Review Report of the

"Development of Geological Models for the Clarion-Clipperton Zone Polymetallic Nodule Deposits"

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The area between the Clarion and Clipperton Fracture Zones (called CCZ) has been the focus of much international attention for many years since it is there where obviously the largest and richest manganese nodule occurrences exist.
The main task of the presented ISA reports is therefore to improve the ISA`s resource data bank and assessment for this CCZ region as well as to present the state of the art about the formation of these deposits.
The idea of the work is that if assumed relationships between certain environmental and oceanographic data and nodule grade as well as abundance could be statistically tested, the results could be used as proxies for further high-grade nodule deposits in areas not yet studied in detail. However, this work hypothesis demands that there is a good and provable understanding of how economically interesting nodule deposits form.
Both volumes represent very important undertakings since they summarize for the first time all knowledge about the CCZ area with regard to the abundance and grade of the manganese nodule deposits. Many features, observations and results are well described and some highly interesting interdependences are presented. The volumes have been distinctly improved by the mentioned changes and additions. Also the presented glossary is very well written and improves significantly the value of the whole work.

Regarding the presented biogeochemical model I like to go a little bit more into the scientific details. The model is based on the geographical distribution and variability of nodule abundance (kg/m^2) and nodule metal content (Mn, Cu, Ni, and Co) in relation to some known proxy variables such as chlorophyll concentrations in surface waters (indicator of primary bioproductivity), distance from the East Pacific Rise (indicator for volcanogenic influence), and Carbonate Compensation Depth (CCD, as indicator for the change in sediment facies with increasing water depth).

The main Mn source for the nodule growth in the deep water is the organic matter flux of fecal pellets which originate from surface water bioproductivity. Only a small percentage of these fecal pellets reach the pelagic deep-sea floor, most of them are oxidized and decomposed on their way down to the O_2-minimum zone. The high content in dissolved Mn in the O_2-minimum zone also derives to a great extent from the fecal particle decomposition. But nevertheless, there is enough Mn which finally is deposited into the pelagic sediments underneath the CCD to form nodules by early diagenetic processes.

Another point is the consideration of a volcanogenic source by using the distance to the East Pacific Rise as a proxy. There is no doubt that the hydrothermal plumes of the EPR volcanism contribute considerably to the Mn budget of the eastern Pacific ocean but I believe that there is no direct flux connection between the Mn supply to nodule growth in the CCZ and the EPR hydrothermal activity.

I think that **the main source for Cu as well as Ni are not fecal pellets but more likely siliceous skeletons** (opaline matter) dominated by radiolarians which form the largest part of the siliceous mud to ooze sediments which are distributed underneath the CCD in that specific area where the richest nodules with regard to Cu and Ni exist. Siliceous plankton also is a product of surface water bioproductivity, however, the productivity rate is significantly less than that of the calcareous plankton. Thus, a remarkable enrichment of siliceous plankton can only take place underneath the CCD in the pelagic environment of the deep-sea floor with very low sedimentation rates. Since the opaline skeletons are the main carrier phases for Cu and Ni, these two metals were set free during and by early diagenesis and were selectively incorporated into the 10 Ǻ-manganate (todorokite) or 7 Å-manganate (birnessite) lattices; however todorokite is the dominating Mn mineral in the diagenetic parts of the nodules. It is noteworthy that the Ni and Cu model predictions are very similar.

The fact that the growth rate of the diagenetic nodule parts is mainly controlled by early diagenesis is positively related to the biological surface productivity. This increases from W to E and ESE in the CCZ. Maximum values of surface bioproductivity, growth rate and nodule abundance exists, for example, in the Peru Basin located ESE of the CCZ. However, the nodules from the Peru Basin do not have best quality regarding the minor metals Cu, Ni and Co but are very rich in Mn with Mn/Fe rations distinctly above 5.

On the other hand, nodules richest in Cu and Ni have Mn/Fe ratios around 5 and exist in the central part of the CCZ. The main reason for the Mn enrichment in the Peru Basin nodules is the very pronounced diagenetic Mn flux. This leads to reduced Cu and also Ni concentrations in the manganate mineral lattices since also dissolved hydrated Mn^{2+} cations can enter in this layered crystal structure and compete with Cu and Ni for interlayer positions. Due to the high Mn^{2+} concentrations in the pore water, which leads consequently to reduced Cu and Ni concentrations, the diagenetic nodule substance is very rich in Mn but depleted in Cu and Ni compared to the CCZ nodules. But we observe that even at very high surface water bioproductivity manganese nodules can grow.

If we use these geochemical observations to describe the environmental conditions for best-quality nodule deposits we can state that nodules with intermediate growth rates and located underneath intermediate bioproductivity values offer the optimum conditions for the growth of Cu- and Ni-rich nodules.

Summarising we can state that the optimum for high-quality nodule growth is not related to maximum growth rates or maximum Mn concentrations but rather to intermediate biogeochemical conditions.

