The United States relies on imports for dozens of commodities in everyday use. Often enough, that reliance is 100%. This book provides awareness of the hidden geology and mineralogy behind common things, and develops an appreciation for the global resource distribution that underpins our society. While concerns about oil import reliance are in the news every day, our needs for other minerals are comparable, and are typically unknown even to technologically aware Americans.

## WHAT THINGS ARE MADE OF: America's Global Dependency on Just About Everything

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# What Things Are Made Of

America's global dependency for just about everything



Richard I. Gibson

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## Acknowledgements

THE DATA COMPILED BY SCIENTISTS AT THE U.S. GEOLOGICAL SURVEY lie at the core of this book. I've tried to blend historical narrative and geology with the statistics, but without their information on production and imports, my main point about global interdependency would be lost. So I owe hugely to those ongoing efforts.

I owe a philosophical debt to James Burke, presenter of the BBC/PBS program *Connections* and author of numerous books. While I'd never compare my own effort to his, I admire the way his stories juxtapose and connect scientific discovery in unexpected ways, and I've consciously attempted to emulate that approach. And information in some of his books pointed me toward a few topics to include here.

The cover photos and design, incorporating Butte's Mountain Con Mine headframe and the hoist engine at the Anselmo Mine, are by me. The photo of me is by Kathryn Langmyer Henderson. Crystal drawings at chapter heads and section breaks are from 19<sup>th</sup> Century mineralogical textbooks. I did the initial formatting and layout for the PDF electronic version, for better or worse.

Early versions of some chapters were read and critiqued by Dick Berg, Steve Koehler, Pat Dickerson, and others, all of whom I thank profusely. Of all the early readers, Sally Lawrence gave me the greatest guidance, pointing out my obnoxious use of "of," passive voice, and other literary sins; her suggestions have made the book far more readable. Any factual errors or disgusting instances of bad style remain mine, of course.

## **About the Author**

Richard Gibson is a consulting geologist and historian. His college geology education was mostly at Indiana University and IU's Judson Mead Geologic Field Station in Montana. After four years analyzing the mineralogy of kidney stones, he entered the oil exploration business as a geophysicist, a professional career that spans more than 35 years and covers the world from the Former Soviet Union to Nevada. He's worked on environmental geology projects as well as diamond and iron ore exploration studies. As a geological educator, he has informed audiences ranging from elementary school children to State Geologists of the United States. He's been a geological Study Leader on Smithsonian Journeys and the Education Director at the World Museum of Mining. Gibson taught college field geology for 14 summers, and explains history, geology, and mining on tours in and around his home town, Butte, Montana. He lives at the corner of Quartz and Crystal Streets.



## 1

### All the Ships of the World Mineral products in home construction

Ask why God made the gem so small, And why so huge the granite? Because God meant, mankind should set That higher value on it. — Robert Burns

INE SHAFTS BREATHE THEIR HOT VAPORS into a forty-belowzero Montana winter. The copper miners, grimy and tired from their efforts to free a bit more ore from the granitic rock, ascend from the depths of the Steward Mine's "Chinese Laundry," where temperatures of one hundred degrees Fahrenheit and a hundred percent humidity exhaust a man in much less time than the 12-hour shift he works

for \$3.50. But copper underpins a growing industrial world, and \$3.50 per day is a decent wage in 1905.

The hazards and hard work of mining are not new. Primitive mining and metal working laid the groundwork for modern civilization. Early humans first pounded pure native copper into knives and scrapers nearly 10,000 years ago, and early smeltermen cast copper objects in Turkey's Anatolia region some 8,400 years ago. Early Egyptian metallurgists had learned how to alloy copper with tin to produce bronze by about 2600 B.C., when they fabricated a rod in the Bent Pyramid at Meidum. Bronze, harder and more resistant to corrosion than pure copper and easier to melt and cast, gave its name to an age extending from about 3000 B.C., when large-scale production began, until 800 B.C. when rudimentary iron working signaled an important change in metallurgy.

Some of the earliest copper miners discovered the metal on the island now known as Cyprus in the eastern Mediterranean; in fact, the word copper comes from Latin *cuprum* and earlier *Cyprium*, meaning "metal of Cyprus." We still live in a copper and bronze age, although many other metals and natural mineral compounds also underpin today's industrial world. Building construction ranks high on the list of copper uses, so let's start this exploration by investigating your home's hidden corners. Together with its alloys brass and bronze, half the copper used in the United States goes for construction of homes and other buildings.

Most plumbing pipe consists of corrosion-resistant copper, while many of the joints and connectors are brass. Both metals are much less likely to rust than steel compounds, and their flexibility allows pipes to curve. Brass, a copper-zinc alloy, became popular during the time of Augustus (27 B.C. – 14 A.D.); a coin from this time is among the oldest known brass objects. Because zinc vaporizes at typical smelting temperatures, recovering pure zinc metal was difficult; many earlier objects, dating back to the early Bronze Age and chemically brass, probably represent accidental inclusion of zinc from mixed ores. Metallurgists in

India learned how to separate pure zinc by the 4<sup>th</sup> Century B.C., after which deliberately fabricated brass became more common.

Another well-known and almost omnipresent copper use is in wires. The invention of the telephone (1876) and the electric light (1879) created a huge market for copper wire. The resulting mining boom put Butte, Montana, on the map. From a busted gold camp with only 60 hardy souls in 1874, Butte exploded to 23,000 people in 1890, mostly on the strength of copper and silver mining. By the early 1900s, Butte's mines yielded about a third of all the copper produced in the world, and growth continued until World War I ended and wartime demand disappeared. Combined with vast copper discoveries in Chile, decreased demand drove the U.S. copper industry into a long, generally downward spiral. In 2009 more than a third of all the copper mined on earth came from Chile and the U.S. imported a quarter of its needs, a dramatic increase in dependency from being a net exporter of copper in 1991 but down from pre-recession copper import levels exceeding 40%. Copper mining in the U.S. was a \$9.4-billion industry in 2008, employing nearly 12,000 mine and mill workers. That made copper the #4 mineral business by value, after iron and steel, crushed stone, and cement. The recession in 2009 reduced domestic copper's value to \$6.2 billion, and fifth place as gold's price surged.

It isn't just the wire itself that requires mineral products. Most wires are drawn through tiny dies manufactured from very hard, tough materials, including diamonds. Diamond is the hardest mineral known, and tiny pieces of single crystals have carefully machined holes (drilled with lasers and ultrasonic machines) that shape wires into the necessary uniform diameter. Simultaneously, diamond dies polish the wire's surface to ensure good electrical connections. Holes as small as a few thousandths of an inch yield the finest wires, such as those that constitute light-bulb filaments.

The U.S. led the world at consuming copper throughout the 20<sup>th</sup> Century. China's burgeoning economy is increasing its needs, helping to drive the world price of copper to record levels above \$3.00 a pound in 2006

and again in 2010, up from  $71 \notin$  in 1999. In 2002, China surged into position as the world's leading copper consumer. China's copper habit soared from about 5% of world consumption in the early 1990s to 21% in 2007.

