Iron Ores

General Remarks

Advanced

- This planet consists of iron (32.1%), oxygen (30.1%), silicon (15.1%), magnesium (13.9%), sulfur (2.9%), nickel (1.8%), calcium (1.5%), and aluminium (1.4%); the remaining 1.2% are "trace amounts" of the 80 or so remaining elements. Most of that iron constitutes the core of the planet but we will not run out of iron compounds or *iron ore* found near to the surface for some time to come.
    - Why is iron so prominent in this (and other) planet ? Because planets were formed from the stuff bred inside the first stars. The reaction chain for generating energy by nuclear fusion starts with hydrogen and stops after iron has been bred. Iron, if you like, is the ash eventually produced by fusing hydrogen to helium, helium and hydrogen to lithium, and so on. When those first stars "burnt out" after a few billon years, some of them coughed up their ashes in a mighty supernova explosion. In time, new stars were formed. Some of these are still burning and visible at night. One (our very own sund) is only visible during the day from a clumped-together iron-rich ash ball called earth.
- From the viewpoint of chemistry, iron (like copper) is a tricky element that can form many oxides, sulfides, carbonates, and so on. All these compounds could be used for smelting iron but some are better for that purpose than others.
  Sulfides are usually bad news. We know that from smelting copper and expect similar problems when smelting iron. Moreover, sulfur in iron is really bad news, and I therefore will only mention iron sulfides briefly in what follows.
    - **Rich ores** are better then poor ores. What makes an ore rich? In the first place, the relative amount of iron it contains. I will give that number in percent (%). One kilogram of magnetite, for example, contains 0.724 kg of iron. If you get about 700 g of iron for every kilogram of magnetite ore you put into your smelter, you have a smelting efficiency of almost 100 %. That is far from the reality of ancient smelting, however.

Name	Formula	wt % Fe
Magnetite	Fe_3O_4	72.36
Hematite	Fe_2O_3	69.94
Goethite	FeO(OH)	62.58
Limonite	$FeO(OH) \cdot n(H_2O)$	52 (n = 1)
Siderite	$FeCO_3$	48.2
Bog iron	Limonite plus dirt	? Low
Pyrite	FeS_2	46.5
Wüstite	FeO	79

The better known iron minerals

- I have included FeO or **wüstite** even so, strictly speaking, it is not an iron ore since is not found in nature (forget some rare exceptions). It is, however, the iron compound that gets reduced in a smelter because it forms from all the other ores put into the smelter before the final reduction step that produces elemental iron takes place. It is also found in the slag produced during smelting.

- Below are pictures of "nice" ores. What went into real smelters can be seen here.

Major Ores

- **Magnetite; Fe_3O_4** (Lodestone).
  German: Magneteisenerz; Magneteisenstein, Hammerschlag.
  Magnetite is actually a mixture of Iron(II) oxide FeO and iron(III) oxide Fe_2O_3; summing up nominally to Fe_3O_4. The "II" and "III" refer to the number of bonds (= "arms" extended to meet other atoms) an iron atom will provide. Since oxygen has always 2 bonds, FeO is fine. Since 2 and 3 don't match, you need 2 Fe atoms with 6 bonds meeting 3 oxygen atoms with also 6 bonds for a match.
  Magnetite gets its name because it has the (rare) property of being magnetic. More to the point, magnetism got its

name because there was magnetite, possibly named after the place it was first found, for example ""Magnesia" in present day Turkey.
Magnetite melts at 1535 °C (2795 °F) and has a density around 5.2 g/cm^3.

- The German name "Hammerschlag" ("hammer blow") refers to the stuff coming off your hot iron when you beat it with your hammer. It's either iron oxide that has formed on your iron, or iron particles spritzing off that immediately oxidize in air. In either case the stuff is mostly magnetite.
  Here is a picture of rare magnetite single crystals:

Magnetite crystals

Source: Photographed in the Goslar; Germany museum.

