## LECTURE #5

# IRON (Fe = Ferrum)

## METALS Year of Discovery

- 6000 BC GOLD
- 4000 BC SILVER
- 4200 BC COPPER
- 3500 BC LEAD
- 1750 BC TIN
- 1500 BC IRON
- 750 BC MERCURY
- 1746 ZINC
- 1751 NICKEL
- 1753 BISMUTH
- 1755 MAGNESIUM
- 1757 PLATINUM

- 1781 MOLYBDENUM
- 1789 URANIUM
- 1791 TITANIUM
- 1797 CHROMIUM
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## **Metals in Earth Crust**

	Parts per million
Iron	50,000
Copper	70
Lead	16
Tin	2
Silver	0.1
Gold	0.005

#### **Bronze and Iron Ages**



## IRON

35% of Earth's mass as Fe-Ni alloy 5% of Earth's crust Fourth most abundant in the Earth's crust Found as oxides: *hematite* (oxide), *limonite* (hydroxide), *magnesite (carbonate)*, and *siderite* (carbonate) Large deposits of iron sulfate (pyrite) Easily oxidized  $\Rightarrow$  rust  $\Rightarrow$  red spots and bands on rocks Pure iron is soft. Hardened with addition of coal Important element in human body (hemoglobin in the red blood cells, myoglobin in muscle cells)

## **Iron Timeline**

- 3,500 BC Egypt Meteoritic iron (7.5% nickel) soft 3,000-2,700 BC - Mesopotamia - First iron production Heating and hammering was used ~1,500 BC - Melting point was too high for ancient furnaces:
- Copper's melting point = 1,085°C
- Tin's melting point = 232°C
- Iron's melting point = 1,538°C
- 1,500-1,200 BC Hittites Made high temperature kilns First to smelt iron ⇔ IRON AGE

## Iron Timeline (cont'd)

India 1,200 BC - Greece 1,100 BC - Roman Era - Celtic expansion - Europe

Large scale iron production – 1,200-1,000 BC

1,000 BC - Charcoal was added to iron ⇒ steel

513 BC – Chinese made furnace capable of melting iron

18<sup>th</sup> Cent. England - Industrial Revolution - Refining pig iron to wrought iron (less carbon) ⇒ steel

## **Iron Age**

Started in Anatolia ~1,200 BC

Changed the civilization and culture because

of the new tools introduced

- Agriculture methods Metalsmithing
- Lifestyle many new objects
- Alphabetic characters 
   ⇒ Written language
- Religious practice Vedas, Hebrew Bible
- Artistic styles ⇒ decorations, designs
- Weapons, wars ⇒ destruction

### Diffusion of Metallurgy from Asia Minor in the Neolithic Era



### Copper, Bronze, and Iron Ores in Sub-Saharan, Central, and South Africa



## Iron furnace



## **Alloys of Iron**

Mixture of two or more elements in which the main component is a metal Modifying the properties for a desirable effect: Harder, non-corrosive, luster, color, cost Alloys of iron: Steel, stainless steel, cast iron, tool steel <u>Stainless steel</u>: carbon steel + chromium, nickel, molybdenum Cast iron: iron + silicon Tool steel: Iron + tungsten, chromium, vanadium, molybdenum High strength-to-weight: Alloys of aluminum + titanium + magnesium

## **Iron Uses**

Found in a wide variety of oxides (rust) Relatively soft metal Smelting process carbon added (2.1% = steel) Made possible our progress in construction and modern life. All means of transportation, appliances, etc. Core of modern civilization

#### **Iron in Humans**

From nutrition, iron passes into blood – attached to transferrin Iron deposits in **bone marrow** where red blood cells are formed Hemoglobin in red blood cells and Myoglobin in muscles cells ⇒ oxidation **Hemoglobin** = **heme** + globin (a protein) Heme has iron in its molecule In the lungs: Blood red cells (hemoglobin + oxygen) = oxyHb.  $\Rightarrow$ tissues  $\Rightarrow$  carboxyHb.  $\Rightarrow$  lungs  $\Rightarrow$  oxyHb. Chronic loss of blood  $\Rightarrow$  **Iron deficiency anemia** (heavy periods, lack of iron intake by children). Treatment: Iron by mouth for 1 yr. Overdoses of Fe by mouth are not recommended is iron overload + peroxides  $\Rightarrow$  free radicals  $\Rightarrow$  DNA damage

## MERCURY [Hydrargyrum (Hg)] (also Known as Quicksilver)

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## MERCURY



## MERCURY

Only liquid metal at standard temperature. Heavy. Found in the mineral cinnabar (mercuric sulfide) red pigment - vermillion **Extremely rare.** Mines in Italy, USA, Mexico Does not blend with other metals. May be kept in iron containers. Concentrated in ores. Dissolves gold and silver Extremely toxic – uses declined b/o environmental **safety.** Water through abandoned mines  $\Rightarrow$ ecological danger. Minamata disease in Japan.

