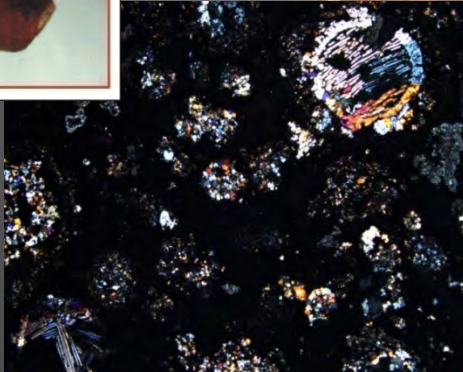


# Mineralogical Co-Evolution of the Geo- and Biospheres



Robert M. Hazen, Geophysical Laboratory  
April 28, 2010 – Bradley Lecture  
Geological Society of Washington



CARNEGIE  
INSTITUTION FOR  
SCIENCE

# Mineral Evolution

*American Mineralogist* v.93, 1693-1720 (2008).

Robert Hazen, CIW

Dominic Papineau, CIW

Wouter Bleeker, GSC

Robert Downs, UA

John Ferry, JHU

Tim McCoy, NMNH

Dimitri Sverjensky, JHU

Hexiong Yang, UA

# **What Is Mineral Evolution?**

**A change over time in:**

- The diversity of mineral species**
- The relative abundances of minerals**
- The compositional ranges of minerals**
- The grain sizes and morphologies of minerals**

# **What Is Mineral Evolution?**

**Focus exclusively on near-surface (<3 km depth) phases.**

- **Accessible to study on Earth**
- **Most likely to be observed on other planets and moons**
- **Direct interaction with biology**



# Why Mineral Evolution?

- Reframe mineralogy in a dynamic historical context.
- Classify terrestrial planets and moons
- Identify mineralogical targets for planetary exploration
- Explore general principles related to complex evolving systems

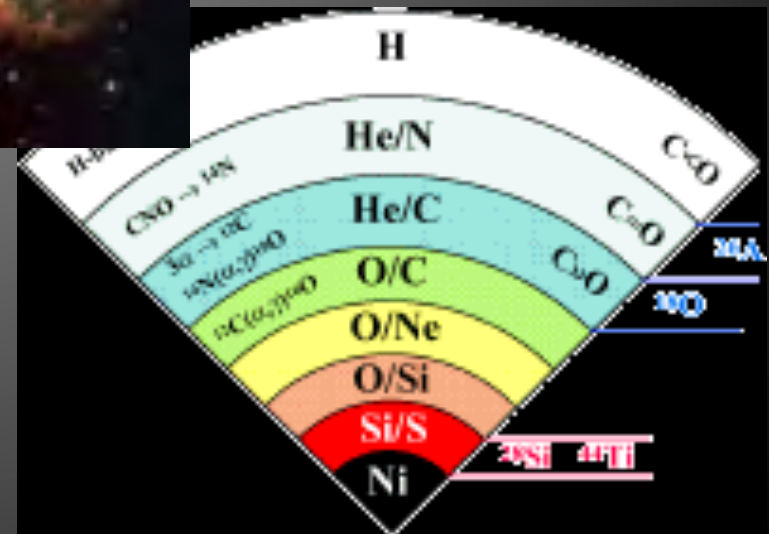
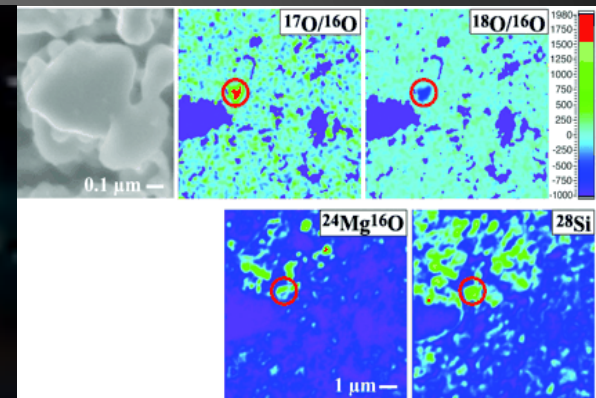
# A Comment on “Evolution”

- The word “evolution” has several meanings
- Change over time, as in Bowen’s “*Evolution of the Igneous Rocks.*”
- Implication of complexification
- Congruency
- But NOT Darwinian evolution!

# “Ur”-Mineralogy

Pre-solar grains contain about a dozen micro- and nano-mineral phases:

- Diamond/Lonsdaleite
- Graphite (C)
- Moissanite (SiC)
- Osbornite (TiN)
- Nierite (Si<sub>3</sub>N<sub>4</sub>)
- Rutile (TiO<sub>2</sub>)
- Corundum (Al<sub>2</sub>O<sub>3</sub>)
- Spinel (MgAl<sub>2</sub>O<sub>4</sub>)
- Hibbonite (CaAl<sub>12</sub>O<sub>19</sub>)
- Forsterite (Mg<sub>2</sub>SiO<sub>4</sub>)
- Nano-particles of TiC, ZrC, MoC, FeC, Fe-Ni metal within graphite.
- GEMS (silicate glass with embedded metal and sulfide).



# **Mineral Evolution:**

**How did we get from a  
dozen minerals to  
>4400 on Earth today?**



# **What Drives Mineral Evolution?**

**Deterministic and stochastic processes  
that occur on any terrestrial body:**

- 1. The progressive separation and concentration of chemical elements from their original uniform distribution.**

# **What Drives Mineral Evolution?**

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- 2. An increase in the range of intensive variables (T, P, activities of volatiles).**

# What Drives Mineral Evolution?

Deterministic and stochastic processes that occur on any terrestrial body:

1. The progressive separation and concentration of chemical elements from their original uniform distribution.
2. An increase in the range of intensive variables (T, P, activities of volatiles).
3. The generation of far-from-equilibrium conditions by living systems.

# Three Eras of Earth's Mineral Evolution

1. The Era of Planetary Accretion
2. The Era of Crust and Mantle Reworking
3. The Era of Bio-Mediated Mineralogy





# Three Eras of Earth's Mineral Evolution

## 1. The Era of Planetary Accretion



## 2. The Era of Crust and Mantle Reworking



## 3. The Era of Bio-Mediated Mineralogy

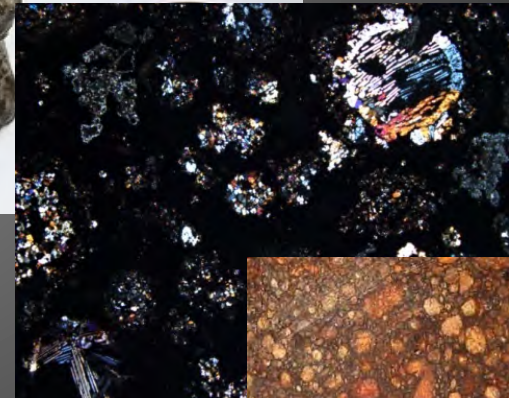


# Stage 1: Primary Chondrite Minerals

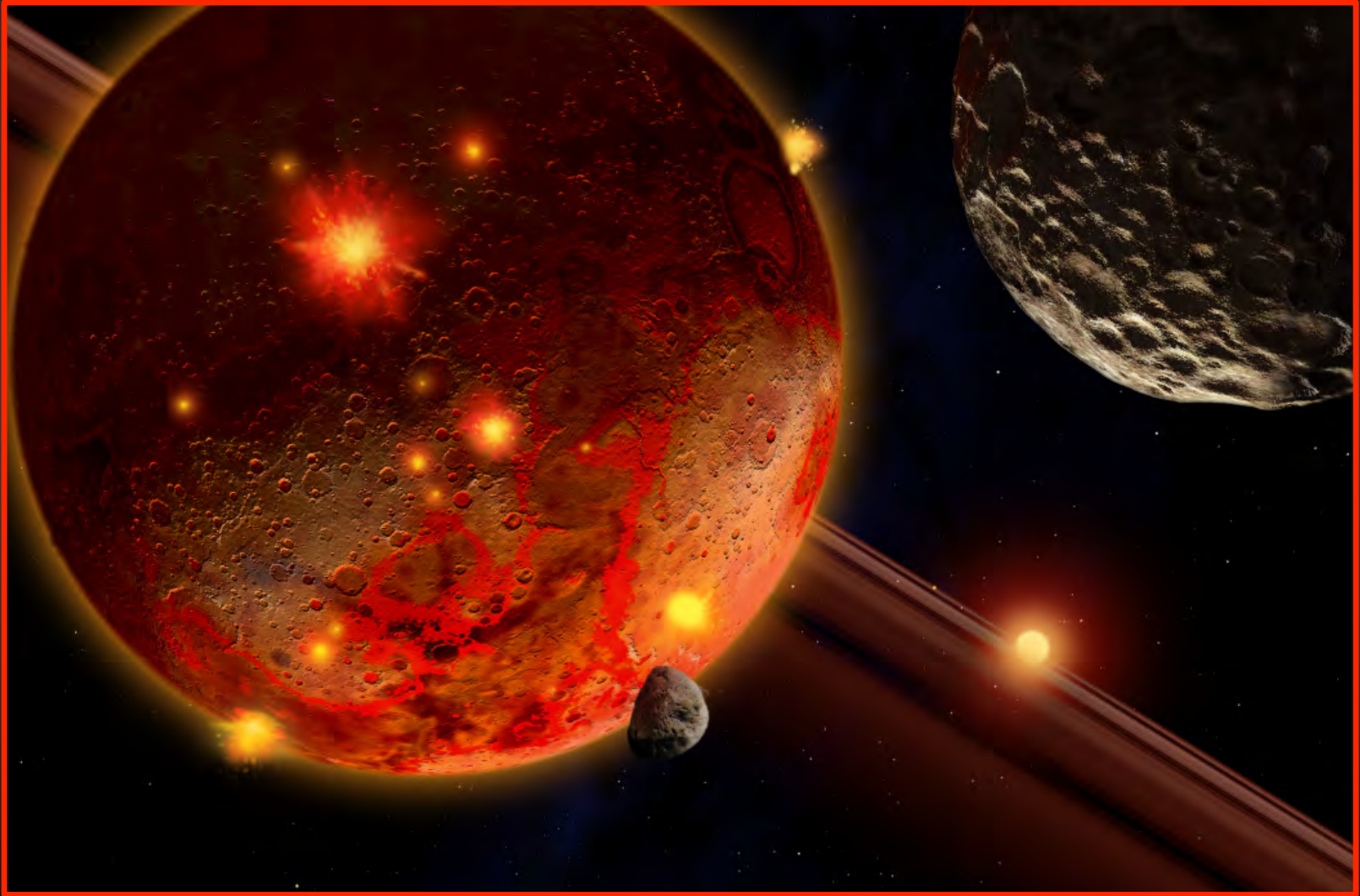
Minerals formed ~4.56 Ga in the Solar nebula “as a consequence of condensation, melt solidification or solid-state recrystallization” (MacPherson 2007)

~60 mineral species

- CAIs
- Chondrules
- Silicate matrix
- Opaque phases



## Stage 2: Aqueous alteration, metamorphism and differentiation of planetesimals

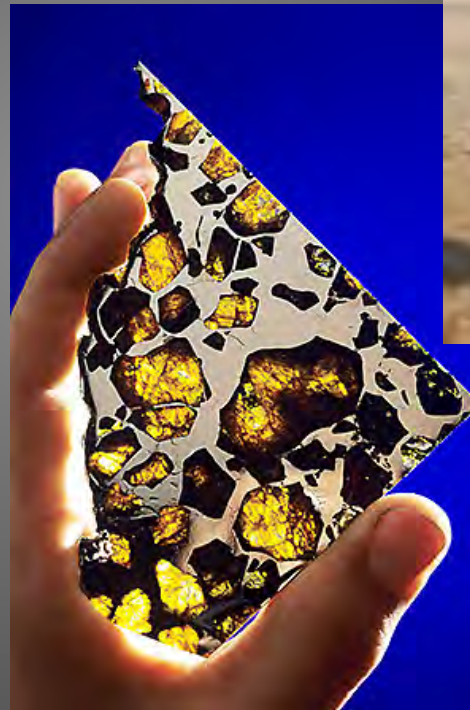




# Stage 2: Aqueous alteration, metamorphism and differentiation of planetesimals

~250 mineral known species: 4.56-4.55 Ga

- First albite & K-spar
- First significant  $\text{SiO}_2$
- Feldspathoids
- Hydrous biopyriboles
- Clay minerals
- Zircon
- Shock phases





