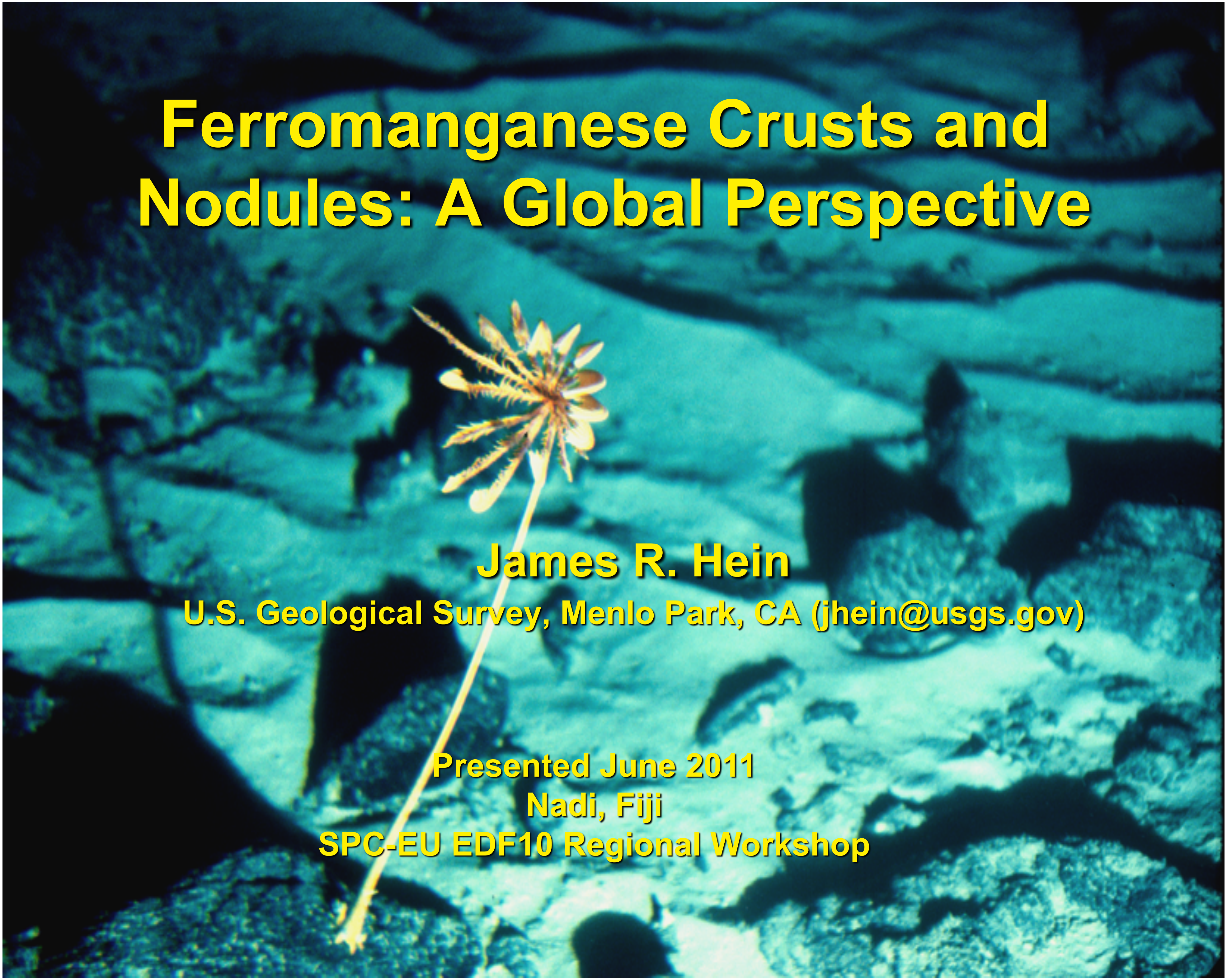


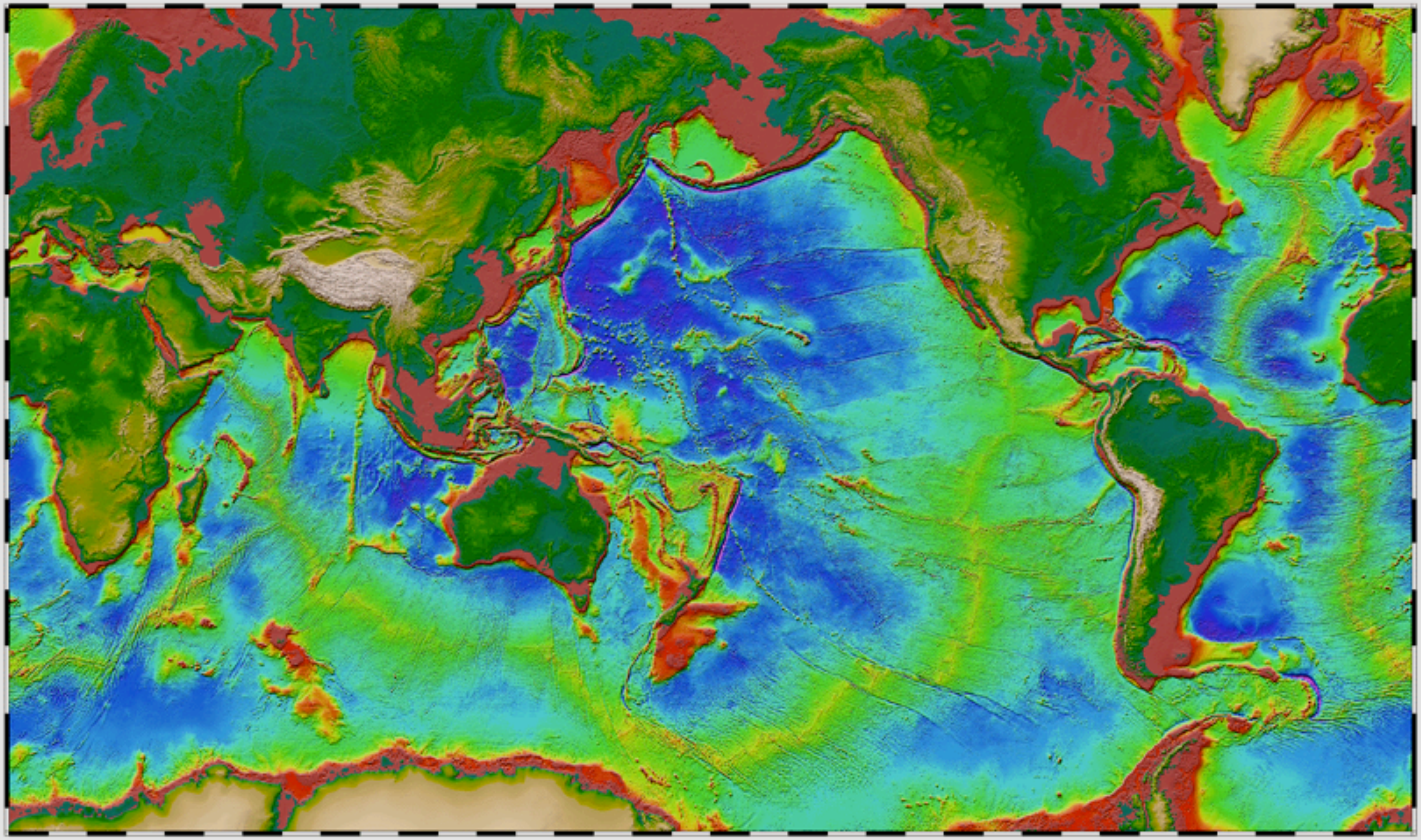
# Ferromanganese Crusts and Nodules: A Global Perspective


**James R. Hein**

U.S. Geological Survey, Menlo Park, CA (jhein@usgs.gov)


Presented June 2011
Nadi, Fiji
SPC-EU EDF10 Regional Workshop

# Location of Crusts and Nodules



# Deep-Ocean Ferromanganese Deposits

**Manganese nodules**

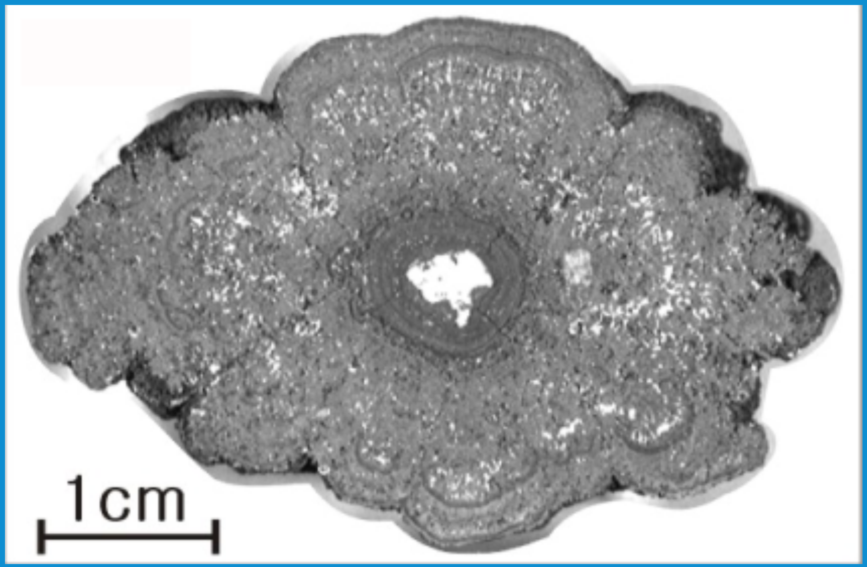
- **Form on the vast deep-water abyssal plains**

**Ferromanganese crusts**

- Form on 50,000 seamounts

# Manganese Nodules

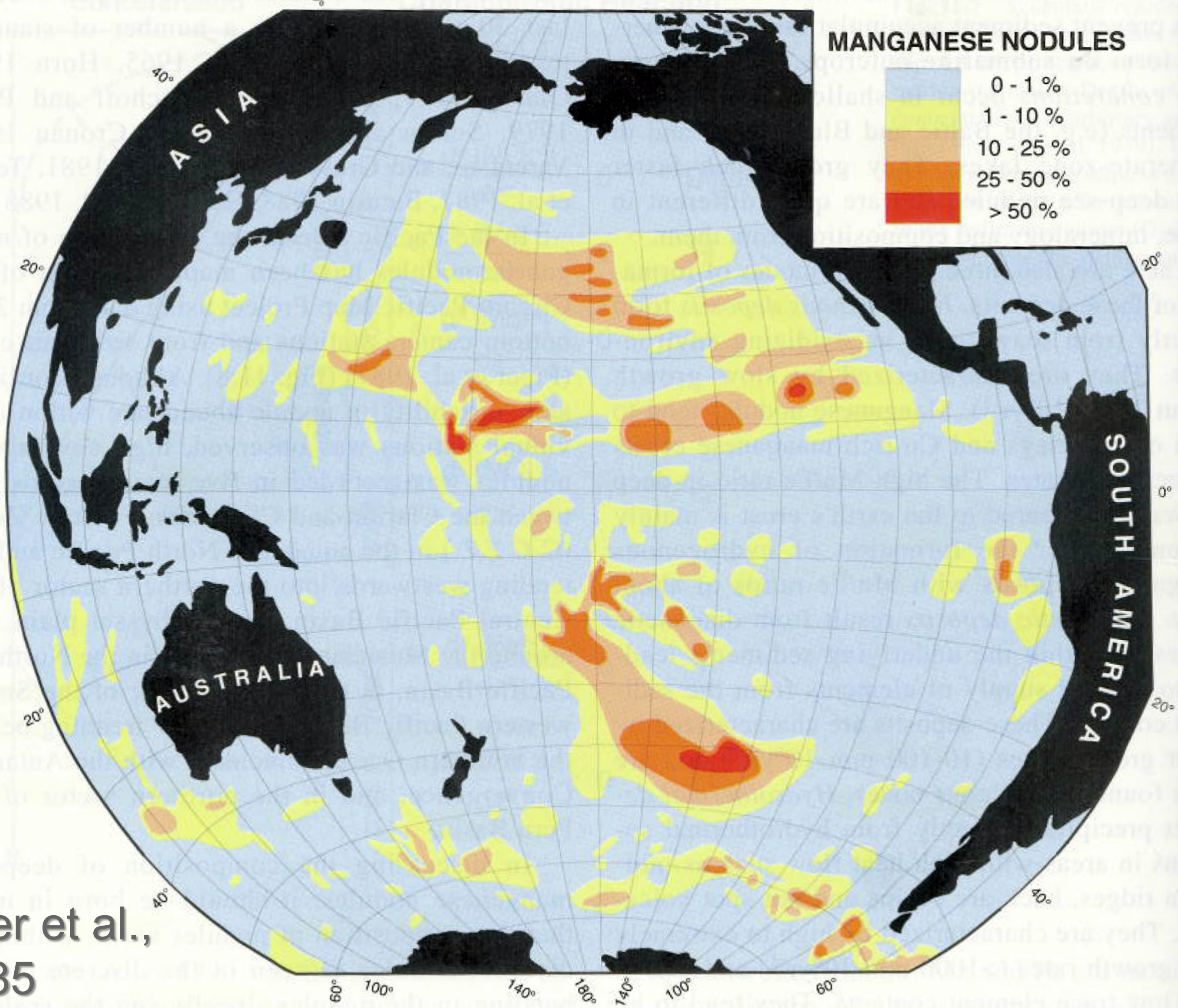
- Form on sediment-covered abyssal plains (4,000-6,500 meters water depths)
- Composed of manganese-iron oxides, with significant amounts of nickel & copper
- Form by precipitation from cold ambient bottom water & from sediment pore fluids



