

Feature

Element of the Month

Manganese

Synthesized in massive stars shortly before a supernova explosion, manganese, a Group 7 metal with 25 protons in its nucleus, is the 11th most abundant element in the Earth's crust.

First isolated by Swedish chemist Johan Gottlieb Gahn in 1774 by reducing pyrolucite with carbon, manganese (Mn) derives its name from the region of Greece called Magnesia (as is the names for *magesium* and *magnetite*). Too reactive to be found as a free element in nature, manganese occurs in numerous primary and secondary minerals—often in combination with closely related iron—comprising 0.1% of the the planet's crust. It most commonly occurs in oxides and carbonates, but also to a lesser extent in sulfides and silicates.

Manganese is a silvery gray, multivalent “s-block” transition metal that resembles iron. It is hard, heavy, and brittle; fuses with great difficulty (1246° C; 2275° F); but oxidizes easily in air, gaining a dark brown surface tarnish. Despite its occurrence with and resemblance to iron, the element and its common ions are *paramagnetic* (attracted by externally induced magnetic fields).

The most important manganese mineral from an economic viewpoint is the dioxide pyrolucite (usually found as *wad*, which is a mixture of manganese oxides much like *limonite* is a mixture of iron minerals), but other important ore minerals include braunite, psilomelane (romanachite), and

rhodochrosite.

South Africa hosts about 80% of the world's known manganese deposits, mainly near Hotazel in the Northern Cape Province with an estimated 15 billion tons in reserves. The country produced 3.4 million tons in 2011. However, other important sources include Ukraine, Australia, India, China, Gabon, and Brazil.

It is interesting to note that while seawater itself contains only about 10 ppm (parts per million) of dissolved manganese, an estimated 500 billion tons can be found on the ocean floor in the form of manganese nodules! Unfortunately, it is for all practical purposes unavailable for mining due to the great depth of the ocean. Attempts to find economically viable methods of harvesting manganese nodules were abandoned in the 1970s, but not before one very interesting historical footnote.

In 1972, the CIA, under a plan called Project Azorian, commissioned Howard Hughes' ship, the *Hughes Glomar Explorer*, to harvest manganese nodules from the sea floor. That event coincidentally triggered a rush of activity to collect manganese nodules, which, of course, was not actually feasible. The real mission of *Hughes Glomar Explorer* was to



raise a sunken Soviet submarine, the *K-129*, with the goal of retrieving Soviet code books!

Chemistry

Like nickel, which was covered in an earlier issue of *Discover Minerals*, manganese is part of the iron group of elements, with similar qualities.

Common oxidation states of manganese are +2, +3, +4, +6, and +7. The most stable of these is +2, which imparts a pink coloration to its compounds. Many manganese(II) compounds are known, such as manganese sulfate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), an important commercially produced inorganic compound used as a precursor to obtaining metallic manganese. In nature, this oxidation state is also recognized in the minerals rhodochrosite (a carbonate) and rhodonite (a silicate).

The +3 oxidation state is known in inorganic compounds such as manganese(III) acetate, but these are powerful oxidizing agents that are quite prone to *disproportionation* (a specific type of redox reaction in which an element from a reaction undergoes both oxidation *and* reduction to form two different products), forming manganese(II) and manganese(IV) compounds. Solid compounds of manganese(III) are characterized by a distinctive purple-red color.

The +5 oxidation state is produced by dissolving manganese dioxide in molten sodium nitrate, and manganate(VI) salts are produced

by dissolving Mn compounds, such as manganese dioxide, in molten alkali while exposed to air. These compounds are blue and green respectively, are strong oxidizing agents, and are also vulnerable to disproportionation.

Those compounds where manganese is in oxidation state +7, which are restricted to the unstable oxide Mn_2O_7 and compounds of the intensely purple permanganate anion MnO_4^- , are also very powerful oxidizing agents. Permanganate compounds are purple, thus they are used to give glass a violet color. Potassium, sodium, and barium permanganates are all potent oxidizers. Potassium permanganate, also called Condy's crystals, is used as a laboratory reagent, because of its oxidizing properties; it is also used as a topical medicine.

In nature, manganese occurs in one stable isotope, Mn-55. However, eighteen radioisotopes have been discovered, the most stable being Mn-53 with a half-life of 3.7 million years. Others include Mn-54 with a half-life of 312.3 days, and Mn-52 with a half-life of 5.591 days. All of the remaining radioactive isotopes have half-lives on the order of minutes to a few hours.

Manganese also has three metastable states (a phenomenon in chemistry and physics when a dynamic system spends an extended time in a configuration other than the system's state of least energy),

primarily Mn-53 that decays to Cr-53 with a half-life of 3.7 million years. Mn-53 is relatively rare, produced by *cosmic ray spallation* (a form of naturally occurring nuclear fission and nucleosynthesis that occurs when ions of various elements, protons, and/or electrons collide with other nuclei) on iron. The others are Mn-46 and Mn-65. The Mn/Cr relationship provides evidence for nucleosynthetic processes just before coalescence of the solar system.