# Three Eras of Earth's Mineral Evolution

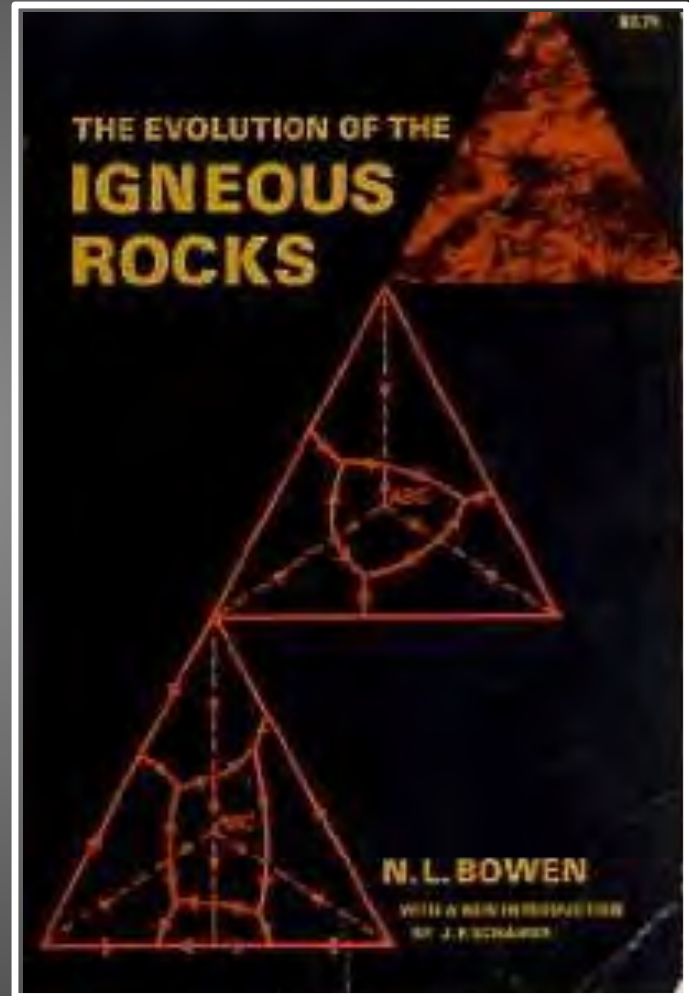
1. The Era of Planetary Accretion
2. The Era of Crust and Mantle Reworking
3. The Era of Bio-Mediated Mineralogy



# Stage 3: Initiation of Igneous Rock Evolution (4.55-4.0 Ga)

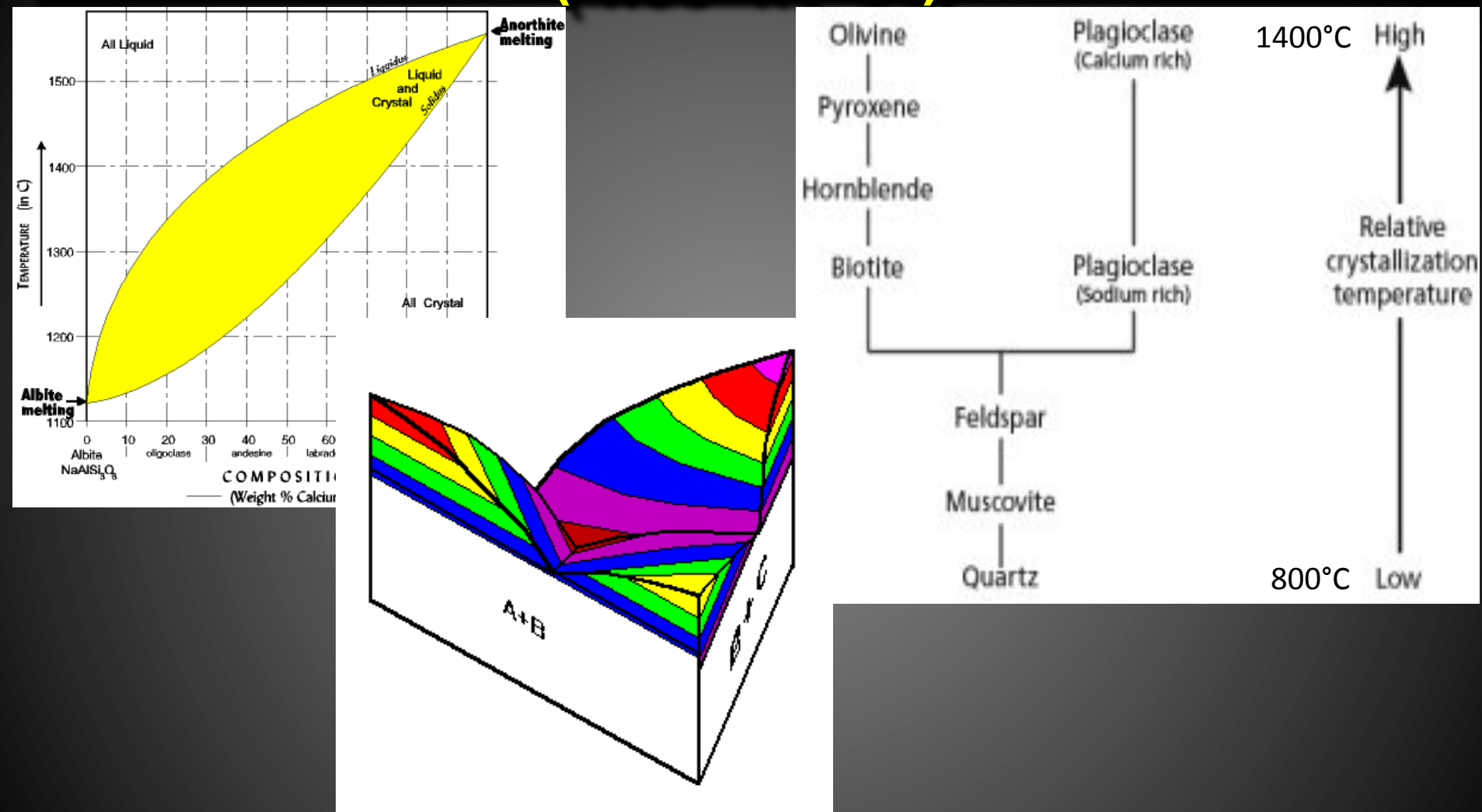


**Norman Bowen (1887-1956)**



**Bowen (1928)**

# Stage 3: Initiation of Igneous Rock Evolution (4.55-4.0 Ga)



**Partial melting, fractional crystallization  
and magma immiscibility**



# Stage 3: Initiation of Igneous Rock Evolution Volatile-poor Body

~350 mineral species?



Is this the end point of the Moon and Mercury?



# Stage 3: Initiation of Igneous Rock Evolution

## Volatile-poor Body

Are there any OH-bearing mineral phases?



Is this the end point of the Moon and Mercury?

## Stage 3: Initiation of Igneous Rock Evolution on a Volatile-rich Body (4.55-4.0 Ga)



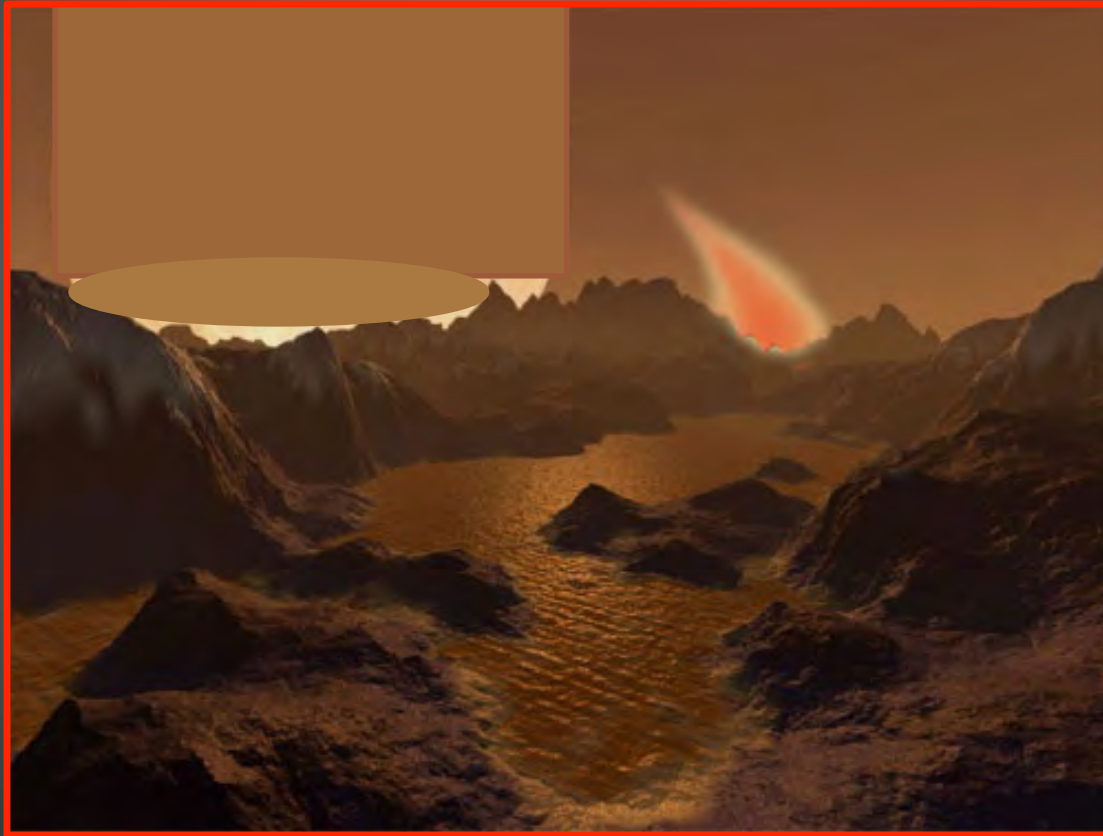
**Volcanism, outgasing and surface hydration.**



# Stage 3: Initiation of Igneous Rock Evolution

## Volatile-rich Body

>500 mineral species (hydroxides, clays)



Volcanism, outgasing, surface hydration, evaporites, ices.

# The Formation of the Moon



# Stage 3: Initiation of Igneous Rock Evolution

## Volatile-rich Body

**>500 mineral species (hydroxides, clays)**



**Volcanism, outgasing, surface hydration, evaporites, ices.**



## **Stage 3: Initiation of Igneous Rock Evolution Volatile-rich Body**

**Important Point:**

**Sudden or gradual changes  
in environments can lead to  
mineral “extinctions”.**

# Stage 3: Initiation of Igneous Rock Evolution

## Volatile-rich Body

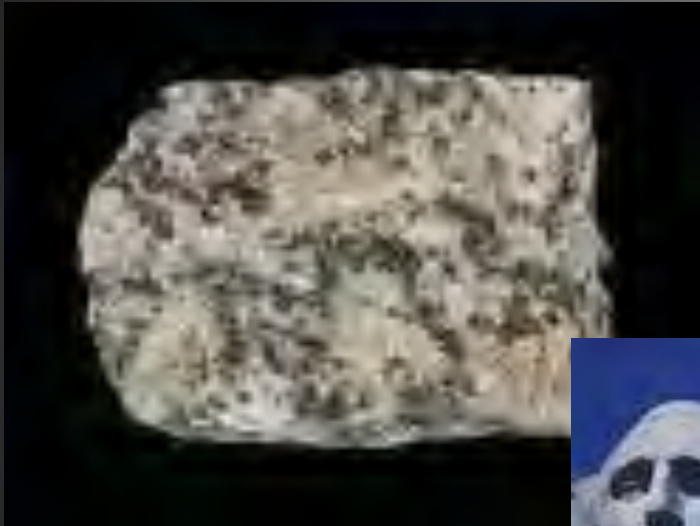
Is this the end point for Mars?



**Volcanism, outgasing, surface hydration, evaporites, ices.**

## Stage 4: Granitoid Formation (>3.5 Ga)

>1000 mineral species (pegmatites)

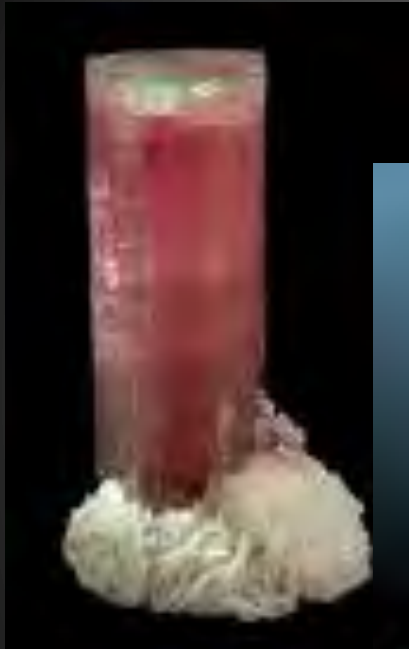


Partial melting of basalt and/or sediments.



# Stage 4: Granitoid Formation (>3.5 Ga)

>1000 mineral species (pegmatites)



Tourmaline



Spodumene



Beryl



Pollucite



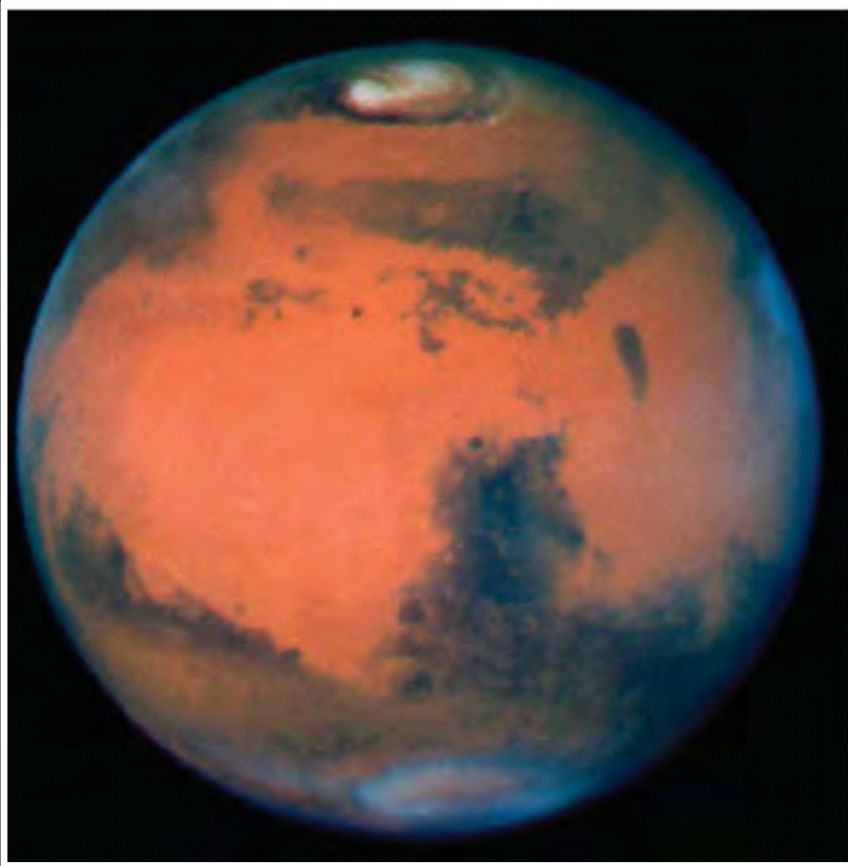
Tantalite

Complex pegmatites require multiple cycles of eutectic melting and fluid concentration.