# Requirements for formation of manganese nodules

- Slow rates of sedimentation
- Availability of material for nuclei
- Mechanism for turning

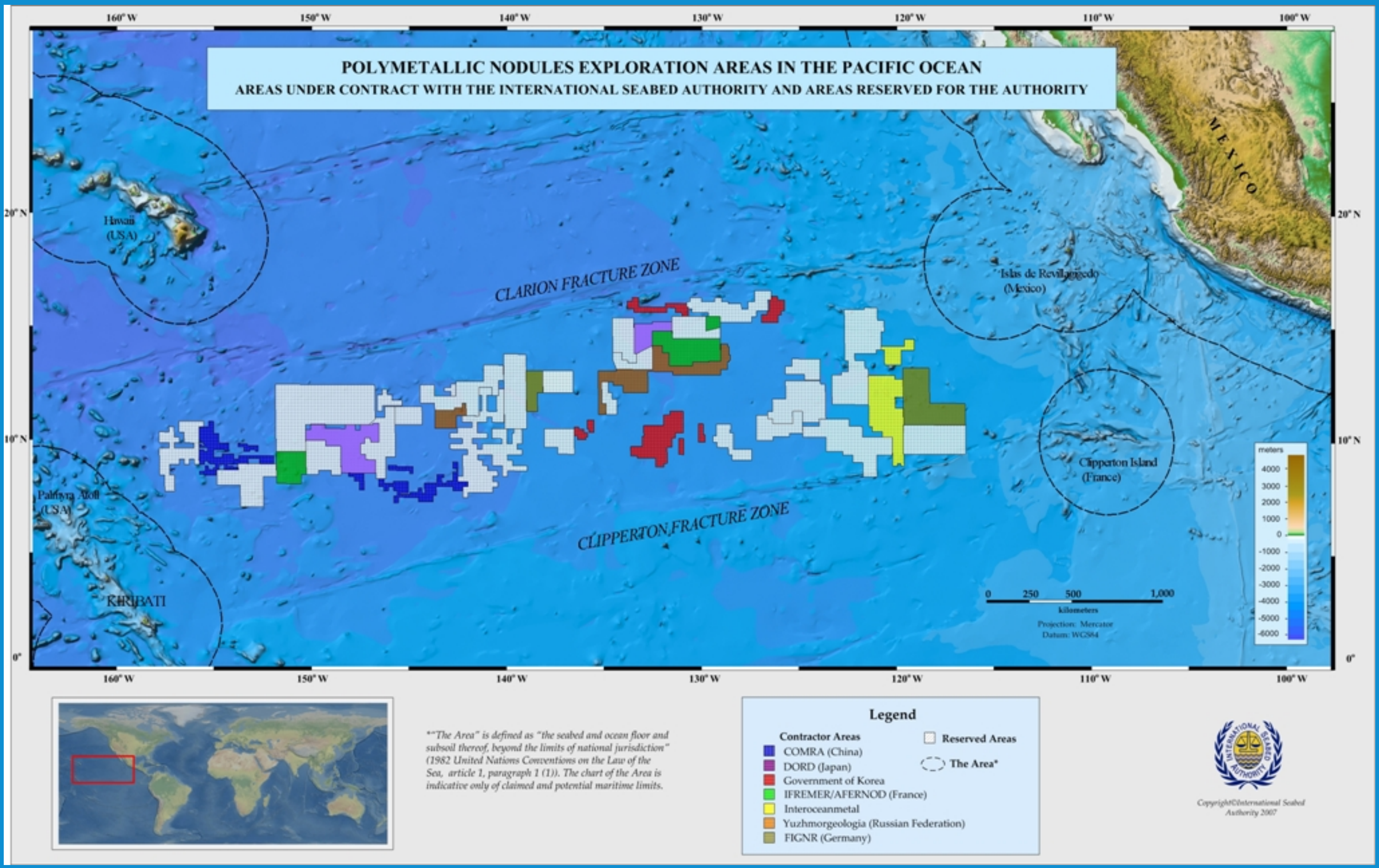
# Pacific/Indian nodule distribution

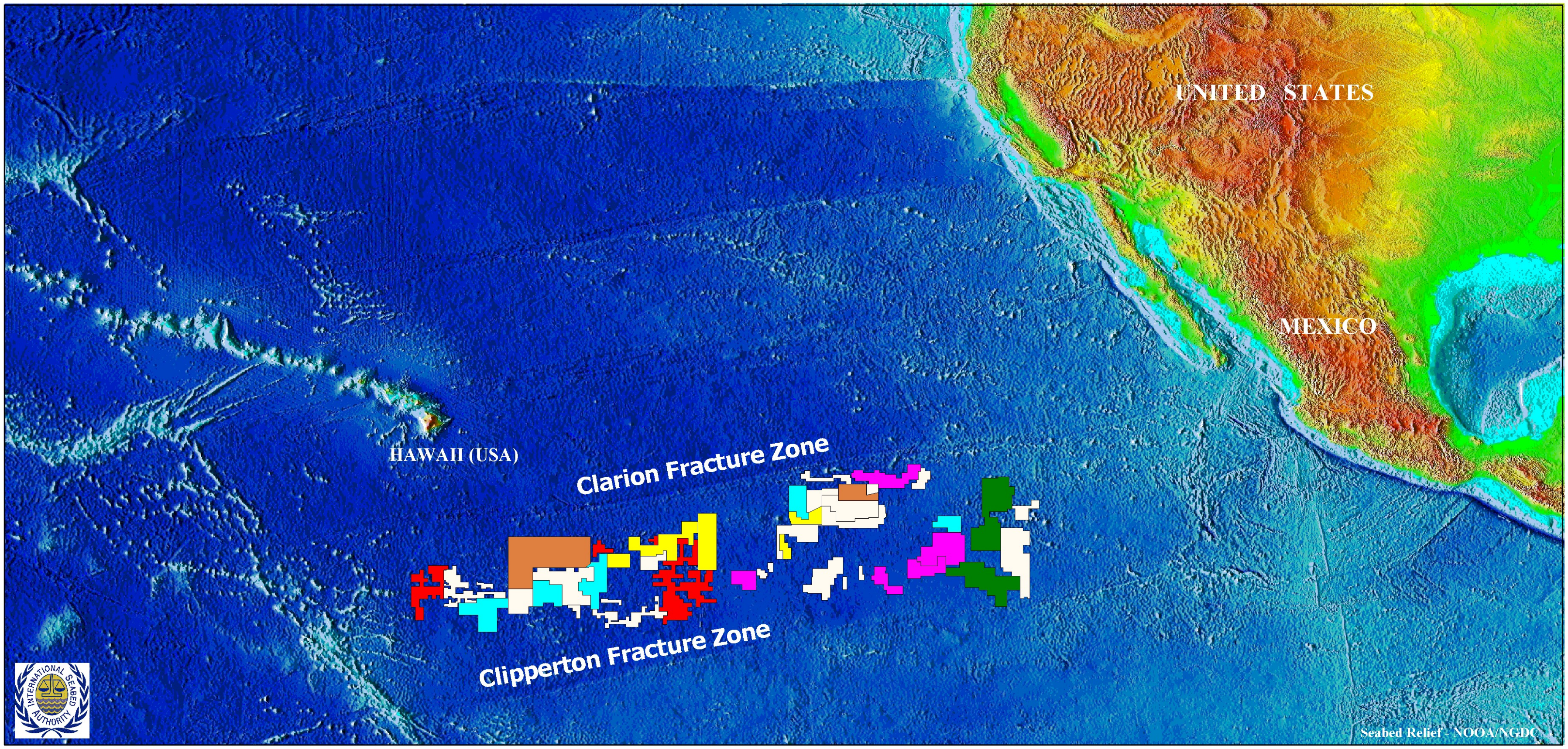



Piper et al., 1985

**Fig. 11.8** Schematic map showing the distribution of manganese nodules in the Pacific Ocean compiled as part of the Circum-Pacific Map Project (Piper et al. 1985). The contours represent the percentage cover of the ocean floor by manganese nodules.

# Clarion-Clipperton Zone



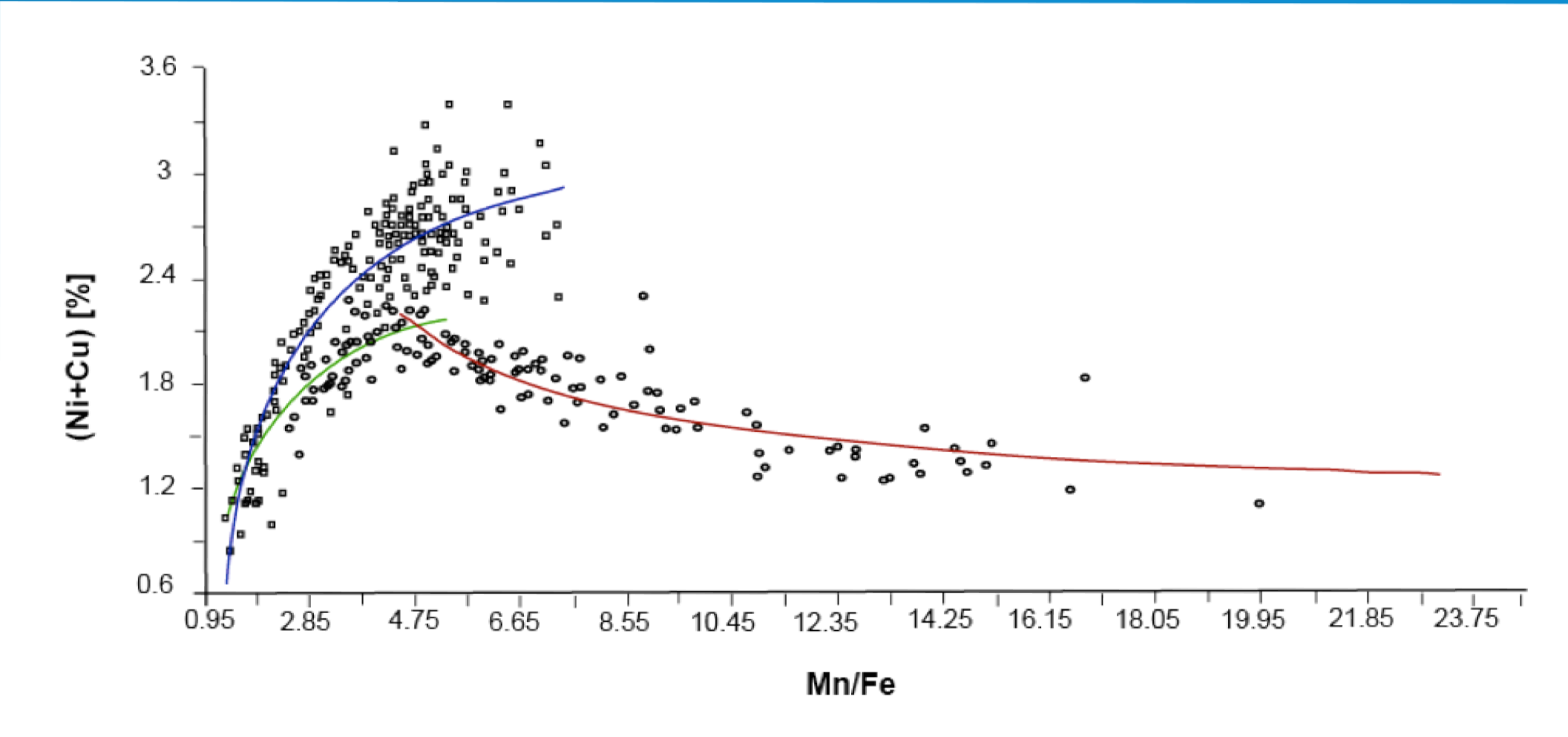



# AREAS RESERVED FOR CONDUCT OF ACTIVITIES BY THE INTERNATIONAL SEABED AUTHORITY IN THE PACIFIC OCEAN

- From COMRA (China)
- From DORD (Japan)
- From IFREMER/AFERNOD (France)
- From YUZHMORGEOLOGIA (Russian Fed.)
- From Government of Korea
- From INTEROCEANMETAL (Bulgaria, Cuba, Czech Rep., Russia Fed., Slovak Rep., Poland)
- CONTRACTORS AREAS

