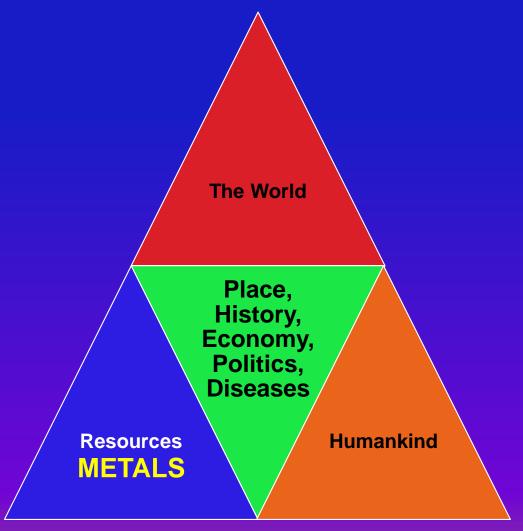
### LECTURE #4

### The World, its Resources, and Humankind Topics of Study



### METALS

### An Opinion on the Discovery of Metals

Need + Serendipity

Observation ⇒ Imagination +

THINKING OUTSIDE THE BOX

#### **HUMANKIND** and **METALS**

Metals made possible advances in

- agriculture,
- transportation,
- communication,
- technology, and
- warfare

The industrial revolution has been entirely dependent on metallurgy

#### **METALS**

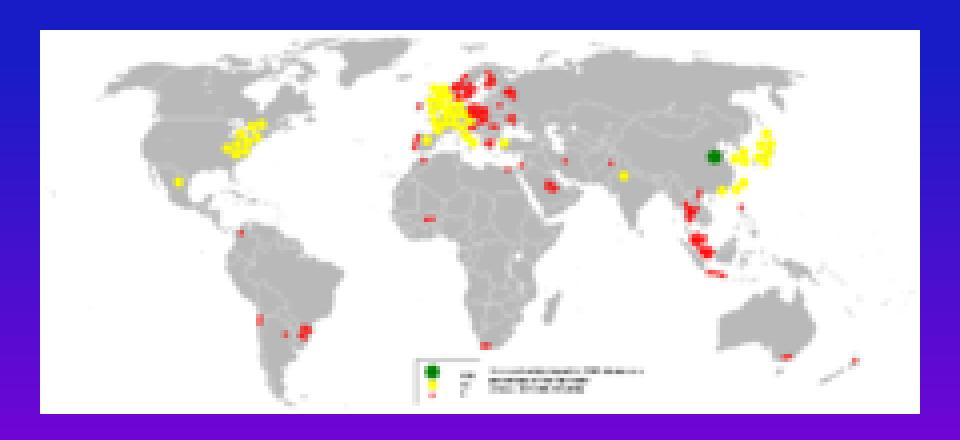
Metals - Greek: "metallon" = mine, quarry

Definition: Materials hard, dense, opaque, shiny, with good electrical and thermal conductivity

Fusible, malleable, ductile

Gold leaf transmits green light Lithium = least dense; Osmium = densest

### **Metals and Ore Imports - 2005**



### **Metals in Earth Crust**

Parts per million

Iron 50,000

Copper 70

Lead 16

Tin 2

Silver 0.1

Gold 0.005

### **Metal Ores and Properties**

Prospecting techniques ⇒ exploration ⇒ examination ⇒ mining (surface or subsurface)

Metals are found in ores (mixed with other metals)

Pyrometallurgy or Hydrometallurgy – purifying methods

#### **Melting temperature:**

Tin 231°C

Lead 328°C

Silver 961°C

Gold 1063°C

Copper 1083°C

Iron 1538°C – not possible in antiquity

# Timeline of materials in human life and technology (1)

- 29,000 BC First pottery Mesopotamia
- 28,000 BC First jewelry
  - 3,000 BC Copper metallurgy
  - 2,000 BC Bronze for weapons and armor
  - 1,600 BC Crude iron metallurgy Hittites
  - 1,300 BC **Steel** invented (iron + charcoal)
  - 1,000 BC Glass invented Phoenicians
  - 1,000 BC Pewter used in China and Egypt
  - 1,000 BC Vegetable dyes Phoenicians
    - 50s BC Glassblowing Phoenicians

# Timeline of materials in human life and technology (2)

- 3rd Cent. Cast iron China
- 671 CE First missile weapon ("Greek fire") Byzantium
- 8th Cent. Porcelain invented China
- 1000 Gunpowder invented China
- 1340 First blast furnaces iron production Liège, Belgium
- 1540 First book on metallurgy Della Pirotechnia V. Biringuccio
- 1555 De Re Metallica G. Agricola Mining, metallurgy
- 1590 Glass lenses Netherlands. Antonie van Leeuvenhoek Father of Microbiology (1632-1723) made first microscope
- 1664 Water pipes of cast iron Versailles

### The Fertile Crescent in Mesopotamia



### Assyria 2500 - 612 BC

The Assyrian kingdom was well organized

Major source of metal ore, as well as lumber

The <u>priesthood</u> became a major power in the Assyrian society

Long wars fought that helped build Assyria into a warrior society

Social position of women was lower than in the neighboring societies.