Must they be younger than 3.5 Ga?



## Stage 4: Granitoid Formation



**Are there pegmatites on Mars?  
If so, how old are they?**

## Stage 4: Granitoid Formation



**Aqua-Rose Beryl Pit,  
Quadville, Ontario, Canada**

**What is the oldest complex pegmatite on Earth?  
Does that age place constraints on the extent and  
rate of Archean fluid-rock interactions?**



# Stage 4: Granitoid Formation

What is the oldest complex pegmatite on Earth?

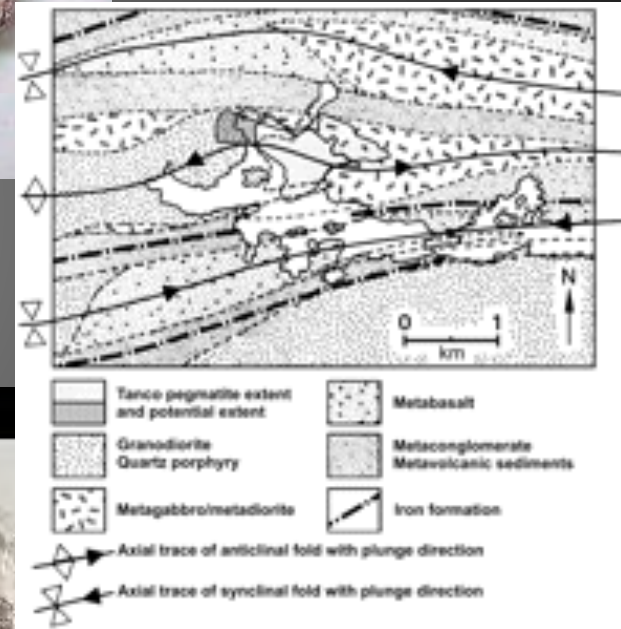
David London (2008):  
Tanco pegmatite,  
Manitoba, is 2.67 Ga  
in age and represents  
at a minimum  
reworking of 18,000  
km<sup>3</sup> of metapelites!



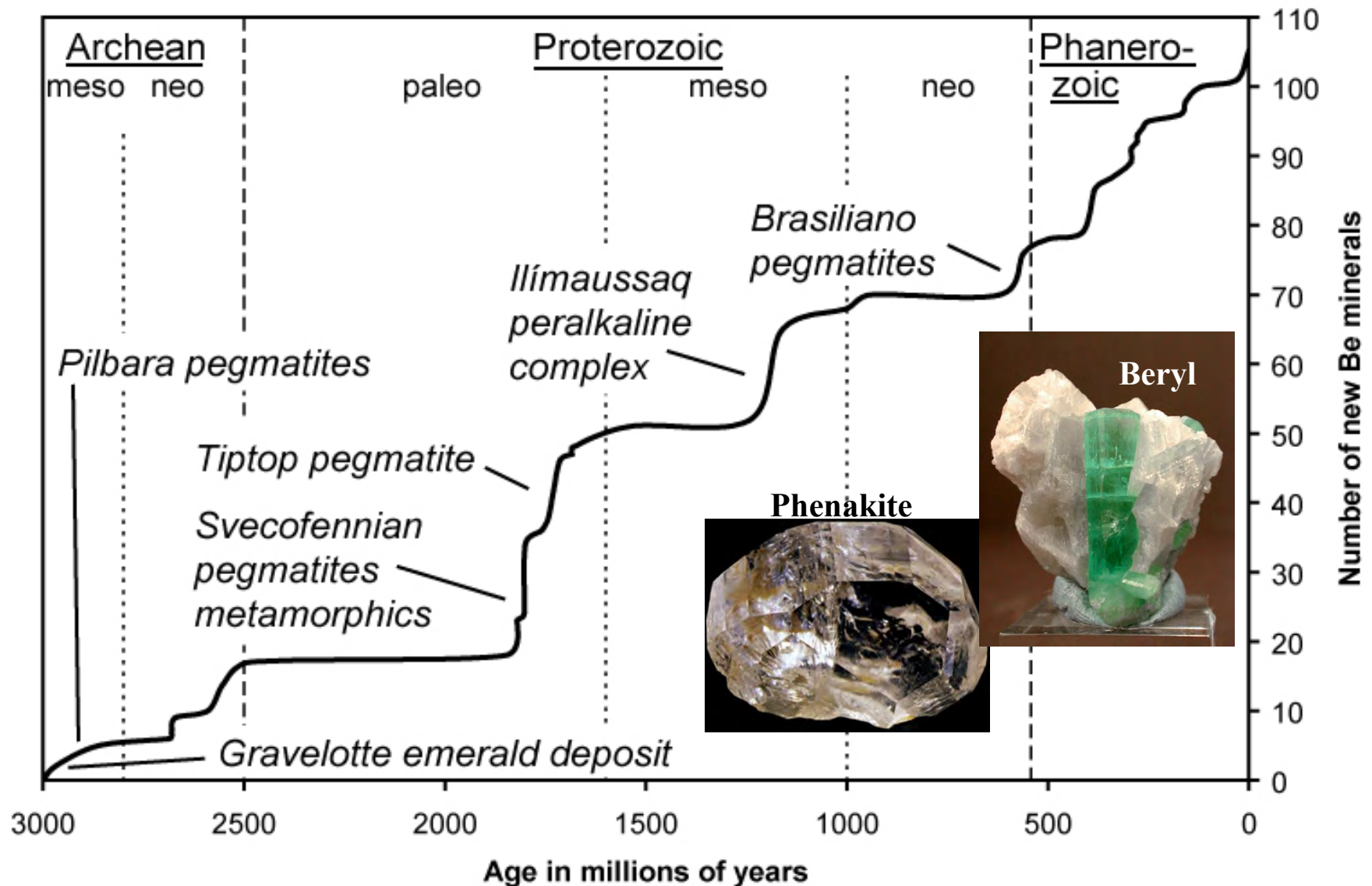
Rossmannite  
(Li-tourmaline)



Cs-Beryl

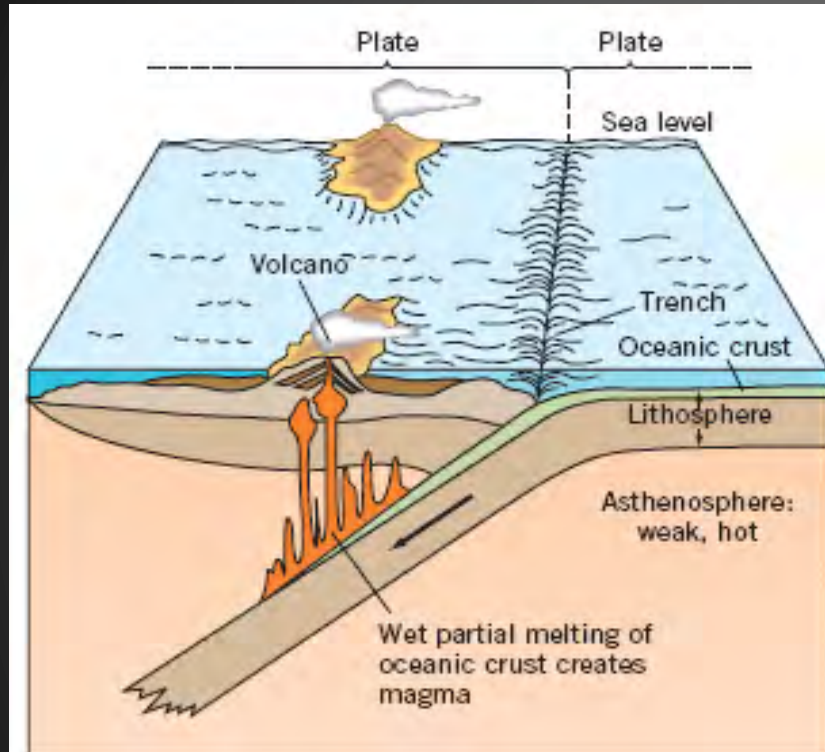


# Be Mineral Evolution (Grew & Hazen 2009)





# Stage 5: Plate tectonics and large-scale hydrothermal reworking of the crust (>3 Ga)



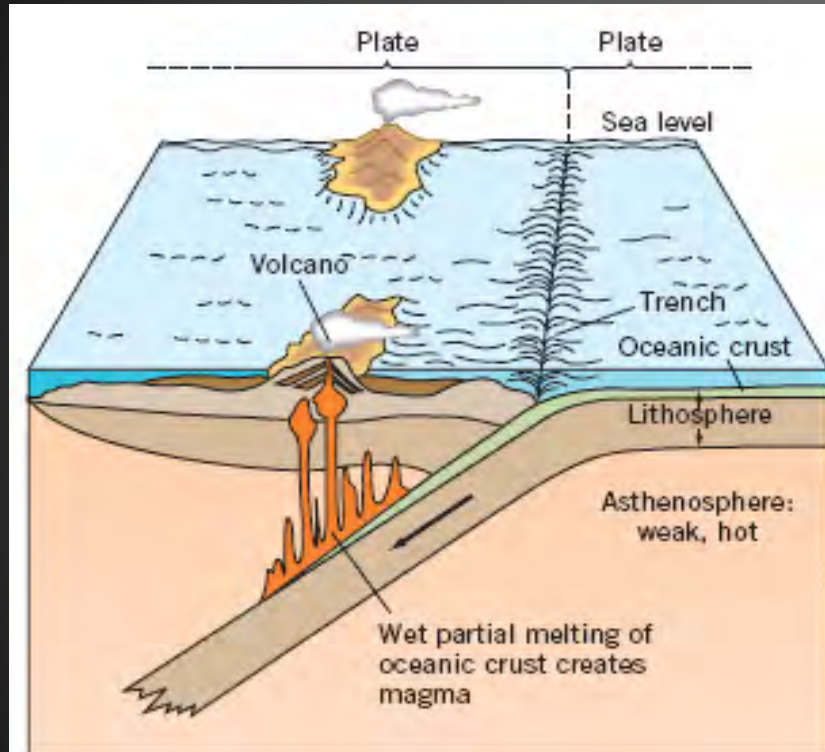
$\sim 10^8 \text{ km}^3$  of reworking



Mayon Volcano, Philippines

## New modes of volcanism

# Stage 5: Plate tectonics and large-scale hydrothermal reworking of the crust (>3 Ga)



Rio Tinto. Spain

**New modes of volcanism**

**Massive base metal deposits (sulfides, sulfosalts)**



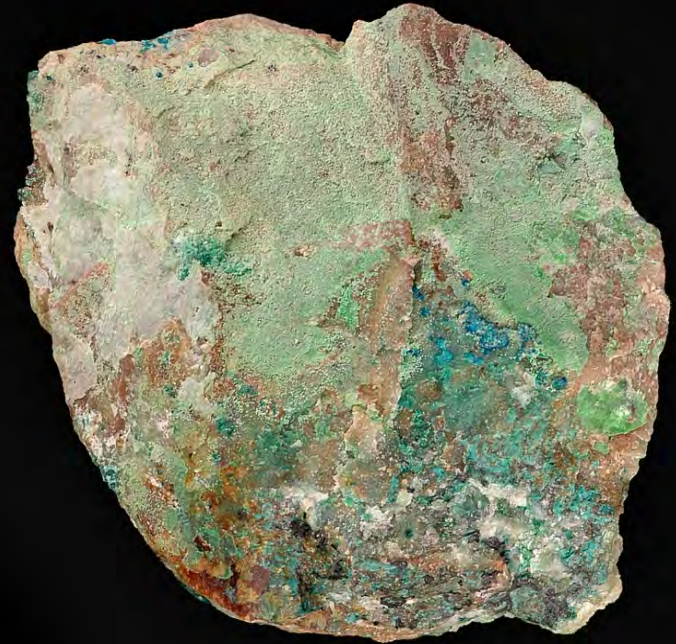
# Stage 5: Plate tectonics and large-scale hydrothermal reworking of the crust (>3 Ga)