# Hyperbolic regression curves of Ni+Cu against Mn/Fe for nodules from the Clarion-Clipperton F.Z. region

(upper curve and Peru Basin) (lower curve) (after Halbach et al., 1981)



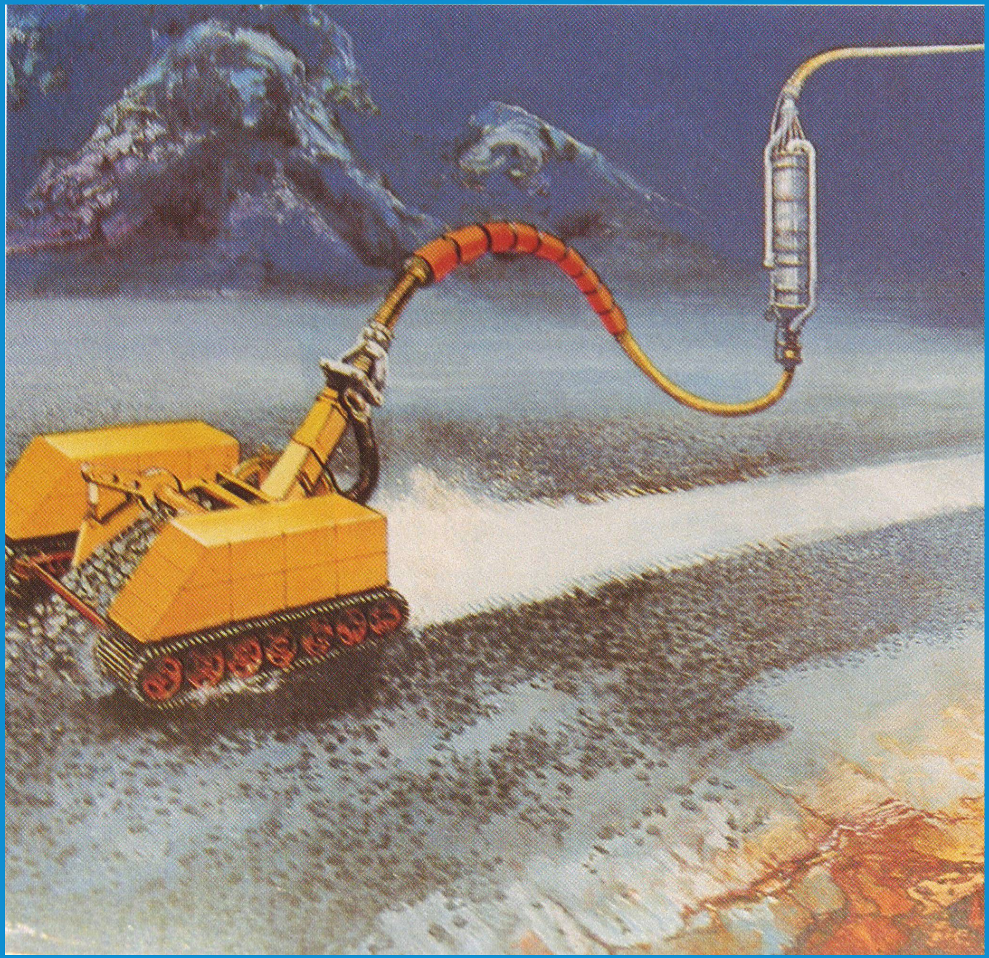
# Unsolved Mystery

How is it that nodules remain at the sediment surface for millions of years without being buried?

»Seismic shaking?

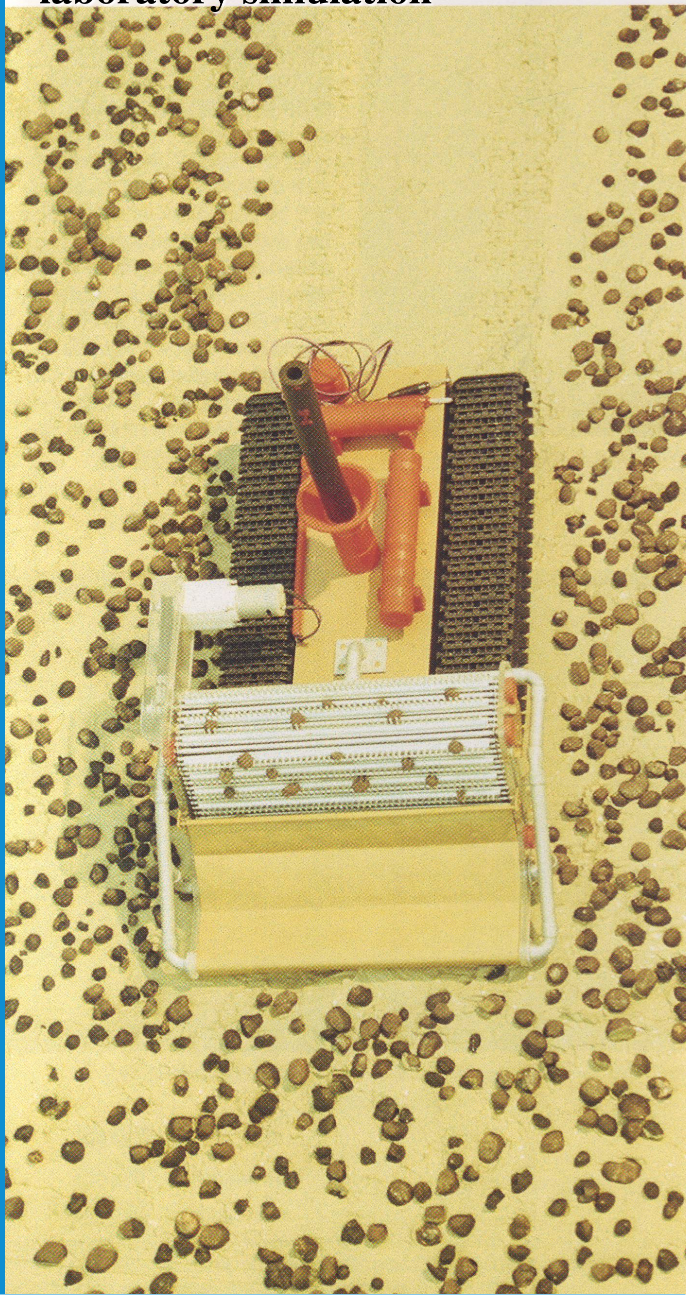
»Collision with animals?

# Mining manganese nodules on the seafloor



System for collecting manganese  nodules, a support stand and a hose connection to the up-flow pipe goes to the transport vessel.  Another pipe goes `from` the vessel bringing particles and waste water back to the deep ocean (**from Andrea Koschinsky**)

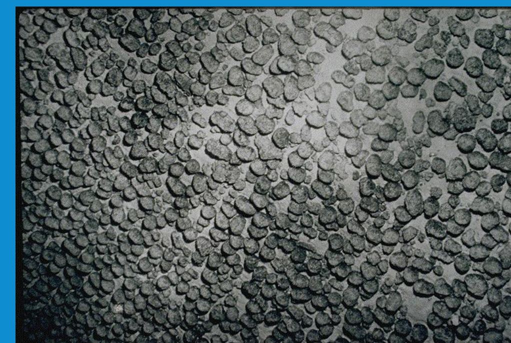
**Model of a collector in a laboratory simulation**



