Ferromanganese Crusts

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Limited Sources of Many Critical Metals

China is The Leading Producer of 30 Strategic And Critical Metals

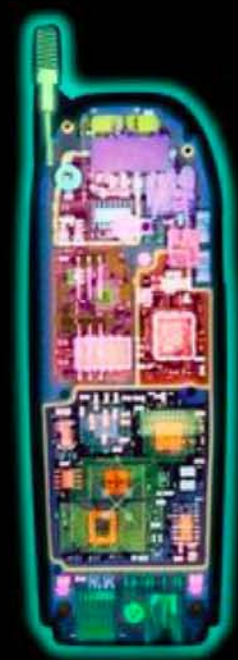
Leading Global Metal Producers, with China highlighted

Element	Leading Producer	2nd Producer	3rd Producer
Aluminum	Australia (31%)	China (18%)	Brazil (14%)
Arsenic	China (47%)	Chile (21%)	Morocco (13%)
Cadmium	China (23%)	Korea (12%)	Kazakhstan (11%)
Chromium	South Africa (42%)	India (17%)	Kazakhstan (16%)
Cobalt	Congo (40%)	Australia (10%)	China (10%)
Copper	Chile (34%)	Peru (8%)	USA (8%)
Gallium	China	Germany	Kazakhstan
Germanium	China (71%)	Russia (4%)	USA (3%)
Gold	China (13%)	Australia (9%)	USA (9%)
Helium	USA (63%)	Algeria (19%)	Qatar (12%)
Indium	China (50%)	Korea (14%)	Japan (10%)
Iron	China (39%)	Brazil (17%)	Australia (16%)
Lead	China (43%)	Australia (13%)	USA (10%)
Lithium	Chile (41%)	Australia (24%)	China (13%)
Manganese	China (25%)	Australia (17%)	South Africa (14%)
Molybdenum	China (39%)	USA (25%)	Chile (16%)
Nickel	Russia (19%)	Indonesia (13%)	Canada (13%)
Niobium	Brazil (92%)	Canada (7%)	--
Palladium	Russia (41%)	South Africa (41%)	USA (6%)
Platinum	South Africa (79%)	Russia (11%)	Zimbabwe (3%)
Rare Earths	China (97%)	India (2%)	Brazil (1%)
Selenium	Japan (50%)	Belgium (13%)	Canada (10%)
Silver	Peru (18%)	China (14%)	Mexico (12%)
Tellurium	Chile	USA	Peru
Tin	China (37%)	Indonesia (33%)	Peru (12%)
Uranium	Canada (21%)	Kazakhstan (19%)	Australia (19%)
Vanadium	China (37%)	South Africa (35%)	Russia (26%)
Zinc	China (25%)	Peru (13%)	Australia (12%)

(Data from J.G. Price, SEG Newsletter, 82, July 2010; as presented by Hein et al., 2013)

25% of a Mobile Phone is Metal

~1.5 Billion Cell Phones
sold in 2010



60 kg Tantalum
510 kg Platinum

22.5 tons Palladium
51.0 tons Gold
525 tons Silver
24,000 tons Copper

Plus many others e.g. REEs

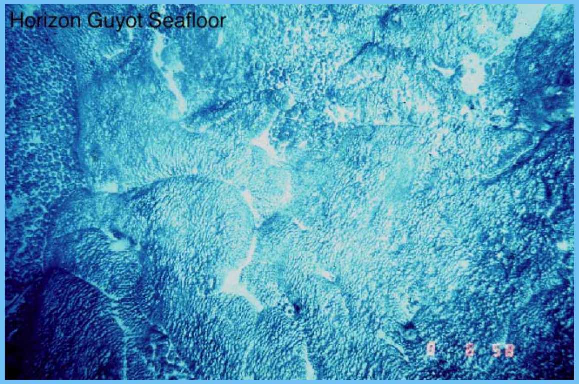
There will be only 20 years supply of tantalum if the global per capita use rises to 50% of the current U.S. per capita use; 40 years for copper

Modified from Hein et al. (2013)

Deep-ocean mineral deposits

Manganese nodules

Form on the vast deep-water abyssal plains



Ferromanganese crusts

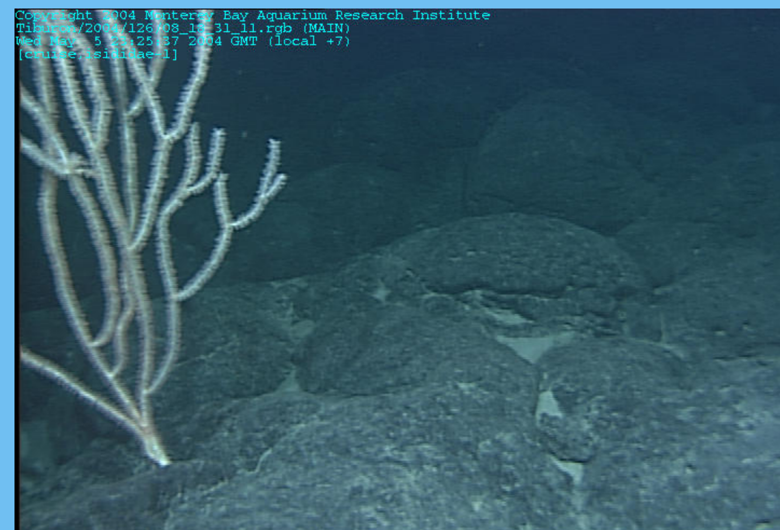
Form on 100,000 seamounts

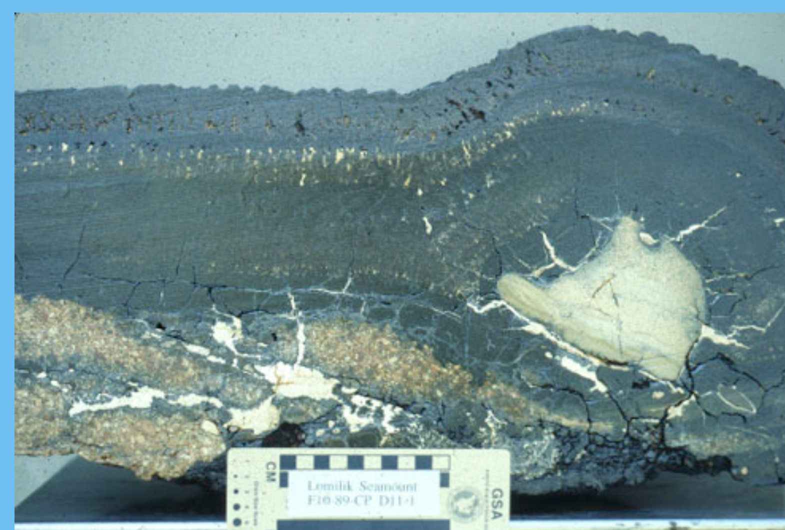
Seafloor massive sulfides

Form at hydrothermal vents along 89,000 km of ridges

Ferromanganese Crusts

- Grow on hard-rock surfaces on seamounts, ridges, and plateaus
- Found at water depths of ~400-7,000 meters
- Thicknesses range from <1 to ~260 millimeters
- Precipitate from cold ambient bottom water



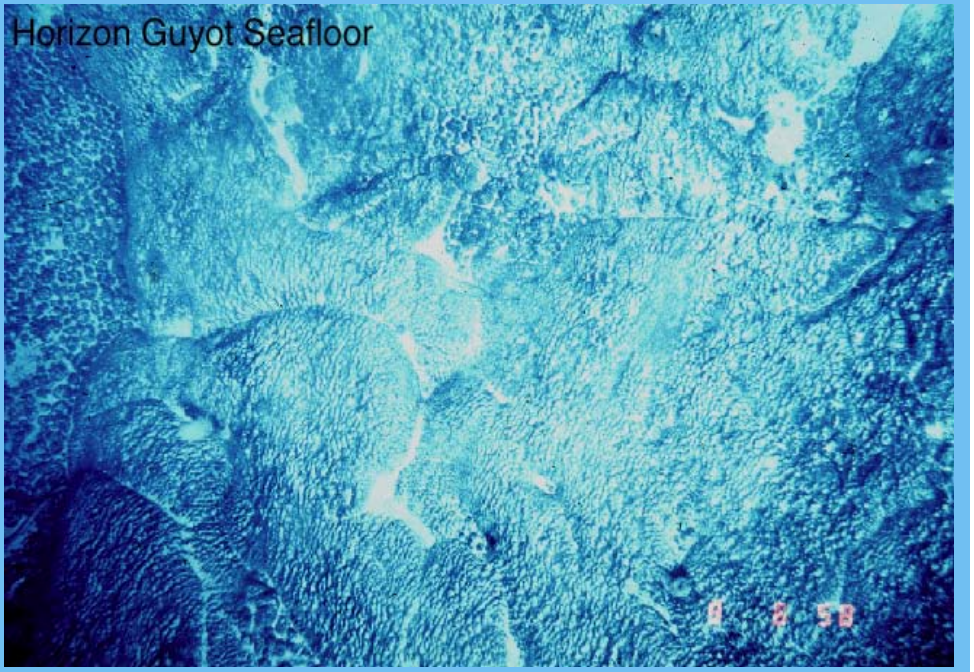


Distribution of Ferromanganese Crusts

- Arctic to Antarctic on seamounts, ridges, and plateaus

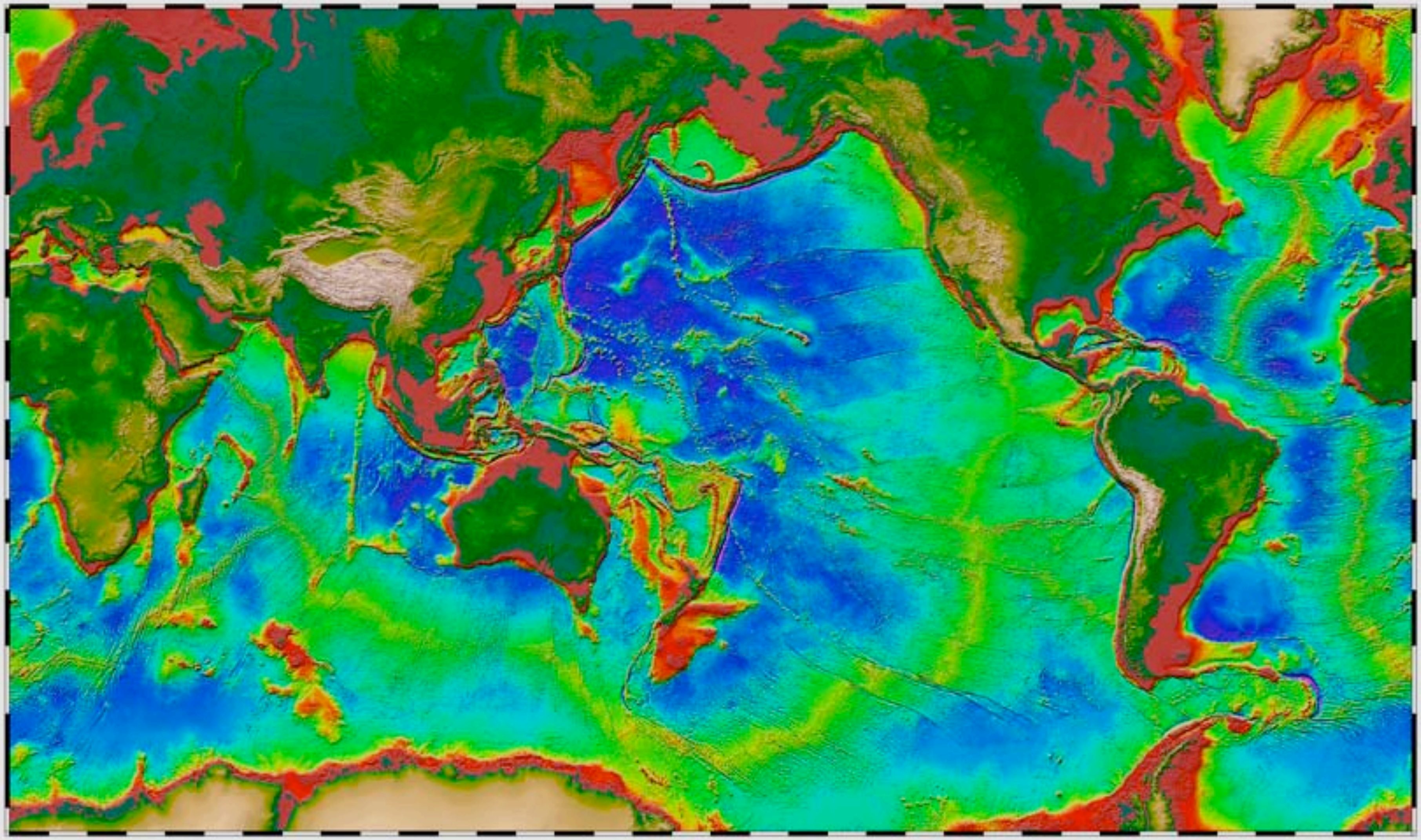
- Thickest crusts occur between water depths of 1500-2500 m, the area of the outer rim of the seamount summit

