

## Review Article

# Keeping Chemical Elements C,N,P Combined in Biomass: Evolution Maintains Biological Stoichiometry Against Chemical Thermodynamics by Controlling Metal Access

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## Abstract

The key ratios of ecological stoichiometry, namely [C/N] and [C/P], are no independent variables but are controlled by different metabolic pathways, environmental factors and the presence and (pertinent [bio-] catalytic) reactivity of several essential metals. In some cases certain metabolic pathways take place only above some [M/C]- or [M'/N] threshold value, like with methanogenesis. Biomass and different kinds of related organic and nitrogenous organic matter are shown to be unstable towards disproportionate into  $\text{CH}_4$ ,  $\text{CO}_2/\text{HCO}_3^-$  and some C-free N compounds. Thus, biomass and the entire biota can only persist and undergo further reproduction, evolution given that catalysis of inter-conversion of organic compounds, including their oxidation yielding  $\text{CO}_2$ , did remain a rate-limited process ever after biogenesis. This does imply levels of catalyst metals be limited in all of biomass although its key components are good to excellent ligands for most essential metals save K, Ca (Sr), expecting efficient retention. Both [C/N] and [C/P] are shown to decrease with evolution going on due to metabolic implications of a multitude of novel processes. However, large parts of biogenic organic matter both below soil surface and in the ocean are effectively decoupled from biological C, N cycling. The very small [C/N] ratio in Earth's atmosphere compared to Mars, Venus and volcanic vents reflects a C limitation in growth of organism on Earth aggravated by this decoupling and biological formation of carbonate minerals while living biomass now represents some 25% of carbon within easy biological access now. Comparably large shares are observed with few other elements, namely, PGMs while < 1% of most other essential elements is retained by biomass. Several elements are identified which do catalyze the said "destructive" transformations on DON, PON in clostridia, pseudomonades and other organisms, implying low levels or uneven distributions are crucial for biosphere stability. These include W, Se, Co and among "non-bimetals" particularly Ru.

## INTRODUCTION

The principal relationships considered in ecological stoichiometry are [C/N] and [C/P]; yet biology depends on availability and (often catalytic) activities of a sizable number of other elements, both metals and some non-metals. As a rule, a multitude of both heterotrophic and (mainly photo-)autotrophic organisms have to be considered within some ecosystem; in water, DON is about 10 - 20 times the mass of living biomass + PON combined. Thus the [C/N] ratio available to detritus feeders, bacteria in a normal lake is mainly controlled by  $[\text{C/N}]_{\text{DON}}$ , and the same holds for energy to be gained from its processing. While several ecosystems based on chemo litho autotrophy, e.g. in caves such as Movile Cave (Romania) and near "black smokers" in deep oceans, are known, only a single one was reported to consist of but one species, namely *Desulforudis audaxviator* reducing sulfate and  $\text{CO}_2$  (and likely  $\text{N}_2$ ) using radiogenic  $\text{H}_2$  in warm deep rocks of South Africa (in abandoned Mponeng gold mine) and at many other sites. Metabolism is a general feature of

living beings, hence uptake and loss terms (excretion, exhalation) must be considered in C and N (and sometimes S) levels, and the same holds among different species linked to each other within one or adjacent ecosystems. Then stability of mixed C;P and C:P compounds without which living beings could not persist or exist becomes an issue. We are going to show here that biosphere stability is a matter of "imperfect" catalysis.

Every actively living being maintains its gross composition within narrow limits [1]. Differences among these genetically controlled ratios within a trophic chain or network will cause release or environmental depletion of some of the elements. N release is common [2] while most of C previously fixed by photo- or chemosynthesis (e.g. in cave-, "black smoker"<sup>1</sup> communities)

<sup>1</sup> <sup>2</sup>Note that in black smoker vent conditions  $\text{H}_2\text{S}$ , metal sulfides can be used as reductants for  $\text{HCO}_3^-$  to yield  $\text{CH}_4$ , biomass organics and sulfate at about 100°C while in colder regions, including those just several dm apart from the vents, the C/S redox reaction goes the other way round (sulfate oxidation of biomass). There are no data for [C/N] in fishes, crabs, worms, clams or bacteria in black

is directly re-converted into  $\text{CO}_2$  on every consumer trophic level. Some set of additive metals and other micronutrients is required for running its enzymes as well as maintaining structural integrity ( $\text{CaCO}_3$ , Ca phosphates,  $\text{SiO}_2$  [sponges, green plants],  $\text{SrSO}_4$ , etc.); uptake and handling of these elements is controlled by complexation properties mainly and thus can be expected to depend on N and P and S contents of biomass, too.