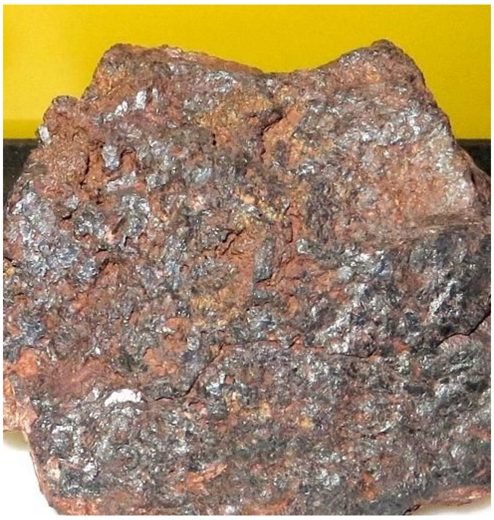
- Magnetite is the "richest" iron ore, it contains a bit more iron than haematite. It is rather common and found in large deposits. It may also be a part of the sand of "black beaches".
- The English name "**lodestone**", from "'leading stone" refers to the magnetic properties of magnetite. It is one of only two natural materials that can be permanently magnetized and thus are permanent magnets. In a compass, it shows the way.

Haematite or Hematite; Fe_2O_3 (Red Iron Ore).
German: Hämatit, Eisenglanz, Roteisenstein, -erz, Roter Glaskopf, Blutstein, Rötel.
Haematite is the most common iron oxide. It melts at 1565 °C (2849 °F) and has a density around 5.2 g/cm^3,

- The word "haematite" contains the Greek word "haima" for blood. You know this from words like "haematoma" = localized collection of blood outside the blood vessels or "haematologists" = (expensive) people who deal with bloody things. The reference to blood simply acknowledges that the stuff is red. Blood is red because its "working" molecule haemoglobin contains 4 iron atoms.
  Humankind used haematite because it supplies the color to ochre, some (powdered) clay colored yellowish / reddish by large amounts of incorporated haematite. Powdered ochre was used quite early - more than 100.000 years ago - for painting things red, reddish or yellowish
  Here are some pictures of haematite:

Haematite in a dense "glassy" form and Mesopotamian weights made from haematite

Source: Liverpool Museum, Merseyside, UK; Wiki commons



Haematite as it goes into smelters

Source: Photographed in the Schmalkalden "Neue Hütte" Museum

- Solid haematite doesn't look all that red but that changes when you powder it. Haematite is rather common and you find it in all kinds of shapes and forms, including dense and sort of glassy appearing pieces, used for making sculptures and jewelry as shown above.
  Haematite is the main ore for present iron smelting. It is neither the richest ore (that would be magnetite) nor the easiest to smelt (that might be siderite) but the most common one.

Goethite FeO(OH) (Brown Iron Ore, Brown Ironstone).
German: Ghoetit, Nadeleisenerz, Brauneisenstein, Brauner Glaskopf
Goethite was named in honor of **Johann Wolfgang von Goethe** (1749 - 1832), Germany's most famous writer. Goethe was also a "naturalist" and dabbled in science, including mineralogy. He also was a politician, e.g. "Minister of mining" in Weimar.
Goethite transforms to haematite before it melts, It has a densiy of 4.3 g/cm^3.

Goethite

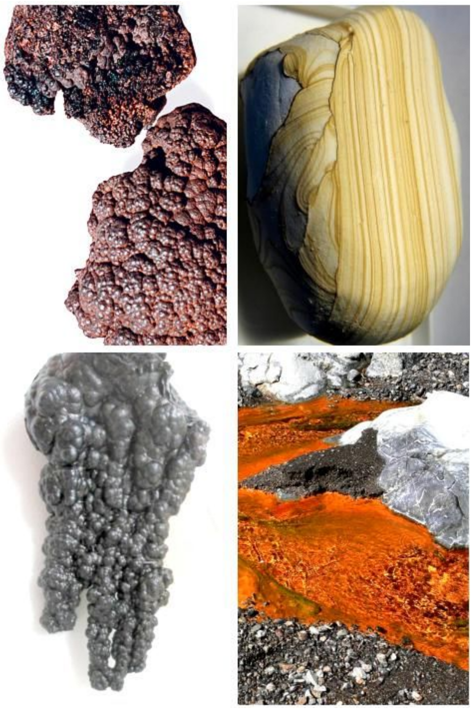
Source: Photographed in the Goslar Museum

- Goethite is related to limonite and bog iron (see below), and it was not before 1806 that it was recognized as a mineral in its own right. To honor Goethe, some dignities suggested to name the "new" mineral after him, and there is a certain irony in the fact that the freshly found specimens were quite likely not what goes for Goethite today but "Lepidokrokit" (lepidocrocite), a mineral with the same composition but different structure. After a few gyrations the name eventually stuck and even made in into plenty of other languages.