- Most cobalt-rich at ~800-2200 m water depths



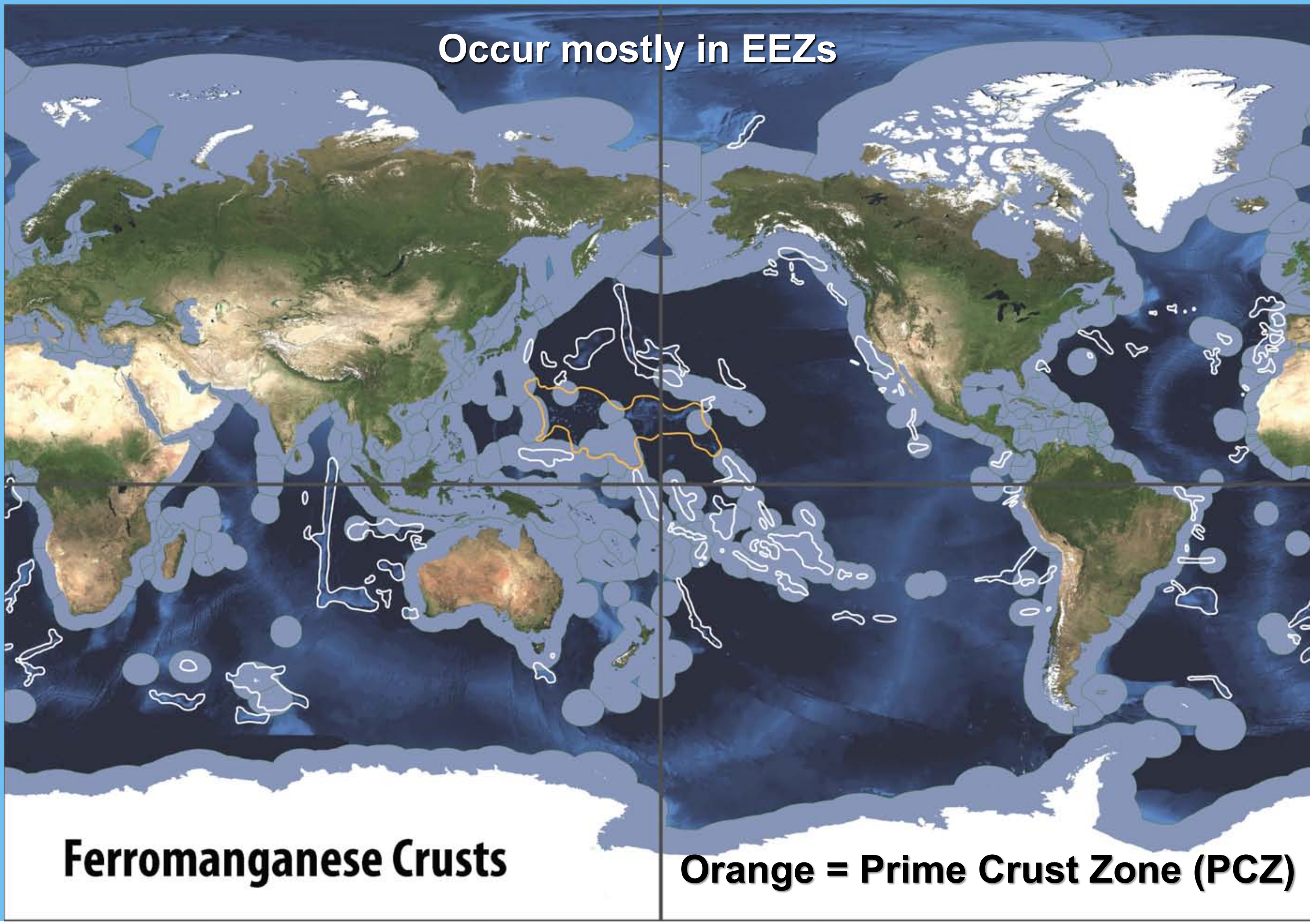
Fe-Mn crust pavement at 2,000 m water depth

Distribution of Fe-Mn Crusts

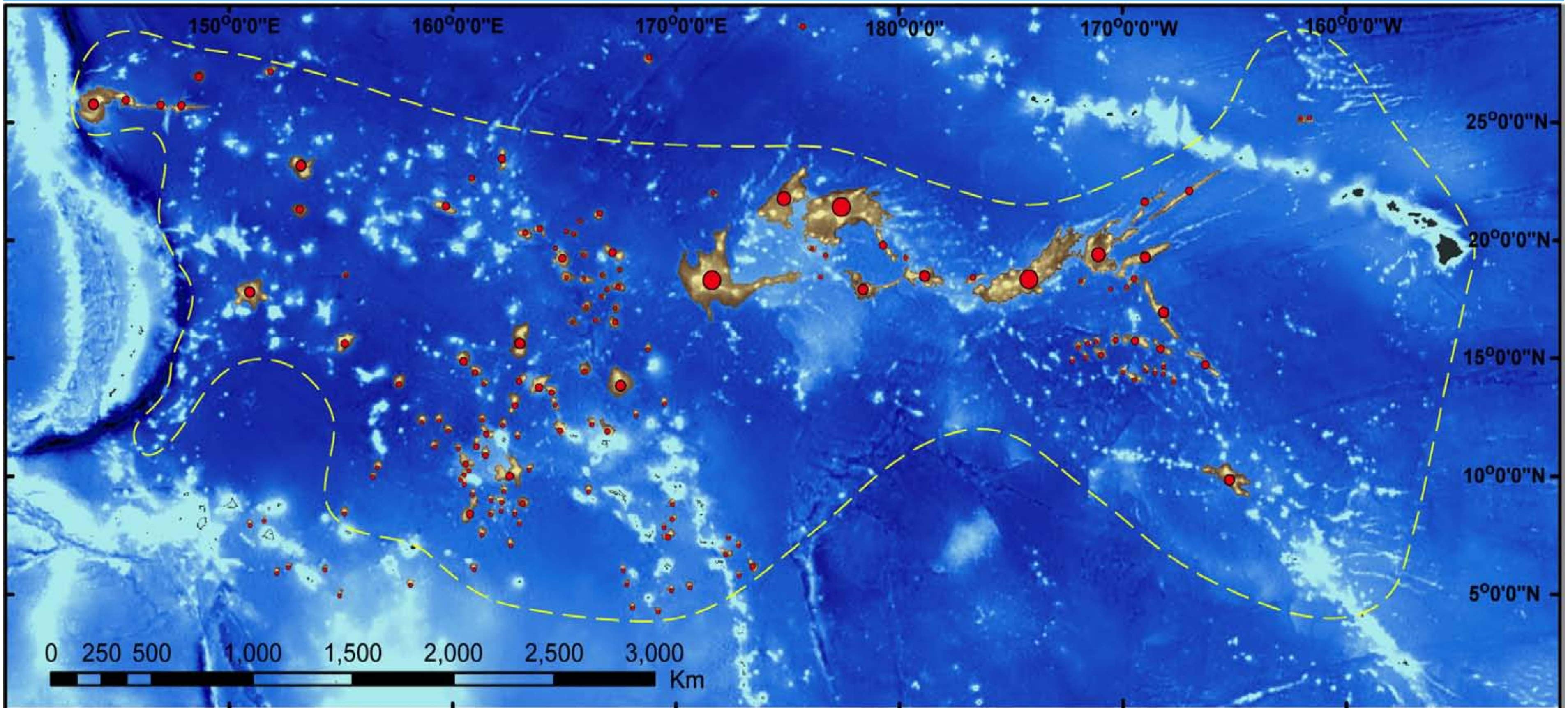


Global Permissive Areas for Ferromanganese Crusts

(From Hein et al., 2013)



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 <u>thick Fe-Mn crusts</u>

From Hein et al. (2009)

Average Seamount (Surface Area Statistics for 155 Seamounts)

	Total Surface Area (km^2)	*Surface Area above -2500m water depth*	*Surface Area above -1500m water depth*
Mean	3,389	1,039	117
Median	1,553	355	71
SD[1]	5,354	1,943	252
Minimum	233	0	0
Maximum	35,519	13,443	1,211

[1] Standard Deviation

25 km^2/yr mining area
500 km^2/20 yrs mining site
3000 km^2 for exploration

Common Shipboard Operations

Sampling rock/sediment

- dredging
- coring (box, gravity, piston, spade)
- rock drilling
- grabs
- sediment pore fluids

Water column

- CTD
- oxygen sensor
- Eh sensor
- water sampling rosette
- hydrothermal fluids
- tow-yo surveys

Geophysics

- multibeam mapping
- side-scan sonar and back scatter
- gravity and magnetics
- single channel and multichannel seismic stratigraphy

Imagery

- bottom camera/video

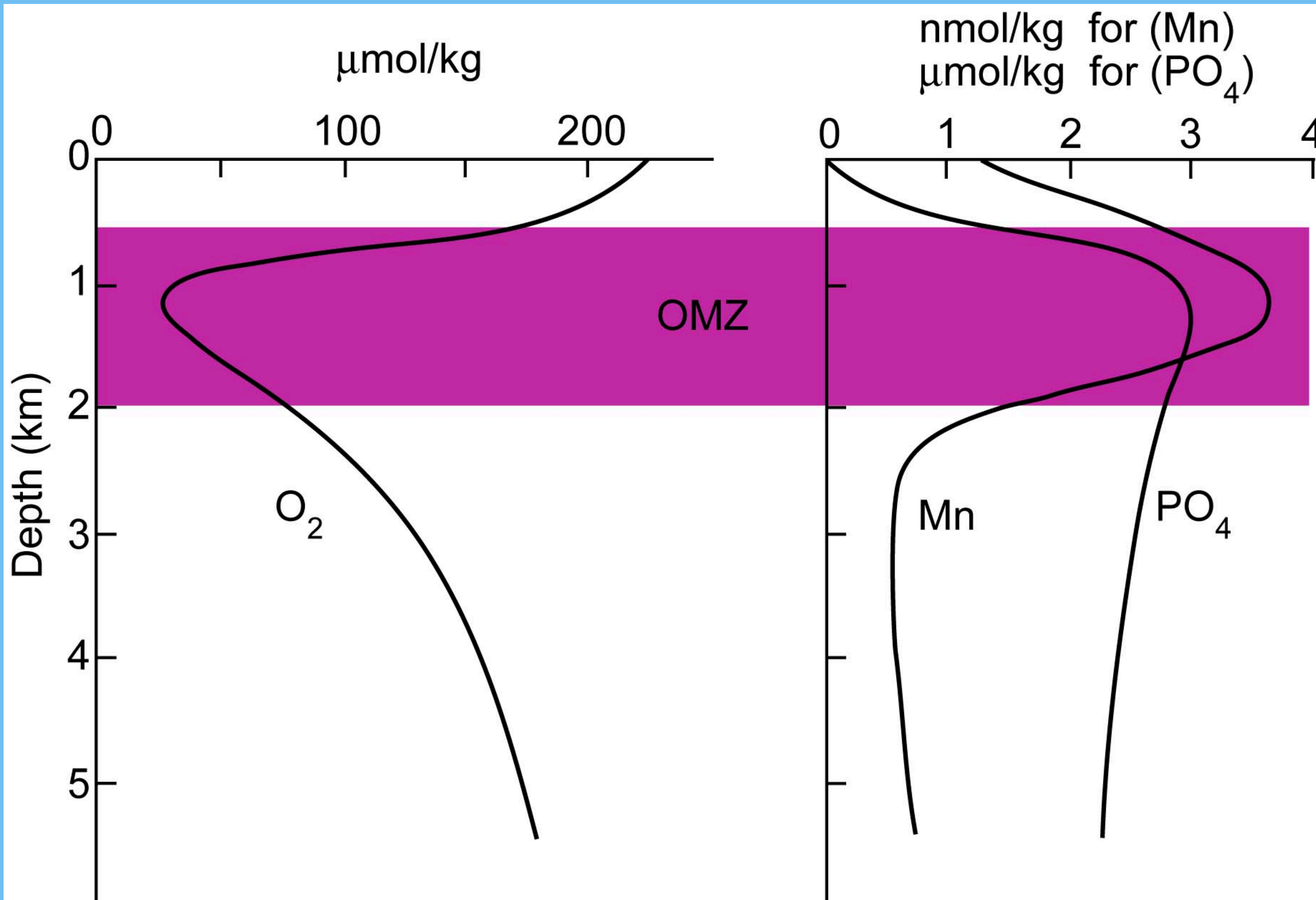
Vehicles

- ROV
- AUV
- Hybrid (e.g. Nereus)

