Cobalt-rich ferromanganese crusts: global evaluation and exploration in the Atlantic and Southwest Indian Ocean

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Outline

- Introduction
- General characteristics
- Global distribution & Geological setting
- Morphology & Formation
- Mineralogy, Metal Grades (e.g. rare-metals) and Age
- Economical issues
- Exploration methods
- Conclusing remarks

Characteristics of deep-sea minerals

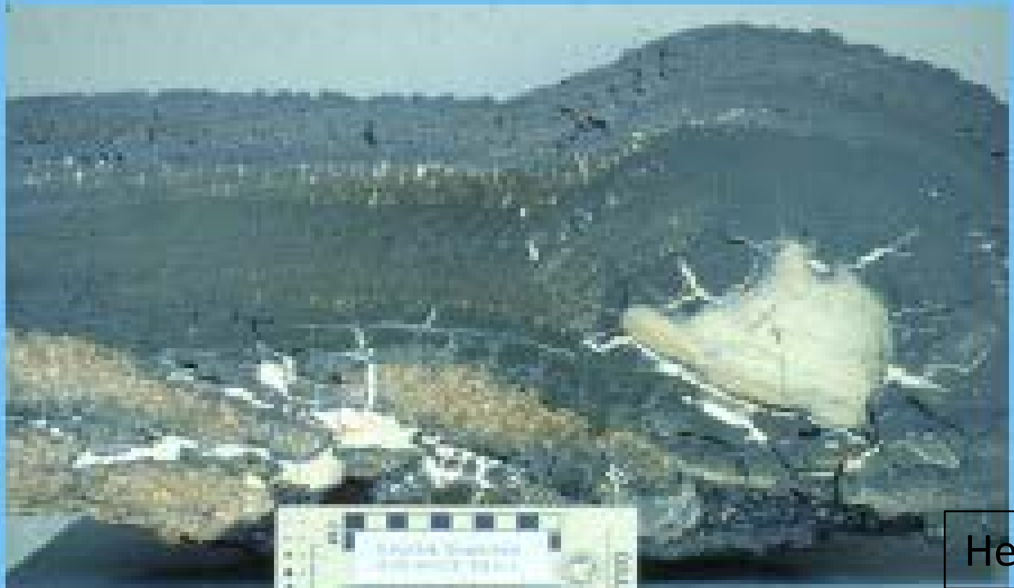
Type of marine minerals	Setting/ Depth, м	Main metals	Age, years
Nodules	Abissal plains (4000-5000)	Copper, nickel, manganese	$n \times 10^6$ - $n \times 10^7$
Crusts	**Seamounts (1000-2500)**	**Cobalt, nickel, manganese**	**$n \times 10^6$ - $n \times 10^7$**
Massive sulfides	Volcanic structures (1500-4000)	Copper, gold, zinc, silver	$n \times 10^0$ – $n \times 10^5$

Co-rich ferromanganese crusts

Crust on the deck	**Crusts on the slope of the seamount**
	

Co-rich ferromanganese crusts – General data

- 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

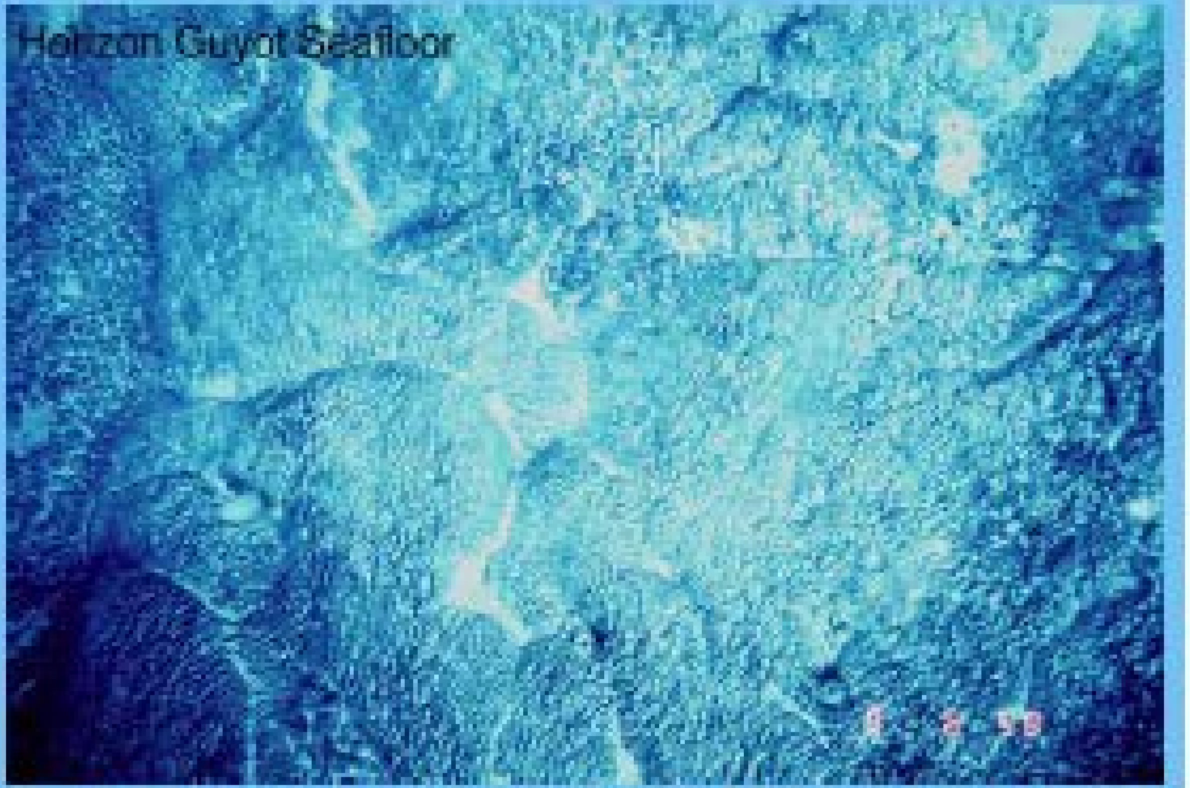


Hein, 2013

Global distribution & Geological setting

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

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Global Distribution of Large Seamounts

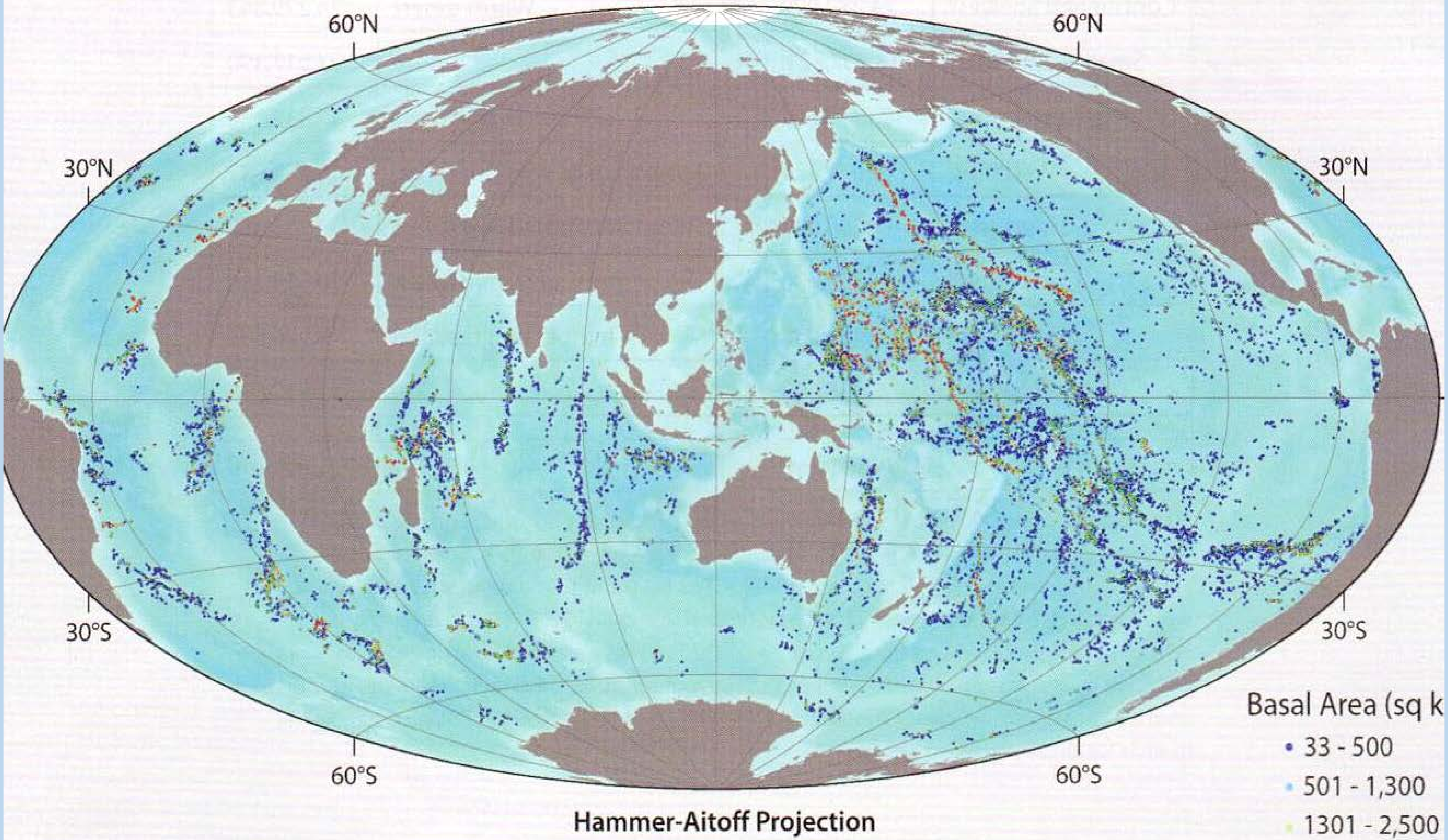
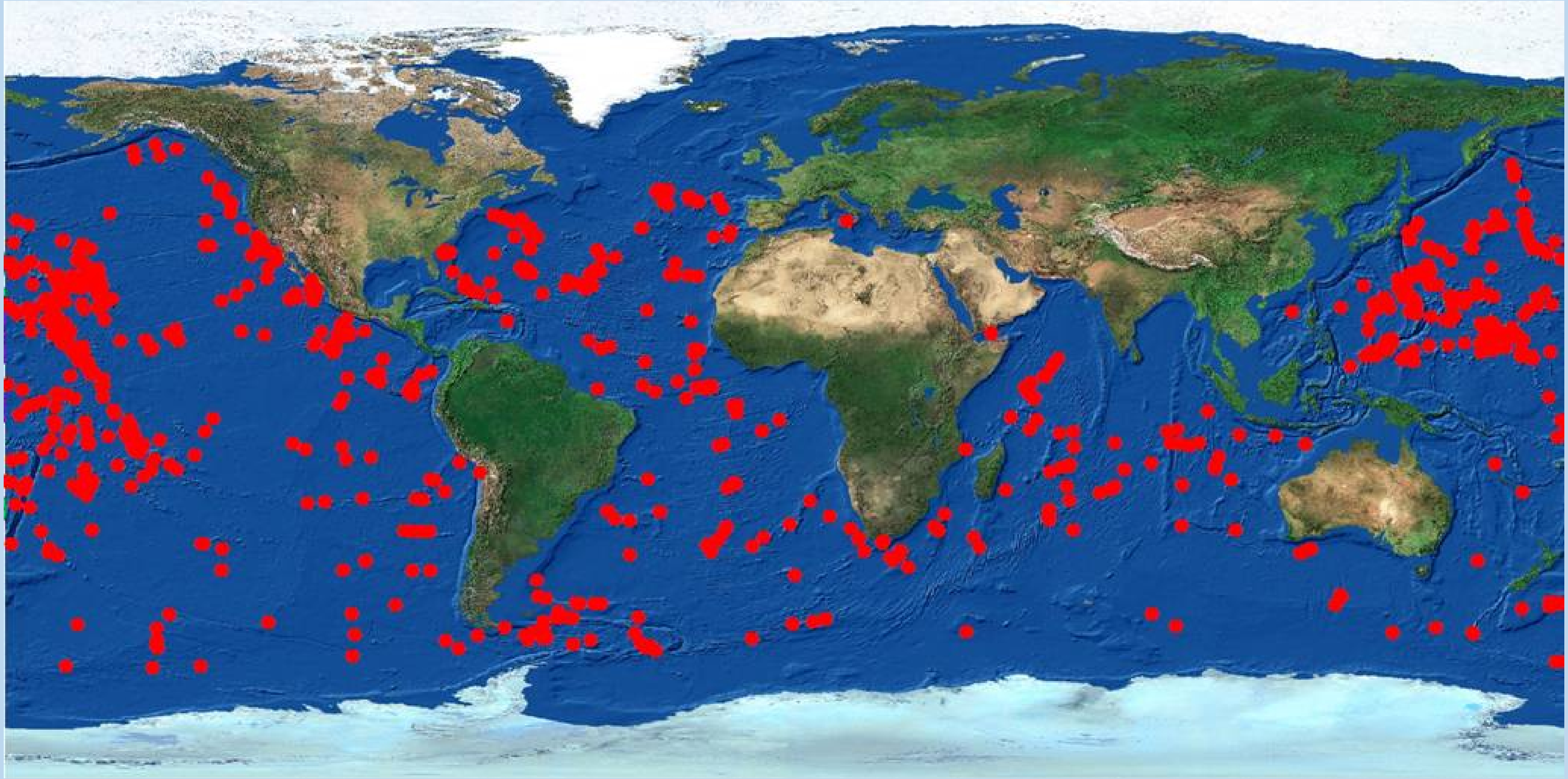


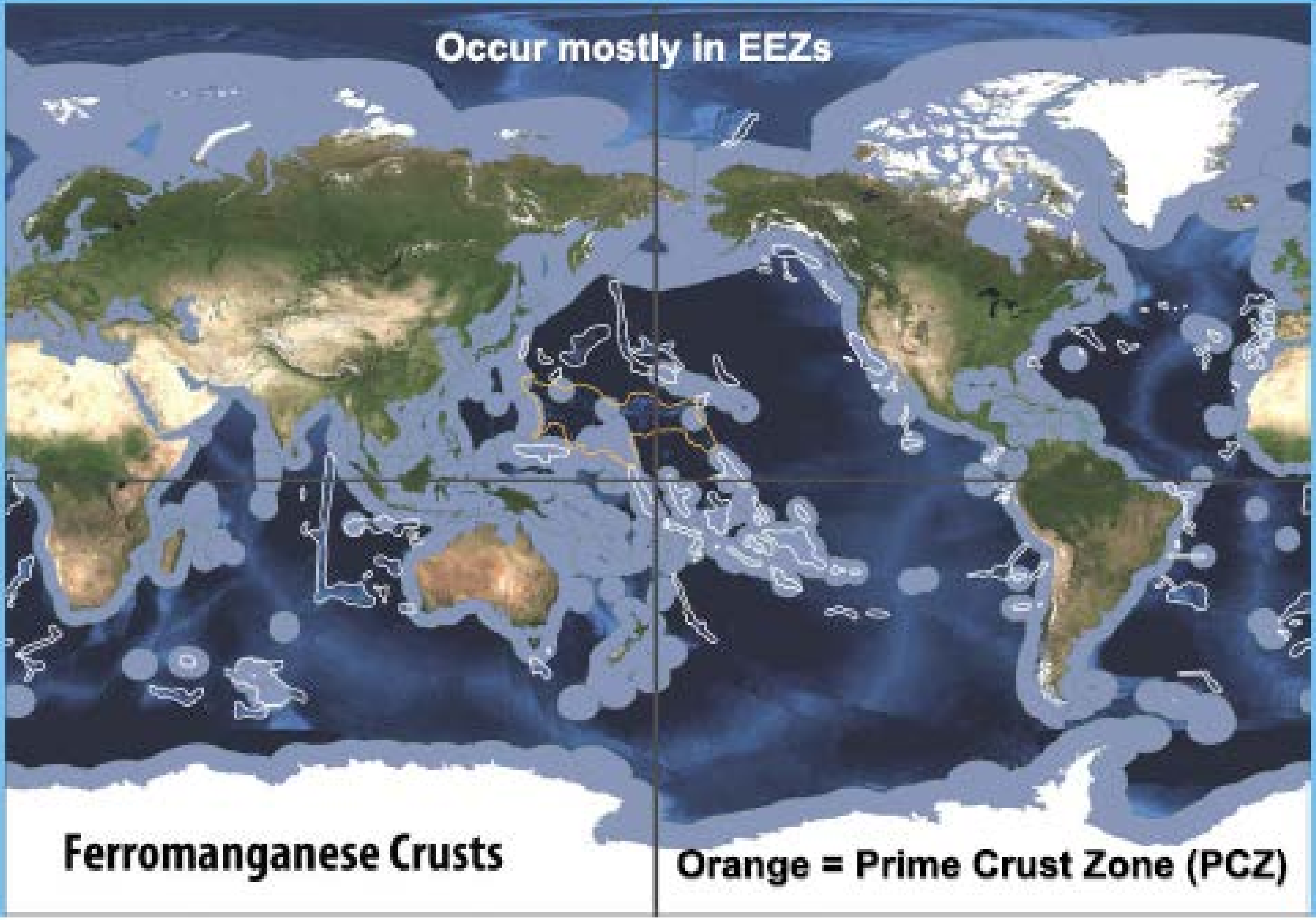
Figure 1. Global equal-area map of 11,880 recognized seamounts with ≥ 1000 m vertical relief (Wessel, 2001).