- Goethite is no longer important in iron making. Its importance in older times is unclear to me because it was not distinguished from siderite or bog ore. Goethite forms by "weathering" of more primary iron ores like magnetite or pyrite, involving a change from Fe(II) compounds to the more stable Fe(III) form. It thus is often found in the "gossan" (Eisenhut = iron hat) of iron ore deposits.
  Goethite then can be "pseudomorph", meaning it keeps the shape of the iron compound it formed from. It thus may appear in shapes (including nice "crystals") that do not express its own structure.
- While few people have ever heard of Goethite or know what it is, everybody knows about "**rust**". Rust is often a mix of iron oxides and hydroxide but primarily is Goethite.

Limonite $FeO(OH) \cdot n(H_2O)$ (Brown hematite, brown iron ore (also used for Goethite); lemon rock, yellow iron ore (if its orange / yellow).
German: Limonit, Brauneisenerz, -stein; Brauner Glaskopf .
Limonite, it appears, is Goethite (FeO(OH)) plus ***n*** molecules of "**crystallization water**" 1). Well **-** it isn't! It is actually not a real mineral or defined chemical compound. So why is there a good name for something that doesn't seem to exist?

- Because it is easy to find iron minerals in nature, often bright orange, that are *not* magnetite, haematite, goethite and so on, but "somehow" iron hydroxides. The tendency then is to name that stuff, and the name that stuck is *limonite*, after the Greek "leimon" = meadow. This alludes to its appearance in "*bog iron*", found in meadows and marshes.
  Limonite is some mixture of iron oxides and hydroxides, including goethite that one could also write as $Fe_2O_3{\bullet}H_2O$, i.e. as haematite with crystallization water and, e.g., lepidocrocite (also called esmeraldite or hydrohematite), jarosite (a pottassium-iron sulfate), haematite, maghemite (a kind of Fe(II)-deficient magnetite), hisingerite (a "watery" iron(III) silicate), pitticite (a "watery" iron-arsenic sulfate / oxide), and God knows what else. It is typically not recognizably crystalline but amorphous or simply "messy". You might also call limonite "natural rust". Here are a few pictures:



Limonite (Lower right: dried up rivulet)

Source: Internet at large

- Limonite, as the pictures show, comes in many variants, and some of the stuff shown as "limonite" might actually be Goethite proper. Some people subsume "bog iron" under limonite but here I will give it its own paragraph.
  Limonite, like goethite, usually forms from the weathering of more primary iron ores like hematite or magnetite, but also from the oxidation and hydration of iron-rich sulfide minerals and more complex stuff like olivine (iron plus some other metal silicate; extremely common in the earth's crust but not stable close to the surface).

Bog Iron

German: Raseneisenerz, -stein

Bog iron is often the only available iron *ore* in regions without mountains. This includes my area ("North German Plain"), pretty much all of The Netherlands, large parts of Hungary, and so on. It is not a well-defined substance but typically "dirt" like clay, sand, peat and mixtures thereof that got impregnated with limonite and compacted to a smaller or larger degree.

- Bog iron was neither formed way back when rocks and primary ores were formed in the teenage time of the planet, nor was it formed by direct "weathering" of those ores like goethite or limonite. It was formed by *first* dissolving some ore completely in oxygen-free water deep down in the bowels of the earth or in bogs, and *second,* by precipitating the dissolved iron as some kind of (hydrated) oxide whenever oxygen was available, i.e. whenever the water made it to the surface.