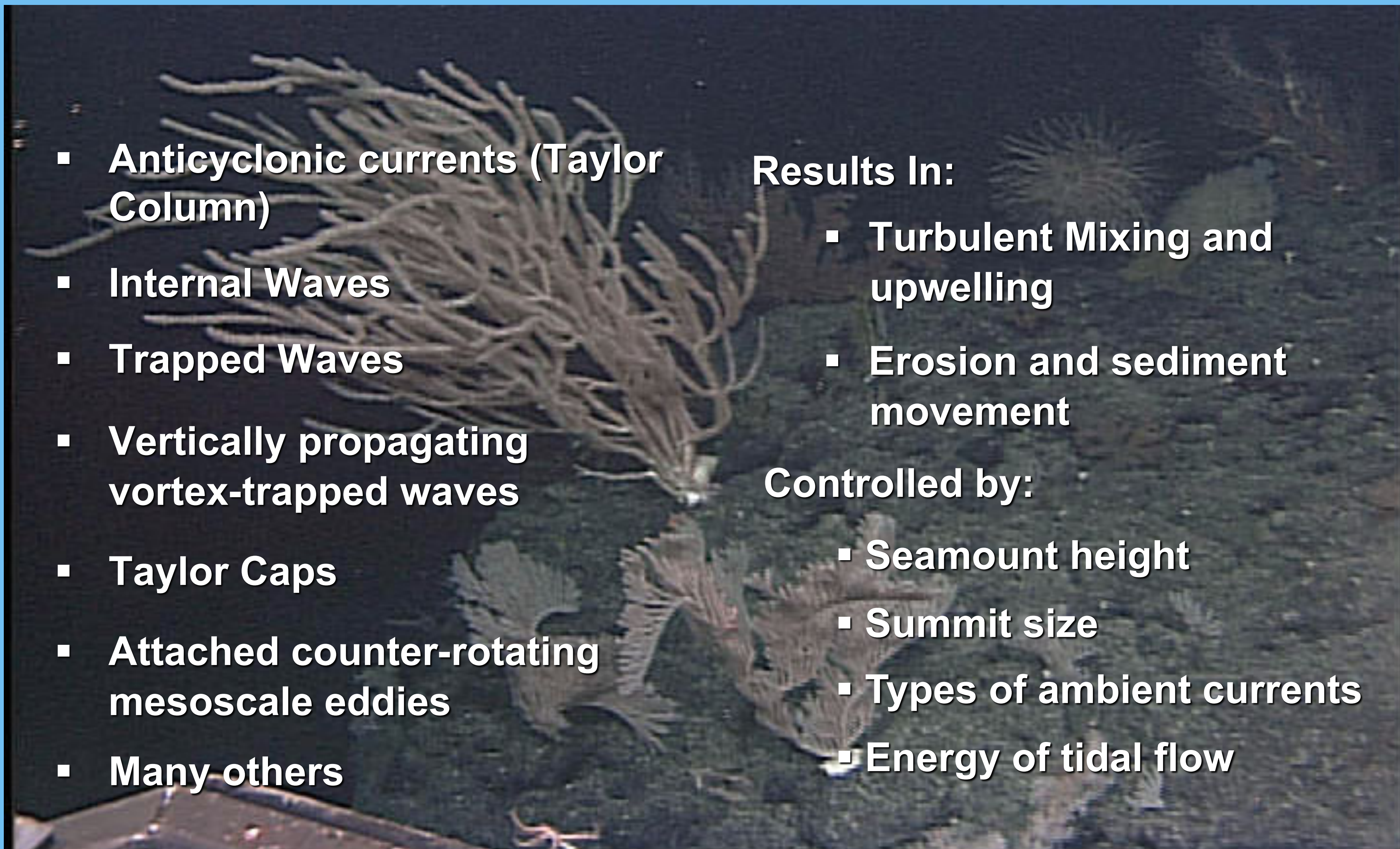
Shipboard sample labs

- Sample description & processing
- Geotechnical properties
- Hand-held XRF scanner

Seawater Profiles for O_2, Mn, and PO_4



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

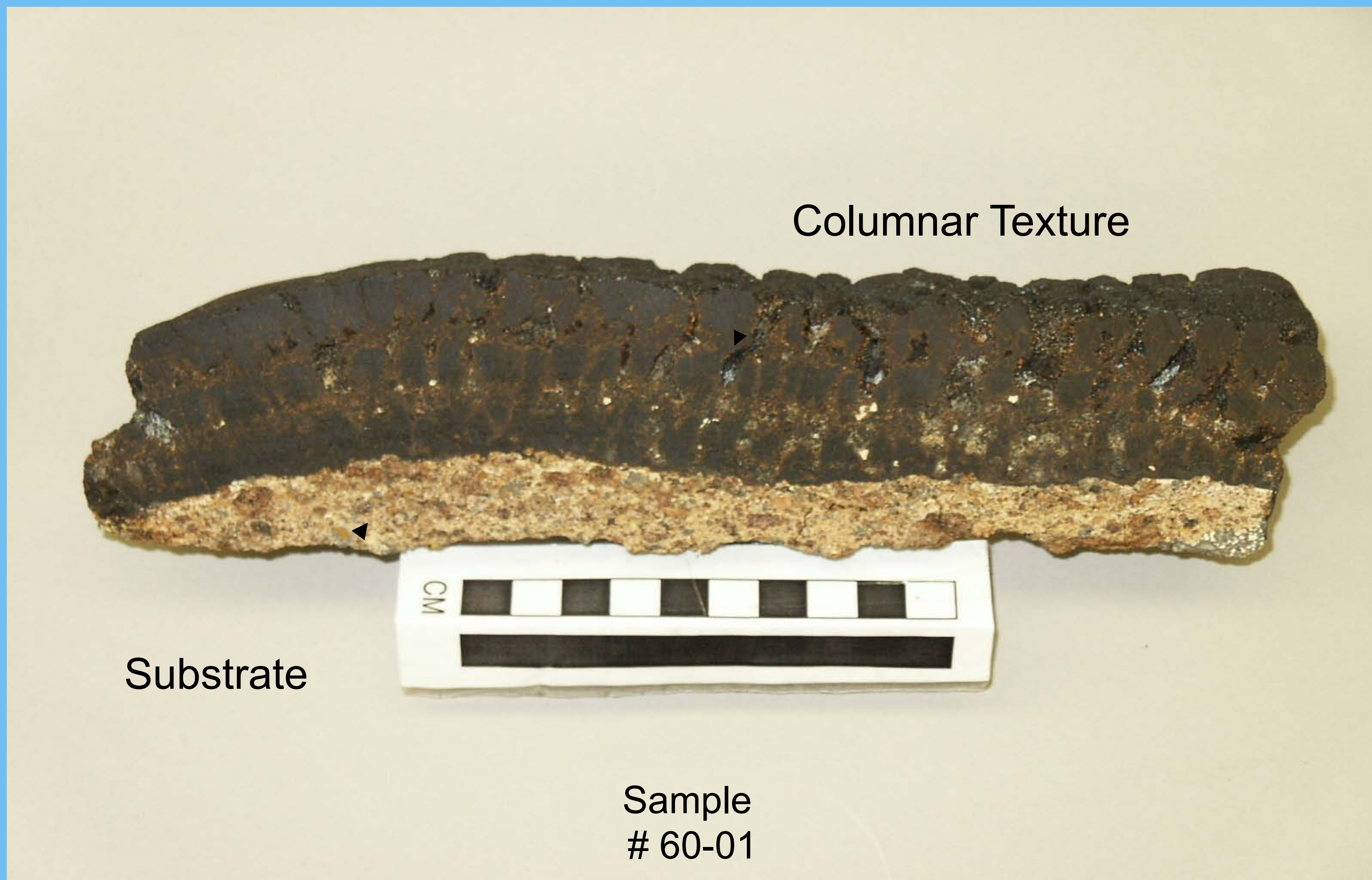
Seamount Biology

- Different communities occur on adjacent seamounts at the same water depth
- Sediment versus rock communities
- Low density and low diversity populations where crusts are thick and cobalt-rich (beneath OMZ)
- Seamounts are not habitats with highly endemic faunas that comprise unique communities distinct from other deep-sea habitats (Rowden et al., 2011)

Evidence for extensive mass movement on seamount slopes

(1) Crust dislodged from seabed, (2) moved down-slope, (3) landed in carbonate sand, (4) sand was then phosphatized

Fe-Mn Crust



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***

Fe-Mn Crust Surface Textures and Internal Textures

Fe-Mn Crust Surface Textures

Botryoidal
Microbotryoidal
Modified botryoidal
Smooth
Granular
Lizard skin
Cauliflower
Fluted
Polished
Porous granular

Fe-Mn Crust Internal Textures

Massive
Porous
Vuggy
Columnar
Dense
Mottled
Laminated
Asicular
Dendritic
Radial
CFA-filled vugs/pores
CFA veinlets
Fe-filled vugs/pores
Fe-oxide veinlets

CFA = carbonate fluorapatite

Typical botryoidal surface of a Fe-Mn crust

Current-smoothed crust surface (modified botryoidal)

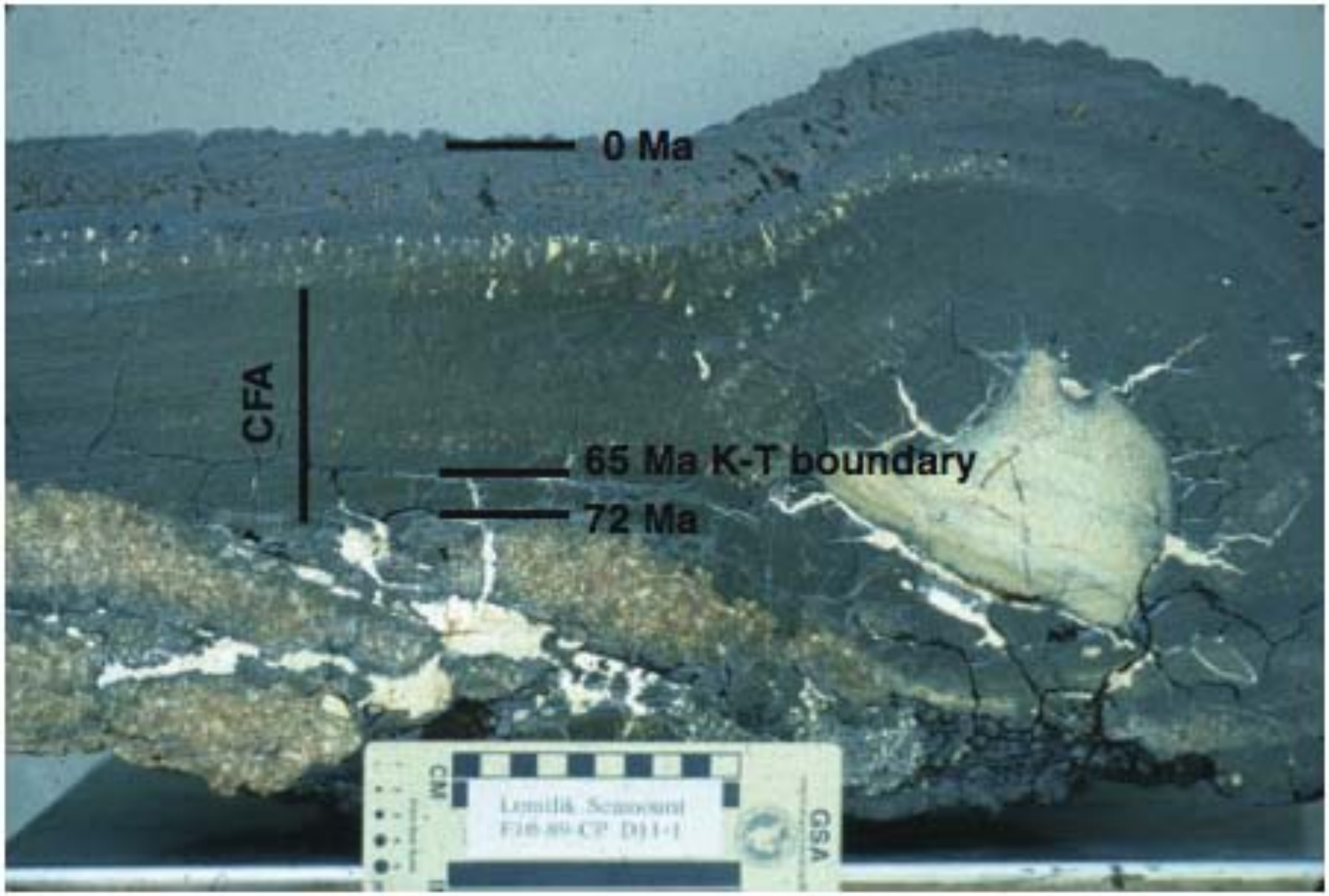
Current-polished and fluted crust surface

Marshall Is. EEZ, F10-89-CP, dredge D11

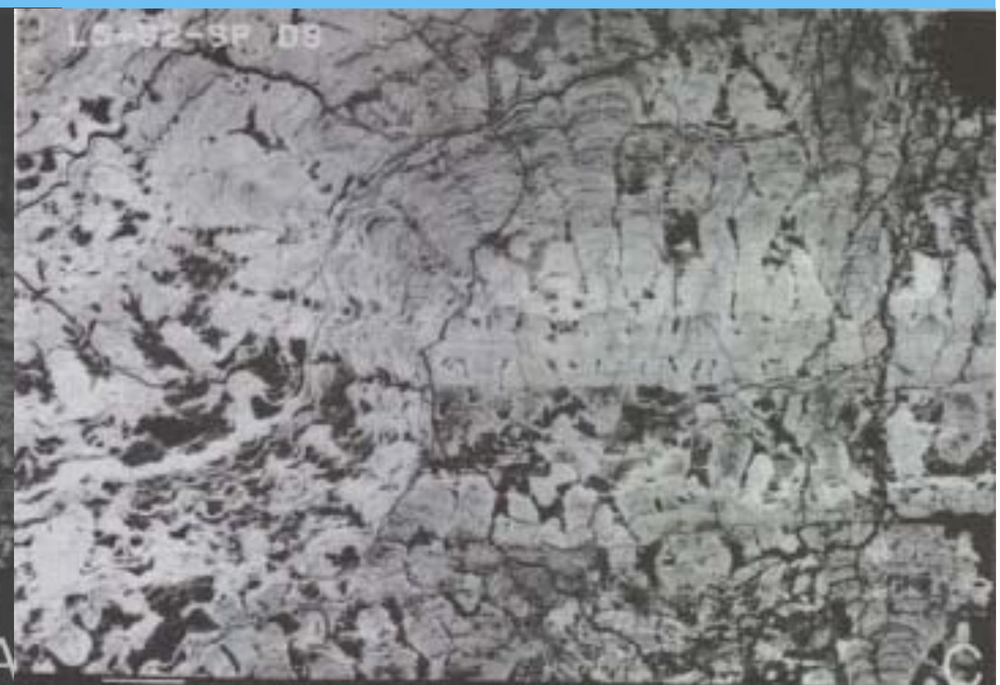
Marshall Islands EEZ

F10-89-CP, Dredge D11

Phosphatization and age of Marshall Is. Crust (D11) that began growing 72 Ma ago (18 cm thick)



