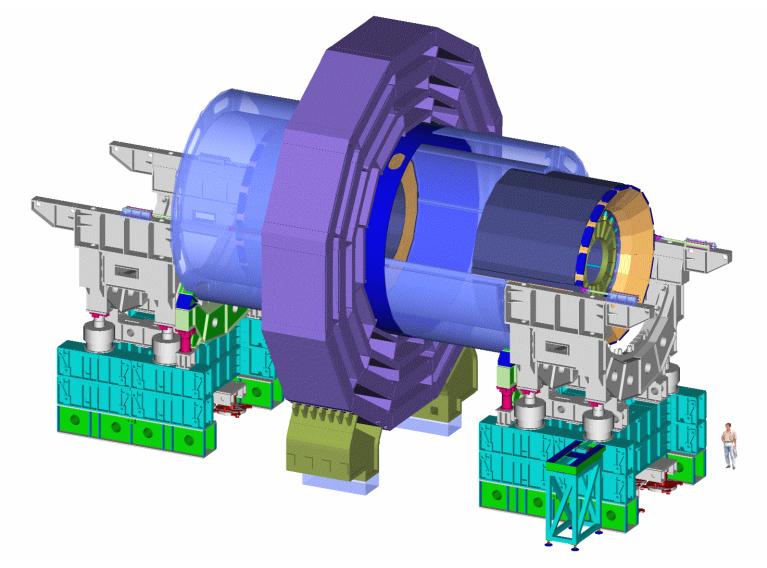


A Rambling Walk through CMS HCAL, where its copper came from, and its scale compared to other large copper works.

> Jim Freeman Fermilab

### HCAL being installed into the CMS Superconducting Magnet



#### The inside of the CMS superconducting magnet



## HCAL : HE and HB





# HCAL Copper

We bought the copper for HCAL in Bulgaria. This caused me to start thinking: Why Bulgaria? And thinking about the role and history copper has had in this region. Later, I also thought about the scale of HCAL compared to other things built out of copper. The answers to these questions are in this talk.

### Southern Balkans



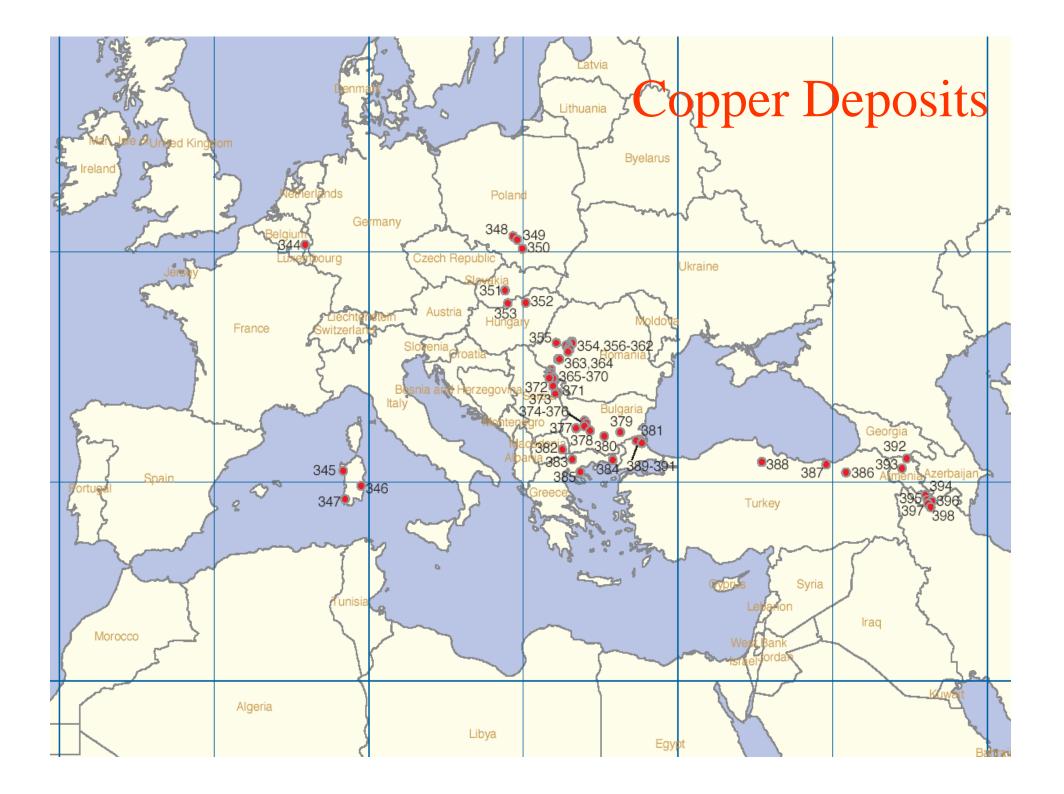
### Open Pit Copper mine in Bulgaria



## Copper in the Balkans

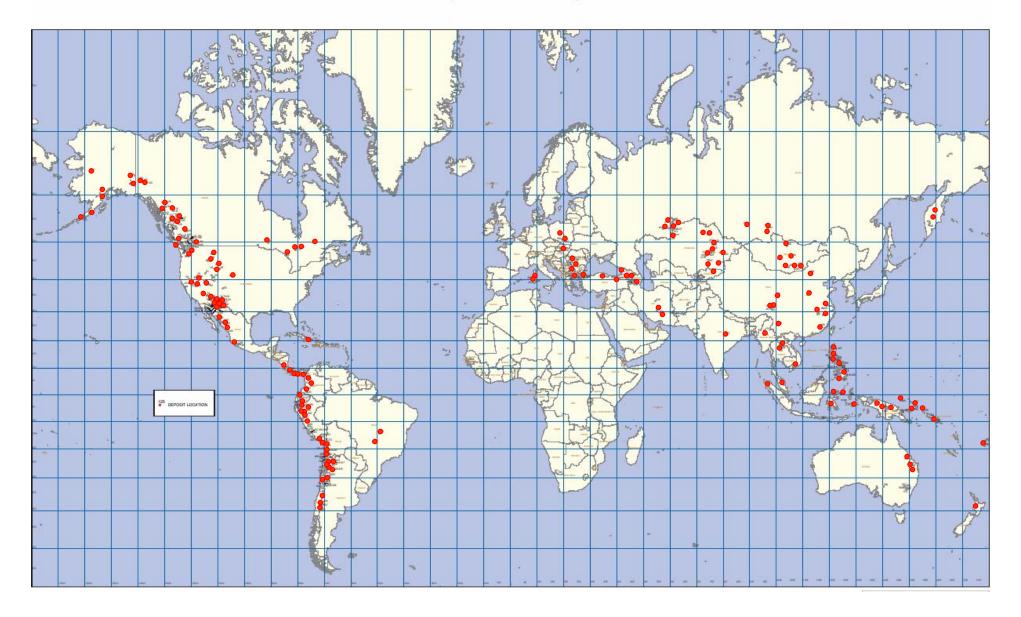
Copper is plentiful throughout the Balkans: Macedonia, Bulgaria, Albania. The Bronze age came into Europe through this region. Lots of copper ore is (or was) close to the surface, so mining is easy.

Question: Why is copper plentiful there?

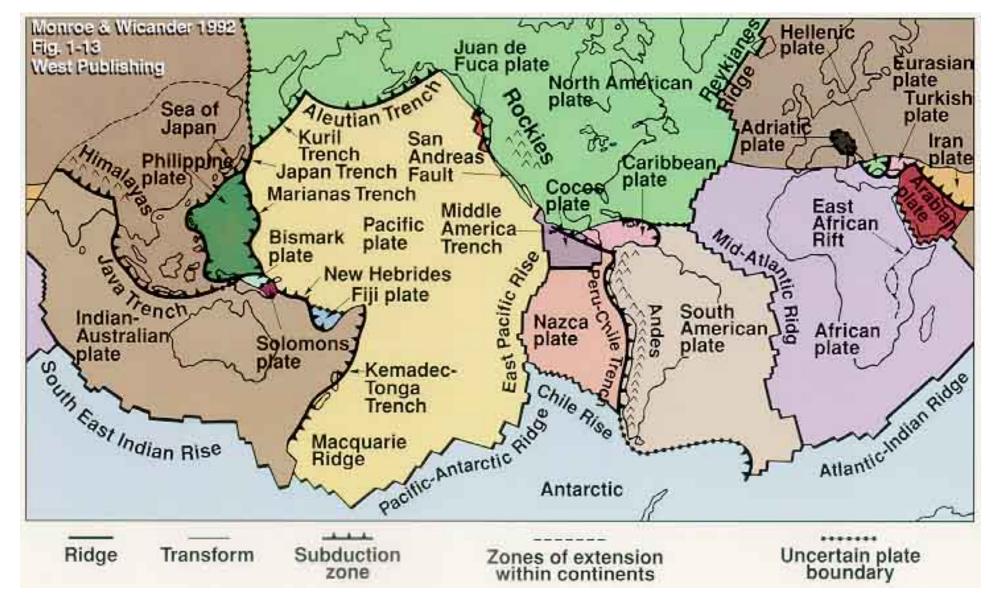


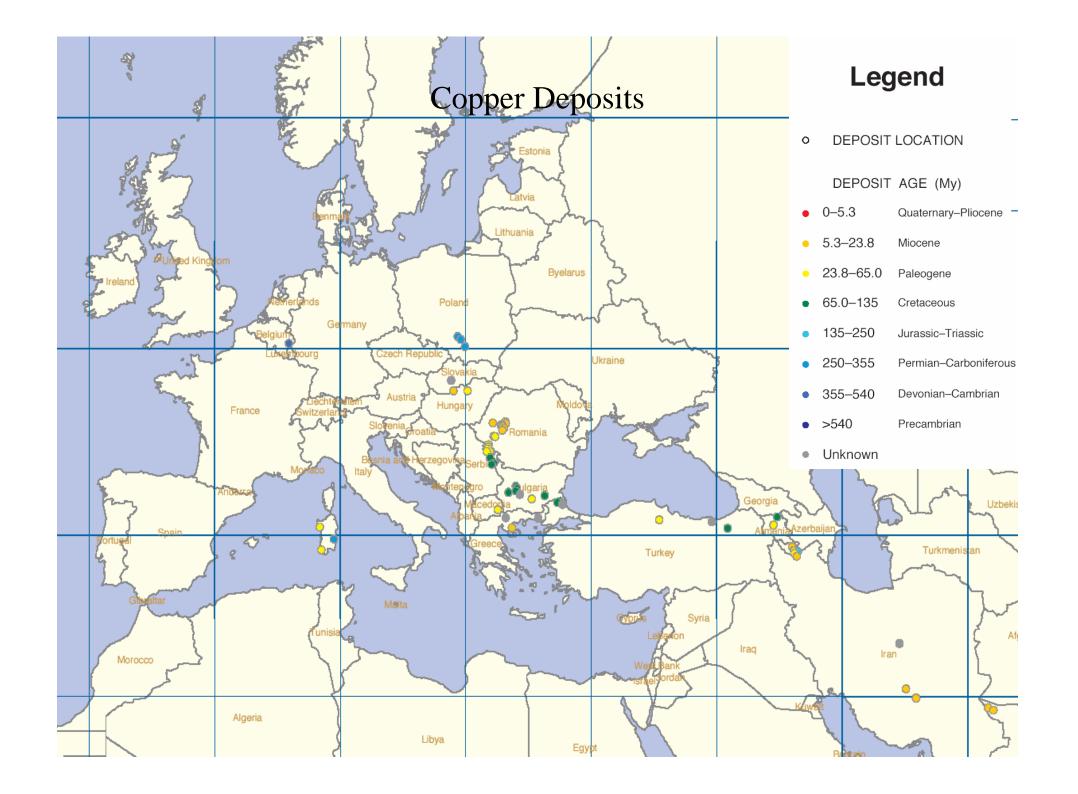
# World Copper Deposits

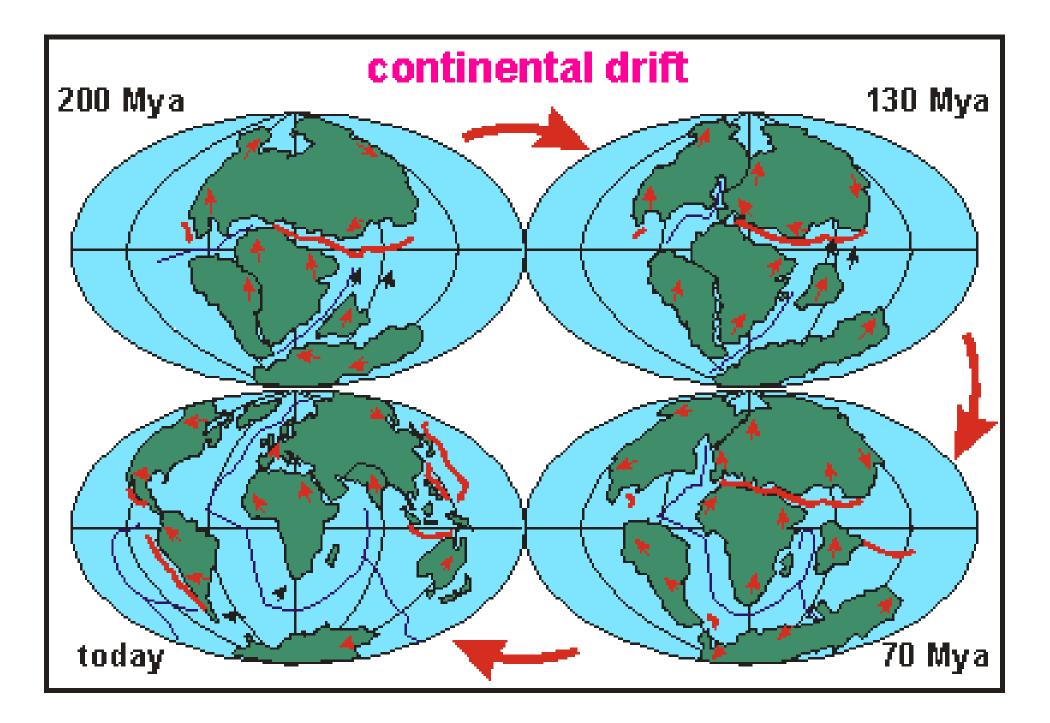
PORPHYRY COPPER DEPOSITS OF THE WORLD (SEE DETAILED MAPS FOR CLUTTERED AREAS)