Assyria was open to homosexual relationships between men

Assyrian domination spanned from the Caucasus Mountains in the north to Egypt, Libya, and Arabia in the south, and from Cyprus in the west to Persia and the Caspian Sea in the east

Decline due to <u>civil wars</u> and <u>political instability</u>

Assyria conquered by Alexander Macedon in 322 BC

### The Akkadian Empire and the direction of its military campaigns



### Akkadian Empire and Sargon of Akkad (2334–2279 BC)

Trade extended from the **silver mines** of Anatolia to the **lapis lazuli** mines in modern Afghanistan, the **cedars** of

Lebanon, and the **copper** of Magan

Consolidation of the city-states of Sumer and Akkad ⇒

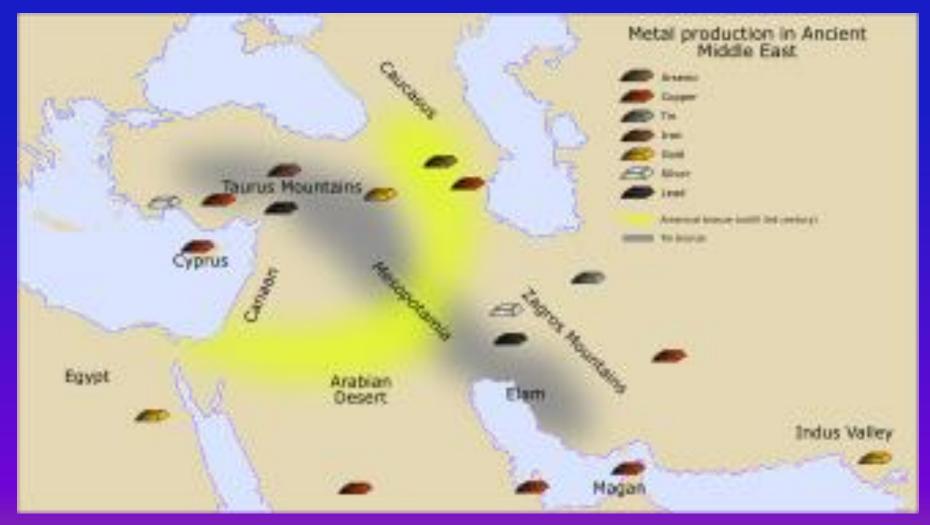
**Growing economic and political power** 

The empire's breadbasket was the rain-fed agricultural system of Assyria and a chain of fortresses built to control the imperial wheat production

Many cruel battles

**Resources** ⇒ **Trade** ⇒ **Dominance** 

### Metal Production in Ancient Middle East



### Mycenaean Civilization

Innovations in: Engineering, Architecture, Military infrastructure

- ⇒ **Metal work**, defensive walls
- ⇒ The script = first written record of the Greek language

**Gold** ornaments

Homer's *Iliad* written in 8th cent. BC

Extensive trade and political influence in Asia Minor (Hittites)

#### Well-defined three classes:

- King and his court
- People
- Slaves

#### **MESOAMERICA**

6000 BC - the early inhabitants of Mesoamerica were domesticating plants

**Barley and wheat** cultivated

All regions of Mesoamerica cultivated the base crops of maize, beans, and squashes

All Mesoamerican cultures used stone age technology

c.1000 AD copper, silver, and gold were worked

Mesoamerica lacked draft animals. Did not use the wheel, and possessed few domesticated animals

The principal means of transport were on foot or by canoe

# 1500 BC – 1697 CE – Mesoamerica – Olmec, Maya, Zapotec

**OLMEC – Southeast Mexico (Veracruz and Tabasco)** 

Well-watered alluvial soil ⇒ **High soil productivity** ⇒ Rich class The elite class demanded the production of the symbolic and sophisticated luxury artifacts

Luxury artifacts made from materials such as jade, obsidian,

magnetite (iron oxide) ⇒ extensive trading network in

Mesoamerica

Colossal heads and jewelry

- Bloodletting
- First writing 900 BCE 650 BCE
- The concept of zero
- Calendar

Decline caused by earthquake

### METALS Year of Discovery

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### **ALLOYS**

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: Bronze, brass

Hundreds of alloys have been produced

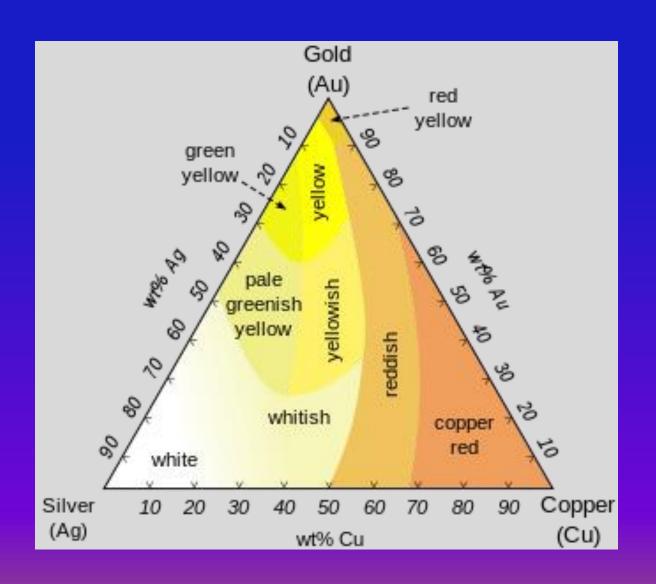
Alloys of iron: Steel, stainless steel, cast iron, tool steel

