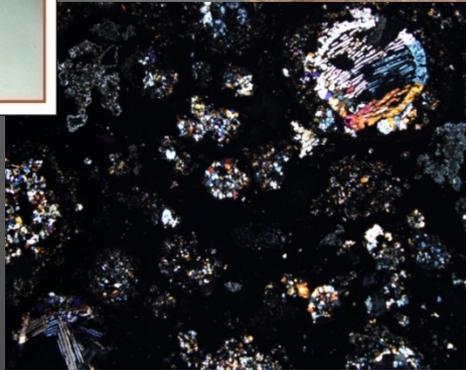
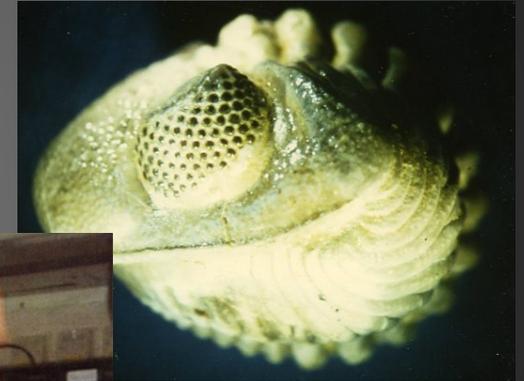


# Paleomineralogy of the Hadean Eon: What Minerals Were Present at Life's Origins?



Robert M. Hazen—Geophysical Lab  
1<sup>st</sup> ELSI International Symposium  
Tokyo Institute of Technology  
March 30, 2013



# CONCLUSIONS

**As many as 90% of the 4700 known mineral species were not present on Earth prior to the origins of life before ~4.0 billion years ago.**

**Origins-of-life models that rely on minerals for catalysis, selection, concentration, protection, or other processes must employ plausible prebiotic mineral species.**

# List of 420 Mineral Species

R. M. Hazen (2013) “Paleomineralogy of  
the Hadean Eon: A Preliminary List”  
*American Journal of Science*, in press.

# What Is Mineral Evolution?

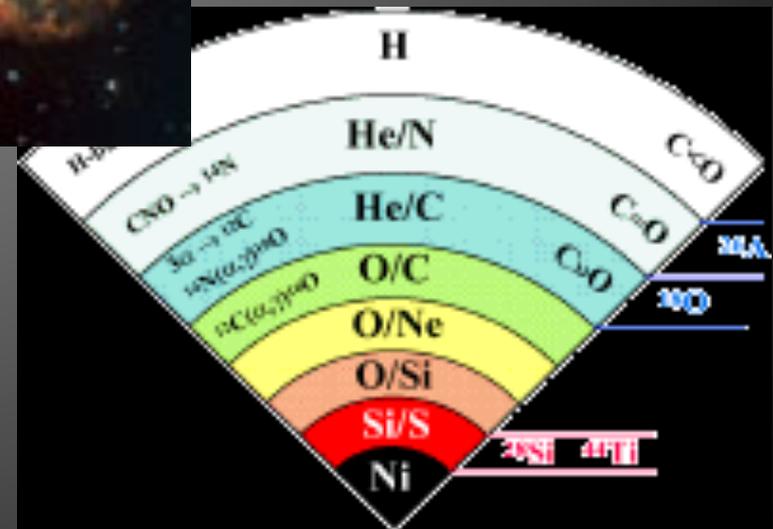
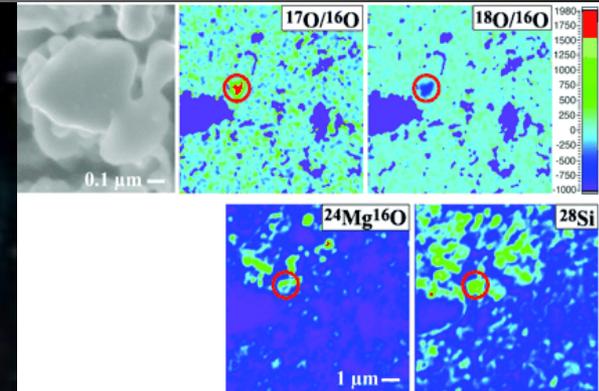
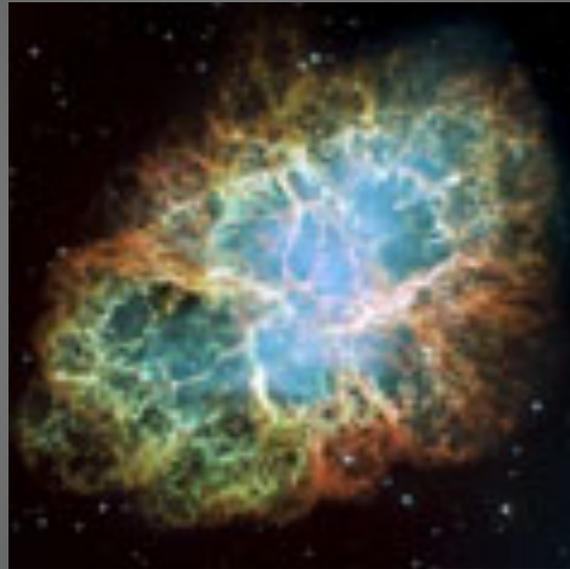
A change over time in:

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

# “Ur”-Mineralogy

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

- Diamond/Lonsdaleite
- Graphite (C)
- Moissanite (SiC)
- Osbornite (TiN)
- Nierite ( $\text{Si}_3\text{N}_4$ )
- Rutile ( $\text{TiO}_2$ )
- Corundum ( $\text{Al}_2\text{O}_3$ )
- Spinel ( $\text{MgAl}_2\text{O}_4$ )
- Hibbonite ( $\text{CaAl}_{12}\text{O}_{19}$ )
- Forsterite ( $\text{Mg}_2\text{SiO}_4$ )
- Nano-particles of TiC, ZrC, MoC, FeC, Fe-Ni metal within graphite.
- GEMS (silicate glass with embedded metal and sulfide).

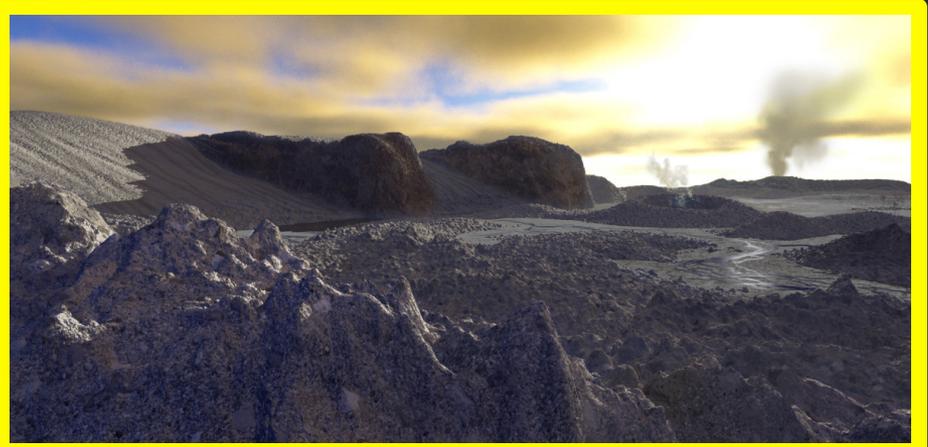


# Mineral Evolution:

How did we get from a dozen minerals to >4700 on Earth today?