### Cinnabar



## **Mercury – Timeline**

Found in Egyptian tombs ~1500 BC 500 BC - Amalgams Used in Egypt, Greece, Rome as cosmetic Medieval Age Alchemists : Hg = "First matter" Widely used by alchemists to obtain gold 1558 – Mercury used in silver extraction by Spain in Peru 2005 - Mines in China  $\Rightarrow$  2/3 of world producer using prison labor

### Minamata Disease

1936-1968 - Industrial pollution of water with methyl -mercury in Minamata Bay.

Severe neuro-muscular symptoms.

2000+ affected, 2000 died.

Chisso Corp. (chemical industry) not cooperating with the investigation.

Paid financial compensations

Cause: Methyl-mercury released in water ⇒ poisoned

fish and shellfish ⇔ eaten by fishermen

1965 – Second Minamata disease in Niigata

#### **Minamata Bay and Chisso Factory**



## **Mercury - Uses**

Dental filings – Amalgam with silver

Mercury-vapor lamps – electricity – Hg. vapor ⇒ S/W UV

light waves light ⇒ phosphor in tube ⇒ fluorescence

High temp. thermometers

Many medical uses have been **discontinued**:

- Thimerosal (vaccine preservative)
- Mercurochrome (topical antiseptic)
- Diuretics, anti-syphilis medications
- Glass thermometers
- Blood pressure cuffs

## **Dental Fillings**

#### 1. Dental amalgam fillings:

- Mercury 50%, silver, tin, and copper.
- 150 years experience,
- Solid, easily prepared, low cost.
- **2.** Resin Composite fillings:
  - 10 years experience,
  - Durable, cosmetic
  - Expensive

## Dental Filing = Amalgam of Mercury and Silver



## **Mercury lamps**



NICKEL (Ni)

## NICKEL

Rare metal in Earth's crust Usually iron-nickel mixture Corrosion-resistant Used in alloys Necessary in industry, metallurgy

#### **Nickel Production**



#### **Nickel Ore Reserves**





## **CHROMIUM**

Known to Chinese 3<sup>rd</sup> cent BC – Xi'an weapons without erosion because of chromium oxide coating of the bronze
Found in mineral crocoite (1761)
Extracted as iron chromate oxide
Resists tarnish

#### **Chromium - Uses**

Stainless steel and plating = 85% of commercial use Dye and pigment chrome yellow - aerospace

Diet - not sufficient information Chromium in drinking water: 25/35 cities = higher than the California proposed limits

#### **Chromium World Production**



## ZINC (Zn) (from German "Zinke" = prong)
### Andreas Sigismund Marggraf Discovered Zinc - 1746





Found as zinc ore *sphalerite* (zinc sulfide) Ores, associated with other metals (copper, lead) Large deposits: Iran, Australia, Canada, USA Refined zinc production increased 80% in 2009 Reserve lifetime is OK **Corrosive-resistant zinc plating of iron = galvanization** Important for humans "Exceptional biologic and public importance"

Zinc deficiency: Exercising, childhood growth, pregnancy, and diarrhea increase utilization

Zinc toxicity known

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## **Zinc - Timeline**

#### Alloy with copper ⇒ Brass

- 3,000 BC Aegean islands, Mesopotamia, Caucasus
- 2,000 BC Persia, Mesopotamia, Judea, W. India

#### **Pure zinc:**

- 900 CE Rajasthan, India
- 1,300 CE India
- 1,600 CE Europe

Alloy of copper + zinc (zinc identified only in 1746)

1746 – Isolated and described by Margraf, a German chemist

1800 – Galvani & Volta discovered electrochemical

properties of Zn I Plating of iron = "galvanization"

### **Zinc Uses**

**Brass** - Superior corrosion-resistant - More ductile and stronger than copper Many industrial and home appliances, musical instruments Various alloys, semiconductor (ZnO) white pigment Batteries - Luigi Galvani experiment and Volta's pile. - Plates of copper and zinc  $\Rightarrow$  static electricity Galvanization - Zinc coating iron to protect from rust **Dietary supplement -** Effect in prostate cancer (?) **Topical uses -** Calamine lotion