Cast iron: iron + silicon

<u>Stainless steel</u>: carbon steel + chromium, nickel, molybdenum

High strength-to-weight: Alloys of aluminum, titanium, magnesium

### **Alloys for Different Colors of Gold**



### **Metals in Earth Crust**

Parts per million

Iron 50,000

Copper 70

Zinc 64

Lead 16

Tin 2

Silver 0.1

Gold 0.005

#### **Noble Metals**

Gold, silver, platinum, palladium, rhodium, iridium, osmium, rhutenium

Precious metals: Rare

Do not oxidize

Uses: Investment, art, jewelry, medicine, dentistry

GOLD (Au = Aurum)

### A Gold Nugget



#### **GOLD**

4600 BC - Oldest thesaurus of gold – Lake Varna,
Bulgaria

2800 BC - Egypt first miners of gold in Nubia – gold
for international trade

610 BC - Coinage in Lydia (Asia Minor)

1091 CE - China – First to introduce gold coins

5000 BC. - Sumer civilization used gold for jewelry

E. MORAN - 2017 27

Roman empire 25 BC - 106 CE: Hispania and Dacia (Rosia

Montana, Romania)

### Gold History (cont'd)

Middle Ages: Gold for coinage and jewelry

Alchemists trying to make gold

European colonization of Americas: Gold shipped to Spain

Legends of El Dorado cities filled with gold

Western Europe fairytales: Bro. Grimm's

Rumpelstiltskin (hay ⇒ gold) and

Jack and the beanstalk (hen ⇒ golden eggs)

Uses: Royal crowns, temples, statues, decorative, rings, valuables

Top prizes: Olympics, Nobel Prize

#### **Gold Sites**

Gold as flakes or micro particles or nuggets. Usually found in Ores - mixed with silver or other metals or minerals

Earthquakes ⇒ gold, water, and silica through faults

Oceans and seas contain gold = 15,000 tonnes (?)

Gold-mining: China, Australia, USA, Russia, Peru, South Africa

- Witwatersand basin in South Africa had the richest deposits ⇒
   1886 Gold Rush
- Boer War (1899-1902) Rights of Boer miners and gold in Transvaal and Orange states
- Gold rushes 19<sup>th</sup> cent. N. Carolina, California, Colorado,
   Klondike

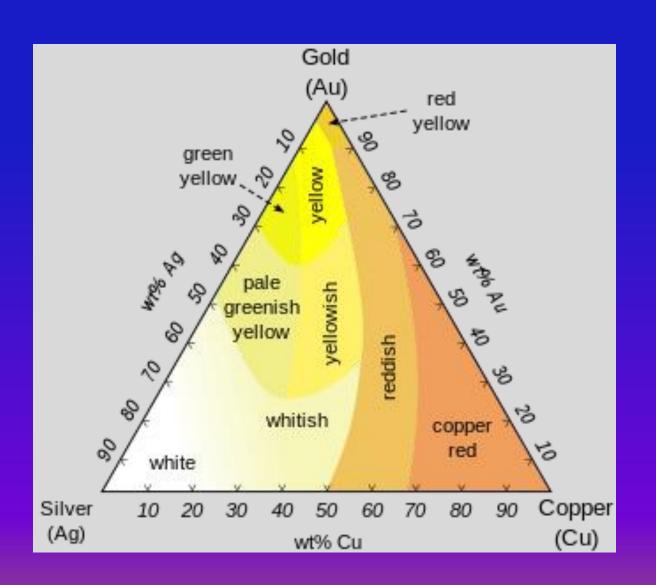
### Relative size of an 860 kg block of gold ore and the 30 g of gold extracted



# Gold malleability – A 5 mm (1/5") nugget may be expanded by hammering into a 0.5 m<sup>2</sup> (~ 5 sq ft) foil



### **Different Colors of Gold**



### **Gold Production**



#### **Gold Economics**

Precious metals measured in troy ounces

One troy ounce = 1.09714 regular (avoirdupois) ounces = 31.1034768 g

Karat indicates the gold purity 24 k = pure gold (0.995)