  Many modern humans, in particular those of the American persuasion, have degenerated to a point where they drink water, in particular mineral water, without a good reason (e.g. like being stranded on a small uninhabited island). If you look at a mineral water bottle, you usually find that on the one hand there is lot of strange stuff in there that you would hate to meet outside the bottle [2)], but that the bottling company "***de-ironed***" its product, even so imbibing iron is supposed to be healthy. The reason is that usually there is too much of it. If you don't take it out, the water tastes bad and looks brownish.

  What we learn is that water from deep down can (and typically will) contain a lot of dissolved iron (and other stuff). In the formation of bog iron three things need to be considered:

  1. Dissolving iron bearing minerals in water.
  2. Precipitating iron bearing minerals from water.
  3. Forming big solid pieces of bog iron, i.e. a rocky matter containing a lot (up to 70 %) of limonite.

  This looks like straight-forward elementary chemistry. It's not, or only up to a point.

- The straight-forward part includes *dissolution* of iron compounds in hot "mineral" water, or water saturated with carbonic acid (H_2CO_3). You know it as carbonated water or "soda", a solution of carbon dioxide (CO_2) in water that also produces carbonic acid. The iron will be dissolved as iron (II) or Fe^{2+}, i.e. it is an ion with two positive charges. This iron-carbonate saturated water then gets stuck in a bog, maybe, where it will become "oxidized" to iron (III) or Fe^{3+} under the influence of oxygen and because the water turns more acidic since organic stuff rots in it and produces humic acid (you don't want to know the formula). Water cannot dissolve a lot of iron(III) and precipitation starts, forming solid limonite or some kind of iron oxide / hydroxide. This happens primarily at whatever solids are bordering the water, and mixtures of sand / clay / peat with iron ore particles form; with the iron ore part increasing as time goes on. The process of bog iron formation may take thousands of years, but some bogs can be "harvested" about once a (human) generation.

  So much to the easy (not really) part.

  The tricky part, not really fully understood at present, consists of Mother Nature interfering, showing the chemists a trick or two. The real process of bog iron generation must include the role of *living beings*, weird kinds of bacteria in this case. Some of these guys live from eating iron-sulfur minerals (they are after the sulfur), pooping iron(III) and sulfuric acid in turn. That's why we get iron (III) dissolved in water. If you see a kind of iridescent and oily film on the surface of bog water, it signifies the presence of those bacteria (or just oil pollution). If you own a bog with this "iron slick" on top (the Icelandic name for this film), you have best conditions for growing your own bog iron.

  Now let's look at some pictures:

Bog iron and the bog iron wall of the Neuhardenberg parish office.

Source: SITSCHICK, H., LUDWIG, F., WETZEL, E., LUCKERT, J. & TH. HÖDING: "Raseneisenerz – auch in Brandenburg ein mineralischer Rohstoff mit bedeutender wirtschaftlicher Vergangenheit" (Bog iron ore – also in Brandenburg a raw material with important economical history), Brandenburg. geowiss. Beitr., **12** (2005), 1/2S. 119-128

- In areas containing the huge bogs from the wet end of the Ice Age that are now meadows or grass-land (German "Rasen"), the iron-rich layer was solidified and compacted into a more rock-like consistence, found right below the "Rasen". Huge deposits of bog iron in many "lower lands", formerly bogs, allowed these areas not only to have an early iron production, but also supplied "rocks" or stones for buildings, a commodity also in short supply in these parts of the world. However, bog iron might be a rather inferior ore, making iron and steel production more difficult. Low-land warriors in the North thus needed to be more inventive for getting good swords, e.g. by raiding and killing the guys in the South.
  However, Darrel **Markewitz**, a blacksmith running the **Wareham Forge** in Ontario / Canada and one of the early practitioner of iron smelting we know form other modules, pointed out to me that there are quite rich ores out there - 58 % - 68 % - that are designated "bog iron", and that it is sensible to distinguish between "primary" bog ion and the rest. One might need to look at its history: was it produced during the last few (thousand) years or in the remote past, what has happened since its primary production, and so on. Darrell also supplied an interesting article about bog iron formation that I'm happy to share with you. So good iron and steel can result from (primary) bog iron and North Europeans may have been aware of that.
- Bog iron contributed to the economical success of some in many ways. For example, "it was smelted at Lynn, Massachusetts with oyster shells and charcoal to be hammered into bars (*of iron*) to be traded for slaves in Africa, which were sold in the Caribbean for sugar to be brought to New England for fermentation and distillation into rum to be sold to the Indians, making the fortunes of Boston and Providence", knows Wikipedia.
  The nobility in my state, by the way, also made fortunes from the slave and rum trade. I doubt, however, that bog iron was involved.