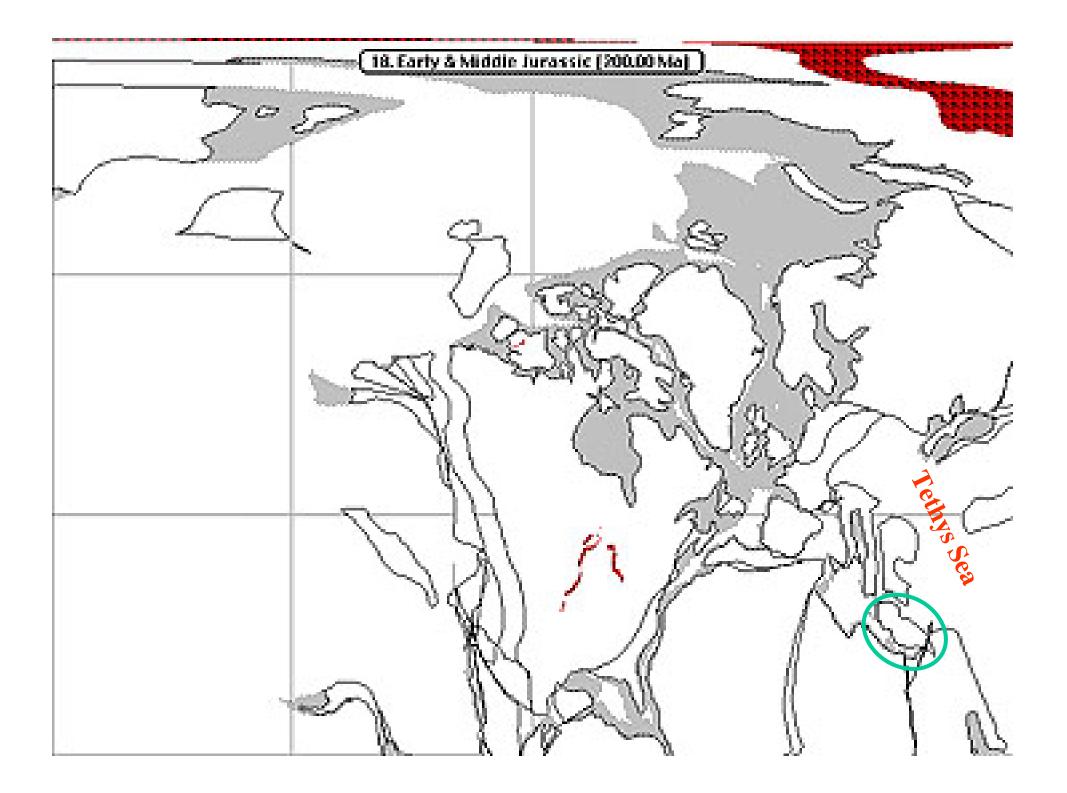


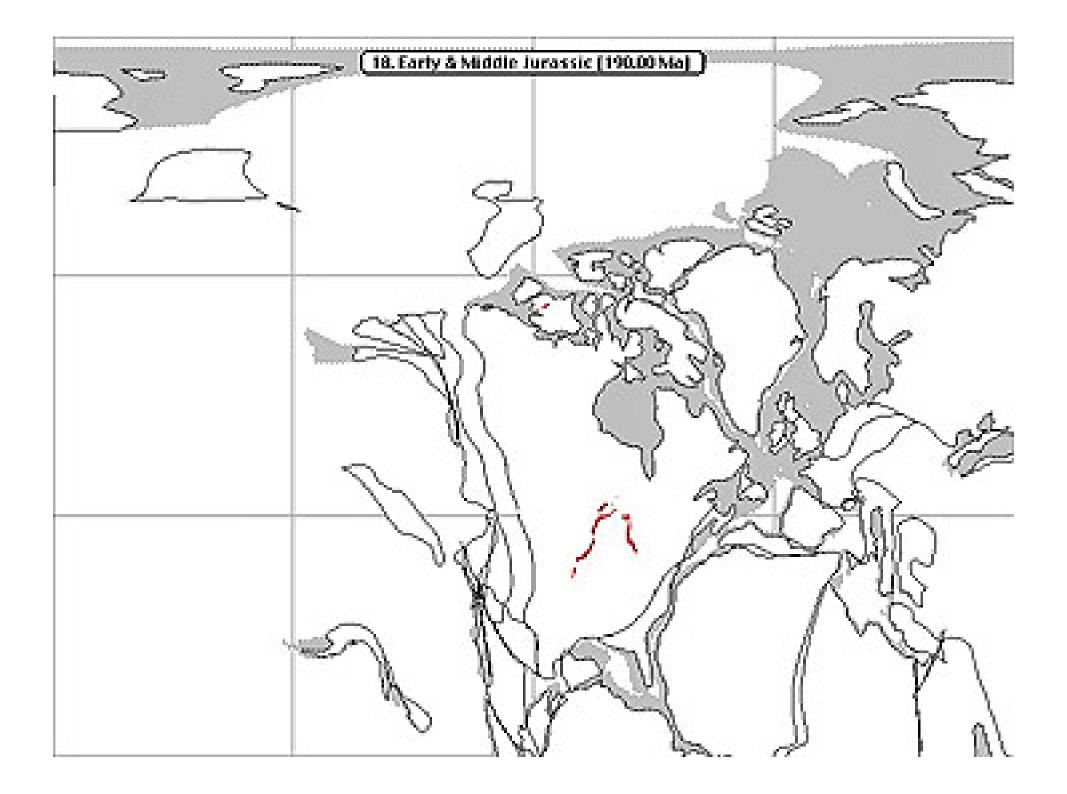
### **Plate Tectonics**

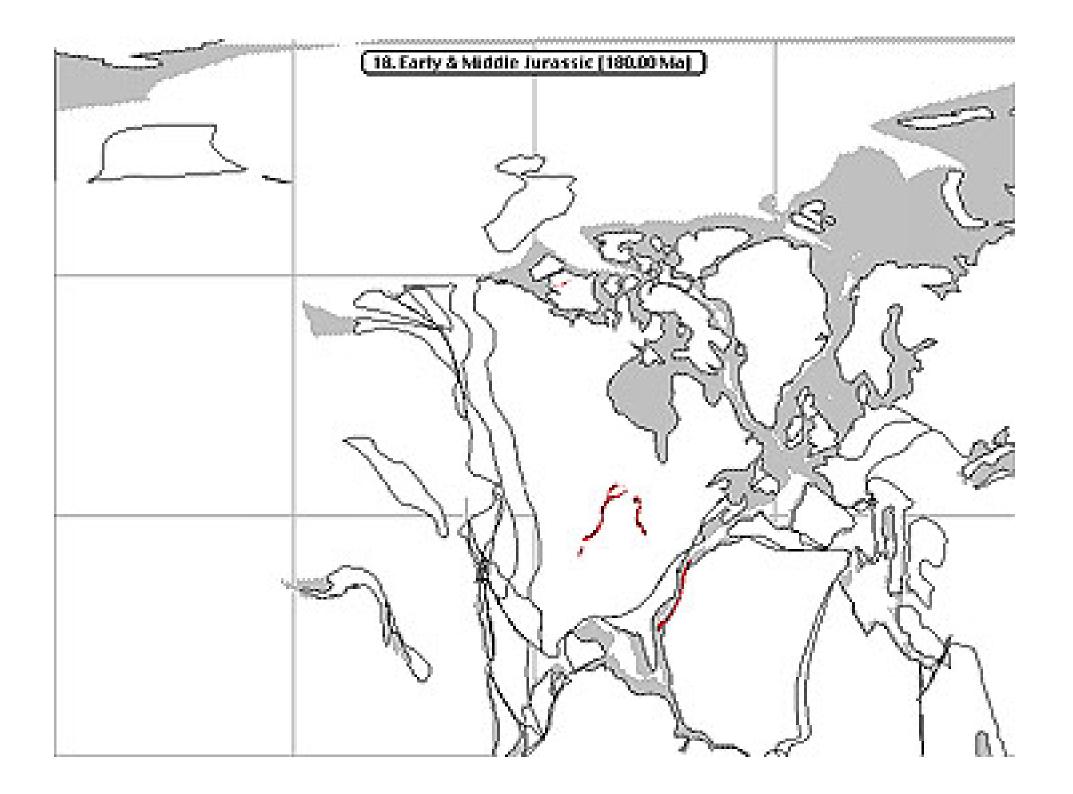


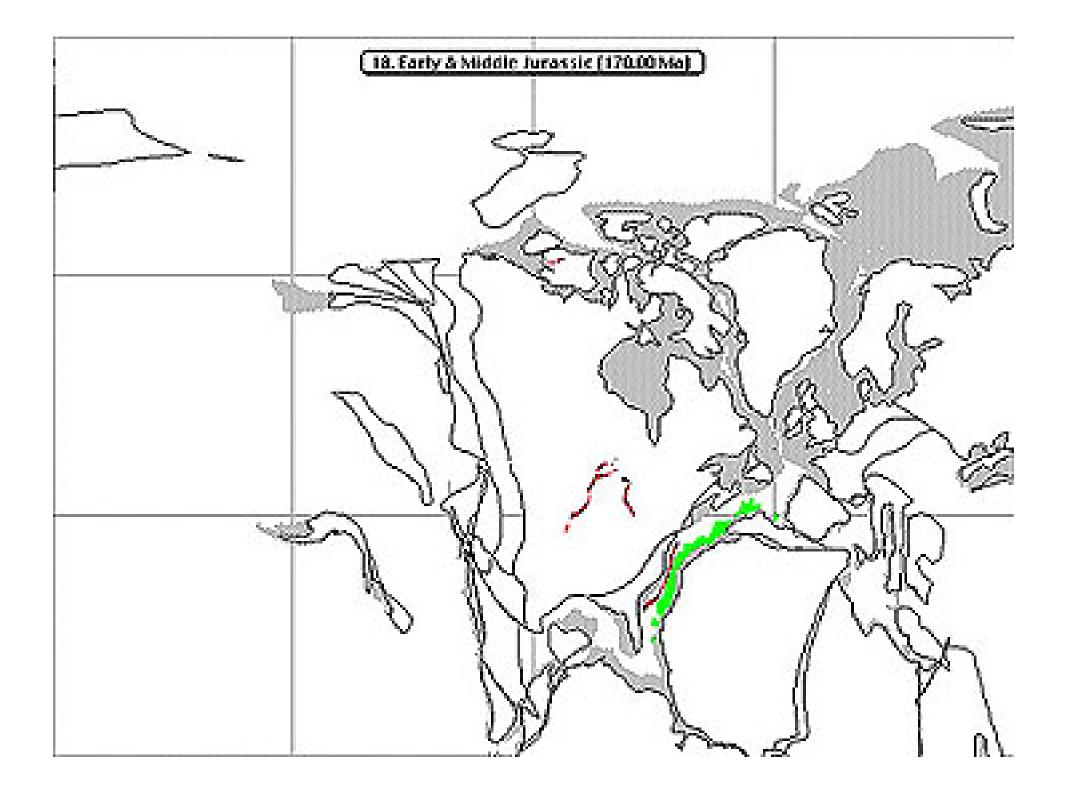


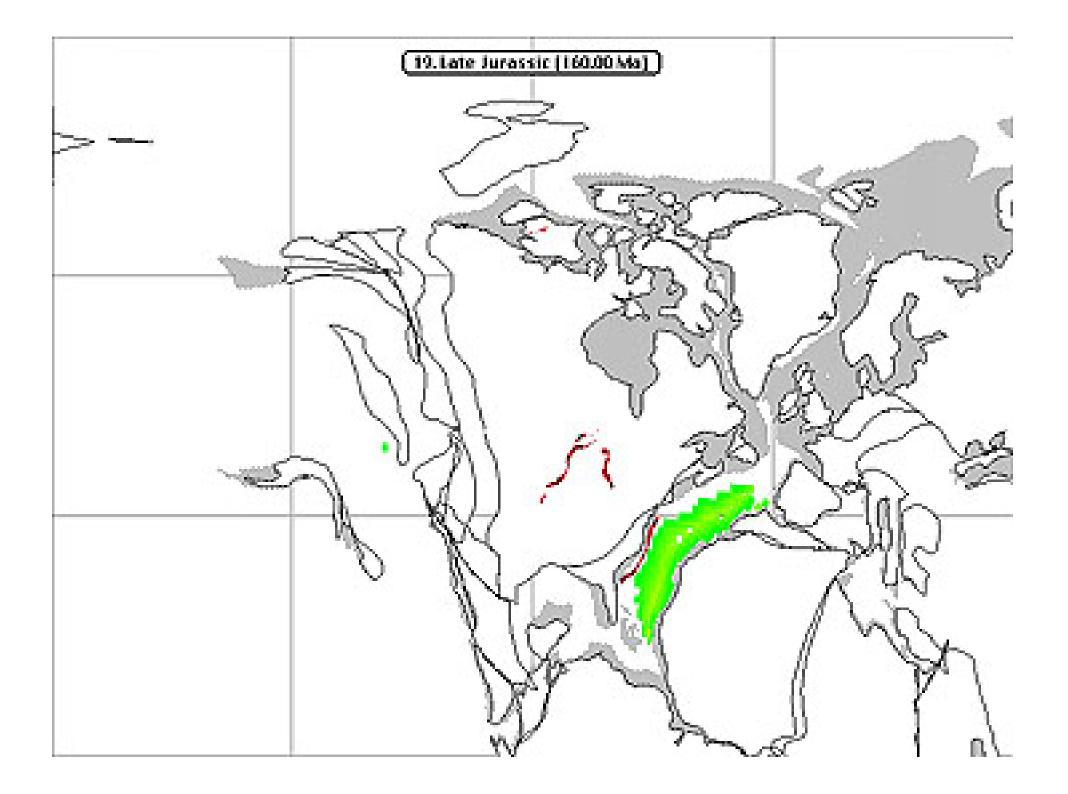


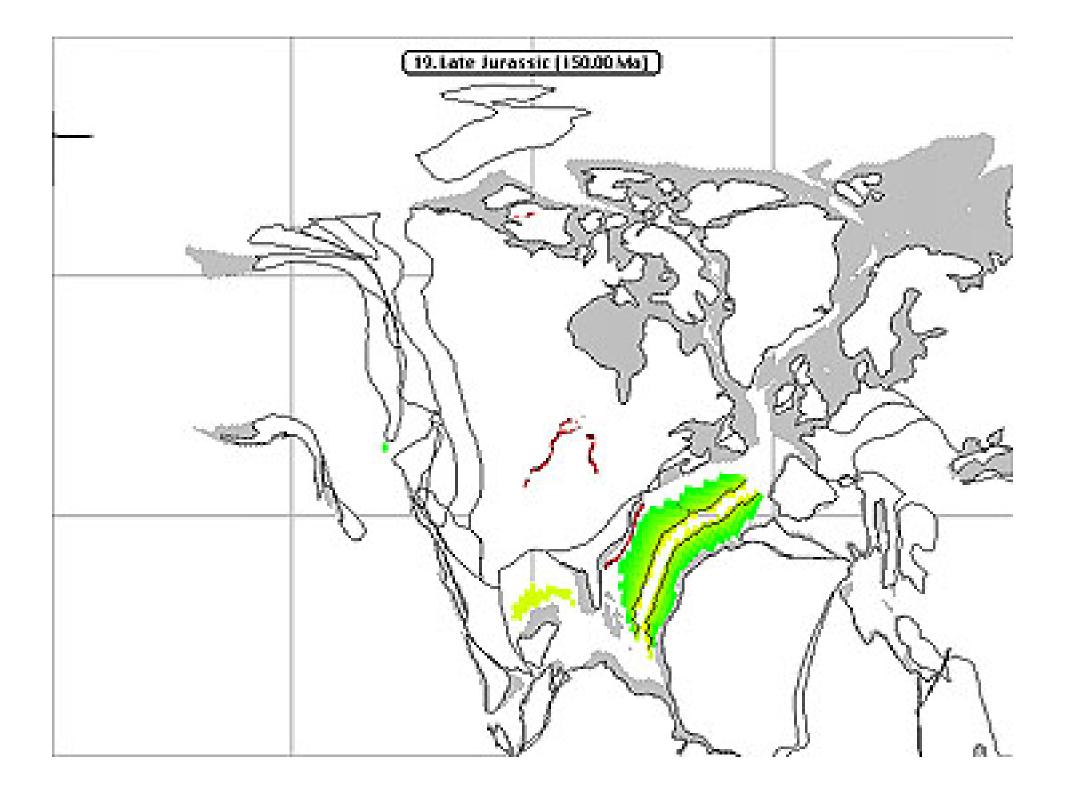


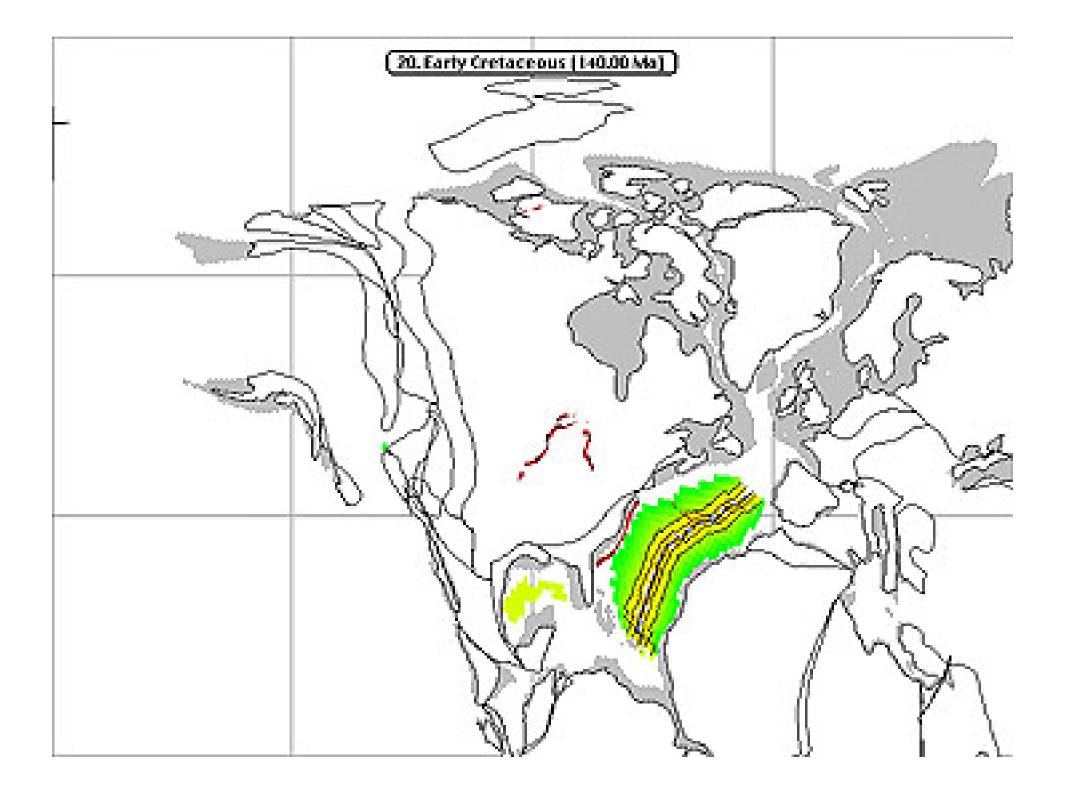


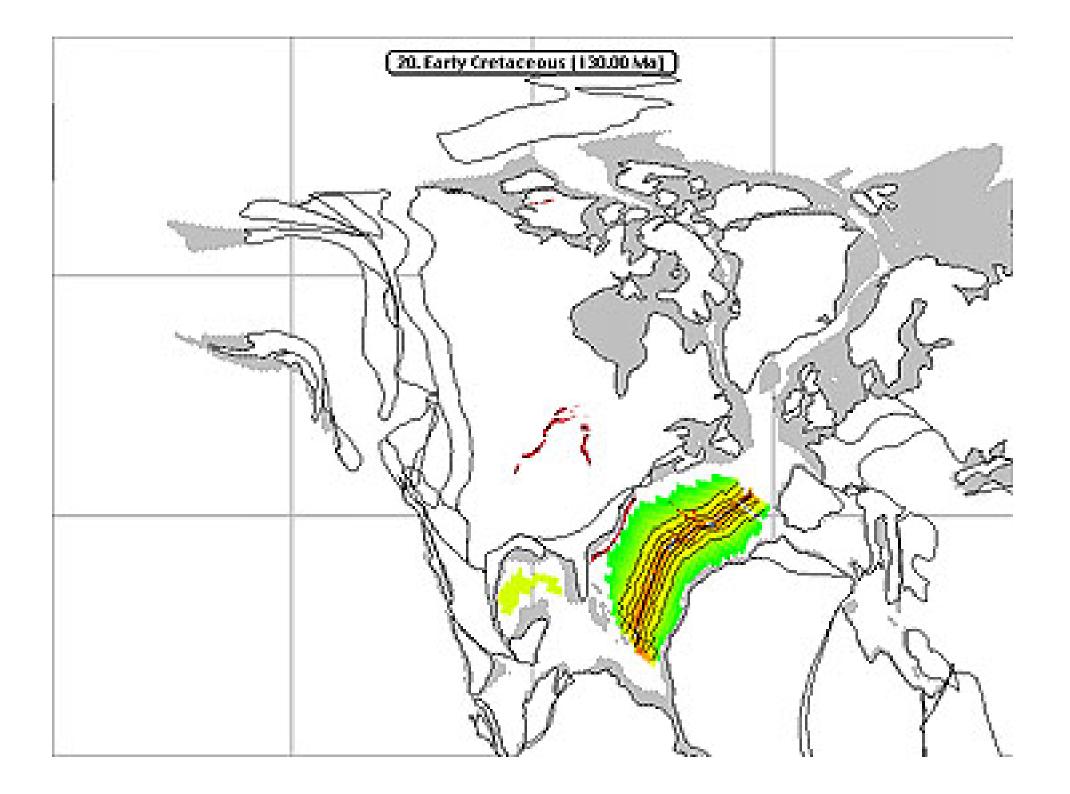


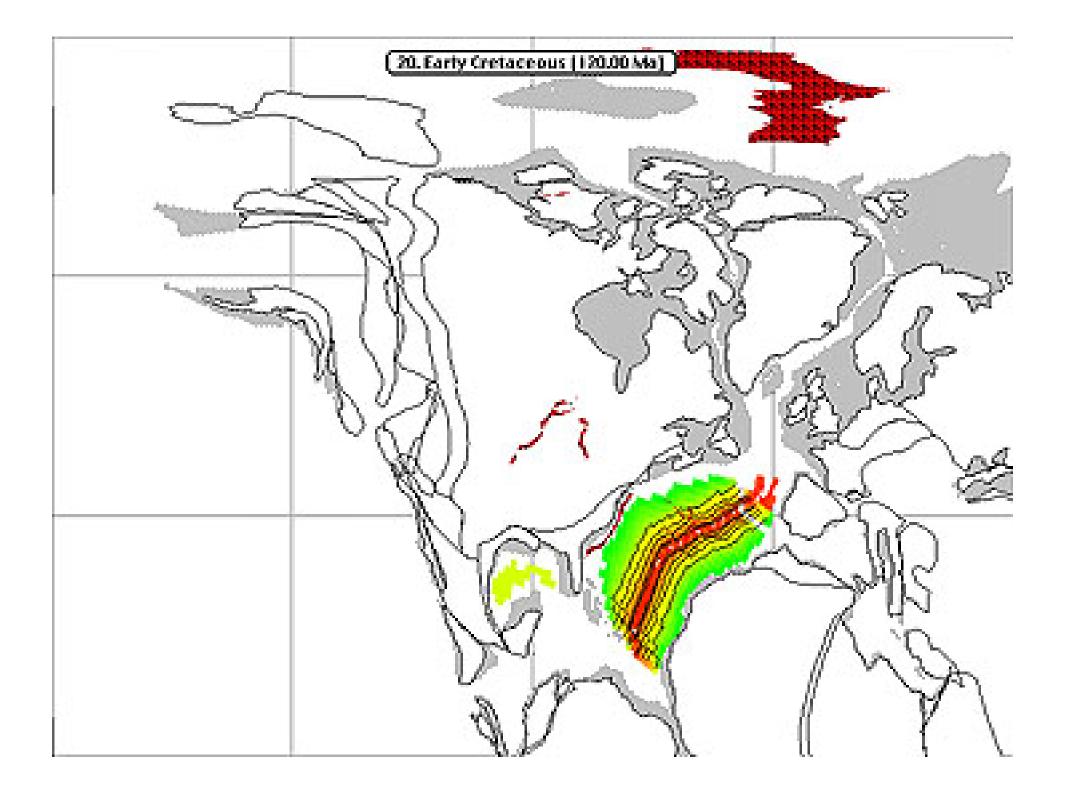


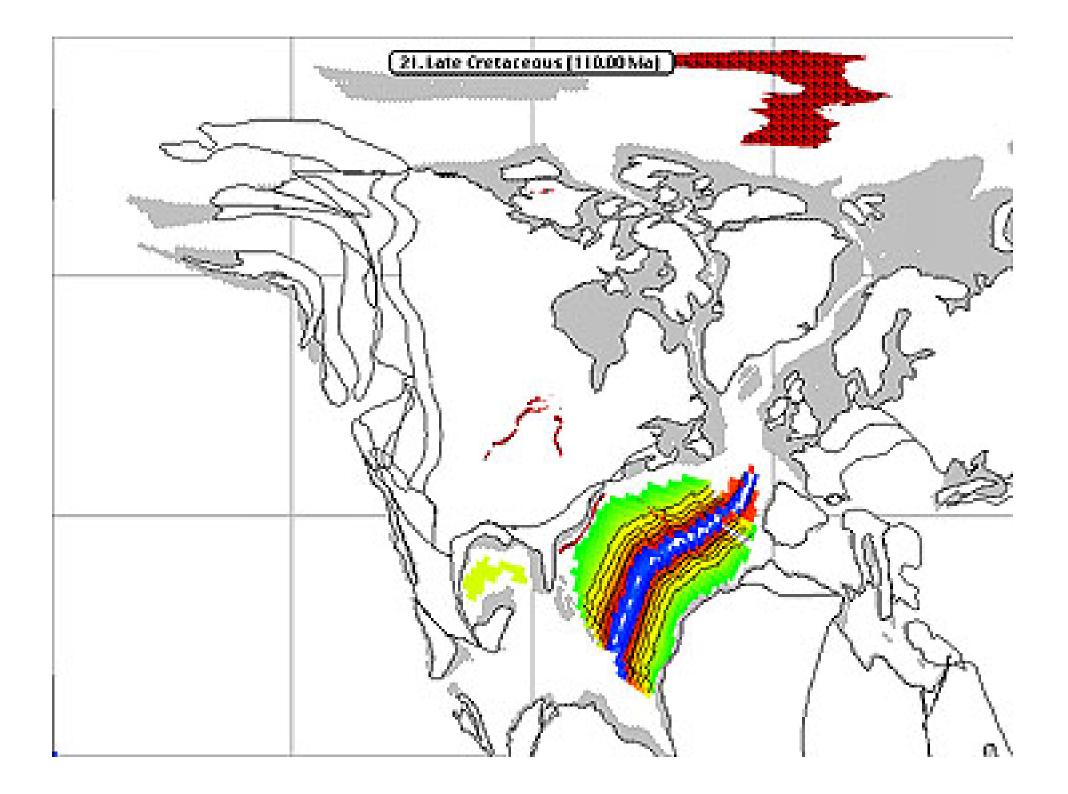


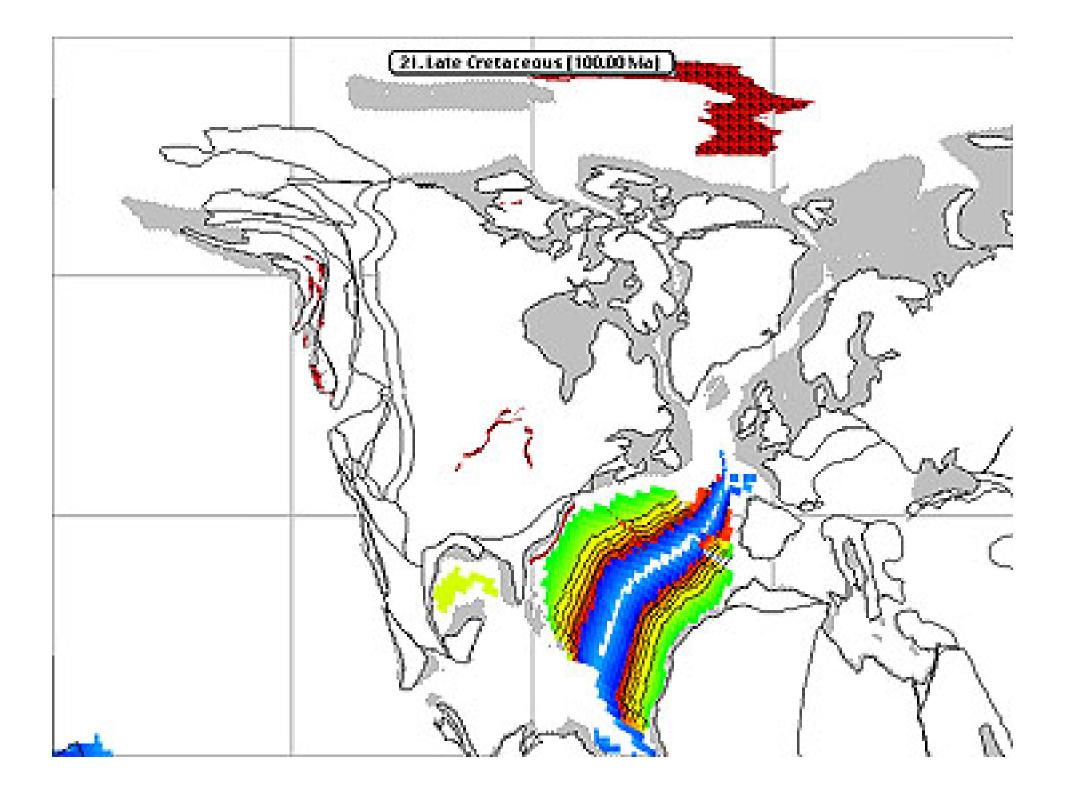


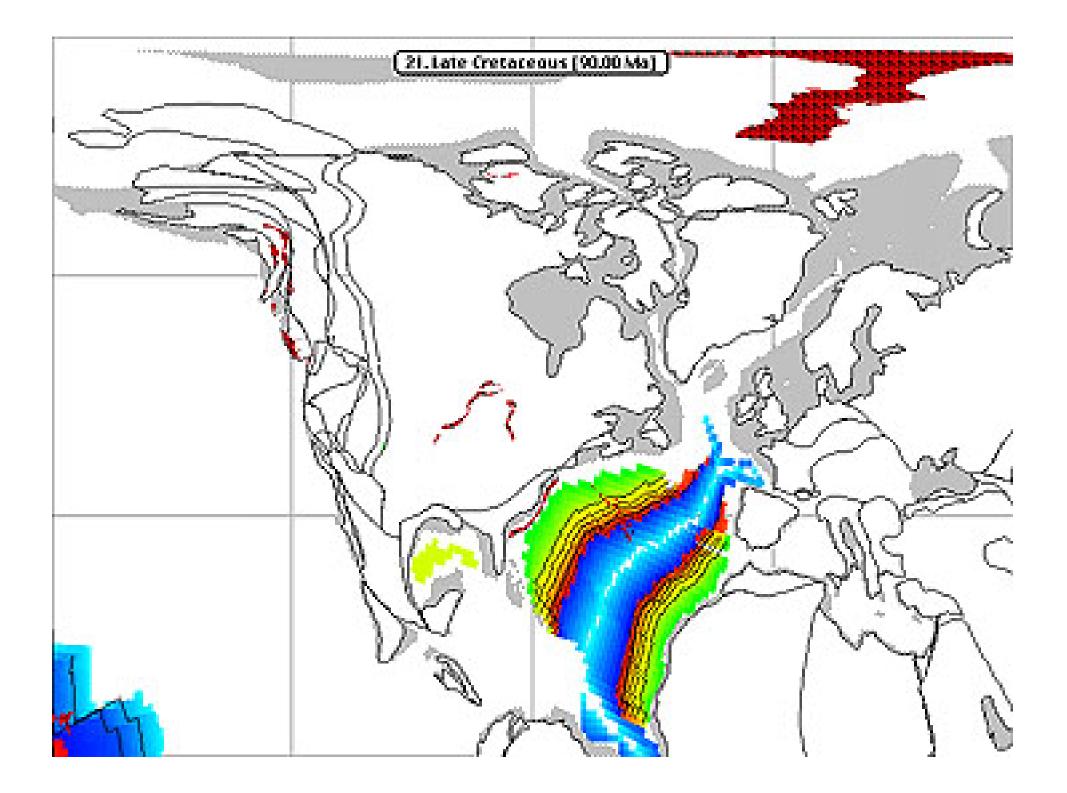