# Deep-Ocean Ferromanganese Deposits

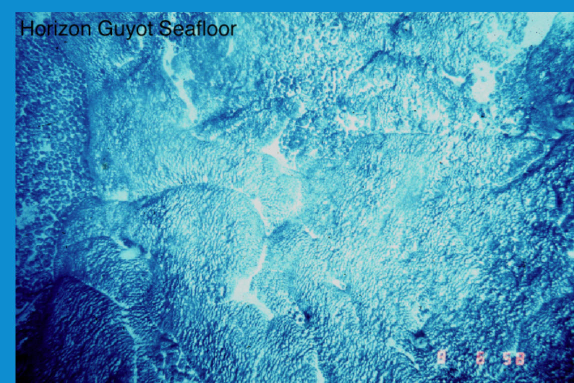
## Manganese nodules

- Form on the vast deep-water abyssal plains



## Ferromanganese crusts

- Form on 50,000 seamounts



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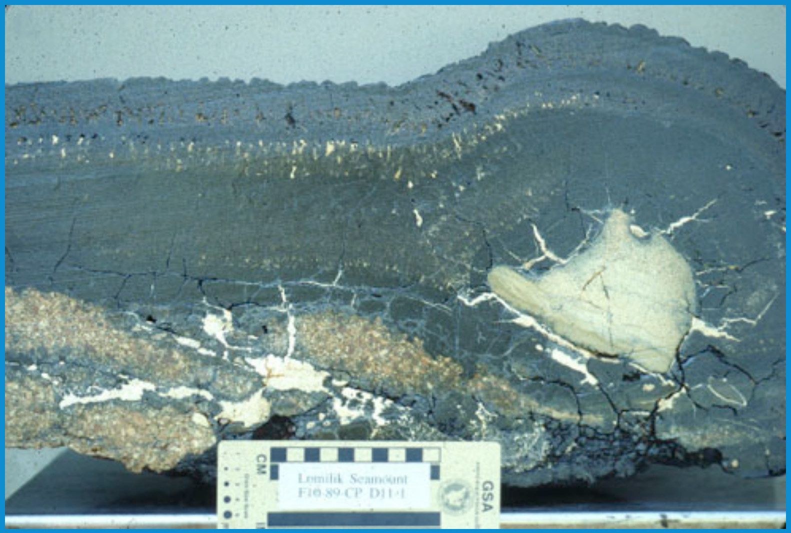
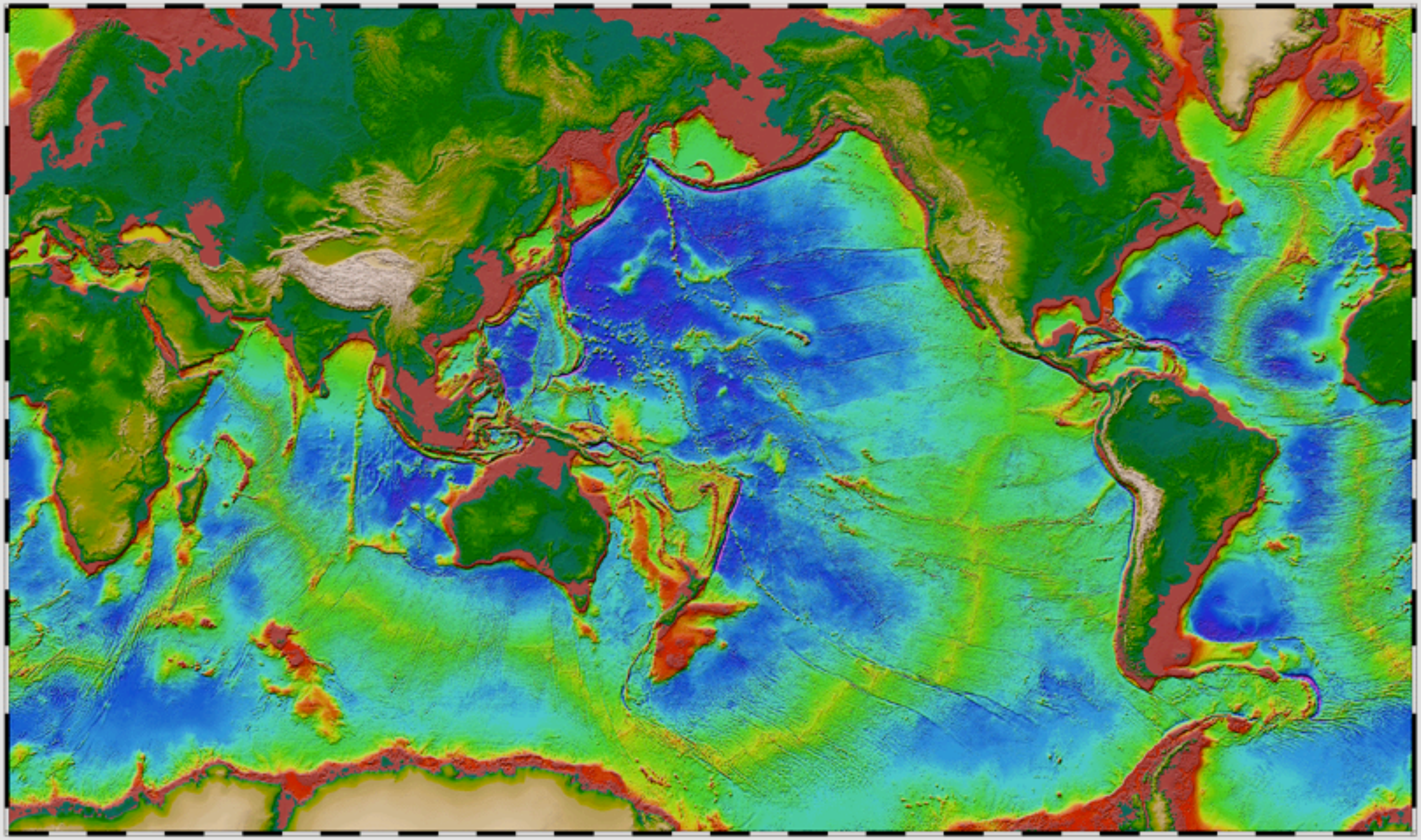
# Ferromanganese Crusts

- Grow on hard-rock surfaces on seamounts and flanks of islands
- Found at water depths of ~400-7000 meters
- Thicknesses range from <1 to ~250 millimeters
- Precipitate from cold ambient bottom water

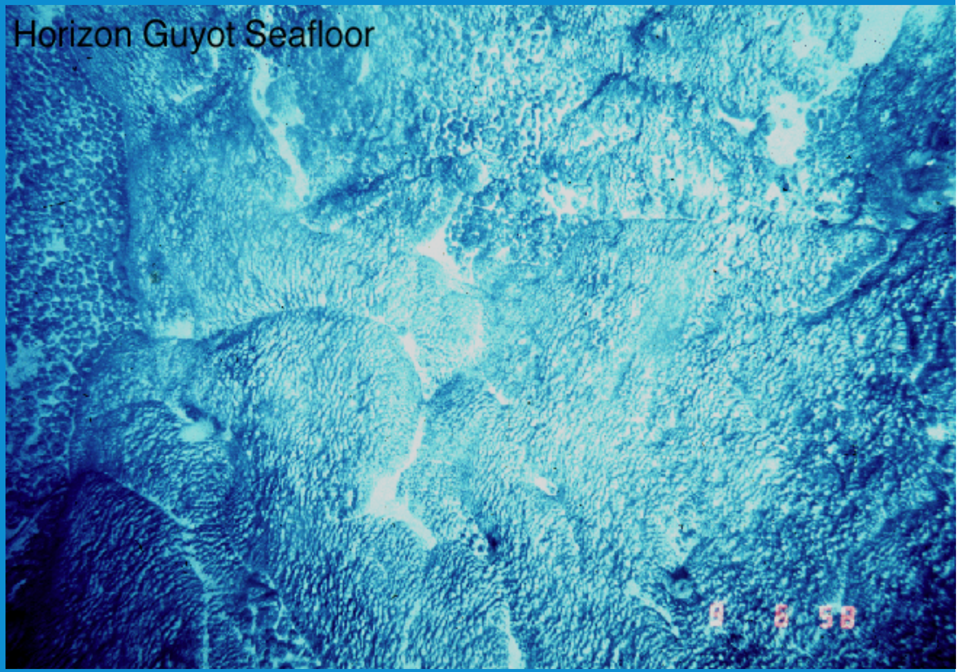


# Distribution of Fe-Mn Crusts



# Distribution of Ferromanganese Crusts

- Arctic to the Antarctic on seamounts, ridges, and plateaus
- Thickest crusts occur between water depths of ~1500-2500 m, the area of the outer rim of seamount summit
- Most cobalt-rich at ~800-2200 m water depth, in and just below oxygen-minimum zone (OMZ)



# Mining Scenario: Rationale for seamount selection parameters

- Mining operations will take place around the summit region of guyots on flat or shallowly inclined surfaces: summit platforms, terraces, and saddles
  - These are the areas with the thickest and most cobalt-rich crusts
    - Much thinner crusts occur on steep slopes
  - Conical seamounts are too small, with rugged summits

- Seamount summits will not be much deeper than about 2,200 m; terraces will not be deeper than about 2,500 m
  - Slopes are more rugged below 2,500 m
  - Crusts are thinner below 2,500 m
  - The contents of Co, Ni, Cu, etc. in crusts are less below 2,500 m

- Little or no sediment will occur on the summit platform, therefore, a region of strong and persistent bottom currents

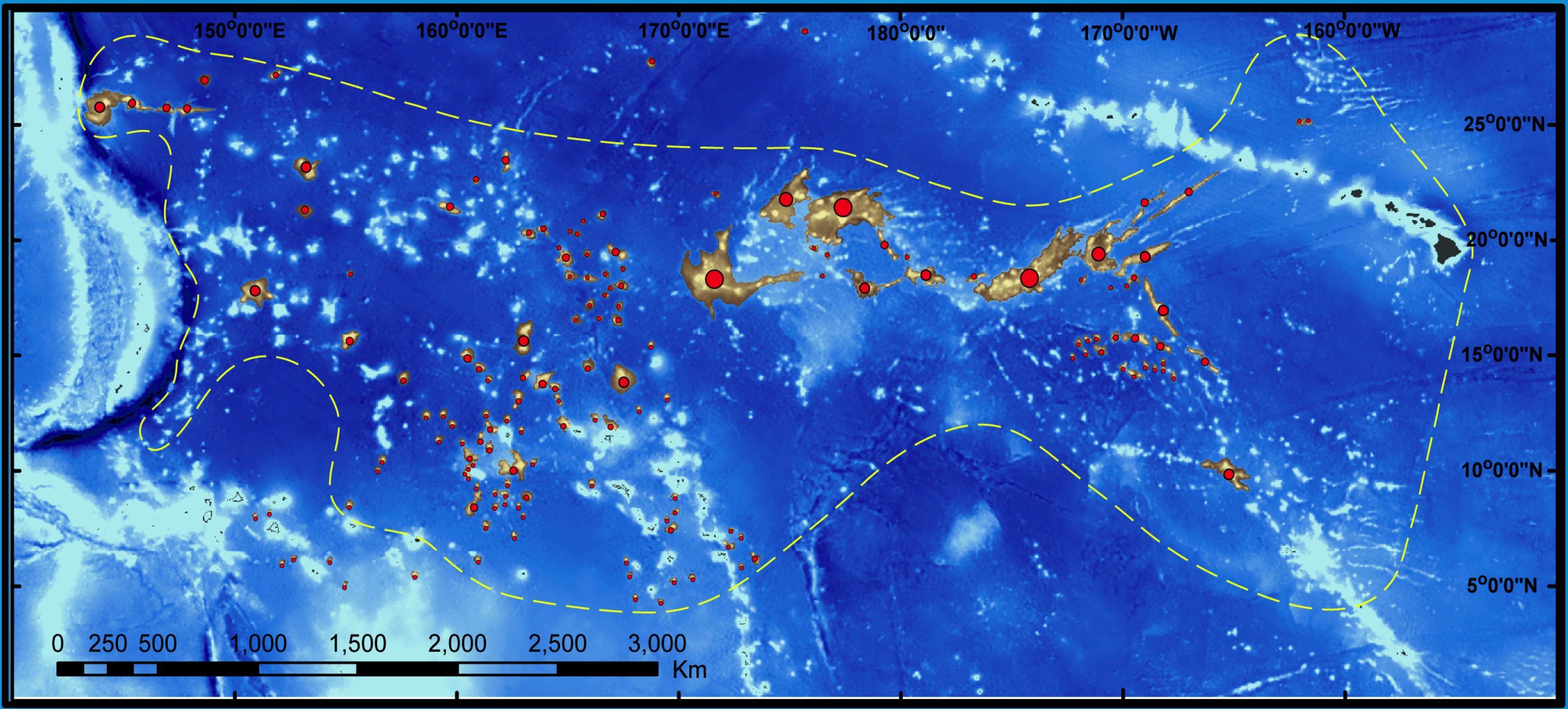
**(From Hein et al., 2009)**

# Rationale (continued)

- The summit region above 2,500 m will be large, more than 400 $km^2$
  - Yields fewest seamounts needed to be mined
- The submarine flanks of islands and atolls will not be considered for mining
- Clusters of large seamounts will be favored
- The seamounts will be old, of Cretaceous age
  - Crust thickness, slope stability, guyots with large summit areas
- Seamounts with thick crusts and high grades (Co, Ni, Cu, etc.)
- The central Pacific best fulfills all these criteria

(From Hein et al., 2009)

# Map of most permissive area in global ocean




Location of seamounts, guyots, ridges, & plateaus used for surface area measurements; brown areas were measured & are marked by red circles indicating relative sizes; dashed line encloses largest region in global ocean with permissive conditions for development of thick Fe-Mn crusts

(From Hein et al., 2009)

# Average size of random set of equatorial Pacific seamounts, guyots, ridges, and plateaus

(n=155; n=52 for guyots)

| | *Surface Area All Edifices ($km^2$)* | *Surface Area of Guyots ($km^2$)* | *Surface Area of Guyots above 2,500 m water depth ($km^2$)* |
|---|---|---|---|
| **Mean** | 3,389 | 3,495 | 1,152 |
| **Median** | 1,553 | 2,905 | 832 |
| **Minimum** | 233 | 590 | 0 |
| **Maximum** | 35,519 | 11,761 | 4,088 |