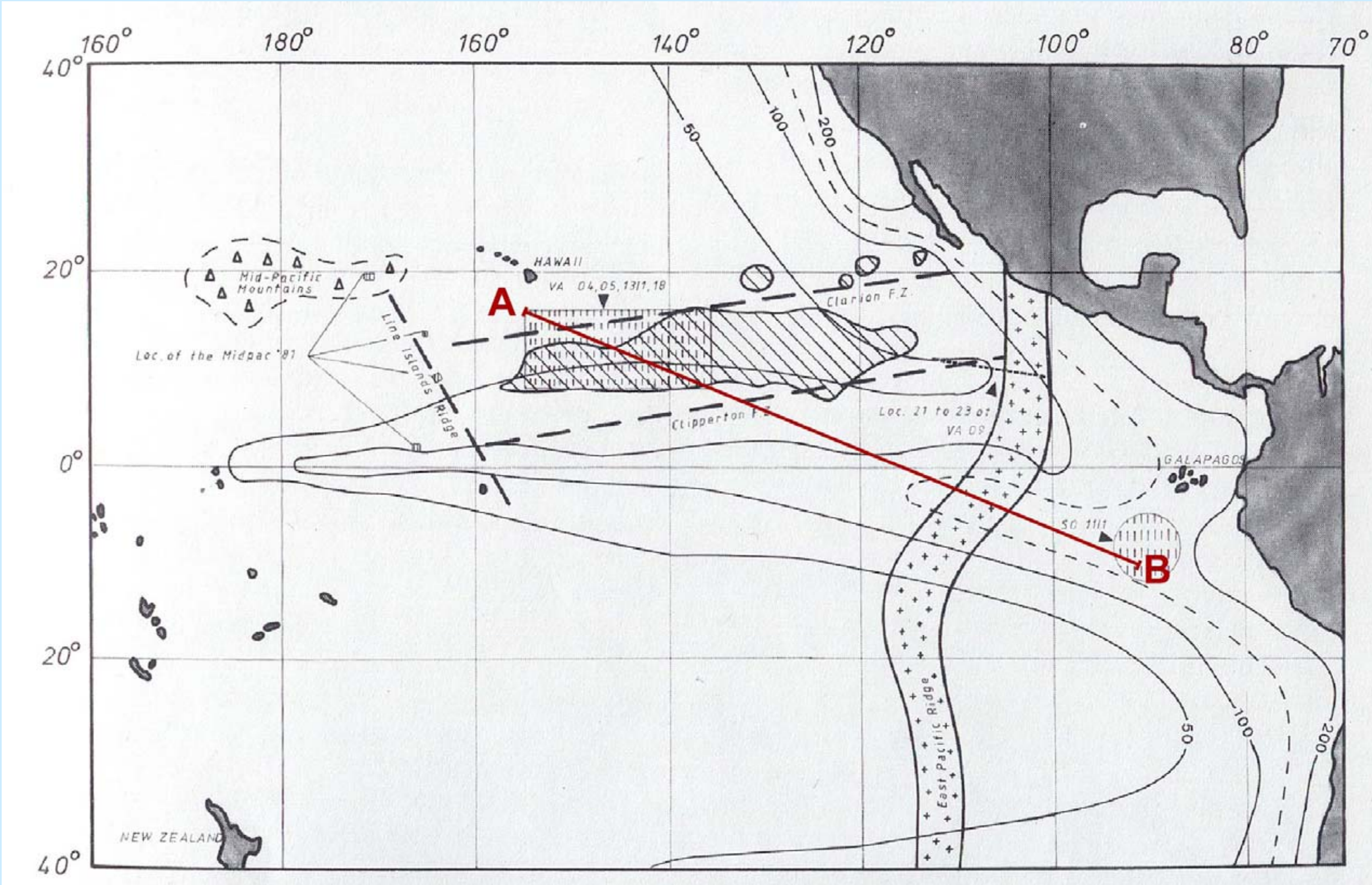


Fig. 1: Map of the eastern part of the Pacific Ocean showing the areas investigated: (cruises: VA 04, 05, 09, 13/1, 18, SO 18 – Midpac 81); the 50-, 100-, and 200 g/m^2x yr isolines mark the primary biological productivity in surface waters (after *Schmithüsen* 1976).