Leading Copper Producers, 2008	Leading Copper Consumers,1990	Leading Copper Consumers, 2007	Main Sources of US Copper Imports, 2008
Chile (35%)	USA (19%)	China (21%)	Chile (40%)
USA (8%)	Japan (14%)	USA (12%)	Canada (33%)
Peru (8%)	Germany (10%)	Germany (8%)	Peru (13%)
Australia (6%)	USSR (10%)	Japan (7%)	Mexico (6%)
China (6%)	China (5%)		
Russia (5%)			
Canada (4%)			
Indonesia (4%)			

With nearly a third of the world's estimated copper reserves (compared to just 7% in the U.S.), Chile will continue to dominate the copper mining industry for the foreseeable future, and China will be the biggest user. Some analysts foresee \$5-a-pound (or even \$10) copper, a price that will affect home construction costs; already, theft of copper and aluminum from building sites is common in the U.S.

In the copper country of the Keweenaw Peninsula, upper Michigan, pure, or native copper predominates in the mines. In most rich deposits, however, copper combines with sulfur, and sometimes with iron, arsenic, and other elements, to form many different minerals. Chalcopyrite is a brassy-looking copper-iron sulfide, CuFeS<sub>2</sub>; change the proportions a bit to  $Cu_5FeS_4$  and you get purple-iridescent bornite, called peacock ore. Sulfur is common in the earth's crust (about the 16<sup>th</sup> most abundant element), and its mobility and reactivity produce a wide variety of sulfides. These sulfide minerals can form when molten rock deep within the earth begins to solidify.

As the molten granite works its way upward, intruding into pre-existing rocks, pressure reduces. Superheated fluids carrying the metals escape into cracks in the rocks, like holes in the lid of a pressure cooker, where they crystallize into mineralized veins. These hydrothermal ("water, hot") veins result directly from plate-tectonic processes. (See Chapter 2 for a discussion of subduction.) In many deposits, the minerals near the surface oxidize to other minerals. This process can also lead to concentration and enrichment of the ores.

Almost all U.S. copper is produced by 20 major mines in five states: Arizona, Utah, New Mexico, Nevada, and Montana. The world's first largescale open-pit mine, started at Bingham Canyon, Utah, in 1906, continues as the second-largest copper producer in the United States, after a mine at Morenci, Arizona. Bingham Canyon has produced around 29 billion pounds of copper over its century of mining, enough to pave about 600 miles of Interstate highway with pure copper four inches thick. But all the U.S. deposits pale in comparison to those of Chile, where just four huge open-pit mines provide most of the country's copper output. The oldest mine, at Chuquicamata, began major production in the 1920s when the Anaconda Company purchased it. A century earlier, in 1810, the year Chile became independent, the nation exported 19,000 tons of copper, but the industry was erratic throughout the 19th Century. With demand increasing because of World War I and the industrialization of Western Europe and the United States, Chile's foreign-controlled copper mining began to take off in 1910-1930, continuing until (and after) nationalization in the 1970s. The pit at Chuquicamata lies about 9200 feet above sea level, and measures almost three miles long by two miles across and a half mile deep, making it the largest open-pit mine in the world. Chile's copper mines together produce around twelve billion pounds each year.

Up and down the mountainous backbones of the Western Hemisphere in the Andes and the Rockies, porphyry copper deposits abound. What's a porphyry? It's an igneous rock like granite with large crystals

(usually feldspar) embedded in a fine-grained matrix – a three-dimensional constellation of crystals scattered throughout a granular firmament. Often the outsized crystals, called phenocrysts, precipitated from the molten rock at a different time from the matrix. This can happen as feldspar crystals grow slowly over thousands or even millions of years while the magma cools deep within the earth, but some late event forces the remaining melt to solidify quickly with no time for large grains to develop, producing the matrix. Derived from a Greek word referring to Tyrian purple, "porphyry" first described reddish-purple rocks in Egypt that contained large feldspar crystals, but today it means any rock with that bimodal texture. Porphyry copper deposits are veins and scattered concentrations of copper minerals associated with rocks of porphyritic texture. Hot hydrothermal fluids and late-stage magma emanated from granites as they cooled, carrying copper minerals into veins and crevices where rich ores formed.

Most of the granitic bodies scattered throughout the Andes and Rocky Mountains are gigantic blobs of formerly molten rock that rose like globules in a lava lamp above subduction zones along the western margins of the continents, the result of North and South America plowing incessantly westward over denser oceanic crust. Oceanic crust plunges down beneath lighter continental crust until it reaches depths where high temperatures drive off water, reducing the melting point and creating magma. At Butte, a dozen or more discrete blobs of granite fused together to form the Boulder Batholith, nearly 80 miles long and 40 miles wide (and small at that size, as batholiths go), but with richly mineralized zones in only a few places. The Boulder Batholith's granite blobs solidified about 76,000,000 years ago; the lava lamp is no longer pumping, but porphyry is common enough to give its name to one of Butte's city streets. A few other mining towns around the world promote this geologic term in street names, including Telluride and Ophir, Colorado, and Springsure, Queensland, in Australia's gold, copper, and gem country.

Butte's miners in 1917 and 1918, the peak of Butte's copper boom, knew they were part of an industry vital to America's war effort as well as to a rapidly developing industrialized society. But they could hardly have imagined the pervasive, critical needs that copper and other minerals would satisfy in the early 21<sup>st</sup> Century. Just think of all the door knobs made from brass, one of the most important alloys of copper and zinc. A typical single-family home in the United States contains some 440 pounds of copper, ranging from bathroom pipes to air-conditioning systems.



IN APRIL 2000, BROTHERS ELOY AND JAVIER DELGADO were driving a new tunnel in the Naica silver-lead mine in Chihuahua, Mexico. A thousand feet below the surface they broke into a cavern filled with sparkling crystals even larger than those in the nearby Cave of Swords, discovered in 1910. The new Cave of Crystals abounds with translucent gypsum crystals 40 feet long and 6 feet in diameter — lots of them stacked like giant jackstraws throughout a 60-foot cavity. These huge crystals of selenite, a variety of gypsum, rank among the largest crystals of any type ever discovered.

Although not produced from crystals found in caves, gypsum is an essential material in most houses, where it forms the walls. More than 20 million tons of gypsum, 85% of all the gypsum consumed in the U.S., goes to manufacture wallboard and plaster each year. Oklahoma, Arkansas, Iowa, California, Nevada, Texas, Indiana, and Michigan account for about threequarters of domestic production, but our domestic gypsum mining cannot sustain America's demand. In 2008, The U.S. imported about a quarter of its gypsum from Canada, Mexico, and Spain.

Gypsum is hydrous calcium sulfate (CaSO<sub>4</sub>  $\cdot$  2H<sub>2</sub>O). Thanks to the water (H<sub>2</sub>O) in its chemical formula, gypsum serves as a fire retardant, making it ideal for building construction. Gypsum's use as a wall coating is nearly as old as mankind's exploitation of copper. Frescoes on smooth, white gypsum-coated tomb interiors in Egypt date to 3700 B.C., and gypsum plaster also served as a mortar and joint compound; the great pyramids have it between the limestone blocks.

The French chemist Antoine-Laurent Lavoisier was just 32 years old in 1775 when he determined gypsum's chemical makeup in his private laboratory after working on the problem for at least a decade. Lavoisier is most famous for recognizing oxygen's role in combustion, a discovery that paved the way for much of modern chemistry — and he went to the guillotine in 1794 for investing in the company that collected taxes in revolutionary France. But his first presentation to the French Academy of Sciences, in 1764, described gypsum's chemistry and the properties of plaster. It took more than a century for those properties to be utilized on a grand commercial scale.