Cobalt-Rich Crusts – Sampling Locations
ISA Central Data Repository

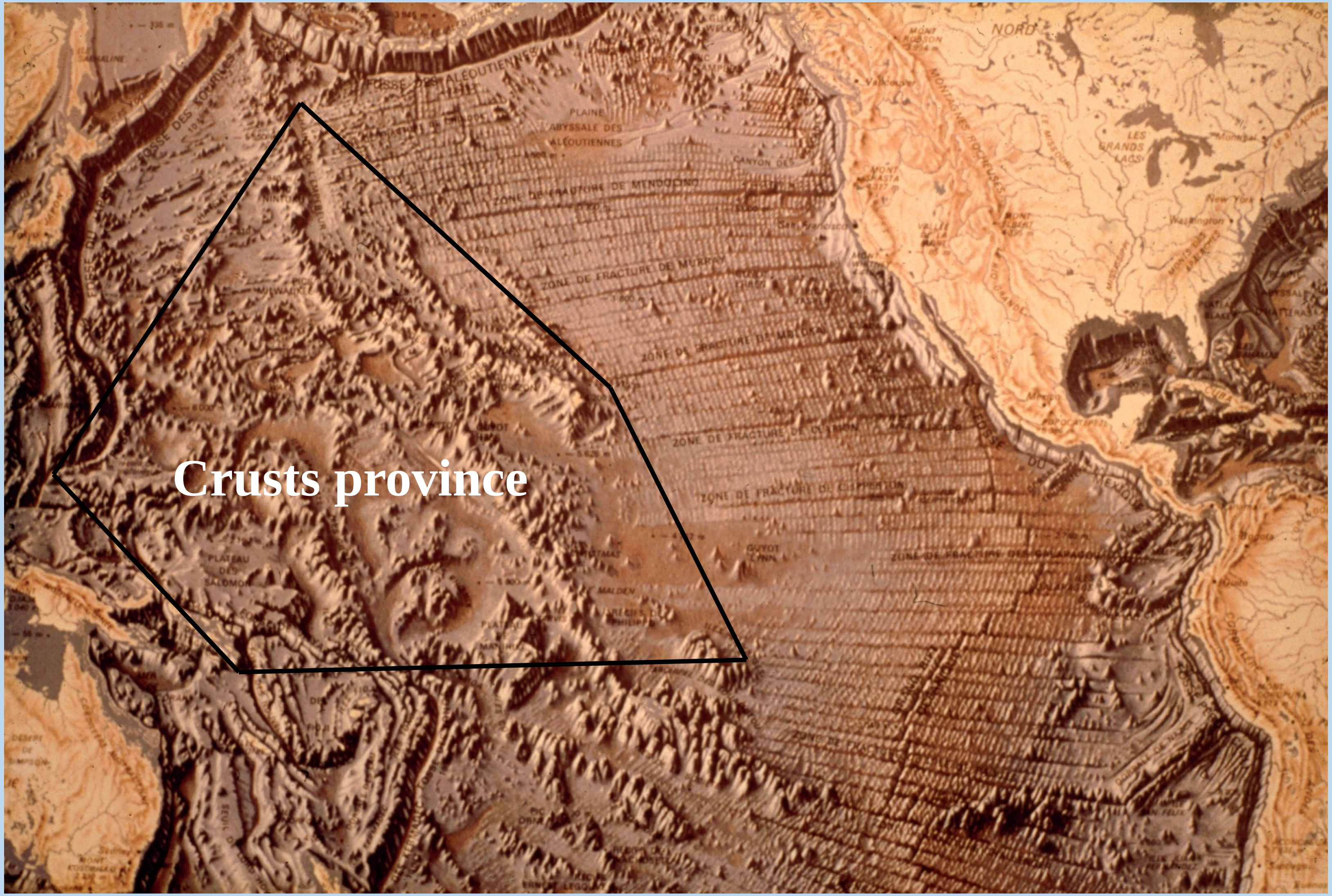


Global Permissive Areas for Ferromanganese Crusts

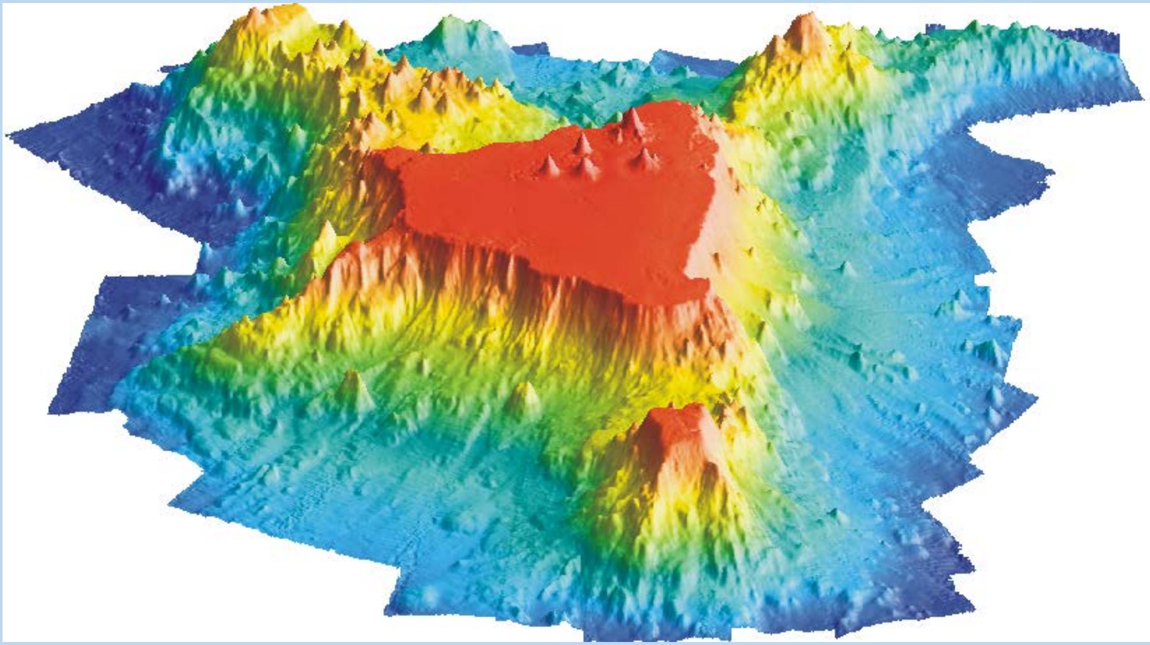
(From Hein et al., 2013)



Seamounts at Western Pacific – main province of crusts distribution

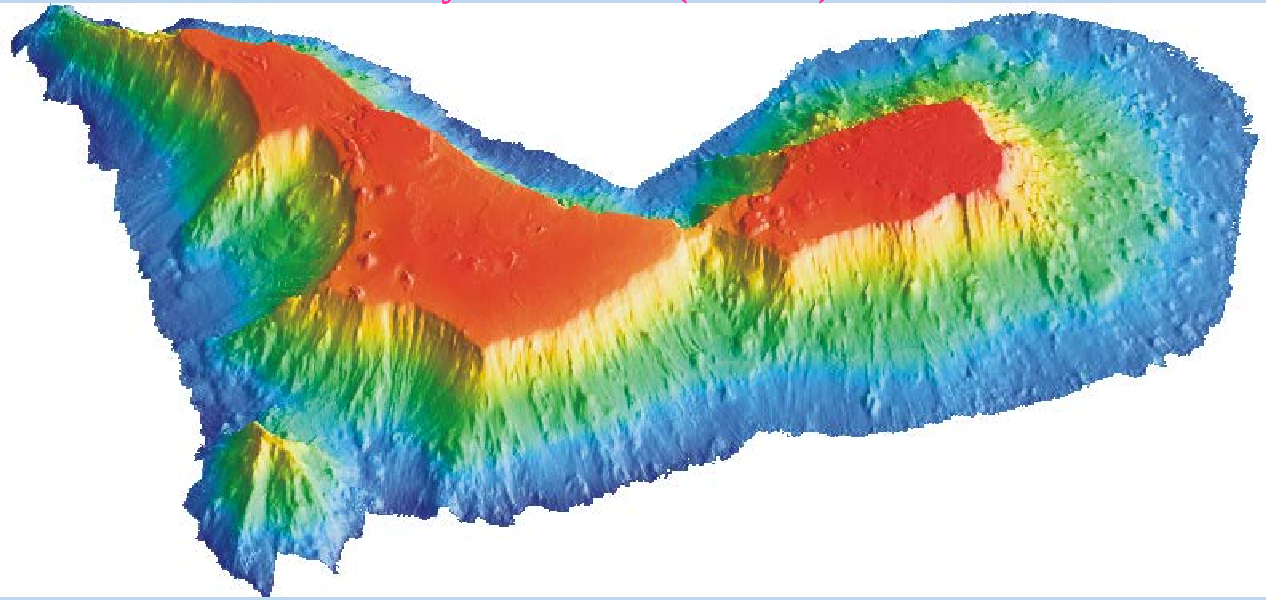


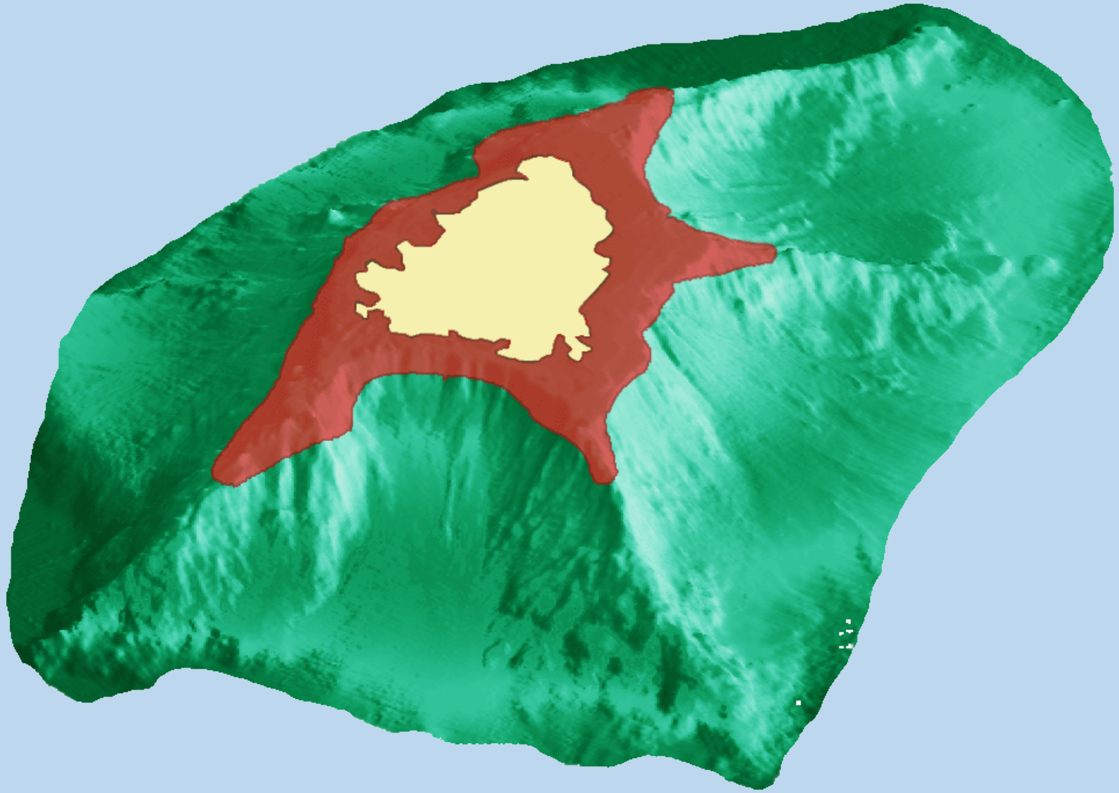
Guyot «Dalmorgeologia» (MA-15)



Flat summit seamounts (Guyots) – substrate for the Co-rich crusts

Guyot «IOAN» (MG-35)





Gramberg Guyot with Co-rich crusts deposits (Magellan smts, Western Pacific)

Morphology & Formation

Typical botryoidal surface of the crust

Large crust sample (diameter ~ 40 cm) with typical botryoidal/knotty surface texture

Current polished surface of the crust

Current polished (originally – botryoidal) crust surface

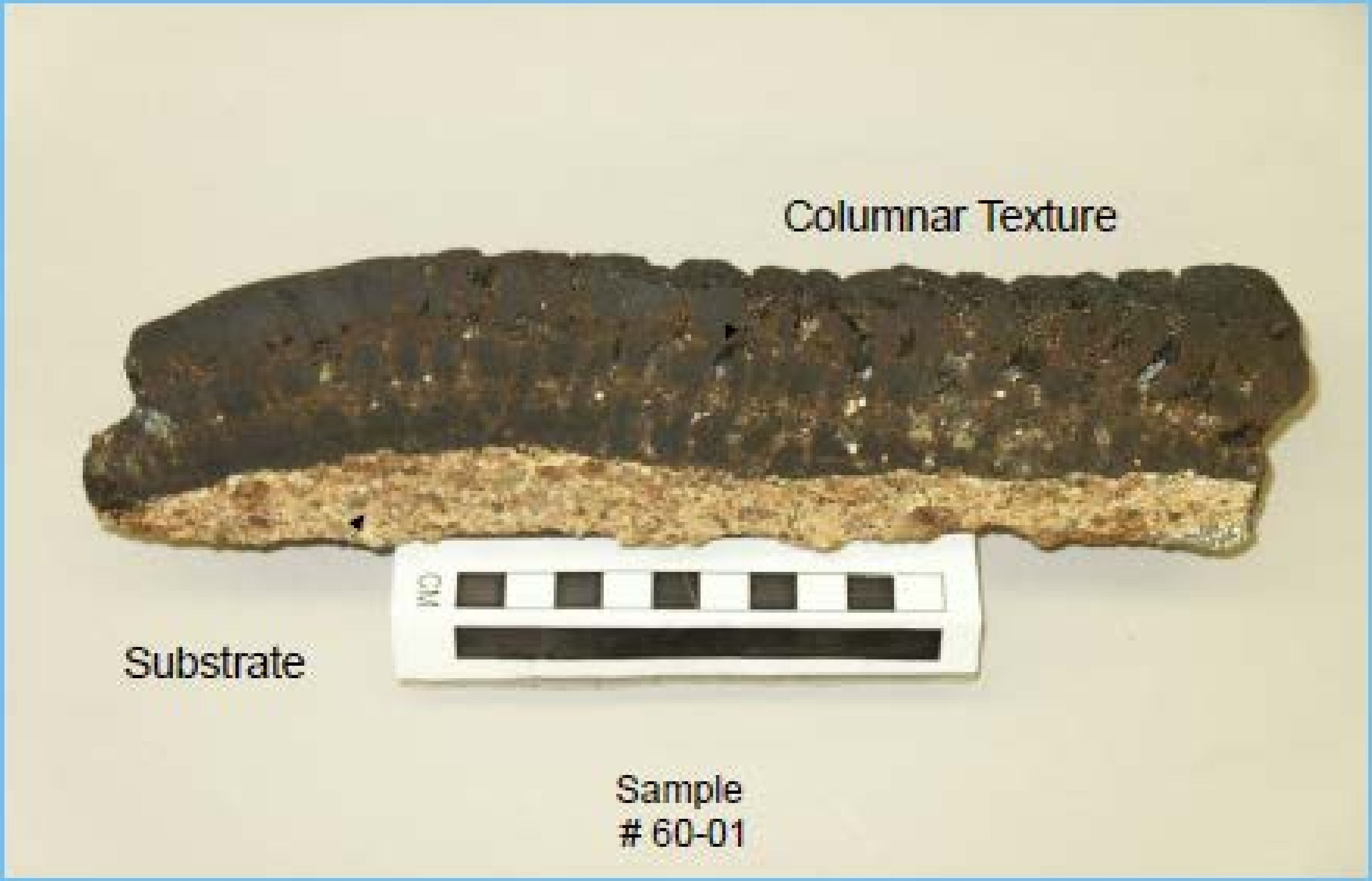
Crusts in Cross-Cut Sections

Cobalt-rich manganese crust covering a hyaloclastic substrate rock; thickness of the crust about 8 cm; sample from a seamount slope in the Central Pacific Basin

Co-rich manganese crust covering a hyaloclastic substrate rock; thickness of the crust about 7 cm; two apatite- filled cracks crosscut the substrate rock and the older crust generation. Sample from the Central Pacific.

Co-rich manganese crust from the Central Pacific. The crust layer covers a substrate rock consisting of a basaltic breccia cemented by carbonate-fluorapatite.

Sample from the Tropic Seamount (tropical east Atlantic) with a Co-rich manganese crust layer of about 4 cm thickness covering a layer consisting almost of pure carbonate-fluorapatite (Oligocene to Middle Miocene age).