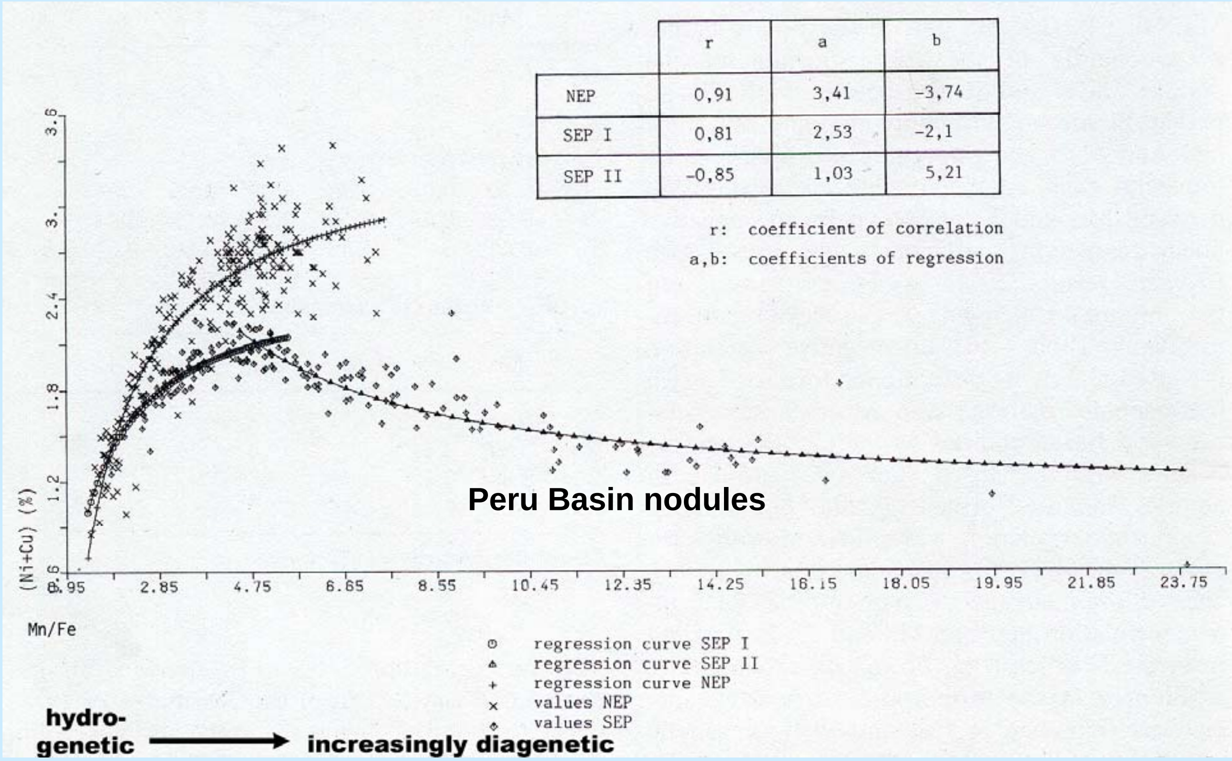


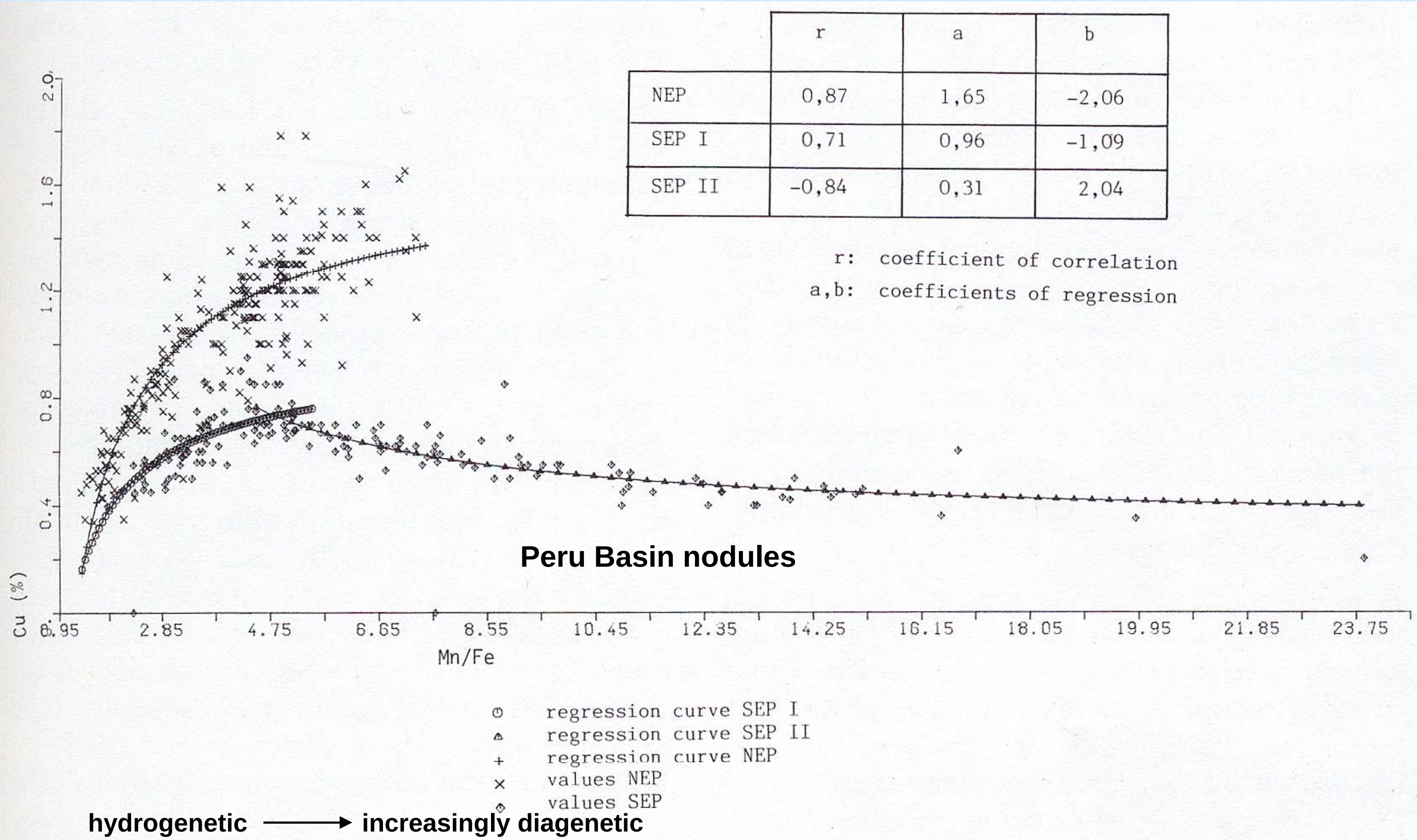
Fig. 2: Hyperbolic regression curves for Mn/Fe versus (Ni + Cu) for nodule samples from different Pacific areas (NEP = NE Pacific nodule belt; SEP = Peru Basin in the SE Pacific).