What minerals were not present at the origin of life (~4.0 Ga), and why?

# Mineral Evolution



# **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.**

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

# What Drives Mineral Evolution?

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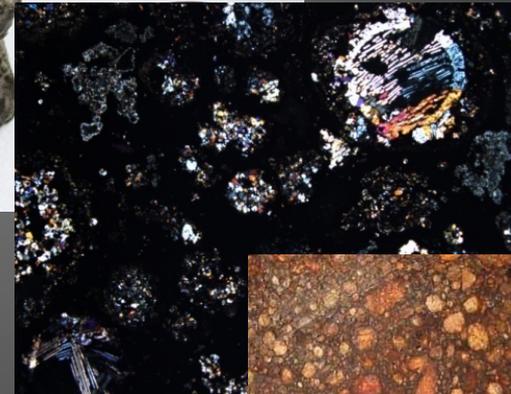
1. The progressive separation and concentration of chemical elements from their original uniform distribution.
2. An increase in the range of intensive variables (T, P, activities of volatiles).
3. The generation of far-from-equilibrium conditions by living systems.

# 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

~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
- Carbonates

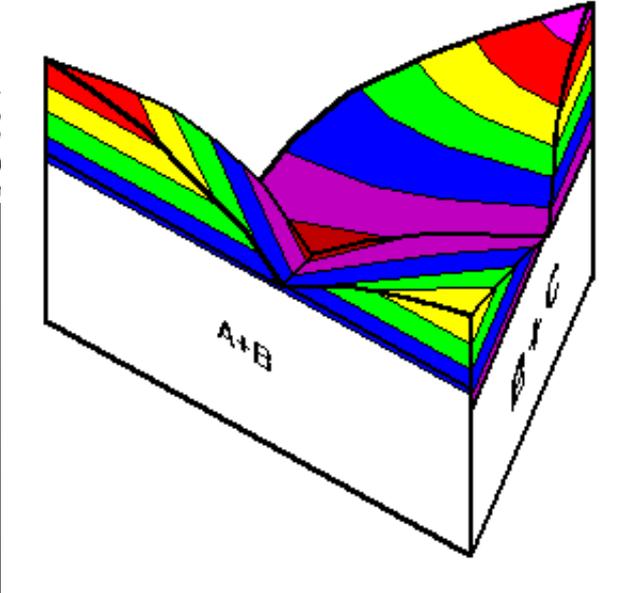
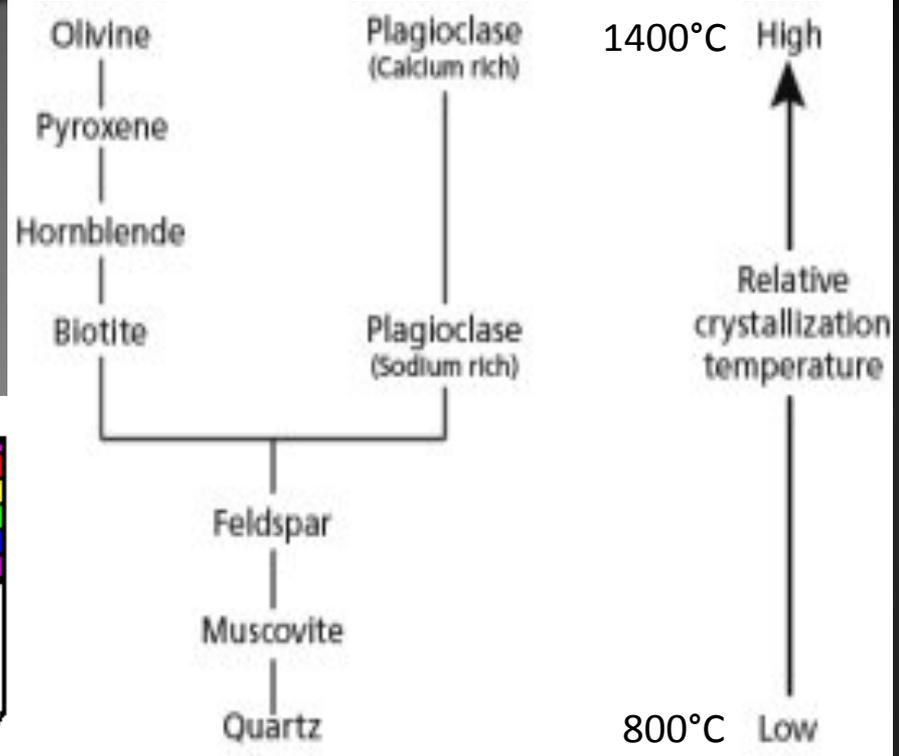
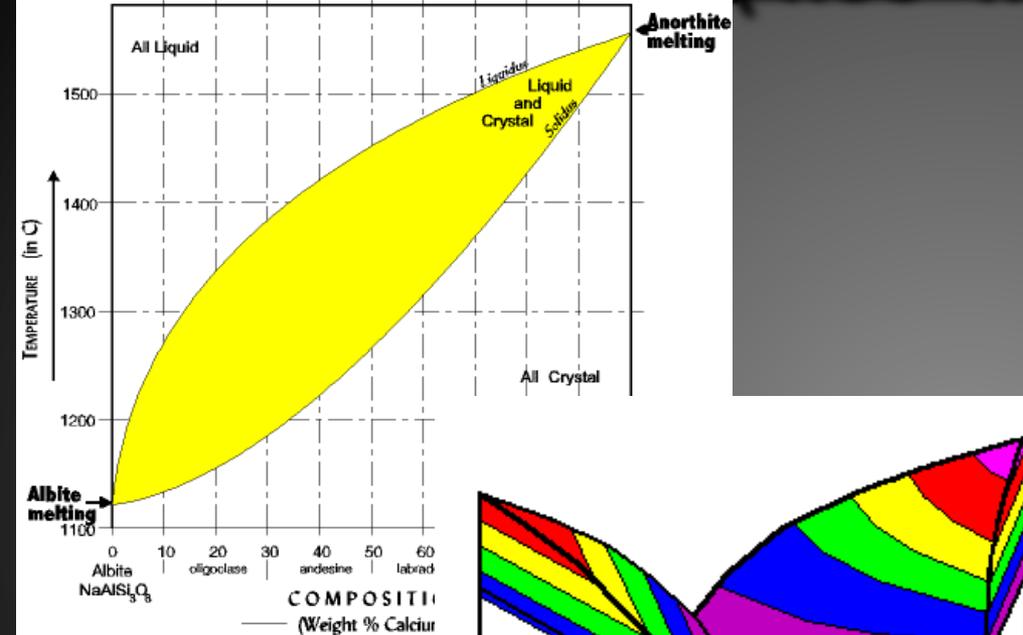


# Stages 1 and 2: Planetary Accretion



**All of the >250 meteorite mineral species were present at life's origins.**

# 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-rich Body

>400 mineral species (hydroxides, clays, ices, evaporites, sulfates, carbonates)



Volcanism, outgasing, surface hydration, evaporites, ices.