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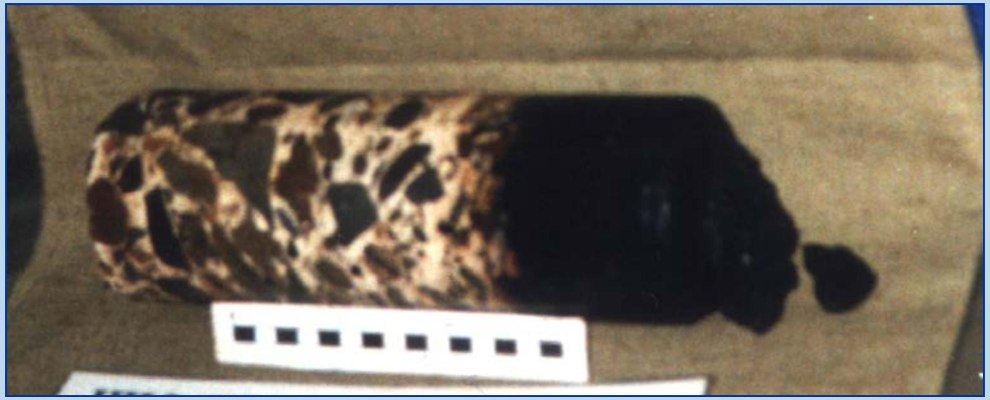
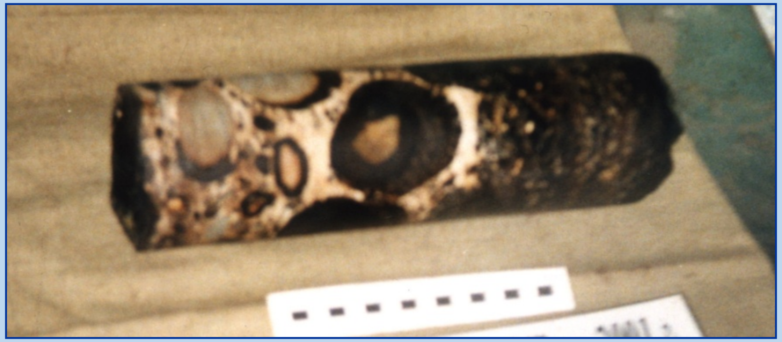
0 2 4 6 8 10

Two halfs of a crust sample with 7 cm thickness. The hyaloclastic substrate rock is pervaded by apatite-filled crack.

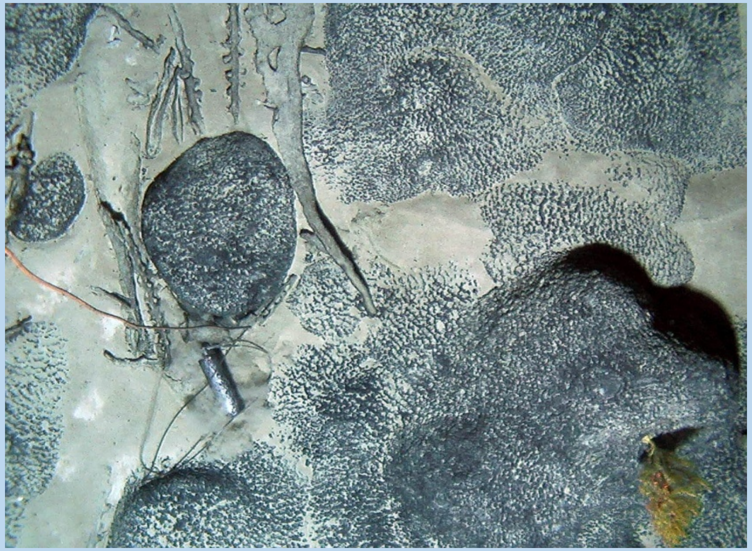
Large crust recovered near Marshall Islands