In 1890 Augustine Sackett and his colleague, Fred L. Kane, employed by the New York Tar Chemical Company, had an invention in search of a use. It was a large wheel-like mechanism they hoped would make a new waterproof wall lining. The problem lay not with the machine, but with the formula: straw paper soaked with pitch, a black, viscous, tarry compound made from coal and petroleum. The pitch made the paper waterproof, but it also soaked through the paper and impregnated printing, paint, or designer wallpaper that decorated it. Kane suggested using Manila paper and Plaster of Paris, a product made from heat-treated gypsum with three-fourths of the water driven off. When the powdered material is mixed with water and allowed to set, it turns back into tightly bonded gypsum faithfully mimicking the shape of any mold. While still fluid, it can be poured into molds to shape wallboard or to cast plaster figurines. Sackett and Kane poured the fluid plaster onto their wheel, rotated it to spin it into

flatness, and a few hours later they had created an ideal new product: plasterboard, or sheet rock, initially called Sackett Board. The patent, granted in 1894, is in Sackett's name.

Sulfur in gypsum drywall may lead to problems, especially when other factors are present like moisture and bacteria. After hurricanes hit U.S. Gulf Coast states in the mid- to late 2000s, drywall imported from China was implicated in generation of corrosive hydrogen sulfide gas (H<sub>2</sub>S) and other household problems. As of 2009, the precise mechanism of H<sub>2</sub>S generation remained uncertain, but reactions involving elemental sulfur are likely. Bacteria may liberate sulfur or it could come from trace materials like strontium sulfide, found in some Chinese drywall. Alternatively, in a purely chemical reaction, sulfur can combine with carbon monoxide to produce carbonyl sulfide (OCS), which gives off H<sub>2</sub>S when it reacts with water. Why the problem arose only recently is not clear, since gypsum wallboard has been around for more than a century.

Although  $21^{st}$  Century drywall is little changed from Sackett's gypsum sandwiched between heavy sheets of paper, a new innovation points the way to longer life for walls: sodium pyrithione (C<sub>5</sub>H<sub>4</sub>NOSNa) impregnates mold- and mildew-resistant wallboard. When combined with zinc the anti-fungal properties of pyrithione, a sulfur-bearing organic compound, make it common in pharmaceuticals for athlete's foot, dandruff, and other conditions.

"Plaster of Paris" takes its name from gypsum deposits in the Montmartre district of the city. Gypsum itself is a name applied to both a specific mineral and the rock composed primarily of the mineral gypsum. The word comes from a Greek term, *gypsos*, ultimately derived from Arabic *jibs*, meaning plaster.

Many homes in Europe in the 1300s and 1400s had walls and ceilings made of wattle and daub. Wattle was a latticework of interwoven poles made of reeds or slender branches. Daub was initially simple natural clay smeared into the lattice to plug the gaps. Lime plaster, made from

roasted limestone, came into use by the late 1400s. The English Plaisterers' Guild, chartered in 1501, used both lime and gypsum plaster in their work with London's home builders. Because lime took days or weeks to harden, workers sought methods for speeding up the setting time. Adding water allowed lime to set overnight, but gypsum plaster's setting time of a few hours ultimately made it the material of choice, and Sackett's gypsum board, or drywall, changed the nature of house construction in the early 1900s.

Gypsum crystallizes in nature when sea or mineral-rich lake waters evaporate. Shallow areas near oceanic shorelines or in lakes that have higher-than-normal concentrations of salts are good candidates for formation of gypsum, salt (halite) and other minerals called evaporites. Hot climates produce high evaporation rates, which result in the minerals precipitating out of the water and depositing in compact layers. Sabkha, an Arabic word for salt flat, has come to have a technical meaning in geology: a flat, tidal plain usually adjacent to the sea, alternately inundated and exposed to the atmosphere. Such locations are ideal for precipitation of evaporites like gypsum, found in the modern sediments of the Umm Said sabkha in Qatar and many other parts of northern Africa and the Middle East.

Southern New Mexico's gypsum White Sands record a complex history: following a drop in sea level, a sabkha or closed basin formed along the sea's margin during Permian time, about 265,000,000 years ago, laying down thick gypsum layers in what is now south-central New Mexico. Much later uplift, about 70,000,000 years ago, eventually allowed the gypsum to be dissolved and washed into a lake with no outlet; for the past 25,000 years or so, wet conditions (from rains during glacial epochs) alternated with dry desert-like times, recrystallizing gypsum on the lake's dry bed. Modern desert conditions prevent water from dissolving the gypsum, and winds blow the crystals into dunes that began to develop around 6,500 years ago during an especially warm, dry period called the Holocene Climactic Optimum, when temperatures may have been warmer in some regions than we see today.

The Permian Period was a time of great evaporation: evaporite deposits of this age in the United States reach more than twice the thickness of similar Jurassic rocks, which rank second in volume of evaporites including gypsum.

Oklahoma is the leading domestic producer of gypsum-nearly 3,500,000 tons of it, worth more than \$26 million in 2007. Like those in New Mexico, most of the gypsum beds in Oklahoma and Texas formed during the Permian Period, about 250,000,000 to 260,000,000 years ago, when dinosaurs were beginning their long reign. Prevailing arid conditions during that period meant that when shallow seas and lakes did form in what is now western Oklahoma, they often evaporated to leave behind the salts that they carried. In Oklahoma's Blaine Formation four to six gypsum layers, each as much as 10 feet thick, separate thin red shale beds. Shale solidifies from mud, and its red color reflects exposure to the atmosphere as evaporation proceeded: the iron in the mud oxidized to hematite-red iron oxide, essentially rust. In today's arid Oklahoma, when groundwater dissolves ancient gypsum and re-deposits it, beautiful crystals form. Oklahoma's official state crystal is selenite, a type of gypsum found most notably at Great Salt Plains State Park near Jet, a town in northwestern Oklahoma.

Similar conditions in Michigan, Indiana, and Iowa during the Mississippian Period, about 340,000,000 years ago, resulted in the thick gypsum layers found there. Gypsum is not valuable enough to warrant expensive underground mining; surface quarries yield most commercial gypsum.

Gypsum also forms beautiful, fanciful growths in caves, known as helictites. The giant selenite specimens in the Cave of Swords and Cave of Crystals a thousand feet beneath the Mexican landscape are special cases. Hot sulfurous waters associated with the nearby lead and silver deposits combined with the calcium in the limestone country rock to create gypsum in solution, a solution that became supersaturated. The crystals probably

reached such extraordinary size because they had cavities in which to grow. The temperature in the Cave of Crystals exceeds 110° F (43° C), far higher than the cool air of even deep caves. And the humidity is 100 percent. The high temperature indicates that a heat source is still present at depth. As a general rule, the larger a crystal's size, the longer it took to grow. Growth-rate studies together with uranium-thorium age dating by Stein-Erik Lauritsen at the University of Bergen, Norway, suggest that these crystals were growing for 400,000 to 500,000 years.