**(From Hein et al., 2009)**

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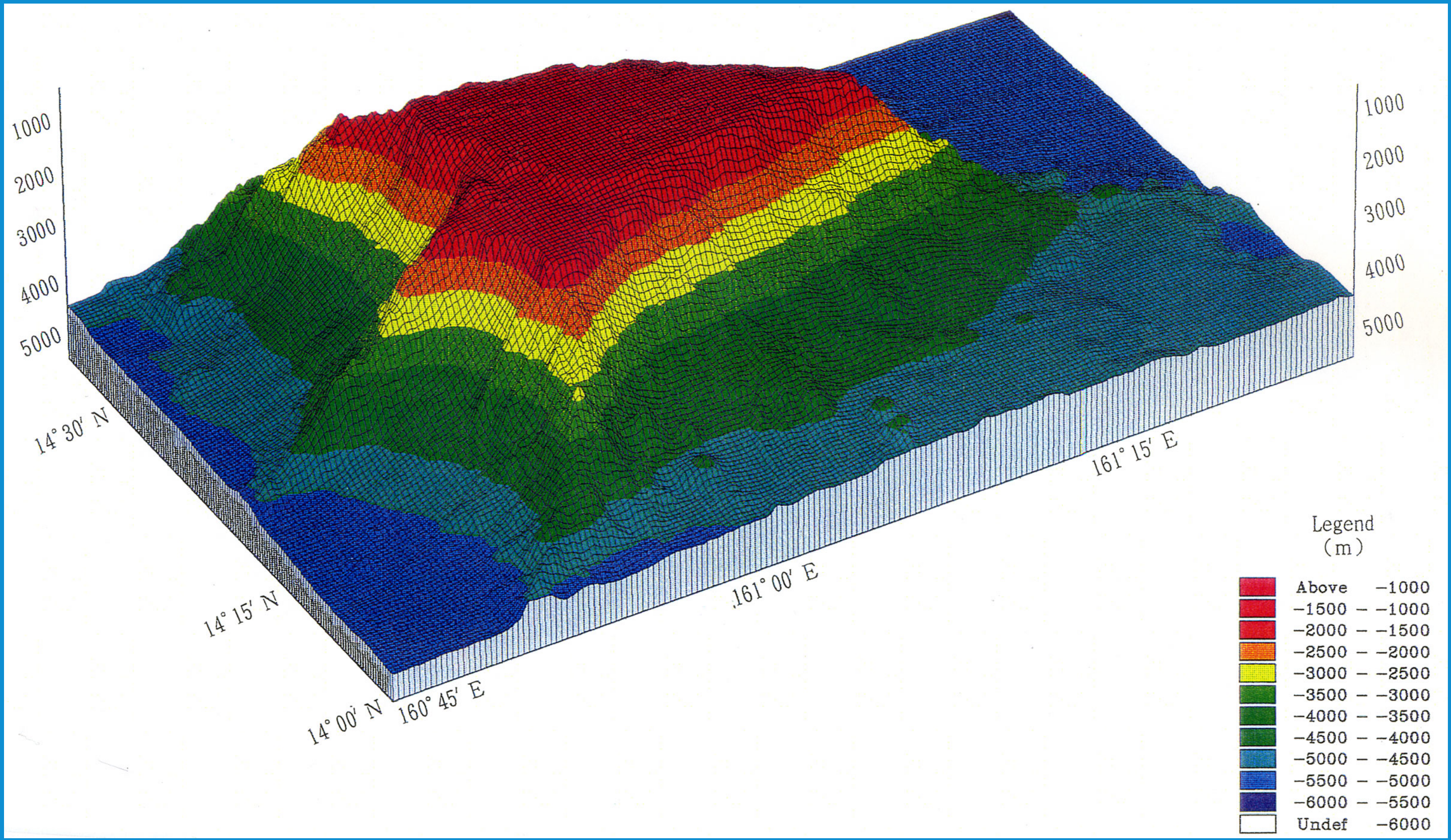
# Typical Guyot

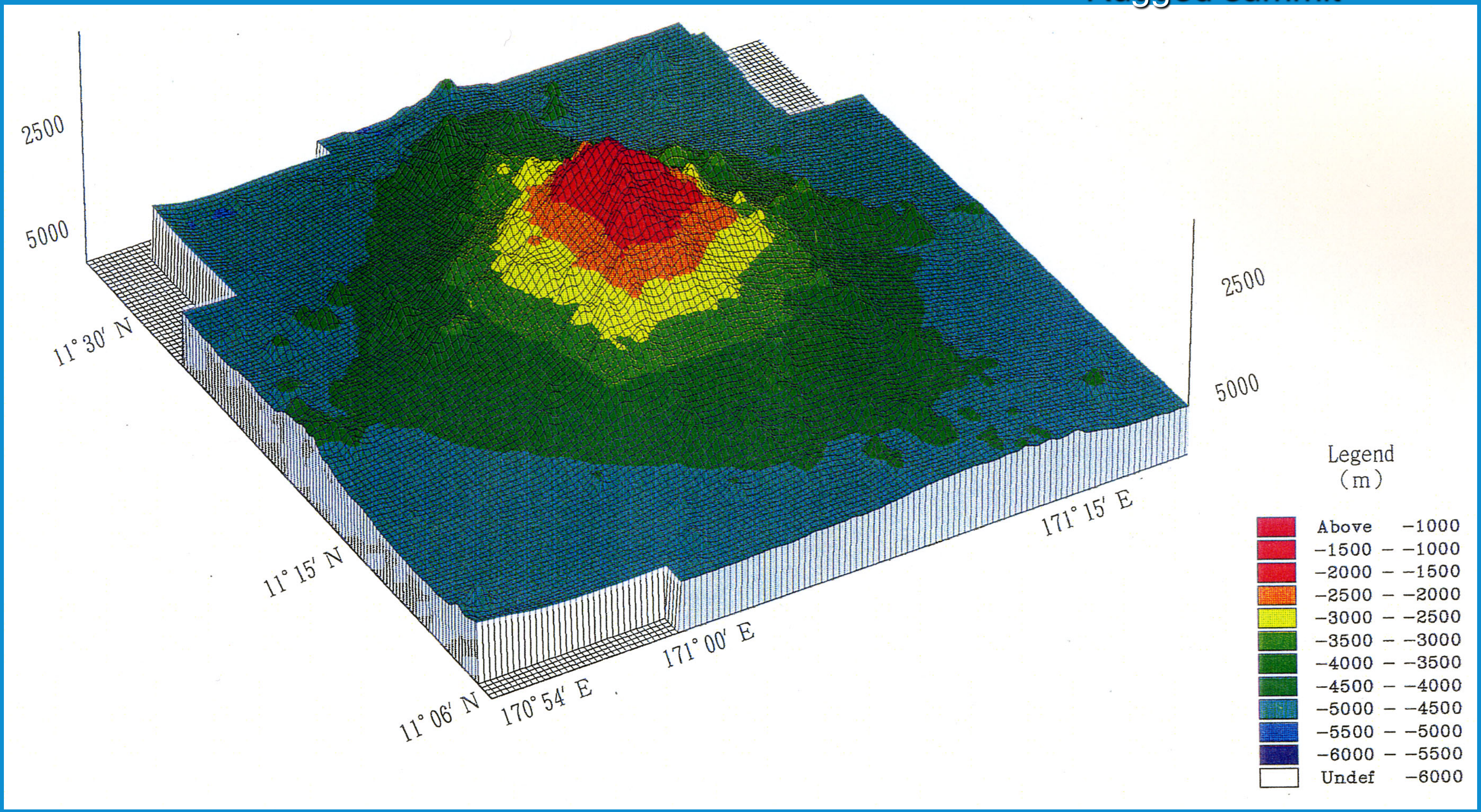
56 kilometers long
Terraces-smooth and rough
Large area above 2500 m
Debris apron