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



**All of the ~420 Stage 3 minerals  
were present at life's origins.**

## 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

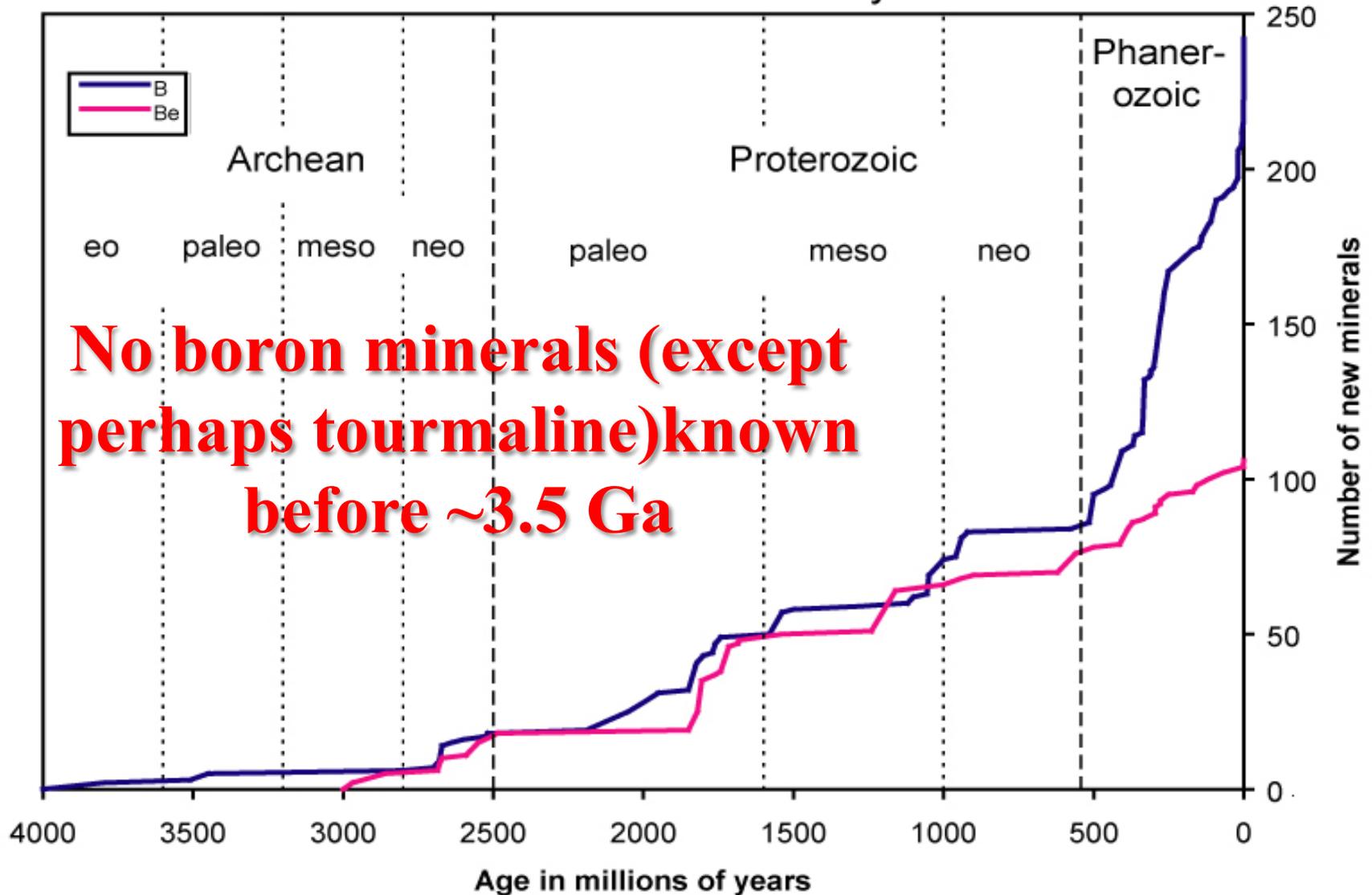
Complex pegmatites require multiple cycles of eutectic melting and fluid concentration.

**All complex pegmatites are younger than 3.5 Ga.**



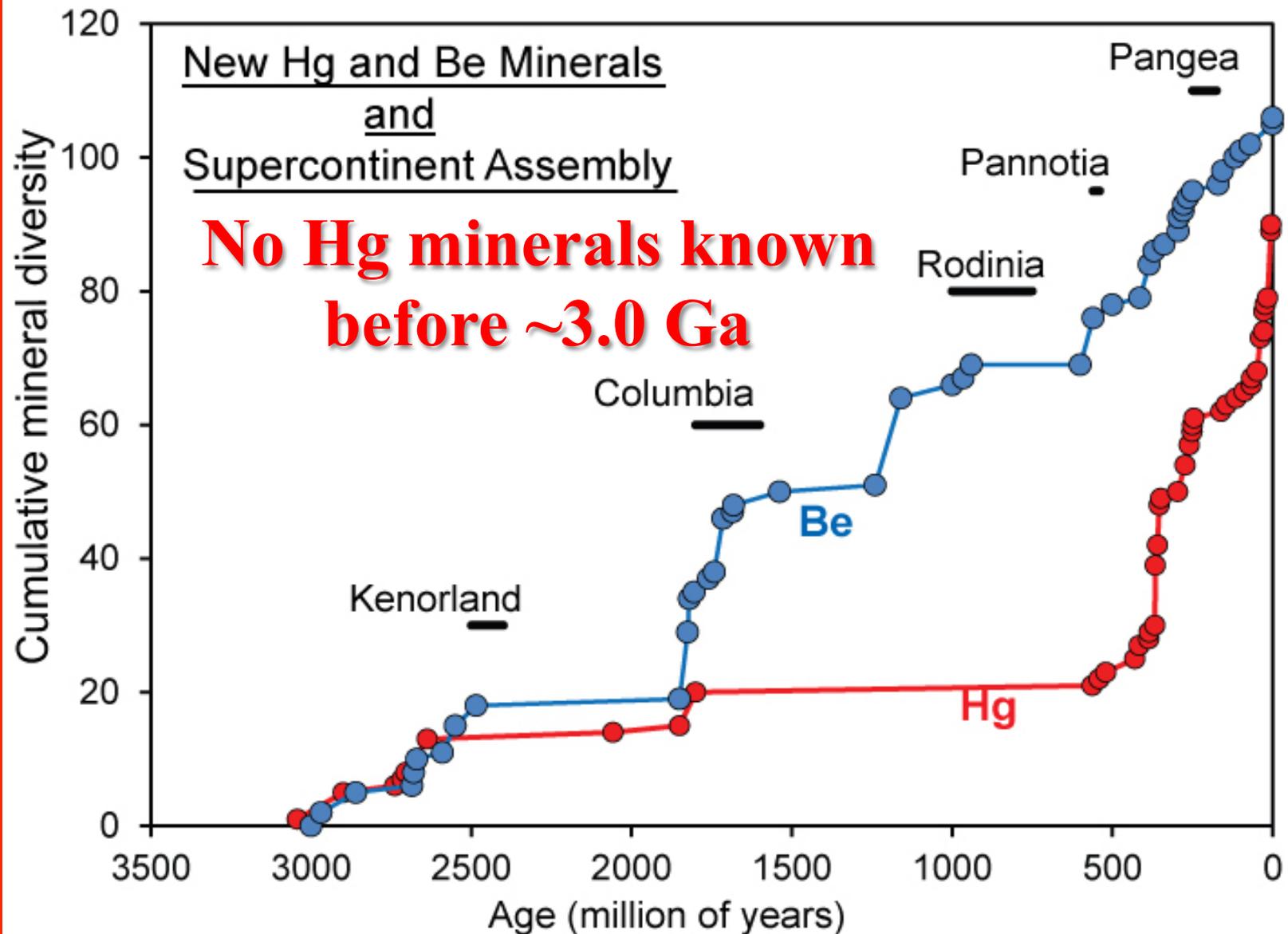
# B Mineral Evolution (Grew & Hazen 2010)