$$12\ Mn^{2+} + \tfrac{11}{2}\ O_2 + 25\ H_2O + 2\ Me^{2+} \rightarrow$$

$$2\left\{\left[Mn(IV)_5\begin{pmatrix}Me(II)\\ Mn(III)\end{pmatrix}O_{12}\right]^+ \cdot [OH(H_2O)_5]^-\right\} + 28\ H^+$$

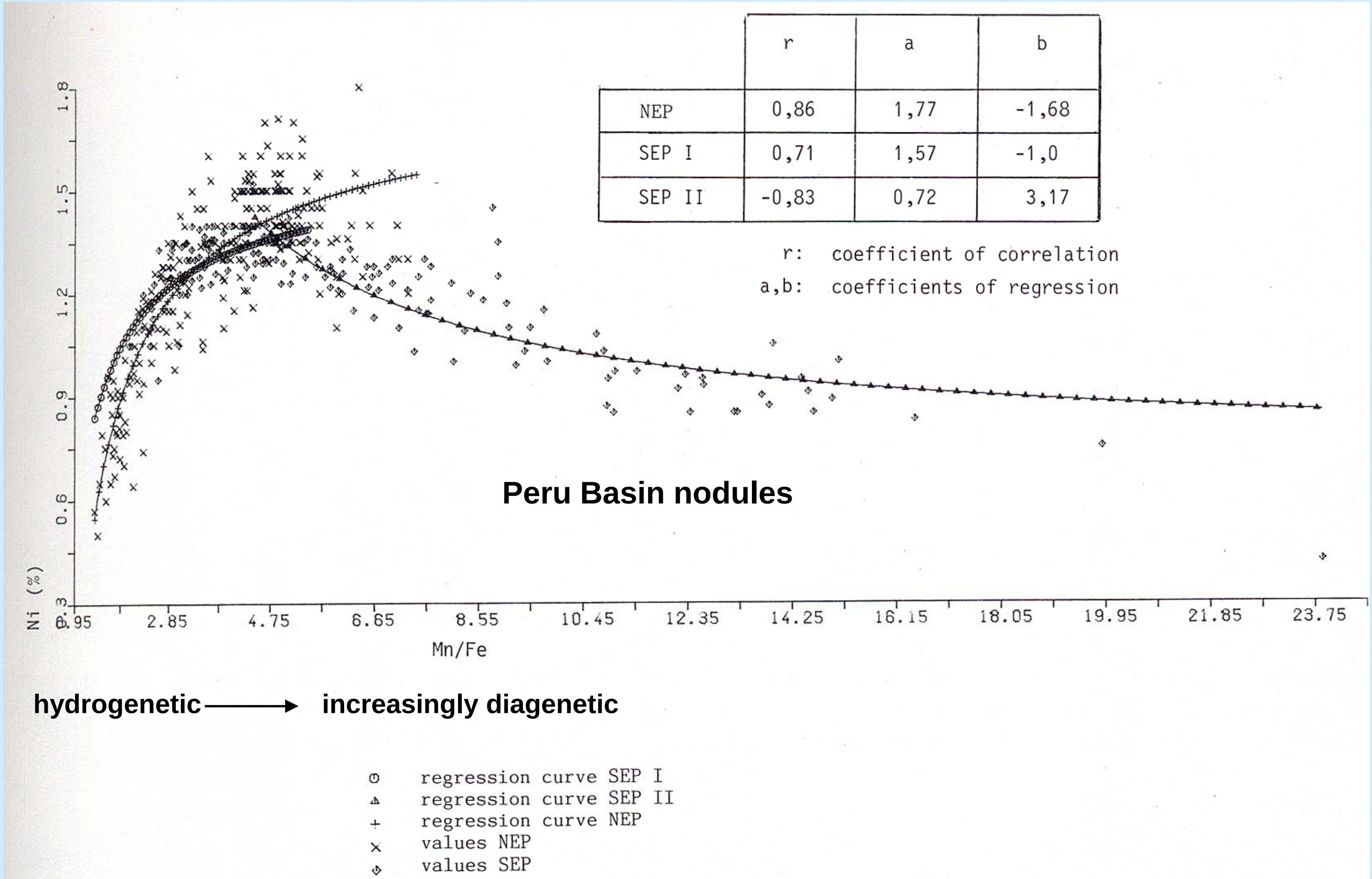
10 Å-manganate

Model reaction to explain the saturation of the 10 Å-manganate lattice with respect to Me (II): Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Mg^{2+}.



	r	a	b
NEP	0,87	1,65	-2,06
SEP I	0,71	0,96	-1,09
SEP II	-0,84	0,31	2,04

Fig. 3: Hyperbolic regression curve for Mn/Fe versus Ni for nodule samples from different Pacific areas.



	r	a	b
NEP	0,86	1,77	-1,68
SEP I	0,71	1,57	-1,0
SEP II	-0,83	0,72	3,17

Fig. 4: Hyperbolic regression curve for Mn/Fe versus Cu for nodule samples from different Pacific areas.