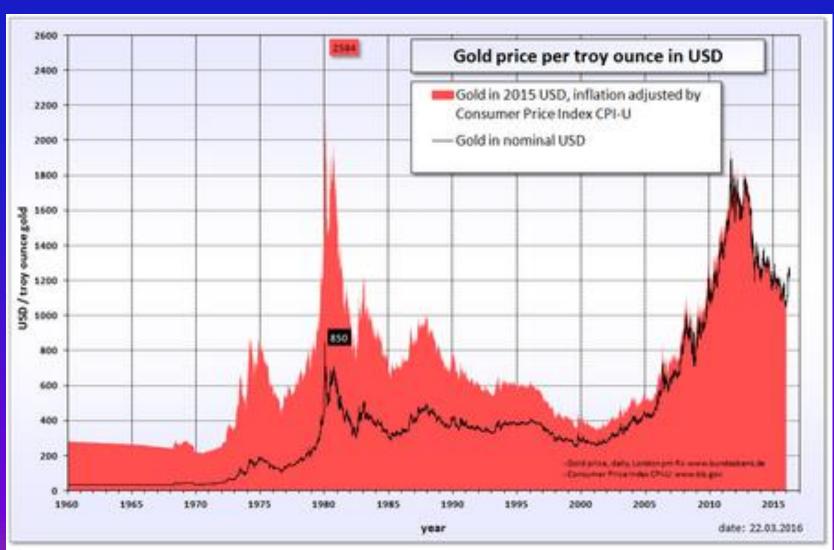
For many years money had to be backed by gold

1930 - Gold Standard Act established gold as international trade standard (USA Dollar = 25 8/10 grains of 90% gold)

1944 – Bretton Woods Conference: USA major influence
US dollar = International Standard. No more gold standard

Price fluctuated. Since 1975 gold price depends on free market Inflation and bear or instable markets increase its price.

### Gold price per troy ounce - 1940-2015



### Mycenaean Gold Earing – 1600 BC



## Mask of Agamemnon – 1600 BC National Archeological Museum, Athens



### Funerary Mask of Tutankhamun c.1325 BC



#### **Gold bullion**



### The Largest Gold Bar – 250 kg Toi Museum, Japan



#### **More About Gold**

Toxicity: Gold salts are toxic to liver, kidneys, skin (Chrysiasis)

Drinks: Danziger Goldwasser - flakes of gold are inert

Medicine: Much used in the past for treatment of

tuberculosis- ineffective

Some gold salts have been used in the treatment of rheumatoid arthritis

Symbolism: "Gold standard", "golden rule", "golden age",

"golden years"

Wedding rings – eternal vows

SILVER (Ag = Argentum)

#### **Metals in Earth Crust**

Parts per million

Iron 50,000

Copper 70

Zinc 64

Lead 16

Tin 2

Silver 0.1

Gold 0.005

# METALS Year of Discovery

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### **Native Silver**



#### **SILVER - History**

```
4000 BC - Separated from lead. One of the 7 metals of antiquity.
```

1500 BC - Egypt - Silver more expensive than gold

700 BC – Kingdom of Lydia (Asia Minor) coins of silver alloy with gold ("electrum")

Silver sources: Phoenicians - Spain, Greeks - Laurium, Romans - Sardinia

Silver in the money of many nations in Europe, China, India, Japan

Pound sterling of UK(£) = Sterling silver

In many languages the word "silver" = money

19th cent. - Much silver mined in Americas

1947 - Most coins made of cupro-nickel

1970 - Last circulating silver coin (US half-dollar)

#### Silver - Uses

- More abundant than gold. 94%-pure = "0.940 fine" sterling silver (0.925)
- Old use: currency, ornamental, silverware, jewelry, coins and medals
- Modern use: Solar panels, photo film, X-ray film, jewelry, (plated with a coat of .999-fine Ag), tableware, silverware. Antiseptic (silver nitrate)
- Best electrical conductivity
- Silver compounds Silver + oxygen + hydrogen sulfide = silver sulfide (tarnish) + H<sub>2</sub>O
- WW2 Electromagnets for enriching uranium Manhattan Project

#### Silver in Technology

**Solar energy - Photovoltaic panels** 2015 - 100,000,000 oz. used in solar energy Air Conditioning - Mirror-like panels on buildings **Electrical conductivity - Highest of all metals** Water purification - Eliminates the need for chlorine **Dentistry** - Alloy with mercury for dental fillings **Telescopic mirrors - for thermal or infrared telescopes** Windows - "Sputtering" silver is applied to glass ⇒ high-performance insulated glazing. High-quality musical instruments - Best flutes

#### **Silver production**



### Silver bowl, Persia, 6th century BC



# Silver 1000 troy ounce (~31 Kg) Bullion Bar



#### **Silver Solar Panels**



# Canada's Maple Leaf 1 troy ounce Silver Bullion Coin



## PLATINUM (Pt)

# METALS Year of Discovery

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#### **PLATINUM**

16 cent. - Spaniards found it in Mexico but thought that it was impurity of gold and discarded it.