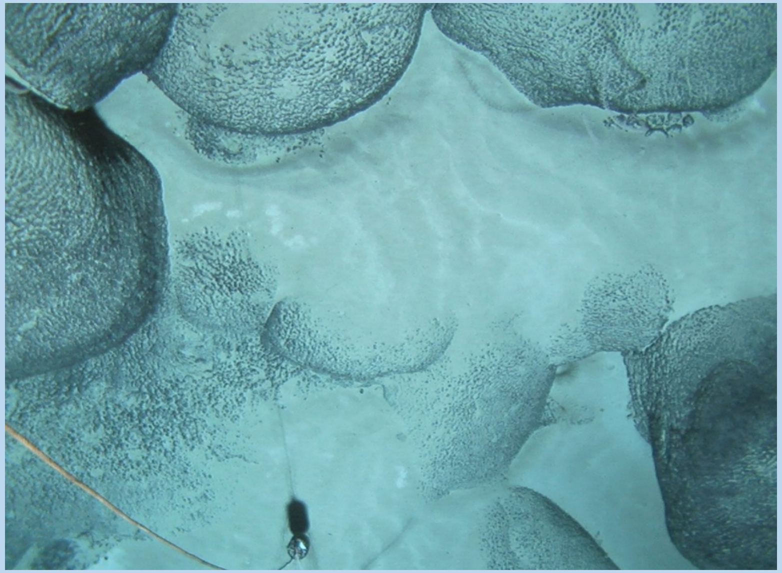
Shallow drilling Cores of crusts

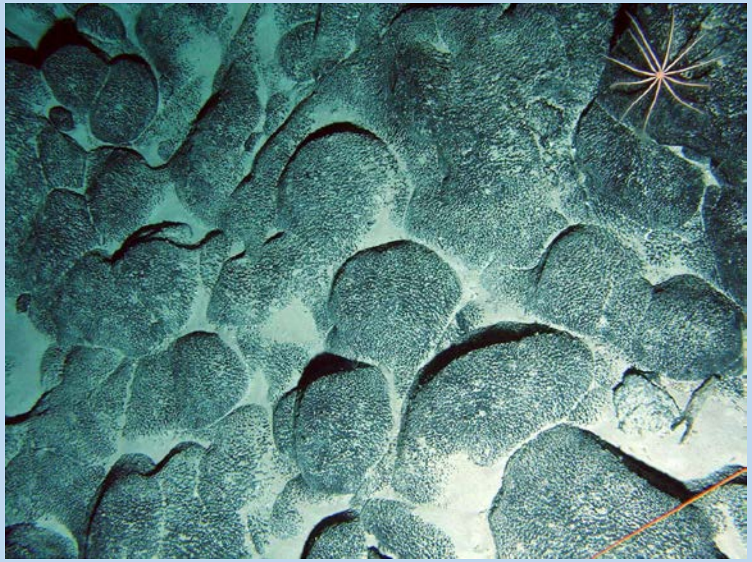


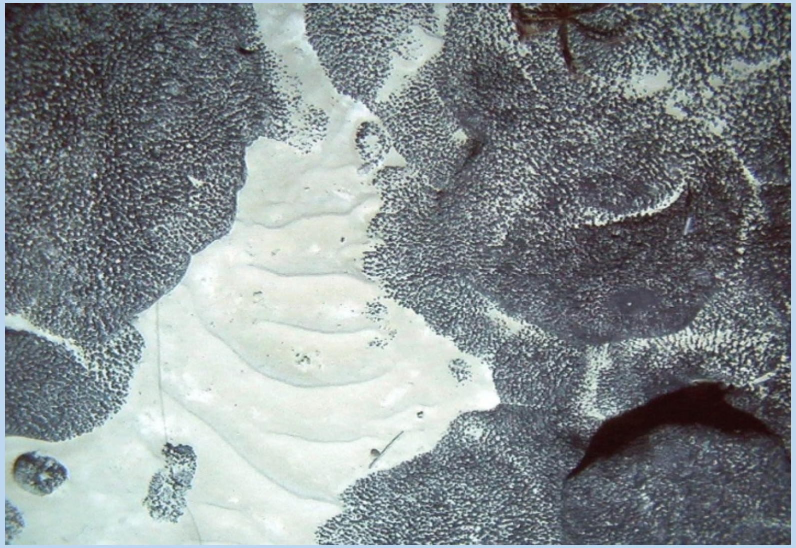


Underwater photos of crusts

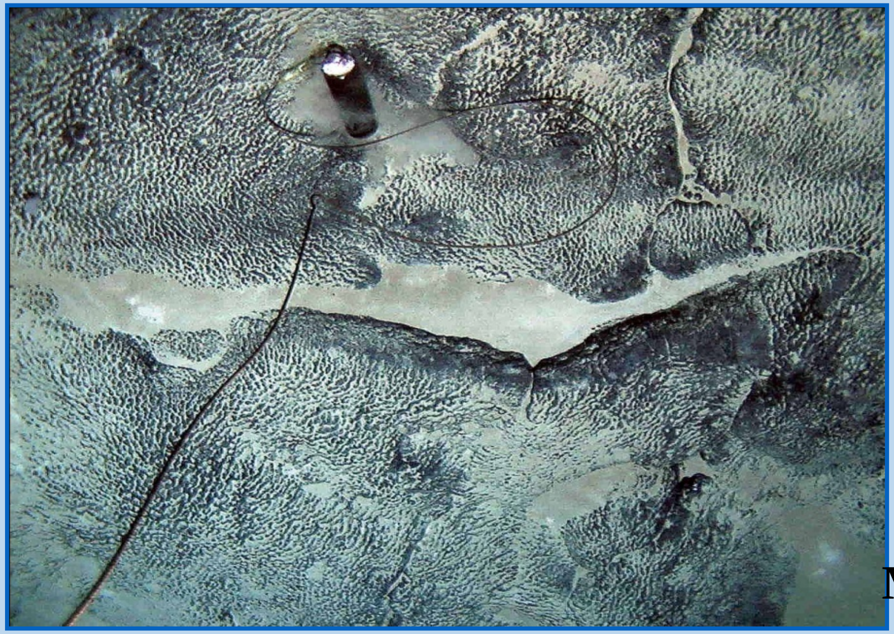






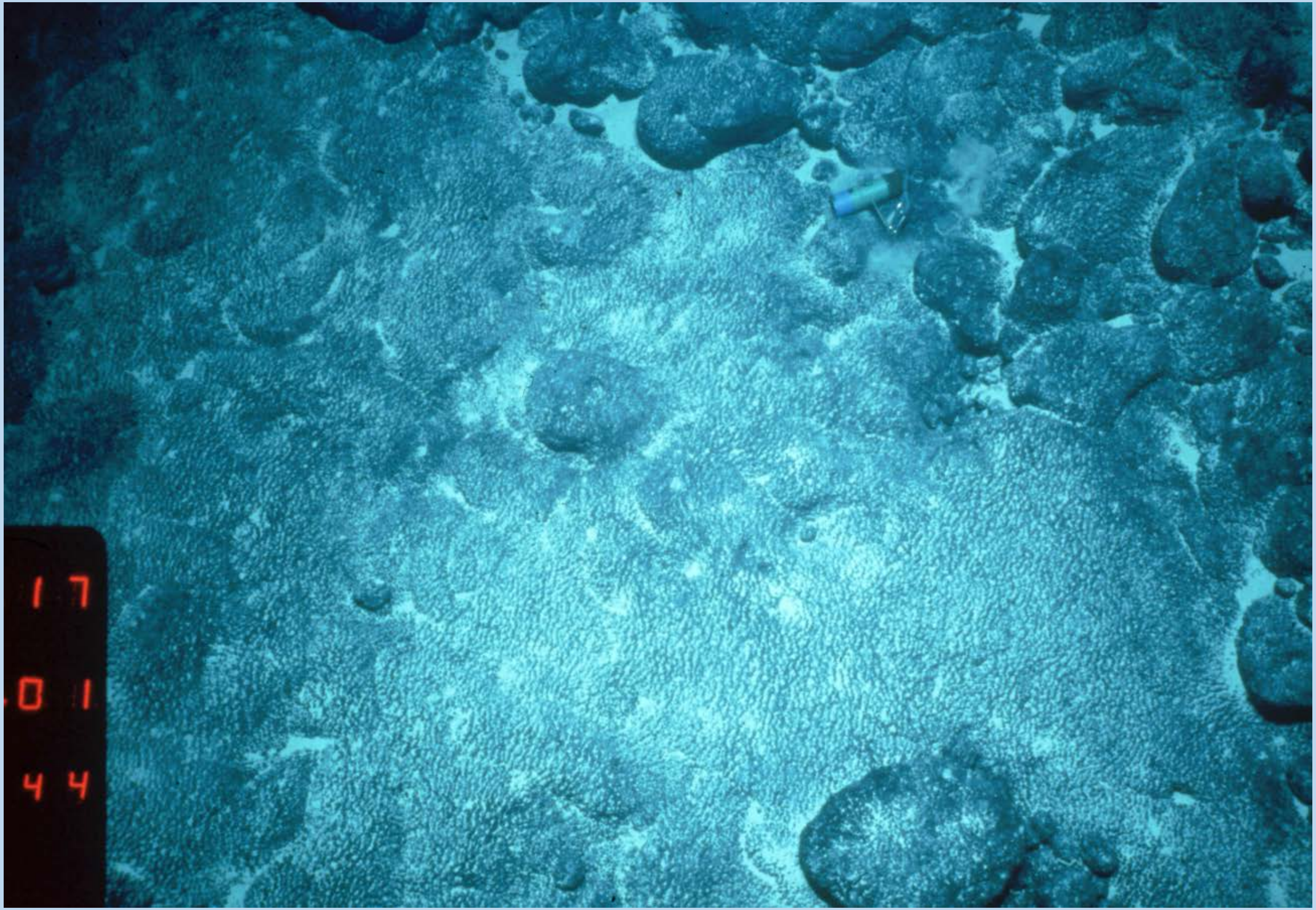


Melnikov, 2010



Melnikov, 2010

Melnikov, 2010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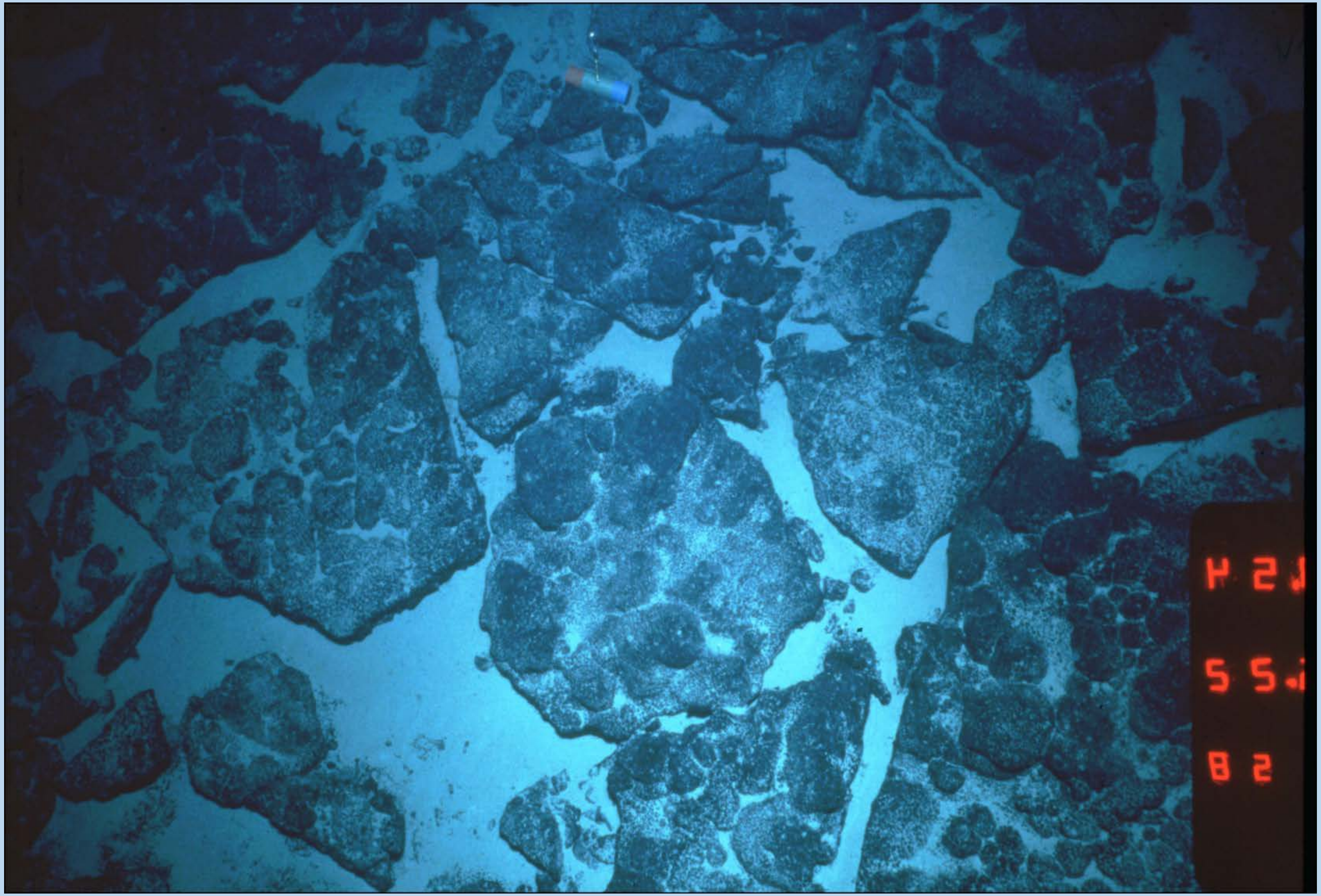
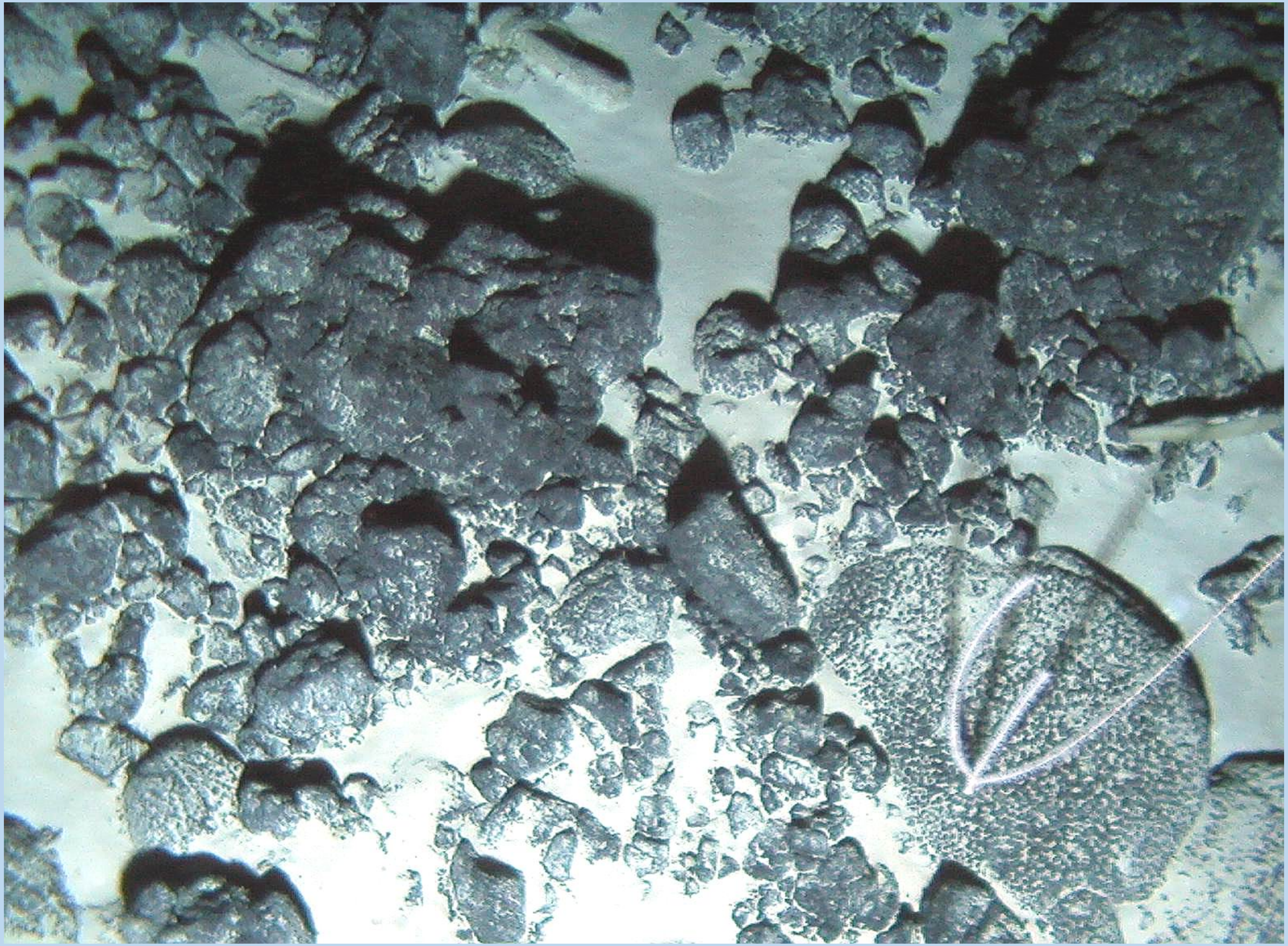
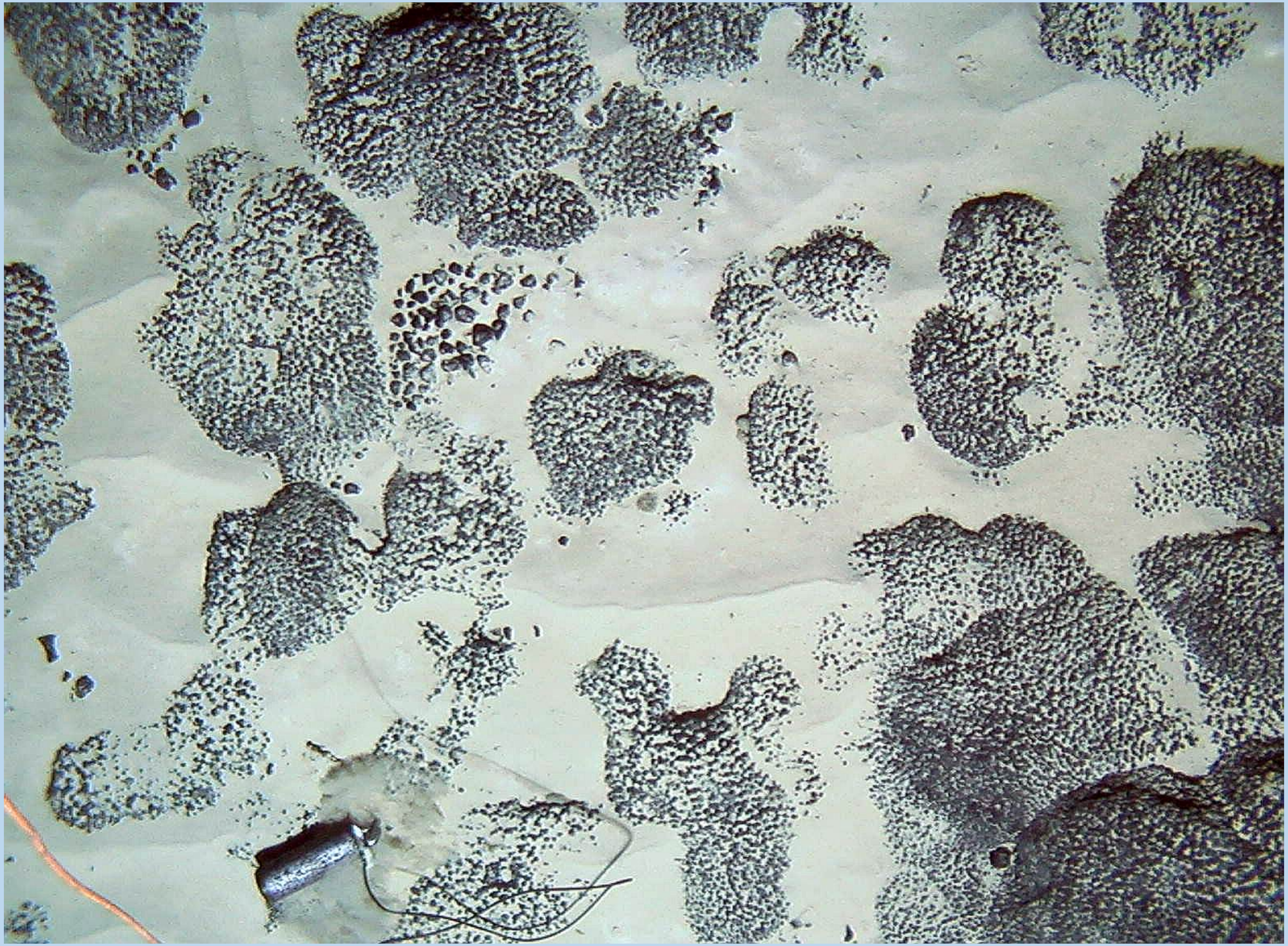
Crusts with sediments