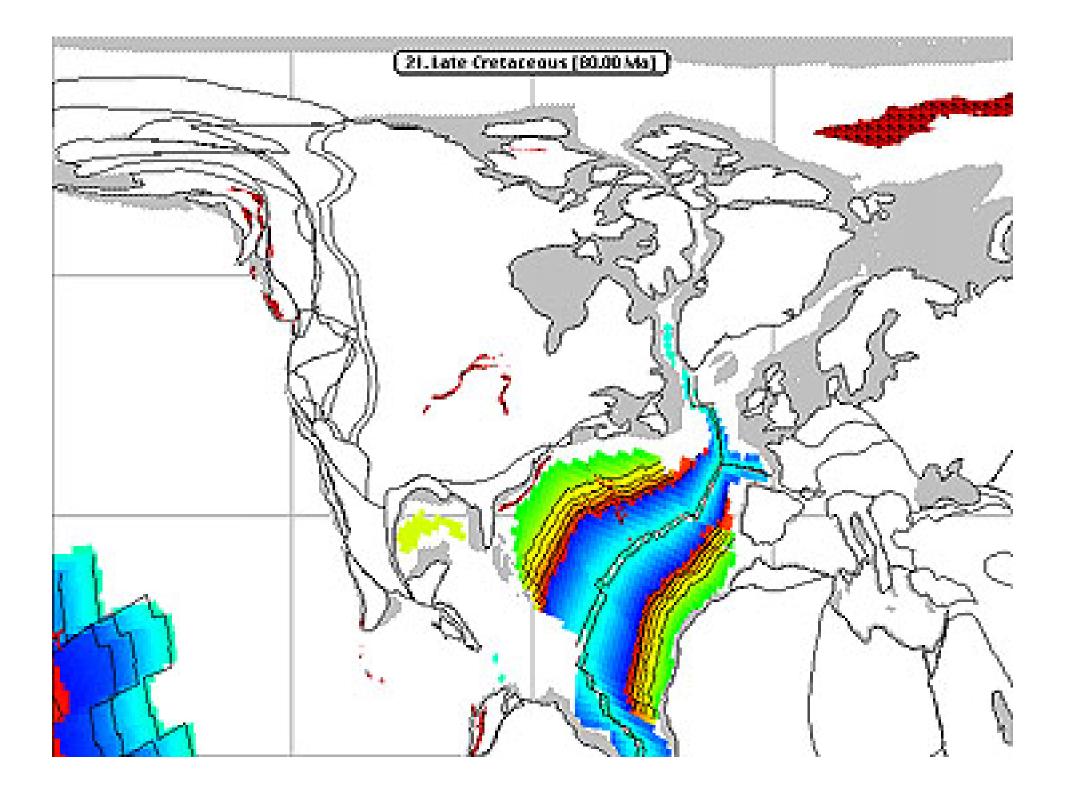


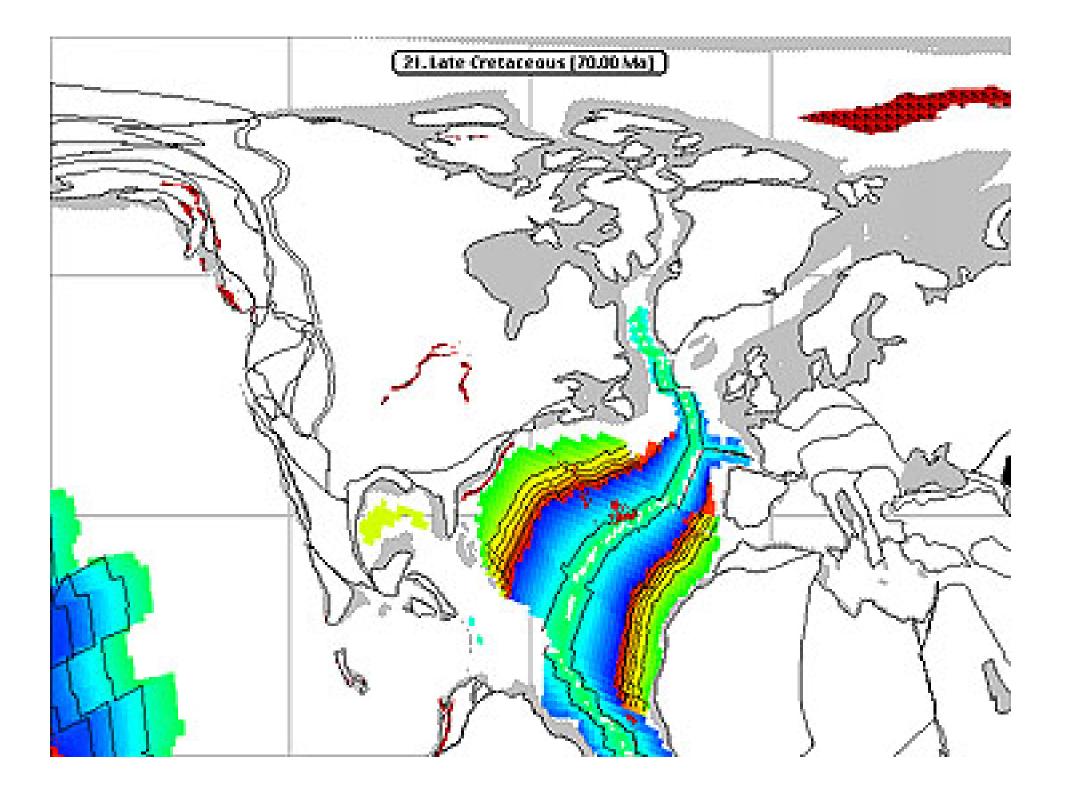


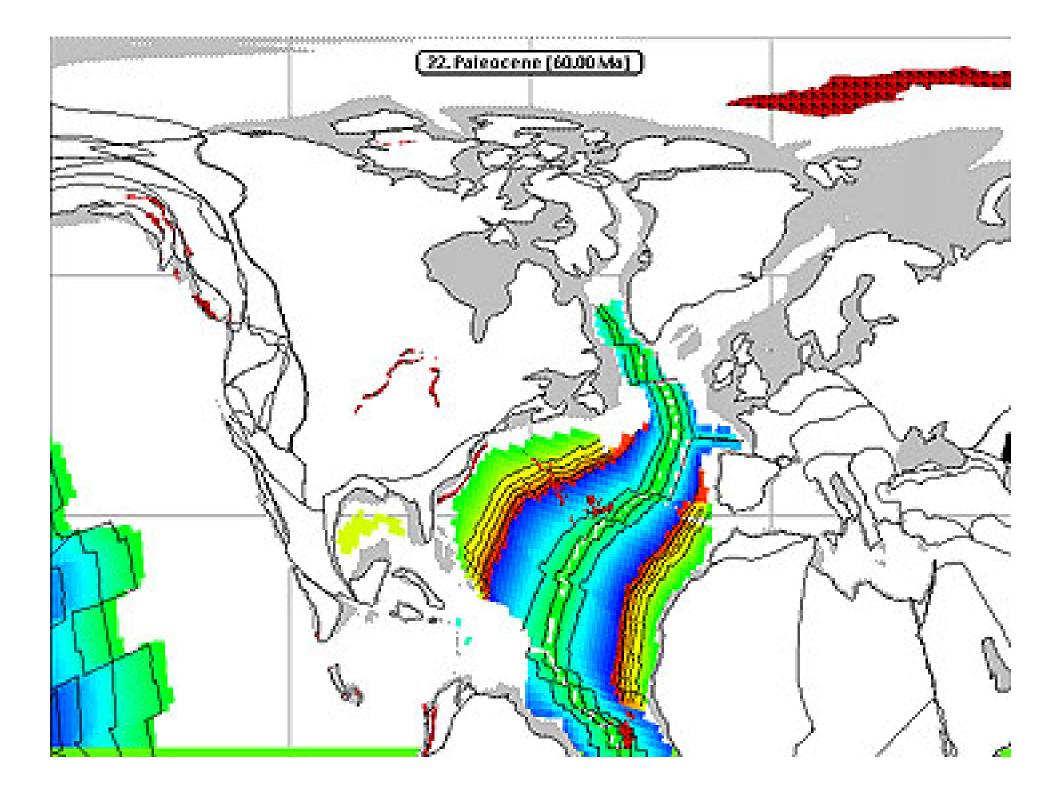


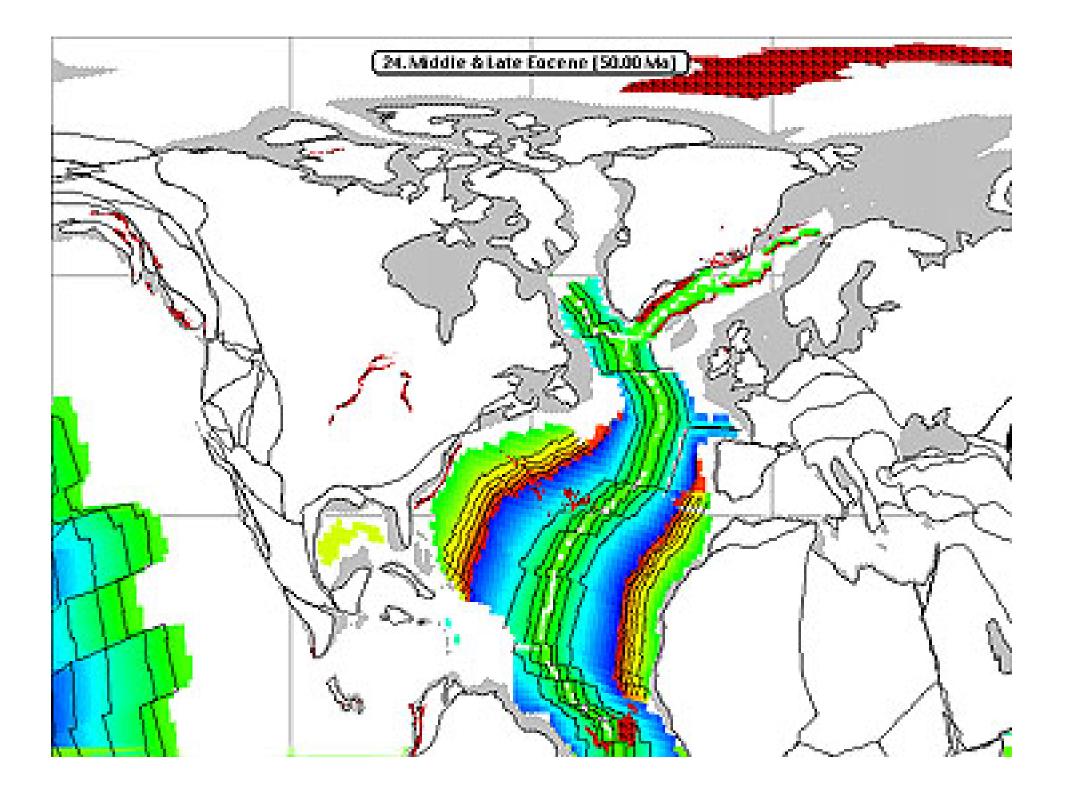


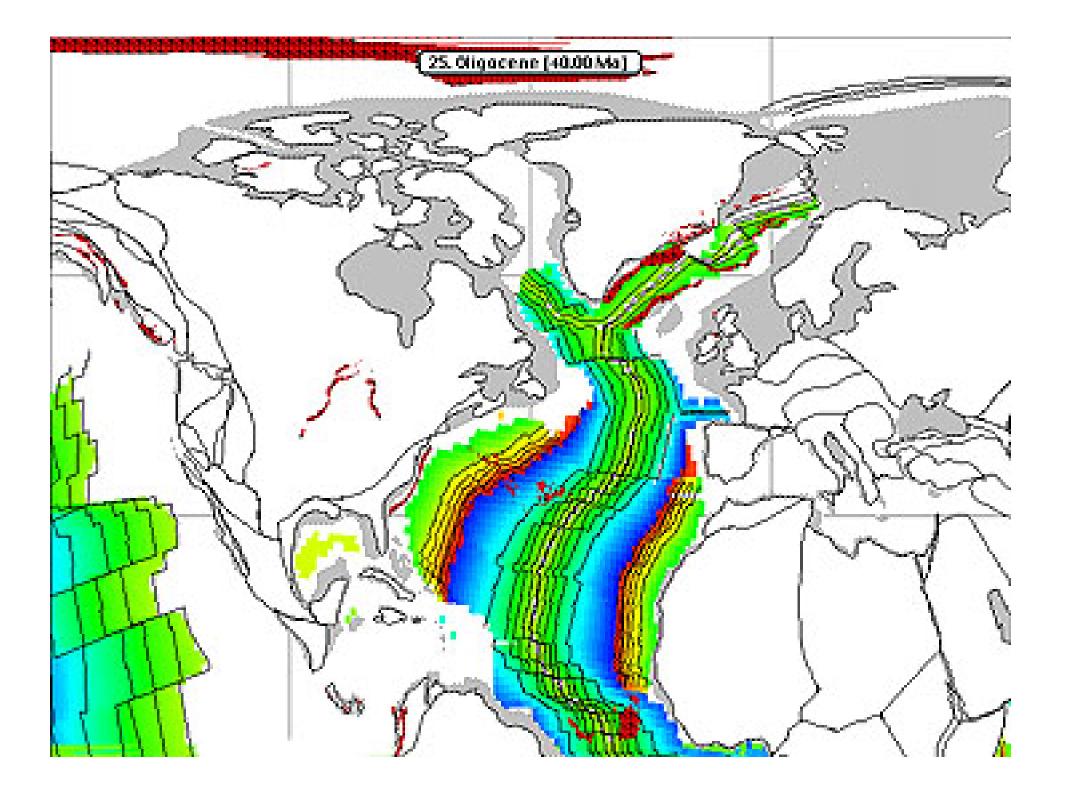


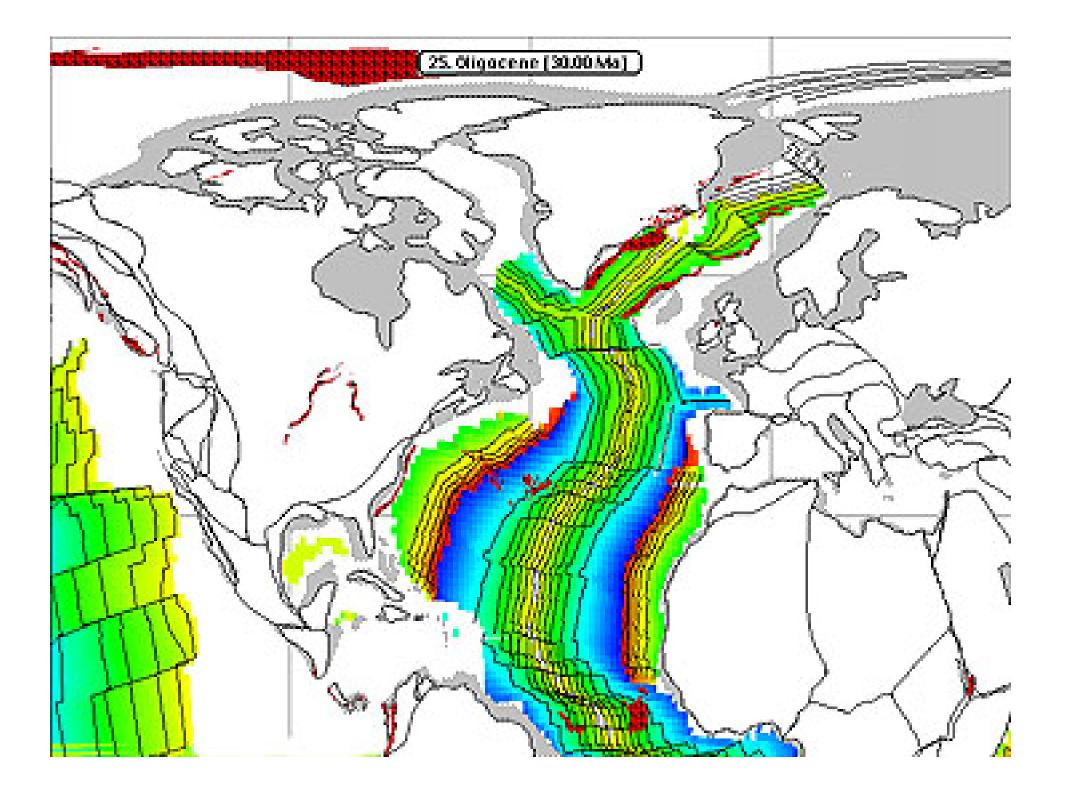


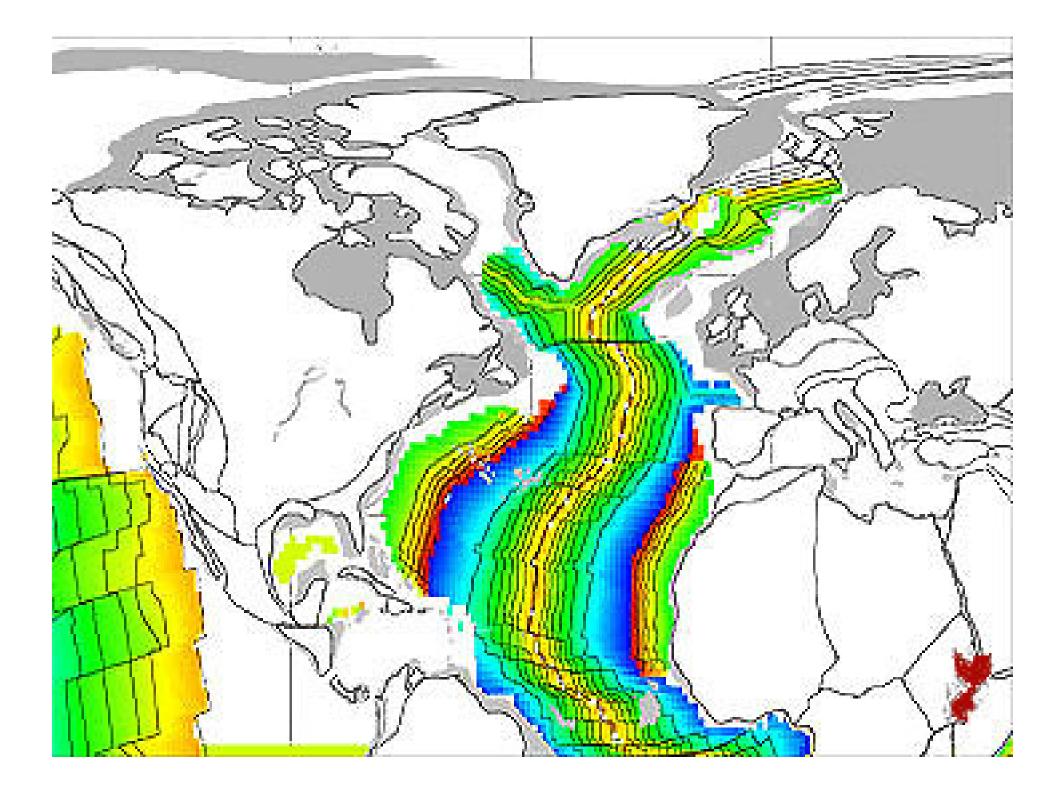


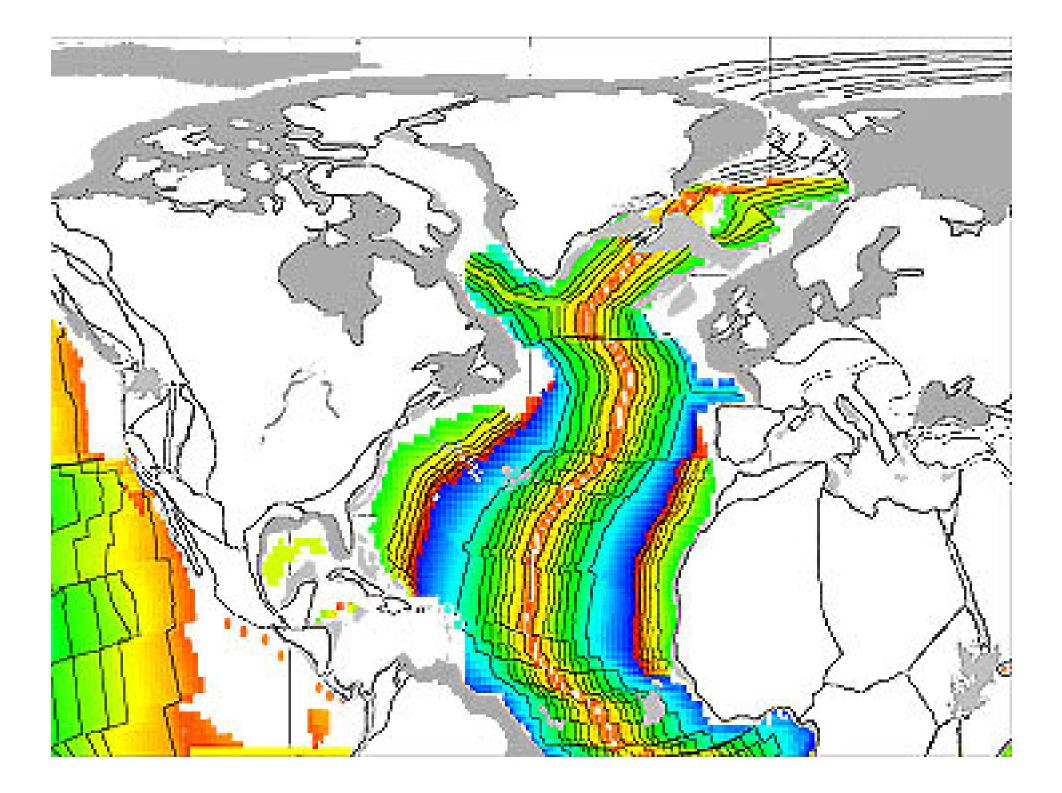


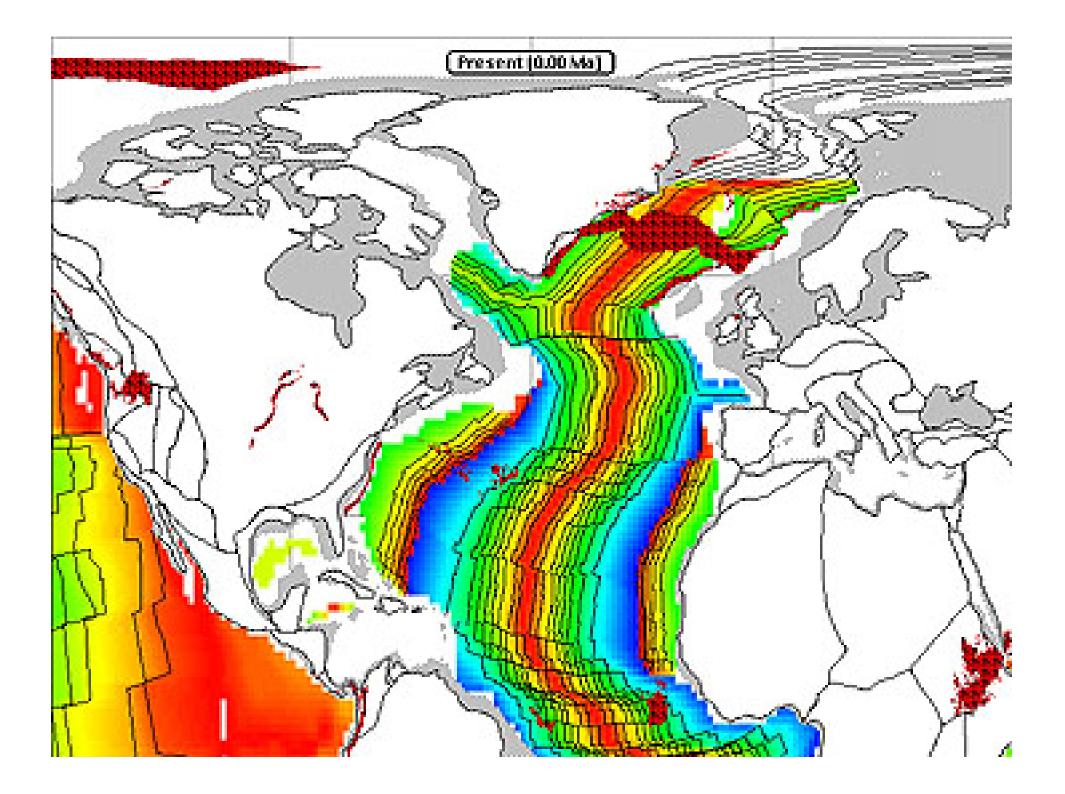




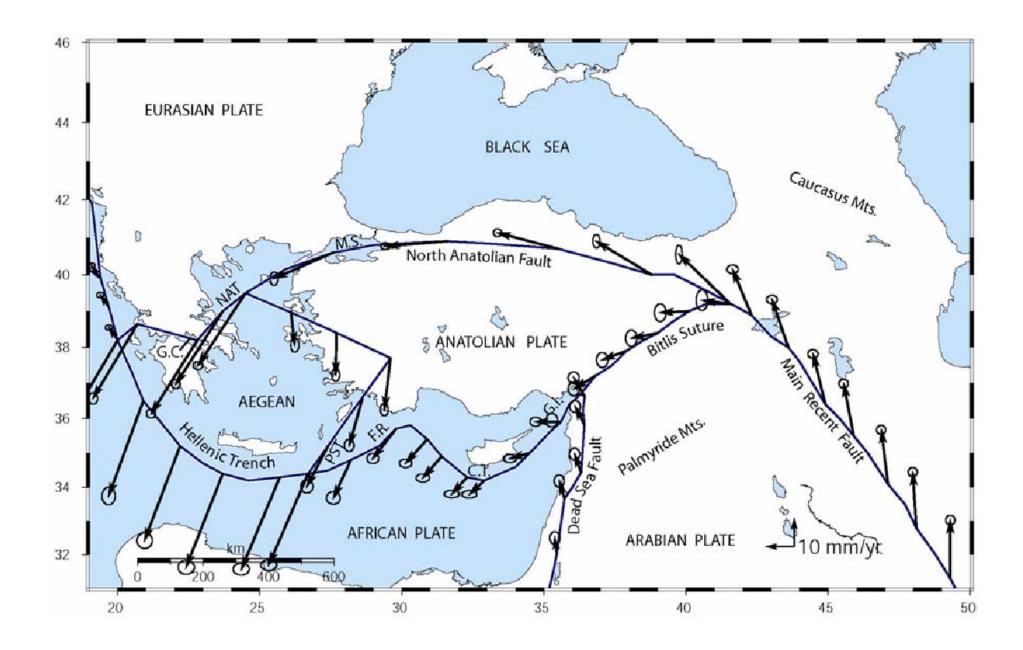




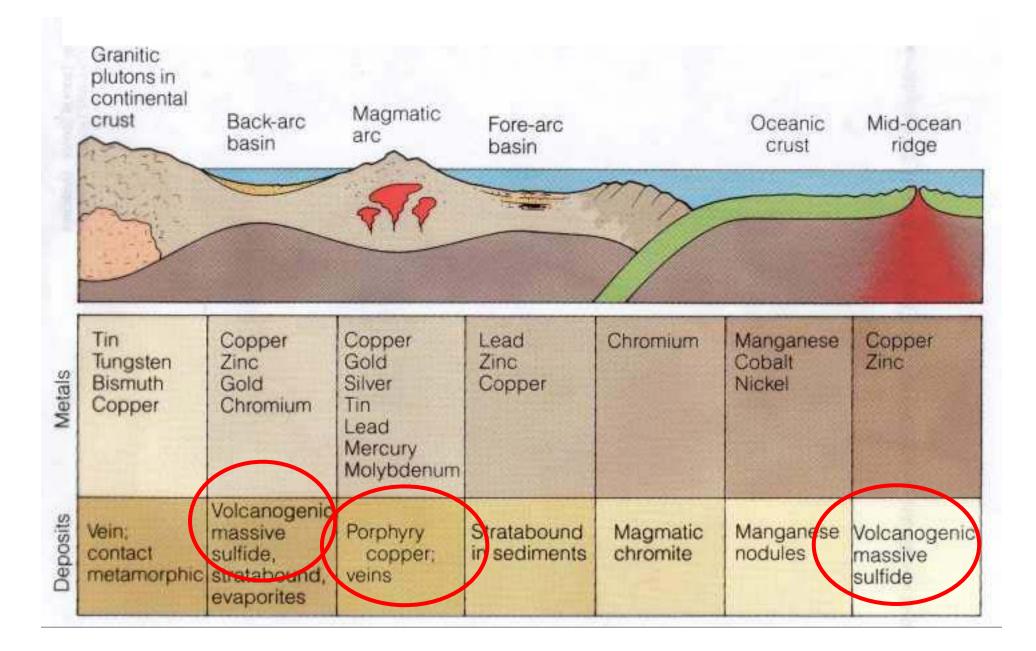




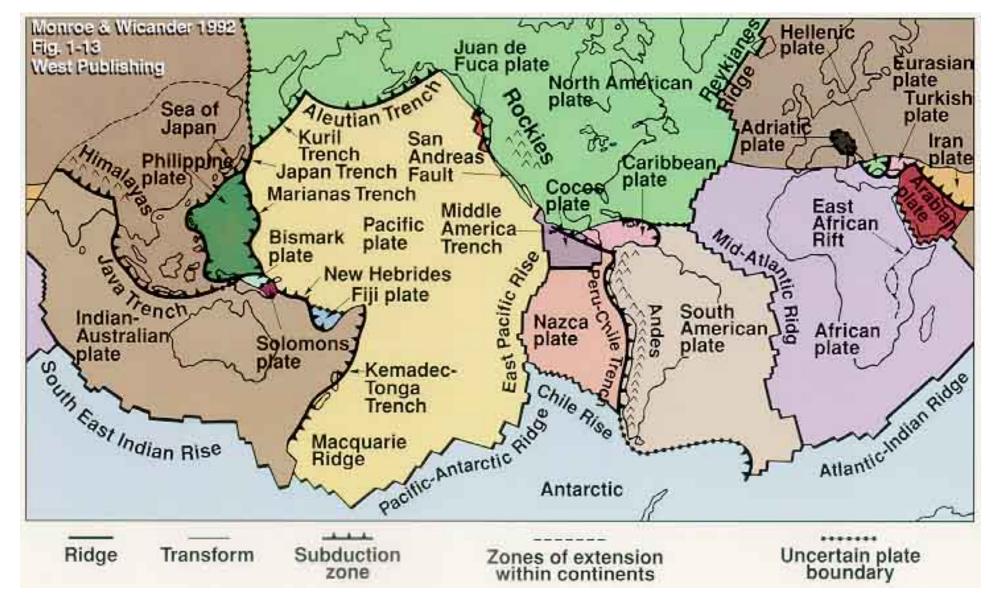