Scanning Electron Microcrographs of polished sections of Fe-Mn crusts

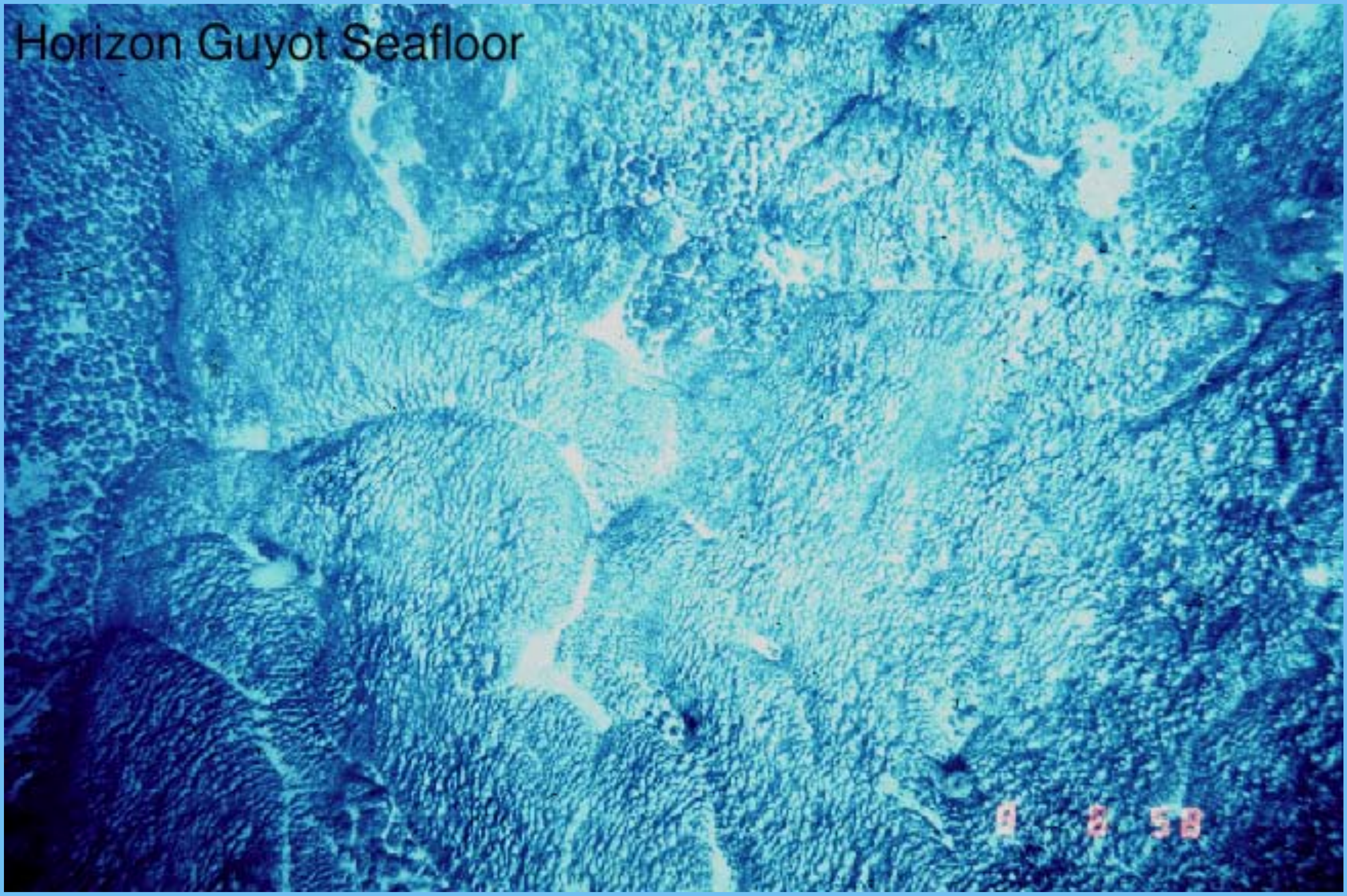


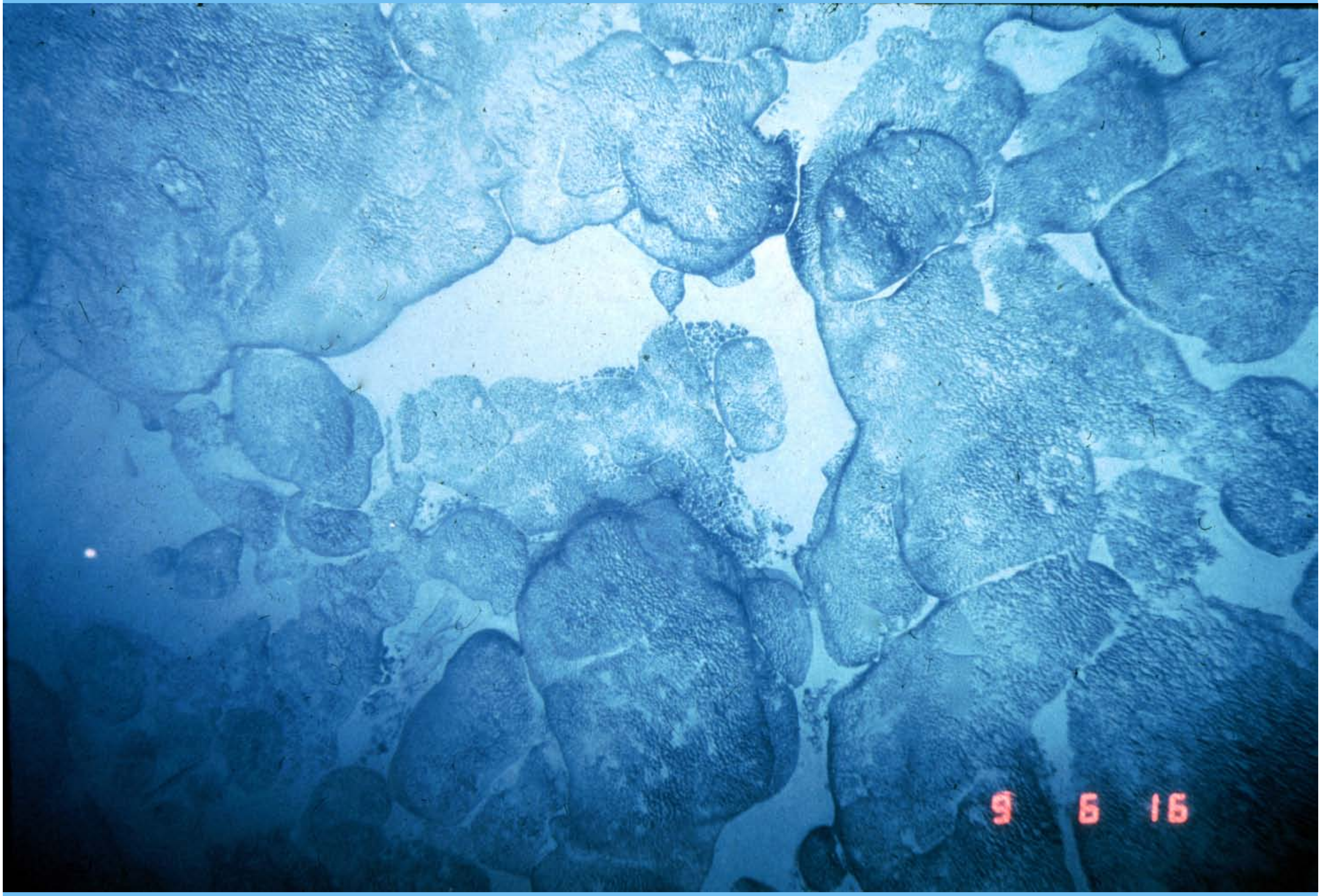
First-order laminated structure with loosely packed botryoids & columnar structures; high porosity in lower part and closely packed botryoids with little porosity in the upper section

Angular erosional discordance; laminae-parallel hiatuses are also common

From Hein et al. (1990)