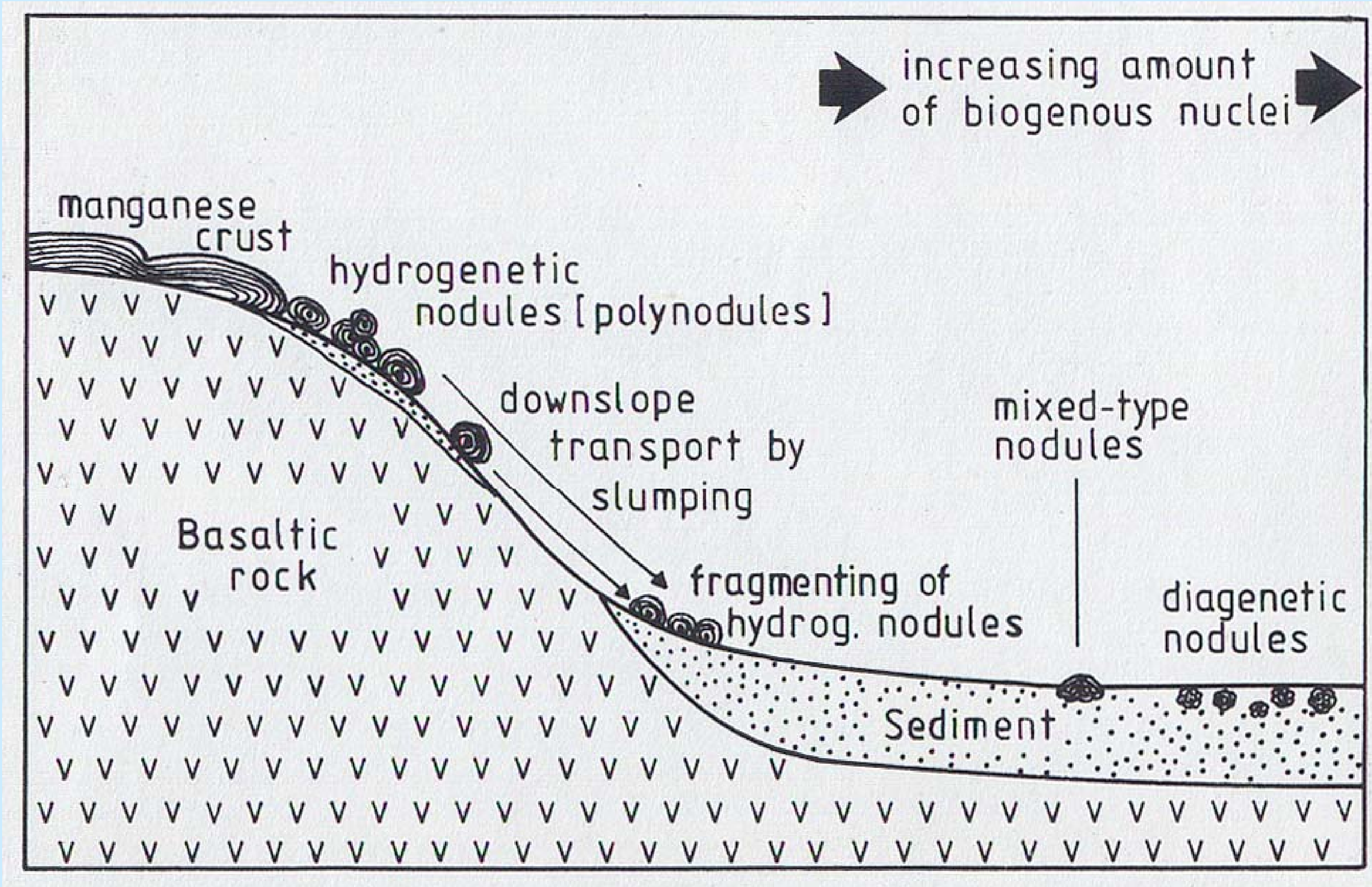


Fig. 5: Relationship between submarine topography, type of nucleus, and type of nodule. The hydrogenetic nodules mainly have basaltic rock fragments as nucleus material. Fragments of hydrogenetic nodules serve as nucleus material mainly for mixed-type nodules. Diagenetic nodules often have biogenic or cemented sediment particles as nucleus material.

So my suggestion for the hypothesis chapter is as follows.

5.4 Hypothesis

The general hypothesis for metal accumulation (specifically Mn, Ni, and Cu) in the Clarion Clipperton Zone (CCZ) polymetallic nodule deposits is illustrated in Fig. 5.1 (has to be revised, see below). It is based on ideas originally introduced by Greenslate, Frazer and Arrhenius (1973), which have been refined here as the basis of a regression model. Co, which also is an important valuable metal of nodule composition, is not included in this statistical study, since it is believed to accumulate via hydrogenetic processes that are independent from the biogeochemical model described below. Fe which is the main antagonist to Mn in nodule composition, exists in the ocean water as colloidal Fe-oxyhydroxide particles and is mainly supplied to Mn nodule growth after release to the water column due to dissolution of calcareous skeletons.

The general sequence of metal transport and accumulation proposed is as follows: The primary metal sources of Mn, Ni, and Cu to the oceans, and presumably for these deposits, are believed to be from continental run-off , volcanogenic, and atmospheric sources. The terrigenous metals exist as dissolved hydrated ions and complexes or are adsorbed to the surfaces of fine-grained particles which carry them westward within the North Pacific current. Volcanogenic metal from the East Pacific Rise probably consists entirely of Mn. Some portion of this is dissolved and adsorbed Mn may reach surface waters, and be then transported to the west. By the time these metals reach the deposits sites in the CCZ, the postulated terrigenous, volcanogenic, and atmospheric sources would not be distinguishable from each other.