JAMSTEC

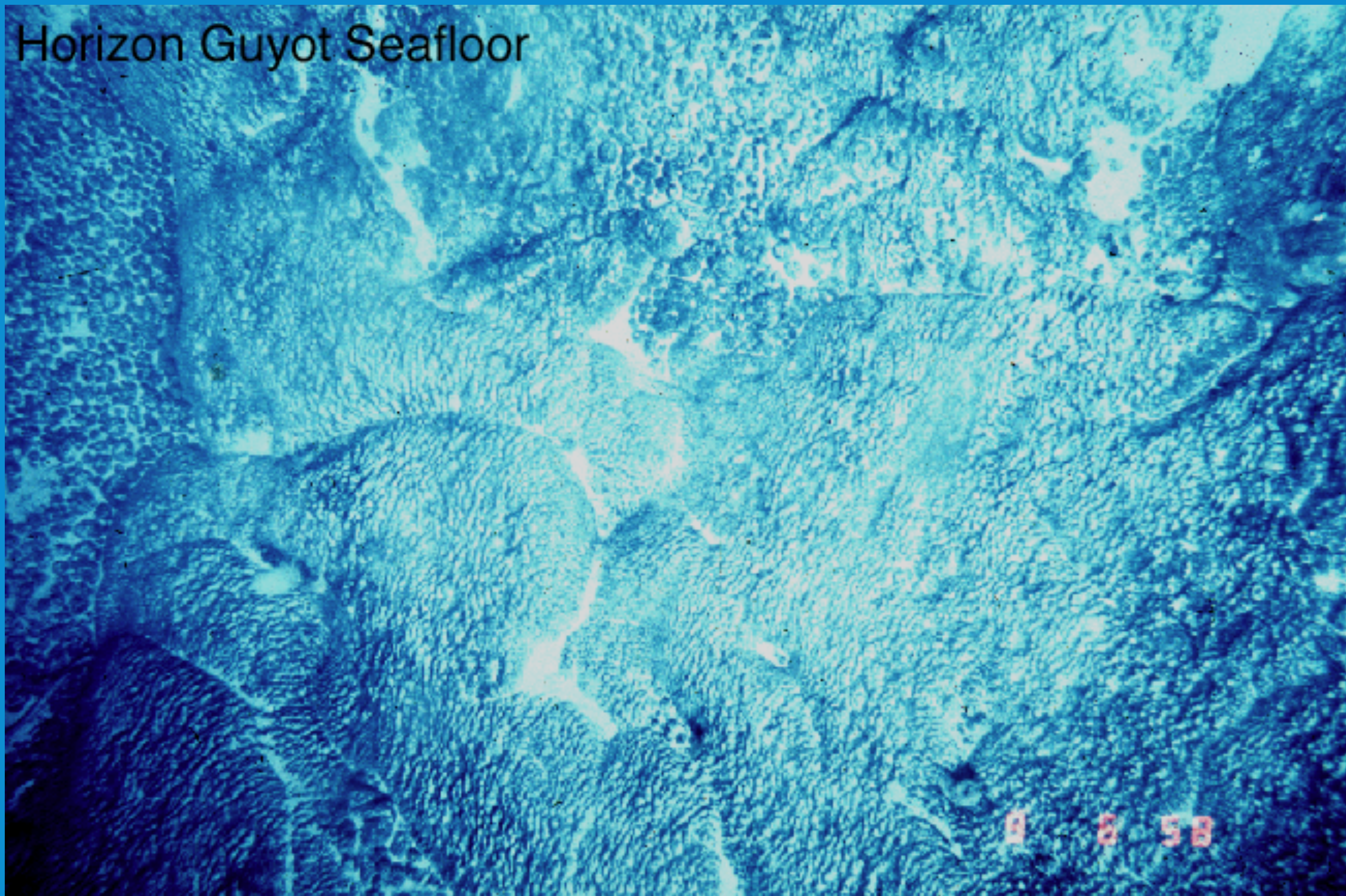
# Typical Conical Seamount

14° slopes
Small area above 2500 m
Rugged summit

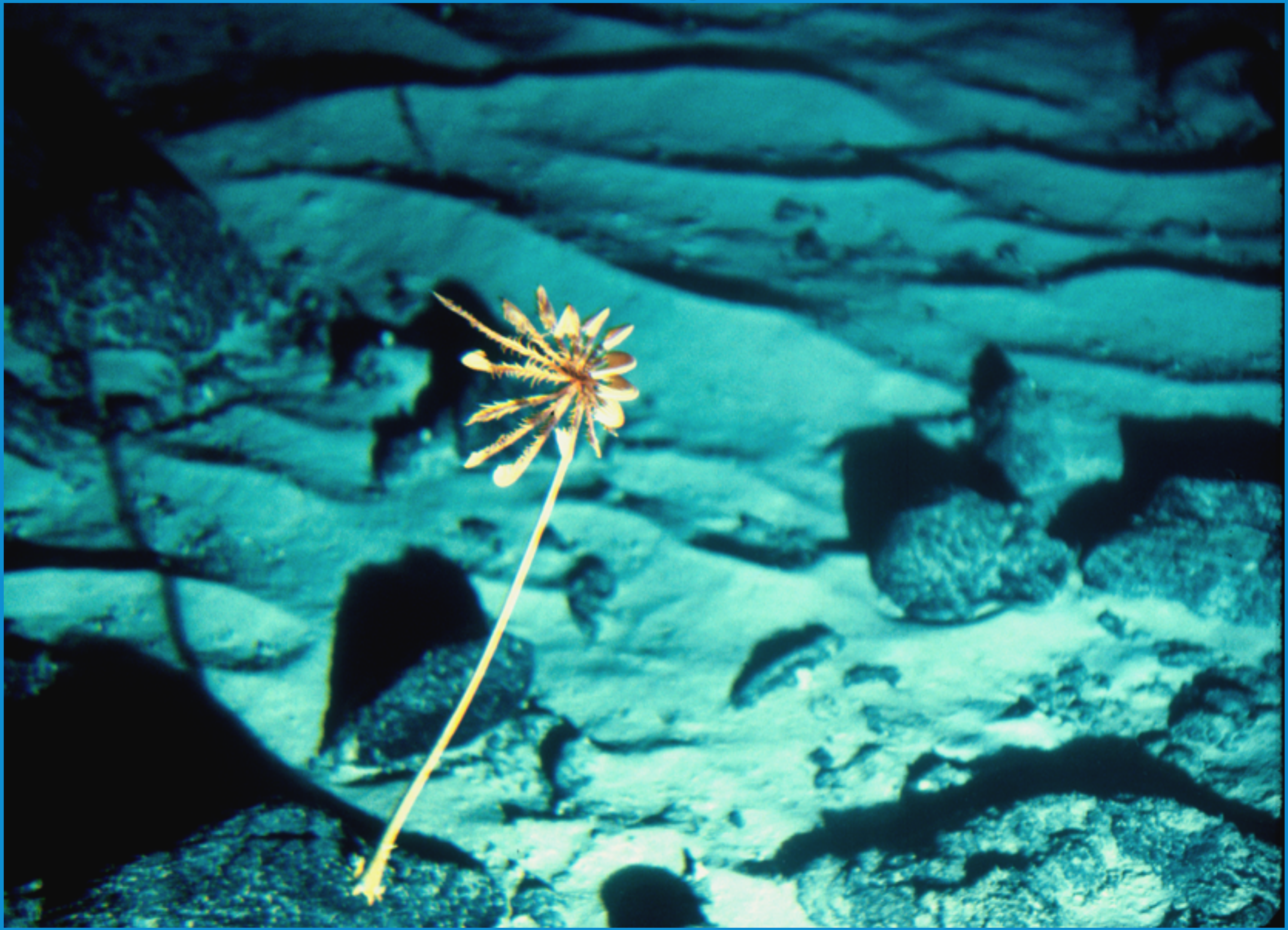



JAMStEC

# Fe-Mn pavement at 2000 m water depth



# Sediment fills lows between Fe-Mn crust Outcrops at 2000 m



# Types of seamount-generated currents

- Anticyclonic currents (Taylor Column)
- Internal Waves
- Trapped Waves
- Vertically propagating vortex-trapped waves
- Taylor Caps
- Attached counter-rotating mesoscale eddies
- Many others

Results In:

- Turbulent Mixing and upwelling
- Erosion and sediment movement

Controlled by:

- Seamount height
- Summit size
- Types of ambient currents
- Energy of tidal flow

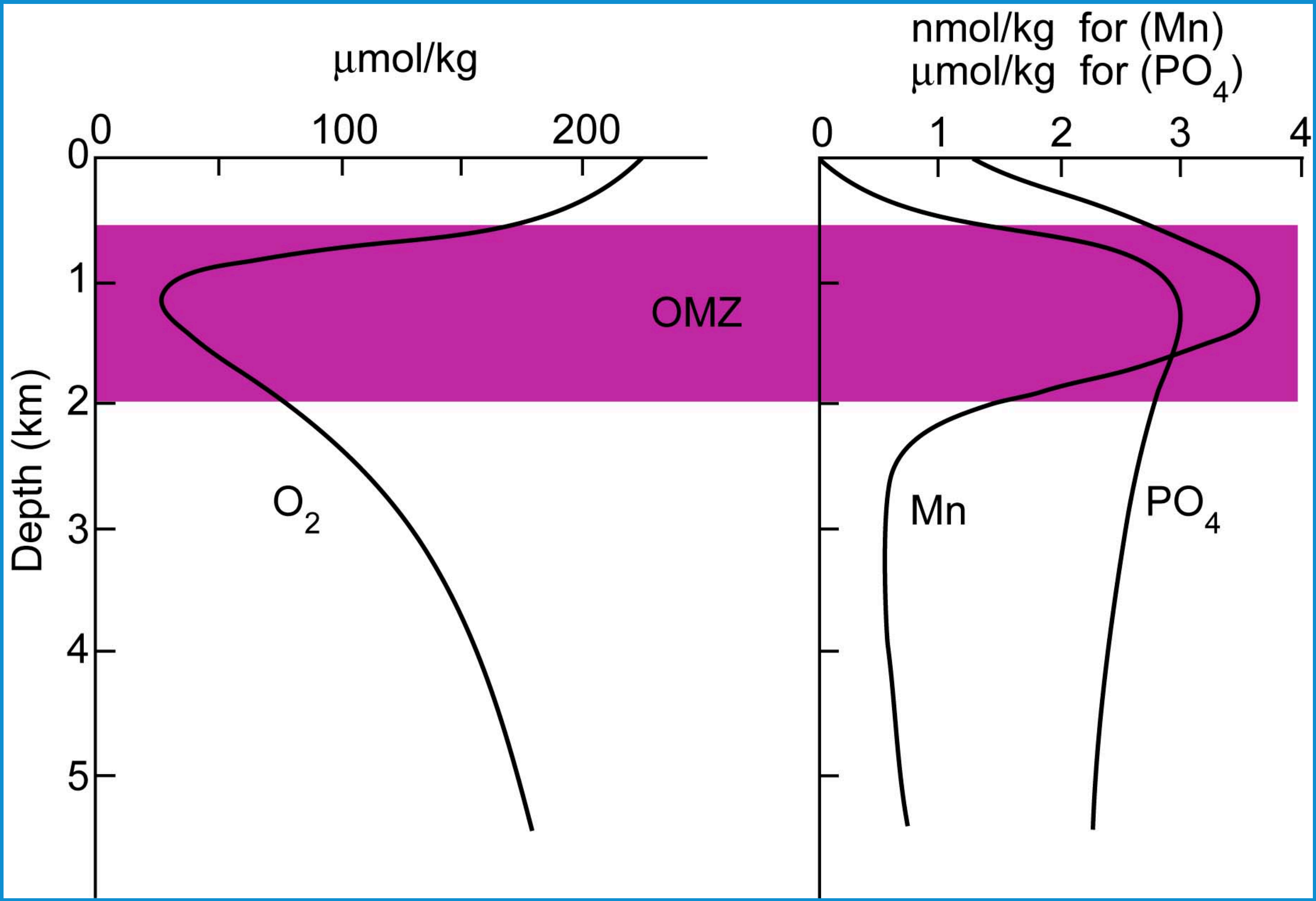
# Seamount Biology

- Different communities occur on adjacent seamounts at the same water depth
- Sediment-hosted versus rock-hosted organisms
- Low density and low diversity populations beneath OMZ where crusts are thick and cobalt-rich
- High-energy summit margins can inhibit biological activity, but can also enhance some groups, such as corals & sponges
- Bacteria may promote uptake of metals in crusts
- Density and diversity are controlled by current patterns, topography, bottom substrate, seamount size, water depth, and size of OMZ, which is related to primary productivity

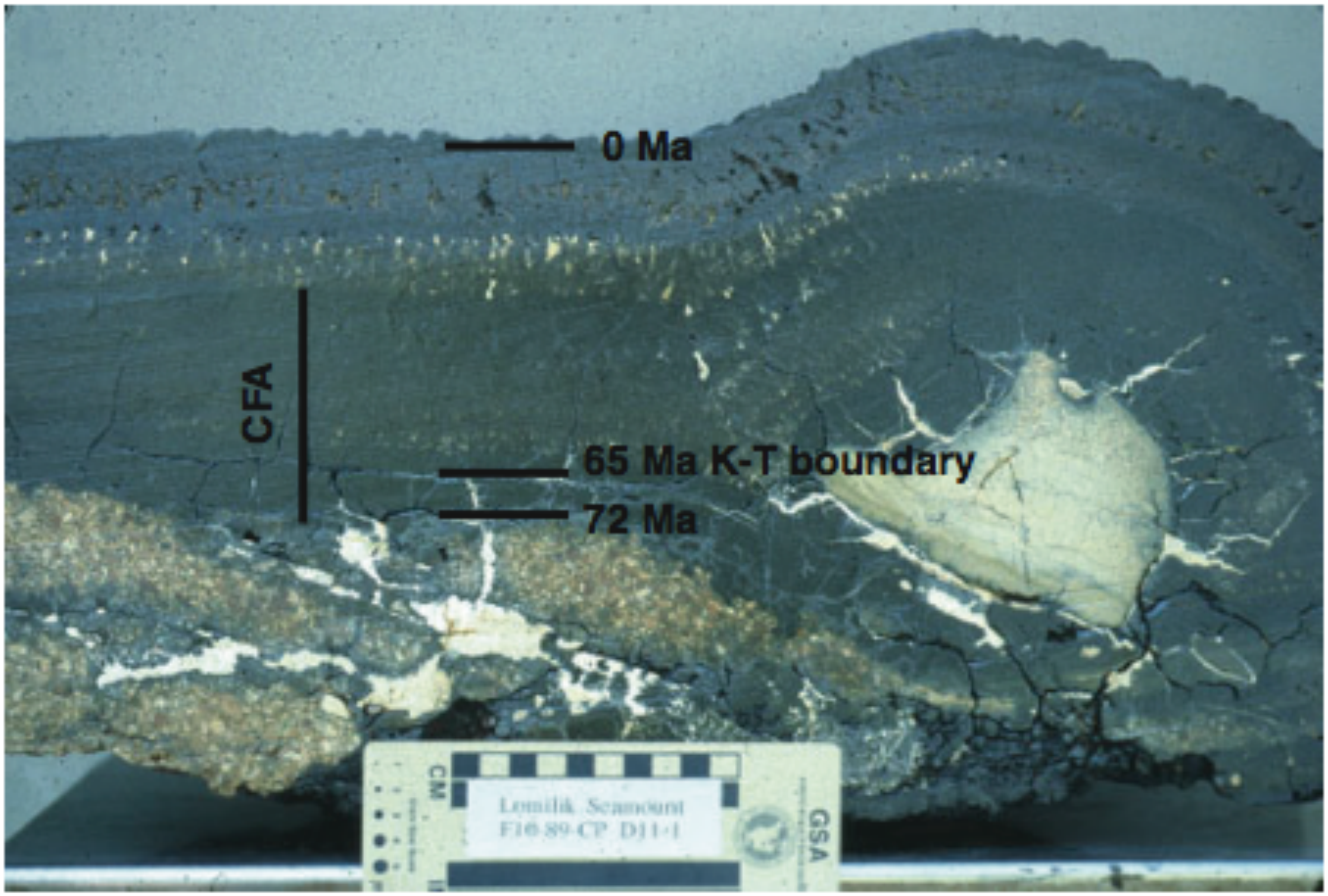
# Potential causes of high variability in colonization patterns

- Circulation that traps larvae and diminishes spread to other seamounts
- Abbreviated larval stage that remains near bottom
- Varying ages and stability of volcanoes
- Varying environmental conditions

# Seawater Profiles for $O_2$, Mn, and $PO_4$



18 cm-thick Fe-Mn crust began growing 72 Ma ago, Marshall Is.