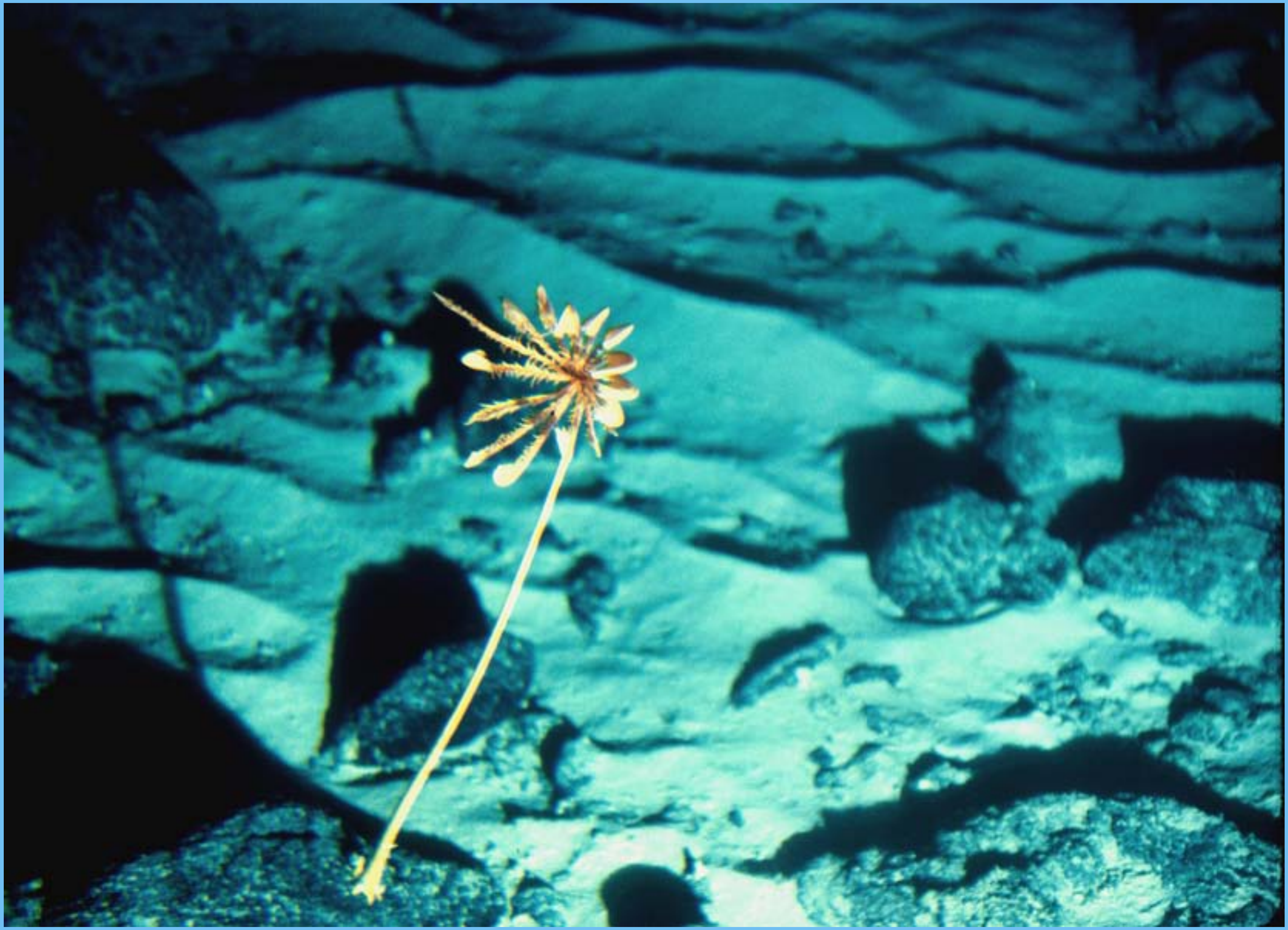
Fe-Mn pavement at 2000 m water depth




9 6 16


9 5 57

Sediment fills lows between Fe-Mn crust outcrops, 2000 m



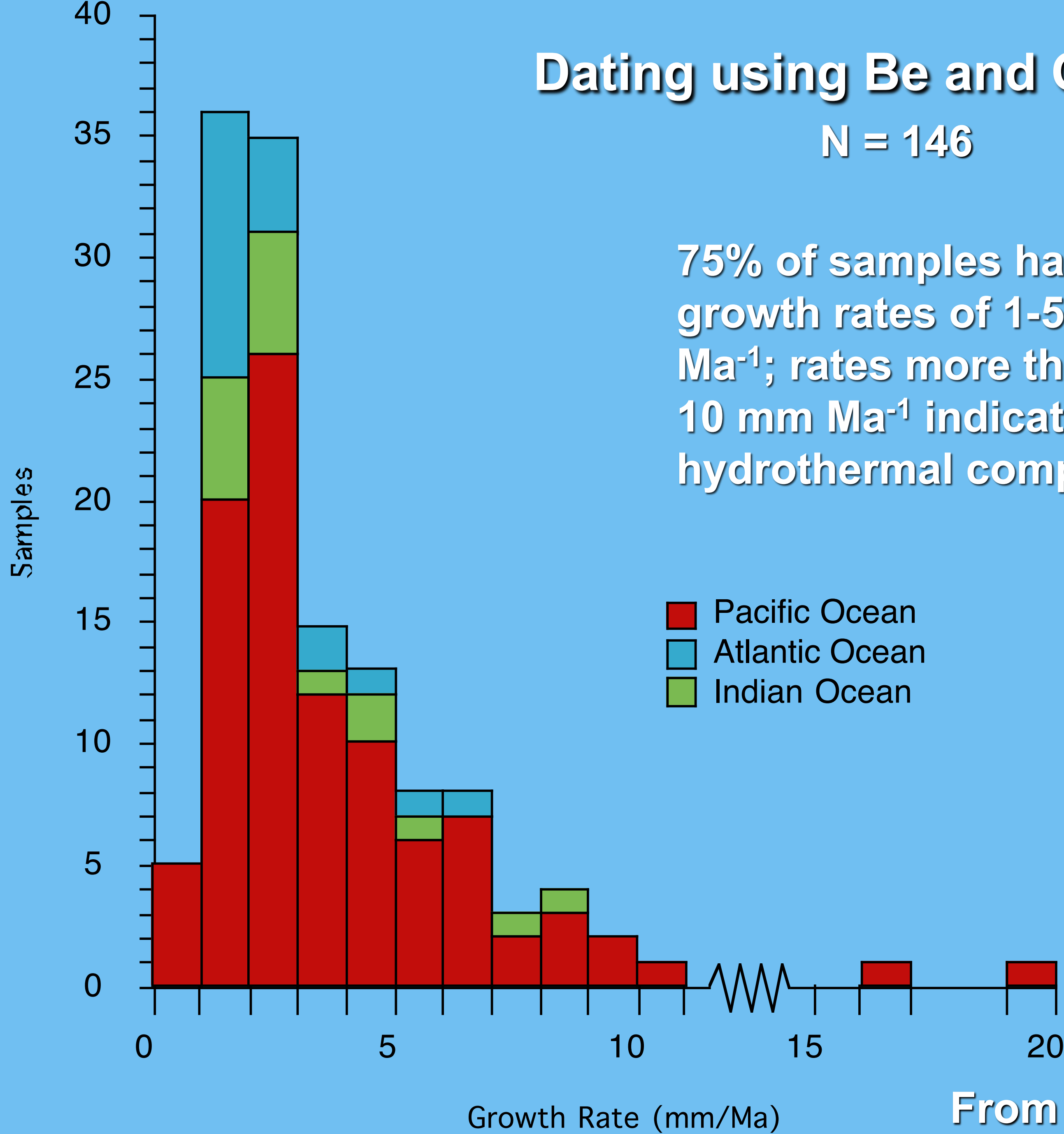
Fe-Mn Crust Mineralogy

- δ-MnO_2
- X-ray amorphous Fe oxyhydroxide: $FeO(OH)$
- Carbonate fluorapatite (CFA)
- Minor detrital/eolian silica & aluminosilicates
- Minor biogenic debris, opal and calcite

Dating using Be and Os isotopes

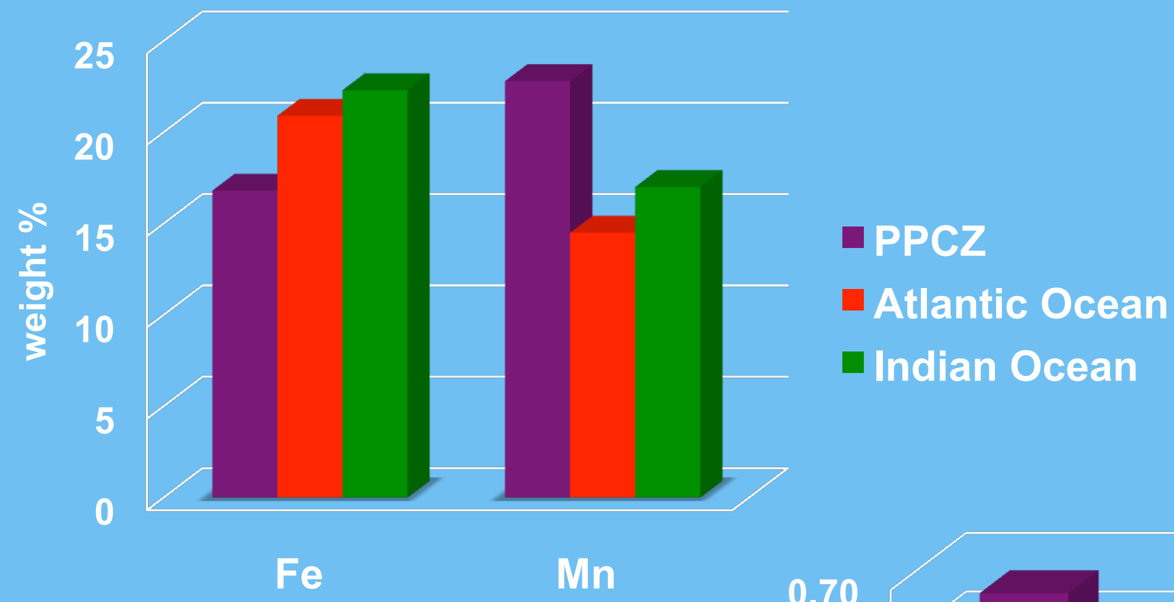
N = 146

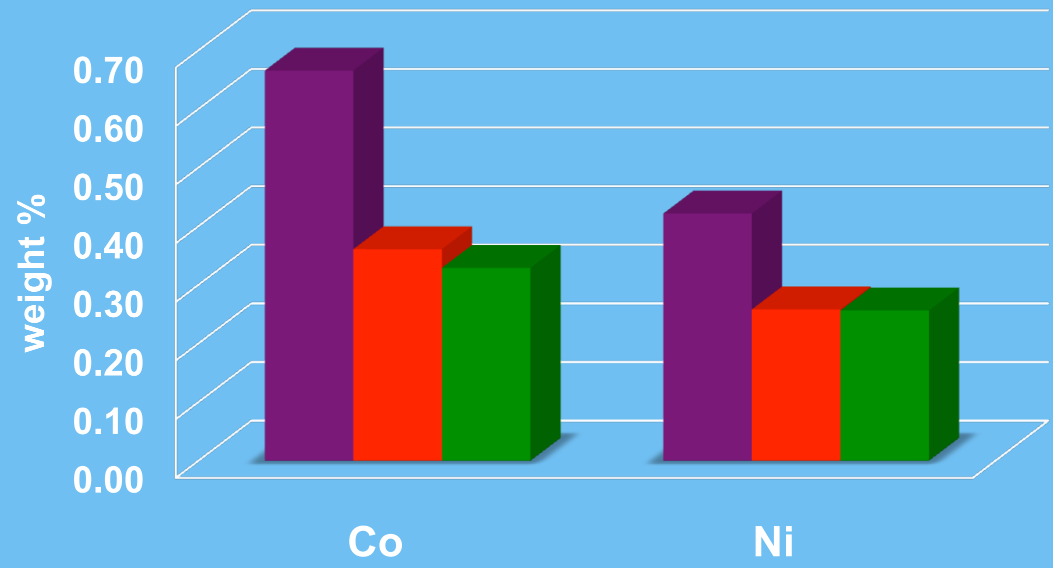
75% of samples have growth rates of 1-5 mm Ma^{-1}; rates more than about 10 mm Ma^{-1} indicate a hydrothermal component



From Hein et al. (2000)

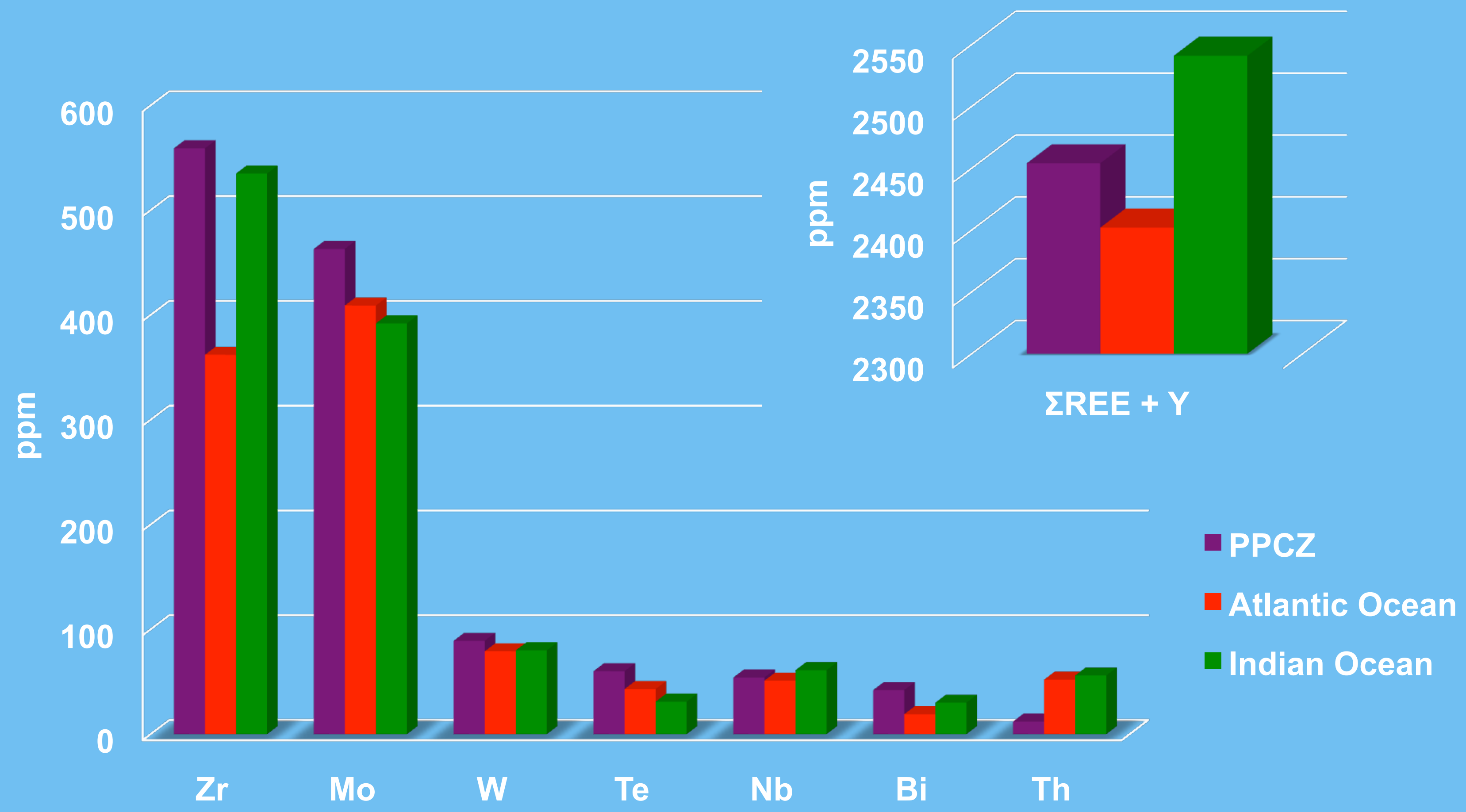
Crusts in the Global Ocean (wt %)



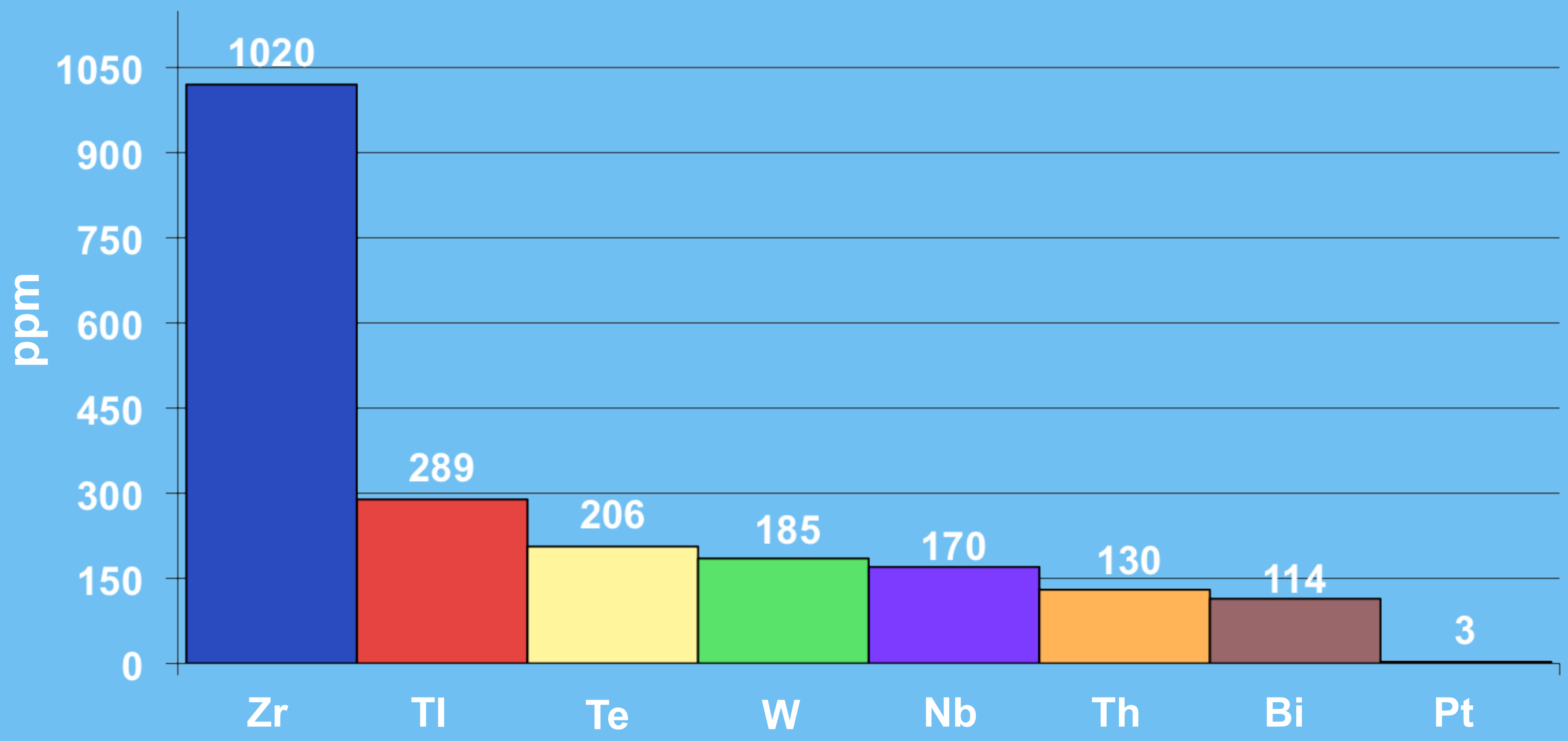


Greatest economic interest for cobalt, nickel, manganese

Crusts in the Global Ocean (g/tonne = ppm)