Neither any kind of biomass nor its constituents do represent thermodynamically stable entities, neither "as such" nor in reducing or oxidizing environmental conditions. The said instability will provide a source of metabolic energy for consumers but likewise compromise the existence of organisms at all trophic levels if transformations concerning carbon and nitrogen (and C oxo species) would be catalyzed right down to the thermodynamic equilibrium states of either element. Some questions arise:

- which would be stable or "highly metastable" forms of N in the combined Pourbaix diagram of C and N (C and N exposed to elements of water at various levels of redox potential and pH, not just the physiological range), and which would be their [C/N] ratio, and
- How is the latter changed by common and un-common biochemical transformations?
- How abundant or bioavailable are those elements involved in possibly complete N loss from biomass?
- And what about the stability of the third "classical topic" element of ecological stoichiometry, namely, phosphorus within organic matter?

Most of respective biomass are phytoplankton, green plants and (soil, marine) bacteria, while animals represent a negligible part of total biomass, as do fungi. It is remarkable that all aerobic bacteria, fungi and animals have very similar [C/N] values (commonly, 4.5 – 8) [1] regardless of their size and relative metabolic activities, that is, regardless of highly different throughput rates. Accordingly the "challenge" of keeping [C/N] both finite and N "inside" the chemical network apparently is tackled in some similar way, although pertinent reactions may differ from each other. While accumulation of lipids or polysaccharides save chitin might increase [C/N], the small range of actual [C/N] ratios in heterotrophs indicates there are robust chemical limits. Chitin is an interesting material in understanding both levels and biochemical activities of elements in some ecosystem [4] and apparently indicates related effects in metal transport between inundated sediment (permanent or perennial) and its overhead water body. Reactions involved in putting C/N phases nearer thermodynamic stability (that is, partial oxidation plus complete cleavage of C-N- or  $\text{C}\equiv\text{N}$  bonds) are summarized in Table (1) below:

Thus some "forcing" by  $\text{N}^{\text{red}}$  input maintains biomass N content provided levels of certain elements in biota and environment stay low.

Table (1) shows that N loss pathways in biochemistry are catalyzed by rather rare elements, or even require combinations among them.  $\text{NH}_4^+$  released by urease is going to be fixed to some 2-oxo carboxylate; hence the fairly abundant Mn in urease (which exists in all organisms) does not compromise withholding N inside an organism. In addition, reduced N is not volatile at physiological pH.

Generally speaking, C-N bonds are less stable (lower BDE) than either C-C-, C=C-, N-H or C-H bonds. Hence thermodynamic stability (heat of combustion) of amines increases (decreases) according to trimethyl amine < methyl ethyl amine < n-propyl amine < isopropyl amine, and ethyl or higher amines/ammonium ions readily undergo elimination of olefins (Hofmann elimination). Yet, CN bonds can be introduced starting with  $\text{NH}_3$  or  $\text{RNH}_2$  when appropriate acceptors (oxidants or electrophilic reagents) are there, producing nitriles from alkenes (ammonoxidation) and isocyanides from  $\text{RNH}_2 + \text{trihalomethanes}$  ( $\text{Hal} \neq \text{F}$ ), respectively. But as rule nitrogen tends to "slip out" of organic compounds, hence biota must control the effect or compensate it by corresponding N inflow "propelled" by redox (nitrate,  $\text{N}_2$  reductions) or solvolytic reactions. The former is mainly accomplished by Mo, the latter by Zn. Thus environmental levels of either metal will serve to stabilize biomass while  $\text{N}_2$  reduction is additionally caused by and thus dependent on Fe (which is unlikely to run short) and Co and reductive desamination of  $\alpha$ -amino acids takes both W and Se [5].

## STABILITY OF DOC AND DON IN THERMODYNAMIC TERMS

$\text{CH}_4$  and  $\text{CO}_2$  are directly connected in the Pourbaix diagram (Figure 1), which means that none of the intermediate oxidation states of carbon is actually stable in any conditions if combined with water. Accordingly, there should be no condensed or solid forms of carbon other than carbonate rocks<sup>2</sup> whereas all kinds of biomass and other organic matter including fossil fuels are but metastable even if not brought near some oxidant or reductant; clostridia gain their metabolic energy from this fact. To start with a simple case, all species which are minima on the  $\text{C}_2\text{H}_5\text{NO}_2$  hyper surface are unstable towards decomposition into methylamine and  $\text{CO}_2$  while glycine is not the most stable form (this being carbaminic acid methyl ester, followed by glycolic amide and glycine only third [6]). Hence one should rather consider methylamine stability, the latter being a substrate of biological methanogenesis [7], like methanol and sec., tert. Methyl amines but not quaternary methyl ammonium salts;  $\text{NH}_3$  released thereby suppresses  $\text{N}_2$  fixation. In turn, you need not consider reductive formation of any  $\text{C}_2\text{H}_5\text{NO}_2$  isomer from  $\text{CO}_2$  unless that of methylamine or methyl ammonium ion proved exothermic.