Most of the fine-grained organic and inorganic particles (e.g. nannoskeletons) in surface waters which are mainly products of the bioproductivity in the photic zone, are too small to directly sink to the seafloor, but these, as well as dissolved metals can be taken up by the zoo- and microplankton in their organic tissue and shells during their life and growth, and later through adsorption processes after death. Some of the dissolved metals are also taken up at the particle surfaces and are partly released throughout the deeper water column. One very important particle type for the proposed vertical transport, especially for Mn and organic matter to the seafloor, are fecal pellets.

Some portions of these metal-laden organic particles are sedimented on the seafloor where they are metabolized by benthic animals, are degraded through bacterial metabolic processes and metals will be released. The main process of metal fractionation takes place under early diagenetic conditions in the pelagic siliceous clay to ooze sediment. The organic material of the fecal pellets gets degraded causing suboxic conditions in the pore water environment of the upper sediment layer consisting of a semi-liquid surface layer and a sublayer with suboxic to reducing conditions reaching down to about 30 cm.

Under these circumstances, Mn is reduced, and other metals like Ni and Cu are leached from their surface positions of e.g. opaline skeletons. Thus, the pore water in the sublayer contains enhanced concentrations in dissolved metals. Since oxidizing conditions prevail at the surface of the sediment, the metals migrate upwards with the oxidation gradient. Mn is then oxidized in the uppermost surface layer, and forms phyllomanganates like todorokite or birnessite. These phyllomanganates have interstitial layers which are capable to scavenge metals like Cu^{2+}, Ni^{2+},and others, thus a selective incorporation into this mineral lattice is taking place. <u>This is the main biogeochemical process which takes place in a sediment redox system, and explains the particular enrichment of Mn, Ni and Cu in the diagenetic parts of the mixed-type nodules.</u>

On the other hand, the hydrogenetic part of the nodules is controlled by colloidal chemical and particle surface processes: the positively charged metal ions or metal complexes are readily absorbed by the negative surface charge of the hydrated manganese oxides at the pH of seawater.