Trace Metal Maxima

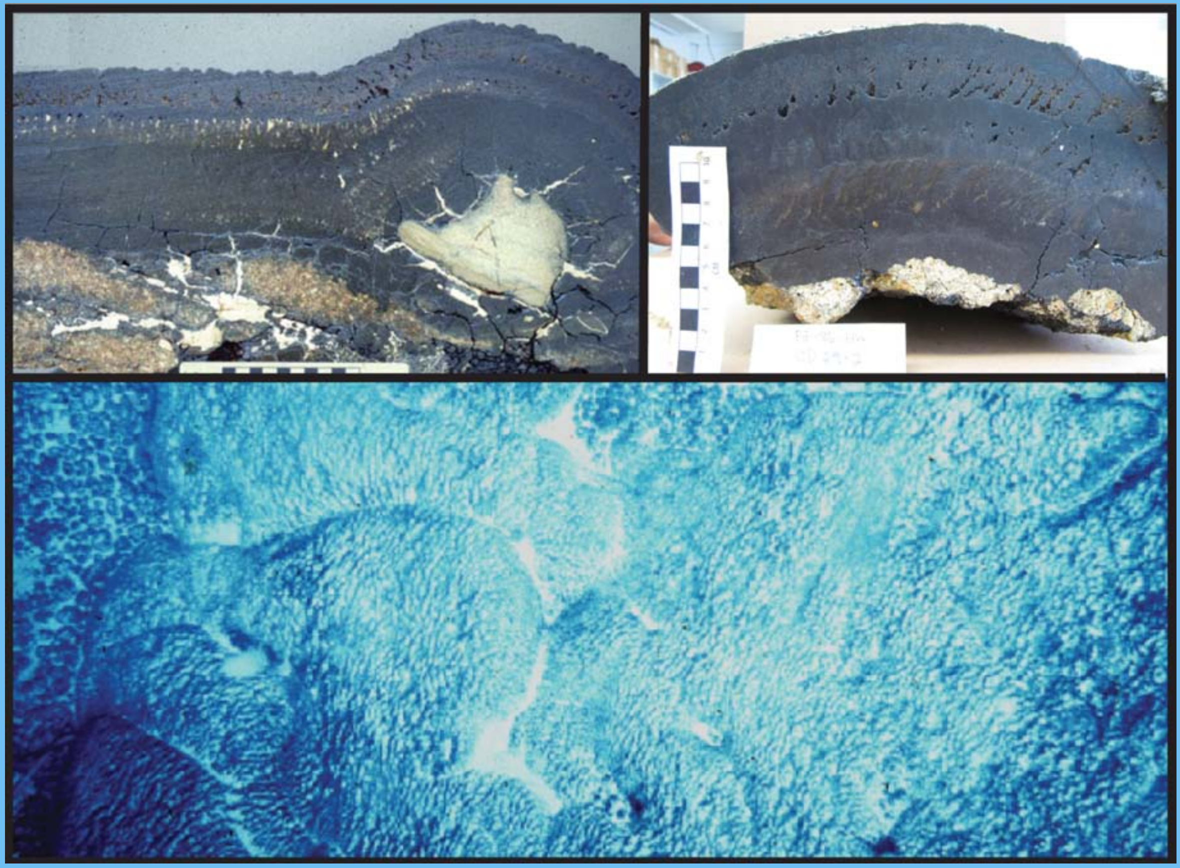


*Ce is 11,000 ppm = 1.1%

From Hein et al. (2010)

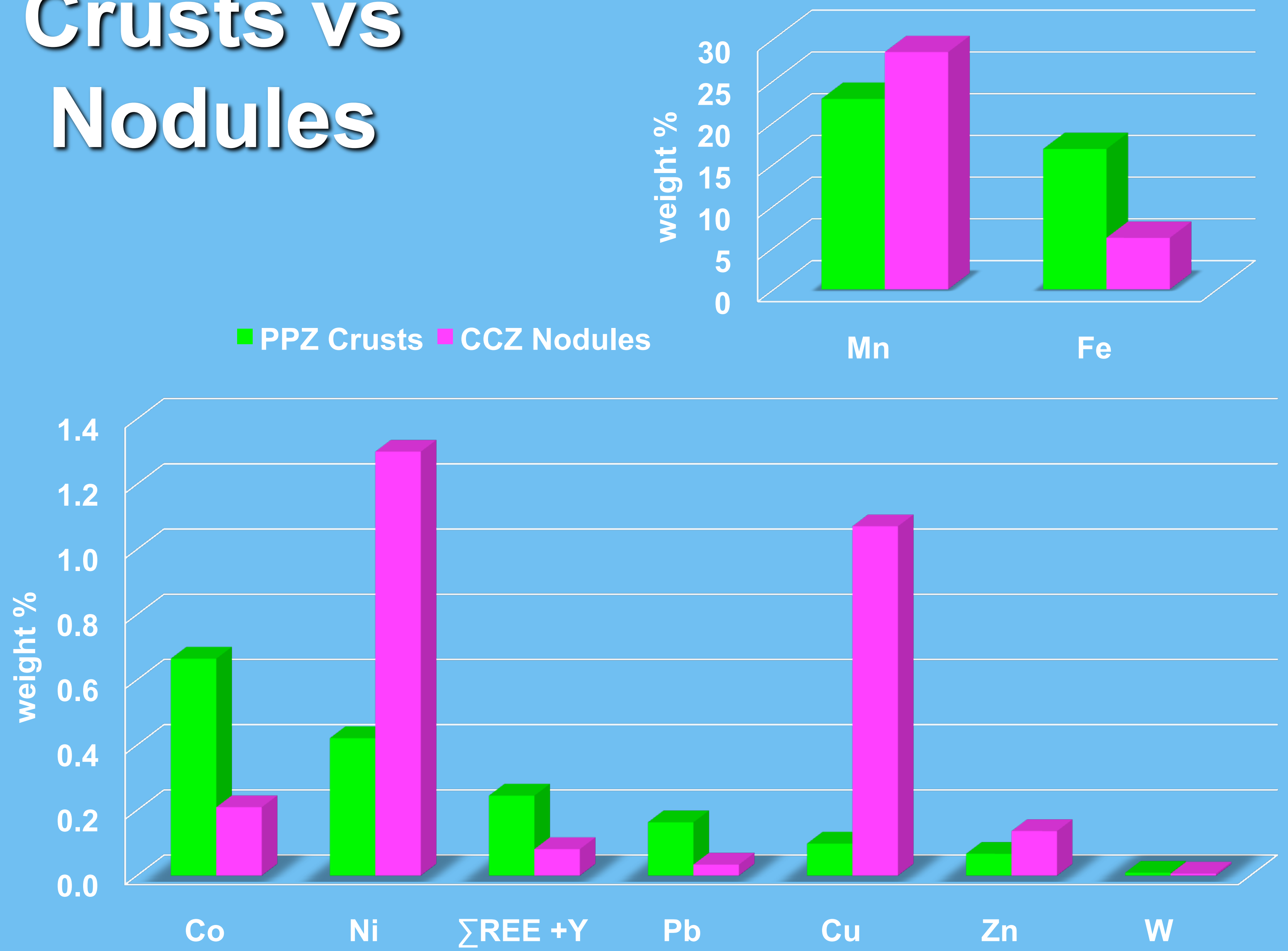
Rare Metals in Ferromanganese Crusts As Potential Byproducts

Rare-Earth Elements
Bismuth
Niobium
Molybdenum
Platinum
Tellurium
Thorium
Titanium
Tungsten
Zirconium

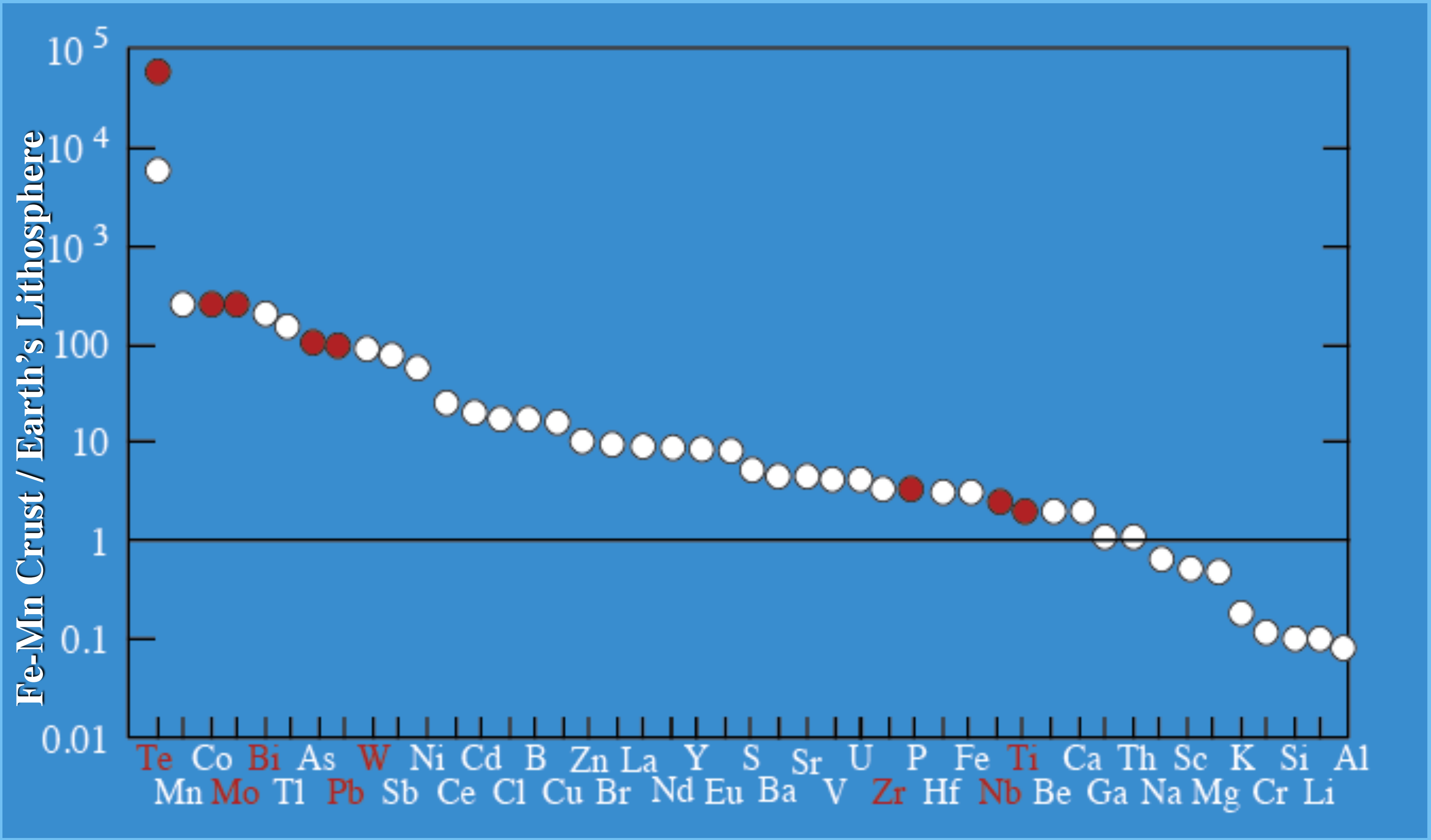


From Hein et al. (2013)