R070750

1 cm

Vallerite  $2[(\text{Fe,Cu})\text{S}] \cdot 1.53[(\text{Mg,Al})(\text{OH})_2]$



R070739

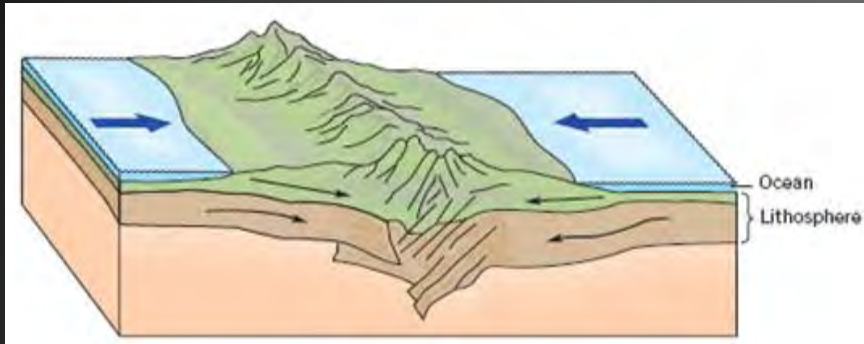
1 cm

Orickite  $\text{CuFeS}_2 \cdot n\text{H}_2\text{O}$

**New modes of volcanism**  
**Massive base metal deposits**

**New hydrated species (hydrated sulfides)**

# Stage 5: Plate tectonics and large-scale hydrothermal reworking of the crust (>3 Ga)



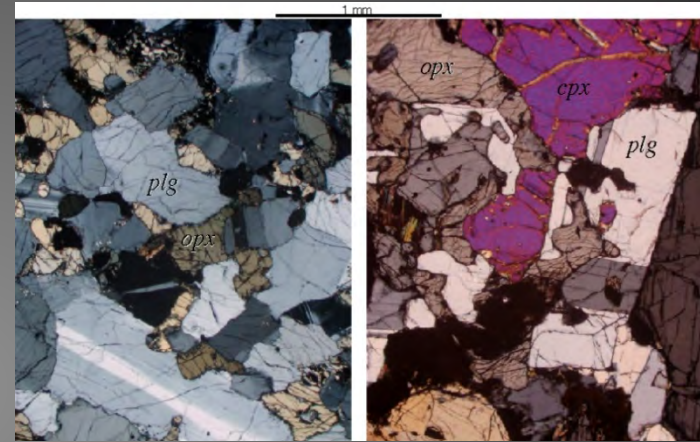
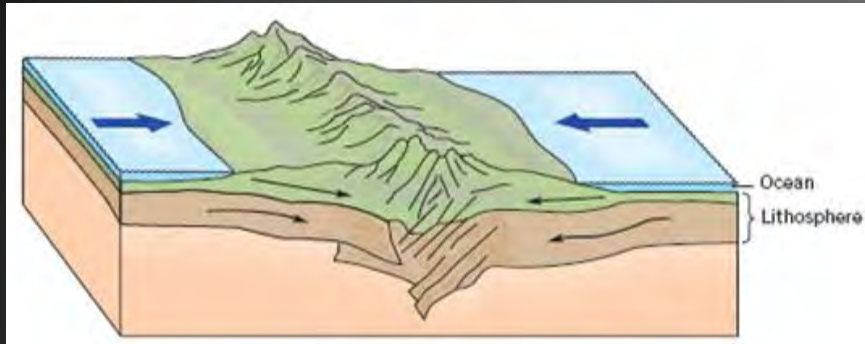
Glaucophane, Lawsonite, Jadeite



**High-pressure metamorphic suites  
(blueschists)**



# Stage 5: Plate tectonics and large-scale hydrothermal reworking of the crust (>3 Ga)



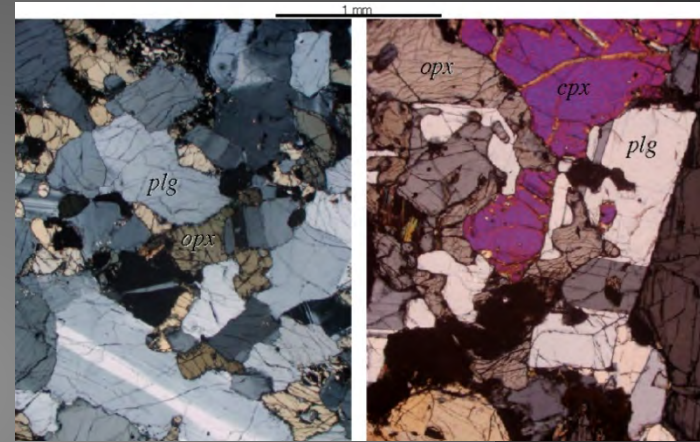
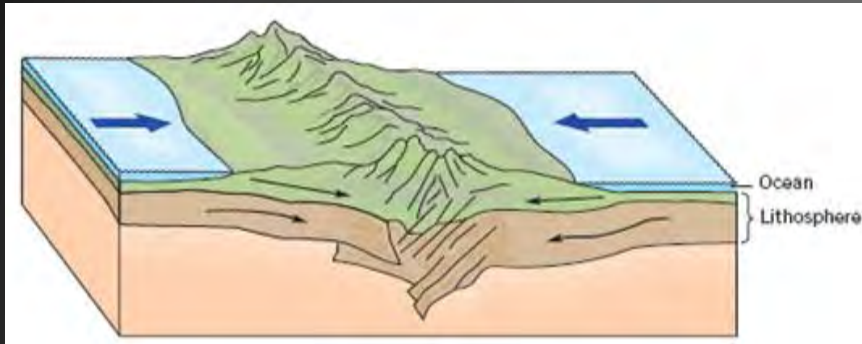
Glaucophane, Lawsonite, Jadeite



**High-pressure metamorphic suites  
(blueschists; granulites)**

# Stage 5: Plate tectonics and large-scale hydrothermal reworking of the crust (>3 Ga)

1,500 mineral species



Glaucophane, Lawsonite, Jadeite



Coesite  $\text{SiO}_2$

High-pressure metamorphic suites  
(blueschists; granulites; UHP phases)



## Stage 5: Plate Tectonics

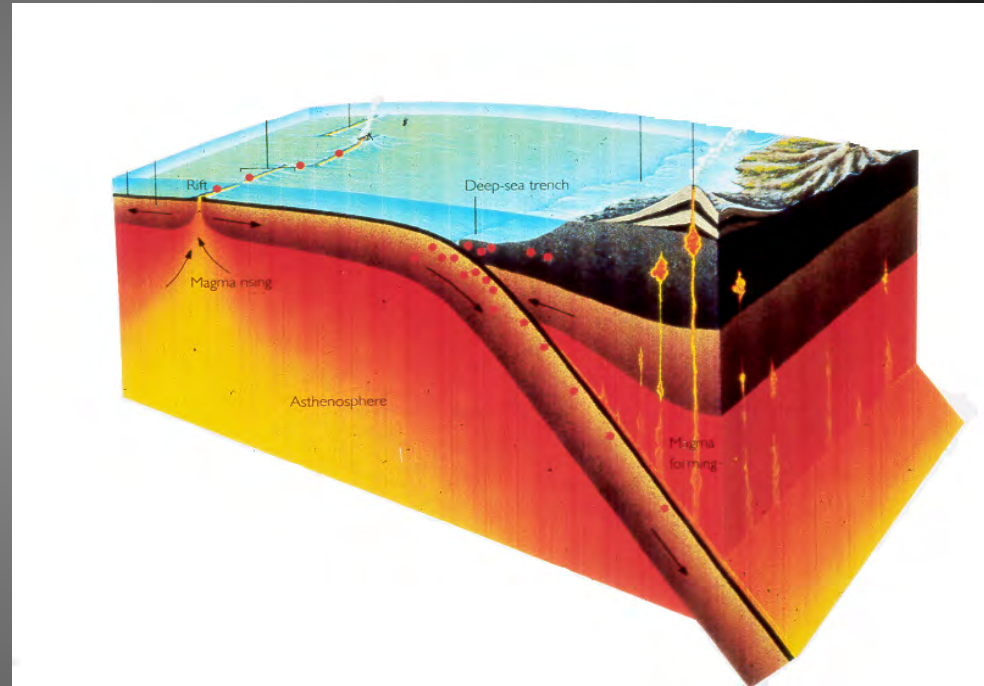


**Did Venus progress to some variant of Stage 5?**  
**Did a loss of water change its mineral evolution?**  
**Are there massive sulfide deposits on Venus?**



# Stage 5: Plate tectonics and large-scale hydrothermal reworking of the crust (>3 Ga)

1,500 mineral species



A volatile-rich planet with plate tectonics can progress at least this far in mineral diversity. Is that the limit? What other minerals might form?

**The origin of life may require some minimal degree of mineral evolution.**

**Sulfides**



**Clays**

**Borates**



**Conversely, does further mineral evolution depend on life?**

**Hence the co-evolution of the geo- and biospheres.**

# Three Eras of Earth's Mineral Evolution

## 1. The Era of Planetary Accretion



## 2. The Era of Crust and Mantle Reworking



## 3. The Era of Bio-Mediated Mineralogy





# Stage 6: Anoxic Archean biosphere (3.9-2.5 Ga)

~1,500 mineral species (BIFs,

Temagami BIFs, ~2.7 Ga



Photo credit: D. Papineau



# Stage 6: Anoxic Archean biosphere (3.9-2.5 Ga)

**~1,500 mineral species** (BIFs, carbonates,



**Photo credit: D. Papineau**



**Photo credit: F. Corsetti, USC**

## **Stage 6: Anoxic Archean biosphere (3.9-2.5 Ga)**

**~1,500 mineral species** (BIFs, carbonates, sulfates, evaporites,



**Death Valley evaporites  
(courtesy Smith College)**



# Stage 6: Anoxic Archean biosphere (3.9-2.5 Ga)

**~1,500 mineral species** (BIFs, carbonates, sulfates, evaporites, skarns)



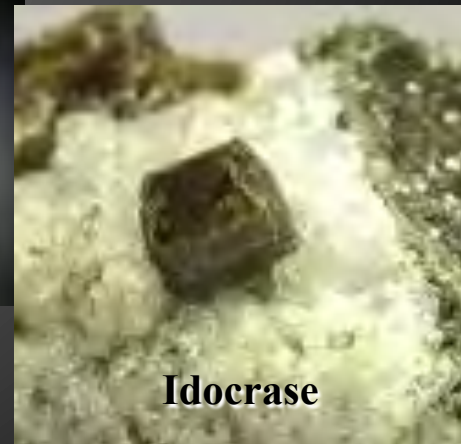
Death Valley evaporites  
(courtesy Smith College)



Diopside



Grossular



Idocrase

# Stage 7: Paleoproterozoic Oxidation (2.5-1.9 Ga)

>4000 mineral species, including perhaps  
>2,000 new oxides/hydroxides



Negaunee BIF, ~1.9 Ga

Rise of oxidative photosynthesis.



## **Stage 7: Paleoproterozoic Oxidation (2.5-1.9 Ga)**

**>4000 mineral species, including perhaps  
>2,000 new oxides/hydroxides**



**Rise of oxidative photosynthesis.**

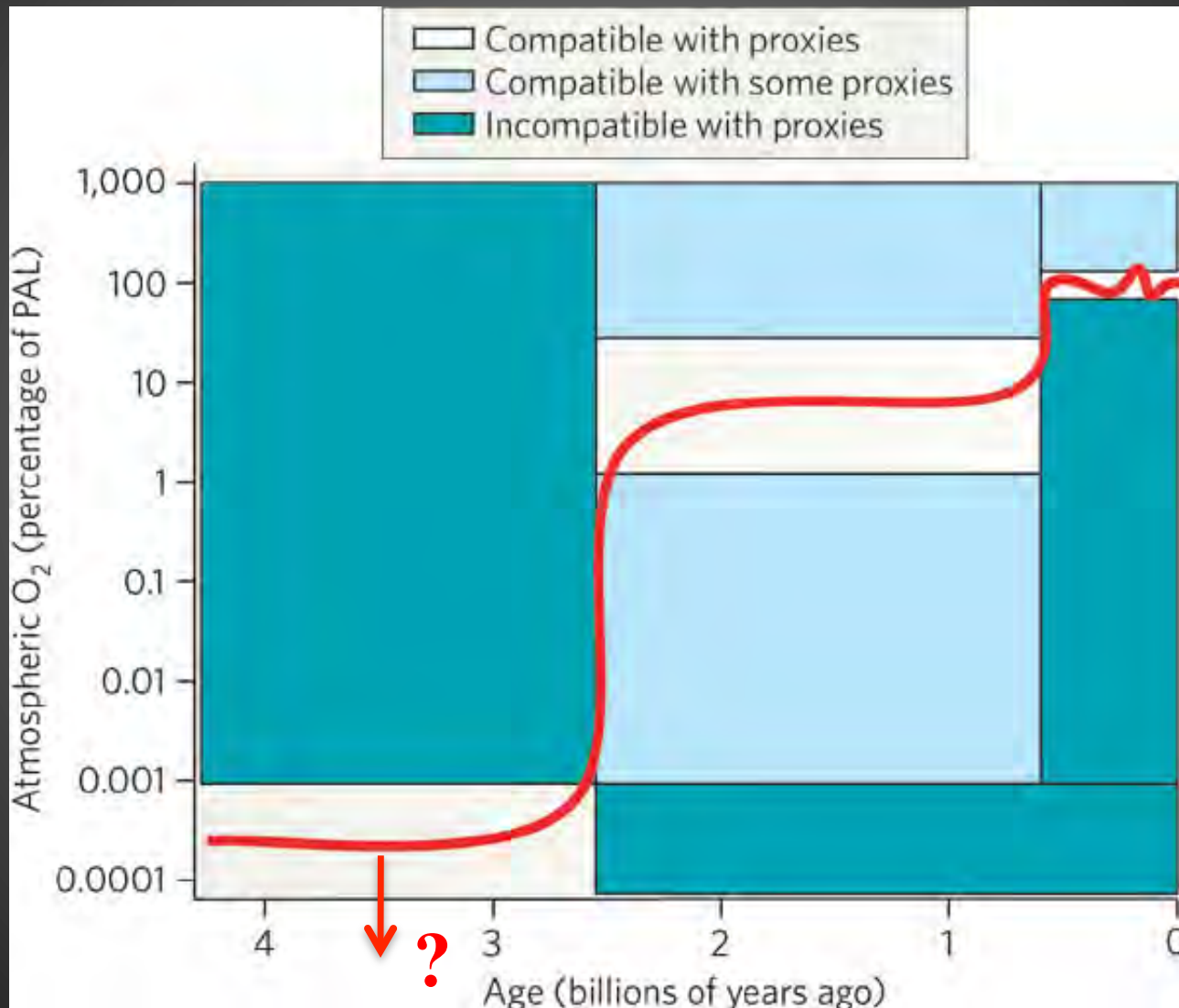


# **Hypothesis**

**Approximately 2/3rds of all known mineral species cannot form in an anoxic environment, and thus are the indirect consequence of biological activity.**