Mica is filler in much of the gypsum wallboard in homes. It is a non-reactive, inexpensive, fire-resistant material that simply makes the gypsum go farther. Joint compound for sealing wallboard consumes the greatest volumes of scrap and flake mica, and North Carolina mines about a quarter of the 90,000 tons of such mica produced in the U.S. During most of the 2000s U.S. import dependency for scrap and flake mica was around 25%, imported about equally from Canada and China with India and Finland providing some supply. Lower demand during the 2009 recession made the United States only 11% dependent on foreign sources for mica. Additives like mica, vermiculite, and perlite increase the strength of gypsum plaster while making it lighter, and they also help control its setting time. Sand and lime (calcium oxide, made from limestone) can also be added for some uses, such as making plaster a bit more resistant. Gypsum's softness, 2 on the hardness scale, is the reason cardboard or paper coatings cover and protect wallboard.

Vermiculite, a lightweight mica-like mineral added to wallboard and acoustic tiles, improves insulating properties as well as fire resistance. Heating vermiculite expands it as much as 15 times its original volume. The U.S. was the world vermiculite leader in the late 1980s, with close to half the total production thanks mostly to the world's largest vermiculite mine at Libby, Montana. Unfortunately the vermiculite at Libby was contaminated with asbestos, resulting in something like 300 deaths among workers and townspeople. The mine there closed in 1990 but lawsuits continue.

Libby's vermiculite deposit, called the Rainy Creek igneous complex, is nearly unique in the world. Similar to carbonatite intrusions at Magnet Cove, Arkansas, (see Chapter 4) it contains strange rocks including nepheline syenite (quartz-poor, but otherwise much like granite) and abundant magnetite (magnetic iron oxide). It even seems to be similar in age to the Magnet Cove intrusion, about 90 million years ago, but the setting of northwest Montana at that time offers little to guide our understanding of its genesis and it could be significantly later, about 50 million years before present, a time when such rocks are more widespread in Montana. Many geologists believe the molten rocks that forced their way upward came ultimately from the earth's mantle. The vermiculite, exposed at the surface, weathered from the original biotite mica in the rocks.

Today, the U.S. is #3 in vermiculite production, after South Africa and China. Our 39% import dependency for asbestos-free vermiculite comes mostly from China (59%) and South Africa (39%), and most domestic production is from South Carolina and Virginia.



CAULKING COMPOUNDS USED TO SEAL GYPSUM WALLBOARD and to glaze windows are largely calcium carbonate and clay but often contain talc and ground silica sand as filler. Their bright white color comes from titanium dioxide pigment.

An unknown artist about 35,000 years ago took reddish ocher containing iron oxide and applied it to the walls of a cave in what is now northern Italy, near Verona. He or she designed pictures of four-legged animals and an animal-headed person. With that simple act, this early human created the first known wall decoration. Paint and pigment are

among the oldest uses of mineral materials, in use at least 20,000 years before the Verona wall pictures appeared.

Gypsum wallboard in most buildings is painted. Paint has two parts: a pigment, and some kind of liquid to carry the pigment. The oldest paints used simple natural coloring agents, including various plant juices and tinted earths. Most non-biological pigments were made from iron oxides, because iron is the most common source of colors in rocks. Tans, yellows, reds, greens, and purples all usually derive from relatively small amounts of iron oxide in the rocks. The famous cliff-forming Redwall Limestone in the Grand Canyon is actually a brownish gray rock, stained bright red by the iron oxide in the overlying Hermit Shale. The iron leaches out of the shale and colors the rocks below.

In 2005, archaeologists discovered the oldest known pigment factory at Sibudu rock shelter, a cave near Durban, Natal, South Africa, where Stone Age workers 58,000 years ago maintained a thriving ochre business. Ochre is a yellowish to red powdery material sometimes called limonite. Limonite is not a discrete mineral, but a rock containing a mixture of iron oxides, hydrates, and hydroxides, often with enough iron to serve as an ore. The artisans at Sibudu may have used the ochre to stain leather garments. Mixed with animal fats ochre makes glue, probably used to help bind stone or bone items to handles or shafts. Lyn Wadley, archaeologist at the University of Witwatersrand (South Africa) who led the investigation, speculated that it could also have had medicinal, preservative, and personal decorative uses.

The ochre at Sibudu probably came from the Ecca Group, a subset of the Karroo Supergroup of rocks. The Karoo strata reach thicknesses of up to 12 kilometers in total, and were laid down in a large basin over a time span of 50 to 100 million years, mostly during Permian time (about 300 to 250 million years ago). The Ecca Group dates to around 280 million years ago and includes iron-rich shales that could weather to form ochre. The Ecca rocks also contain *Glossopteris* fossils, ferns whose remains in South Africa,

South America, India, Australia, and Antarctica provided early evidence for continental connections in a supercontinent called Gondwana, leading ultimately to modern ideas of plate tectonics.

The older rocks in the Karoo Supergroup show evidence of the Permian glaciation, a time when South Africa and adjacent parts of Gondwana lay near the South Pole. By the time the Ecca Group sediments were deposited, the continent had moved north to the tropics and the climate had changed. Coal swamps and iron-rich bogs dominated the environment. The Ecca Group holds about a third of the coal in the southern hemisphere; South Africa ranks #7 in world coal production. The swamps, shallow lakes, mud flats, and river flood plains of the Karoo 250 million years ago are the result of a mountain range, today's Cape Fold Belt, that uplifted when parts of Antarctica and Patagonia collided with South Africa and central South America during the assembly of Gondwana and eventually the larger supercontinent, Pangaea (see Chapter 2). The uplifted mountains shed so much eroded debris onto the ancient South African craton that the crust subsided under the weight, making a foreland basin, a depression that sinks under the weight of material eroded or tectonically pushed from an actively uplifting mountain range. The plains of northern India south of the Himalayas are a modern example of a foreland basin.

While natural ochre in South Africa was easy for stone-age people to use as pigment, modern white paint's color comes from titanium dioxide which requires significant processing, from mining to chemical reactions. Titanium dioxide constituted the ninth most valuable mineral business in the US, at \$3.7 billion in 2008; even though it lost a billion dollars in value in 2009's recession titanium dioxide rose to the #8 position as other commodities lost even more value. The titanium industry in the U.S. employs about 4,000 workers. In addition to paints (almost two-thirds of all the TiO<sub>2</sub> used), it is an important component in white papers, white sidewall tires, plastics, ceramics, coated textiles, sun block, and floor coverings. The U.S. is the world's leading producer of titanium dioxide pigments, with

almost a third of the 5.3 million tons produced annually. This makes the United States a net exporter of this useful commodity. Other important producers include China, Germany, Japan, and the United Kingdom. However, the U.S. imports most of the basic concentrates of titanium minerals to produce pigment, primarily from Australia and South Africa. Australia leads the world in producing these concentrates.

Nature collects titanium minerals into economic deposits. The two most important compounds, ilmenite (FeTiO<sub>3</sub>) and rutile (TiO<sub>2</sub>), are much denser than common quartz so they become concentrated in beach sands and dunes by wave action and to a lesser extent by wind. Both waves and wind move the lighter quartz sand grains more easily, leaving a concentrated lag of titanium minerals. This is similar to the mechanism by which water localizes gold in pockets called placers in river beds.

