER/TM-96/R2, variously paged, accessed March 3, 2013, at <http://www.esd.ornl.gov/programs/ecorisk/documents/tm96r2.pdf>.
- Taylor, S.R., and McLennan, S.M., 1995, The geochemical evolution of the continental crust: *Reviews of Geophysics*, v. 33, no. 2, p. 241–265. [Also available at <http://dx.doi.org/10.1029/95RG00262>.]
- Tebo, B.M., Bargar, J.R., Clement, B.G., Dick, G.J., Murray, K.J., Parker, Dorothy, Verity, Rebecca, and Webb, S.M., 2004, Biogenic manganese oxides—Properties and mechanisms of formation: *Annual Reviews in Earth and Planetary Science*, v. 32, p. 287–328.
- Tivey, M.K., 2007, Generation of seafloor hydrothermal vent fluids and associated mineral deposits: *Oceanography*, v. 20, no. 1, p. 50–65. [Also available at <http://dx.doi.org/10.5670/oceanog.2007.80>.]
- Tsikos, Harilaos, and Moore, J.M., 1997, Petrography and geochemistry of the Paleoproterozoic Hotazel iron-formation, Kalahari manganese field, South Africa—Implications for Precambrian manganese metallogenesis: *Economic Geology*, v. 92, p. 87–97. [Also available at <http://dx.doi.org/10.2113/gsecongeo.92.1.87>.]
- Tsikos, Harilaos, Beukes, N.J., Moore, J.M., and Harris, Chris, 2003, Deposition, diagenesis, and secondary enrichment of metals in the Paleoproterozoic Hotazel iron formation, Kalahari manganese field, South Africa: *Economic Geology*, v. 98, p. 1449–1462. [Also available at <http://dx.doi.org/10.2113/gsecongeo.98.7.1449>.]
- Tyler, Germund, 2004, Vertical distribution of major, minor, and rare elements in a Haplic Podzol: *Geoderma*, v. 119, nos. 3–4, p. 277–290. [Also available at <http://dx.doi.org/10.1016/j.geoderma.2003.08.005>.]
- Urban, H., Stribny, B., and Lippolt, H.J., 1992, Iron and manganese deposits of the Urucum district, Mato Grosso do Sul, Brazil: *Economic Geology*, v. 87, p. 1375–1392. [Also available at <http://dx.doi.org/10.2113/gsecongeo.87.5.1375>.]
- U.S. Environmental Protection Agency, 2011, Miscellaneous uses of carbonate: Washington, D.C., U.S. Environmental Protection Agency Information Sheet EPA-430-F-09-007R, 3 p.
- U.S. Environmental Protection Agency, 2013, National primary drinking water regulations: U.S. Environmental Protection Agency Web page, accessed February 15, 2013, at <http://water.epa.gov/drink/contaminants/index.cfm>.
- U.S. Geological Survey, 1996, Global 30 arc-second elevation (GTOPO30): Reston, Va., U.S. Geological Survey dataset (digital elevation model), accessed March 13, 2014, at <https://lta.cr.usgs.gov/GTOPO30>.
- Varentsov, I.M., 1996, Manganese ores of supergene zone—Geochemistry of formation: Dordrecht, Netherlands, Kluwer Academic Publishers, 343 p.
- Viers, Jérôme, Dupré, Bernard, and Gaillardet, Jérôme, 2009, Chemical composition of suspended sediments in world rivers—New insights from a new database: *Science of the Total Environment*, v. 407, no. 2, p. 853–868. [Also available at <http://dx.doi.org/10.1016/j.scitotenv.2008.09.053>.]
- World Health Organization, 2011, Guidelines for drinking-water quality (4th ed.): Geneva, Switzerland, World Health Organization, 541 p. [Also available at http://www.who.int/water_sanitation_health/publications/2011/dwq_guidelines/en/.]

For more information concerning this report,
please contact:

Mineral Resources Program Coordinator

U.S. Geological Survey

913 National Center

Reston, VA 20192

Telephone: 703-648-6100

Fax: 703-648-6057

Email: minerals@usgs.gov

Home page: <https://minerals.usgs.gov>

Prepared by the USGS Science Publishing Network
Reston Publishing Service Center

Edited by J.C. Ishee

Illustrations by Caryl J. Wipperfurth

Layout by Caryl J. Wipperfurth and Cathy Y. Knutson

Posting by Angela E. Hall

