

# Oxides and Hydroxides

The Earth's Crust - the Ultimate Reservoir  
of Oxygen and Hydrogen in the Planet



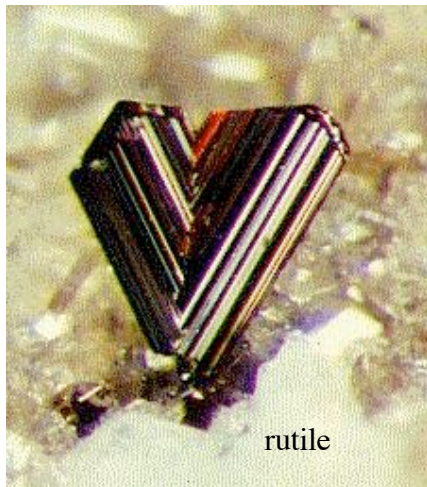
## Oxides and Hydroxides

- Oxides
  - Hard, dense, refractory minerals
  - Generally occur as accessory igneous and metamorphic minerals, and resistant detrital sedimentary grains
- Hydroxides
  - Lower in hardness and density
  - Dominantly occur as secondary alteration and weathering products

# Oxides

<b><math>X_2O</math> and <math>XO</math> types</b>			
Cuprite	$Cu_2O$		
Periclase (Zincite)	$MgO$ $ZnO$		
<b><math>X_2O_3</math> type</b>		<b><math>XY_2O_4</math> type</b>	
<b>Hematite Group</b>		<b>Spinel Group</b>	
Corundum	$Al_2O_3$	Spinel	$MgAl_2O_4$
Hematite	$Fe_2O_3$	Gahnite	$ZnAl_2O_4$
Ilmenite	$FeTiO_3$	Magnetite	$Fe_3O_4$
		Franklinite	$(Zn,Fe,Mn)-$ $(Fe,Mn)_2O_4$
		Chromite	$FeCr_2O_4$
<b><math>XO_2</math> type (excluding <math>SiO_2</math>)</b>			
<b>Rutile Group</b>			
Rutile	$TiO_2$	Chrysoberyl	$BeAl_2O_4$
Pyrolusite	$MnO_2$	Ferrocolumbite	$(Fe,Mn)-$ $(Nb,Ta)_2O_6$
Cassiterite	$SnO_2$		
Uraninite	$UO_2$		

## Rutile $TiO_2$

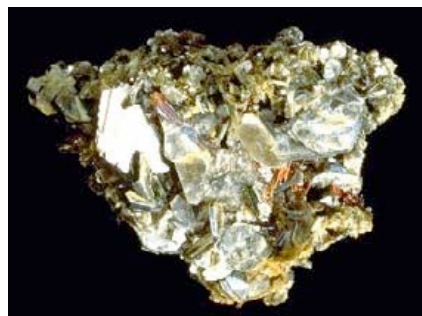


Occurs in granites and mica schists; an important Ti ore

Tetragonal, adamantine luster

Hardness: 6-6.5

Density: 4.18-4.25



## Rutile ( $\text{TiO}_2$ ) in Quartz ( $\text{SiO}_2$ )



Other Ti oxide polymorphs:  
Anatase, brookite (orthorhombic)

## Rutilated Quartz



### Health Qualities

Regeneration of tissue throughout body.  
Enhances life-force. Strengthens immune system. Stimulates brain functions.

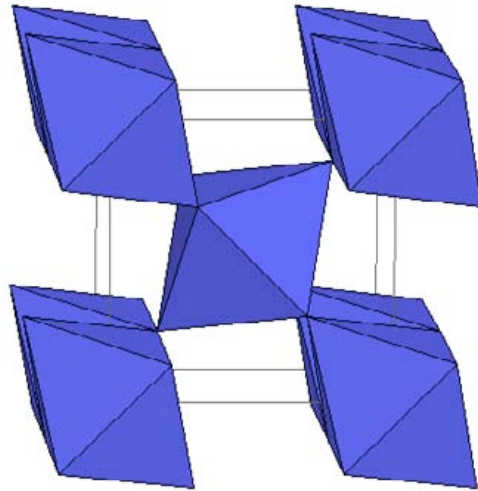
Eases depression, facilitates inspiration.  
Increases clairvoyance. Highly electrical, more intensity than clear quartz.