In Australia, the ultimate source of the titanium minerals is probably granite bodies in northeastern New South Wales. The granite solidified during the Permian Period, about 260,000,000 years ago, and has been eroding for much of the time since then. The Clarence River carries concentrations of modern sediment, including ilmenite and rutile, to the coast. The black sands there are enriched in these minerals because the sub-tropical environment has chemically removed some of the less-resistant but more common compounds such as iron oxides. Most of the world's greatest titanium sand deposits lie in sub-tropical regions. About 95% of the titanium produced in the world goes to making pigments; the rest generates titanium metal.

Red and red-brown mineral pigments are usually made from iron oxide, either chemically synthesized or as the mineral *hematite* (Fe<sub>2</sub>O<sub>3</sub>). At the Mather Mine, Upper Michigan, about 1% of the mine's iron output goes to the paint and pigment industries. This is among the primary domestic sources for these coloring agents. Red iron pigment also comes from famous localities near Linares in Jaen Province, Spain, and (formerly) from Ormuz or Hormuz Island, in the Iranian Persian Gulf, the source of Persian Red for

the Roman Empire. Because iron oxide is in effect already rust, its use in covering pigments such as paint also serves as an effective rust inhibitor.

Wollastonite, calcium silicate (CaSiO<sub>3</sub>), added to some acrylic latex paints, helps stabilize the pH or acidity of the solution and prevents acid corrosion of the paint cans. Much U.S. production is from Willsboro, New York, where wollastonite occurs in 1-billion-year-old metamorphosed limestone in the northeastern Adirondack Mountains.

Lead chromate produces bright chrome yellow; chromium occurs in only one important mineral, chromite, and we import most of our needs from South Africa, Turkey, and Zimbabwe. Crocoite, a commercially unimportant but beautiful chromium mineral that forms brilliant orange stick-like crystals, occurs in magnificent collectible form in Tasmania. Cadmium gives color to most corrosion-resistant yellow and orange paint. Cadmium sulfo-selenate serves as a red pigment that is common in plastics, ink, and paint. Cadmium is similar to zinc in its atomic properties; it is not mined directly, but comes from smelting sphalerite (zinc sulfide) which contains cadmium in holes within its crystal lattice. In the U.S., some zinc and most cadmium production is ultimately from Mississippi Valley deposits in Wisconsin and Illinois, and the Tri-State District of Kansas, Missouri, and Oklahoma, but the cadmium is produced by metal refineries in Tennessee, Ohio, and Pennsylvania. The U.S. is a net exporter of cadmium.

The silvery appearance of oil tanks and water towers is due to aluminum flake paint. Not only does such paint reduce the possibility of corrosion of the tank, it also reduces temperature by being reflective.

The workhorses of blue and green pigments in plastics (see Chapter 4) are synthetic phthalocyanines, copper-based organic compounds. Many common copper minerals are blue and green, so these colors are no surprise. Bromine is sometimes included in some of the green colorants using phthalocyanine as a starting point. The carbon and hydrogen in the mix come from petrochemicals manufactured using oil and natural gas.



**I**RON'S COLORING POWER IS DESIRABLE IN PAINT, but not when transparency is the goal, as in glass. Common window glass is a noncrystalline (amorphous) material composed primarily of quartz (silica, SiO<sub>2</sub>) from clean sand. If the sand contains just 0.02 percent iron oxide, decolorizing is required to produce clear glass, and most deposits contain more than that. The Romans discovered a decolorizing technique during the first century A.D., by adding manganese to glass to reduce its amber tint. But glass manufacturing dates to 4000 B.C. in Egypt, where the sands of the Sahara melted into glassy glazes on ceramic figurines.

Alexandria was among the most important glass-making centers in the world from 300 B.C. until early Imperial Roman time. The Alexandrians used state-of-the-art molding techniques, but manufacturers in rival Sidon apparently invented glass blowing during the first century A.D. Pliny the Elder wrote that sailors camping at the mouth of the Belus River, modern Nahr Na'mân near Akko or Acre in northern Israel, used blocks of soluble natron (Na<sub>2</sub>CO<sub>3</sub> · 10H<sub>2</sub>O) for their fire stones. The soda supposedly combined with the clean sand of the river bed to yield a nearly transparent glass. Other sources suggest that the Sidon glass makers used ashes from burned seaweed as a soda source together with the Belus River sands, but in either case they developed melts that could be blown into patterned molds to make attractive vessels and containers. Sidonese glass-making techniques spread across the Roman Empire within a few decades.

Glass was once such a valuable product that until the 17<sup>th</sup> Century, people took window panes with them when they moved. In the 21<sup>st</sup> Century, it takes about one ton of quartz sand to make the window glass in an average American house, totaling almost seven billion square feet of flat glass in

North America every year. That's about 250 square miles, nearly the area of St. Louis, Philadelphia, and Washington DC, combined.

Today, the best glass sands in the United States come from the 400million-year-old Devonian Oriskany Sandstone of West Virginia, Pennsylvania, and Virginia, and in the Ordovician St. Peter Sandstone in Illinois, Missouri, and Arkansas. Named for occurrences along the St. Peter River (now called the Minnesota River) not far from its junction with the Mississippi near Minneapolis, the St. Peter formation was deposited as a broad sheet of sand from Minnesota, Wisconsin, and Michigan south to Arkansas and Kentucky, and from Ohio and Indiana west to South Dakota and Nebraska. It likely started out as a near-shore or beach deposit, wavewashed and sorted for thousands if not millions of years, resulting in excellent rounding and uniformity of grain size as well as high purity.

The Ordovician Period, 470,000,000 years ago, was a time of no life on land: no plants, no animals, short of possible bacterial and algal mats in moist, rocky soils. All life existed in water. A transgressive sea in what is now the U.S. Midwest crept slowly over a low-lying continent, bringing beach and tidal environments progressively further and further eastward. Occasional regressions, or drops in relative sea level, took the shoreline in the other direction at times. It all added up to a sheet of St. Peter sandstone, hundreds of miles wide and averaging 150 feet thick. In some places, the rock is about 99.5% pure silica – the quality that makes it outstanding as glass sand. Across the country, many other minor or lower-quality deposits are also mined for silica sand. The U.S. leads the world in glass-sand production at about 28% of the world's total of 40 million metric tons, with Texas the leading state and Illinois second. Nearly a third of U.S. industrial sand and gravel production goes to glassmaking, the largest use (ahead of oil well operations; see Chapter 8). Italy is the second leading world producer of industrial sand and gravel of all sorts including glass sands, and Germany, Austria, United Kingdom, and Australia rounded out the top six sand producers in 2008.

It is nearly impossible to remove all the trace amounts of iron from silica (quartz) sand used to make glass. Iron gives a greenish or reddish brown tint to glass (seen in some 19th Century window glass and old bottles), but the addition of other compounds in tiny amounts can neutralize this coloration. Today selenium replaces the Romans' manganese in making glass transparent.

Another additive, sodium sulfate or "salt cake," pumped from underground brines in Texas and California, prevents the formation of undesirable scum on the surface of the molten glass mixture. It is used especially for window glass production. Sodium sulfate can provide soda (Na<sub>2</sub>O), but soda is more commonly introduced into glass melts using sodium carbonate, or soda ash. Derived from vast deposits in Wyoming which hold about 95% of the world's sodium carbonate reserves, soda lowers silica's unmanageably high melting point (about 1650°C, or 3000°F), but has the undesirable side effect of making glass soluble in water. Yet another additive, lime (calcium oxide), overcomes this problem, and most common glass manufactured today is a soda-lime-silica glass.