Cumulative Number of Boron and Beryllium Minerals

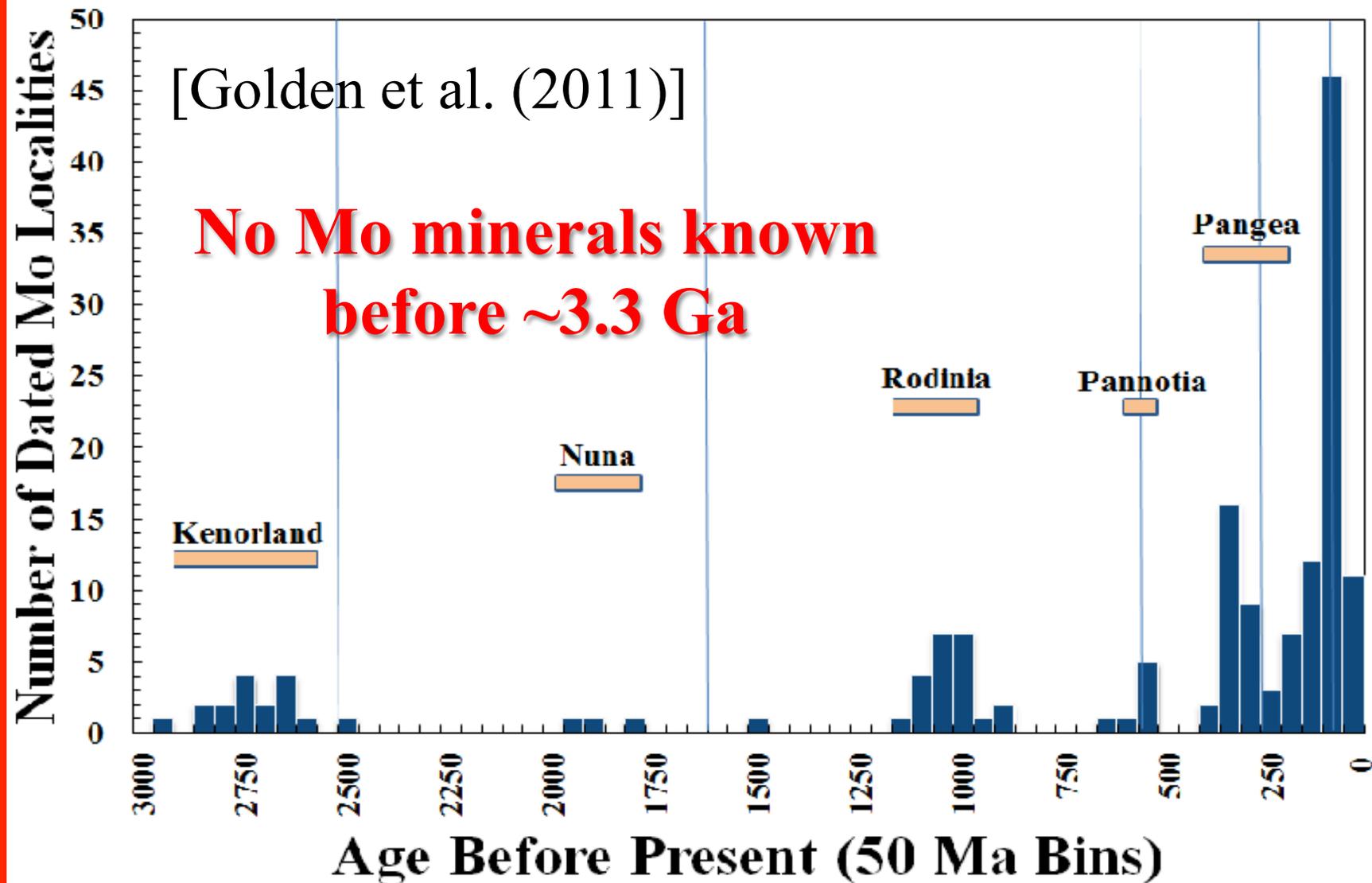


**No boron minerals (except perhaps tourmaline) known before ~3.5 Ga**

# RESULTS: Hg & Be Mineral Evolution



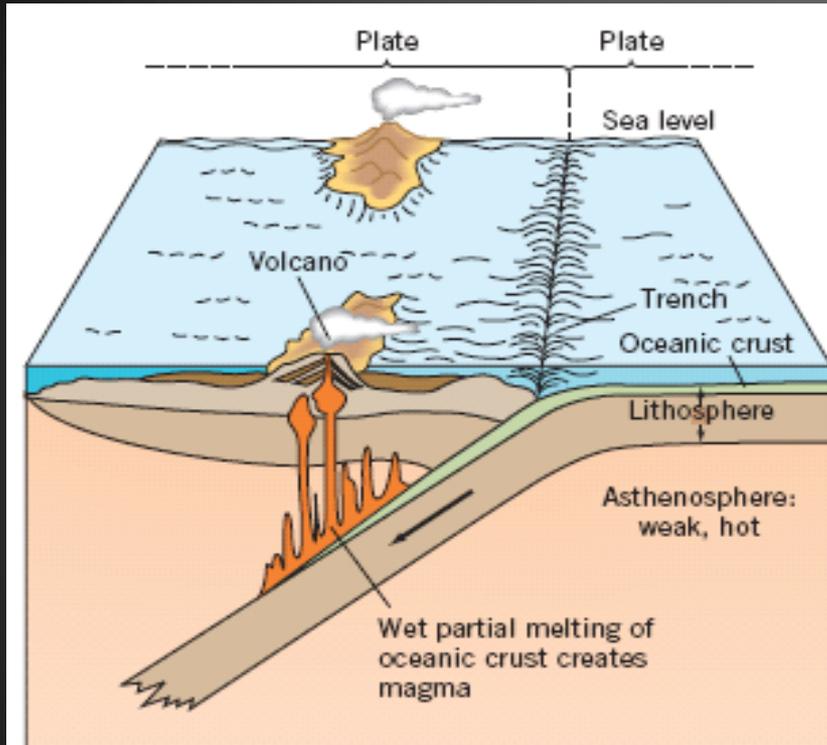
# RESULTS: Molybdenite ( $\text{MoS}_2$ ) through Time