Pierces through layers of physical/emotional/mental density.  
Transmutes negativity.

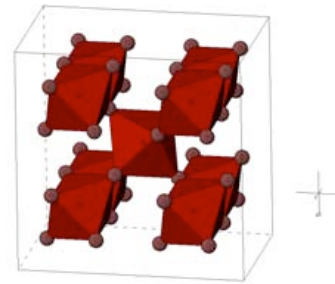
Enhances communication with Higher Self and Spirit Guides.

(<http://www.wicca.com/celtic/stones/stonep-s.htm>)

## Rutile - Octahedral Coordination of Ti with O



Oxygen  
octahedrons on Ti



Isostructural with stishovite (SiO<sub>2</sub>), pyrolusite (MnO<sub>2</sub>), and cassiterite (SnO<sub>2</sub>)

## Corundum Al<sub>2</sub>O<sub>3</sub>

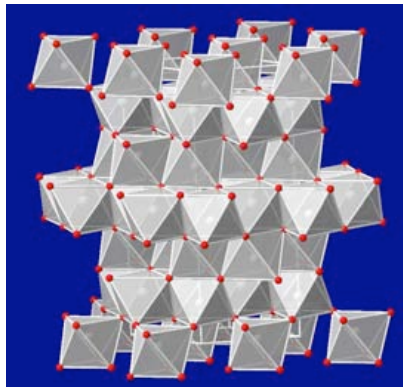


## Ruby and Sapphire



Corundum is often used as an abrasive, but colored by certain ions gives precious stones. When the  $\text{Cr}^{3+}$  replaces some of the  $\text{Al}^{3+}$  it's colored red and is called ruby. When a small amount of the  $\text{Al}^{3+}$  is replaced by  $\text{Ti}^{3+}$  instead, the color is blue and gives sapphire.

## Corundum



Corundum can be described as a hcp structure with the oxygen at the lattice points and two-third of the octahedral holes occupied by aluminum atoms.



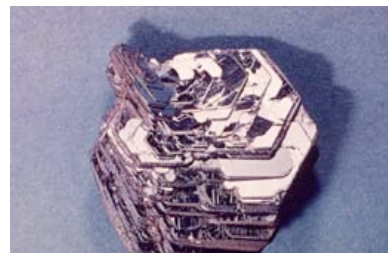
Ruby with Cr zoisite and hornblende

## Hematite $\text{Fe}_2\text{O}_3$



An ore of Fe and cement in sandstones (red beds)

All  $\text{Fe}^{3+}$



var. specularite

NAME: The name "hematite" is from the Greek [haimatites,] meaning "bloodlike," which is in reference to the vivid red color of the powdered mineral.

LEGEND and LORE: Hematite was used by Galen for inflamed eyelids and headaches, and by Pliny for blood disorders. Egyptians valued it as a cure for hysteria.

MAGICAL PROPERTIES: Hematite has long been associated with psychic awareness. In addition, some people believe that it assists in astral travel. "A scrying: In a darkened room, light a red candle. Settle before it and hold a large piece of hematite so that the candle's flame is reflected on it. Gaze at the reflection and visualize a question. The answer will come to you." (Cunningham)

HEALING: Hematite is a principal blood purifier among stone healers. It can be placed anywhere on the body for this purpose, or worn as a ring, pendant or necklace for continuous healing. It is also considered a grounding stone, which makes it useful for those people who have difficulty concentrating on the "here-and-now". Shamans historically have believed that Hematite, placed over the location of an illness, will draw the "spirit" of the illness out of the patient and into itself.