# Fe-Mn Crust Mineralogy

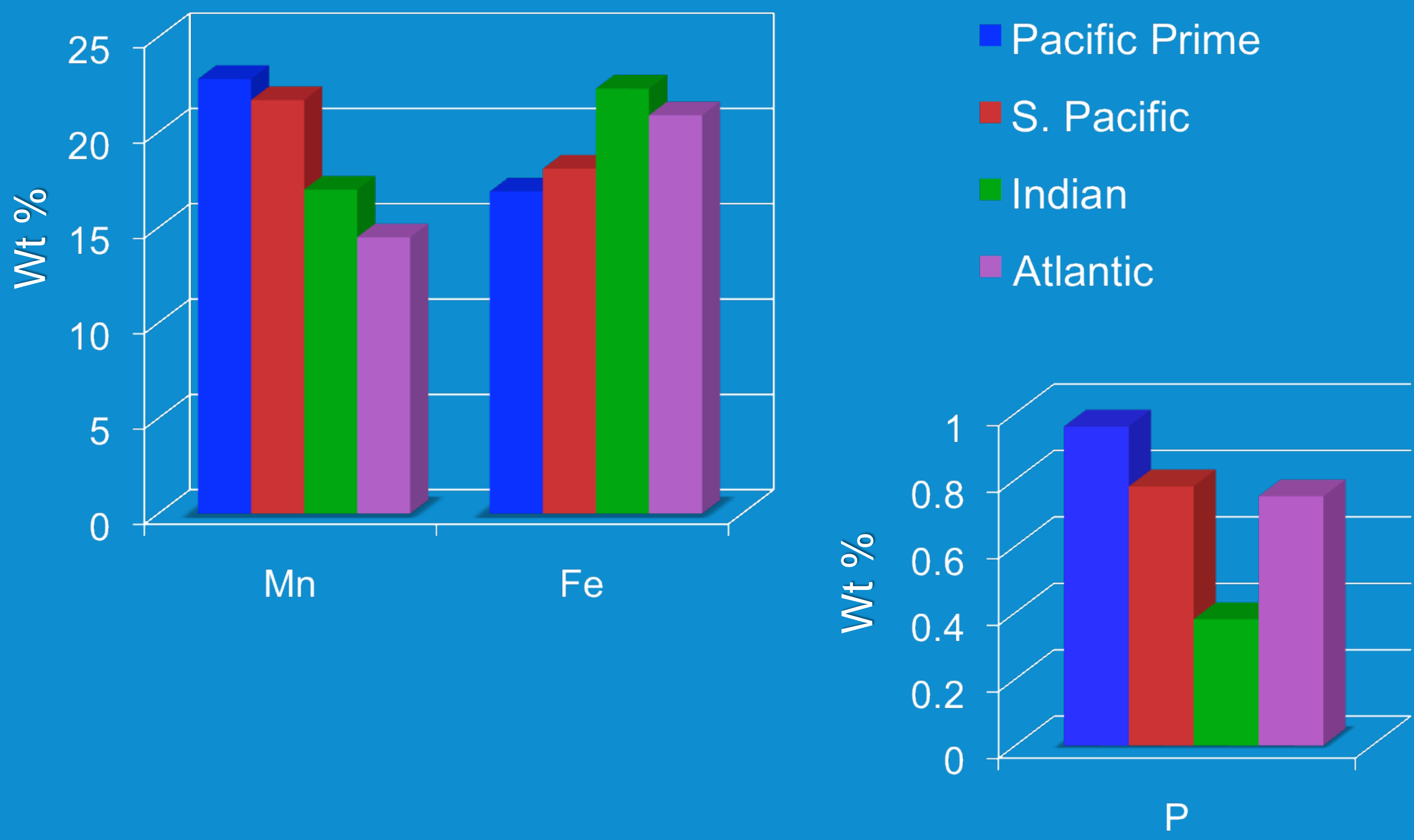
- $\delta$-$MnO_2$ (vernadite; turbostratically disordered hexagonal birnessite)
- X-ray amorphous Fe oxyhydroxide (feroxyhyte)
- Carbonate fluorapatite (CFA)
- Minor detrital/eolian silica & aluminosilicates
- Minor biogenic debris: opal and calcite

# Important Properties of Fe-Mn crusts

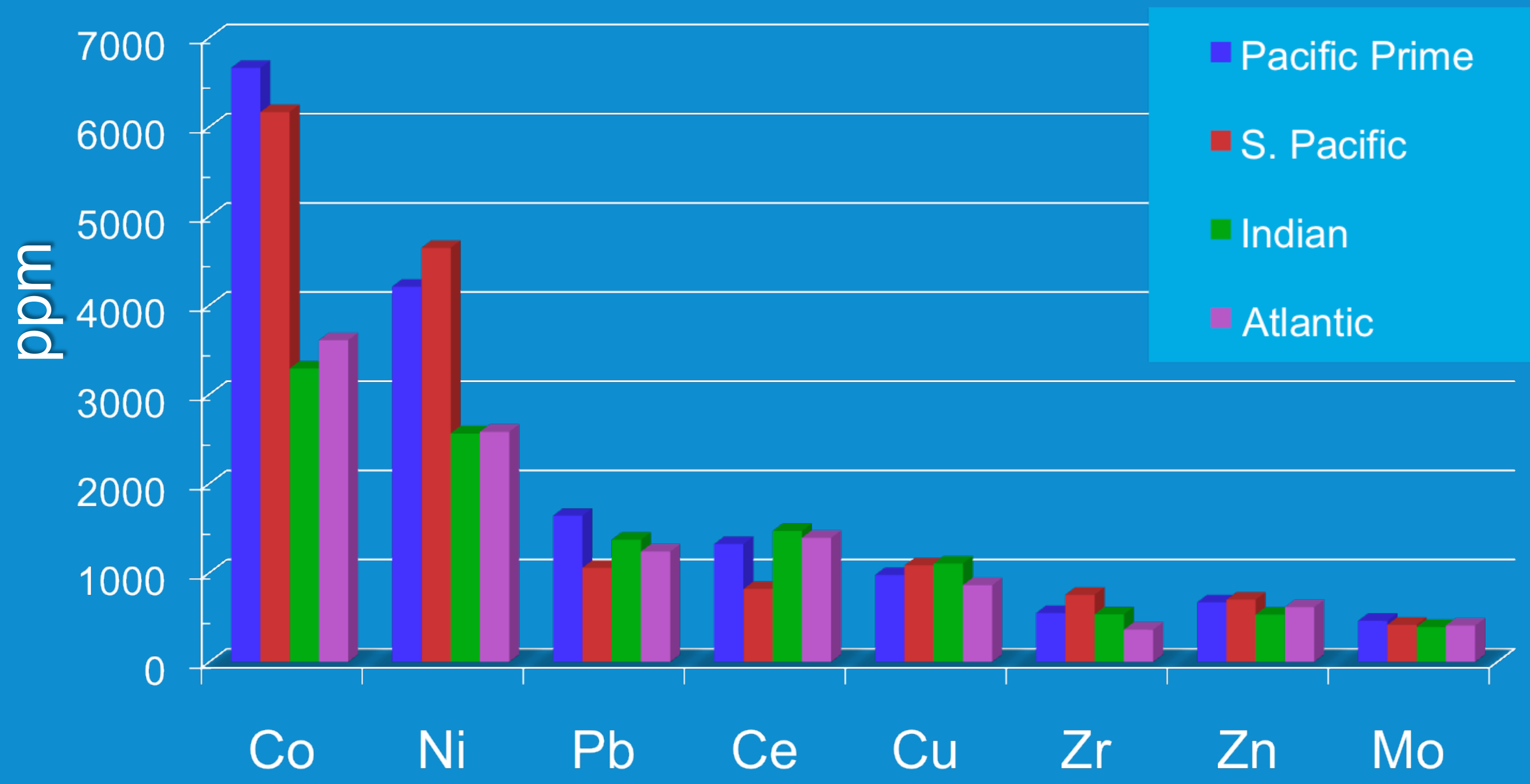
- Very high porosity (60%)
- Extremely high specific surface area (mean 325 $m^2/g$)
- Incredibly slow rates of growth (1-5 mm/Ma)