# RESULTS: Mo Mineral Evolution



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



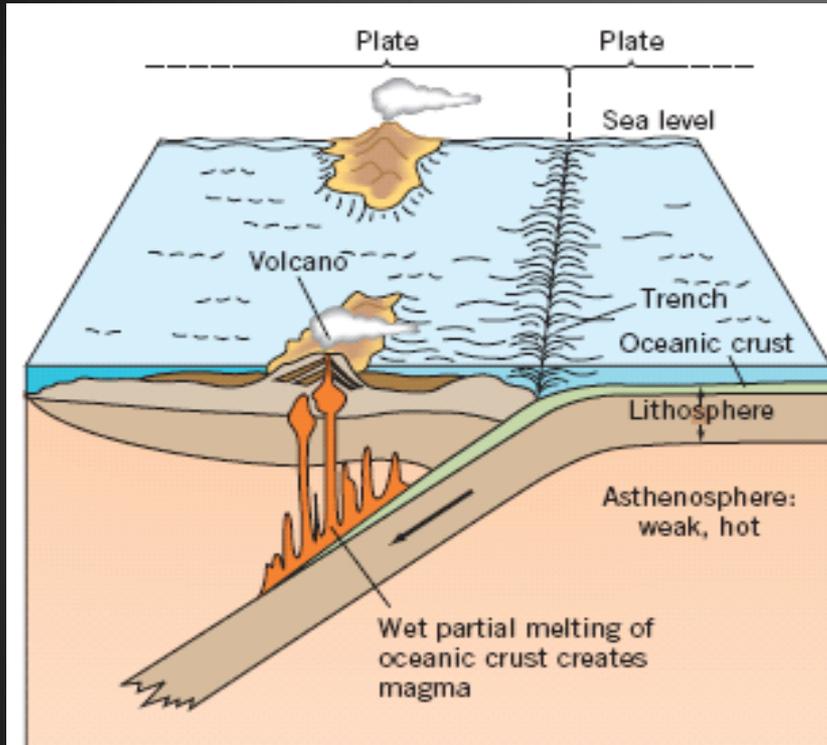
$\sim 10^8 \text{ km}^3$  of reworking



Mayon Volcano, Philippines

## New modes of volcanism

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



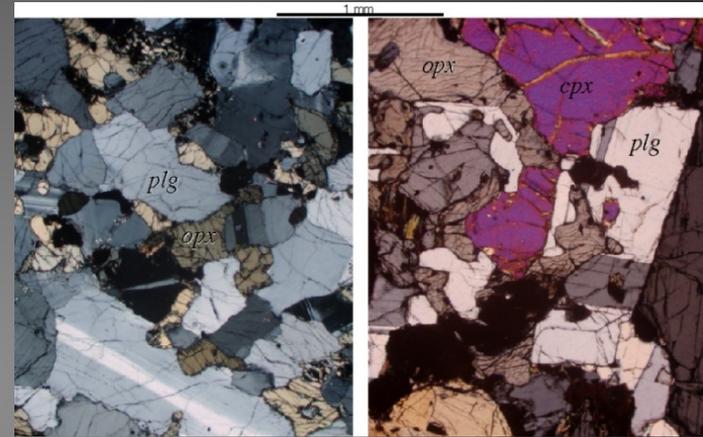
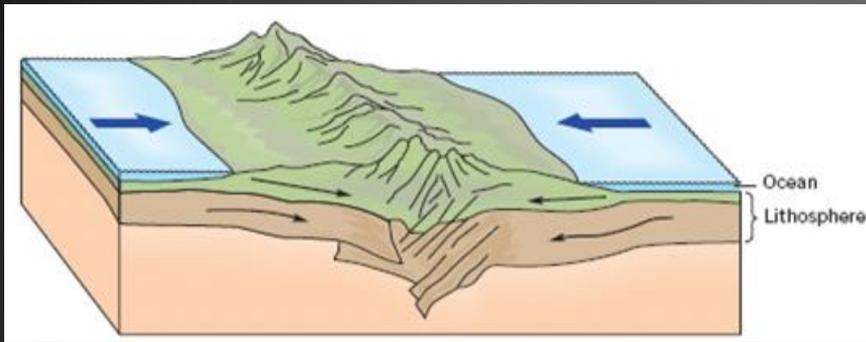
Rio Tinto. Spain

New modes of volcanism

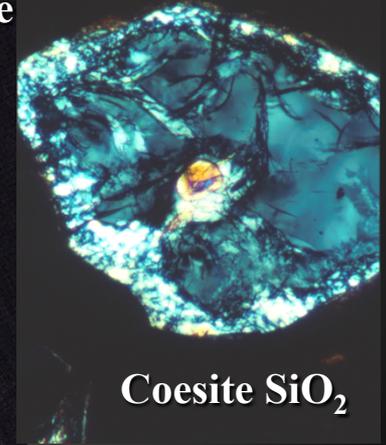
Massive base metal deposits (sulfides, sulfosalts)