## Hematite



The red streak is diagnostic!



Red Beds - Hematite Cement in Sandstone

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UTAHREDOCKS.COM

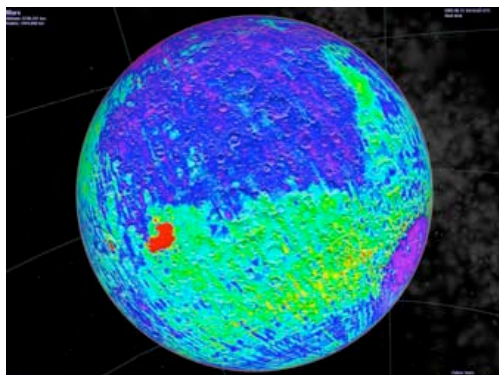


## Hematite on Earth

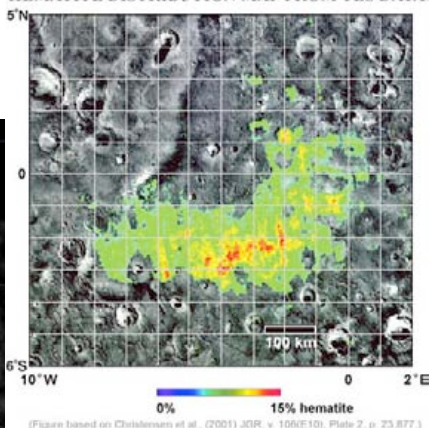
Navajo Sandstone, Monument Valley

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# Hematite on Mars



HEMATITE DISTRIBUTION MAP FROM TES DATA



(Figure based on Christensen et al., (2001) JGR, v. 106(E10), Plate 2, p. 23,877.)