History

Manganese compounds have found extensive use since prehistoric times. In Gargas, France, cave paintings that are over 25,000 years old indicate that pyrolucite had been in use as a pigment since at least the Stone Age! It is speculated that the famous Spartan steel derived its superior strength and hardness from the manganese content of Greek iron ores. Egyptian and Roman glassmakers used manganese compounds to either add or remove color from glass, a practice that continued through the Middle Ages to modern times, as evidenced in 14th-century Venetian glass.

Since manganese dioxide was already in use by glassmakers, the compound was thus available to alchemists who converted it to permanganate, a useful laboratory reagent. In 1774, Swedish chemist Carl Wilhelm Scheele discovered a new element, chlorine, by reducing

A Collection of Manganese Minerals

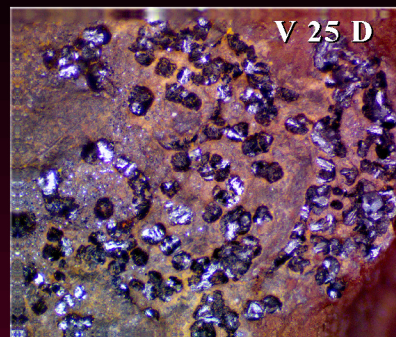


Hausmannite

*Aggregate of crystals with
Andradite and Calcite.*

Specimen 1 x 1.5 inches
N'Chwaning II Mine
South Africa

Rhodochrosite
Granular aggregate with Calcite.
Specimen 5.25 x 3.25 inches
Unknown location



Chalcophanite

Spear-shaped crystals.

Mohawk Mine
Mountain Pass, CA



Rockbridgeite

*Radiating crystal mass with
white Feldspar.*

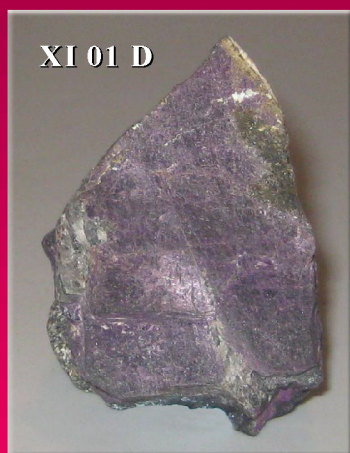
Specimen 2 x 1.25 inches
Bavaria, Germany

Rhodonite
Compact massive specimen
Specimen 2.125 x 1 x 1.75 inches
Silverton, CO



Psilomelane

Solid botryoidal mass.
Specimen 2.25 x 1.5 inches
Unknown location



Purpurite

Massive cleavage fragment.
Specimen 1.25 x 1.75 inches
Black Hills, SD

Franklinite
Euhedral crystals in Calcite.
Specimen 4 x 3 inches
Sterling Mine
Ogdensburg, NJ



Pyroxmangite

Compact massive specimen
Specimen 2.5 x 1.5 inches
Sunnyside Mine
Silverton, CO

All specimens from the G. Miles Lehman Collection

A Collection of Manganese Minerals

Some minerals that do not normally contain manganese do so as an impurity that often accounts for a change in color, or response to short-wave UV radiation.



VII 08 D

Manganocalcite

Marble with Franklinite and Zincite.

Specimen 3 x 2.75 inches

Sterling Mine

Ogdensburg, NJ



VII 27 C

Manganoan Hydrozincite

Purple carbonate with colorless Smithsonite crystals..

Specimen 3 x 2.25 inches

Argentana Mine

Goodsprings, NV



IV 07 D

Zincite

Red crystals with black Franklinite in Calcite.

Sterling Mine

Ogdensburg, NJ

All specimens from the G. Miles Lehman Collection

manganese dioxide with hydrochloric acid (though he did not actually recognize his discovery as a new element, thinking instead that it was an oxide). Scheele and others were aware that manganese dioxide contained a new element, but none were able to isolate it until Gahn later in 1774.

Applications

Manganese has no satisfactory substitute in its major applications in metallurgy, although zinc and vanadium can sometimes substitute for the element in its minor applications (e.g., manganese phosphating). It is essential in the steel industry for its ability to remove excess sulfur, oxygen, and phosphorous from iron in order to improve malleability.

In fact, steelmaking accounts for nearly 90% of the demand for manganese, which is a key component in stainless steel. The workability of steel at high temperatures is improved by adding a small amount of manganese, which forms a high-melting sulfide that prevents the formation of iron sulfide, thus making the steel easier to work with.