Ammonia as such will convert  $\text{CO}_2$  into carbamate, urea at any pH rather than reduce it. Since not even methane (the most stable hydrocarbon) can be produced directly (irrespective of Ammanox reactions) by converting  $\text{NH}_4^+$  into  $\text{N}_2$ , the same will hold for every other kind of organic compound. Processes mixing/combining or separating C and N in organic compounds

smokers but the feed water in Loki's Castle (Northern Atlantic Ocean) site has [C/N]  $\approx$  6.8 and ample sulfide [3], hence neither N nor S (acting as a reductant) will limit the rate of C fixation there.

<sup>2</sup> Biosynthetic pathway of cyanide in myriapods is unknown. The same holds for source of cyanide in sponge isocyanides biosyntheses (possibly symbiotic bacteria?)

**Table 1:** Nitrogen transfer processes and redox reactions involving amines, catalyzing enzymes/metals and their ramifications for biochemistry. Note for a direct comparison that the value given for seawater corresponds to about one metric ton whereas that for soil is given per gram.

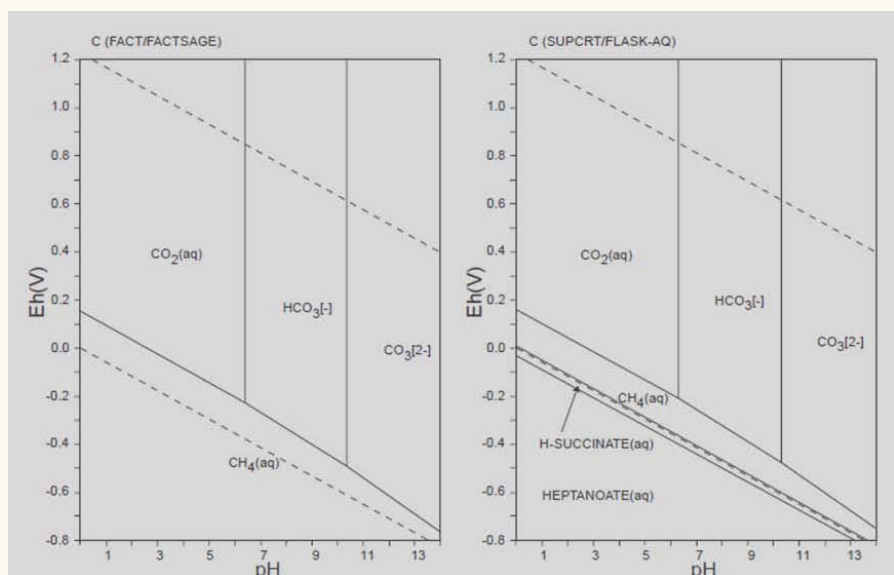
Substrate, products	[C/N] before and after	Organisms involved	metals in enzymes involved	Technical-chemical equivalent	Ocean abundance of metals [ $\mu\text{g}\cdot\text{m}^{-3}$ ]	Soil abundance of metals [ $\mu\text{g}/\text{g}$ ]
glycine $\rightarrow$ HCN + CO <sub>2</sub>	2 $\rightarrow$ 1	Pseudomonads, arthropods, sponges <sup>1</sup> , plants (seeds, roots [e.g. apricot stones, manioc])	Probably Fe	Ru complexes dehydrogenating primary amines or reducing nitriles	Fe 30 Ru $5\cdot 10^{-3}$	Fe: some 30,000 Ru $3\cdot 10^{-6}$
glycine $\rightarrow$ acetate + NH <sub>4</sub> <sup>+</sup>	2 $\rightarrow$ $\infty$	clostridia	W + Se	None known	Se 100 W 10	Se 5 W 2.5 $\rightarrow$ it takes 2 rare elements and a low local $\epsilon$ to cause CN bond cleavage; also occurs with sarcosine and betaine (then producing [tri-]methyl amine and acetyl phosphate)
RCONH <sub>2</sub> $\rightarrow$ RCOO <sup>-</sup> + NH <sub>4</sub> <sup>+</sup>	x $\rightarrow$ $\infty$ (x = small integer)	bacteria	Fe + Co, inhibited by iodoacetate or ICH <sub>2</sub> CONH <sub>2</sub>	Simple acid catalysis	Fe 30 Co 1.2	Fe: some 30,000 Co 8
RC $\equiv$ N $\rightarrow$ RCOO <sup>-</sup> + NH <sub>4</sub> <sup>+</sup>	x $\rightarrow$ $\infty$ (x = small integer)	bacteria	In bacteria: commonly Co	Simple acid catalysis	Co 1.2	Co 8
aspartate $\rightarrow$ carbamoyl aspartate	2 $\rightarrow$ 1.25		Carbamoyl transferase, hydantoinase: both Zn		Zn 360	Zn 50
reduction of N <sub>2</sub> , RNC to NH <sub>3</sub> (RNH <sub>2</sub> + CH <sub>4</sub> )	No direct effect for S = N <sub>2</sub>	Fe + Mo or V (nitrogen-ases are not equivalent)		Activated Fe oxides or Mo or W [ML <sub>2</sub> X(N <sub>2</sub> )] complexes (L' = bidentate phosphanes)	Mo 10,000 V 2,000	Mo 2 V 100, i.e. Mo prevails in ocean while V prevails in soil
NO <sub>3</sub> <sup>-</sup> $\rightarrow$ NH <sub>4</sub> <sup>+</sup>	No direct effect	universal	Mo in nitrate reductase		Mo 10,000	Mo 2
RCO-COOH $\rightarrow$ RCH(NH <sub>2</sub> )COOH	Plants: $\infty \rightarrow 2$ , animals: $\infty \rightarrow 5$	universal	none required (who does transfer electrons to pyridinium salt pyridoxal?)		-	- most metals were shown to inhibit reaction, Al <sup>3+</sup> does alter [C/N] by RCHO elimination from alcoholic amino acids
arginine $\rightarrow$ ornithine + urea	1.5 $\rightarrow$ 2.5 (cycle species) + 0.5 (urea)	universal	Mn, in some plants: Ni		Mn 20	Mn 440
2 NH <sub>2</sub> -CHR-COO <sup>-</sup> $\leftrightarrow$ dipeptide	No change for some symmetr. system (peptide bond replaces O)		In metallo-proteases: Zn, sometimes Co; process can be catalyzed omitting metal ions, too	SIPF reaction (Plankensteiner et al. 2002): Cu	Zn 360 Co 1.2	Zn 50 Co 8