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

1,500 mineral species



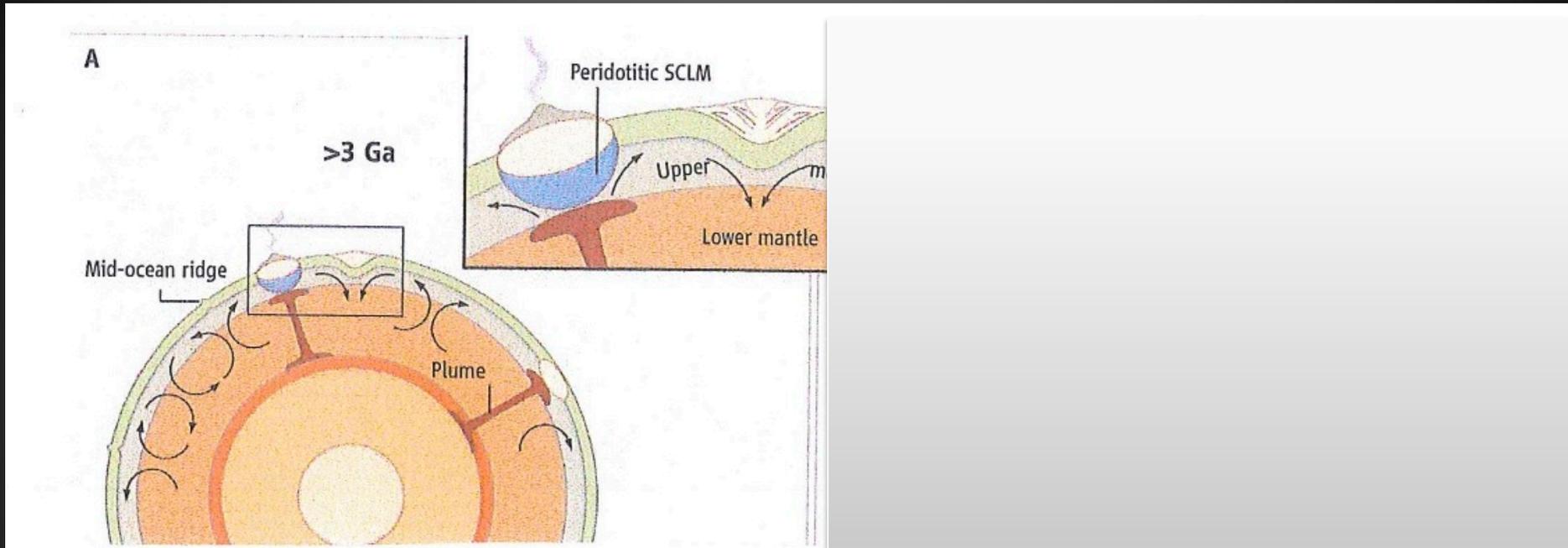
Glaucophane, Lawsonite, Jadeite



Coesite SiO<sub>2</sub>

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

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

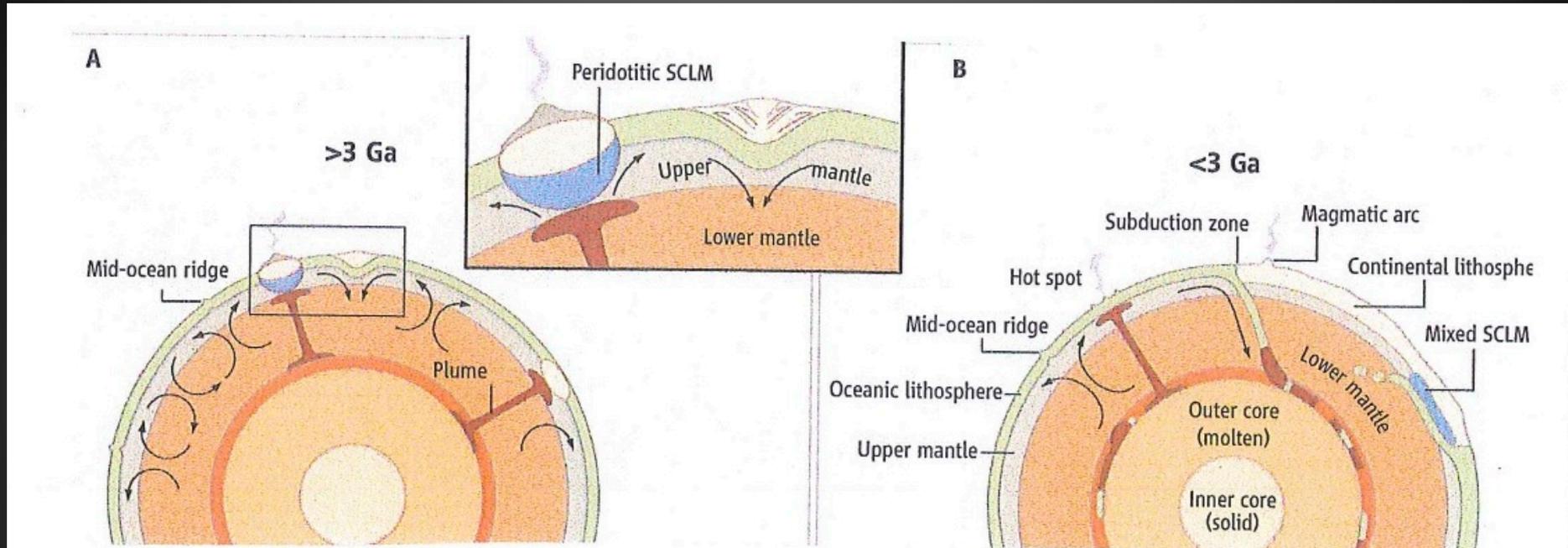


Van Kranendonk (2011)

> 3 Ga

When did subduction begin?

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



Van Kranendonk (2011)

> 3 Ga

< 3 Ga

Recent research suggests that global-scale subduction did not begin until ~3 Ga.

## Stages 3-5: Era of crust-mantle processing (igneous evolution; plate tectonics)



# **What was the Role of Impacts?**

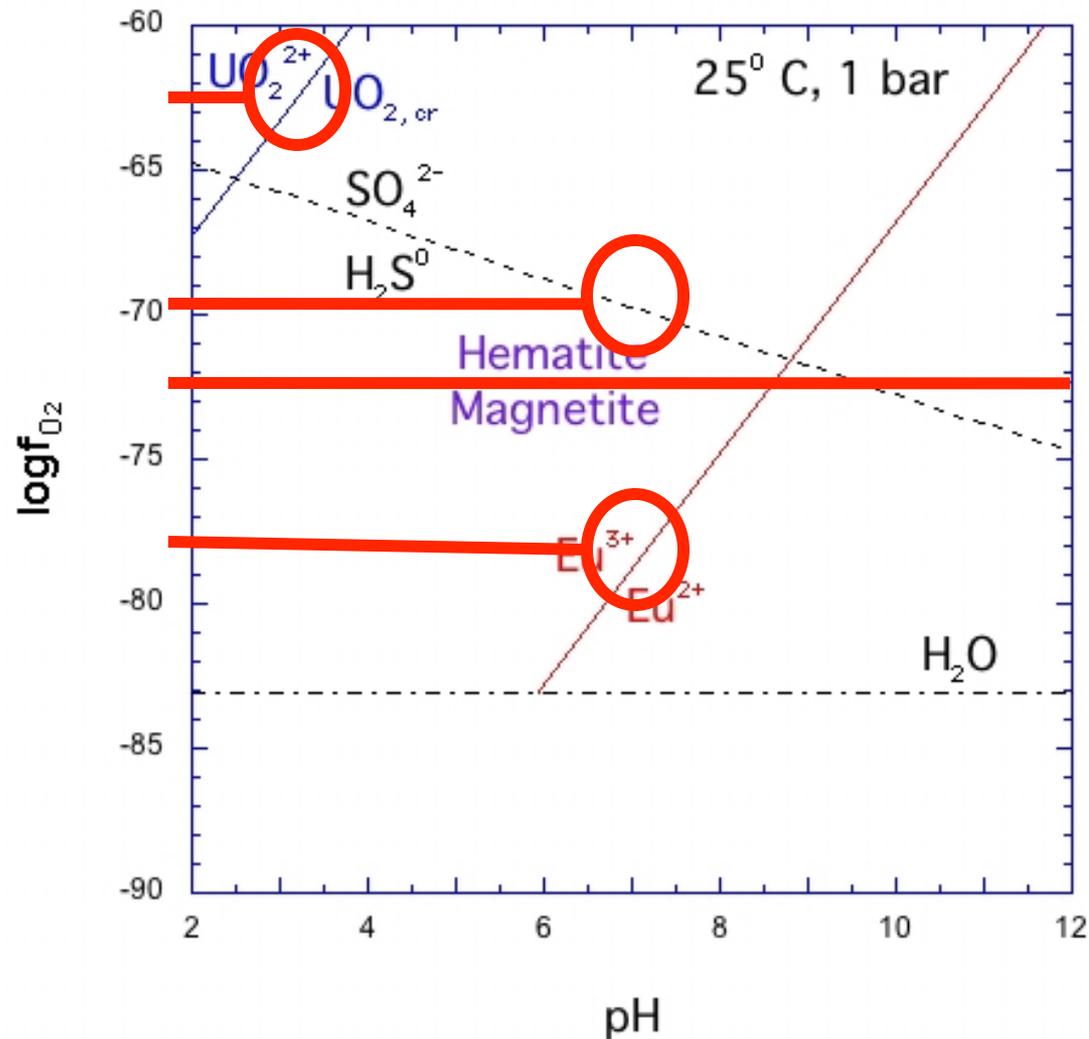
- 1. Formation of shock minerals.**
- 2. Excavation of deep igneous and metamorphic terrains.**
- 3. Creation of deep subsurface hydrothermal zones.**