Spanish "platina" = "little silver"

1748 – Antonio de Ulloa discovered platinum in Colombia

Rare element – major precious metal

Dense (heavy), malleable, ductile, highly unreactive

Mined in South Africa ⇒ 80% of world production

Alloy with palladium, rhodium, iridium, osmium, and ruthenium

#### **PLATINUM**

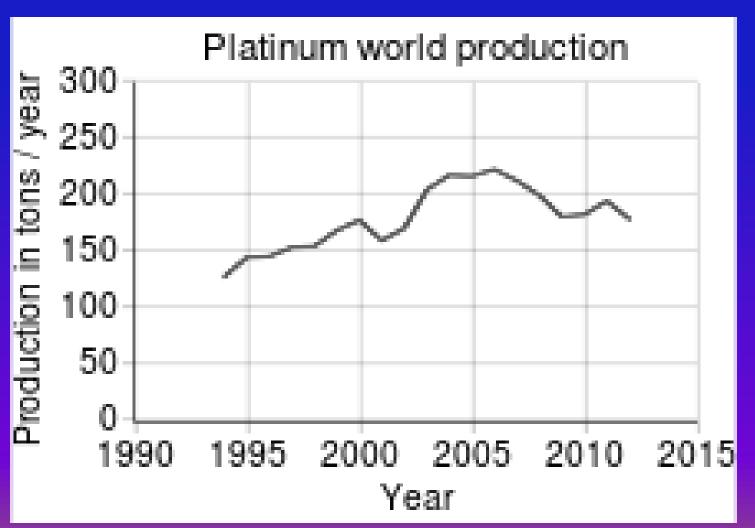
**Uses: Jewelry** 

Catalyst for auto and industrial plant emissions

Organic chemicals

**Cancer medications** 

#### **Platinum World Production**



## 1,000 Cubic Centimeters of 99.9% Pure Platinum, Worth About US \$696,000 at 29 June 2016 Price



## COPPER (Cu = Cuprum)

#### **Metals in Earth Crust**

Parts per million

Iron 50,000

Copper 70

Zinc 64

Lead 16

Tin 2

Silver 0.1

Gold 0.005

# METALS Year of Discovery

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#### COPPER

Discovered ~ 9,000 BC in 99.9% pure form Found by serendipity - "Some stones" being fired melted and new objects could be cast **Replaced stone tools**: crude knives and sickles ⇒ The "Chalcolithic Age" or "Copper Age" 4000 - 1000 BC - "Old Copper Complex" of the Western Lakes - copper 99% pure Old use: Spearpoints, tools, decorative objects

#### 2700-1200 BC - The Minoan Civilization



A Minoan copper ingot

#### The Snake Priestess



### **Native Copper**



#### **Timeline of Copper**

- 5,000 BC World oldest copper smelting Rudnic Mt. (Serbia)
- 3800 BC Copper mines in Sinai peninsula
- 3000 BC Ores of copper in Cyprus and in Cornwall -
  - Phoenicians bring copper to Judea for the Temple of Solomon (~1000 BC)
- 2800 BC Ores of copper and tin ⇒ harder metal ⇒ Bronze Age
- 2800 BC Sinai 

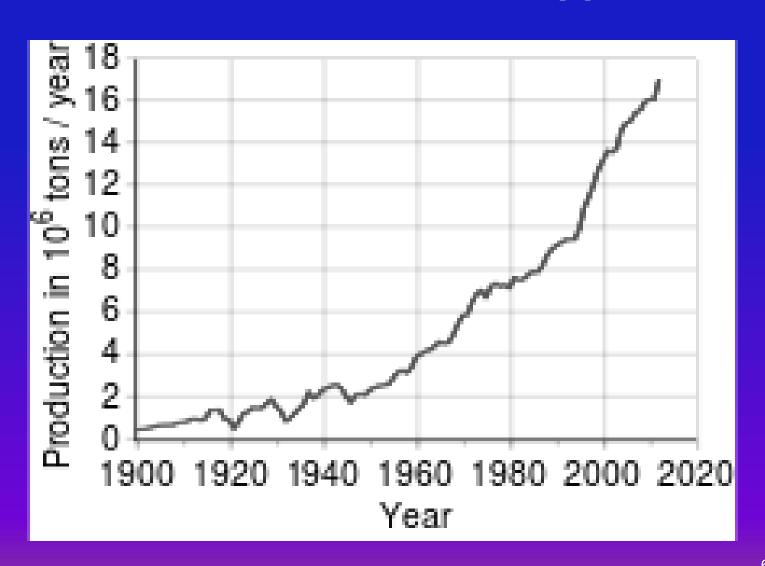
  ⇒ Sumer 

  ⇒ Anatolia 

  ⇒ Europe 

  ⇒ Indus valley
- 2500 BC ⇒ China (Shang dynasty) 1500 BC
- 2750 BC Copper water pipes in a temple in Egypt

#### **World Production of Copper**



#### **Old and New Copper**



ROYAL OBSERVATORY – EDINBURGH, SCOTLAND COPPER OF 1894 AND OF 2010

### LEAD (Pb = Plumbum)

#### **Metals in Earth Crust**

Parts per million

Iron 50,000

Copper 70

Zinc 64

Lead 16

Tin 2

Silver 0.1

Gold 0.005

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### **Lead nuggets**



#### **LEAD**

Great availability (16 ppm). Found in ore (galena)

Mined since 7000 - 6500 BC

Ancient civilizations - Various uses: Cosmetics, currency, contraception

Mined in China 1000 BC

Rome great producer of water pipes. Lead intoxication (?) (saturnism)

16<sup>th</sup> cent. CE - Important for the **Gutenberg printing press Gun bullets** 

Whitened face ⇒ Lead poisoning ⇒ Lead teeth ⇒ Lead intox.