# Mars or Mojave?

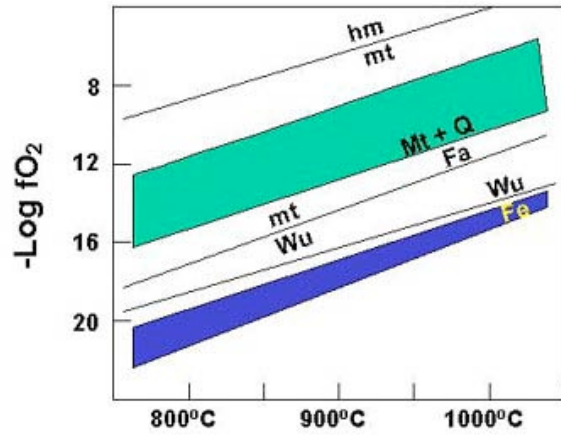




# Moon, Earth, Mars

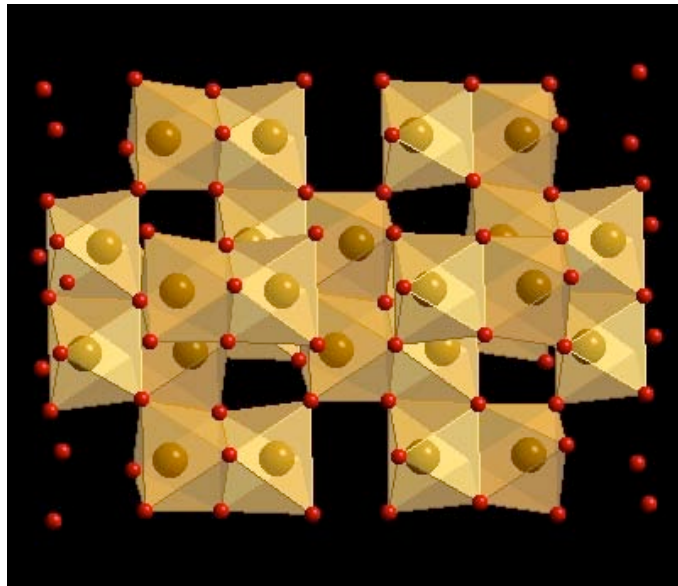
Hematite: Earth, Mars

Ilmenite: Moon

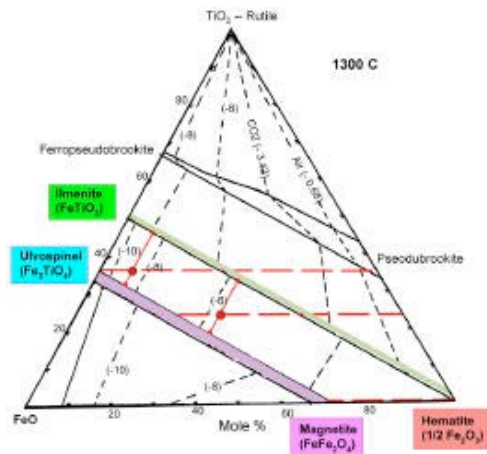


... a contrast in stages of oxidation

## Hematite - Isostructural with Corundum



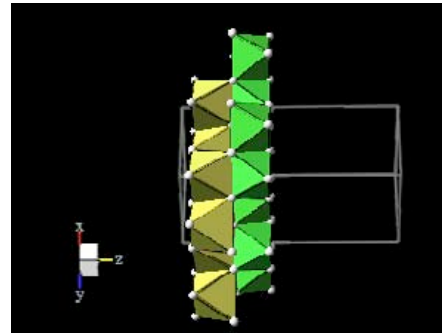
## ...and in Solid Solution with Ilmenite $\text{FeTiO}_3$ $\text{Fe}^{2+}$



Ilmenite, an important ore of Ti

## Ilmenite $\text{FeTiO}_3$

Alternating layers of  $\text{Fe}^{2+}$  and  $\text{Ti}^{4+}$  octahedra



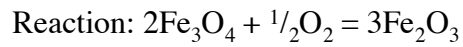
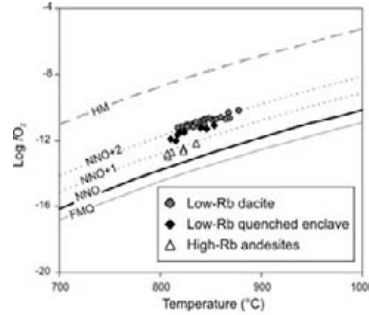
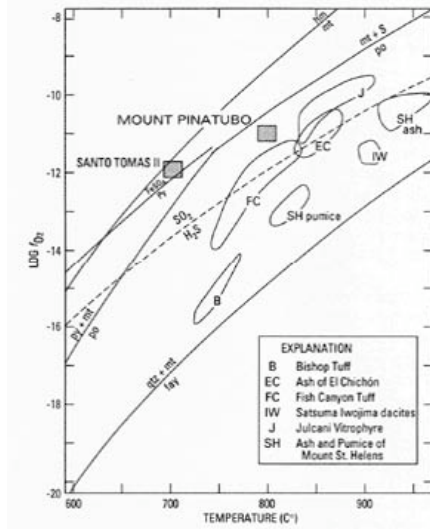
Ilmenite ore



Tins of paint

Ilmenite is the a source of titanium dioxide which is used in paints, fabrics, plastics, paper, sunscreen, food and cosmetics

# The Hematite - Magnetite Buffer

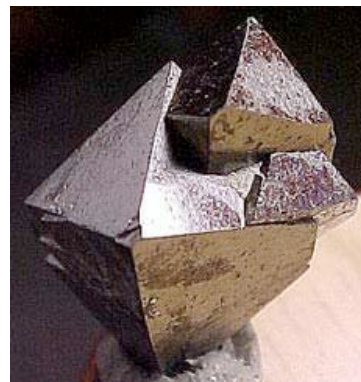
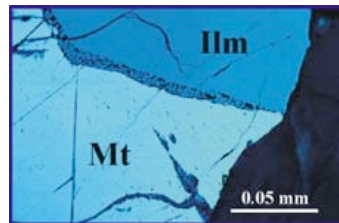