### Plates in motion



### Plate Tectonic Ore Deposit Formation

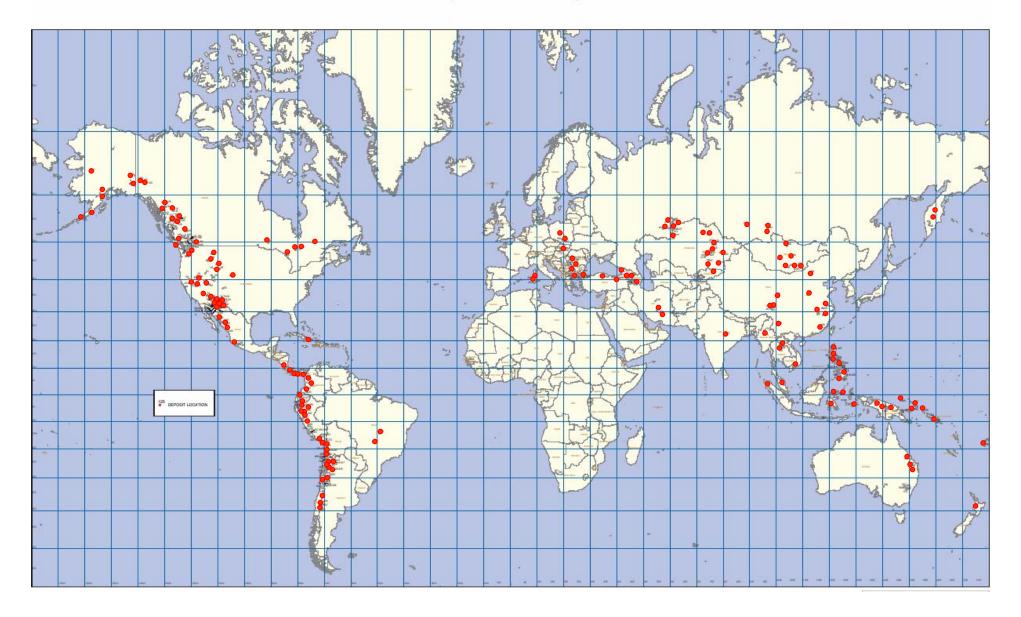


#### **Plate Tectonics**

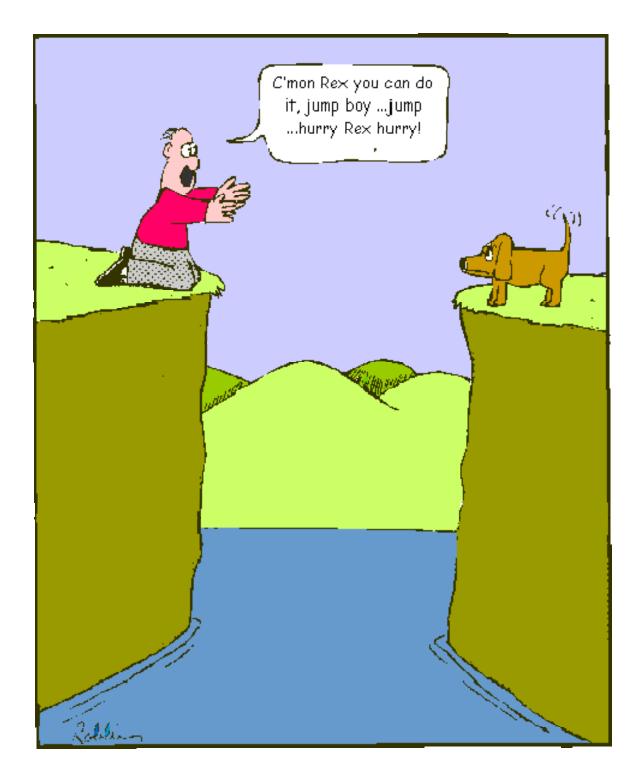


# World Copper Deposits

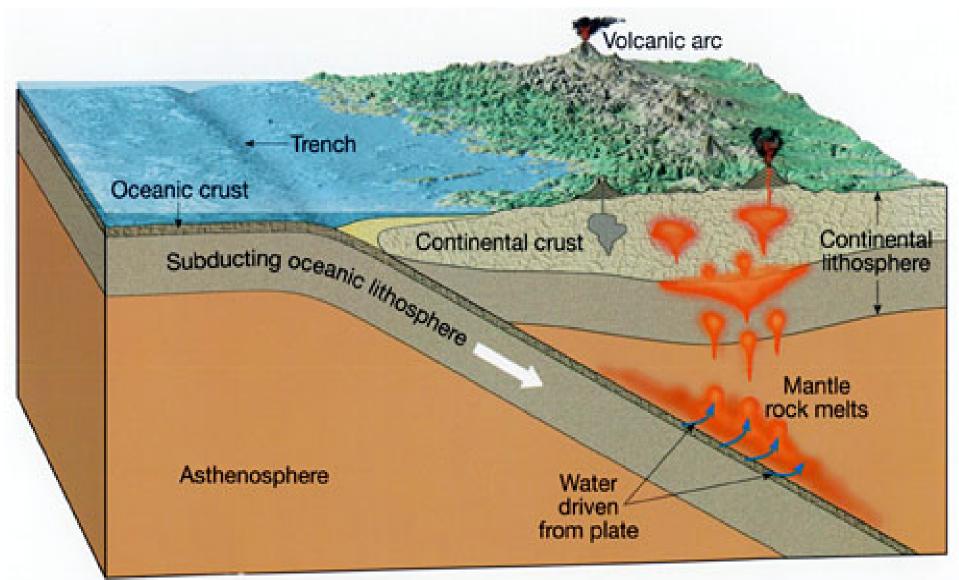
PORPHYRY COPPER DEPOSITS OF THE WORLD (SEE DETAILED MAPS FOR CLUTTERED AREAS)



A down side of continental drift

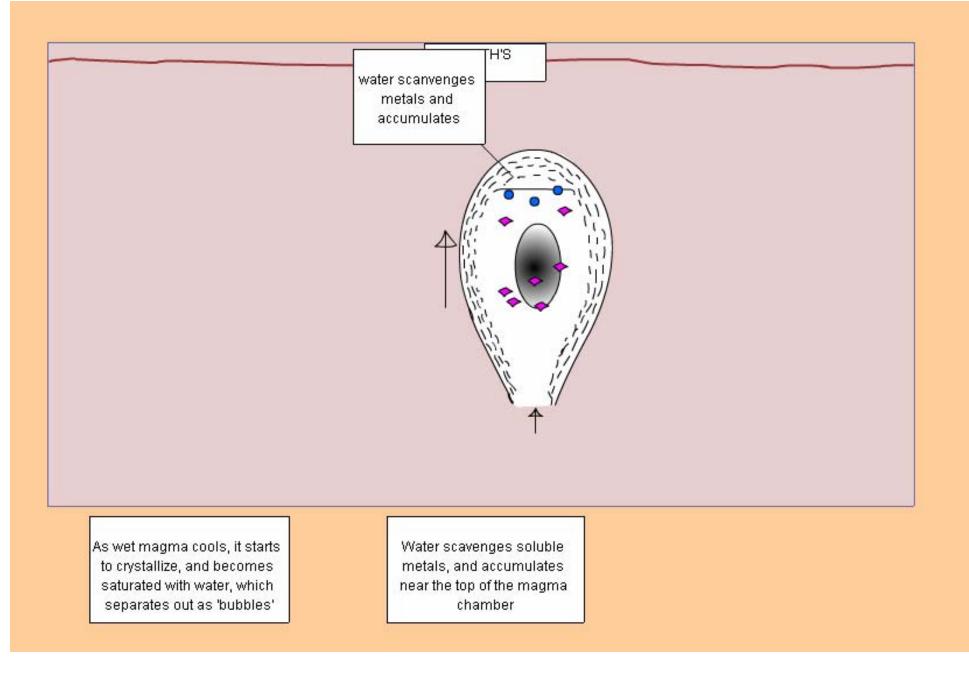


# Ocean-Continent Boundaries →Porphyry Deposits

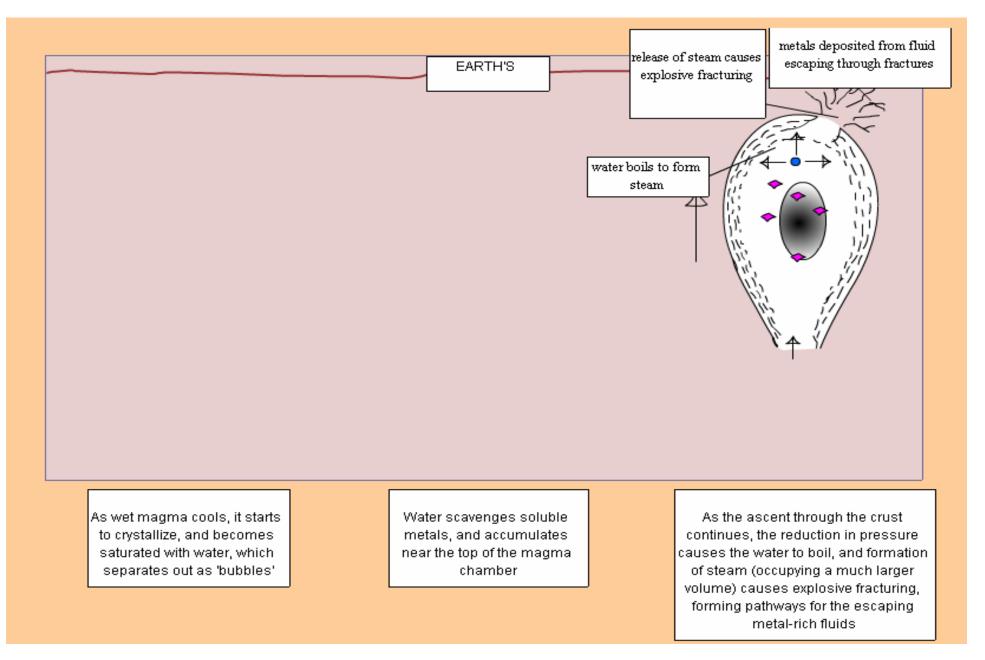


# Development of Porphyry Ore Deposit EARTH'S crystallization RISING MAGMA BODY wet As wet magma cools, it starts to crystallize, and becomes saturated with water, which separates out as 'bubbles'

## Development of Porphyry Ore Deposit

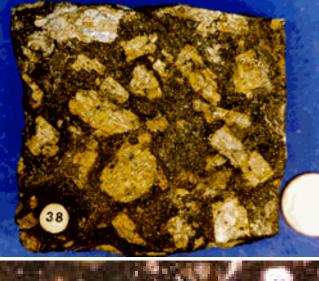


## Development of Porphyry Ore Deposit

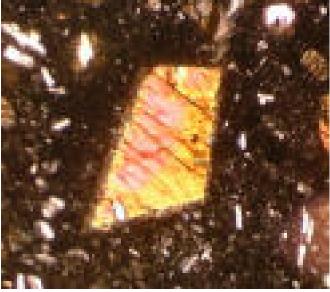


# Characteristic of Porphyry Formation

Large mineral crystals in matrix of fine crystals. Slow cooling at high temperatures followed by rapid cooling at lower temperature.