The U.S. soda ash industry based in southwest Wyoming is the largest in the world, yielding more than 93% of total output. Layers of sodium carbonate minerals, especially trona, Na<sub>3</sub>H(CO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, probably represent evaporating conditions in a large confined lake, Lake Gosiute, that developed during the Eocene Epoch, about 45,000,000 years ago. The sediments laid down in this lake formed 2,000 feet of strata called the Green River Formation, famous for well-preserved fish fossils. By some estimates, Lake Gosiute was remarkably long-lived, possibly lasting as long as 20 million years. Most lakes are ephemeral over geologic time. Extreme evaporation produced layers of almost pure trona as much as 20 feet thick. Trona dissolves easily in water, so most of the water must have disappeared for the minerals to be deposited, much like the crusty deposits laid down by hard water when it evaporates on a faucet.

The soda ash industry is also among the oldest in America. The moniker "ash" is a term applied in the commodities market for any sodium carbonate, no matter what the origin. Before evaporite deposits were mined, sodium carbonate was produced by burning plant products, as the glass makers of ancient Sidon discovered. Settlers at Jamestown, Virginia, in 1608 exported "soap-ashes" in their first shipment back to Britain on behalf of their sponsor, the London Company. Soda ash also helped create a fledgling glass business in Jamestown.

Today's U.S. soda ash business employs 2,500 workers as part of a \$1.4-billion-a-year industry, 19<sup>th</sup> most valuable mineral industry in the United States, with half the output exported around the world, especially to Mexico and Brazil. U.S. reserves account for 96% of known world supplies. Although based on U.S. mining, two-thirds of the domestic soda ash business is controlled by companies based in India, Belgium, Japan, and South Korea. Perhaps surprisingly because of its connections to glass and the building industry, the domestic soda ash business was among only a few that saw essentially no decline in value with the recession in 2009.

Modern glass sheets are flattened and made uniformly thick by floating them on a bath of molten tin or by passing warm, pliable material through rollers. Plate glass polish uses rouge (iron oxide), cerium oxide, or finely crushed garnets like those found in sandpaper. Alumina (aluminum oxide) provided by the mineral feldspar inhibits devitrification, the process by which glass slowly recrystallizes into the quartz from which it was made. Alumina also improves the hardness, durability, and chemical corrosion resistance of the final product. The United States is self-sufficient in feldspar production, with North Carolina the leading state. Nepheline, a lowiron alumino-silicate, replaces feldspar as a source for alumina in glass. Most of it comes from Canada, which exports some 70% of its nepheline production to the U.S. glass industry.

Venice, Italy, a center of Renaissance glass-making, also produced some of the first glass mirrors by 1300 A.D. Early Egyptians used polished

bronze reflectors as mirrors, but today's household mirrors reflect light from a very thin film of silver or aluminum deposited on a sheet of glass. The rear-view mirror in your car has two mirrors at slight angles to each other, with one only partially silvered so that some of the light from bright headlights does not reflect. Mercury has sometimes been used to make mirrors and the platinum-group element rhodium coats some highly reflective surfaces such as those in searchlight mirrors.

In addition to its use in mirrors, aluminum is often the prime constituent of exterior house doors, commonly made almost entirely of aluminum and aluminum alloys. The bare metal may make a typical storm door, or it may be coated or painted for aesthetic purposes. Although the U.S. produces a huge amount of aluminum metal, the raw ore is imported from Jamaica, Australia, Guinea, Suriname, and elsewhere. Processing aluminum from ore (bauxite) is an electrolytic process, so electricity cost is a major consideration. In 2007, Alcoa Aluminum opened a huge plant in Iceland because of the low cost of electricity there. Iceland is the only nation that derives 100% of its heat and electricity from cheap, renewable hydropower or geothermal sources. The Iceland aluminum plant imports bauxite from as far away as Australia, exporting the metal to markets in Europe. See Chapter 4 for more about aluminum.



WHAT ABOUT THE SPACE between the walls of your house? Russell Slayter at the Owens-Corning Company invented modern fiberglass for home insulation in 1938. Molten glass, primarily silica, is blown through tiny bushings or nozzles made from platinum. Platinum is non-reactive at the high temperatures needed to melt silica (around 1450 °C at the nozzle),

but it is not quite durable enough for commercial applications. The addition of some rhodium, a metal related to platinum, helps with this problem. The entire volume of platinum group elements mined in the United States comes from one place: the Stillwater Mine in southwest Montana, the only important platinum mine in the entire Western Hemisphere. This production, while significant, provides less than a tenth of the platinum the U.S. consumes each year; more than a third comes from South Africa. The manufacture of platinum bushings for making fiberglass, nylon, and other filaments is a tiny proportion of all the platinum used, and we'll be talking much more about platinum in later chapters. But without platinum, fiberglass made from silica would be more difficult and more expensive to make.

Silica becomes workable to manufacture fibers only at temperatures above 1700°C. Introducing impurities, such as sodium and calcium, reduces the melting temperature, but the resulting fibers are not resistant to alkaline compounds. In modern fiberglass, aluminum and boron added to the melt help achieve more desirable properties and reduce the working temperature to a typical 1450°C. Boron also works as a flame retardant in cellulose insulation made from plant fibers. Glass production, including fiberglass, consumes three-quarters of all the boron used. It may be more familiar as a component of soap and detergents (borax), but its use in the glass industry is much more important.

Most U.S. boron products come from salty brines and dry lake deposits in California. The Searles Lake area in the Mojave Desert is especially rich in borates, and four producers there supply about 30% of all the boron in the world. Searles Lake's bed lay deep under water during the most recent Ice Age, two million to 12,000 years ago. But the valley was completely surrounded by mountains, giving the lake no outlet, so salts of all sorts, especially borates, built up as the area became arid and evaporation exceeded the influx of water.

Why was Searles Lake rich in borates while Lake Gosiute in Wyoming was rich in trona or soda ash (sodium carbonate)? The chemistry of lakes depends mostly on the chemistry of the rocks weathering around them. Boron at Searles Lake came from hot spring water percolating into the lake beginning about 10,000,000 years ago (Miocene time). The hot water likely dissolved boron-rich granite and volcanic rocks associated with subduction, perhaps enriched in boron by incorporation of sea water into magmas. The mountains surrounding Lake Gosiute were mostly clay-rich limestone, contributing carbonate that reacted with sodium to form soda ash during especially intense periods of evaporation. Searles Lake is also rich in soda ash, just not in as much volume as the Wyoming deposits.

The United States exports boron and borates, supplying 28% of the world's production. Turkey and Argentina are other important sources. Ulexite (NaCaB<sub>5</sub>O<sub>9</sub>  $\cdot$  8H<sub>2</sub>O) is an interesting borate that's also called "television rock" because its parallel crystal rods transmit light almost perfectly in one direction, but they are opaque or translucent in other directions, forming natural optical fibers.