Magnetite

Hematite

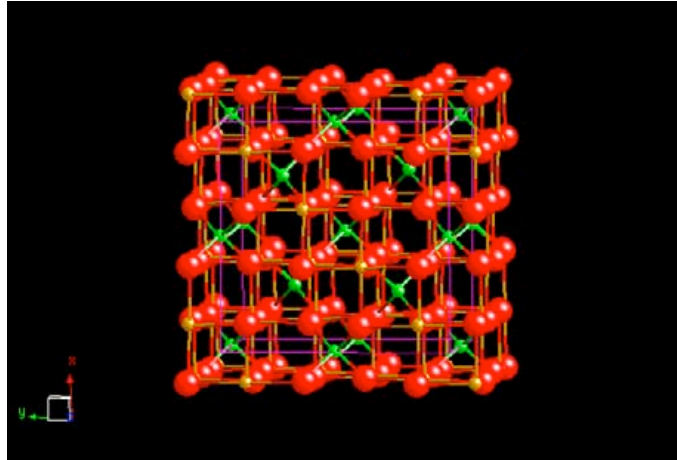
It takes a lot of oxygen to stabilize hematite!!

## Magnetite $\text{Fe}_3\text{O}_4$



..found in granites and the most important ore of iron

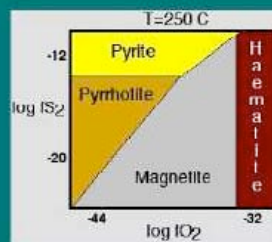
## Magnetite $\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$



An inverse spinel, with  $\text{A}^{2+}$  in octahedral sites,  $\text{B}^{3+}$  in both octahedral and tetrahedral sites

## Fe Oxide - Sulfide Relations

### Oxygen/Sulphur Phase Diagram



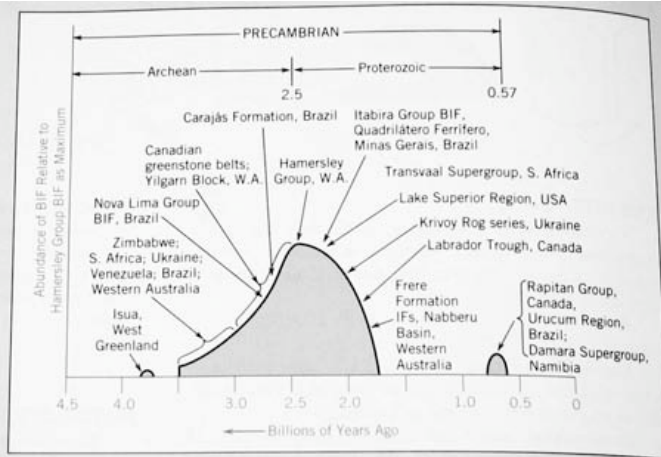
- At even higher sulphur fugacities, all Fe will go into pyrite or pyrrhotite, depending on temp.

Oxides or Sulfides? It all depends on the relative abundance of oxygen and sulfure.

## Banded iron formations- the oxidation of the atmosphere

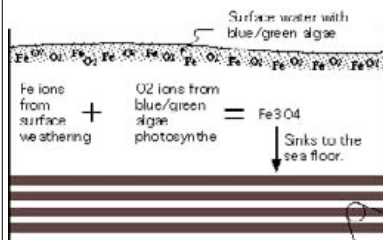
**Major iron ore minerals:**  
Hematite  
Magnetite  
Goethite

**To make steel:**  
Pyrolusite ( $MnO_2$ )  
Romanechite  
Chromite ( $FeCr_2O_4$ )  
Pentlandite ( $Fe, Ni)_9S_8$



Highly schematic diagram showing the relative abundance of Precambrian BIFs versus geologic time with several of the major BIFs or major BIF regions identified by name. The maximum at 2.5 billion years ago is represented by the BIFs in the Hamersley Basin of Western Australia. (From Klein, C. 2005. Some Precambrian iron-formations (BIFs) from around the world: Their age, geological setting, mineralogy, metamorphism, and origin. American Mineralogist 90: 1473-99).