Broken crusts and crust slabs formation

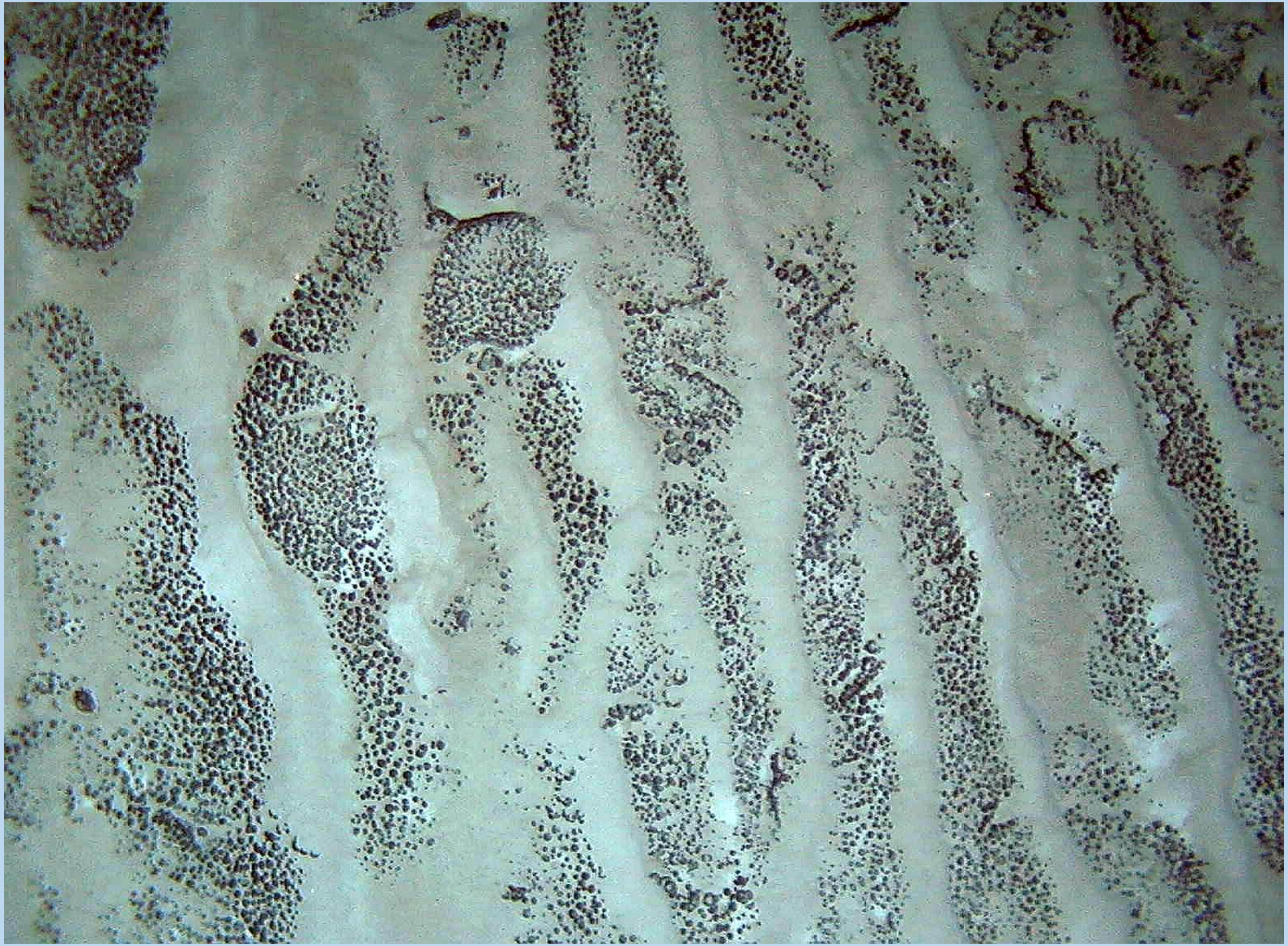




Melnikov, 2010

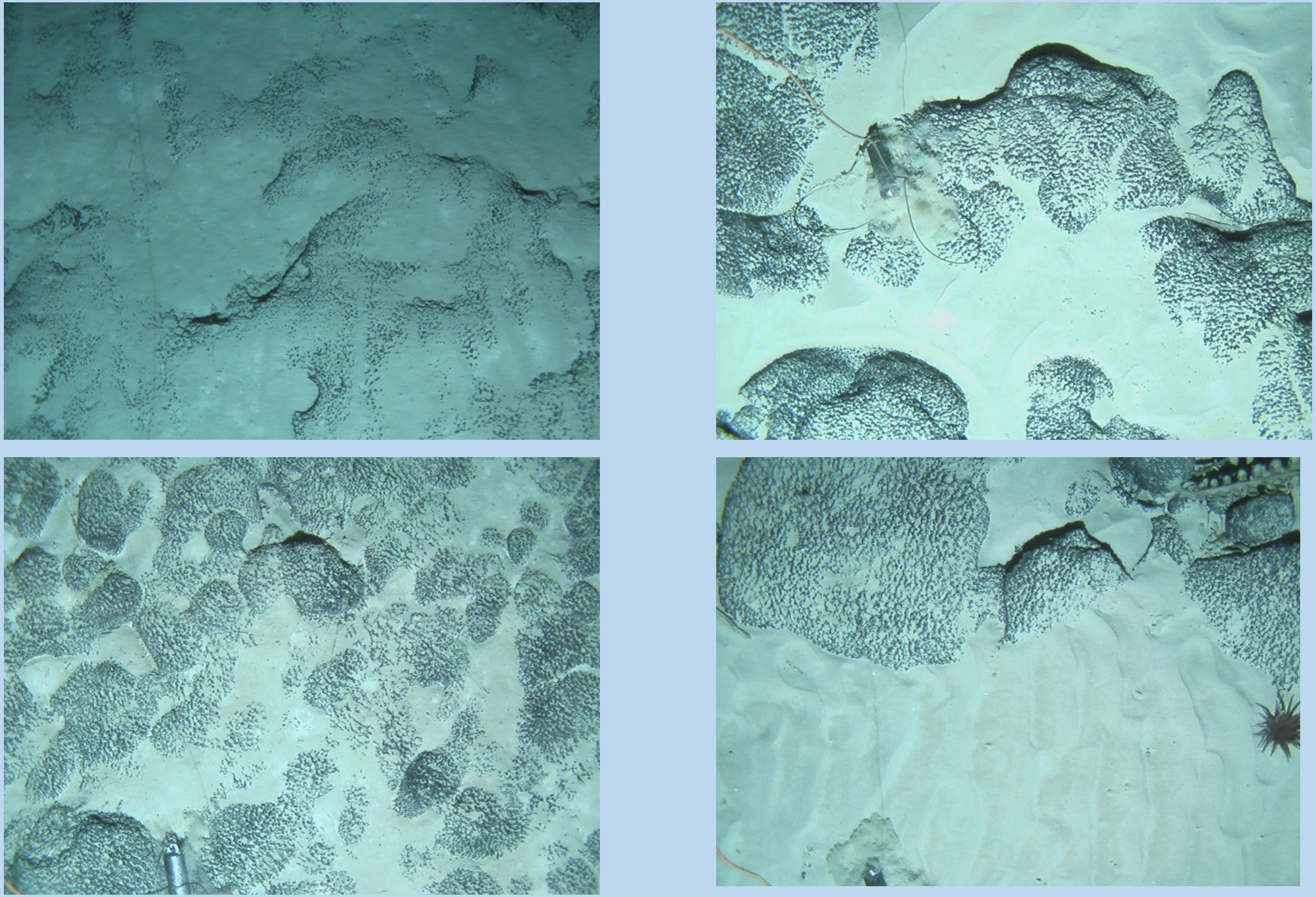


Melnikov, 2010



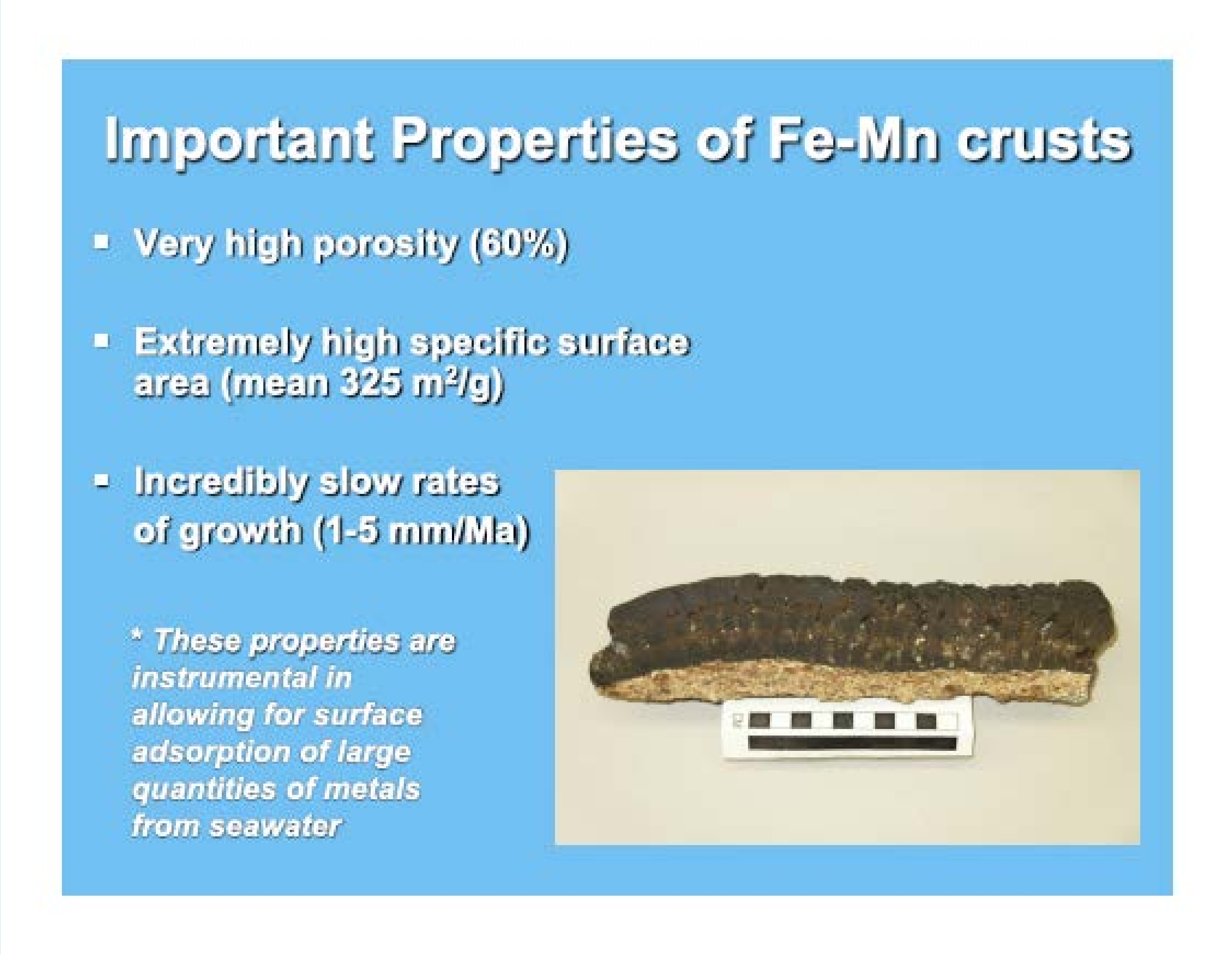
Melnikov, 2010

Various degrees of dusting of crusts by unconsolidated sediments



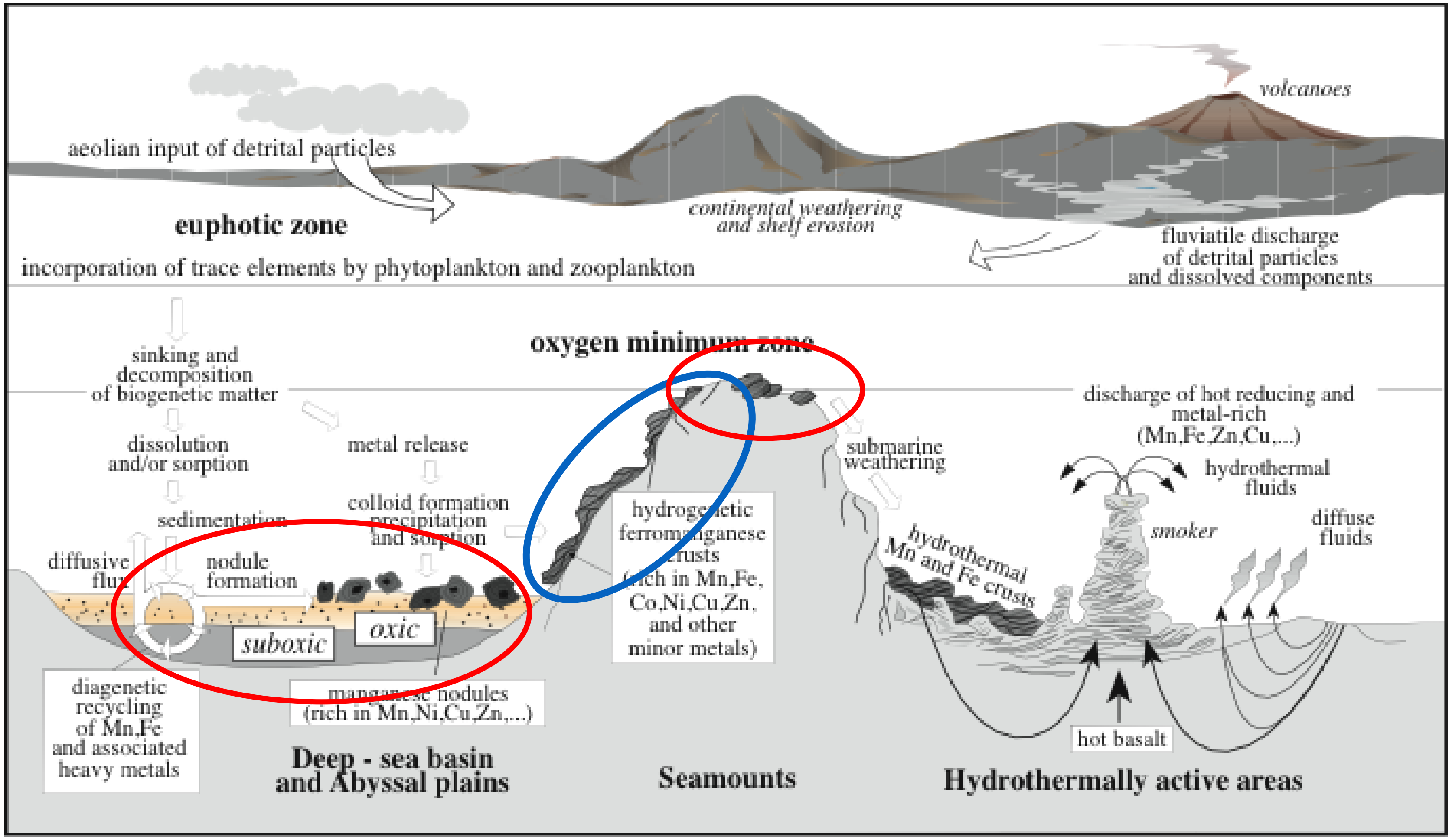
Melnikov, 2010

Crusts and nodules


Important Properties of Fe-Mn crusts
Very high porosity (60%)
Extremely high specific surface area (mean 325 m²/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

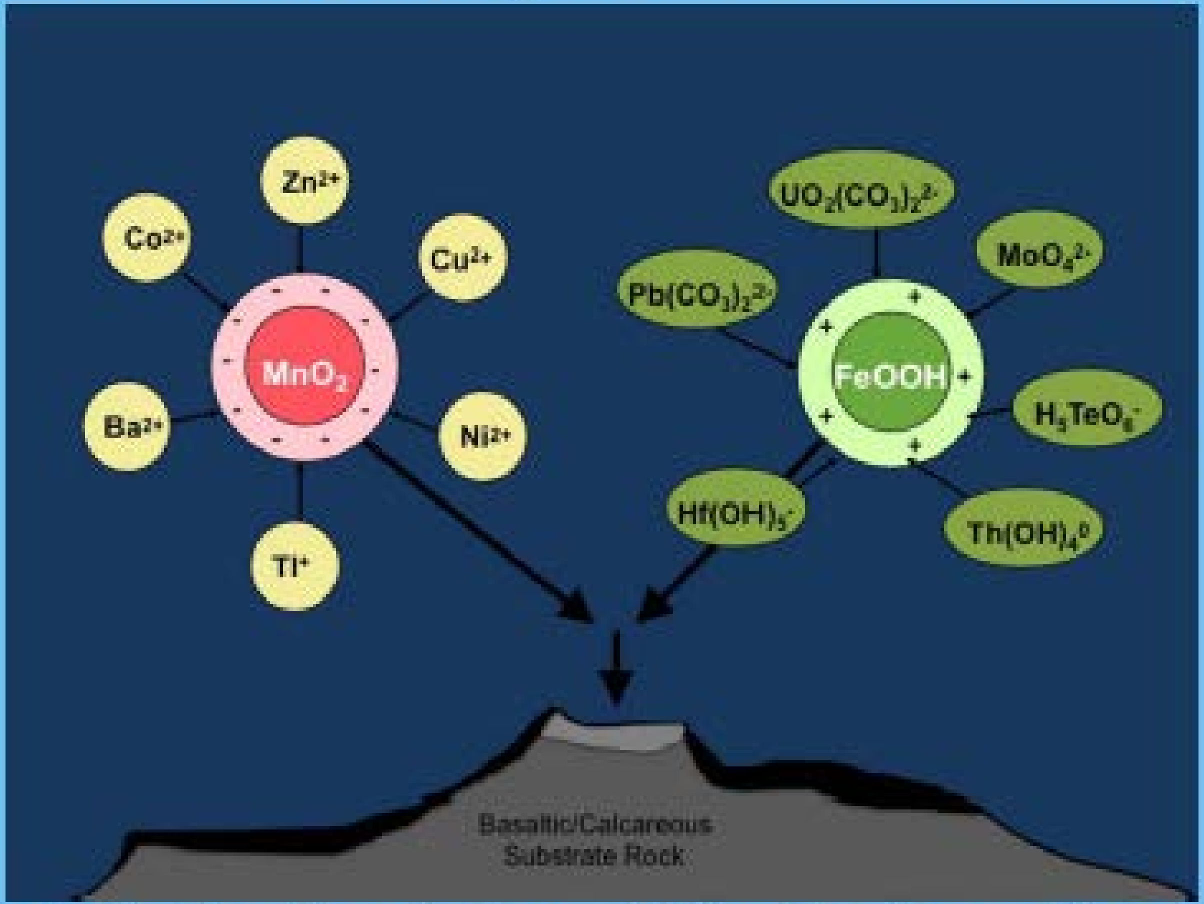
Hein, 2013

Mechanism of marine minerals formation



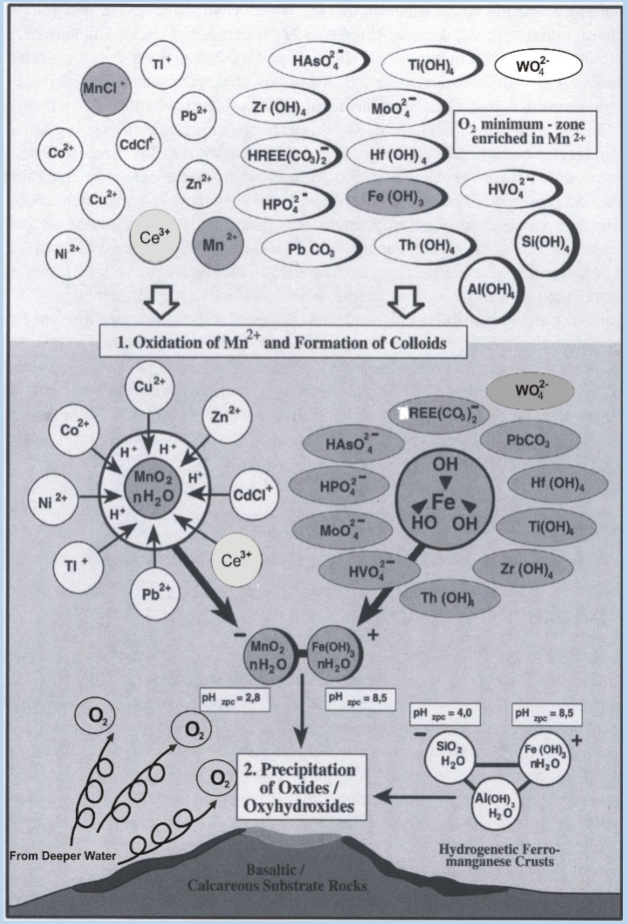
Nodules are mostly found in the deep-sea basins and on abyssal planes, while **ferromanganese crusts** cover the sediment-free slopes of seamounts. Presented are sources and sinks for heavy metals and processes controlling the formation of these deposits.

Crust Formation Begins in the Water Column

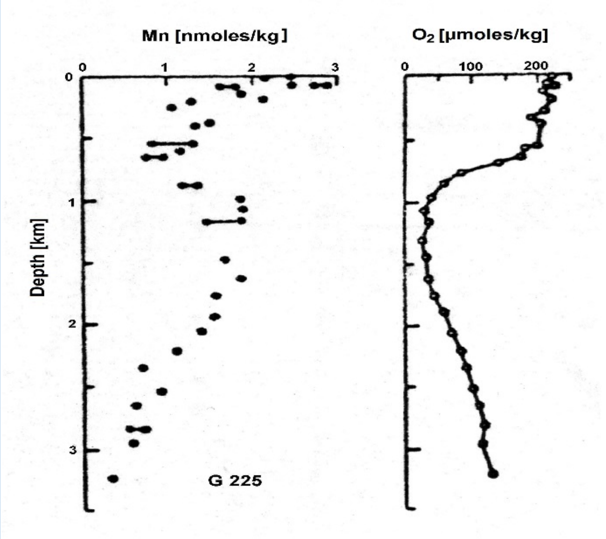


Simplified electrochemical model for the formation of Fe-Mn crusts by adsorption of trace metals on colloidal Mn oxide and Fe oxyhydroxide (From Hein et al. 2013)

The process of hydrogenetic precipitation is basically an inorganic colloidal-chemical and surface-chemical mechanism. Elements in seawater may occur as dissolved hydrated ions or as inorganic as well as organic complexes which in general have either a positive or a negative surface charge depending on the pH of the respective aqueous environment. These complexes form hydrated colloids that interact with each other and with other dissolved hydrous metal ions.



Colloidal-chemical model for formation of hydrogenetic crusts showing the probable hydrated cations, anion complexes and colloidal phases in seawater, adsorption of metals, the pH of the zero point of charge (zpc) and the precipitation of hydrated oxides on substrate rocks (modified from Koschinsky A. and Halbach P., 1995). Dissolved oxygen (O_2) is supplied from deeper water by turbulent eddy diffusion.



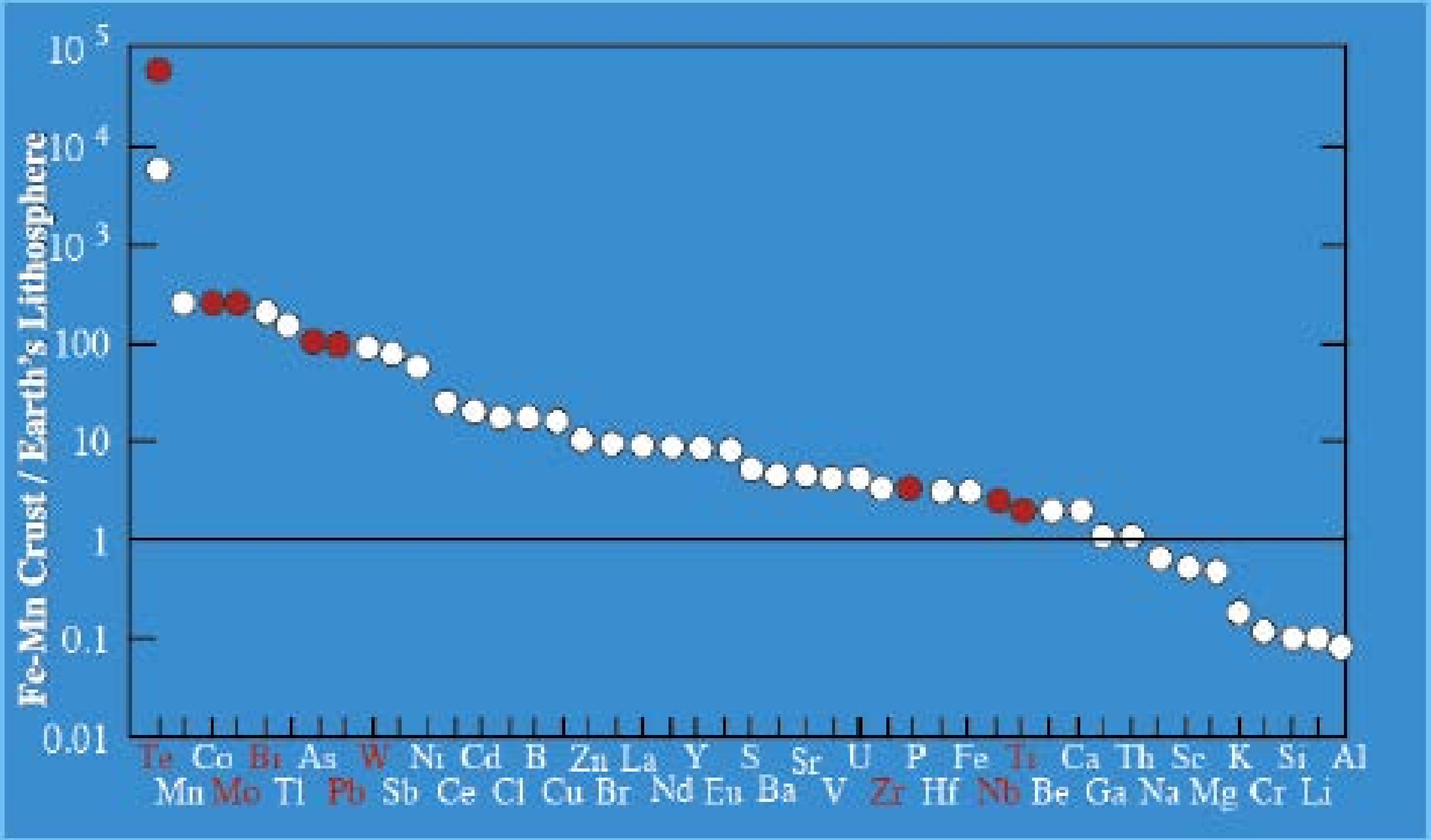
Mineralogy, Metal grades and Age

Fe-Mn Crust Mineralogy

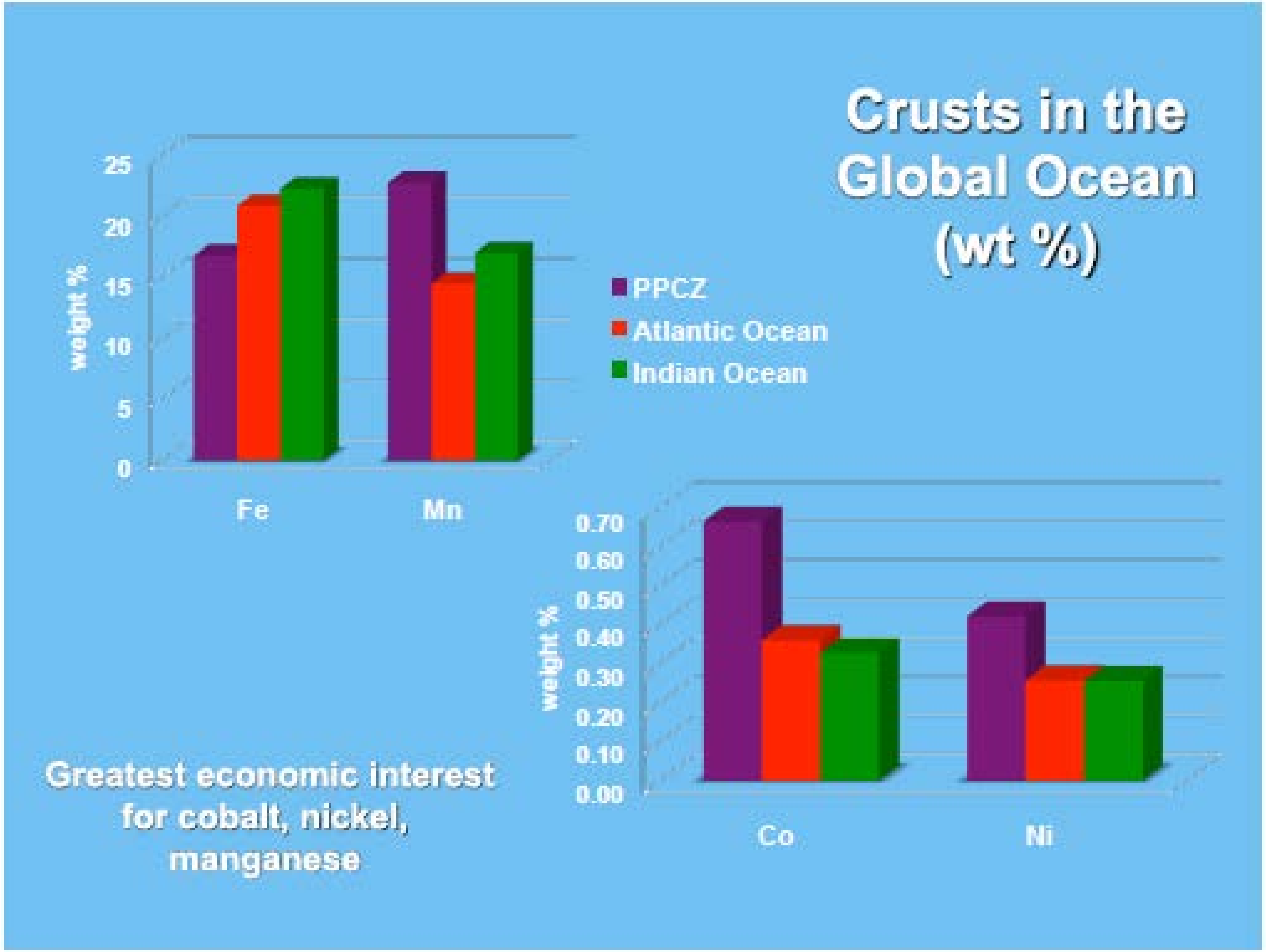
- δ-MnO_2
- X-ray amorphous Fe oxyhydroxide: $FeO(OH)$
- Carbonate fluorapatite (CFA)
- Minor detrital/eolian silica & aluminosilicates
- Minor biogenic debris, opal and calcite