#### **Porphyry Chalcopyrite ore**

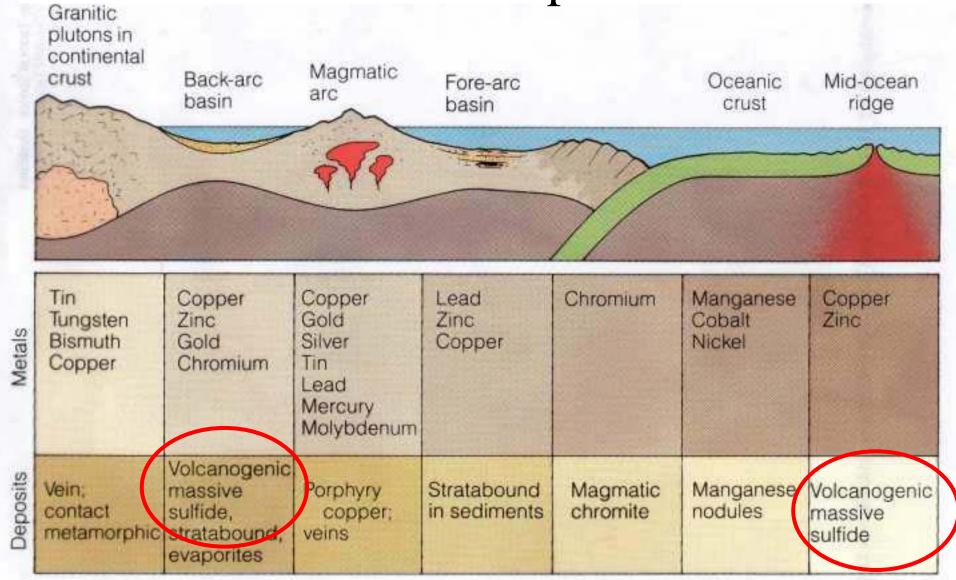
#### CuFeS2



# Porphyry Copper Mining

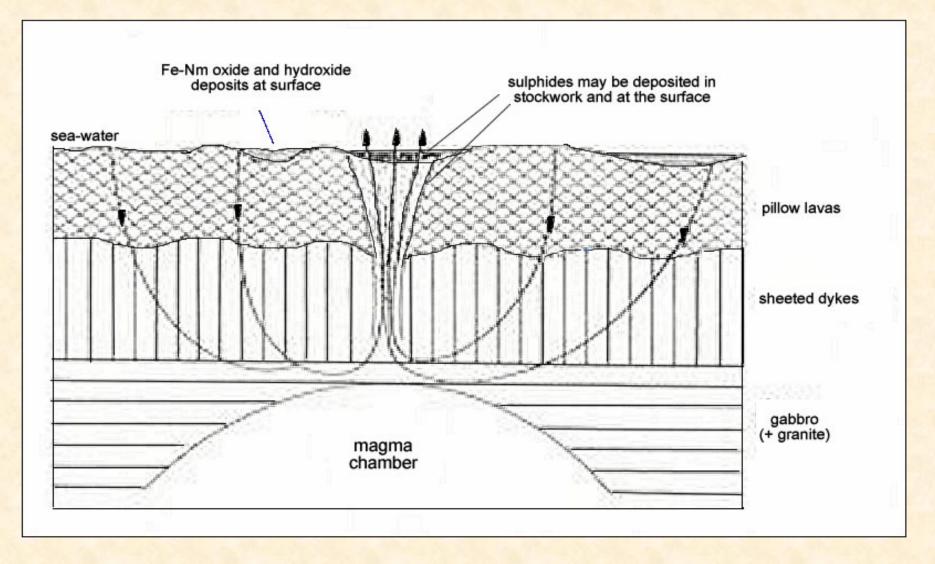


## Plate Tectonic Ore Deposit Formation Massive Sulphide



# Massive Sulphide Ore Deposit

**Cyprus-type Massive Sulphides** 

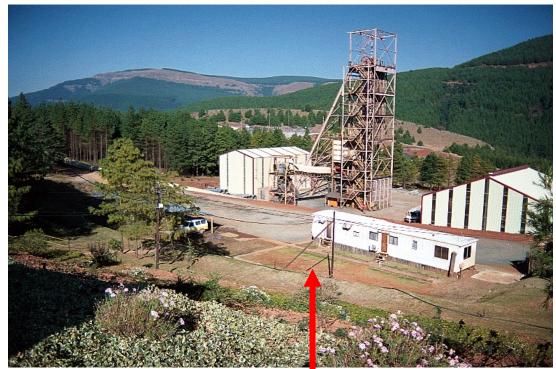


# Black Smokers → Create Volcanogenic massive Sulphides



black smoker.avi

Massive Sulphide Copper Mine much smaller deposits, higher concentration of copper





Mine Head

Ore Vein

## Bronze Age Mining



Bronze age mine entrance, 4000 BC



Burning wood to heat/crack stone copper ore

> Basic tools were stone hammers, wooden shovels, and fire



# Copper and why not Iron?

Copper was one of the first metals used, because it was comparatively easy to refine, and workable into objects. It was difficult to get hot fires to melt iron.

Material	Melting Point	
Copper	1084.62 °C	
Zinc	419.53 °C	
Tin	231.93 °C	
Iron	1538 °C	

### Timeline of Copper/Bronze/Iron Ages

- 7000 BC First evidence of copper production in eastern Turkey
- 4500 BC Copper working in Balkans, Aegean
- 3000 BC Bronze-making in Balkans/Greece/Turkey/Near East
- 2500 BC First iron objects, Turkey
- 1000 BC Widespread use of iron

## Malachite copper ore

#### $Cu_2(CO_3)(OH)_2$





Early miners looked for Malachite, a copper ore that was easy to refine

The green color hints that it has copper inside

# Making Copper I

Start with Copper ore, Malachite:  $Cu_2(CO_3)(OH)_2$ 

Heat in kiln:

 $Cu_2(CO_3)(OH)_2 = 2CuO + CO_2 + H_2O$ 

To get copper oxide, brownish powder

Then reducing fire, charcoal, oxygen-starved (rich in CO) to remove oxygen

At about 1100° C, copper oxide forms copper metal:

 $CuO + CO = Cu + CO_2$ 



Bronze age pottery crucible for metal smelting

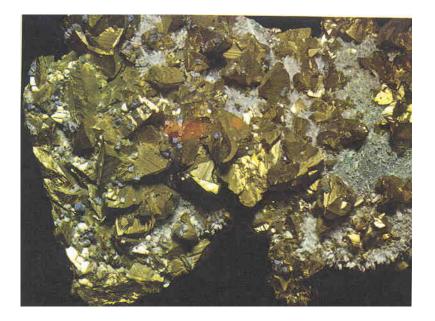
# Making Copper II

Although Malachite was easier to smelt, Chalcopyrite, was more plentiful.

```
Start with Copper Sulfide ore,
CuFeS<sub>2</sub>
```

Heat in kiln while blowing air through

(roasting) :



#### $4CuFeS_2 + 13O_2 \rightarrow 8SO_2 + 2Fe_2O_3 + 4CuO$

Copper oxide was then reduced by stirring with green wood poles (effectively adding carbon to form  $CO_2$ )

Flux of  $SiO_2$  was needed to dissolve the iron and float it to the surface. After cooling, it could be shattered and broken off, leaving copper.

### Bronze

Bronze is an alloy of copper. Normally some Tin (10%) is added. Early bronze was Copper-arsenic, because Arsenic was easier to find. Bronze is a much stronger material than copper, so better for tools, weapons.

(Estimate for total bronze production in bronze age ~ 1 million tons. Cyprus – 200 kt; Rio Tinto – 100 kt )

#### Tin, Arsenic Ores



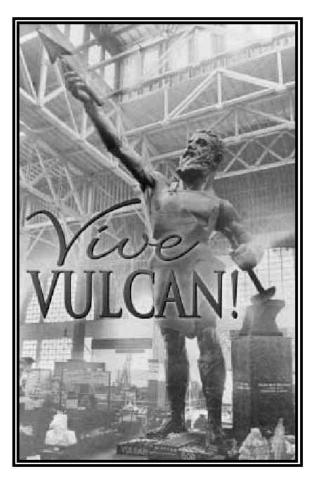


Casserite SnO<sub>2</sub> Not very distinctive Adamite Cu<sub>2</sub>AsO<sub>4</sub>

# Arsenic Poisoning

Early Bronze was Cu-As. Arsenic is much more common that Tin and easier to identify. Smelters worked outside, no problem from the arsenic vapors. However the smiths worked inside, and would contract arsenic poisoning. First symptoms are nerve damage to limbs, crippling. Ultimately Bronze chemistry was switched to tin.

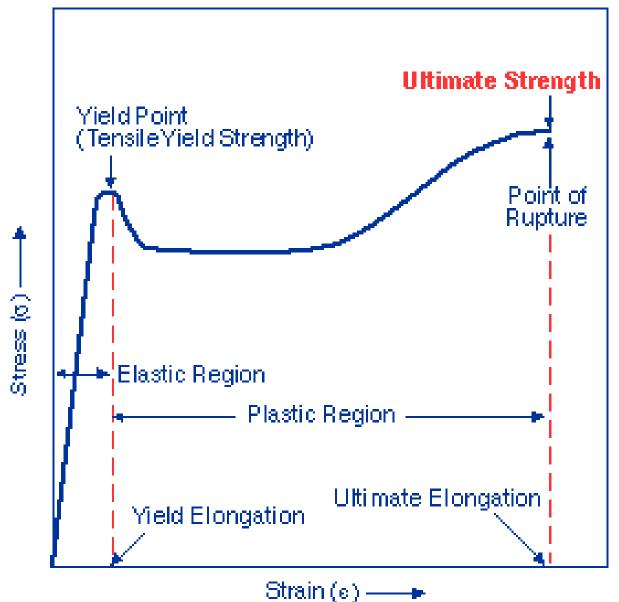
# Vulcan, god of metalworking





Roman god Vulcan and analogous Greek god Hephaestus were always portrayed as lame, probably because many early metalworkers had arsenic poisoning and were crippled.

# Strength of Materials



Change in length (Strain) is measured while pulling on test sample (Stress). Material acts springlike for a while, then deforms (stretches), finally breaks.

# Strength of Materials The advantage of bronze

Material	Yield Strength	Ultimate Strength
Copper	10,000 psi (10 ksi)	30 ksi
Bronze	30 ksi	50 ksi
Wrought iron	18 ksi	25 ksi
Mild steel	35 ksi	50 ksi
Tool steel	100 ksi	150 ksi

# Metal was of great economic importance

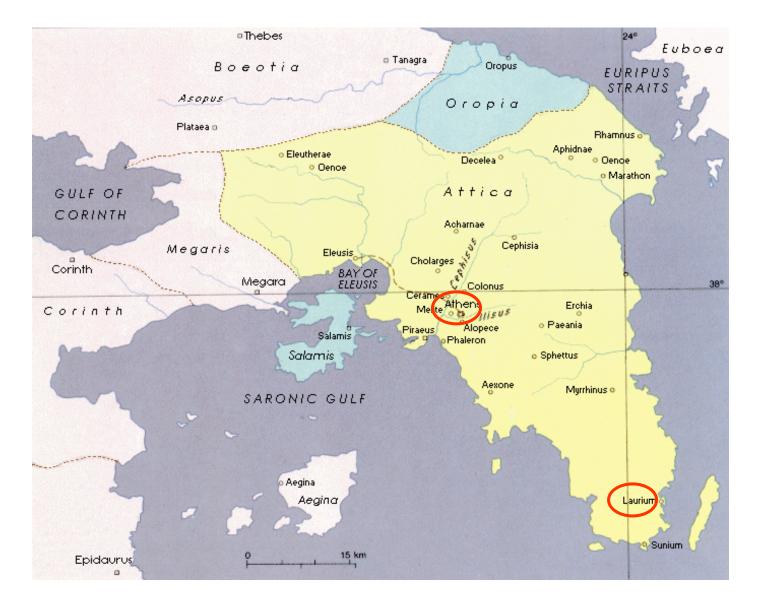
Athens became a great city state because it had a very large silver and lead mine under its control, Laurion Mines. 160 million ounces of silver was mined at Laurion. (A billion dollars worth today, even though silver is much more common now!)

Money was used to buy naval power, armies, as well as civil construction.

20,000 slaves worked the mines.

During Peloponnesian Wars (430 BC), Sparta laid siege to Laurion Mines before Athens.

#### Laurion Mines



#### Laurion Mines





Gallery. Height about 3 feet.

# Athenian silver coin from Laurion

# **Ecological Impact of Mining**

Early metal smelting needed enormous amounts of wood for fuel.

Copper smelting needs a great deal of fuel, especially if the ore supply is dominantly sulfide. About 300 kg of charcoal are needed to produce 1 kg of copper by smelting 30 kg of sulfide ore. A ton of charcoal needs somewhere between 12 and 20 cubic meters of wood, and for each cubic meter of wood a 100-year old tree has to be felled. So 3 large trees per pound of copper.

During life of Laurion Mines, about 300 years from 500 BC to 200 BC, 1 million tons of charcoal and 2.5 million acres of forest were consumed.

# Over-foresting and the fall of Athens

Eventually, all forests around Athens were destroyed. Mine stopped producing, not because of lack of ore, but lack of wood.

Cutting the forests caused erosion.

Plato writes about environment of Athens:

a mere relic of the original country.... What remains is like the skeleton of a body emaciated by disease. All the rich soil has melted away, leaving a country of skin and bone. Originally the mountains of Attica were heavily forested. Fine trees produced timber suitable for roofing the largest buildings: the roofs hewn from this timber are still in existence.

Athens destroyed at end of Peloponnesian Wars. Although Laurion still had silver ore, no wood to use to refine.

With the end of silver production, Athens fell from power.

# Over-foresting in the ancient world

- Cyprus produced 200,000 tons copper. Needed 40 million acres of forest!
- As a scale, recent California fires burned 600,000 acres.
- Current aridity and lack of trees in Cyprus, Greece, Lebanon and lack of trees thought to be aftermath of this deforestation. (Earlier thought due to introduction of goats and overgrazing.)

# End of the Bronze Age

- Bronze Age "officially" ended around 1200BC in the Aegean region. Fall of Troy, end of Mycenaean civilization.
- Result was 400 years of "dark age" before rise of Greek civilization around 800BC. Loss of writing, ...
- Cause(s) under debate:
  - Earthquakes
  - Invasions
  - Change in techniques of warfare (chariot vs infantry)
  - Deforestation
  - Cutoff of tin supply

### Source of Tin for Bronze

Tin is pretty scarce. Where did the tin come from that was used for bronze? It is a question that interests archeologists today. The origin of the tin tells about the ancient trade routes and commerce. Science can be used to find out the source of the tin.