1621 - Lead mining in Virginia

1841 - Lead mining in Australia

### **Lead Uses**

Production increased 31%

Primary by extraction & by recycling

Lead-acid batteries – Environmental hazards:

Vernon, CA

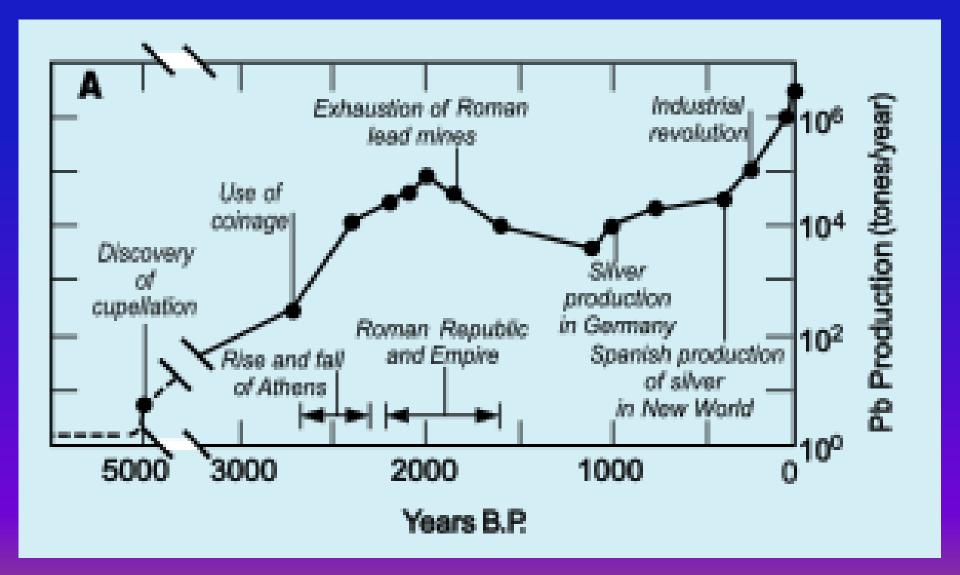
Alloys of copper + lead

Construction industry

Shielding from radiation – Radiation therapy rooms

Ballast keel of sailboats

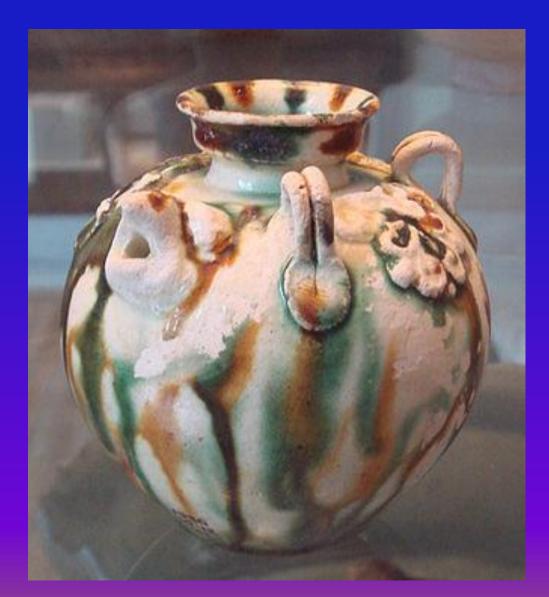
### **Lead production**



## Water lead pipes Emperor Vespasian Villa - Rome



## Multicolor Lead-glaze Paint Tang Dynasty 8th Cent. CE



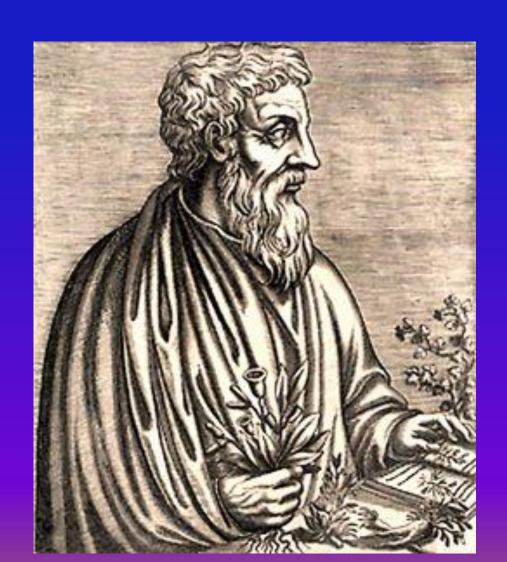
# Elizabeth I of England White Powdering of Face and her Cause of Death