# 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 (ask me).**

# What was the oxygen fugacity in the Archean?



# Key constraints on Archean surface oxygen fugacity.

Detrital uraninite, pyrite and siderite

Paleosols lacking iron oxides

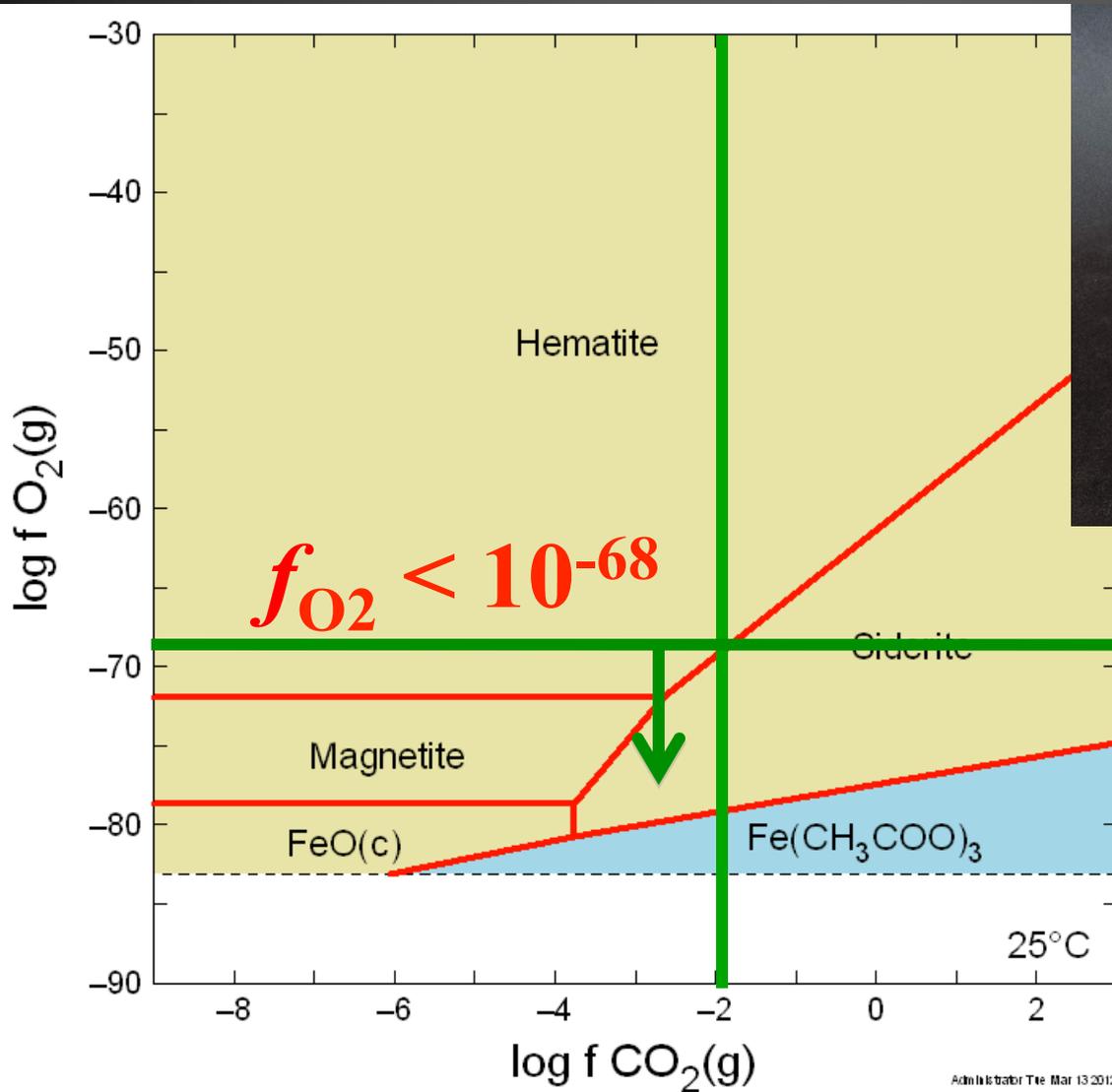
[Surface waters with aqueous  $\text{Fe}^{2+}$ ]