## Chemical Assay used to compare 5 different copper artifacts

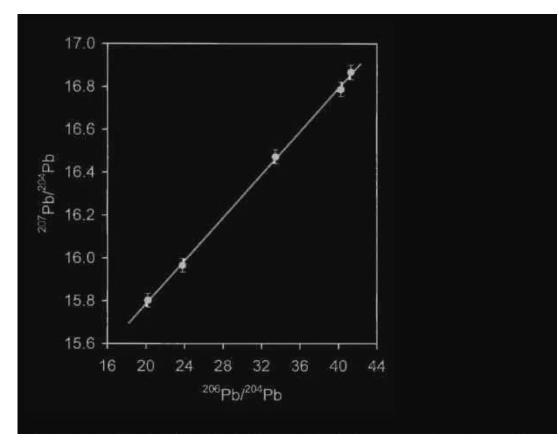
Artefact													
	Cu	Sn	As	Sb	Ag	Pb	Fe	Ni	Co	Zu	Au	Bi	5
WG2060	98.66	0.01	1.17	ㅂ	0.05	0.01	0.02	0.02	tt <sup>2</sup>	nd	0.05	ㅂ	0.01
1905.11.6.3	95.70	0.01	3.77	0.10	0.04	0.03	0.20	0.07	Ъ,	ᇿ	0.02	0.06	0.01
1927.7 - 13.1	97	nd	1.4	0.04	0.02	0.01	0.03 <sup>5</sup>	0.09 <sup>+</sup>	nd	nd	118	0.02	na
84.83 H/1	96.7	nd	3.07	nd	0.05	nd	nd	0.16	nd	nd	nd	0.02	na
84.83 H/3	94.8	nd	4.59	τ	0.02	Г	0.01	0.50	nd	nd	0.02	0.01	na

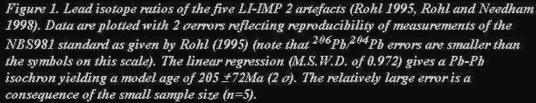
Table 3. Chemical compositions of the five LI-IMP 2 artefacts (wt.%).

# Radioactive decay chains into lead isotopes

<sup>238</sup> U series		<sup>232</sup> Th series		<sup>235</sup> U series	
<sup>238</sup> U	4.47x10 <sup>9</sup> yr	<sup>232</sup> Th	1.40x10 <sup>10</sup> yr	235U	7.04x10 <sup>8</sup> yr
<sup>234</sup> Th	24.1 day	<sup>228</sup> Ra	5.75 yr	<sup>231</sup> Th	25.5 day
<sup>234</sup> Pa	1.18 min	228 <sub>Ac</sub>	6.13 hr	<sup>231</sup> Pa	3.25x10 <sup>4</sup> yr
<sup>234</sup> U	2.48x10 <sup>5</sup> yr	<sup>228</sup> Th	1.91 yr	<sup>227</sup> Ac	21.8 yr
<sup>230</sup> Th	7.52x10 <sup>4</sup> yr	<sup>224</sup> Ra	3.66 day	<sup>227</sup> Th	18.7 day
<sup>226</sup> Ra	1.62x10 <sup>3</sup> yr	<sup>220</sup> Rn	55.6 sec	<sup>223</sup> Ra	11.4 day
<sup>222</sup> Rn	3.82 day	216 <sub>Po</sub>	0.15 sec	<sup>219</sup> Rn	3.96 sec
<sup>218</sup> Po	3.05 min	212 <sub>Pb</sub>	10.6 hr	215 <sub>Po</sub>	1.78x10 <sup>-3</sup> sec
<sup>214</sup> РЪ	26.8 min	212 <sub>Bi</sub>	60.6 min	211 <sub>Pb</sub>	36.1 min
<sup>214</sup> Bi	19.7 min	212 <sub>Po</sub>	3.0x10 <sup>-7</sup> sec	<sup>211</sup> Bi	2.15 min
<sup>214</sup> Po	1.64x10 <sup>-4</sup> sec	208 <sub>Pb</sub>	stable	<sup>207</sup> T1	4.77 min
<sup>210</sup> РЬ	22.3 yr			<sup>207</sup> Pb	stable
<sup>210</sup> Bi	5.01 day				199
210 <sub>Po</sub>	138 day				
<sup>206</sup> РЪ	stable				

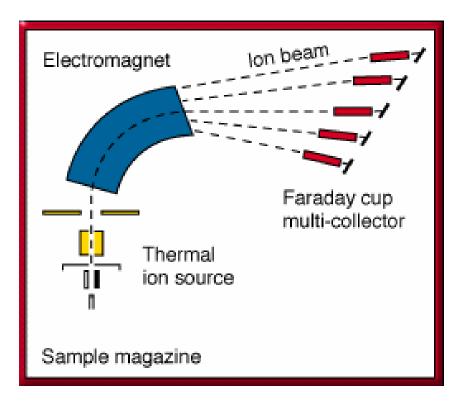
## Radio-isotope comparison of 5 different samples





$$Pb^{207}/Pb^{206} = [U^{235}(e^{L235t}-1)]/[U^{238}(e^{L238t}-1)]$$

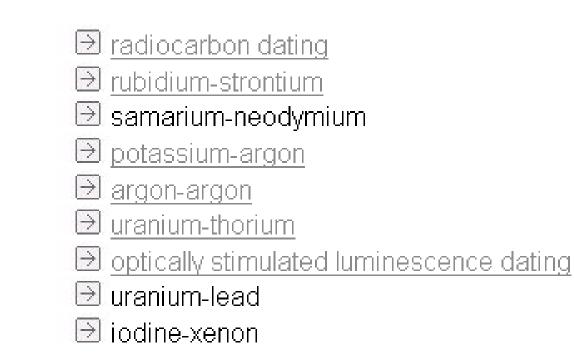
## Mass Spectrometer for determining Isotope concentrations



Features of a mass spectrometer. A mass analysis is obtained by volatilizing the element placed in the *thermal ion source* of the machine, which is kept at high vacuum. The vapor is then ionized and accelerated through a magnetic field produced by an *electromagnet*. The ion beam travels through the analyzer tube and then goes to a *collector*, where it is measured.

## Other Radio-dating Techniques

#### Types of radiometric dating



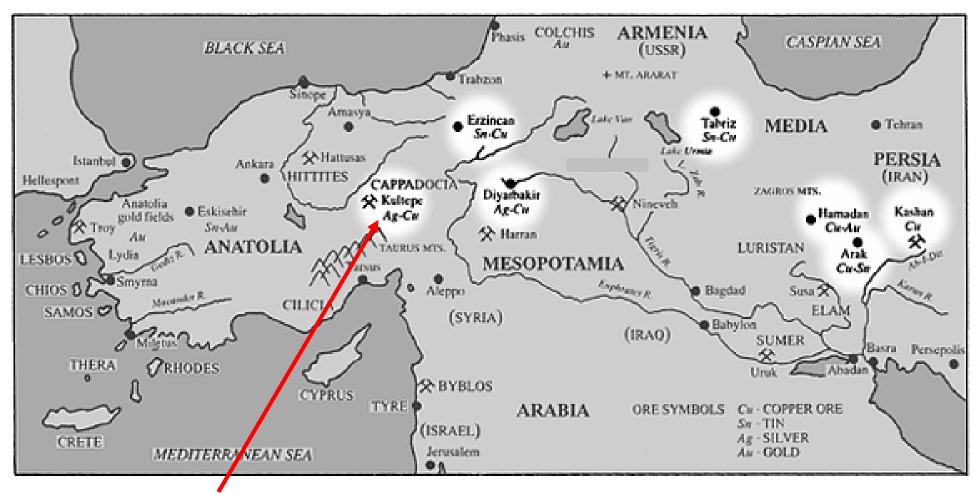
#### Sn Isotope concentrations

Study is currently under way to see if tin ores can be determined by ratios of isotopes. All isotopes naturally occurring, not decay products.

Interesting fact: because there is so much difference in mass of the isotopes, heating and reheating bronze can change isotope ratios by up to 5%. Can tell if bronze was recycled.

Isotope	e Atomic mass (m <sub>a</sub> /u)	Natural abundance (atom %)
<sup>112</sup> Sn	111.904826 (5)	0.97 (1)
<sup>114</sup> Sn	113.902784 (4)	0.66 (1)
<sup>115</sup> Sn	114.903348 (3)	0.34 (1)
<sup>116</sup> Sn	115.901747 (3)	14.54 (9)
<sup>117</sup> Sn	116.902956 (3)	7.68 (7)
<sup>118</sup> Sn	117.901609 (3)	24.22 (9)
<sup>119</sup> Sn	118.903311 (3)	8.59 (4)
<sup>120</sup> Sn	119.9021991 (29)	32.58 (9)
<sup>122</sup> Sn	121.9034404 (30)	4.63 (3)
<sup>124</sup> Sn	123.9052743 (17)	5.79 (5)

### Sources of Bronze Age Tin



Recently rediscovered Kestel mine was the source of near-Eastern Bronze age tin.

The Sumerian word for copper, "urudu", is the same word for the Euphrates, literally, the "copper river."

Compare HCAL to other large constructions

- HCAL is made of brass and stainless steel.
- 1600 tons total for barrel and endcap.
- About 1200 tons copper.
- What other large objects are made of copper alloy?
  - $\rightarrow$  monumental statues
- Look into a little history of famous statues

## Alexander the Great 356–323 BC



•Phillip II of Macedonia

- •Alexander the Great
- •Aristotle
- •Generals Antigous the one-eyed, Seleucus, Ptolemy
- •Cleopatra

#### Alexander the Great bullets

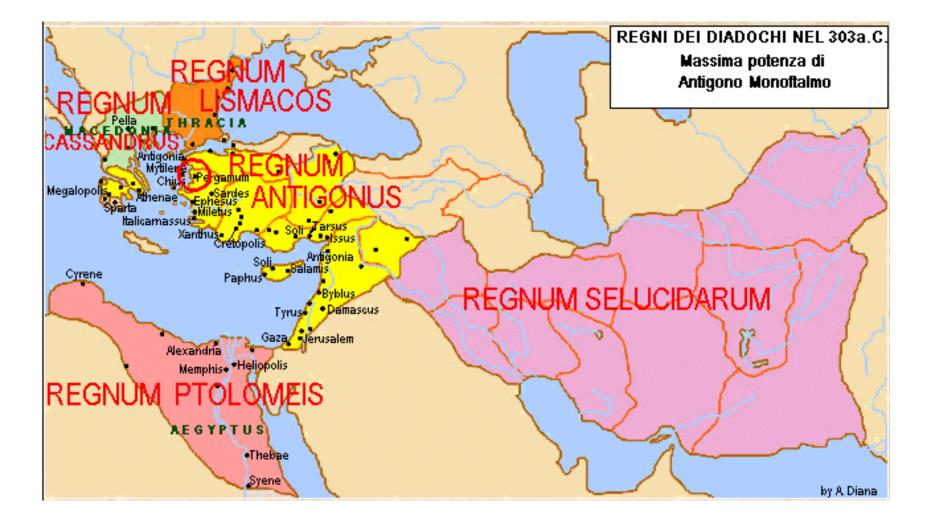


Alexander the Great

•356 –323 BC

- •Took power after the assassination of his father, Philip II.
- •Aristotle was his tutor.
- •Considered very handsome. Short by modern standards, 5'3''.
- •Would bring in philosophers and scholars of conquered lands to discuss and learn from.
- •Was a terrible drunk. He ordered the torching of Persepolis on a whim after a drinking binge.
- •Lived to be 33 years old. Died from illness acquired during drinking bout.

#### Empire of Alexander the Great



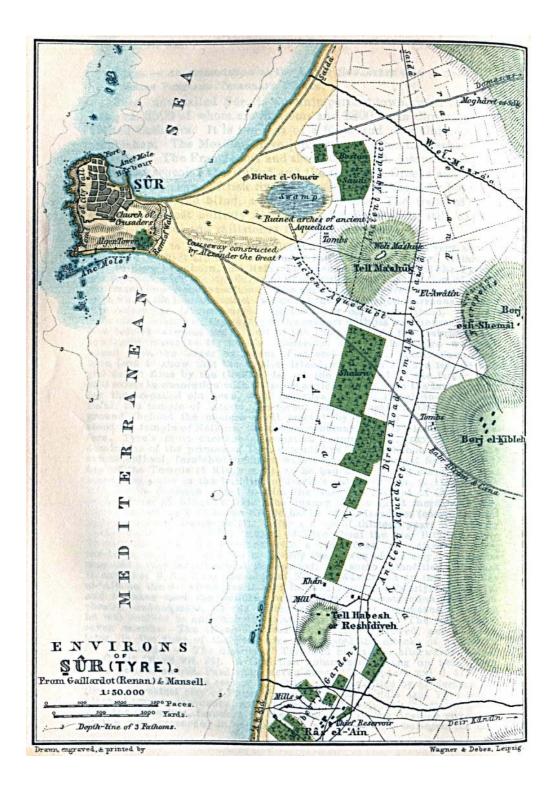
#### Diving at Tyre



Alexander tried to float siege engines to island city of Tyre. Citizens sank ships to block way. Alexander sent down divers (weighted wooden barrels over their heads) to clear wrecks. First record of underwater diving.

He ultimately built land bridge to island.

Map of Tyre from 1700's still shows Alexander's land bridge



#### Colossus of Rhodes

After the death of Alexander (at 33), his empire divided between his three principal generals, Seleucus, Antigous, and Ptolemy. The Rhodians supported Ptolemy (who wound up ruling Egypt) in this struggle. This angered Antigous who sent his son Demetrius to capture and punish the city of Rhodes. Rhodes, off the coast of Turkey, seiged by Demetrius and army of 40,000. After one year, fleet of ships from Egypt, Ptolemy, came to the rescue.

The siege was abandoned and departing soldiers left armor there. Citizens of Rhodes commissioned statue, had the bronze armor melted down and used in the statue, the Colossus of Rhodes. Started in 304 BC.

Statue stood for 54 years until earthquake broke it. Huge pieces lay on the ground for 1000 years. In 700 AD, sold for scrap, 700 camels carried the material away.



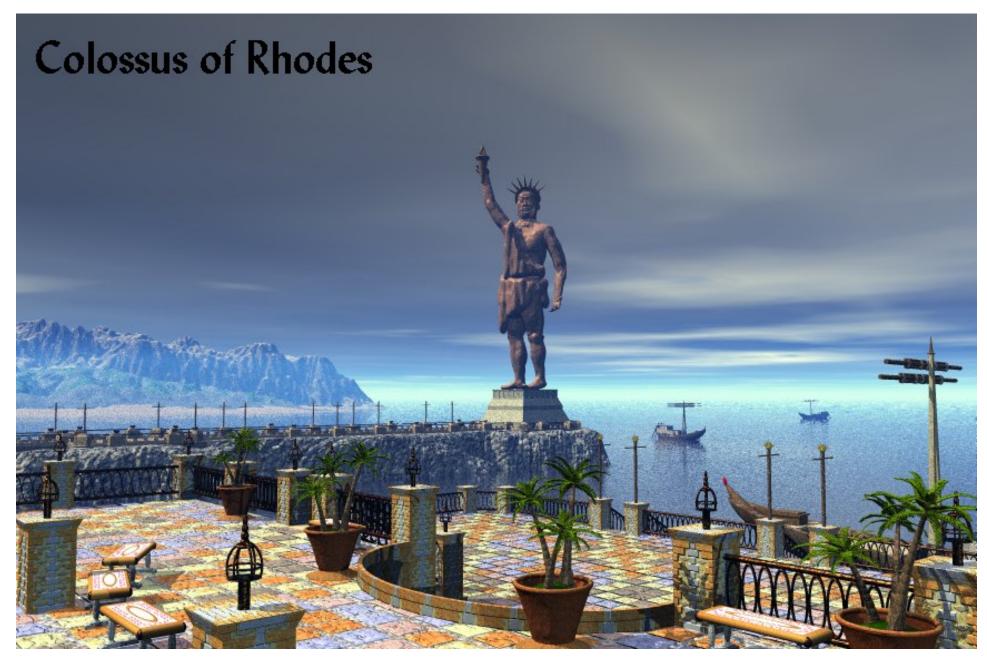






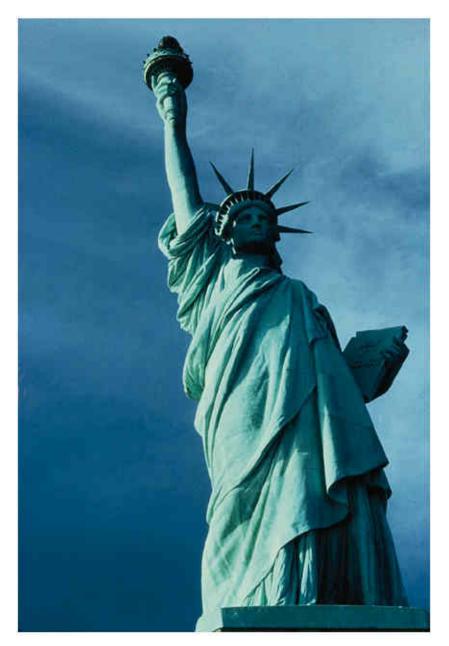


Full armor of soldier was about 80 pounds of bronze



#### **Colossus of Rhodes (40 meters) (200 tons Bronze)**

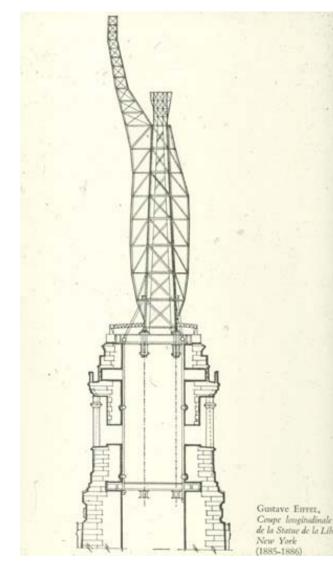
### Statue of Liberty



Statue of Liberty designed by Frederic Auguste Bartholdi, inspired by Colossus of Rhodes. Designed to be the same size. It is 40 meters tall, uses 100 tons copper.