Melnikov, 2010

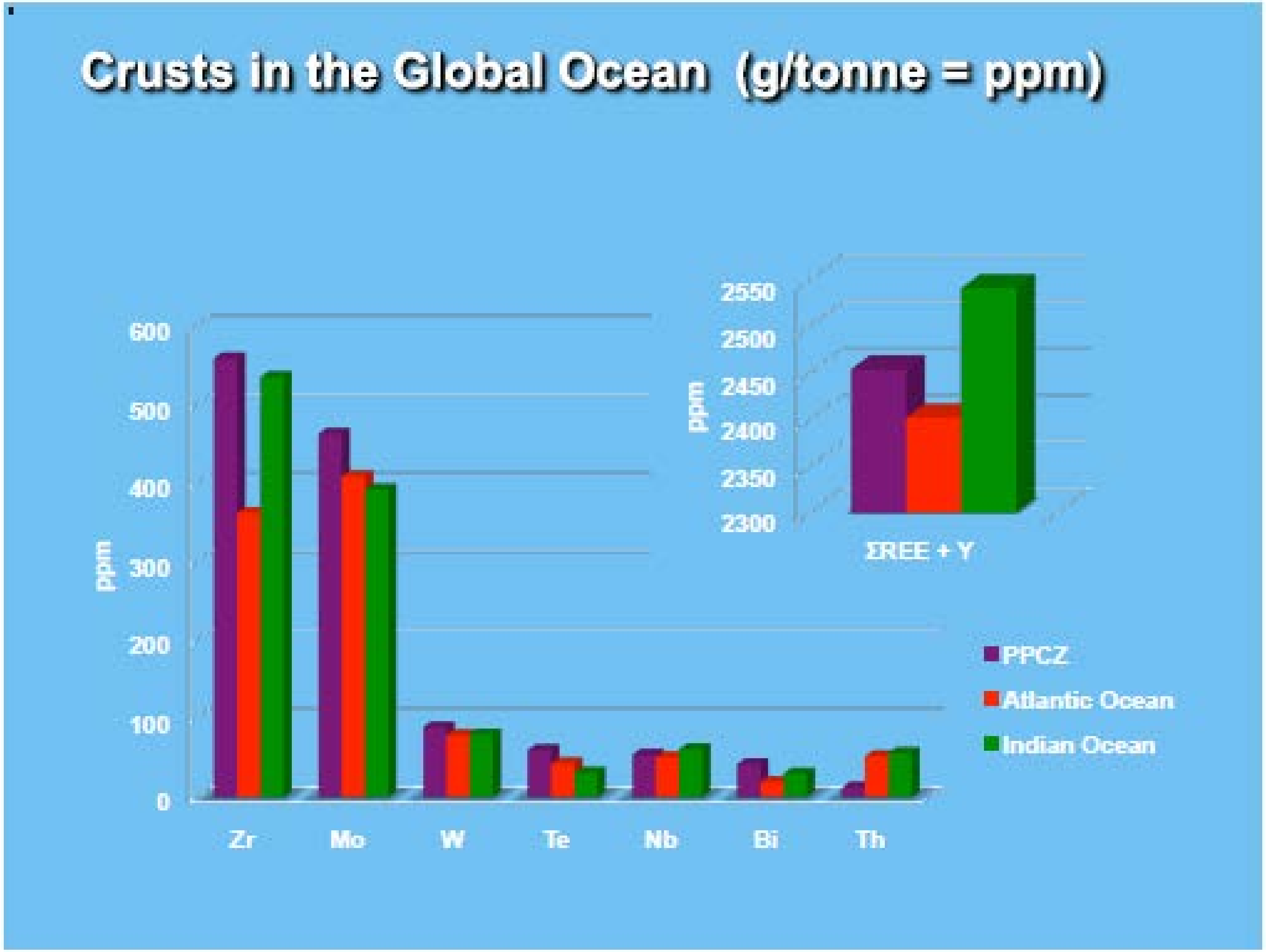
Element Enrichment in Fe-Mn Crusts relative to the Earth's Lithosphere



From Hein et al. (2003)

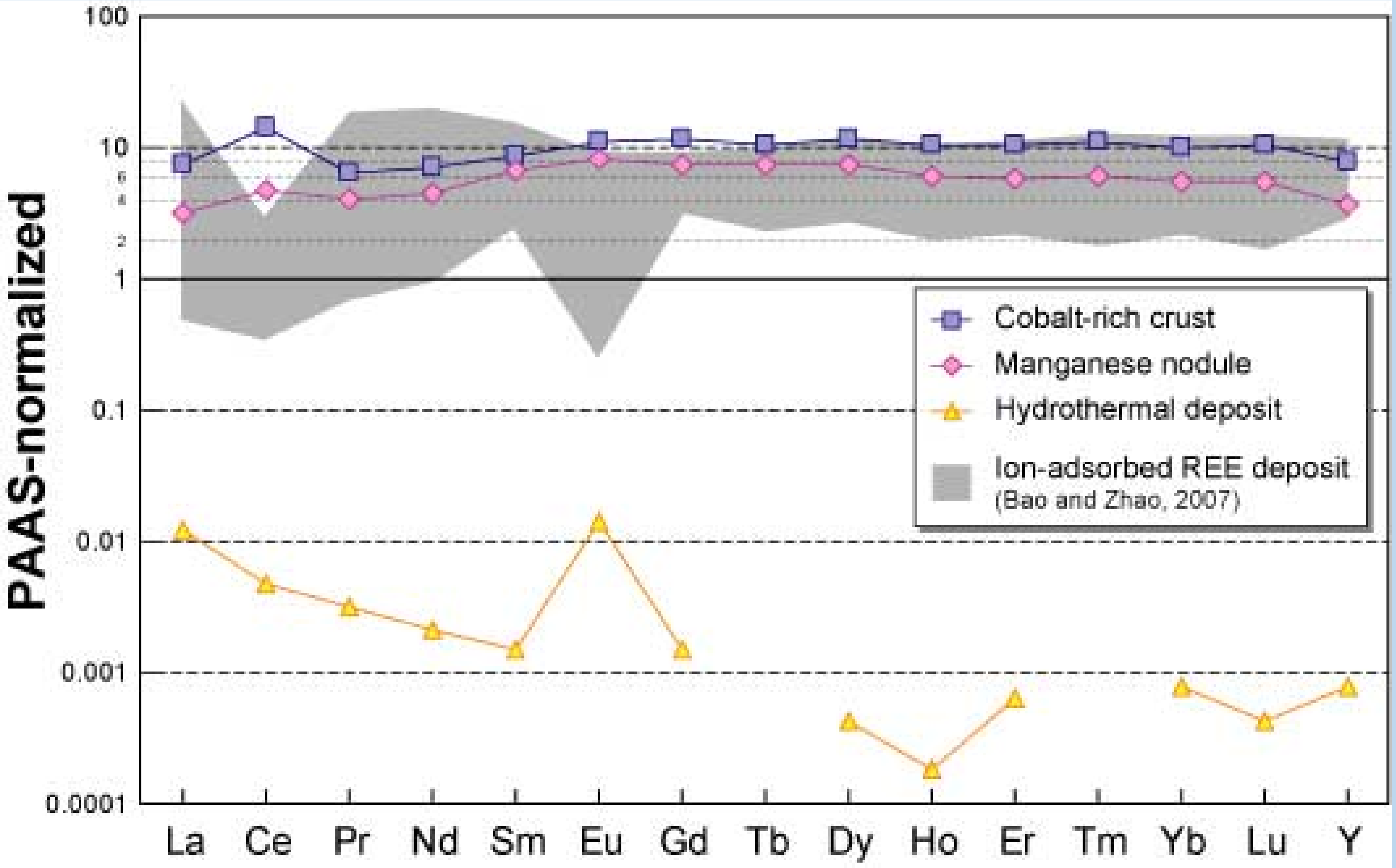


Melnikov, 2010



Melnikov, 2010

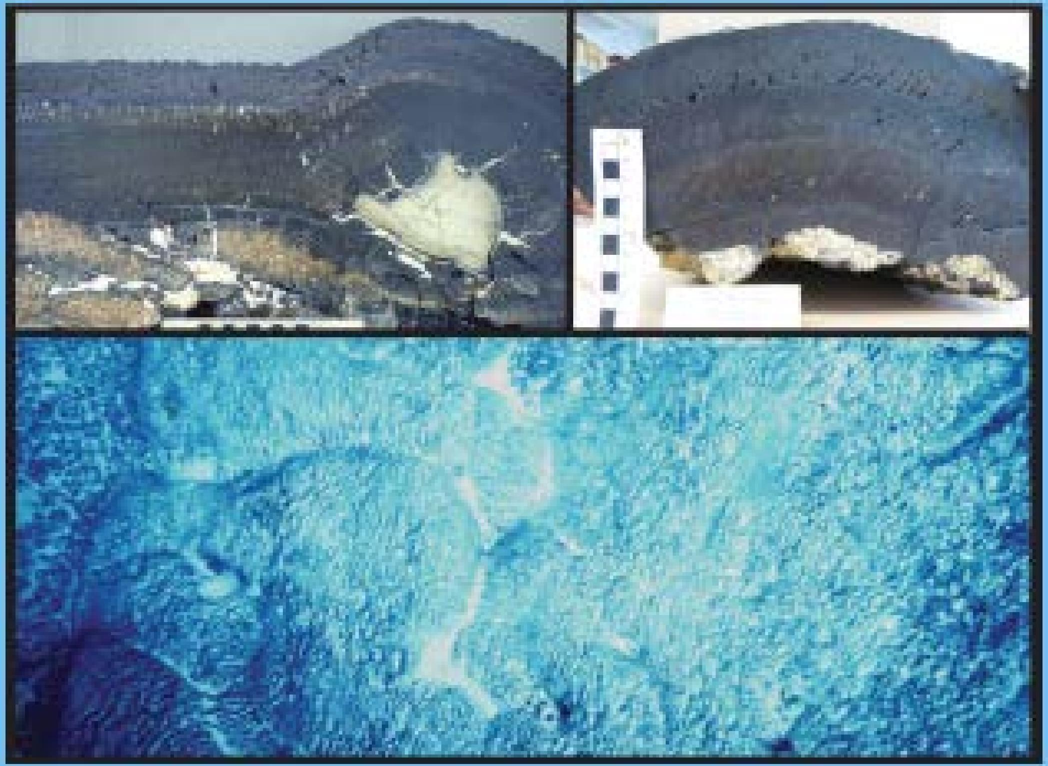
Contents of REE in CRC are equivalent with the ones on-land deposits in China under mining operation.



Source: Awaji, S., personal communication (2009)

Rare Metals in Ferromanganese Crusts As Potential Byproducts

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

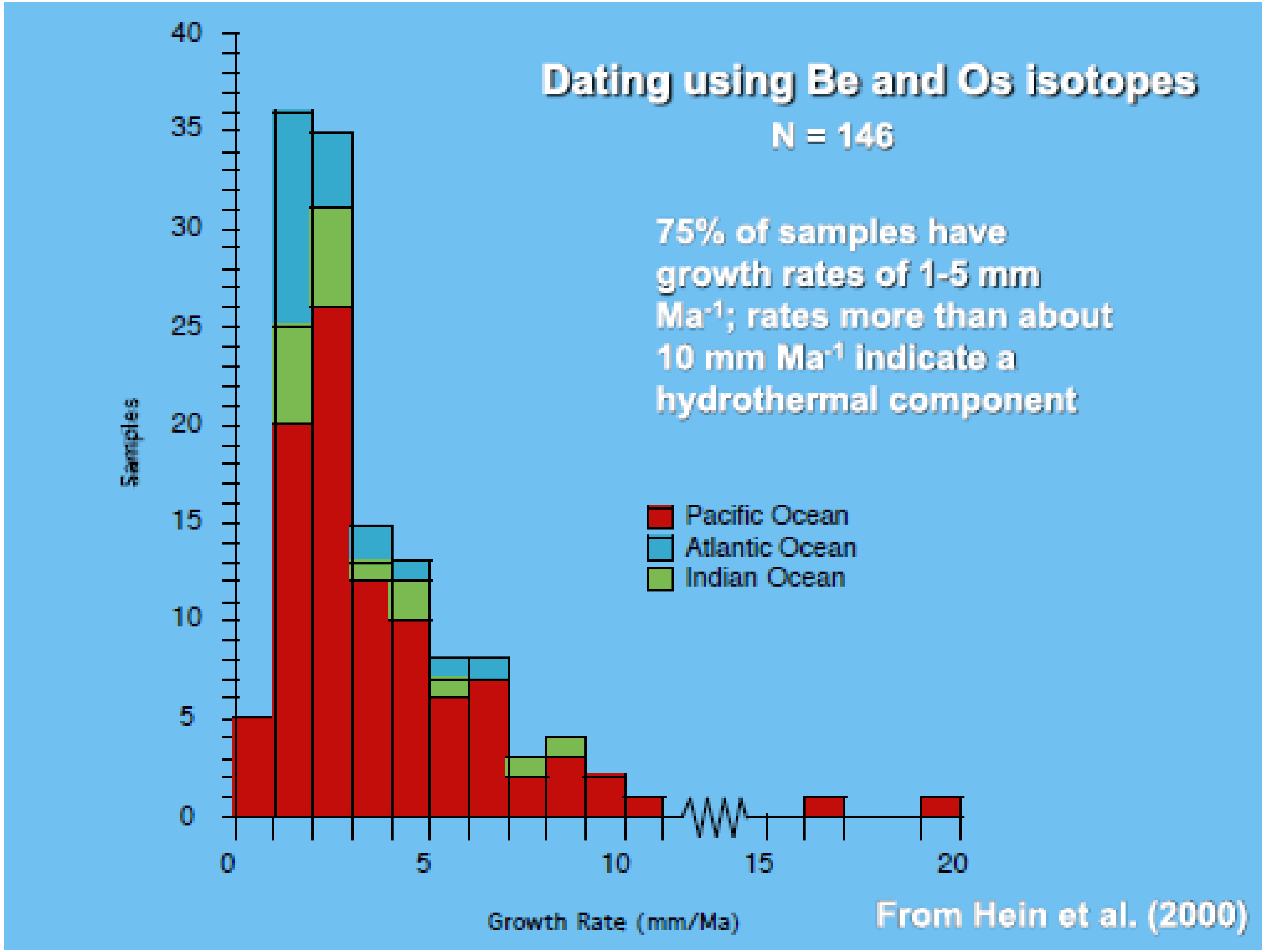


From Hein et al. (2013)