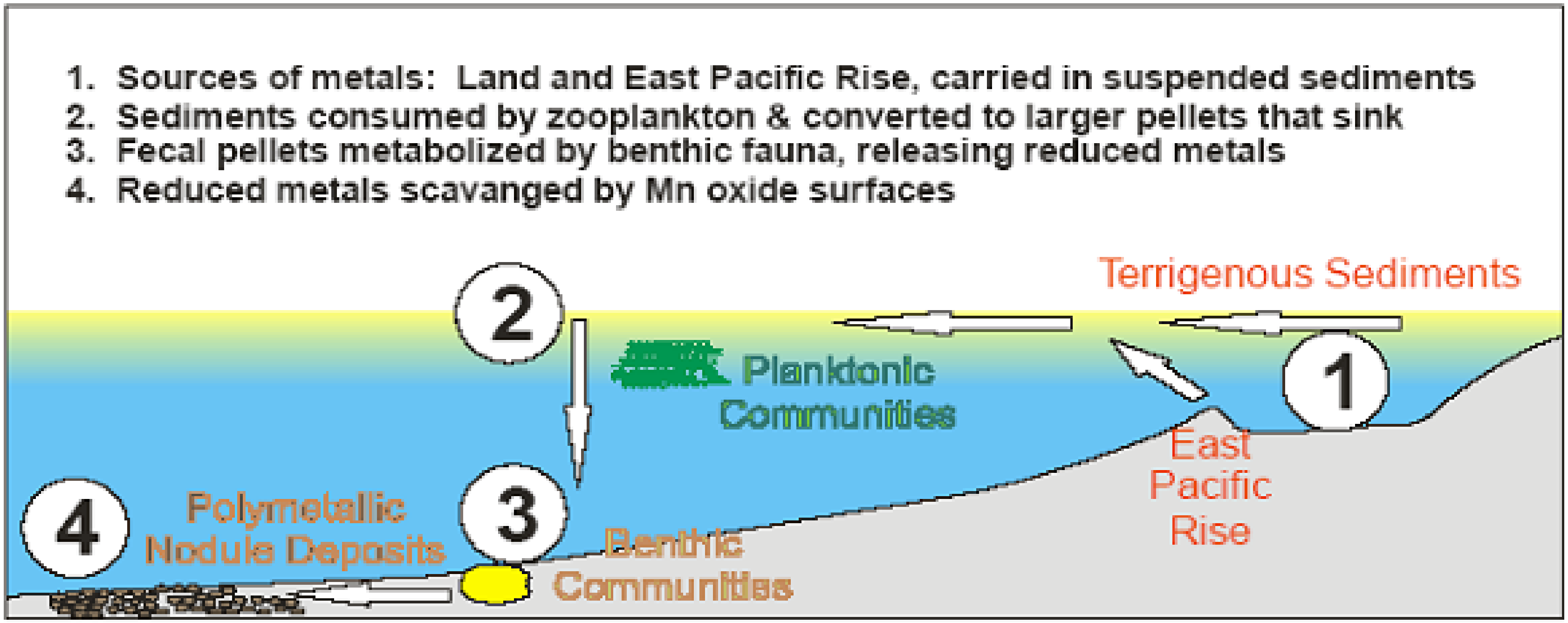
If the diagenetic model is correct, and if the regional trends in surface water circulation and biological primary production have been persistent for the past several million years, then the metal content of the polymetallic nodules in the CCZ should reflect the intensity of the biological processes that are evoked to explain the metal transport from the surface waters to the deep water precipitation sites and the re-arrangement of metals during early sediment diagenesis.

Nodules richest in Cu and Ni have Mn/Fe ratios of about 5, and exist in the central part of the CCZ. Towards the East, in the equatorial belt of high bioproductivity, the surface production increases. This results in the formation of Mn-richer diagenetic nodules, for example in the Peru Basin. Thus, both areas, the CCZ as well as the Peru Basin belong to one common biogeochemical system. The main reason for the Mn enrichment in the nodules of the Peru Basin is the more pronounced diagenetic Mn flux to the sediments. Since reduced Mn^{2+} can also be uptaken by the phyllomanganate lattice, these Mn^{2+} ions enter into the layered crystal structure and compete with Ni and Cu for interlayer positions. The result is that the nodules formed underneath areas of higher surface bioproductivity have more Mn and respectively a higher Mn/Fe ratio, but less Cu and Ni. These considerations show that the optimum for high-quality nodule growth is not related to maximum growth rates or maximum Mn concentrations but rather to intermediate conditions.

Since the data from the very Mn-rich Peru Basin nodules are not included in the ISA data set, this enrichment in Mn and depletion in Ni and Cu caused by very high bioproductivity, does not appear in the regression calculations of the Geological Model and Mn, Ni, and Cu coincide in the plot versus bioproductivity at intermediate surface chlorophyll values (Fig. 5.2).