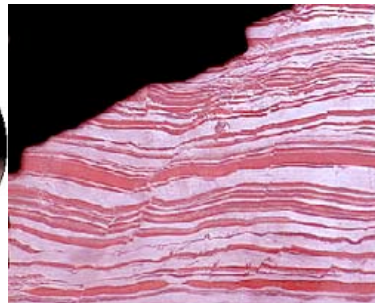
## Banded Iron Formations



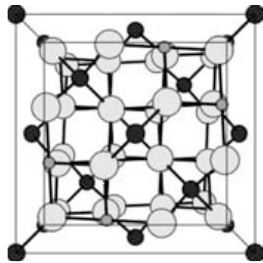
In an ideal setting, you would expect the magnetite-rich layers to exhibit a reversed graded bedding. Looking from the bottom up, this would involve a slow transition into the magnetite rich layers, representing slowly increasing O<sub>2</sub> levels in the upper sea water in response to the increasing population of blue/green algae. The upper contact of each magnetite-rich layer would be relatively abrupt, reflecting the sudden extinction of the population due to O<sub>2</sub> poisoning, and the resulting loss of available O<sub>2</sub> in the water to combine with the iron ions.



After combining the Fe and O<sub>2</sub> ions into Magnetite (Fe<sub>3</sub>O<sub>4</sub>), the mineral grains sink to the sea floor, where they accumulate into iron-rich and iron-poor layers.



## Spinel $MgAl_2O_4$

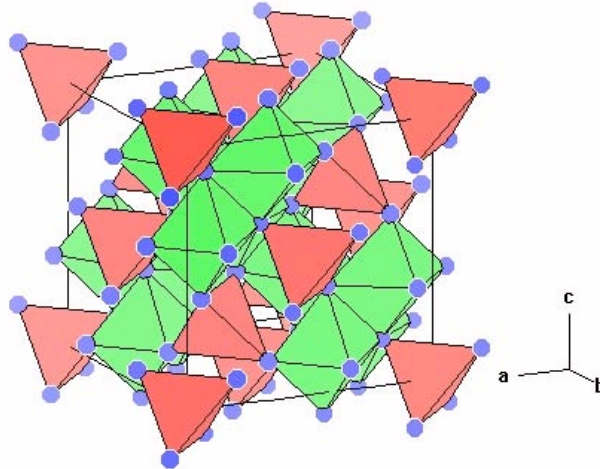


Spinel,  $A^{2+}$  in tetrahedral sites,  $B^{3+}$  in octahedral sites

## The Spinel group

Table 16.2 End Members of the Spinel Group ( $XY_2O_4$ )			
Normal Spinel Structure		Inverse Spinel Structure	
Spinel	$MgAl_2^{3+}O_4$	Magnetite	$Fe^{3+}(Fe^{2+}Fe^{3+})O_4$
Hercynite	$FeAl_2^{3+}O_4$	Magnesioferrite	$Fe^{3+}(Mg^{2+}Fe^{3+})O_4$
Gahnite	$ZnAl_2^{3+}O_4$	Jacobsite	$Fe^{3+}(Mn^{2+}Fe^{3+})O_4$
Galaxite	$MnAl_2^{3+}O_4$	Ulvöspinel	$Fe^{2+}(Fe^{2+}Ti^{4+})O_4$
Franklinite	$ZnFe_2^{3+}O_4$		
Chromite	$Fe^{2+}Cr_2^{3+}O_4$		
Magnesiochromite	$Mg^{2+}Cr_2^{3+}O_4$		

# Spinel



Mg = tetrahedral; Al = octahedral

## Chromite $\text{FeCr}_2\text{O}_4$



Abandon Cr mine in Maryland, 1828-1850



**Chrome Spinel - Ayrshire**

The only source of Cr!