With a content of 8 to 15% manganese, steel gains a high tensile strength that finds valuable use in many specialized products. For instance, in 1882 English metallurgist Sir Robert Hadfield discovered manganese steel (mangalloy), one of the first steel alloys. Also known as *Hadfield steel*, which contains 12% Mn, it is a high-impact steel that's resistant to abrasion once in its work-hardened state. It was used for British military helmets, and later became the famous "Doughboy" helmet worn by the U.S. military in WWI.

The next largest consumption of manganese is alloying with aluminum for producing beverage cans. Manganese increases aluminum's resistance to deterioration by absorbing impurities that lead to galvanic corrosion.

The element finds additional use in many applications in both the auto and chemical industries. For instance, as *methylcyclopentadienyl manganese tricarbonyl*, it is used as an additive in unleaded gasoline to boost octane rating and reduce engine knocking.

Manganese dioxide is used for several purposes, including as a reagent in organic chemistry for the oxidation of benzylic alcohols; the production of oxygen and chlorine; the removal of the greenish tinge in glass caused by trace amounts of iron contamination; to impart a stronger green color—or even pink—to glass; as a brown pigment for paint; and in dry-cell batteries as an electron acceptor from zinc.

The metal also finds usage in coinage. Aside from the war years of 1942-45 when manganese replaced much scarcer nickel, modern dollar coins are made of a brass that contains 7% Mn to duplicate the electromagnetic properties of a previous identically sized and valued coin in the mechanisms of vending machines.

Finally, manganese is an important element for human health, essential for development, metabolism, and the antioxidant system. The human body contains about 12mg of manganese, mostly in the bones; the remainder is concentrated in the liver and kidneys. While the element is a required trace mineral for all living organisms, in greater quantities it is a neurotoxin. Excessive exposure or intake may lead to a variety of impairments. Although manganese compounds are less toxic than other more widespread metals such as nickel and copper, manganese poisoning has been linked to impaired motor skills, cognitive disorders, and a condition known as *manganism*, a neurodegenerative disorder with symptoms similar to Parkinson's disease.

While most specimens of manganese-bearing minerals are rather non-descript, dull in luster, and occur in various shades of unspectacular brown and black, some, such as rhodochrosite, rhodonite, and pyroxmangite are quite attractive pink minerals that find their rightful place in all worthy collections. Naturally, there are others that are quite rare (e.g. chalcophanite, hetaerolite) that are hard to obtain, but should not be overlooked in collections of rare minerals.

The varieties of manganese have attracted the attention of chemists for many years past. Yet the investigations have attained little more than to discover those properties which might serve to distinguish them from other kinds of stones; at least it is not generally known that anything further has been done with them besides the dissertation of the year 1767, in which Westfield undertook to demonstrate their constituents. Nevertheless, my experiments will plainly show that he has been too hasty in this. It is unnecessary to enumerate the many varieties of manganese that I examined, because they all agree in their chief properties.

A clear colorless glass flux always becomes more or less red from manganese, entirely according to quantity; and if the flux is a little alkaline, the color inclines to violet. It is known that arsenic, gypsum, and calx of tin destroy the red color in such a glass and render it clear and colorless. So far as the arsenic is concerned, the reason is evident from its constituents; for in this case the phlogiston of the arsenic unites with the manganese dissolved in the red glass, and takes away the color, and the acid of arsenic unites with the alkali of the glass. In this connection it is observed that the experiment succeeds even in a covered crucible, which would in no case go on with gypsum and calx of tin; but when charcoal powder is added to it, an effervescence arises, the red color disappears, and the glass becomes clear and colorless....

When a solution of manganese is diluted with much water, and is afterwards precipitated by caustic alkali, the precipitate comes down brown at the very beginning, and behaves like pure manganese. It is clearly seen here that the air in the water is sufficient to take up the inflammable principle in the manganese as soon as it is separated from its acid. For the same reason, the manganese precipitated from its solution by lime water, likewise falls down brown, but when more of a concentrated solution of manganese is mixed with it, and it is afterwards precipitated with caustic alkali, a white precipitate is obtained....

When an ounce and a half of phlogisticated manganese was distilled in a glass retort over a strong fire, a large quantity of aerial acid went over, together with some drops of water. While the retort was still warm, the manganese was poured out upon paper, whereupon it immediately became red-hot and kindled the paper.

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Tests for Manganese

Coloration imparted to various fluxes are the only simple tests necessary to confirm the presence of manganese in mineral samples, and are very sensitive and reliable.

Sodium Carbonate Bead Test: a sample fused in sodium carbonate and heated in an oxidizing flame will color the bead a characteristic bluish green color if manganese is present. Add a grain of potassium nitrate (KNO_3) to ensure oxidation. The bead is transparent when cold.

Borax Bead Test: a sample fused in borax and heated in an oxidizing flame will color the bead a characteristic purple to maroon if manganese is present. Bead turns colorless when heated in the reducing flame. The bead is transparent when cold.