Crusts vs Nodules

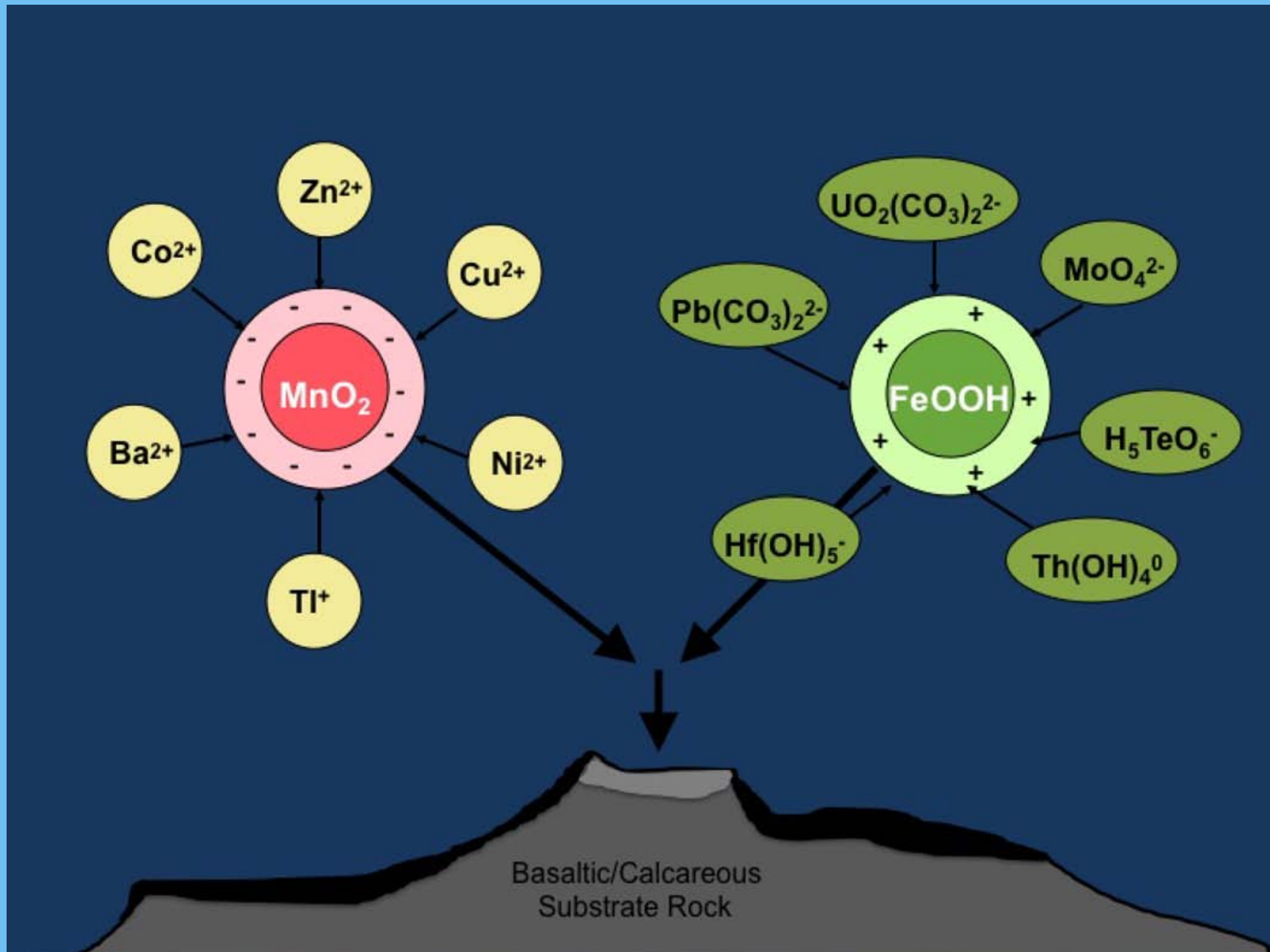


Element Enrichment in Fe-Mn Crusts relative to the Earth's Lithosphere



From Hein et al. (2003)

Crust Formation Begins in the Water Column



Simplified electrochemical model for the formation of Fe-Mn crusts by adsorption of trace metals on colloidal Mn oxide and Fe oxyhydroxide (From Hein et al. 2013)

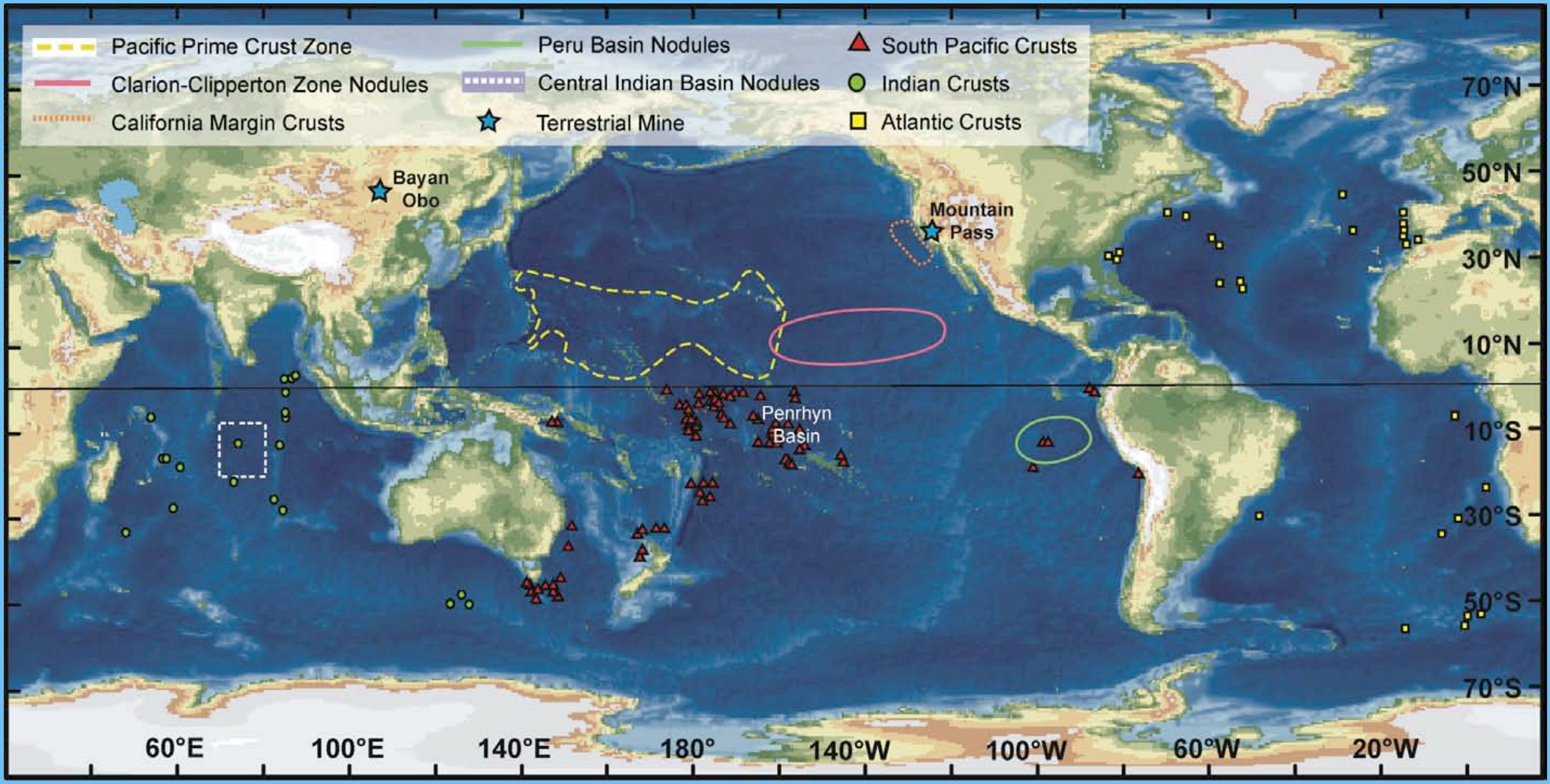
Surface Oxidation of Fe-Mn Crusts

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

Comparisons of CCZ and PPCZ with global land-based reserves



From Hein et al. (2013)

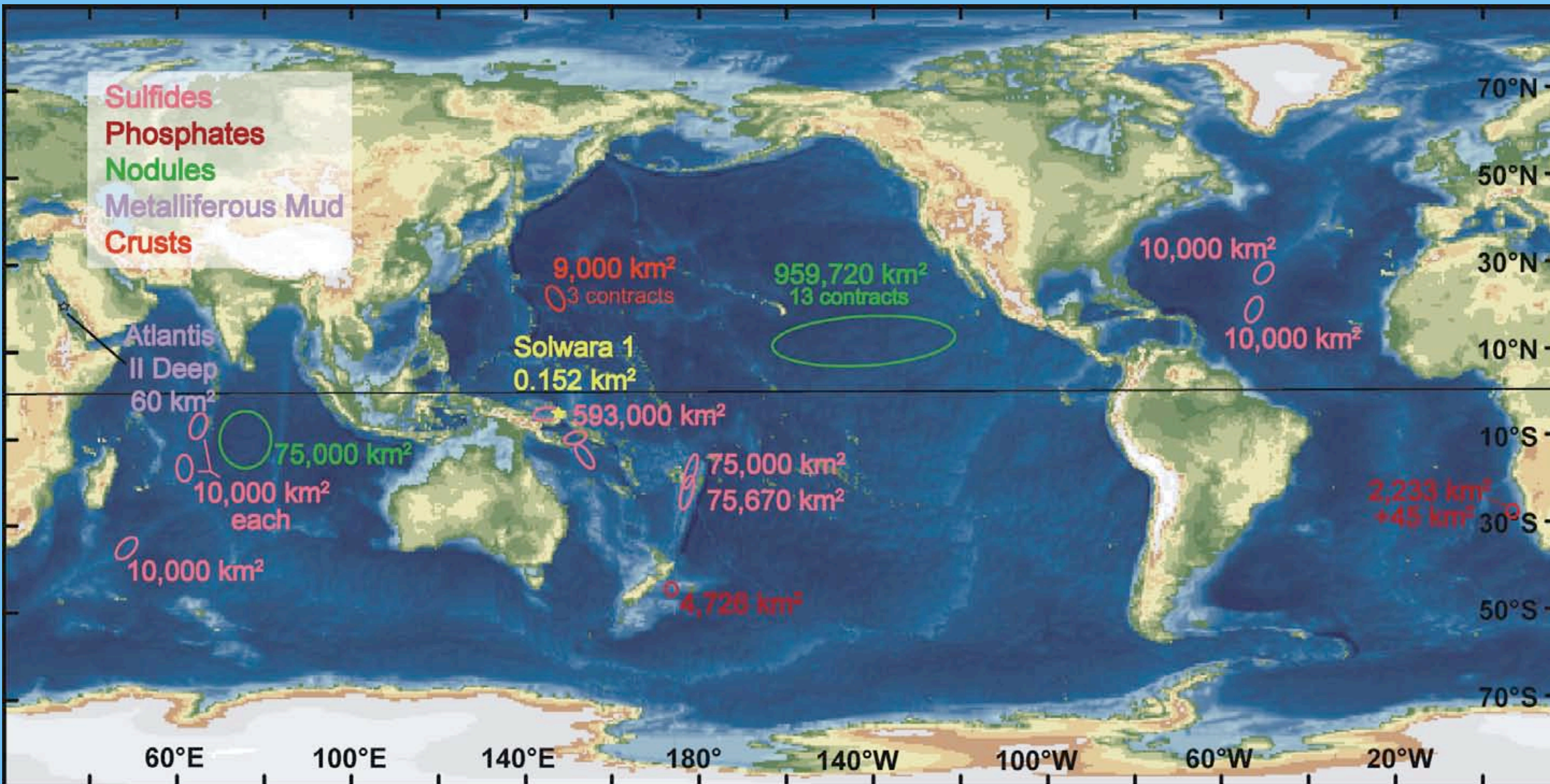
Contained metal tonnages (x 10^6 metric tonnes)

	Prime Pacific Crust Zone	Global Terrestrial Reserves	Global Terrestrial Reserve Base	Clarion-Clipperton Zone Nodules
Manganese	1714	630	5,200	5,992
Copper	7.4	690	1,000+	226
Titanium	88	414	899	67
TREO	16	110	150	15
Nickel	32	80	150	274
Vanadium	4.8	14	38	9.4
Molybdenum	3.5	10	19	12
Lithium	0.02	13	14	2.8
Cobalt	50	7.5	13	44
Tungsten	0.67	3.1	6.3	1.3
Niobium	0.4	3	3	0.46
Arsenic	2.9	1	1.6	1.4
Thorium	0.09	1.2	1.2	0.32
Bismuth	0.32	0.3	0.7	0.18
Yttrium	1.7	0.5	0.5	2
PGM	0.004	0.07	0.08	0.003
Tellurium	0.45	0.02	0.05	0.08
Thallium	1.2	0.0004	0.0007	4.2

From Hein & Koschinsky (2013)

- USGS 2009 reserve base & 2012 reserves (reserve base includes resources currently economic [reserves], marginally economic, and subeconomic)
- Crust tonnage is 7,533 million dry tonnes; Nodule tonnage is 21,100 million dry tonnes

Contracts for Marine Minerals <u>Exploration</u> Total 1,844,454 km²



Total lease area equivalent to area of <u>5.2 "Germanys"</u>

All SW Pacific, Red Sea, phosphate licenses in EEZs, all others in "The Area"

From Hein et al. (2013)

States & companies with deep-ocean minerals contracts

States/State Agencies

China	Nodules, Sulfides, Crusts
France	Nodules, Sulfides
Germany	Nodules, Sulfides
India	Nodules
Japan	Nodules, Crusts
Korea	Nodules, Sulfides
Russia	Nodules, Sulfides, Crusts
Inter-Ocean Metals [e]	Nodules

[e] Bulgaria, Cuba, Czech Republic, Poland, Russia, Slovak Republic

Companies

Chatham Rock Ltd.	Phosphate
Namibian Marine Phosphates Ltd. [a]	Phosphate
Diamond Fields International Ltd.[b]	Metalliferous Mud
G-TEC Sea Minerals NV	Nodules
Nauru Ocean Resources	Nodules
Tonga Offshore Mining [c]	Nodules
UK Seabed Resources Ltd. (2 contracts) [d]	Nodules
Marawa (Kiribati)	Nodules
Nautilus Minerals	Sulfides
Neptune Minerals	Sulfides

[a] Joint venture with UCL Resources Ltd., Minemakers Ltd., & Tungeni Investments c.c.