## (Footnotes)

1 Biosynthetic pathway of cyanide in myriapods is unknown. The same holds for source of cyanide in sponge isocyanide biosyntheses (possibly symbiotic bacteria?)

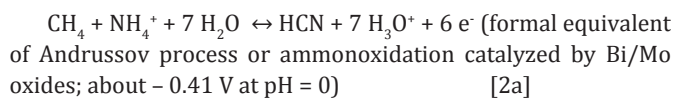
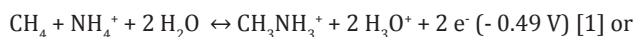
thus merit further thermodynamical considerations for setting limits or conditions of biomass stability, even apart from complete oxidation in an O<sub>2</sub>-rich atmosphere, with O<sub>2</sub> not being the strongest oxidant encountered and tackled with by biota: that is perchlorate [8], common in desert soils. Carbon and

nitrogen Pourbaix diagrams can be combined (superposed) to identify possibly stable assemblies of C, N, (O) and H combined in one molecule besides of (CO<sub>2</sub> + N<sub>2</sub> [cp. Martian, Venusian atmospheres]; CH<sub>4</sub> + N<sub>2</sub> or CO<sub>2</sub> + NO<sub>3</sub><sup>-</sup> [none of these does contain C-N bonds of any covalent order]): Let us first consider whether

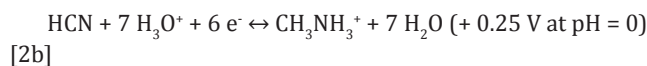
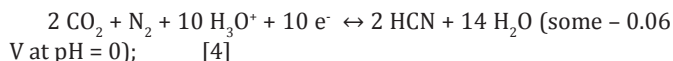
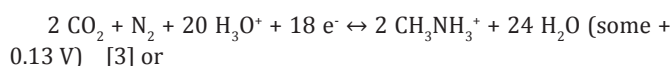


**Figure 1** Pourbaix diagram of carbon which shows CH<sub>4</sub> and CO<sub>2</sub> are directly connected, leaving no space for intermediate oxidation states represented e.g. by alcohols, carboxylic acids or sugars.

HCN or methylamine form some potential window in between



On one hand and



Accordingly, HCN tends to decompose into methyl ammonium ion (or glycine), CO<sub>2</sub> and dinitrogen (combination of [2b] and [4]) whereas CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> is stable towards disproportionation which would yield CH<sub>4</sub>, HCN and NH<sub>4</sub><sup>+</sup> (combination of [2a] and [2b]). In fact, HCN is known to undergo hydrolytic disproportionation affording oxalate, urea, glycin (-ate) and other products upon long-time RT standing in alkaline conditions, besides of polymerization (giving adenine, aminomalononitrile etc.) and hydrolysis to yield formamide, formate [9].