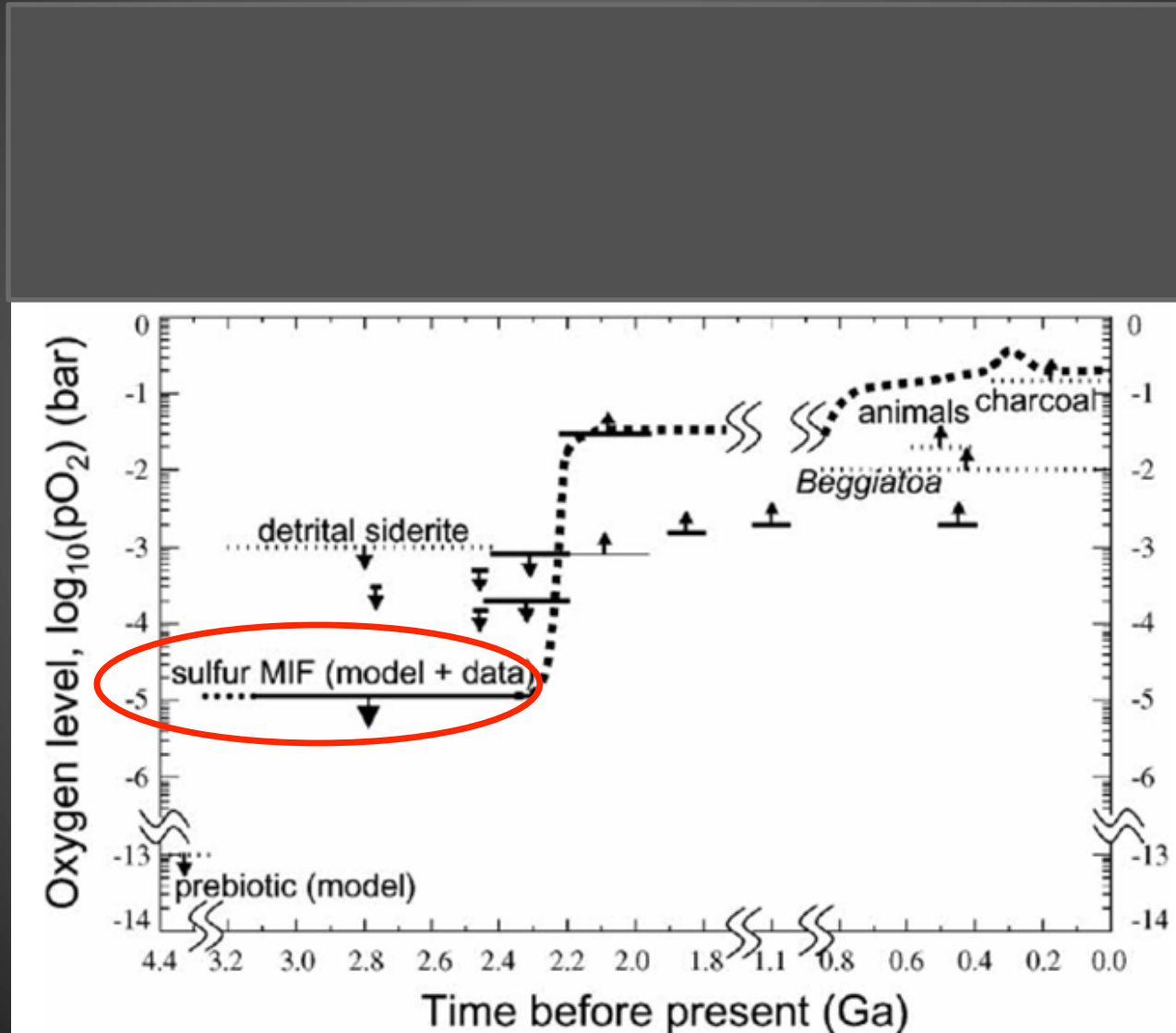
**Many lines of evidence point to an essentially anoxic Archean atmosphere.**

# What was the oxygen fugacity in the Archean?



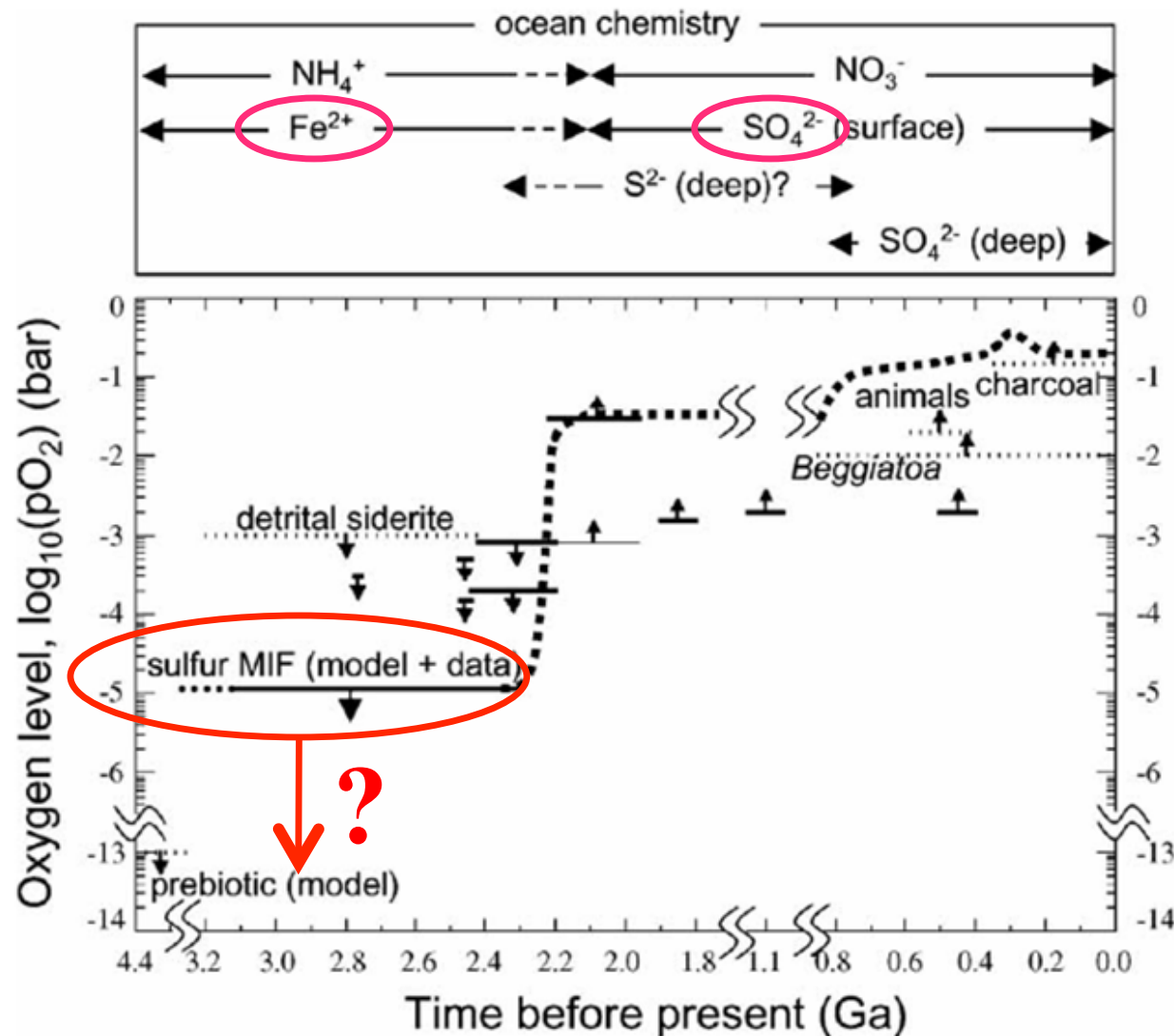
Kump (2008) *Nature* 451, 277-278.

# What was the oxygen fugacity in the Archean?





# What was the oxygen fugacity in the Archean?



# What was the oxygen fugacity in the Archean?

## Published estimates of Archean $\log fO_2$

Ohmoto (numerous refs)	> -2
Farquhar et al. (2000)	< -5
Frimmel (2005)	< -5
Kump (2008)	< -5
C-W-K-H Model (1968+)	~ -13
Sverjensky et al. (2008, 2010)	~ -70

# **Key constraints on Archean surface oxygen fugacity.**

**Detrital uraninite and pyrite**

**Paleosols lacking iron oxides**

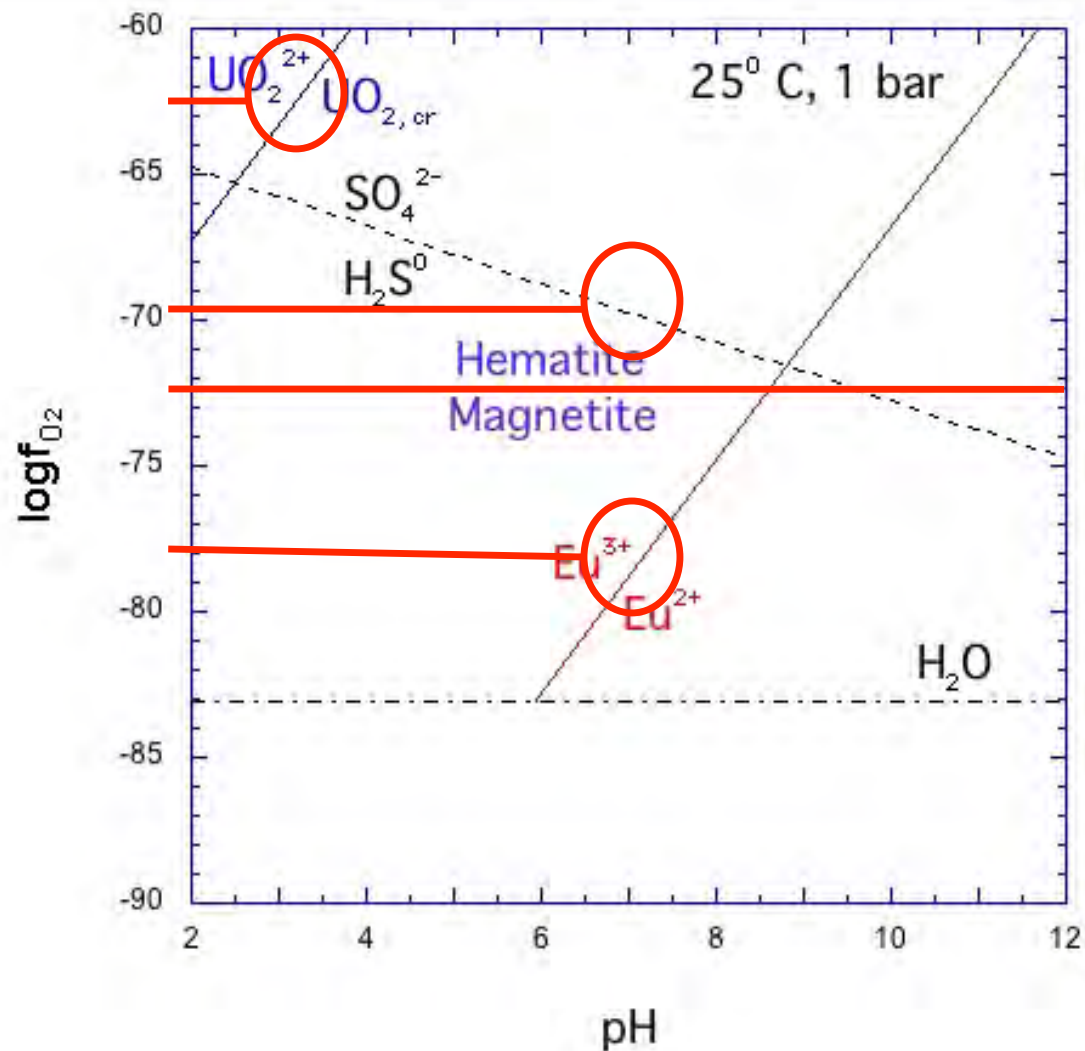
**[Surface waters with aqueous  $\text{Fe}^{2+}$ ]**