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

Melnikov, 2010



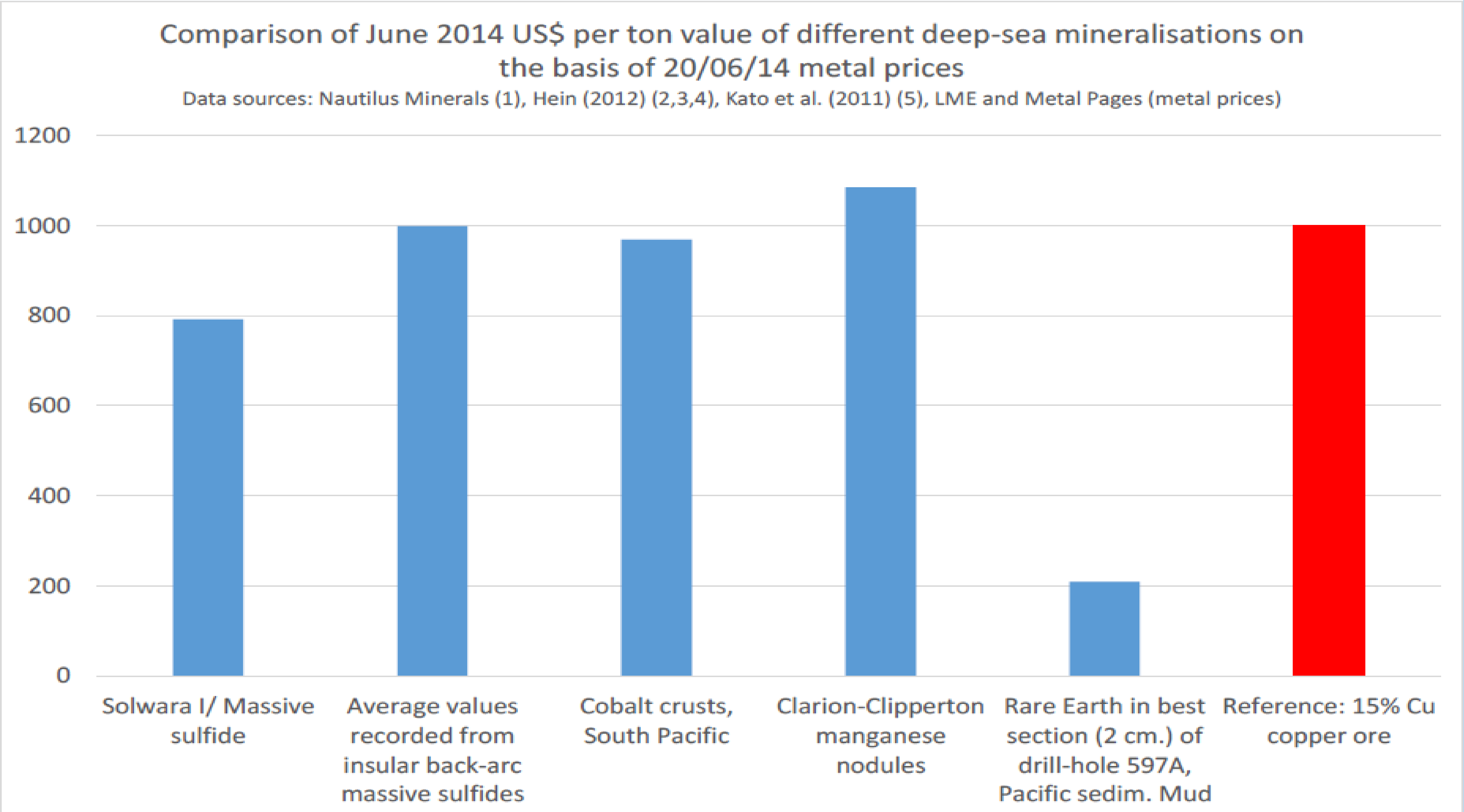
Dating using Be and Os isotopes
N = 146
75% of samples have growth rates of 1-5 mm Ma-1; rates more than about 10 mm Ma-1 indicate a hydrothermal component
Pacific Ocean
Atlantic Ocean
Indian Ocean
Samples
40
35
30
25
20
15
10
5
0
0
5
10
15
20
Growth Rate (mm/Ma)
From Hein et al. (2000)

Economical issues

Value of Metals in 1 Metric Ton of Fe-Mn Crust from the Central-Equatorial Pacific

	Mean Price of Metal (2007 $/kg)	Mean Content in Crusts (g/ton)	Value per Metric Ton of Ore ($)
Cobalt	$61.20	6899	$422.22
Cerium	$125.00	1605	$200.63
Titanium	$15.31	12,035	$184.26
Nickel	$36.32	4125	$149.82
Molybdenum	$73.41	445	$32.67
Platinum	$41,343.58	0.5	$20.67
Zirconium	$25.30	618	$15.64
Tellurium	$123.19	60	$7.39
Copper	$7.67	896	$6.87
Tungsten	$24.95	90.5	$2.26
Total	--	--	$1,042.42

Hein, 2007


Comparison of June 2014 US$ per ton value of different deep-sea mineralisations on the basis of 20/06/14 metal prices
Data sources: Nautilus Minerals (1), Hein (2012) (2,3,4), Kato et al. (2011) (5), LME and Metal Pages (metal prices)
1200
1000
800
600
400
200
0
Solwara I/ Massive sulfide
Average values recorded from insular back-arc massive sulfides
Cobalt crusts, South Pacific
Clarion-Clipperton manganese nodules
Rare Earth in best section (2 cm.) of drill-hole 597A, Pacific sedim. Mud
Reference: 15% Cu copper ore

Exploration methods

1. **Ship-borne investigations** provide the first step of exploration by producing a **high-resolution bathymetric seafloor map** with Multibeam Echosounder Systems in order to identify seamounts and to record the sizes and depths of slopes with their inclinations as well as platforms, ridges and intermediate terraces. In combination with **Parasound** (Sub-bottom Profiler) also the thickness of possible sediments can be measured.

2. After the bathymetric mapping a **seafloor TV-record or foto-imaging** has to be carried out using a Foto/TV-sledge in order **to image the coverage density** of the seafloor crusts, sediments and rock outcrops. A ROV (Remotely Operating Vehicle) or an AUV (Autonomous Underwater Vehicle) can be also be applied. One important aspect of this part of the exploration is also to get **information about the microtopography** of the ore fields. The microtopography is one important parameter which controls the **mineability of crust fields.**

3. Sampling of the deposit can be done by dredging (relatively simple technique), TV-controlled hydraulic grab or ROV system with respective manipulators. Sediment sampling can be done by a Box Corer device.

4. Additional investigations by Side-Scan Sonar Systems can be very helpful to evaluate the local morphology by a reflex-seismic method.

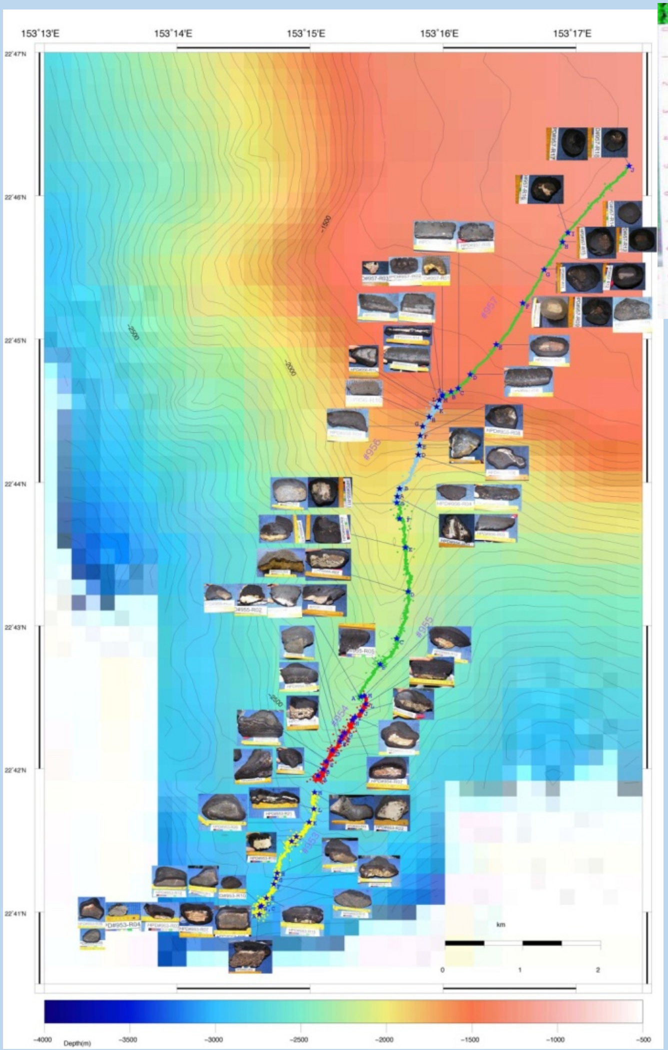
5. Chemical analyses of all the main, minor and trace metals must be carried out.

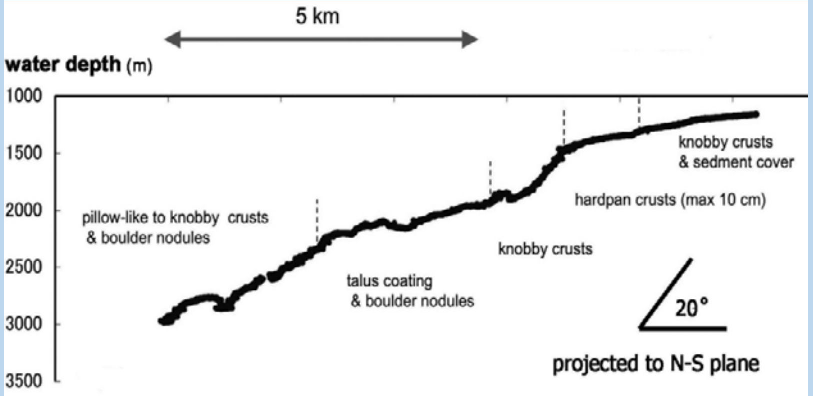
6. The above should result in a final evaluation as to the economic value and mineability of the crust deposits.

ROV equipped by saw can recover up to 200 kg of crusts

Usui, 2010

Crusts sampling along the slope of seamount

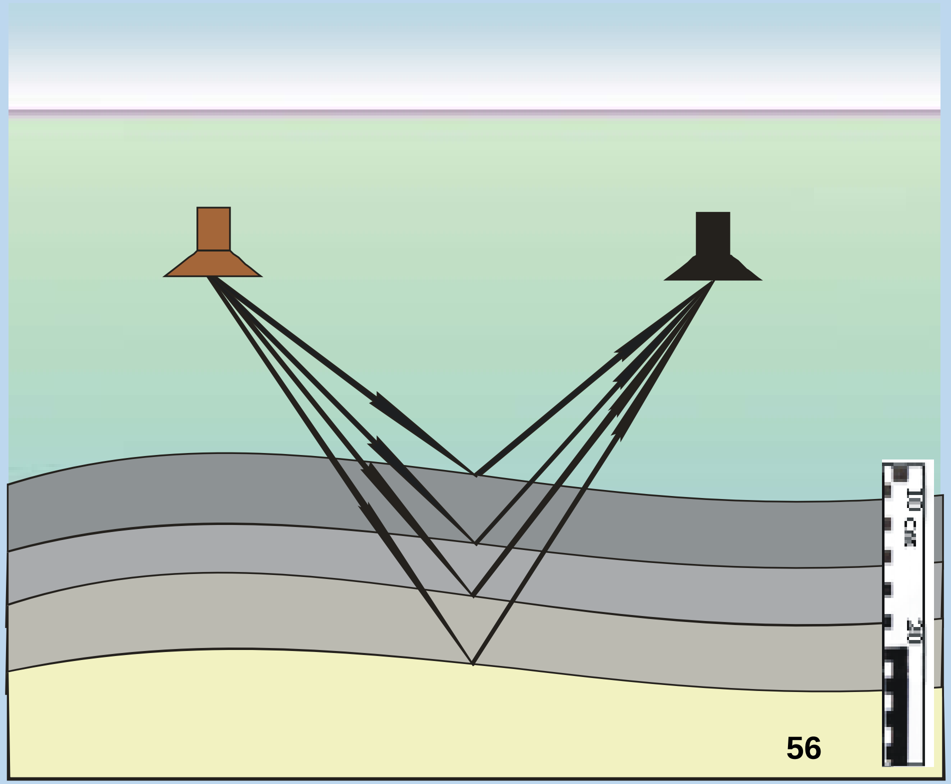




Usui, 2010

- **Local variability of parameters of ore deposition is a factor of most uncertainties in the resource assessment**

- Development of high-resolution remote techniques can help to solve this problem



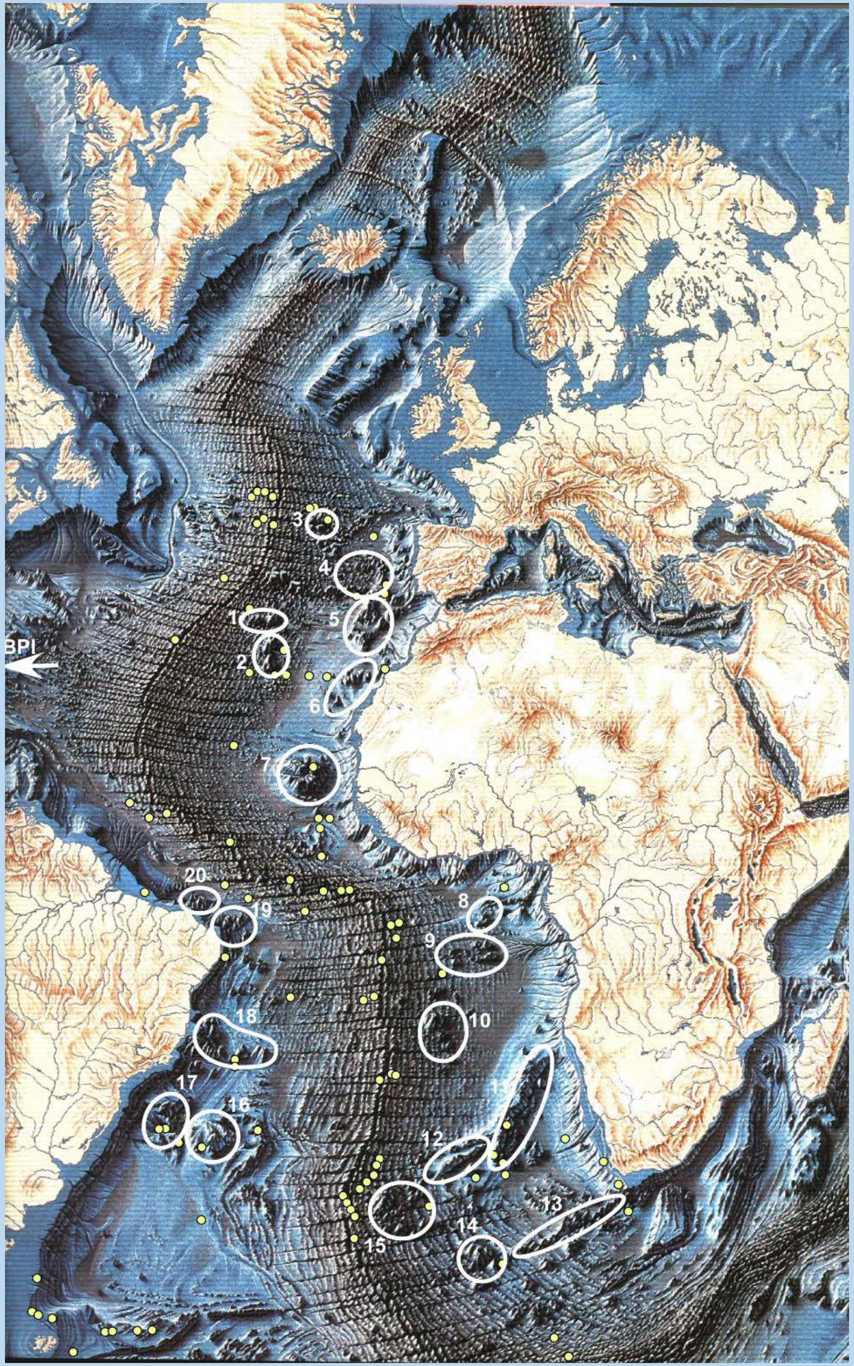
Challenges to Fe-Mn Crust Mining

- 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

Hein, 2013

Crusts in the Atlantic



<u>20 marked sites</u> of potential ferromanganese crust occurrences in the Atlantic Ocean

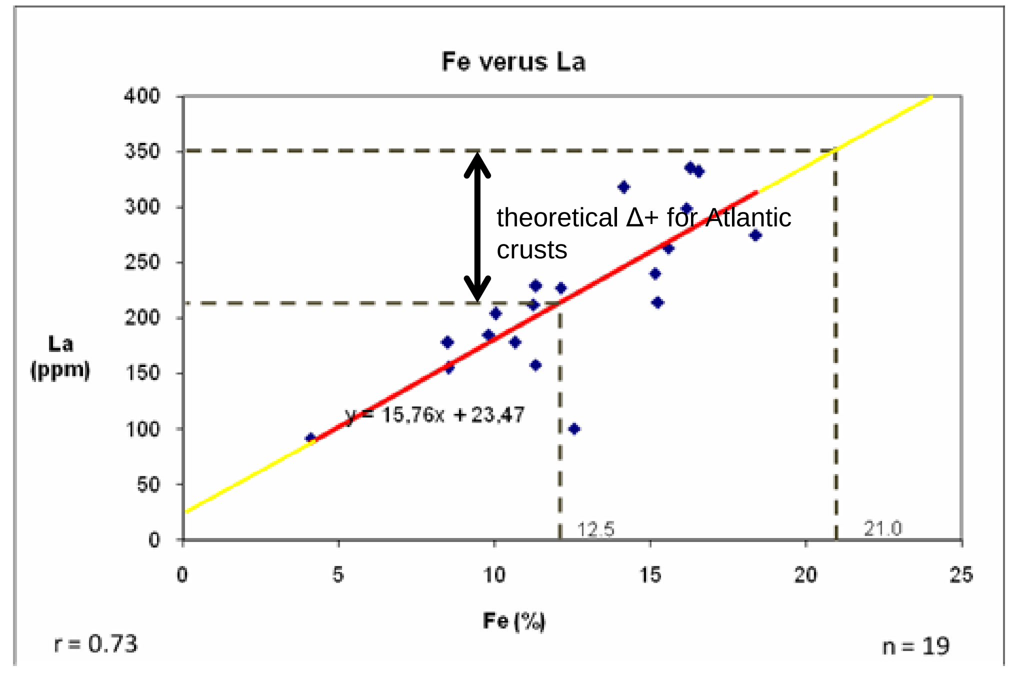
Compared to the Pacific Ocean, the concentrations of Mn are about 4 to 6 % lower, and Fe about 6 to 9 % higher. Correspondingly, the metals Co and Ni which are closely related to Mn, also have lower concentrations in the Atlantic crusts (mean values: Co 4800 ppm, Ni 3300 ppm).