HCN is more stable at pH = 0 than both ammonium ion (albeit slightly so) and methane towards oxidation into CO<sub>2</sub>, N<sub>2</sub> while its formation by co-oxidation of CH<sub>4</sub>, NH<sub>4</sub><sup>+</sup> (essentially Andrussov process [at hot Pt] or promoted by Bi<sub>2</sub>O<sub>3</sub>/O<sub>2</sub>) takes place much more readily than that of methane alone. Thus, once either N<sub>2</sub> assimilation by organisms or some a biotic process including troilite or Fe/Mo systems takes place, [C/N] can be maintained finite (in fact, even down to 1) in acidic conditions, keeping or introducing N in(to) some covalent network. N<sub>2</sub> assimilation commenced less than 1 Ga after biogenesis [10], with limited CO<sub>2</sub>, CH<sub>4</sub> in the atmosphere then and before [11], and it is an

ATP-consuming though exothermic process up to this day. The generally Fe-centered pathways of biological N assimilation thus suggest life had to overcome thermodynamic obstacles already then (with simple model systems also processing HCN and isocyanides, like nitrogenase does), while primary products were rapidly removed from equilibrium by reductive amination or HCN cleavage, addition (Figure 1).

## BIOCHEMICAL EQUIVALENTS OF N-ELIMINATING TRANSFORMATIONS

Catalyzed by both W and Se in clostridia, glycinate undergoes reductive desamination to yield NH<sub>4</sub><sup>+</sup> and acetate [5] while the N-methyl pyridinium salt pyridoxal phosphate effects oxidative desamination to afford glyoxylate and NH<sub>4</sub><sup>+</sup> [12] while Al<sup>3+</sup> addition causes cleavage of 3-hydroxy-2-amino acids to afford RCHO and glycine [13], with either naturally occurring process increasing [C/N]. A small, finite [C/N] (which is almost constant among heterotrophs) cannot be maintained by keeping inside some potential windows (which do not exist as shown before) but rather by (fairly low) abundance/bioavailability of certain metals. This argument can be extended even to the TCA cycle: fumarate which can be hydrogenated into succinate, hydrated to yield malate (normally, both reactions go the other way round) will reversibly add ammonium ions to yield aspartate which in turn reacts with pyridoxal phosphate yielding oxaloacetate. Thus coupled equilibrium in both hydrogenation and oxidation tend to eliminate NH<sub>4</sub><sup>+</sup> once again, at slightly different redox potentials (in between, [C/N] = 4).

Both thermodynamically stable forms of C being volatiles (with CO<sub>2</sub> possibly locked up in carbonates), yet living biomass does share some 25% of total carbon in the regions accessible to a broad range of biota (troposphere, topsoil down to 3 m, Upper Ocean down to photosynthetic limit at some 100 m. The only other elements comparable to this are PGMs Ru, Os, and Ir [4]. Even though none of these is essential, and only Ru does undergo

observable bioaccumulation in marine algae [14], these elements share exceptional chemical features (particularly, catalytic properties with respect to hydrogenation, dehydrogenation and C-H bond activations).

Somewhat like C phase partition, the high inertness of  $N_2$  (average troposphere lifetime some 15 mio. y) brings about  $[C/N]_{\text{troposphere}} \approx 1.9 \cdot 10^{-4}$  prior to industrial revolution and  $2.6 \cdot 10^{-4}$  now, some factor of  $10^5$  less than in plant biomass although plants make use of another N source than the atmosphere (nitrate reduction, mostly taking place within rhizosphere). Aerobic heterotrophs are distinguished by  $[C/N] < 15$ , often much less than 10. We saw before how difficult it is to maintain low  $[C/N]$  unless for good N retention and venting of  $CO_2$ . Fortunately, not all thermodynamically possible reactions do occur rapidly (otherwise neither we nor atmospheric oxygen would be here!), thus the obvious difference between the above reasoning and the actual state of matter(s) is due to imperfect catalysis. In other words, while biomass is thermodynamically unstable and the efficiency of biochemical catalysts (most enzymes) is really admirable, their levels – and thus those of elements other than C, H, O, N, S and P which are involved in some 30 – 40 % of enzymes – are kept so low (although ambient levels might be much higher) as to maintain the biosphere against chemical destruction. Of course it is difficult to activate either  $N_2$  or CH bonds in mild (“physiological”) conditions.