**[Surface waters with low  $\text{SO}_4^{2-}$ ]**

**$\text{Eu}^{2+}$  anomalies**



# What was the oxygen fugacity in the Archean?



# **Key constraints on Archean surface oxygen fugacity.**

**Detrital uraninite, pyrite and siderite**

**Paleosols lacking iron oxides**

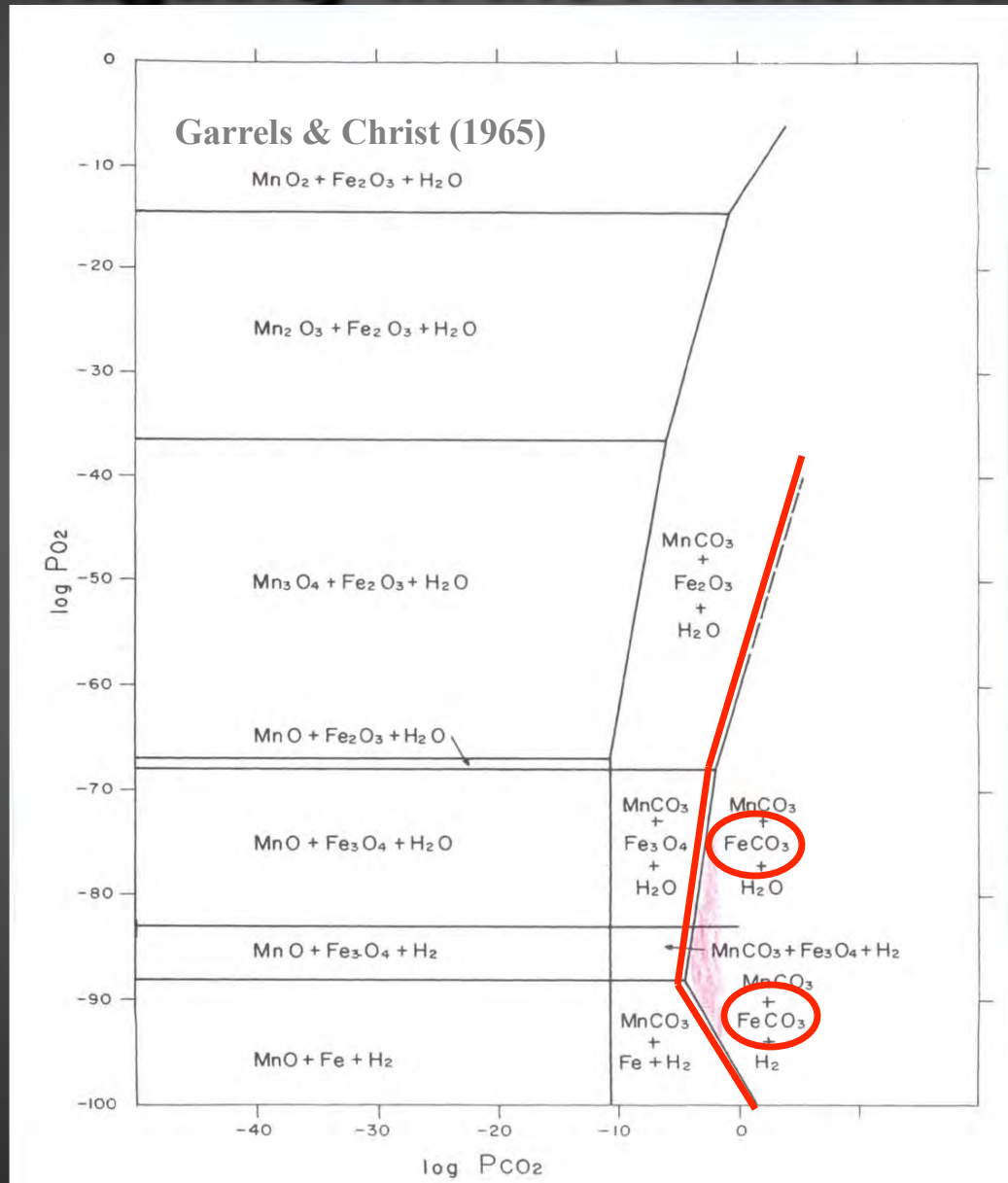
**[Surface waters with aqueous  $\text{Fe}^{2+}$ ]**

**[Surface waters with low  $\text{SO}_4^{2-}$ ]**

**$\text{Eu}^{2+}$  anomalies**

**Precipitation of ferroan carbonates**

# What was the oxygen fugacity in the Archean?



Siderite  
 $FeCO_3$

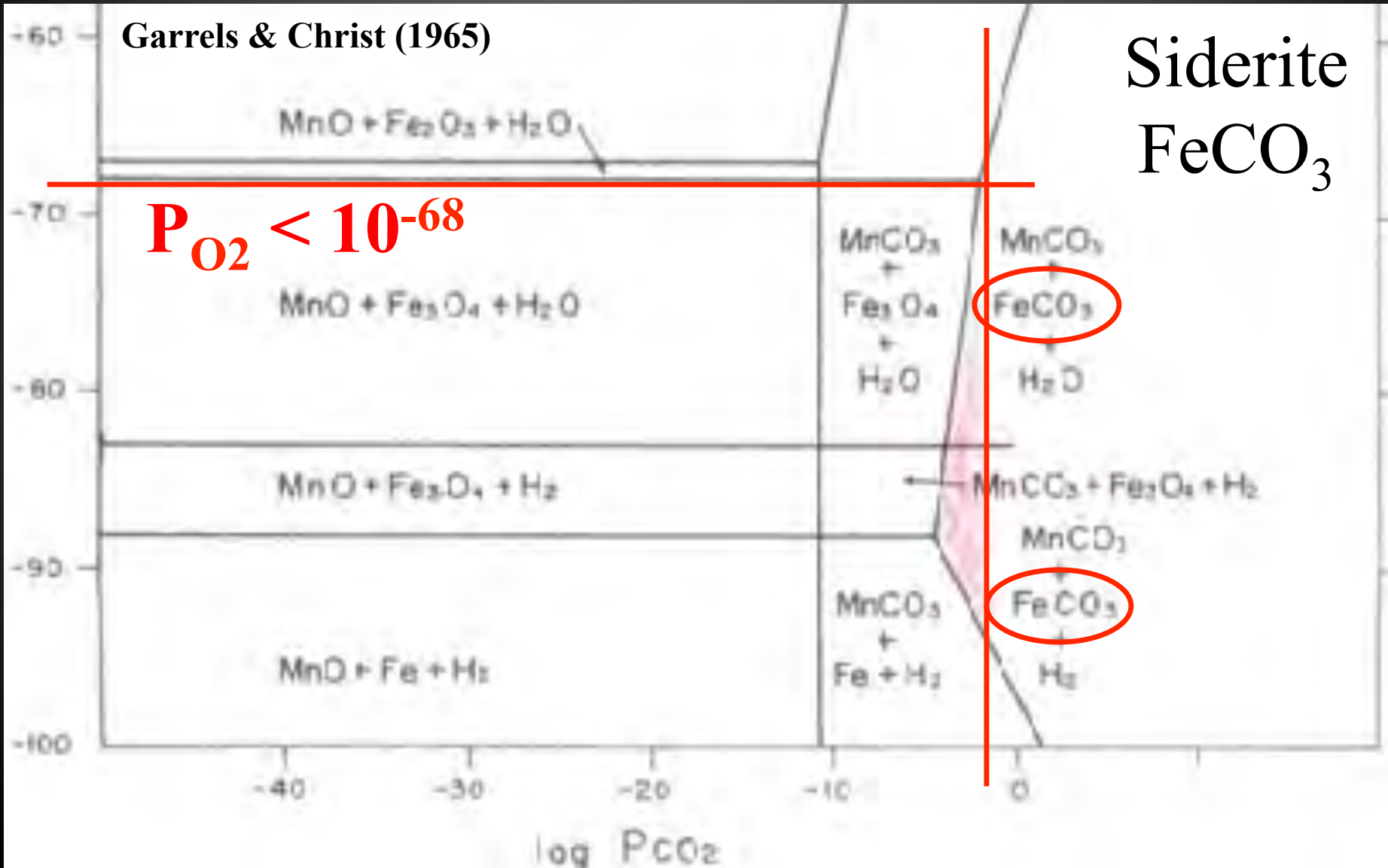


# What was the oxygen fugacity in the Archean?

Garrels & Christ (1965)

$P_{O_2} < 10^{-68}$

Siderite  
 $FeCO_3$



# **Key constraints on Archean surface oxygen fugacity.**

**Detrital uraninite, pyrite and siderite**

**Paleosols lacking iron oxides**

**[Surface waters with aqueous  $\text{Fe}^{2+}$ ]**

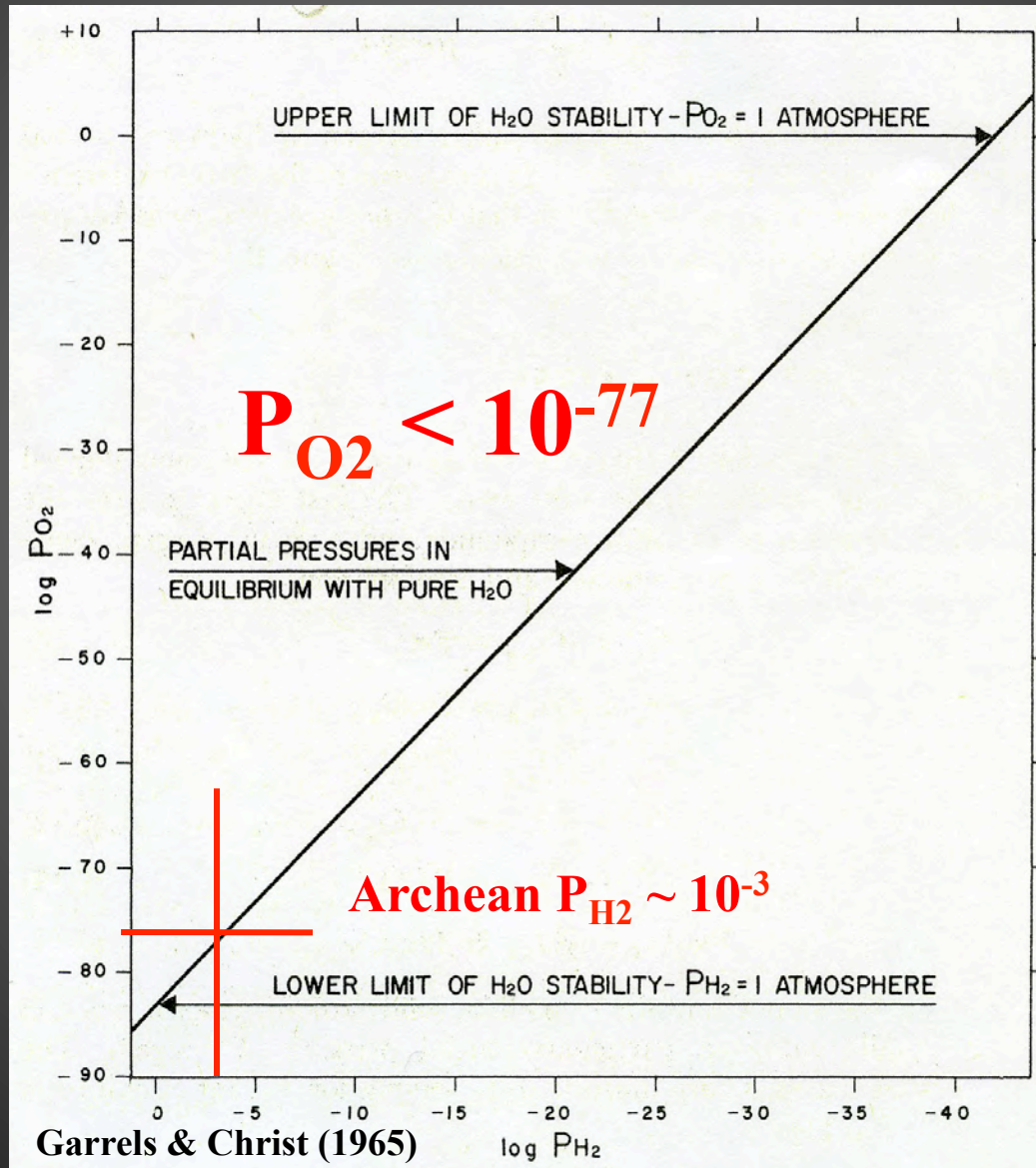
**[Surface waters with low  $\text{SO}_4^{2-}$ ]**