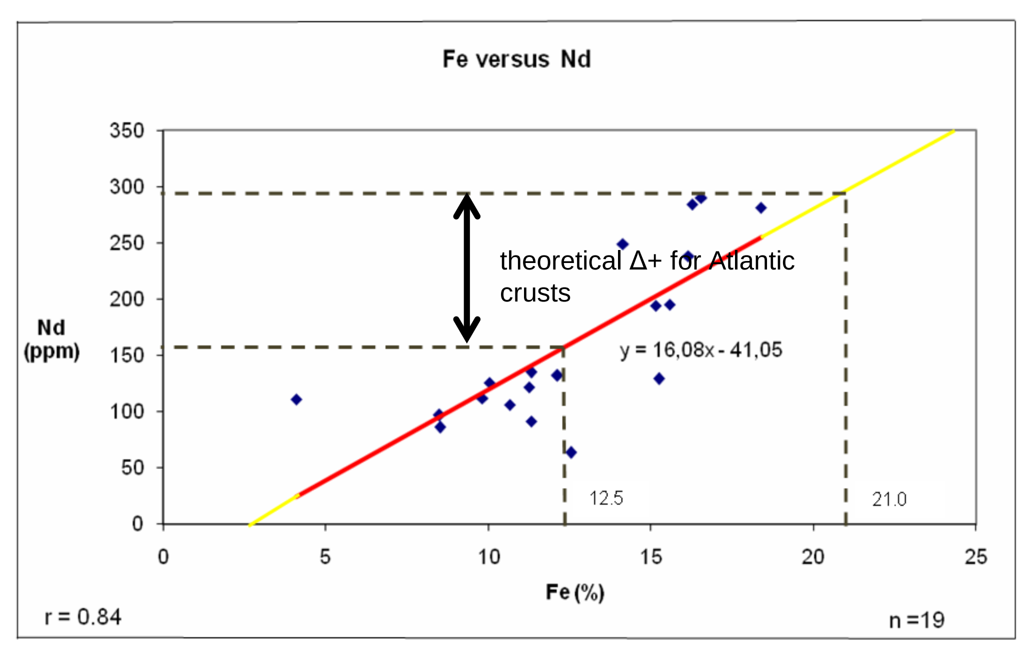
Metals which are controlled by Fe have somewhat higher concentrations in the Atlantic samples (TiO_2 1.5 %, Cu 870 ppm, sum of REEs 2463 ppm).

	Mean
Mn [%]	16.9
Fe [%]	20.9
Mn/Fe	0.8
TiO_2 (Ti) [%]	1.5 (0.9)
Co [ppm]	4800
Ni [ppm]	3300
Cu [ppm]	870
Mo [ppm]	410
WO3 [ppm]	103
Ce [ppm]	1680
Te [ppm]	27
Sum of REEs [ppm]	2463

Estimated mean value metal composition of Atlantic ferromanganese crusts.

Pacific ferromanganese crusts only contain mean concentration of REEs: **1775 ppm**





Fe and REE are positively interrelated.

The mean Fe 12.5 % is typical for Central Pacific crusts.

The Fe concentration of 21.0 % is typical for Atlantic crusts.

It could be predicted an increase of REE concentrations in the Atlantic crusts by **70 to 100%.**

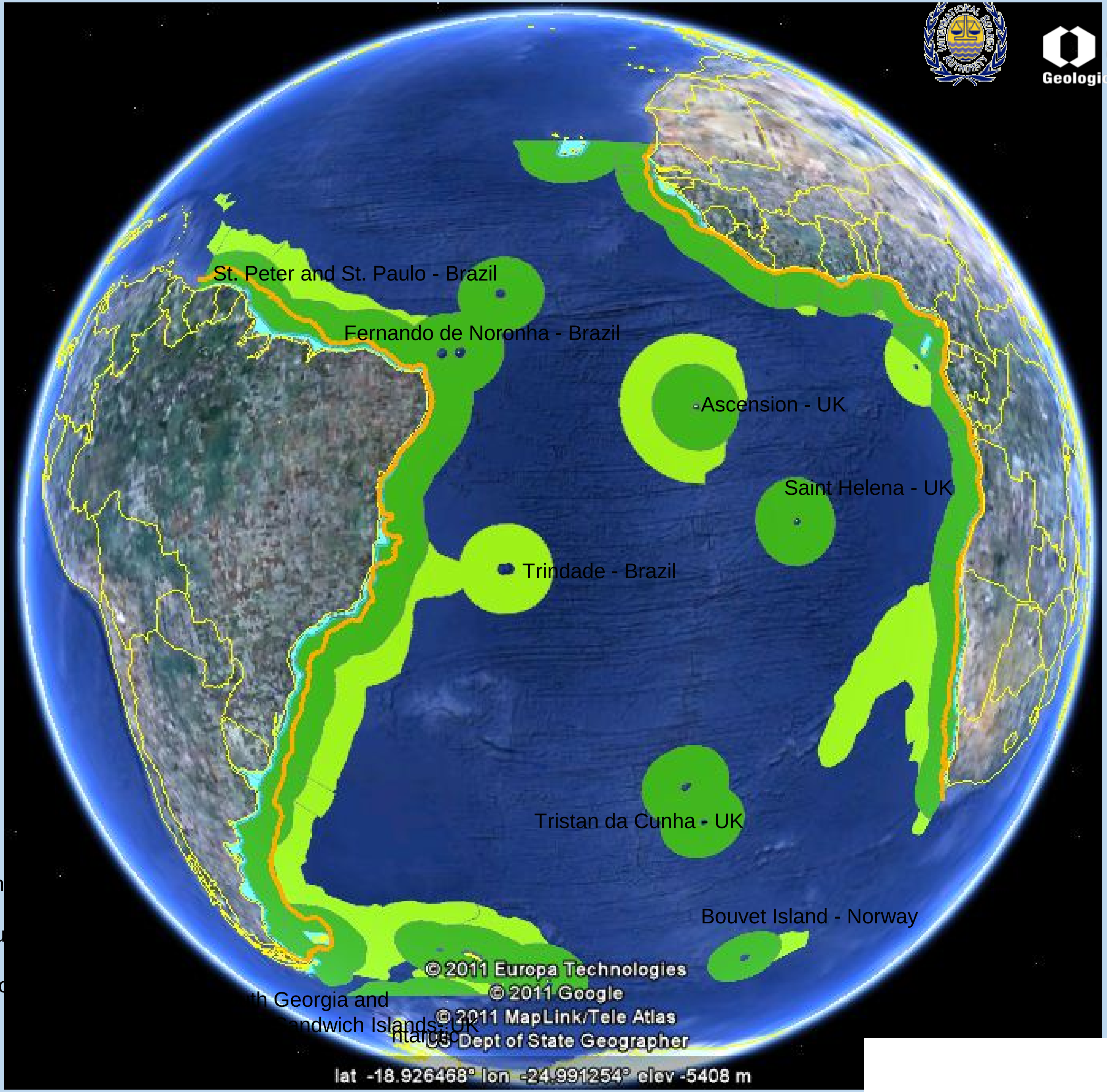
Carbonate-Fluorapatite associated with the ferromanganese crusts

One very pronounced oceanographic feature **in the Atlantic Ocean** is the upwelling of nutrient-rich deeper sea water in the area of the western African shelf. South of the equator, the upwelling system is controlled by the Benguela surface current flowing northward along the southwestern coast of Africa; in the equatorial region exists the Guinea current. In general, coastal upwelling systems are areas where enhanced flux of ortho-phosphate (HPO_4^{2-}) causes apatite formation either by direct precipitation or, more frequently, by replacement of calcareous sediments eventually leading to layers consisting of pure **carbonate-fluorapatite**.

Sample from the Tropic Seamount (tropical east Atlantic) with a Co-rich manganese crust layer (about 3 cm thick) underlain by a 4 cm thick nearly pure phosphorite layer intimately intergrown with the oxide material.

One important future task is to study the extension and the potential of the phosphorite occurrences associated with the Co-rich crust deposits in the Atlantic.

CPRM
Geological Survey of Brazil



Territorial Sea

Contiguous Zon

Economic Exclu

Extension of Co

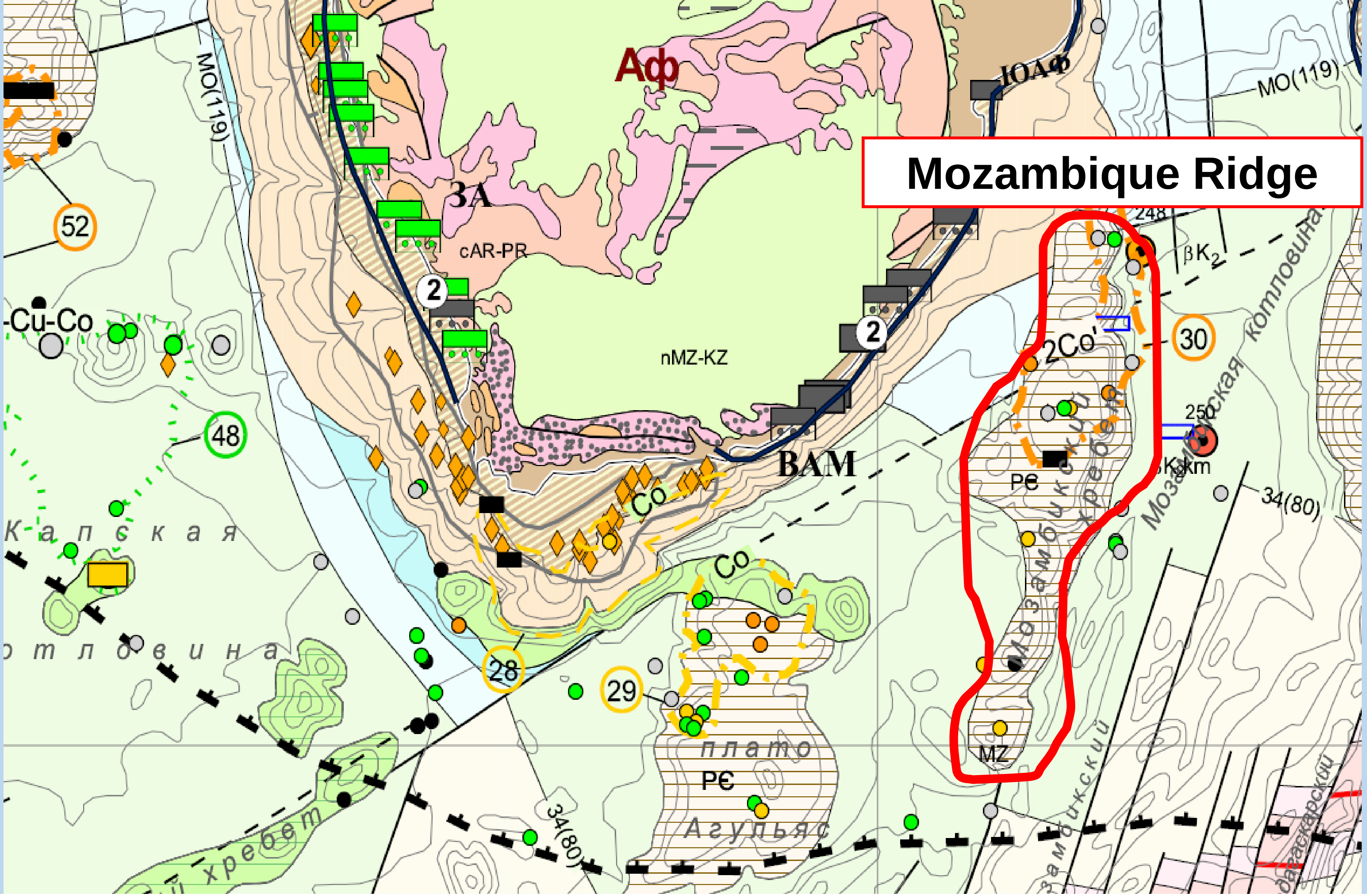
Continental

The Southwest Indian Ocean:

the Mozambique Ridge

Case study

Mozambique Ridge



The Mozambique Ridge is located in the southwestern part of the Indian Ocean offshore the coast of South Africa and Mozambique.

Chemistry of ten ferromanganese crust samples of the **Mozambique Ridge.**

	Mean MR	2s	Min MR	Max MR
Mn %	17.5	2.7	15.4	19.5
Fe %	21.3	2.8	19.1	23.7
Mn/Fe	0.82	0.13	0.73	0.90
Co %	0.52	0.22	0.39	0.72
Ni %	0.26	0.06	0.21	0.30
Cu %	0.08	0.03	0.06	0.10
Ca %	2.0	0.3	1.8	2.3
La	308	54	267	349
Ce	2140	750	1800	3100
Pr	85	106	61	236
Nd	240	134	62	297
Sm	51	10	41	59
Eu	12.6	2.8	10.4	14.8
Gd	64	13	57	74
Tb	9.1	2.4	7.2	11.0
Dy	46	13	36	57
Ho	9.6	3.0	7.4	11.9
Er	24.9	7.2	19.7	30.5
Tm	3.7	1.1	3.0	4.6
Yb	22.5	6.0	17.7	27.1
Lu	3.6	1.0	3.0	4.4
Ce/Ce*	3.4	2.5	0.4	5.5
Sum of REEs	3020	722	2594	3884
Sum of HREE	183	46	151	220
Sum of HREE (%)	6.1	2.0	3.9	7.1

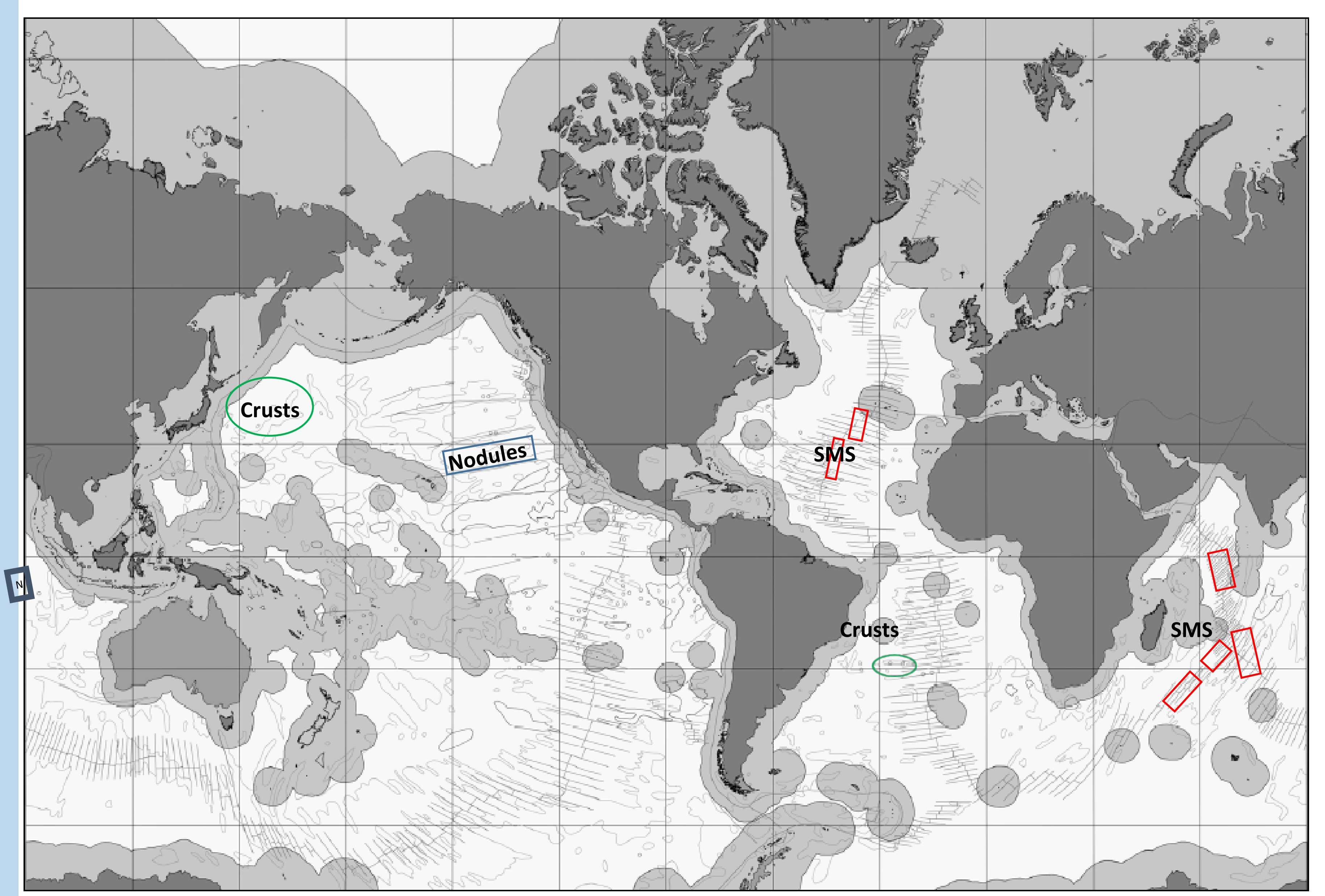
The Southwest Indian Ocean (the Mozambique Ridge): a case study

DATA: 10 crust samples of this ridge from average water depths between 2593 to 3793 m.

The average Co-concentration is 0.52%.
The REE contents are remarkably high: the mean sum of REEs is **3020 ± 722 ppm**

The Mozambique Ridge Co-rich crusts are richer (3020 ppm) in the sum of REEs than the average Atlantic concentration (2463 ppm) and distinctly richer than the average Pacific concentration (1775 ppm).

Exclusive economic zones & application areas



Conclusing remarks

- Ferromanganese Co-rich crusts is globally distributed and present a potential resources for the basic and rare metals which use in hi-tech and green-tech technologies
- Atlantic and Indian Oceans are relatively poor studied compare with Pacific but has high potential of crusts with very specific high grades of REE
- There are still many targets available in Atlantic and Indian oceans which are waiting for study, evaluation and future exploitation

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