**B**RICKS AND TILE CONSTITUTE THE GREATEST SINGLE USE of clay, and much of it goes to home construction. Brick use began by 4000 B.C., when wet clay or mud mixed with straw became adobe, or sun-dried brick. They're still used in arid lands. By about 1000 B.C., manufacturers learned to strengthen bricks by firing them. When salt-saturated driftwood was used to fire bricks, manufacturers noted an attractive, hard, glossy surface, which led to the discovery that salt could produce a glaze on ceramic surfaces. Salt today still creates glazes.

Colored pigments decorated bricks by 600 B.C. The strongest coloring agent is iron oxide; when present in amounts exceeding 5%, it gives a red color to brick, with particular shades developing according to the firing temperature.

Clay of all types added up to a \$1.7-billion industry in the U.S. (\$1.4 billion in 2009 with total mine and mill employment at about 5,300). More than half the value comes from Georgia kaolin, used mostly in the paper business (see Chapter 7). Production of common clay, the type most often used in bricks, is centered in North Carolina, Texas, and Alabama, but 41 states have some production.

Some non-structural facing bricks, roofing tile, and ceramic pipes are made from miscellaneous clay, which can include any mixture of clay minerals. Illite, a clay mineral containing some calcium and magnesium, and a general category of clay minerals, is a common constituent, but adding montmorillonite (a group of hydrated clays) strengthens the final product because it bonds more tightly when the water is driven off during heating. But too much montmorillonite can result in too much shrinking, ultimately weakening the brick. An 8" brick may lose as much as five-eighths of an inch in length in the firing process and remain strong. As with common clay, Texas, North Carolina, and Alabama lead U.S. producers of miscellaneous clay, but illite's name honors the state of Illinois. Montmorillon, a quiet vacation community in western France, gave its name to the montmorillonite group in 1847.

Clay minerals are mostly hydrous aluminum silicates, the result of weathering other aluminous minerals like feldspars. Called phyllosilicates (Greek, *phyllon*, a leaf), they form platy or flaky, leaf-like crystals. Thin laminae, easily separated, are made by silicate (silicon-oxygen) layers that are strong within the sheet, but weakly bonded from sheet to sheet. Micas belong to this mineral clan along with clays. Some clay minerals including montmorillonite are structurally constructed on a molecular level so that they can actually expand, allowing mobile and electrically polar molecules

like water to enter between the sheets, forcing them apart. With dehydration, either natural or induced in a brick kiln, these swelling clays return to their more compact state. This property is a great advantage in natural soils, where clays can stockpile water into dry periods, making it available to plants and animals.

Mortar for bricks is cement (see Chapter 8), a roasted mixture of powdered limestone, sand and clay. After water is added to the resulting gray powder, it turns rock-hard when it dries. Sometimes gypsum (hydrated calcium sulfate) is included in mortar mixes.

In the United States alone about 9 billion bricks are cast each year – more than a million miles of brick, enough to reach from the earth to the moon almost five times. India produces more than ten times that amount. With more than 33 million tons of clay of all types consumed in the U.S. annually, the nation is a net exporter; Canada and Japan are the largest export destinations for U.S. clays, accounting for about a third of the billion dollars in value shipped abroad.



ON FEBRUARY 6, 1595, SIR WALTER RALEIGH, age 41, set sail from Plymouth, England, in search of El Dorado. After a 45-day voyage, he arrived at Trinidad, where he found not gold, but black, fetid tar. He wrote, "At this point, called Tierra de Brea or Piche, there is that abundance of stone pitch that all the ships of the world may be therewith laden from thence; and we made trial of it in trimming our ships to be most excellent good, and it melteth not with the sun as the pitch of Norway, and therefore for ships trading the south parts very profitable." Today the second-largest Pitch Lake in the world indeed provides profits to Trinidad, with exports

worth more than \$3 million sent to 50 countries annually. Local legend has it that an early king killed a hummingbird, offending the gods so much that they buried the tribe's settlement in pitch. But this evil reputation has not kept the 115-acre Pitch Lake from also becoming perhaps the ugliest tourist attraction in the Caribbean, with more than 20,000 visitors each year.

Natural asphalt, tarry petroleum bitumen with the consistency of cold molasses, is fabricated into roofing shingles, and in Trinidad it also paves roads. Much of the material in shingles is also prepared as a distillation by-product of oil refining; several refineries in the U.S. produce asphalt exclusively. Asphalt's granular mineral surface may be composed of many different natural materials, including crushed limestone and slate. For many years asbestos was used, but health risks have reduced asbestos use in shingles, from 2,500 tons in 2005 to 715 in 2009; two-thirds of asbestos in the U.S. goes to the roofing industry. Consumption in 2009 was also impacted by the economic recession and downturn in home construction, but the downward trend in asbestos use has persisted since 2000. No domestic asbestos has been mined since 2002 and most imported asbestos comes from Canada.

Quartz sand, granite, slag from the steel industry, and oyster shells all coat roofs, usually in locations near to the material's source. Many subtle hues in shingles come from the diverse tints in these granules, although more recently the color results from glass or ceramics colored with chrome oxide, copper sulfate, and other compounds. For some roofs, air-blown asphalt, sprayed or mopped directly onto the surface, can be covered with decorative granules, bypassing the need for shingles. This step may also serve as a base coating to which roofing workers nail asphalt shingles.

Asphalt differs from oil primarily in its viscosity, or fluidity. Asphalt can be solid enough for a person to stand on it, or it can flow sluggishly like thick syrup. Asphalts often lack volatiles, chemical components such as gases, water, and very light hydrocarbons that make oil fluid. An asphalt lake or other near-surface deposit is an oil reservoir

exposed to the atmosphere, allowing the volatiles to escape. The pitch lakes of Trinidad and Venezuela, as well as the famous La Brea Tar Pits in southern California, are fed by underground asphalt seeps. Mineral matter, including sand and silt, can comprise as much as a third of some asphalts, and sometimes it is the other way around: you can have sandstone that contains asphalt between the grains. These "tar sands" can often be used directly to pave road surfaces, and the huge deposits in Canada increasingly provide a source for crude oil. Surface tar sands are excavated in quarry fashion by bulldozers and other earth-moving equipment, but some deeper underground deposits are liquefied by steam injection, allowing it to be pumped to the surface where it is refined.

Asphalt shingles are as much as 50% filler (apart from surface granules), usually composed of very finely ground granite or clay. This material strengthens and extends asphalt's volume and makes it heavier, so that shingles can resist being blown off in the wind. Mica flakes dusted on the backs of asphalt shingles prevent sticking. The U.S. and Russia were virtually tied in 2008 as the world's leading producers of such *scrap mica*, and North Carolina produces the most of any state in the U.S.

Some modern roofing shingles made of fiberglass and similar tough non-corrosive materials resist fire. Most ceramic roofing tiles are simply unglazed clay fired in an oven. Wooden shingles, often cedar, are increasingly going out of use because they present significant fire danger.

In 2009, Dow Chemical introduced thin-film cells of copper indium gallium diselenide (CIGS) encased in molded plastic as solar panels integrated into asphalt shingles. They can be installed by roofing contractors. Indium, gallium, and selenium are relatively rare elements with photoelectric properties. Indium forms few minerals, and most indium is a byproduct of zinc smelting. China leads the world in indium production, and also leads in supplying imports to the United States which is 100% dependent on foreign sources for indium. Likewise, virtually all gallium used in the U.S. is imported, in almost equal proportions from China,

Ukraine, Germany, and Canada. Processing bauxite to produce aluminum yields most of the world's gallium. Selenium is also a byproduct, usually of copper refining. One refinery, at Amarillo, Texas, produces all domestic selenium, but the U.S. also imports nearly 600 tons per year, mostly from copper refineries in Belgium; the U.S. produces enough selenium to be a net exporter.