**$\text{Eu}^{2+}$  anomalies**

**Precipitation of ferroan carbonates**

**[Significant atmospheric  $\text{H}_2$ ]**

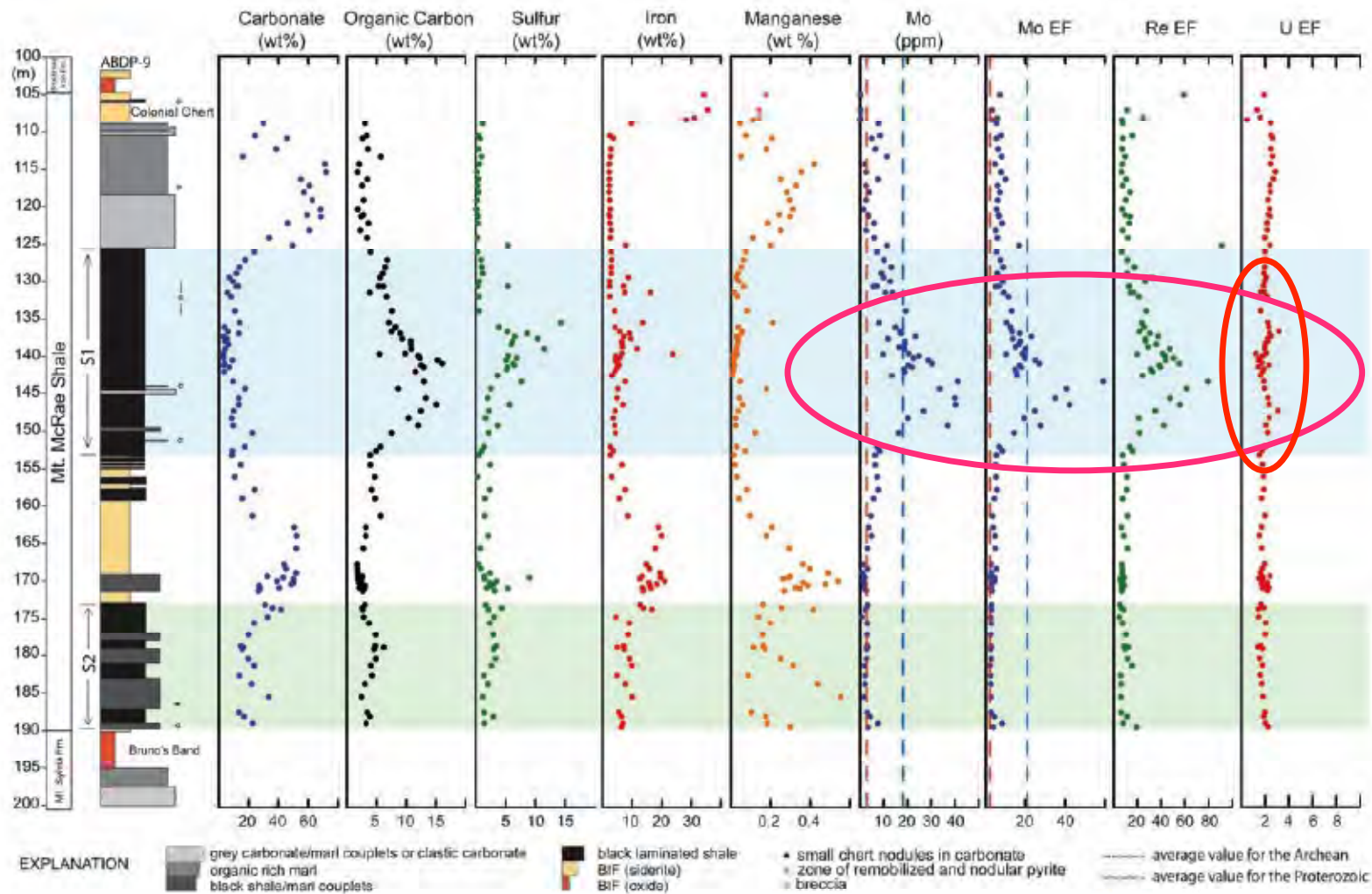
# What was the oxygen fugacity in the Archean?





# “A whiff of oxygen” before the GOE?

[Anbar et al. (2007) Science 317, 1903.]

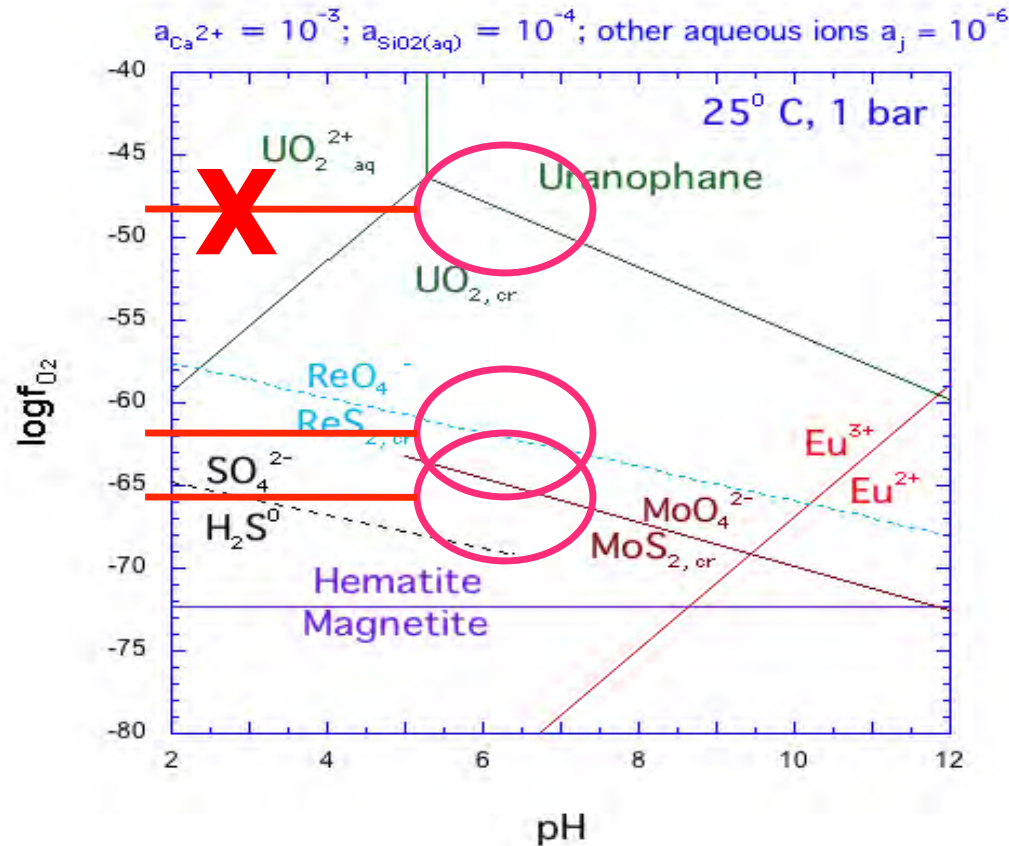


**Fig. 1.** Stratigraphy and geochemistry of the Mount McRae Shale, including percent of carbonate, TOC, S, Fe, Mn, Mo, Re, and U and EFs (24) for Mo, Re, and U (23). The intervals S1 and S2 span 125.5 to 153.3 m and 173.0 to

189.7 m, respectively. For comparison, dashed lines denote mean Mo concentrations and EFs in Archean and Proterozoic pyritic black shales, as indicated in the legend at bottom (18, 22) (tables S1 and S2).

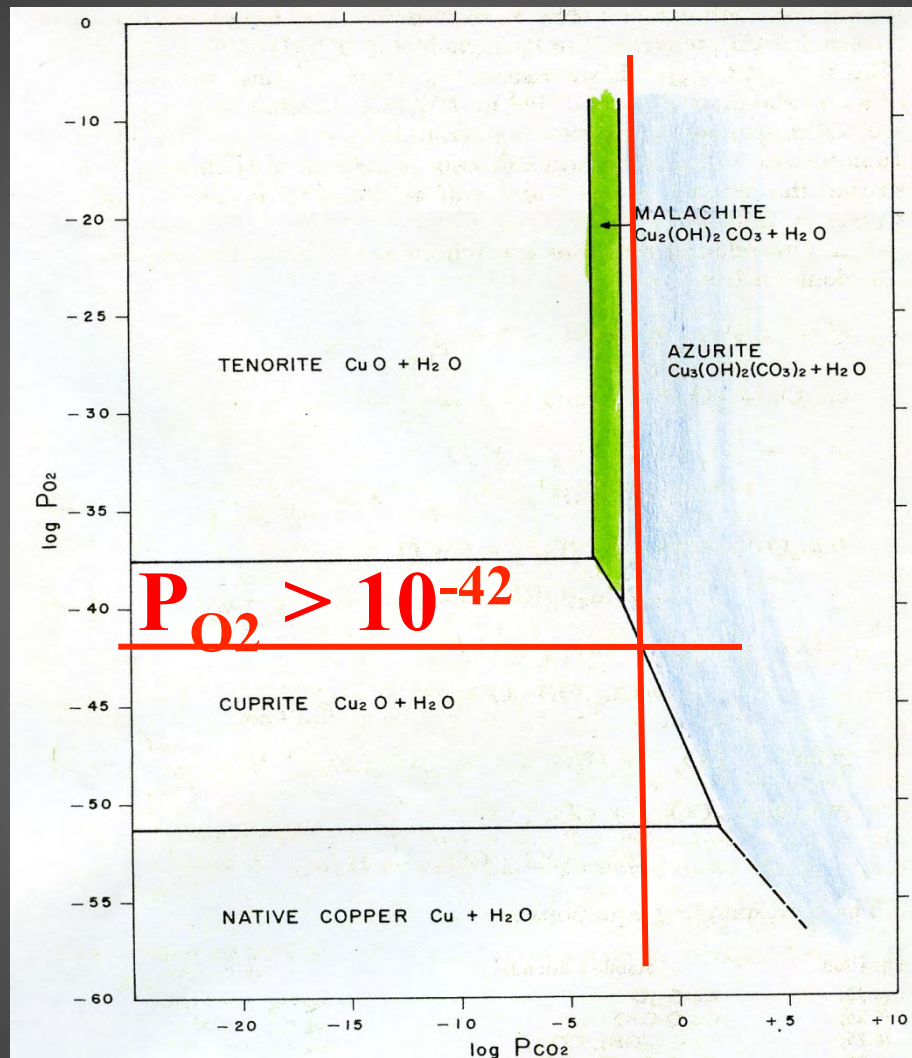
**These results reflect surface weathering conditions.**

# What was the oxygen fugacity in the Archean?



The implication is thus that for most of the Archean the effective surface  $\log f\text{O}_2 < -60$ , and perhaps  $\sim -70$ .

# What minerals won't form?



If the effective  $\log f_{O_2} \sim -70$ , then malachite, azurite and other  $Cu^{2+}$  minerals will not form.



# Stage 7: Paleoproterozoic Oxidation (2.5-1.9 Ga)

$\text{Cu}^{2+}$  Copper minerals (256 of 321)



**When did these minerals first appear?**

# Stage 7: Paleoproterozoic Oxidation (2.5-1.9 Ga)

What mineral species won't form?

202 of 220 U minerals

319 of 451 Mn minerals

47 of 56 Ni minerals

582 of 790 Fe minerals



CARNOTITE



Piemontite



Garnierite



Xanthoxenite

# Conclusion

**Approximately two thirds of all known mineral species are unlikely to form in an anoxic environment, and thus are the indirect consequence of biological activity.**



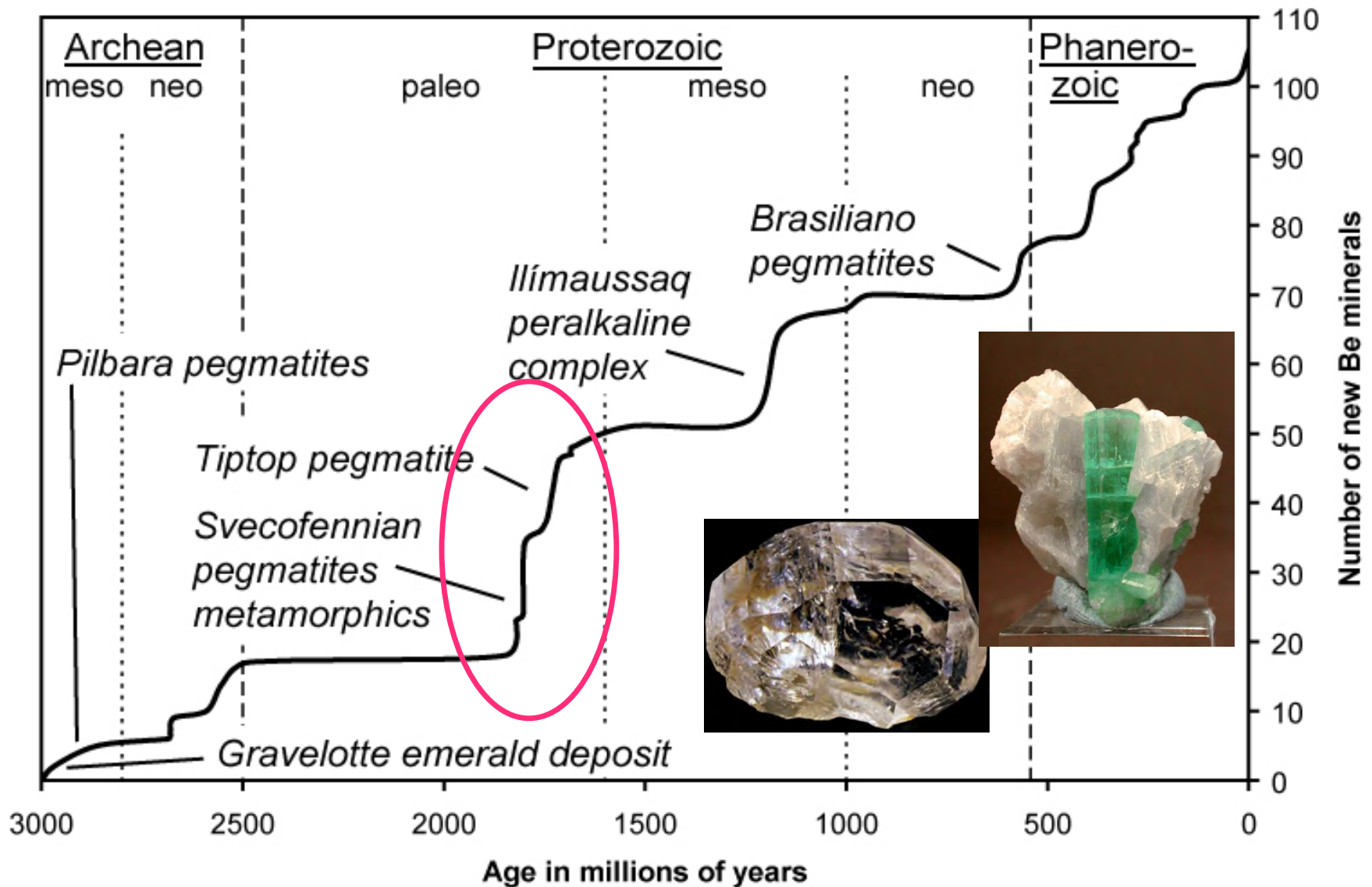
## Stage 8: The “Intermediate Ocean” (1.9-1.0 Ga)