Siderite $FeCO_3$ (chalybite, iron carbonate).
German: Siderit, Eisenkalk, Eisenspat, Spathiger Eisen, Stahlstein, Eisencarbonat, Raseneisenerz (sic!), Spateisenstein, Stahlstein, Weißeisenerz.
Siderite is a well-liked ore because it is relatively easy to smelt, if not as rich as some others. It can be reduced in two simple steps. First, just by getting hot, the carbonate breaks down into FeO and carbon dioxide ($FeCO_3 \Rightarrow FeO + CO_2$). With hot carbon monoxide, metallic iron is produced ($FeO + CO \Rightarrow Fe + CO_2$). That is considerably simpler chemistry than what needs to be going on for the other ores, and that is one of the reasons why siderite is easy to smelt.

- Siderite got its name by some unimaginative Frenchman who just used the Greek "sideros" = iron for naming a mineral that had been know and used for millennia under other names. It is a simple carbonate and quite ubiquitous. One particular well-know huge deposit (400 Mio tons) is in present-day Austria. It has been mined in Roman times and before and it is mined today. 250 Mio tons have been removed so far.

Part of the "Erzberg" (Ore Mountain) in Austria

Source: Internet, Tourist information.

Pyrite (fool's gold)
German Pyrit, Schwefelkies, Eisenkies, Katzengold, Narrengold
Pyrite is the most common iron sulfide and more or less useless for making iron. One could roast it, like the copper sulfides, driving out the sulfur - but why should one? There is enough sulfur-free iron ore around.

- The name pyrite comes from the Greek "pyr" = fire and refers to a special property of pyrite: It creates sparks when struck with anything hard like steel or flintstone. It is called "fool's gold" because it looks just like gold. If you are ever tempted: pyrite is hard and light, gold is soft and heavy.
  Single crystals occur as perfect cubes and are easy to find. The cubes below are about 2 cm in size. The small crystals are embedded in quartz.

Pyrite

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[1] Crystallization water" (or "water of crystallization", "water of hydration") is actually a murky term that describes that many simple inorganic compounds or "salts" exist as water-free "anhydrides" (e.g. copper sulfate $CuSO_4$ or tin chloride $SnCl_2$) but also in "hydrated" form containing "water". The crystal structure of the anhydrides is usually not very complex - in contrast to the "hydrated" forms. Since chemists typically work with liquids and gases, they tend to dissolve everything solid in water or watery stuff like acids, and the result then is the same for compounds with or without crystallization water. The hydrated forms simply release a bit of water upon dissolving. That is the reason why the crystal structure of the hydrated stuff is often not known and the chemical formulae are written like this: $CuSO_4 \bullet 5H_2O$ = copper sulfate pentahydrate, or $SnCl_2 \bullet 2H_2O$ = tin chloride dihydrate. The "•" sign indicates that the structure is unclear but that you get as much water as given behind the sign if you dissolve the stuff or roast it, driving out the water.
"Goethite , for example, could also be written as $Fe_2O_3 \bullet H_2O$, i.e. as haematite with crystallization water.
If you look at the solids, the story is quite different now. The "water" is an intrinisic part of the crystal structure, and that can be quite complicated. In nature the hydrated stuff often is more stable than the anhydrides and might form beautiful crystals. Contrariwise, it also can be amorphous.
We know even more. If you bothered to look at the phase diagram of salt water, you see that the hydrated stuff simply embodies the various phases you can get in the system "salt compound" - water. Nice to know - but it doesn't make things simpler, just clearer.

[2] Look at what you encounter in a bottle of mineral water besides water and hydrogen carbonate: Sodium, potassium, magnesium, chloride, sulfate,..., things you would normally not imbibe while sober. In contrast, the contents of a bottle of beer are: beer. All of it healthy.