#### Structure of Monumental Statues





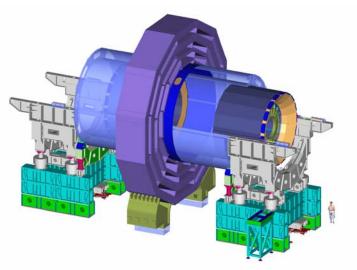
Interior view of Statue of Liberty. Structure is a cast iron framework with 2mm thick sheets of copper riveted to it. Same basic structure as Colossus of Rhodes. (By the way, Statue of Liberty iron frame designed by Gustave Eiffel, of Eiffel Tower fame.)

### Science vs Religion



The world's largest statue, Maitreya Buddha (150 meters tall) (2500 tons bronze) is being contemplated for Buddhgaya, India.

Until then, CMS HCAL, 1600 tons, will be the most massive copper structure ever built.



## Backup

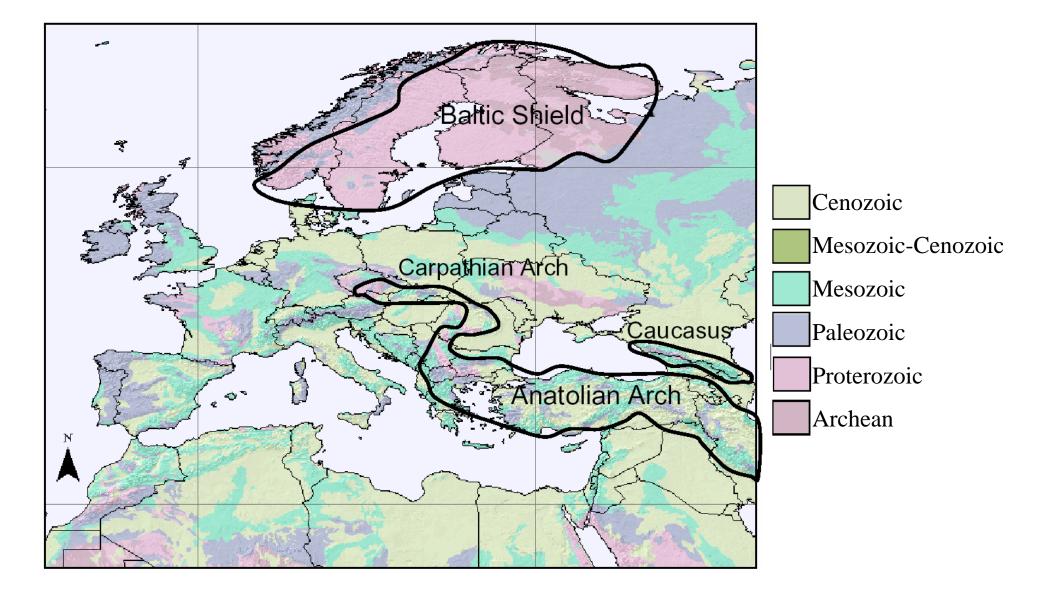
## HCAL

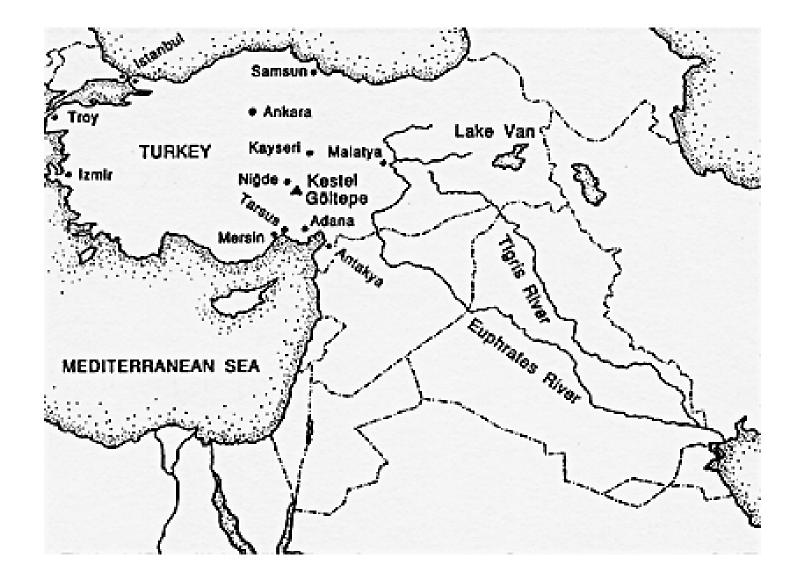


The HCAL is a detector that will be used at the LHC at CERN. It sits inside a huge electromagnet with a very strong magnetic field. Because of this, it needs to be made from nonmagnetic material, stainless steel or copper. We picked copper because it is cheaper and easier to machine.

HB sitting on its cradle in Spain

#### Geology of Europe /Asia Minor



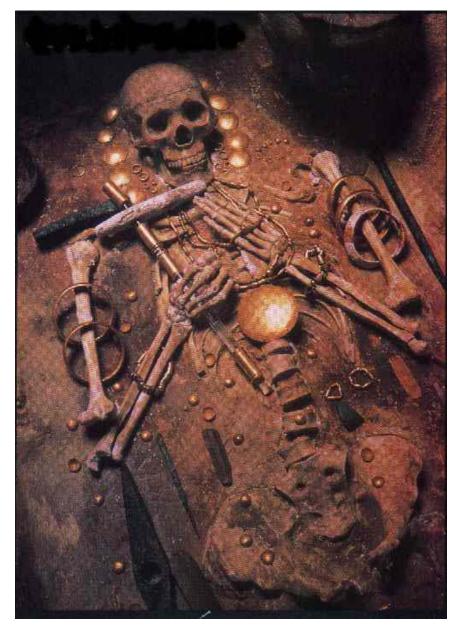


#### Empire of Thrace



Part of present day Bulgaria. It was a powerful country 700 - 50 BC, with gold and copper riches. A pre-Grecian civilization. Kings were buried in mounds, many of which were forgotten about and not plundered.

#### Grave of Pre-Thracian King, 4000BC

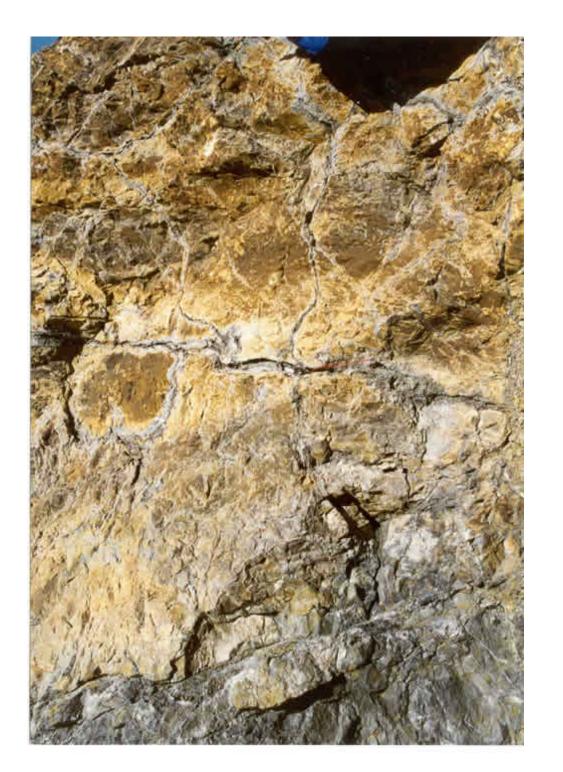


#### Wealth of Thrace







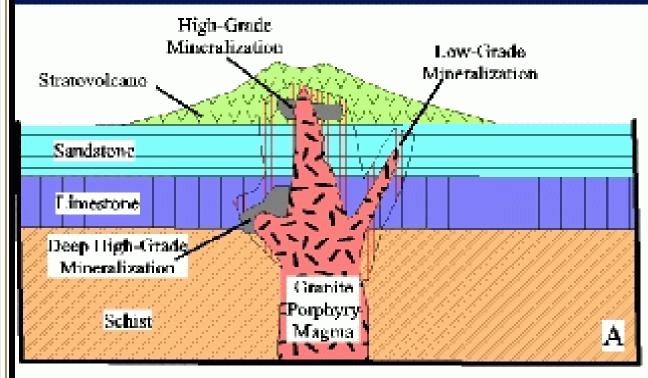


#### Massive Sulphide Ore

much smaller deposits, higher concentration of copper



### Formation of a Porphyry Copper Deposit

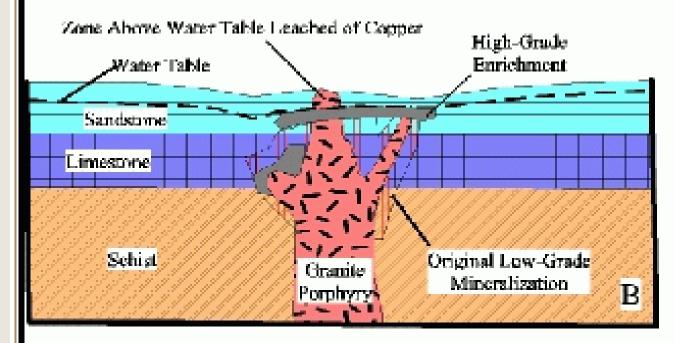


Initial formation of a purphyry copper deposit associated with a magnue chamber beneath a stratovoleano. Hot water circulating near the magnue forms low-grade copper mineralization next to the solidifying magna. Highgrade mineralization forms over the top of the magnue and in chemically reactive wall modes, like limestone.

Arizona State University



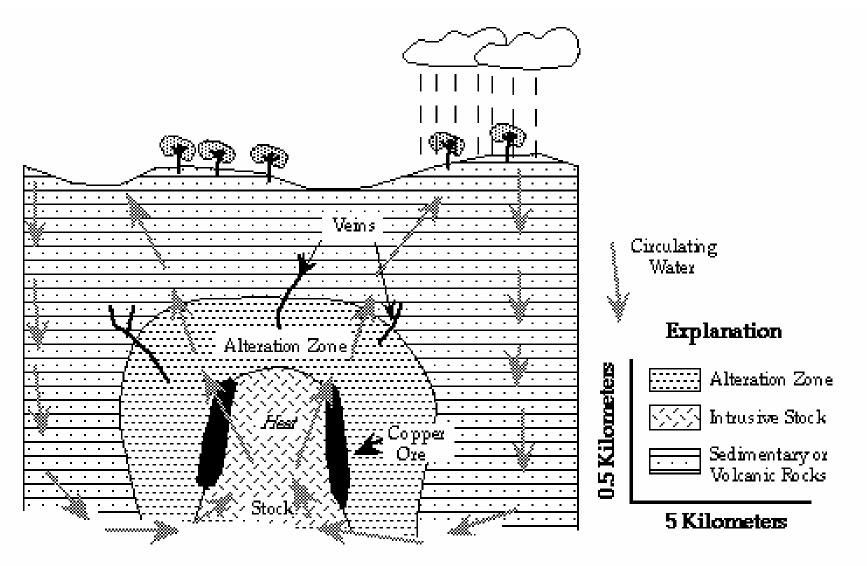
## Formation of a Porphyry Copper Deposit



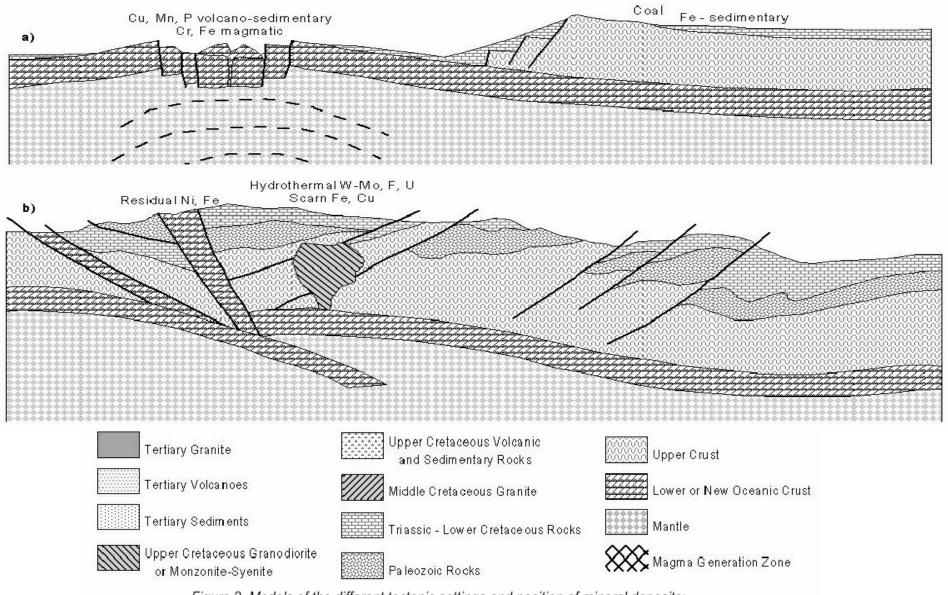
Erosion removes the stratovolcano and top of the original copper deposit. Rainwater and weathering cause copper to be leached from the top of the deposit and redeposited as the downwardmoving groundwater reaches the water table. The resulting enriched zone is commonly high grade and fairly flat.

Arizona State University

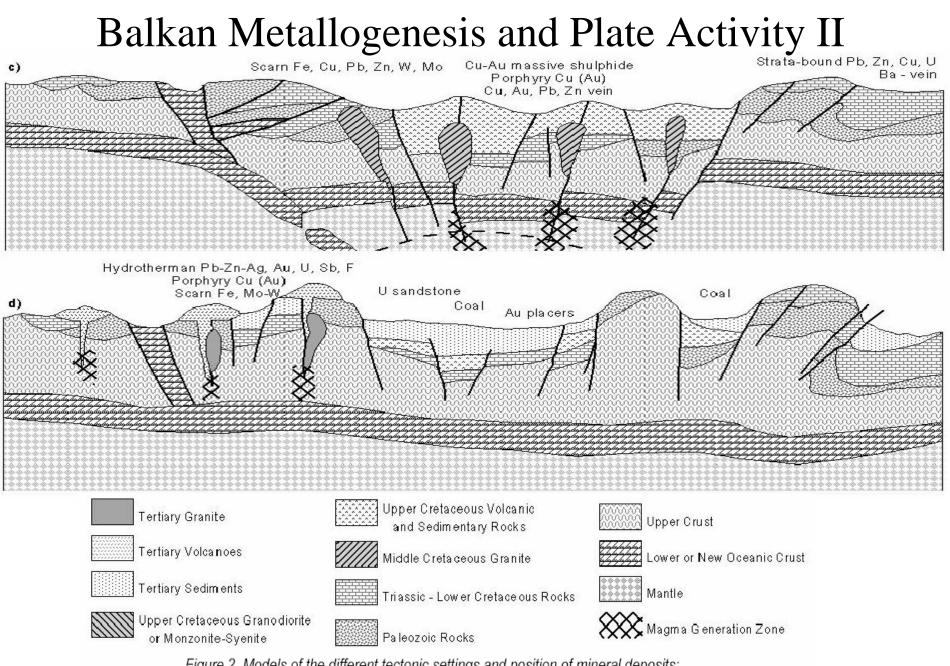
#### Massive Sulphide Formation



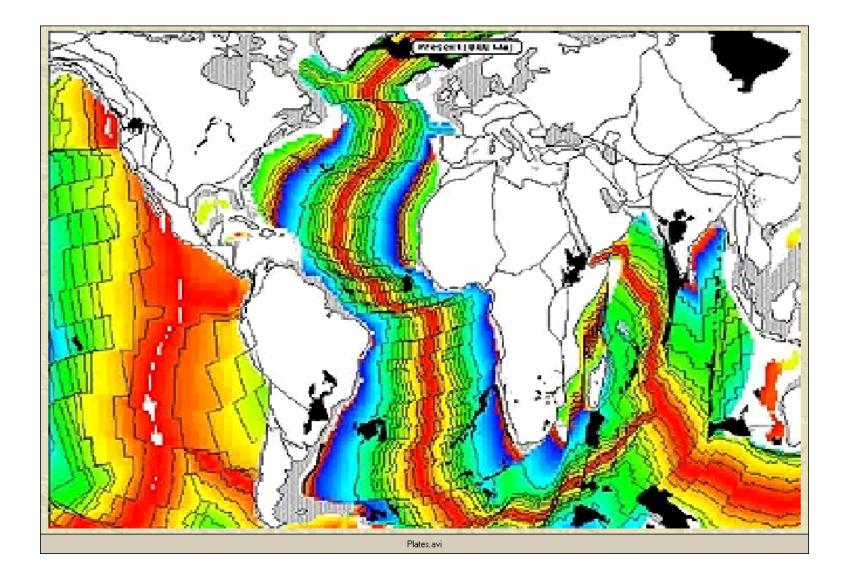
#### Balkan Metallogenesis and Plate Activity I



*Figure 2. Models of the different tectonic settings and position of mineral deposits: a) spreading; b) early collision; c) intracollisional rifting; d) post-collisional orogen.* 



*Figure 2. Models of the different tectonic settings and position of mineral deposits: a) spreading; b) early collision; c) intracollisional rifting; d) post-collisional orogen.* 



#### **Development of Porphyry Ore Deposit**