**>4000 mineral species (few new species)**



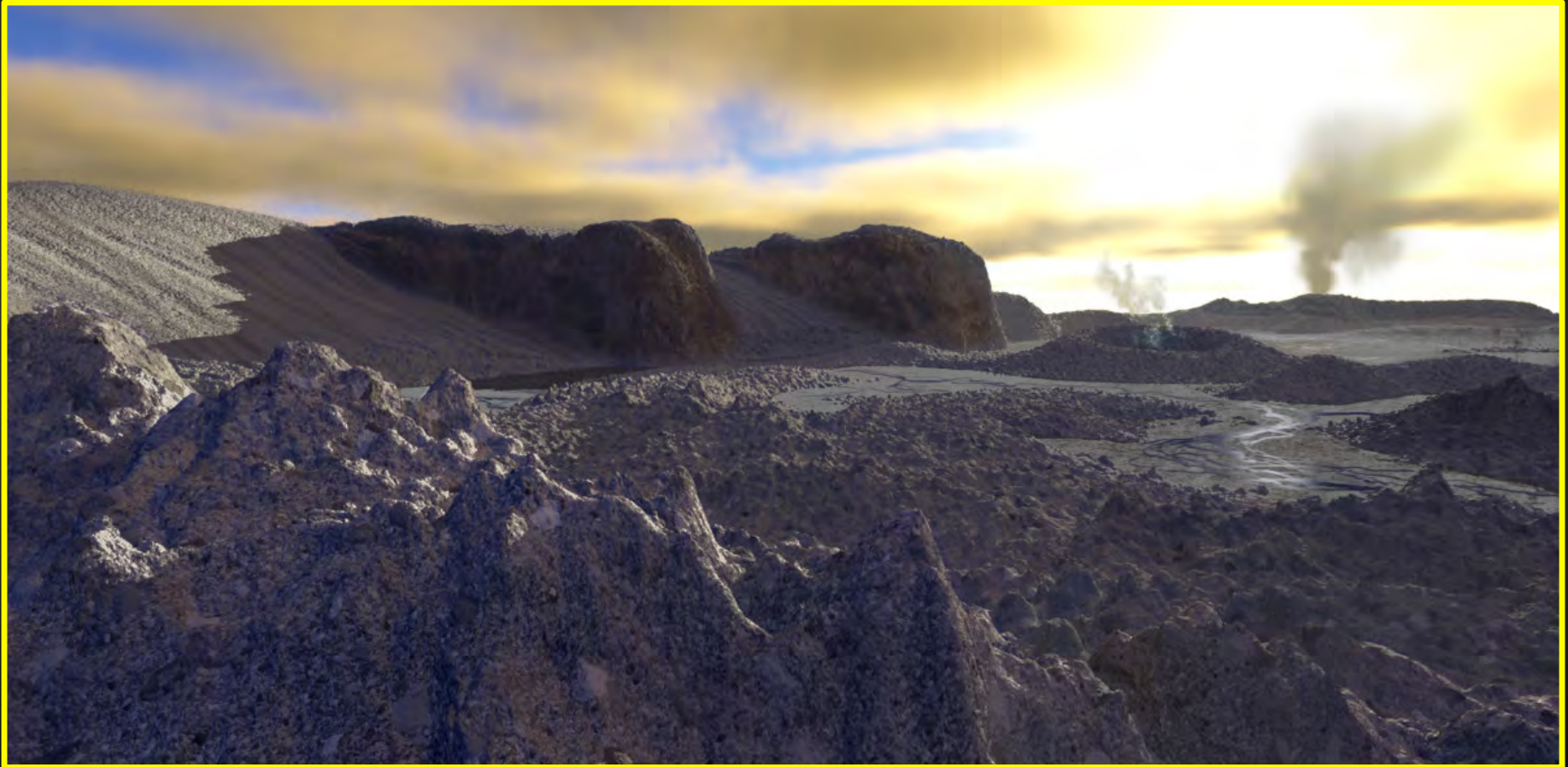
**Oxidized surface ocean; deep-ocean anoxia.**

# Be Mineral Evolution (Grew & Hazen, 2009)



# Stage 9: Snowball Earth and Neoproterozoic Oxidation (1.0-0.542 Ga)

>4000 mineral species (few new species)



Glacial cycles triggered by albedo feedback.



# Stage 10: Phanerozoic Biomineralization ( $<0.542$ Ga)

>4,400 mineral species (Biominerals, clays)



# Stage 10: Phanerozoic Biomineralization ( $<0.542$ Ga)

>4,400 mineral species

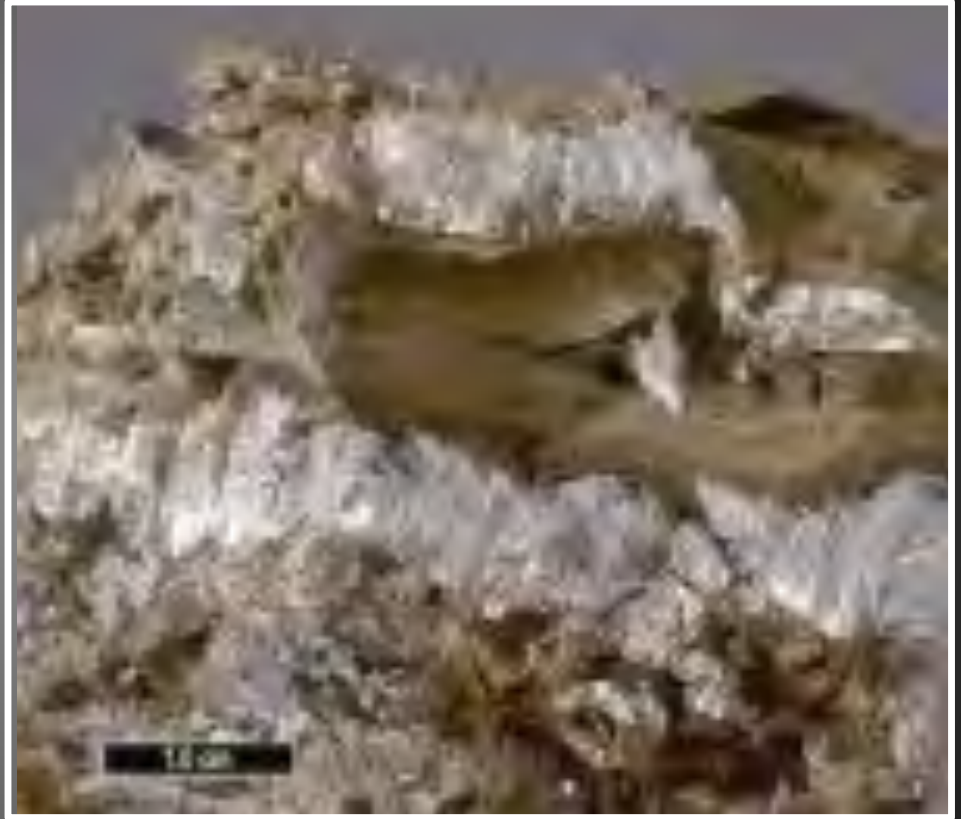




# Wilmot Hyde Bradley (1899-1979)



*W H Bradley*

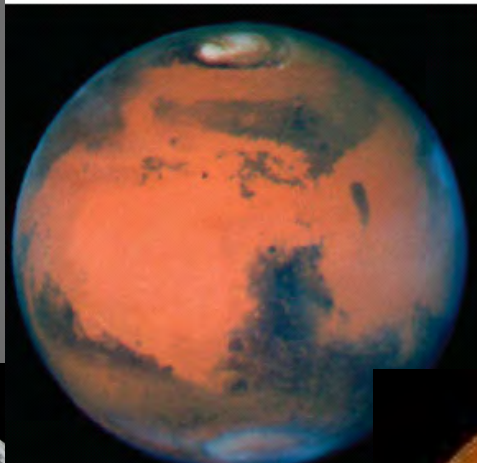
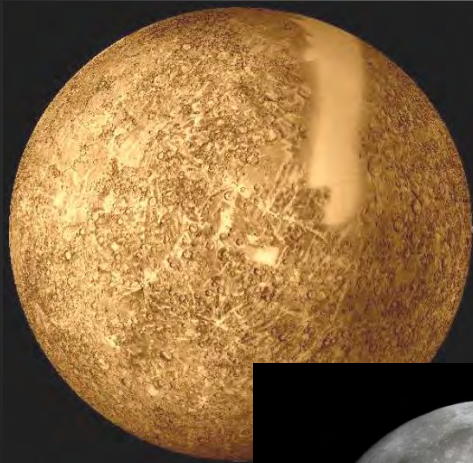


**Bradleyite  $[\text{Na}_3\text{Mg}(\text{PO}_4)(\text{CO}_3)]$   
Green River Formation, WY**



# Implications of Mineral Evolution

1. Mineral evolution suggests a new way to compare and contrast terrestrial planets and moons.



# Implications of Mineral Evolution

2. Mineral evolution points to NASA mission targets: mineral biosignatures (and abiosignatures).



# **Implications of Mineral Evolution**

**2. Mineral evolution points to NASA mission targets: mineral biosignatures (and abiosignatures).**

- Granites (pegmatites)**
- Massive sulfide deposits**
- Carbonates**
- Banded iron formations**
- Evaporites**



# Implications of Mineral Evolution

**3. Mineral evolution provides insights on the evolution of complex systems.**

**Examples:**

- Nucleosynthesis**
- Mineral evolution**
- Prebiotic chemical evolution**
  
- Languages**
- Material culture**
- Biological evolution**

# Implications of Mineral Evolution

3. Mineral evolution provides insights on the evolution of complex systems.

Themes: Combinatorial r  
Selection  
Diversification  
Niches  
Punctuation  
Extinction



# Implications of Mineral Evolution

4. Mineral evolution represents a new way to frame (and to teach) mineralogy.

- **Provides a narrative thrust to the presentation of minerals.**



# Implications of Mineral Evolution

Mineral evolution represents a new way to frame (and to teach) mineralogy.

- Provides a narrative thrust to the presentation of minerals.
- **The “Ur-mineralogy” encompasses most essential principles chemical and structural principles.**

# **“Ur”-Mineralogy**

- Diamond/Lonsdaleite
- Graphite (C)
- Moissanite (SiC)
- Osbornite (TiN)
- Nierite (Si<sub>3</sub>N<sub>4</sub>)
- Rutile (TiO<sub>2</sub>)
- Corundum (Al<sub>2</sub>O<sub>3</sub>)
- Spinel (MgAl<sub>2</sub>O<sub>4</sub>)
- Hibbonite (CaAl<sub>12</sub>O<sub>19</sub>)
- Forsterite (Mg<sub>2</sub>SiO<sub>4</sub>)
- Nano-particles of TiC, ZrC, MoC, FeC, Fe-Ni metal in graphite.
- GEMS (silicate glass with embedded metal and sulfide).

**All major types of chemical bonding**

**Polymorphism**

**Physical properties**

**Cation polyhedra**

**Phase equilibria**

**Solid solution**

**Order-disorder**

# Future Work

- **Conduct comprehensive mineral surveys**
  - Clay minerals (Bish, IU)
  - Hg, Br & I (Sverjensky, JHU)
  - Mo & W (Downs, UA)
  - Carbonates (Kah, UT)
  - P & As (Sverjensky, JHU)
  - Li, Be & B (Grew, UM)
  - Trace/minor elements in amphiboles, garnets, & spinels (anyone interested?)



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- **Conduct comprehensive mineral surveys**
- **Identify mineralogical targets for astrobiological exploration.**
- **Study how geological cycles, fluxes, and gradients transfer information to chemical systems.**
- **Further investigate mineralogical clues to Hadean and Archean environments, and thus the origins of life.**



# Conclusions

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- The mineralogy of terrestrial planets and moons evolves in both deterministic and stochastic ways.
- Different planets/moons achieve different stages of mineral evolution.
- **Three principal mechanisms of change:**
  1. Element segregation & concentration
  2. Increasing ranges of T, P and X
  3. Influence of living systems.



# Conclusions

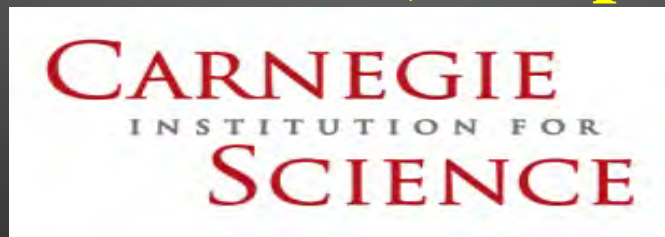
**With mineral evolution, the science of mineralogy once again assumes its rightful place at the center of the Earth and planetary sciences.**



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# What was the oxygen fugacity in the Archean?

Estimates of Archean  $H_2$   
are  $\geq 1000$  ppm:

$$[P_{H_2}]^2[P_{O_2}] = 10^{-83.1}$$

$$P_{O_2} \leq 10^{-83.1}/[10^{-3}]^2 = 10^{-77.1}$$