- Sickle cell disease skin ulcers

### Zinc – Intake

Present in many body enzymes - 1940 - carbon anhydrase contains zinc Present in most organs; highest in prostate, eye, brain US IOM – Est. Ave. Requirements = 8-11 mg/day. RDA = 11 mg.Tolerable Upper Intake Level (UL) = 40 mg/day **Dietary intake:** Oysters, meat, fish, fowl, eggs, dairy, wheat (bran), seeds, beans, nuts, fortified cereals

## **Foods Containing Zinc**



## **Zinc Deficiency**

**Deficiency – Malabsorption**, chronic liver and kidney diseases, sickle cell disease, elderly, Low intake < RDA = 15 mg/day USA – Less than EAR: Women - 17%; Men -11% 2.2 Bil. people are deficient. 800,000 children dead/year **Symptoms:** Retarded growth of children, diarrhea, skin lesions, depression, cognitive and immune system impairment, anosmia

### **Zinc world production**



# MAGNESIUM (Mg)

## MAGNESIUM

Name comes from *Magnesia*, in Greece Eighth most abundant element in Earth's crust Highly reactive – found in minerals Very important in industry Essential for life: human body and plants Important structural metal (3rd after iron and aluminum) Highly flammable, intense white light

### **Magnesium – Production**

1618 – Farmer in Epsom, England, had water rich in Mg. which healed skin lesions

1808 – Isolated in England

China is greatest supplier (80% of world supplier)

Magnesium **Uses: Super-strong lightweight alloys: Aircraft -** (engine, airframe) Automotive (engine blocks, magwheels) **Electronics** Photography, printing **Batteries** Roofing Medicine - important electrolyte **Plants - chlorophyll** 

### **Magnesium - Biomedicine**

#### **Essential to cell functions**

>300 enzymes require magnesium ions 60% in the skeleton; **39% intracellular** RDA = **300 mg/day**; only 32% of US people meet the RDA **Sources:** Green leafy vegetables, cereals, nuts, spices Level maintained by GI absorption/loss, and kidney excretion Magnesium deficiency: Common life threatening intake, GI or kidney dysfunction, ↑ intracellular shift, antacids, alcoholism, diabetes Symptoms: Neuromuscular and cardiac dysfunction

# Foods rich in magnesium



# ALUMINUM (AI)

## ALUMINUM

Third most abundant in the Earth's crust Chemically reactive ⇒ mostly in minerals Chief ore = **Bauxite** Found as oxides and silicates Feldspars are aluminosilicates Aluminum is corrosion-resistant Best known "strength-to-weight" alloy Essential for the aerospace industry, structures, building, transportation

## Bauxite – A major aluminum ore



## **Aluminum - Uses**

- **Transportation** (aircraft bodies)
- Packaging
- Containers (food, beverages)
- Construction
- Household items
- Electronic appliances
- Electrical transmission lines
- Cooking utensils
- Coins
- Metal instruments (guitar resonators, and electric
- guitar speakers

#### **Aluminum - Economics**

2005 – Major producers: China (1/5), Russia, Canada, USA
Recycling: Very active
Melting aluminum saves electrical energy
Aluminum recycling: 42% - 95% in Europe

#### **World Production of Aluminum**



#### **Aluminum - Biomedical**

No known function in biology Excessive use of antacids and antiperspirants ⇒ toxic effects – nervous system and bones No conclusive evidence on role in Alzheimer disease Exposure to powdered aluminum ⇒ pulmonary fibrosis

#### Aluminum absorption by human skin





## SAPPHIRE

Gemstone variety of the mineral corundum (an aluminum oxide) Many colors: blue, yellow, purple, orange, grey, black, clear (white) Natural or synthetic Very hard (grade 9/10) Uses: Jewelry, ornaments, electronics **Producers:** Australia, Thailand, Sri Lanka, China, Madagascar, E. Africa, Montana

## Uncut Rough Sapphire Spokane Sapphire Mine, Helena, MT



## The Blue "Logan Sapphire" 423-carat (85g)



# **The Blue Sapphire**



# **Synthetic Sapphire**



## Synthetic Star Sapphire



# CALCIUM (Ca) from Lat. "calx-calcis" = lime

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## **CALCIUM – NATURAL HISTORY**

Earth metal, soft, grey. Very reactive - found only as compounds (salts of calcium)