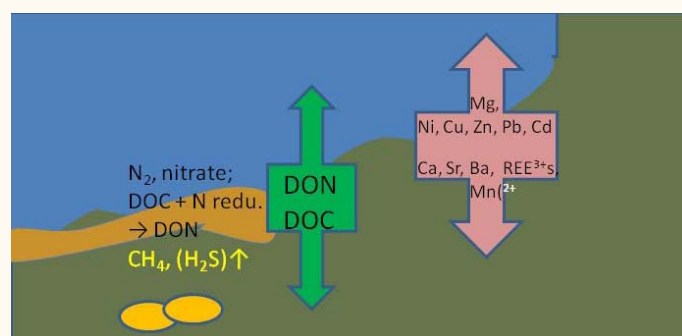
In terms of “Gaia” speculations, this lack of efficiency affords a common and mutual selection advantage: only cellulose and lignocelluloses not previously falling to wildfires keep available as nutrient sources to wood-rot fungi (and the entire bandwagon of organisms depending on their activity), bacteria or certain rodents (e.g. beavers). Likelihood of wildfires critically depends on atmosphere dioxygen levels [15]. Now, both wood decomposition by fungi (the only organisms which ever “invented” this pathway of metabolism, putting an end to hard coal formation some 298 mio. y ago [16]) and oxygenic photosynthesis (PS II) rely upon the same fairly abundant heavy metal, Mn. More Mn in soil (and wood) thus would increase burn down (combustion probability) of wood, enhance nutrient cycling via ash but keep fungi from more subtly exploiting lignified cellulose and hemicelluloses. In turn, balance between electrons from water photo oxidation and their consumption in  $CO_2$  reduction requires a certain range of Mg (chlorophyll, rubisco) and Mn levels in leaves, needles [17].

Common Mn levels in photosynthetic organs of plants are some 50 – 150  $\mu\text{g/g}$ , i.e., some 10 – 35% of average soil level (440  $\mu\text{g/g}$ ), except for some *Vaccinium* scrubs where typical levels are rather 700  $\mu\text{g/g}$  [14,18].

At very low potentials both  $[C/N]$  and  $[C/P]$  may be modified by reductions (cp. trimethyl amine degradation by *Methanosarcina* spp.). This causes us to look for the strongest available biogenic hydride donor (i.e., that one with the lowest formal redox potential) or the most strongly reducing species produced by living beings. Omitting the questionable identification of  $BiH_3$  by GC/MS run [19] in conditions where this compound would last for seconds at most (while the much more stable lower analog  $SbH_3$  never was clearly identified as a bioproduct [20], this compound is stannane  $SnH_4$  afforded by bacteria decomposing *Enteromorpha* algae in anaerobic conditions (ibid.).

### NITROGEN RETENTION IN BIOMASS AND SOLVENT, ENVIRONMENT, N COMPOUND POLARITIES

Water is a highly polar medium which readily produces H bonds while sediment, in particular inundated sediment, is fairly non polar, causing extraction and enrichment of non-polar organic and inorganic compounds adsorbed from an overhead water column or even air. E.g. while benzene or butyric, succinic acids are little soluble in water, replacement of a single C atom with N while maintaining bond topology produces pyridine or sarcosine or  $\beta$ -alanine which are fully miscible or extremely soluble in water. Both open water and submerged sediment are populated by many different kinds of organisms while the latter commonly gets anoxic within a few mm below surface, and both DOC, DON outcompete particular (i.e., detritus mainly), living C, N by far in water. Yet the above exchange and (negative) alteration of  $\log k_{ow}$  (which also holds for complexes) will cause some fractionation and change of  $[C/N]$  ratio near the upper sediment edge and make elements whose cations readily form complexes with amino acids or carboxamides to move from sediment to water while others which are more affinic to carboxylates or hydroxy-carboxylates will be drawn into the sediment (Figure 2). Either process will affect local biota, with depletion of N in sediment being less significant as sulfate reducers are distinguished by very high  $[C/N]$  while metal ion fractionation/transport could



**Figure 2** Partition of N and metals by sediment interface-related metabolic activities. The orange area is the reducing field where  $[C/N]$  is decreased to form a) polar DON (much more abundant than PON, living biomass) and b) non-polar lipids (DOC, POC) which enhance extraction properties of sediment. Metal ions then follow paths according to  $x_{sd}$ .

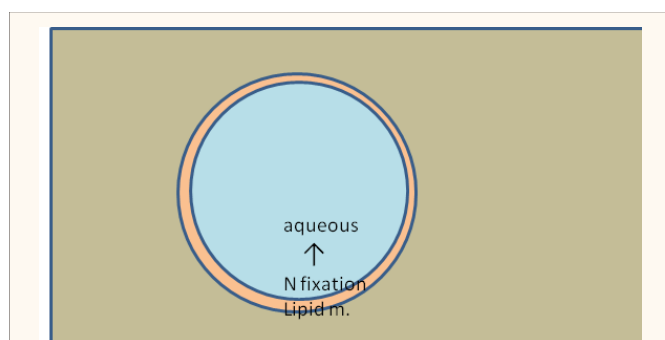
pose limits to living conditions of some specialized organisms<sup>3</sup> (Figure 3).