Sir Walter Raleigh may not have found El Dorado, but today's roofing products industry is a \$9-billion business in the United States alone.



Galvanizing is the process of adding a protective zinc coating to iron and steel products to deter corrosion. Named for electricity pioneer Luigi Galvani (1737-1798), galvanizing is accomplished either by electroplating, often used for coating wire, or by dipping steel sheets, pipes, and fence wire in molten zinc. Zinc reacts with steel forming an undesirable zinc-iron compound, but adding a little aluminum to the mix results in less of the brittle alloy. Galvanizing is one of zinc's main uses, helping to make it the fourth most common metal used in the world today. Among obvious galvanized materials are vents and standpipes protruding from home roofs; many gutters and downspouts are painted galvanized steel plate. Bracings and reinforcements for interior wall corners and window openings often consist of galvanized sheet steel bent at a right angle. The metal is usually invisible because its painted cover matches the wall but it can be located with a magnet.

Although zinc was known in ancient times (the Romans alloyed zinc compounds with copper to make brass) not until the Middle Ages did the pure metal come into common use. As noted above, zinc metal was

probably isolated by the 4<sup>th</sup> Century B.C. in India, and recognized as a new element as early as 1374 by chemists working for the Hindu King Madanapála. Importing Indian smelting techniques, the Chinese probably knew of zinc by 1637. The German chemist Andreas Sigismund Marggraf was the first European to prepare the metal, in 1746.

Leading zinc producers are China (28% of world production), Peru (13%), and Australia (13%). The United States contributes about 7% of the world's zinc mining, with 83% from Alaska. In 2008 zinc was the 18<sup>th</sup> most valuable mineral industry, at \$1.5 billion and employing 2,800 mine, mill, and smelter workers. 2008 marked a recent peak in zinc-related employment: compare 1,900 in 2006 and 1,800 in 2009 when the recession reduced domestic zinc's value to about \$1.2 billion.

Bob Baker was among the hardy bush pilots and miners who frequently flew over northwestern Alaska in search of mineral ores. Accompanied by his rust-colored dog, Baker and others noticed bright colors in the rocks of the western Brooks Range in 1953, but it was not until 1970 that U.S. Geological Survey scientists began documenting the remote deposits, along a creek named for Baker's red dog. A further 19 years would pass before ore production began.

Today, the Red Dog Mine complex, north of Kotzebue, Alaska, contains the largest known zinc reserves in the world. Unlike most copper deposits associated with granitic intrusive bodies, many zinc ores lie in sedimentary rocks. At Red Dog, black siliceous shales and cherts of the Mississippian-Pennsylvanian Kuna Formation host the zinc ores (see Geologic Time Table). Shale is a very fine grained rock that solidified from mud, and chert is a form of silica (quartz, SiO<sub>2</sub>) that probably represents siliceous concentrations derived from sponge spicules and radiolarians, microscopic single-celled animals that secrete silica shells. The ore, mostly the mineral sphalerite (zinc sulfide, ZnS), precipitated from hot waters flowing through layers and cracks in the shale. The waters were probably at

around  $120^{\circ}$  to  $200^{\circ}$  C (248° to 392° F) — not that hot by geologic standards, but hot enough to dissolve and carry a lot of zinc.

Other important zinc producers in the U.S. are Idaho, Missouri, Montana, New York, and Tennessee. Most zinc deposits are also rich in lead, because lead and zinc minerals have similar properties. In the United States, galvanizing by the steel industry consumes more than half of all the zinc used.

The U.S. is the world's largest exporter of zinc concentrates, mostly from Alaska. This is because even with two primary and 12 secondary zinc smelters, the supply from American mines is too large to handle. Consequently, the U.S. is also the world's largest *importer* of zinc metal, with more than 70% reliance on imports for its needs. Canada and Mexico account for more than two-thirds of our zinc metal imports. More about zinc in Chapter 3.



A VITAL COMPONENT OF MOST AMERICAN HOMES that is not fundamentally mineral matter is the wooden frame that forms the backbone of the house. But even here we must look to the world of geology to understand modern lumber. Trees and other plants cannot grow without soil, decomposed rock mixed with decaying organic matter from plant and animals sources. (See Chapter 7 for more on fertilizer and soils.)

A more direct application of mineralogy to lumber lies in the preservatives used to extend the life of a simple two-by-four. Arsenic is a familiar poison: it may have contributed to Napoleon's death in exile, either by murder or accident, entering his system from the green-pigmented wallpaper in his jail cells, or from hair tonic which contained arsenic. Despite this, arsenic in another form, chromated copper arsenate (CCA), has

been a valuable tool in preparing lumber for use in outdoor construction such as decks, playground equipment, and picnic tables. Pressure treatments force the compound into the wood. Inside each plank or board, the chemical helps deter termites, fungi, and molds from attacking the wood. The useful life of wooden boards can be extended by as much as ten times through such treatment. The railroad industry saved nearly \$7 billion from 1900 to 1950 by using wood ties treated with creosote, a coal tar derivative mixed with petroleum.

Studies indicate low health risk, but arsenic residues may accumulate on weathered wood, and they can also be released by burning, so some states have banned the use of CCA-treated lumber. The woodtreatment industry voluntarily stopped using CCA at the end of 2003, and alternatives are being investigated. Most other approaches are not as effective as using chromated copper arsenate, and some, such as creosote, work only in situations where odor and staining of covering material such as paint are not issues. The \$4-billion-a-year market for wood that resists bugs and rot has begun using other copper-based chemicals as preservatives. The leading replacement compound, alkaline copper quaternary, or ACQ, contains copper carbonate as a fungicide combined with ammonium chloride, an insecticide. One drawback to this chemical is its reactivity with steel; galvanized fasteners are recommended in ACQ-treated lumber. Robert Slimak, a 10<sup>th</sup>-grade student in Virginia, researched sodium silicate's water solubility, leading to its initial use in 2005 as a timber treatment. This compound provides moisture, fire, and insect resistance and is a viable alternative to both toxic CCA and corrosive ACQ.

Every bit of America's arsenic is imported -25,000 tons in 2001 - and until 2004, 90% became lumber treatment. Consumption had depended largely on the new housing market in the U.S., but with the elimination of CCA as a wood treatment, demand began to decrease significantly in 2004, to about 3,600 tons by 2009. China and Chile dominate the world arsenic market, producing about one-half and one-

quarter of the total volume, respectively. China and Morocco, the third largest world arsenic producer, provide the primary sources of American arsenic imports.

Although arsenic's well-deserved reputation for human toxicity creates a public fear factor, most American homes rely on arsenic in tiny volumes in an unexpected location: television sets, computers, and CD players, detailed in Chapter 3.

The United States relies on imports for dozens of commodities in everyday use. Often enough, that reliance is 100%. This book provides awareness of the hidden geology and mineralogy behind common things, and develops an appreciation for the global resource distribution that underpins our society. While concerns about oil import reliance are in the news every day, our needs for other minerals are comparable, and are typically unknown even to technologically aware Americans.

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