#### **Geochemical cycling:**

- Calcium-rich rocks erosion ⇒
- Calcium released into surface water ⇒ Oceans ⇒
- Calcium reacts with dissolved CO<sub>2</sub> ⇒ Ca carbonate ⇒
- Limestone is formed

#### **Essential to living organisms**

### **Calcium Timeline and Uses**

- 14,000 7,000 BC Used as lime plaster and statues
- 2,500 BC First lime kiln Mesopotamia
- 1<sup>st</sup> Cent. Romans prepared lime for buildings and statues
- 975 CE Plaster of Paris (Ca sulfate) to set broken bones
- 1808 CE Calcium isolated by Sir Humphry Davy
- Most abundant metal in many animals
- 2000 CE Large scale industry use of various salts

### **Some Calcium Uses**

- Ca carbonate Lime
- Ca hydroxide for detecting presence of  $CO_2$
- Ca arsenate insecticide
- Ca chloride ice removal, additive to canned tomatoes
- Ca citrate food preservative
- Ca hypochlorite swimming pool disinfectant
- Ca phosphate suppl. animal feed, fertilizer
- Ca sulfate (gypsum) blackboard chalk, Plaster of Paris

#### **Green Calcite from Mexico**



### **Red Calcite from China**


# Dolomite (white) + Magnesite (yellow) from Spain



# **Orange Mound Spring, Yellowstone**



## **Travertine Terraces - Mammoth Hot Springs, Yellowstone National Park**



#### **Travertine terraces, Pamukkale, Turkey**



# Pamukkale, Turkey



#### **Calcium - Biomedical**

**Necessary for life** 99.9% of calcium is in the bones and teeth Necessary as a **neurotransmitter**, for **muscle** contraction, cardiac function, and normal blood clotting **Deficiency:** Rickets, osteoporosis, cardiac dysfunction, clotting abnormalities Vitamin D - necessary for calcium absorption and utilization Intake: Dairy products, nuts, some vegetables

**Retention in blood = Medical emergency** 

#### **Rickets and Osteoporosis**

Diseases of calcium deficiency in the bones Calcium needs vitamin D to be absorbed. Vitamin D is activated in the skin from an inactive form If low CA ⇒ Skeletal deformities

Osteoporosis = imbalance btw. production and destruction of bone RDA for >70 y.o. = 1,200 mg

Foods that contain vitamin D include: butter, eggs, fish liver oils, margarine, fortified milk and juice, portabella and shiitake mushrooms, and oily fishes such as salmon, tuna, and herring.



#### MARBLE

Calcium carbonate sedimented in layers (foliation) Mostly calcite and dolomite (aka. limestone) Effect of water: holes and carving the stone ⇔ caves

Uses: Sculpture Construction

## **Carrara Marble**



# Foliation (layering) of Limestone



#### Limestone – Bridges and arches Piatra Craiului, Romania



#### **Limestone Art**





## Carlsbad Caverns, NM



#### Carlsbad Caverns – "Rock of Ages" Photo Ansel Adams - 1941



# The Great Pyramid of Giza. Outer layer (veneer) of limestone (Egypt – 2650 BC)



# Venus of Milo - 400-500 BC (?) The Louvre Museum



#### The Nike of Samothrace Parian Marble (c. 220–190 BC) The Louvre Museum



## Marble Door – Hagia Sophia – 537 CE



#### Travertine Vessels Mexico, 600-900 CE



#### Italian Renaissance – Statue of David by Michelangelo, 1504



#### Taj Mahal - Agra, India – 1648 CE



# LITHIUM (Li)

# LITHIUM

- 1817 Isolated from mineral **Petalite** (lithium-aluminum silicate)
- Lithium is present in ocean water, clays, briny waters
- Lightest and least dense metal
- Highly reactive and flammable stored in mineral oil
- 75% of production used in industry, batteries
- Found in grains and vegetables. RDA = 1 mg/day
- High content in embryo. Activity related to other biochemicals in the body
- Mood-stabilizing drugs Bipolar disorder in humans. Effect on bone marrow ⇔↑ in the white cell production

#### Lithium Floats in Oil



#### Launch of a Torpedo using Lithium as Fuel



#### **World Production of Lithium**



# **RECYCLING OF METALS**

The world use of metals is higher than its production Mining activities are expanding 1932 - 1999 USA copper used/person 73g ⇔ 238g Lower energy for recycled metals

#### **UN Intl. Resource Panel – Environmental Program:**

- 60 metals recycling rates <50%
- 34 metals recycling rates <1%

Battery packs for hybrid cars, mobile phones are in jeopardy

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# **END OF LECTURE # 5**