This will influence the biota the more as many of the former elements are involved in biochemical processes which are typical of submerged sediment, e.g. Ni in methanogenesis. In addition sediment feeders must cope with a higher [C/N] in their diet. Organisms living in reducing conditions tend to accumulate less N in their body, which at first glance does relieve the problem but in the long run means further enrichment of sediment with lipids which thus becomes even more unpolar, increasing the effect mentioned above.

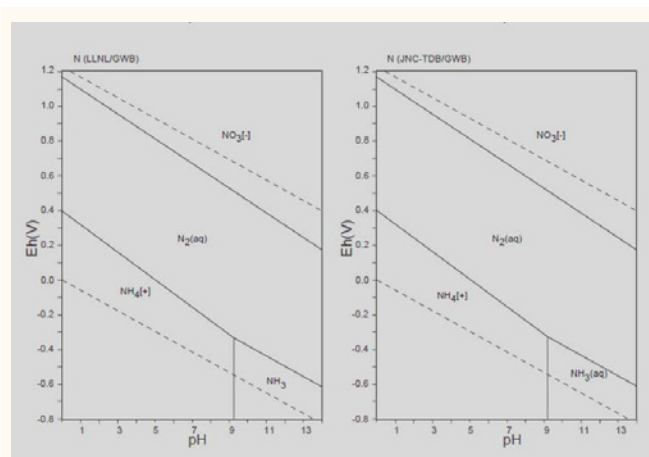
Volatile speciation forms of elements C, N, P, and S are involved in loss of these from biomass, primarily being CO<sub>2</sub>, CH<sub>4</sub>, (non-N<sub>2</sub>) N<sub>2</sub>O, HNO<sub>3</sub>, NO<sub>x</sub>, HCN and CH<sub>3</sub>CN, PH<sub>3</sub> and COS, SO<sub>2</sub>, dimethyl sulfide. Reactivity towards OH radical will control composition of trophic networks by way of nutrient recycling. Troposphere lifetimes of those molecules given in normal letters [23] are sufficient to permit global spreading (or continent-, hemisphere-wide for CO or HCN [ $\tau \approx 100$  d]), and thus airborne exchange among ecosystems, whereas those given in italics will likely recycle N, P, S, respectively, to the same forest or water body. For C, N, S, Cl and other elements most of atmosphere-biota feedback is related to but one speciation form (for relative data on feedback, cycling [24], principal chemical species being NO and NH<sub>3</sub> [nitrogen], SO<sub>2</sub>, H<sub>2</sub>S [sulfur], HCl [chlorine], and oxidation intermediate HCHO besides of CO<sub>2</sub> but not CH<sub>4</sub> [carbon]). N content- and thus [C/N] studies (as [C] is almost invariable in vegetation) show a ready uptake of both ammonia and N oxides by plants (in particular, mosses) depending on air burdens of these short-lived gases. Nutrition status e.g. of reindeer or other moss grazers will be influenced by this. *Sphagnum* mosses respond to N burdens > 0.3 g/m<sup>2</sup>a (which is really a low input) by releasing both inorganic N and DON to surface waters surrounding them, rather than increasing growth (here, [C/N]  $\approx$  30) (Figure 4).

DON and DOC differ in their physicochemical properties. While – except for amino- vs. “plain” carboxylic acids, e.g. comparing sarcosine,  $\beta$ -alanine with butyric acid but not the respective esters - log  $k_{ow}$  is determined by bond topology mainly

<sup>3</sup> Identification of BiH<sub>3</sub> was based on an estimated retention time only; identification of BiH<sup>+</sup> and BiH<sub>3</sub><sup>+</sup> in mass spectra is straightforward when using H<sub>2</sub> as a carrier gas while the reported BiH<sub>3</sub> level in human exhaled breath was reported to be < 10<sup>-13</sup> mixing ratio (< 1 ng/m<sup>3</sup>, < 100 ppqv) [26].



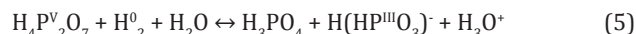
**Figure 3** Migration trends of DON (formed) in a cell. The grey background is sediment matter.