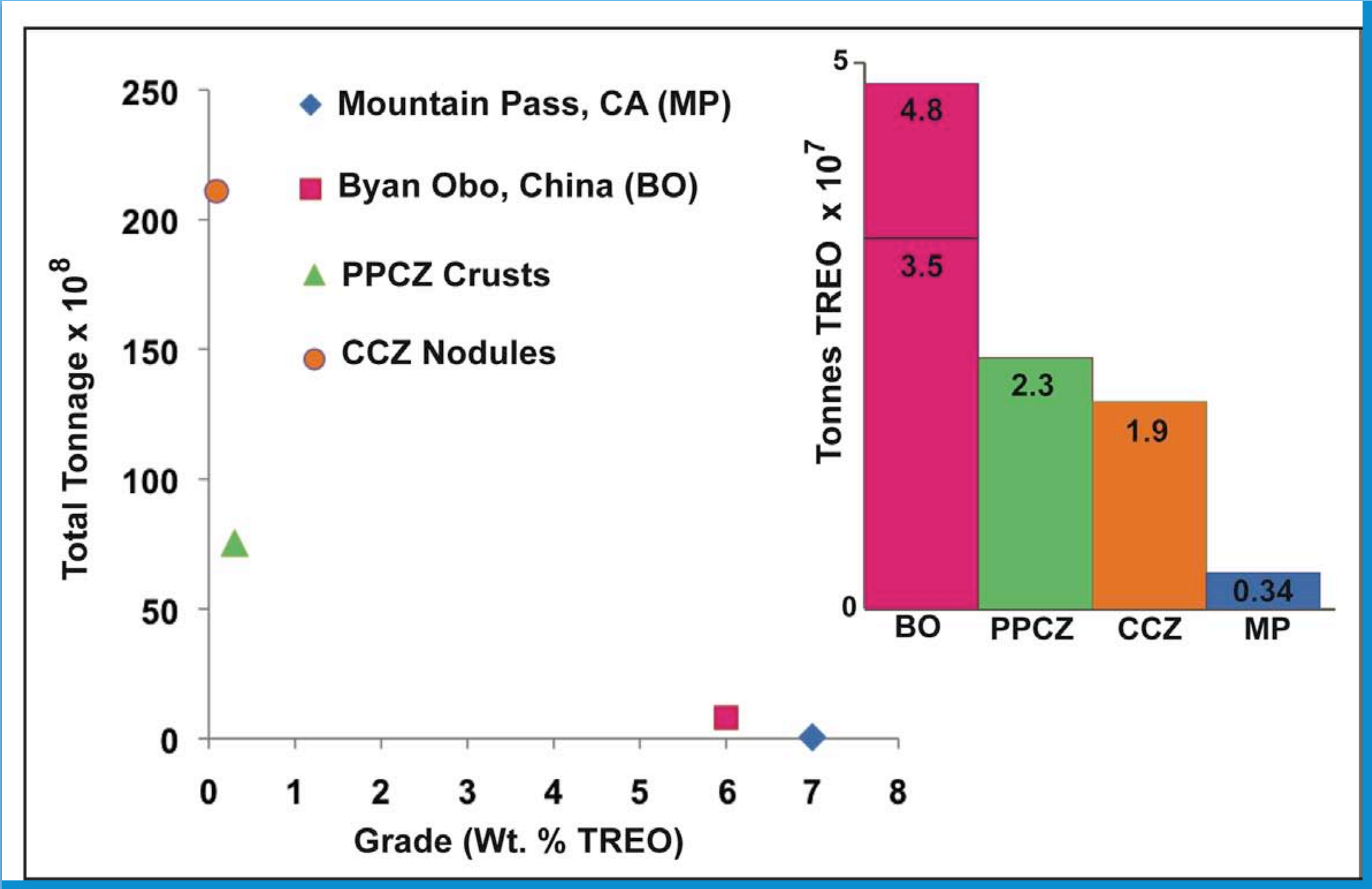
[b] Joint venture with Manfa International

[c] Wholly owned subsidiary of Nautilus Minerals

[d] Wholly owned subsidiary of Lockheed Martin UK Holdings Ltd.

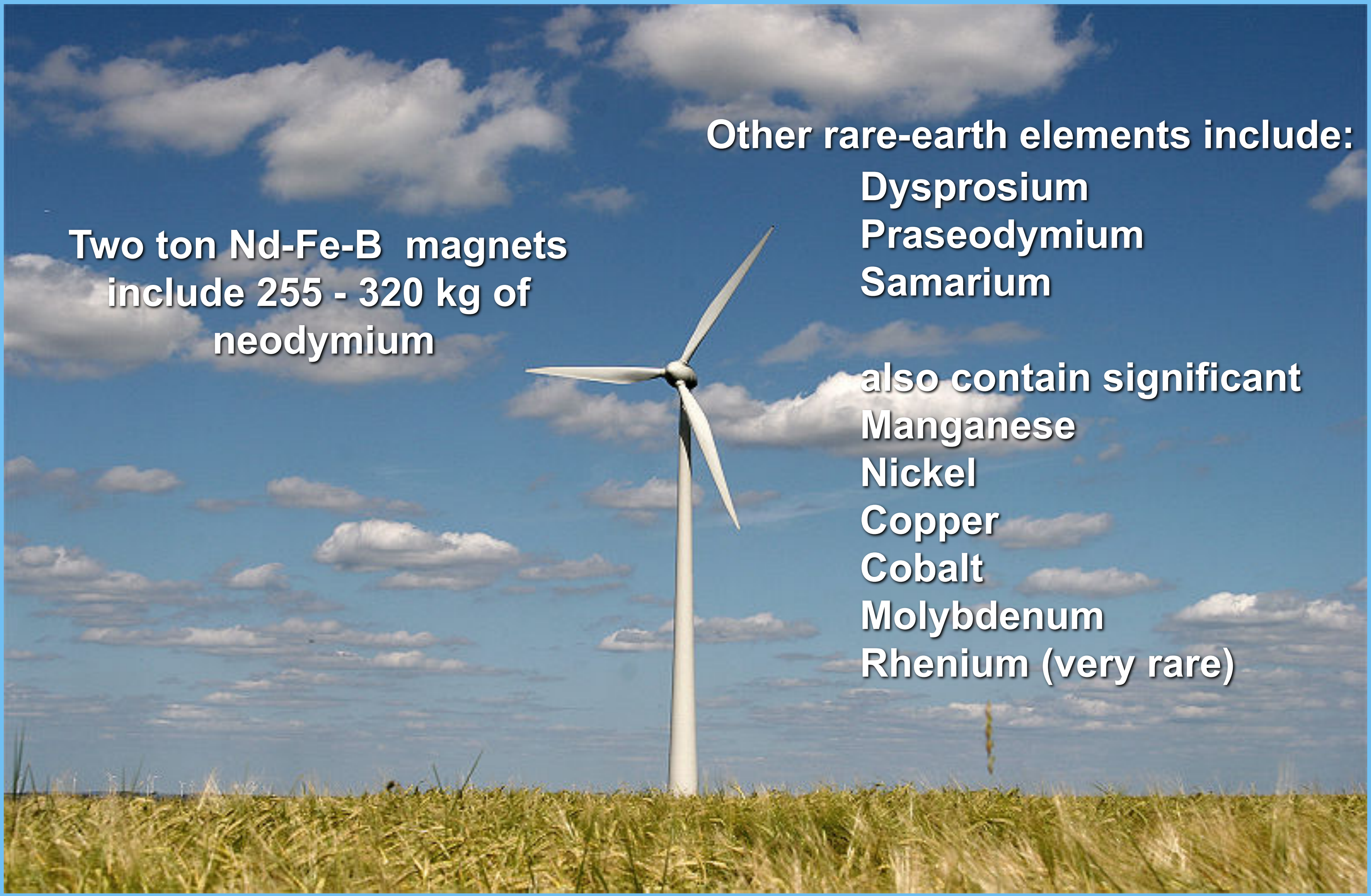
From Hein et al. (2013)

REEs in crusts and nodules would be byproduct of Ni-Cu-Co-Mn mining & the cost of extraction, transportation, and partial metallurgy will be financed by the focus metals; this is not the case for terrestrial REE mines



From Hein et al. (2013)

Wind Turbines



From Hein et al. (2013)

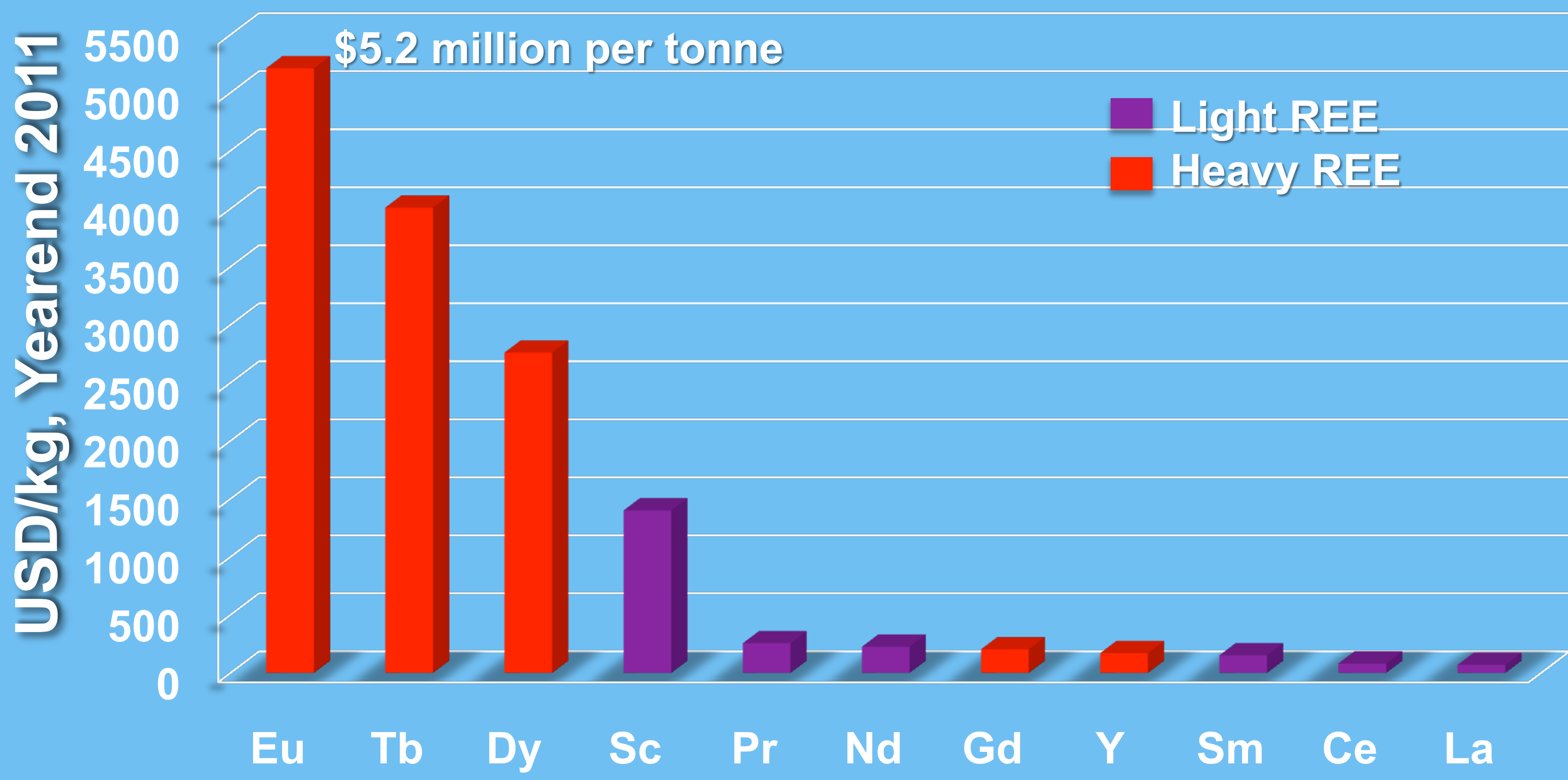
Light versus Heavy REEs

Bayan Obo & Mountain Pass average less than 1% HREEs

PCZ averages 18% HREEs

CCZ averages 26% HREEs

From Hein et al., (2013)



Extractive Metallurgy for REEs

Land-based ores require extensive processing, e.g., 1000 steps to isolate ytterbium metal

Marine FeO(OH) and MnO_2 can be dissolved with simple HCl leach putting all sorbed REEs and other metals into solution

The New York Times December 15, 2010

David Gray/Reuters

Rare Metals for Emerging and Next Generation Technologies

- Tellurium: Photovoltaic solar cells; computer chips; thermal cooling devices
- Cobalt: Hybrid & electric car batteries, storage of solar energy, magnetic recording media, high-T super-alloys, supermagnets, cell phones
- Bismuth: Liquid Pb-Bi coolant for nuclear reactors; Bi-metal polymer bullets, high-T superconductors, computer chips
- Tungsten: Negative thermal expansion devices, high-T superalloys, X-ray photo imaging
- Niobium: High-T superalloys, next generation capacitors, superconducting resonators
- Platinum: Hydrogen fuel cells, chemical sensors, cancer drugs, flat-panel displays, electronics

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