### **Lead Blocks Used for Radiation Protection**



## Dioscorides (Greek physician) noted <u>lead's effects</u> on the mind (1<sup>st</sup> Cent. CE)



### LEAD POISONING

Lead poisoning by air, dust, water, food

Brain is the most sensitive

10% of cases -intellectual disability

Memory problems, anemia, sterility

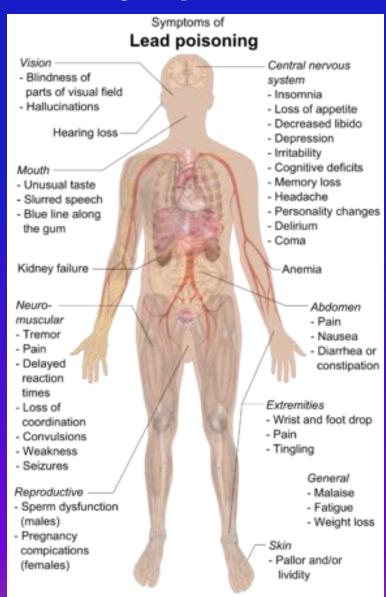
Various multi-system symptoms

Children more affected (by ingestion of paint)

Diagnosis: Gums colored blue and anemia

**Treatment:** Chelating agents

### Symptoms of Lead Poisoning



General Central nervous system Vision Neuro-muscular Intestinal Kidney failure Anemia Reproductive Skin

## Testing kit for lead detection The swab turns red in lead presence



#### The Timeline of Flint Water Crisis

- Feb. 2015 Oct. 2015 <a href="high-levels of lead">high levels of lead</a>: 104 ppb (threshold is 15 ppb) = HHS Violation of the Safe Water Drinking Act
- Oct. 2, 2015 State officials publicly announce high lead content in drinking water of Flint
- Dec. 14, 2015 Flint Mayor Karen Weaver: State of emergency
- Jan. 16, 2016 President Obama: Emergency Declaration
- Apr. 20, 2016 Michigan AG: charges against DEQ employees
- June 2, 2016 DEQ Chief Deputy Director Jim Sygo: "Flint water crisis 'was overplayed"
- June 2016 Gov. Snyder: Apologies to citizens: \$28 Mil. for medical supplies; \$30 Mil. for water bills; + \$165 Mil. for water pipes replacement

### Prof. Mard Edward from Virginia Tech:

"Authorities' actions expose a new level of arrogance and uncaring that I have never encountered"



## The Story of Exide Technologies

Manufacturing and Recycling of Automotive and Industrial Batteries – USA, Pacific Rim, Europe, and Australia

**Vernon, CA - 2015** 

## Exide Technologies Batteries Recycling Plant, Vernon, CA

JOSE GOMEZ at his home in the 1100 block of South Hicks Avenue in East L.A., which is being tested for lead contamination. Crews sample soil from about 15 locations on each property and analyze them for lead.

# 'SOMETHING INTHESOIL'

Brain-damaging lead levels near Vernon battery plant were as much as 100 times above health limits

## Exide Technologies Batteries Recycling Plant, Vernon, CA

in East Los Angeles, including several property owners who shared their testing with The Times. Properties sampled: 269 Classified as Unsafe for residential soil -Safe for hazardous waste state standard residential soil (1,000 ppm or higher) (80 ppm or higher) (Less than 80 parts per million) 11

### Lead Economics, Health, and Politics

Industrial Revolution – Increased demand for plumbing, painting, and gasoline additive

Lead paint – Children lead intoxication

Lead more dangerous if fumes are inhaled

19th Cent. – Lead causes mental disorders

Lead causes blindness

1921 – Tetraethyl lead added to gasoline to avoid "knocking". Phased out

TIN (Sn = Stannum)

### **Metals in Earth Crust**

Parts per million

Iron 50,000

Copper 70

Zinc 64

Lead 16

Tin 2

Silver 0.1

Gold 0.005

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## Known Tin Deposits Exploited in Ancient Times



#### TIN

- First alloy to make bronze
- Discovered ~3000 BC Copper + tin was
  - harder ⇒ Bronze Age
- Found as Cassiterite mineral in river banks
- Soft, malleable, ductile
- Melts at low temp. 232°C (450°F)
- Not easily oxidized in air, not toxic ⇒
  food packaging in tin cans