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

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

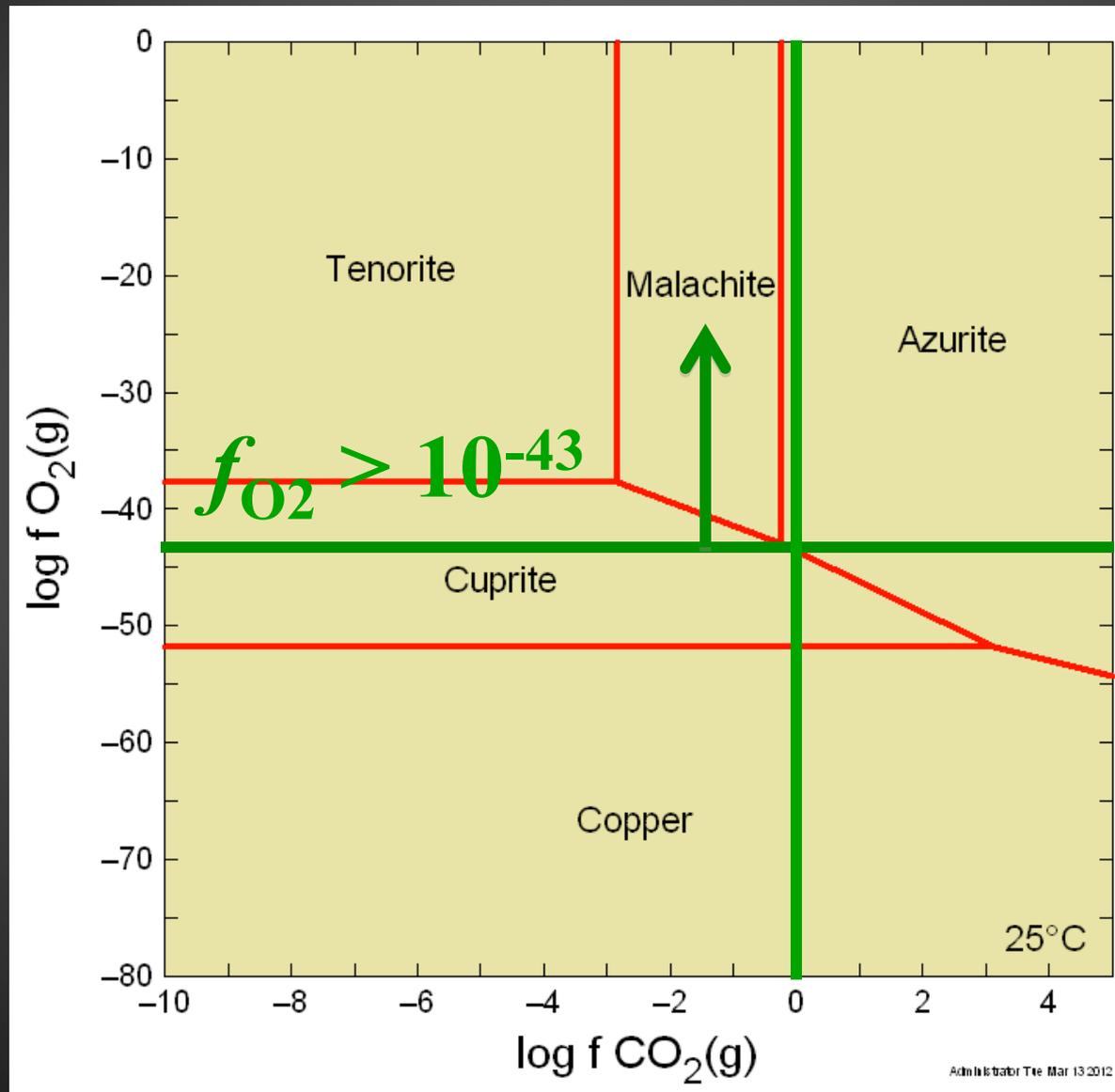
Precipitation of ferroan carbonates

# What was the oxygen level in the Archean Eon?



Siderite  
 $\text{FeCO}_3$

# What was the oxygen level in the Archean Eon?



Azurite  
&  
Malachite



# What minerals won't form?

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



Turquoise



Malachite



Diopside



Azurite



Chrysocolla

# What minerals 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

# What minerals won't form?



(c) Thomas Witzke + Abraxas Verlag

**Abelsonite— $\text{NiC}_{31}\text{H}_{32}\text{N}_4$**



(c) Thomas Witzke + Abraxas Verlag

**Ravatite— $\text{C}_{24}\text{H}_{48}$**



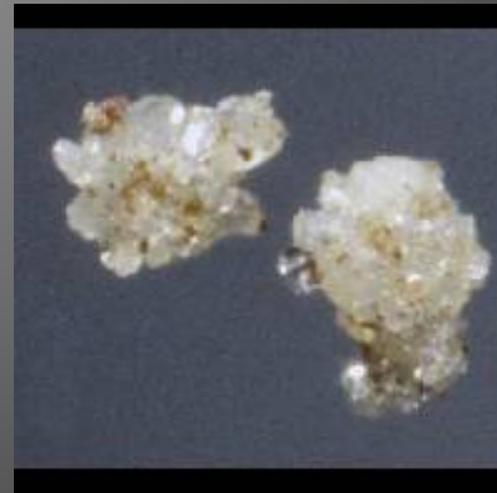
(c) Thomas Witzke + Abraxas Verlag

**Evankite— $\text{C}_{24}\text{H}_{48}$**



(c) Thomas Witzke + Abraxas Verlag

**Dashkovaite— $\text{Mg}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$**



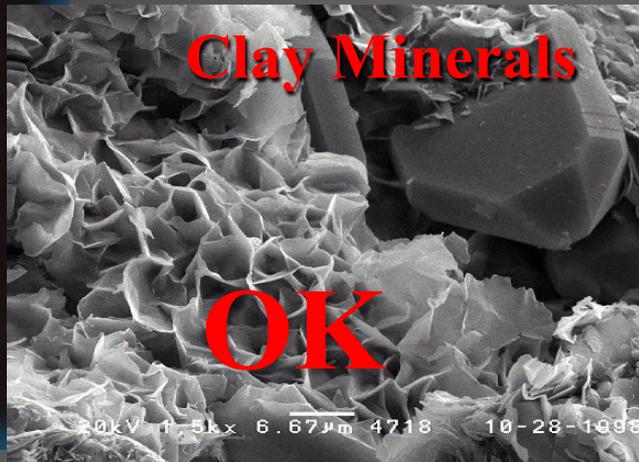
**Oxammite— $(\text{NH}_4)(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$**

**> 50 Organic Mineral Species**

# So what minerals were present at the time of life's origins?

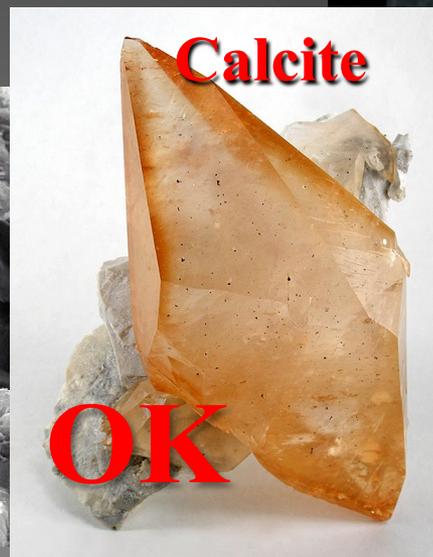
Sulfide Minerals

**OK**



**Clay Minerals**

**OK**



**Calcite**

**OK**



**Quartz**

**OK**



**OK**

**Diopside**



**Rutile**

**OK**



**Borates**



**Molybdates**

# CONCLUSIONS

**As many as 90% of the >4700 known mineral species were not present on Earth prior to the origins of life before ~4.0 billion years ago.**

**Origins-of-life models that rely on minerals for catalysis, selection, concentration, protection, or other processes must employ plausible prebiotic mineral species.**

# Unanswered Questions?

When did an ocean form and what were its physical and chemical characteristics?

When did continents form and what was the dominant lithology (TTG vs. anorthosite)?

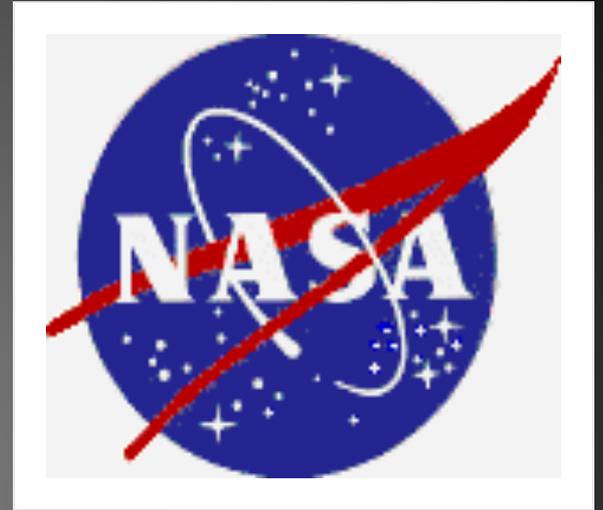
When did plate tectonics begin?

What local reaction path mechanisms might have led to redox excursions?

What was the role of impacts?



Deep Carbon Observatory



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**Carnegie Institution, Geophysical Lab**

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