** These properties are instrumental in allowing for surface adsorption of large quantities of metals from seawater*

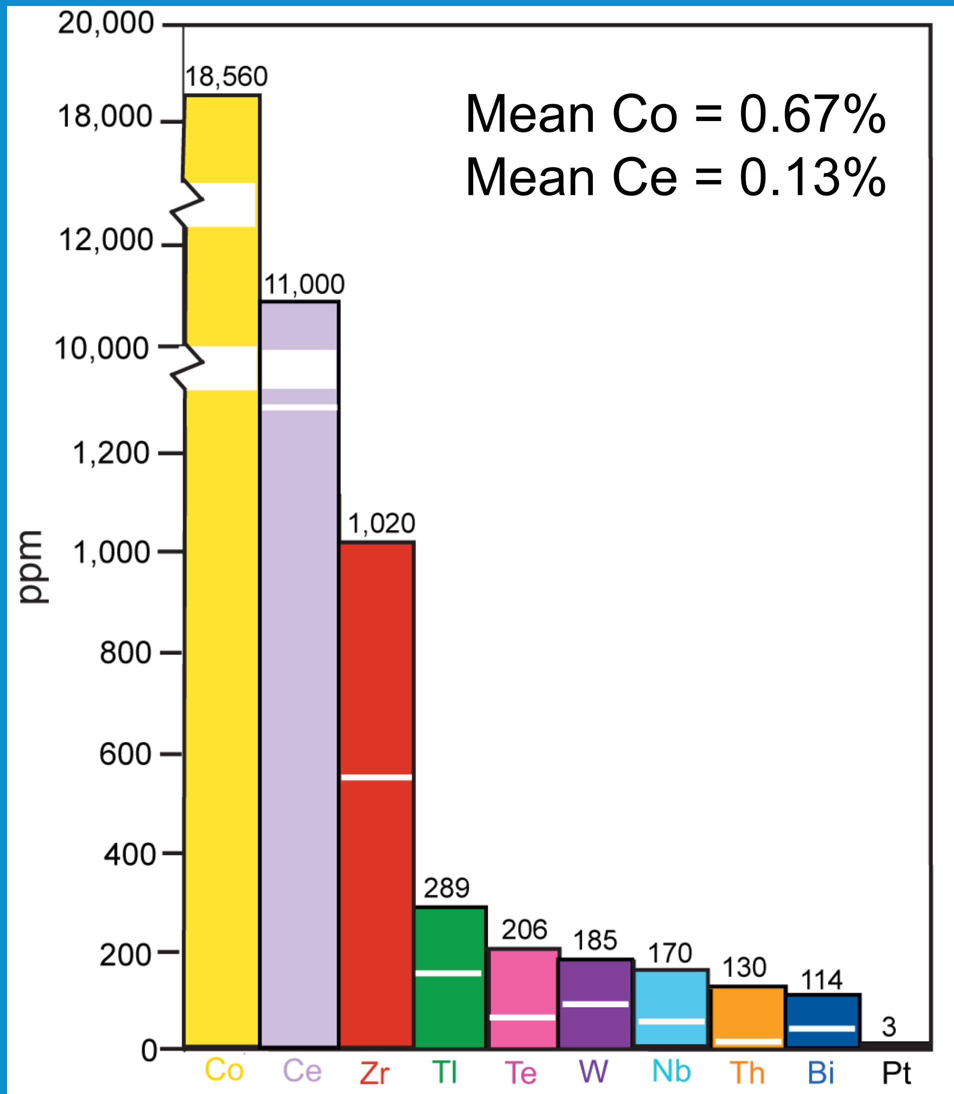
# Crusts in the Global Ocean



# Crusts in the Global Ocean Continued

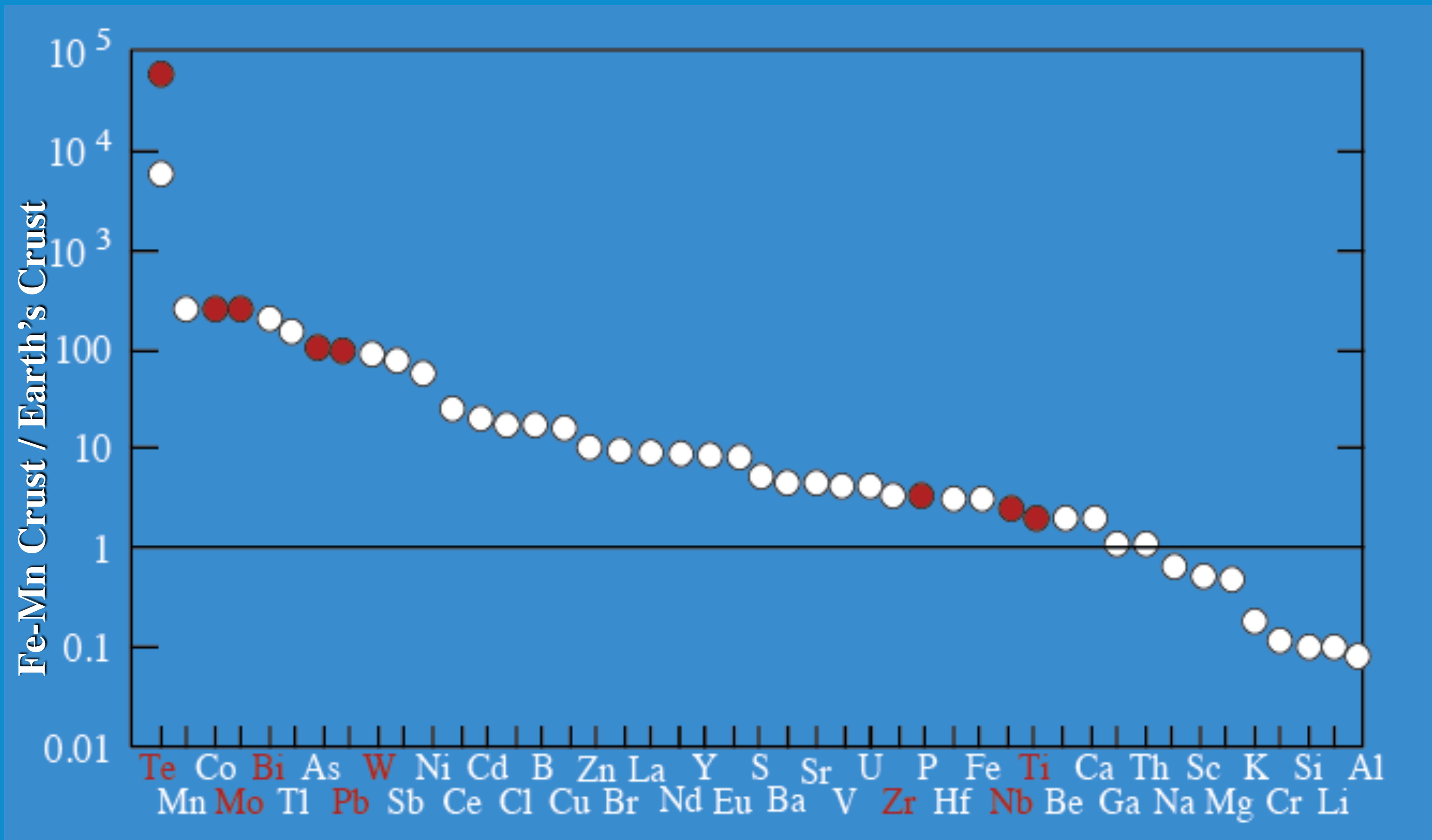


# Trace Metal Maxima




From Hein et al., 2010

# Element Enrichment in Fe-Mn Crusts Relative to the Earth's Upper Crust

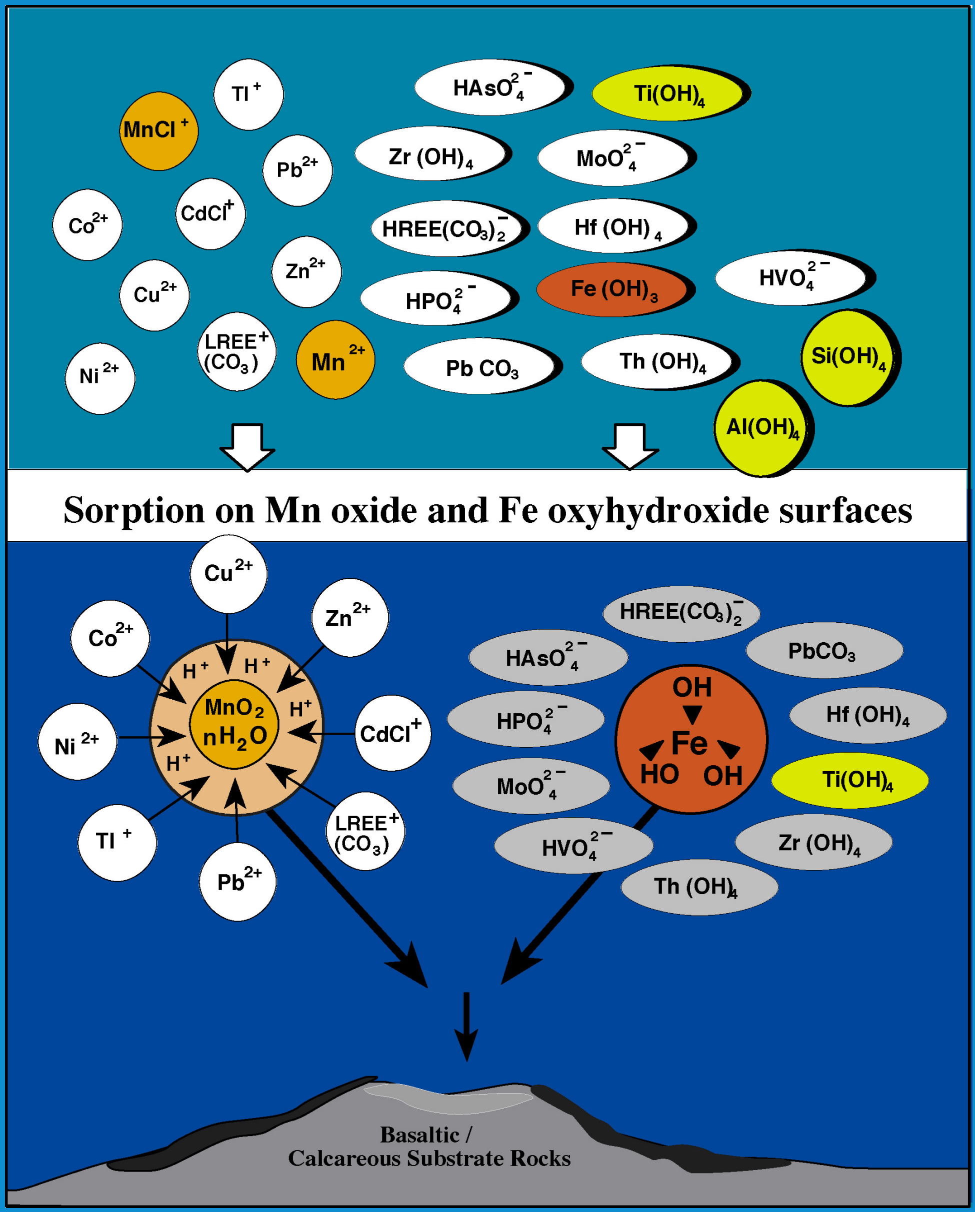



From Hein et al., 2010

# How Do Ferromanganese Crusts Form?

Simplified electrochemical model for the formation of Fe-Mn crusts by adsorption of metals onto colloidal Mn oxide and Fe oxyhydroxide

(From Koschinsky and Halbach, 1995; Koschinsky and Hein, 2003)



# SURFACE OXIDATION

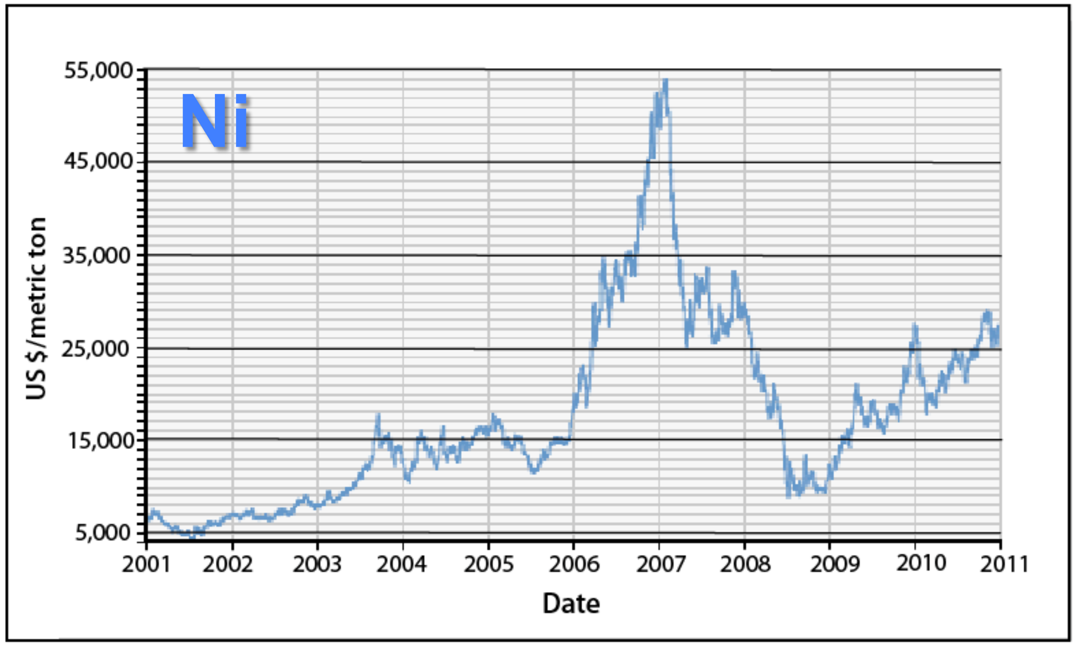
| Oxidation | | | Substrate |
|---|---|---|---|
| $Co^{2+}$ | $\rightarrow$ | $Co^{3+}$ | |
| $Ce^{3+}$ | $\rightarrow$ | $Ce^{4+}$ | $MnO_2$ |
| $Tl^{+}$ | $\rightarrow$ | $Tl^{3+}$ | |
| $Te^{4+}$ | $\rightarrow$ | $Te^{6+}$ | FeOOH |
| $Pt^{2+}$ | $\rightarrow$ | $Pt^{4+}$ | |

To verify:

XANES: X-ray absorption near edge structure spectroscopy
EXAFS: Extended X-ray absorption fine structure spectroscopy

# Ten Year Price Graphs from LME





# Value of Metals in 1 Metric Ton of Fe-Mn Crust from Central-Equatorial Pacific (2008)

| | Mean Price of Metal (2008 $/kg) | Mean Content in Crusts (g/ton) | Value per Metric Ton of Ore ($) |
|---|---|---|---|
| Cobalt | $92.59 | 6899 | $638.81 |
| Cerium | $125.00 | 1605 | $200.63 |
| Titanium | $8.70 | 12035 | $104.70 |
| Nickel | $20.74 | 4125 | $85.55 |
| Molybdenum | $74.96 | 445 | $33.36 |
| Platinum | $64,795.28 | 0.5 | $32.40 |
| Tellurium | $350.00 | 60 | $21.00 |
| Zirconium | $25.30 | 618 | $15.64 |
| Copper | $8.48 | 896 | $7.59 |
| Tungsten | $25.40 | 90.5 | $2.30 |
| Total | -- | -- | $1,141.98 |

## *Ferromanganese crusts provide the richest source of tellurium known* (Hein et al. 2003)

*"Finding enough Te for CdTe is the largest barrier to the multi-terawatt use of CdTe for solar-cell electricity. It is widely regarded as the lowest cost photovoltaic technology with the greatest potential. This is important to the US and the world"*

(Ken Zweibel, National Renewable Energy Laboratory)

| | Import/ Export | | Main Uses | Emerging & Next Generation Technologies |
|---|---|---|---|---|
| Te | 9 | | Steel, Cu, & Pb alloys, pigment | Photovoltaic solar cells; computer chips; thermal cooling devices |
| Co | 4 | | Steel superalloys (e.g. jet engines), batteries, chemical applications | Hybrid & electric car batteries, storage of solar energy, magnetic recording media, high-T super-alloys, supermagnets, cell phones |
| Bi | 6 | | Metallurical additives, fusible alloys, pharmaceuticals & chemicals | Liquid Pb-Bi coolant for nuclear reactors; Bi-metal polymer bullets, high-T superconduct, computer chips |
| W | 3 | | Wear-resistent materials, superalloys, electrical, chemicals | Negative thermal expansion devices, high-T superalloys, X-ray photo imaging |
| Nb | 18 | | Steel & superalloys | High-T superalloys, next generation capacitors, superconducting resonators |
| Pt | 7 | | Catalytic converters, liquid-crystal & flat-panel displays, jewelry, electronics, | Hydrogen fuel cells, chemical sensors, cancer drugs, electronics |

**(From Hein et al., 20100**

# Challenges to Fe-Mn Crust Mining

- The largest impediment to exploration for Fe-Mn crusts is the real-time measurement of crust thicknesses with a deep-towed instrument

- The largest physical impediment to ore recovery is separation of Fe-Mn crusts from substrate rock that occurs on an uneven and rough seabed


Thank You