\*Chromite typically forms in ultramafic complexes and mantle rocks

## Folded chromite layer in mantle harzburgite



Talkeetna Arc  
Alaska

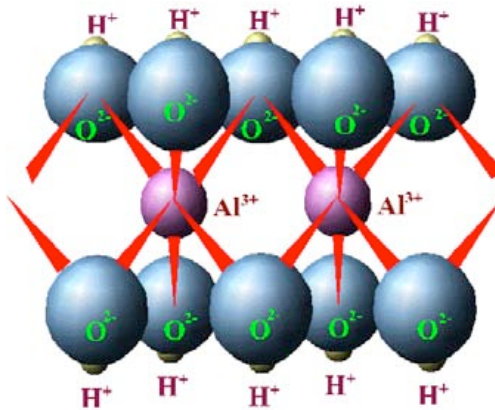
## Chromite “Reef”, Bushveld, RSA



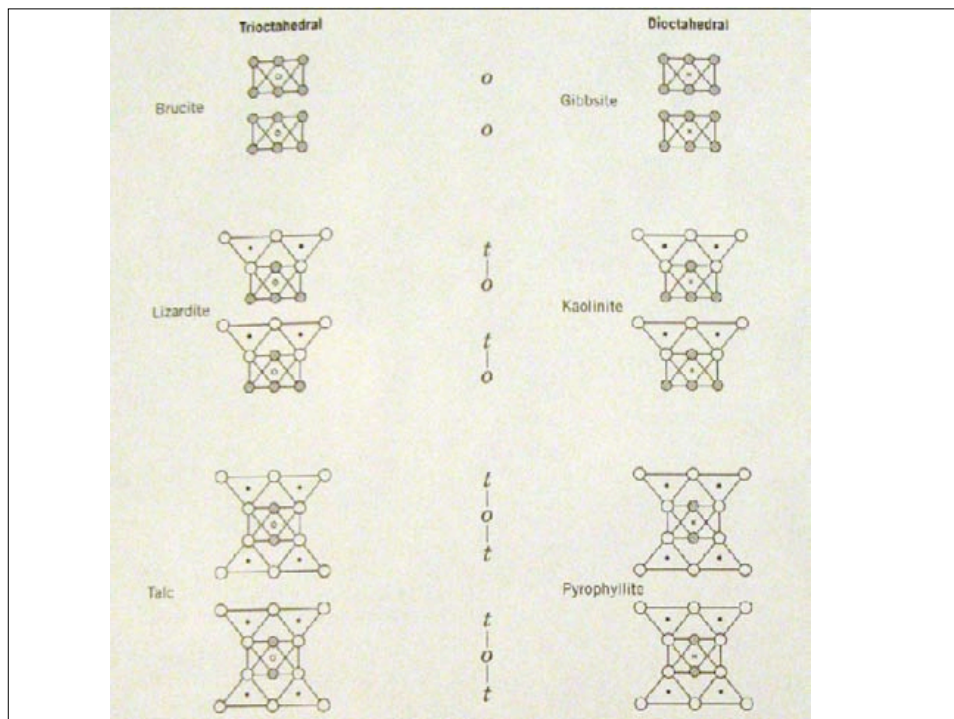
# The Hydroxides

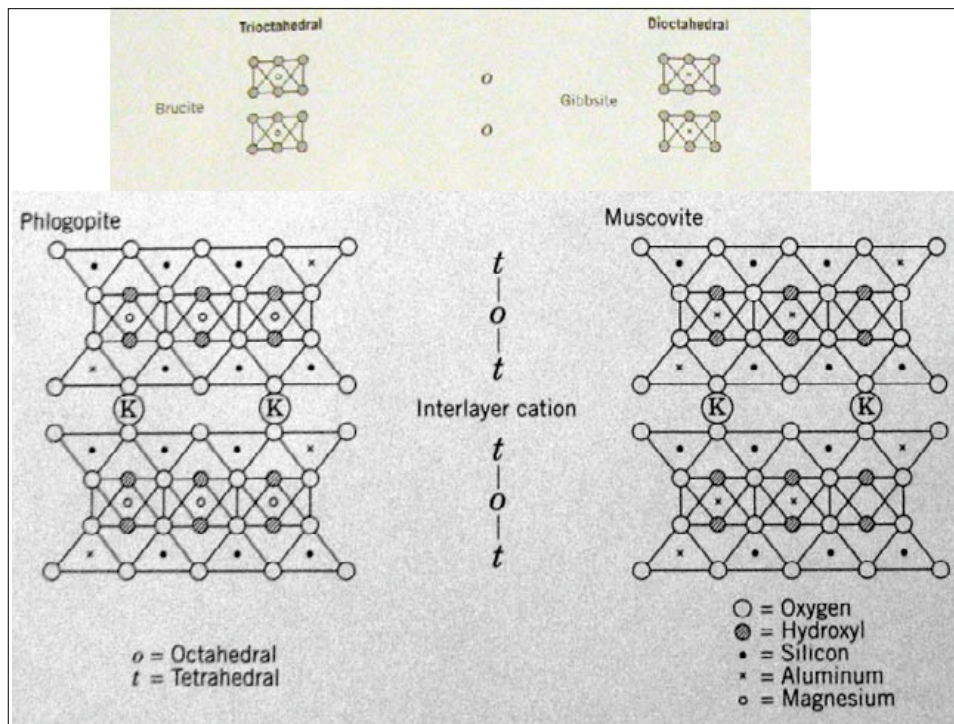


Brucite  
 $Mg(OH)_2$ , a  
 product of  
 serpentinization



Gibbsite  $Al(OH)_3$ , a principle  
 mineral of bauxite Al ore





## Bauxite



## Bauxite Mine, Australia

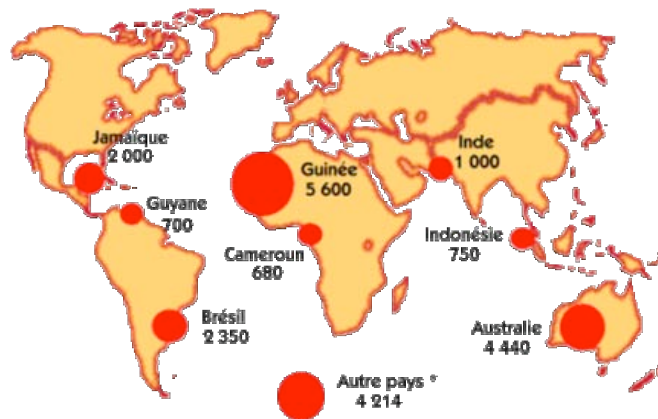


... bauxite ore ship

Composed of:  
Gibbsite  $\text{Al}(\text{OH})_3$   
Diaspore:  $\alpha\text{AlO}(\text{OH})$   
Boehmite:  $\gamma\text{AlO}(\text{OH})$



## World Wide Aluminum



Bauxite - the only Al ore worth it!

## Goethite $\text{FeO}(\text{OH})$



A principle mineral in limonite  
Limonite ( $\text{FeO} \cdot \text{OH} \cdot n\text{H}_2\text{O}$ )

An ore of iron and source of pigment

Yellow streak is diagnostic!

Lepidochrosite is a polymorph of goethite- platy crystals

Picture  
of the  
Day



Navajo Sandstone