Also important to this model is a hypothesized balance between increasing supply of metals from biogenic sedimentation and the increasing dilution of metals from excess biogenic sedimentation (Fig. 5.2). At very low levels of biological activity, the supply of reduced metals to the seafloor is insufficient to produce substantial nodule deposits. At the other extreme, under regions with relatively high biological activity, as found in the eastern tropical Pacific and near the equator, the flux of organic matter will exceed the rates at which the benthic nodule-forming processes can extract the adsorbed metals, and deposits with high values of Mn, but low Ni and Cu will form (e.g. Peru Basin).

Figure 5.1 General Formation Model



The explanations in Fig. 5.1 should be changed as follows:

1. *Sources of metals: Land, East Pacific Rise, and atmospheric input, carried as suspended matter, dissolved ions or metal complexes.*
2. *Particulate material and metal complexes are incorporated in biological metabolism, zooplankton consumes phytoplankton, fecal pellets are produced and sink.*
3. *Fecal pellets are degraded in the sediment, causing early diagenesis and release reduced metals.*
4. *Mn oxide minerals are formed, and take up reduced metals by selective lattice scavenging.*

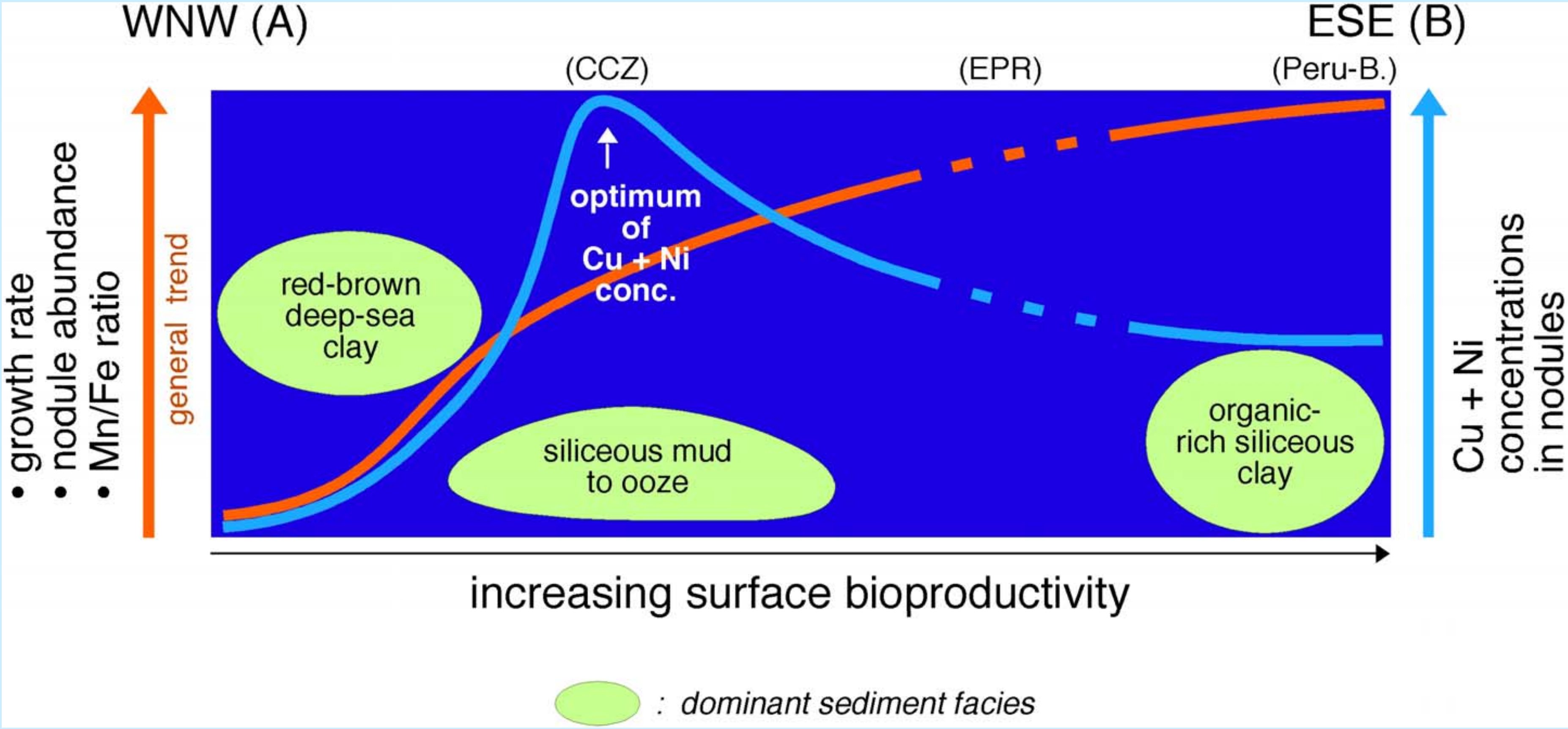


Fig. 7: Hypothesized optimum level of surface bioproductivity for Cu-and Ni-rich nodule growth (general oblique cross section through the CCZ: A-B; situation underneath the CCD).