### TIN ORES

Yunnan province - China

Malaysia peninsula

Peru

Devon, Cornwall - England

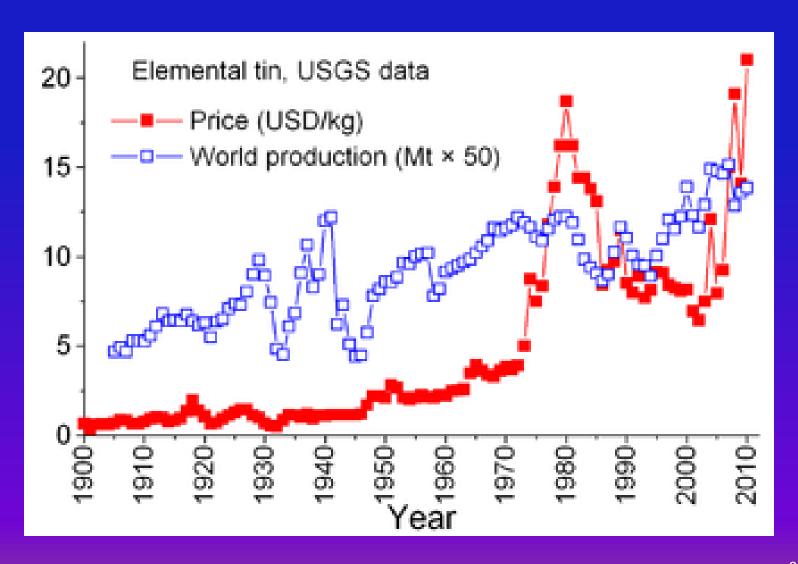
Brittany - France

Central Europe – Erzgebirge

Spain and Portugal

**Central Africa** 

### World Production and Price of Tin



## COPPER ALLOYS: Bronze, Brass, Pewter

## **BRONZE**

### **Bronze Age Timeline**

The Bronze Age started 3,500 - 3,000 BC (after the copper age called the "chalcolithic period")

Casting of metal ⇒ Metallurgy is born

- Mesopotamia c. 4500 BC
- Egypt c. 3500 BC
- China c. 2800 BC
- Central America c. 600 CE
- West Africa c. 900 CE

### **BRONZE**

Italian: *bronza* (bell) ⇒ French: *bronze*Bronze is an alloy of copper + 12% tin

Various alloys ⇒ hardening the copper

Sumer, India, China and Japan - 4000 BC

Followed by the Iron Age (~1300 BC)

- Harder than iron; does not rust
- Iron easier to find and process but requires higher temps.
- Disruption in tin supply (?)

## The Bronze Age of China (2000 – 771 BC)

Started under the Shan dynasty - Henan province Imported technology or invented locally (?)

Bronze artifacts: Utilitarian, rituals, tools, weapons

Taotie motifs (animal-like masks)

Jade carving Irrigation

#### **Bronze Uses**

Tools, weapons, armor, building materials more durable than copper

Sculptures, bronze statues

Works of high art

Musical instruments: Bells, cymbals, stringed instruments: bass, piano, harpsichord, guitar

**Coins and medals** 

## Chinese Bronze Age – Shan dynasty 2500-1800 BC



## Mycaenean Civilization Swords and Cups (1600 – 1100 BC)



## Hittites – <u>Masters of Metal Work</u> in the Bronze Era (1600 – 1100 BC)



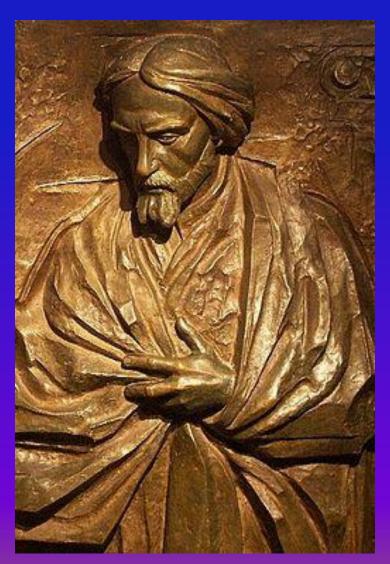
# Bronze Sculptures The Artemision Bronze c. 460 BC The National Archeological Museum of Athens



## Roman cuirass, Grenoble, France



## Bronze relief Wawel Cathedral, Krakow, Poland



## Modern Bronze Statues Degas' Dancers)





## BRASS

### **BRASS**

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

Several alloys in use

Bright gold-like appearance

Higher malleability than copper or zinc alone

Low melting point

Easy to cast

Antimicrobial (?)

90% is recycled

#### **Brass Uses**

Roman empire: Coinage

Medieval Europe: Religious objects

Metal of choice for musical instruments: "the bass

section" (trombone, tuba, trumpet, cornet, horn)

Decorative objects

Household items

### Brass - 7th Cent. Persian Ewer



## Baptismal Font – St. Bartholomew's Church Liège, Belgium, 12<sup>th</sup> Cent.



## **Brass Cracking by Ammonia**



## **PEWTER**

#### **PEWTER**

Malleable alloy. 85-99% tin + copper + antimony + bismuth

Low melting point 170-230°C (338-446°F)

Used in the Near East, c.1450 BC in Egypt

Many household vessels in the Middle Age, mugs

Replaced by porcelain, pottery, and glass

Tin + 15% lead - household items - less used today

E. MORAN - 2017

### **Pewter vessels**





## END OF LECTURE #4