**Figure 4** Pourbaix diagram of nitrogen (two different data bases). There are just four stable entities. The positions of N<sub>2</sub>/NH<sub>4</sub><sup>+</sup> and N<sub>2</sub>/NO<sub>3</sub><sup>-</sup> transitions are such as to preclude both CO<sub>2</sub> reduction by ammonium ion and H transfer to HCN even if N<sub>2</sub> reduction were not inhibited by activation barrier.

(i.e.,  $a \approx 1$ ) the (considerably negative) value of  $b$  determines the additional hydrophilicity of DON (dissolved organic nitrogen) caused by HO-H...N<sub>org</sub> hydrogen bonds; e.g., while benzene is little soluble in water and vice versa, pyridine and water do mix in any volume relationship. The aqueous medium of the interior of a cell, as opposed to its membrane linings, thus augments N withholding (Table 2).

Both pnictogenes which are commonly considered in ecological stoichiometry, N and P, might undergo venting if  $\mathcal{E}$  is sufficiently low; PH<sub>3</sub> was first detected over Wadden Sea plains and in cities like Leipzig [25] (Figure 5).



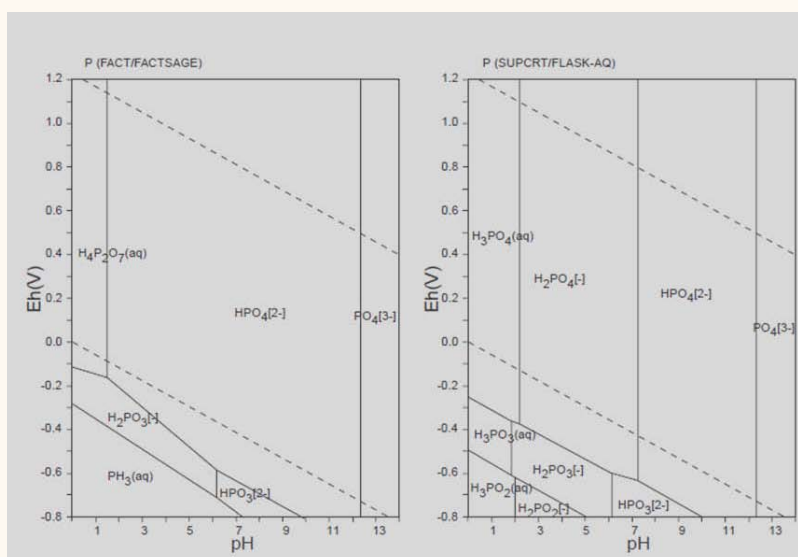
The Mitchell pathway of phosphorylation indirectly transferring energy (and water abstraction equivalents) from any kind of redox process among other chemical species is required to produce biomass. Probably chemolithoautotrophy is very old while there is also evidence for biological N<sub>2</sub> reduction more than 3 bio. y ago. Now let us consider implications for [C/N] and [C/P] from this. At marine pH, HPO<sub>3</sub><sup>2-</sup> and thus PH<sub>3</sub> formation should not occur above -700 mV, well below the potentials for both CH<sub>4</sub> and H<sub>2</sub> formations (-340 and -485 mV, respectively). While phosphine does form there and in ammonia-laden animal excretion sludges, and there are estimate of P venting as PH<sub>3</sub>, the effect on [C/P] of Wadden Sea sediment biota is not straightforward to estimate. Additionally, even more than with CH<sub>4</sub>, it is likely that most of phosphine undergoes either biological reoxidation or formation of phosphide minerals somewhere up the sediment strata, with P never entering atmosphere. Similar arguments hold for PH<sub>3</sub> emissions during nighttime in towns. PH<sub>3</sub> venting is higher on Antarctic shore tundra soils inhabited by penguins than that populated by seals or no marine vertebrates at all [27].

## WHY BIOMASS YET IS METASTABLE: LIMITED LEVELS OF CATALYST METALS

There is no reason to assume that evolution might have

**Table 2:** polarity effects caused by exchanging some C- with an N atom, e.g. during amino group attack on esters or alkyl phosphates or reductive amination which then withhold N within the polar, aqueous interior of some cell or entire organism.

Kind/topology of DOC	topological equiv. among DONs	A*log $k_{ow(doc)}$	b
n-alkanes	Prim., sec. amines	0.899	-0.912
Carboxylic acids	Amino acids	2.063	-3.19
methyl ketones, esters	carboxamides, AA esters	0.863	-2.130
benzene-, naphthalene aromatics	pyridines, quinolines	1.133	-1.877

**Figure 5** The left part of the left Pourbaix diagram shows that diphosphate is a good hydride acceptor even though the equilibrium of the redox couple ( $\text{pH} \leq 1.6$ ).

“avoided” establishment of functions which in the long run might eliminate N from biomass, pushing organics nearer towards thermodynamic stability, that is, either  $\text{CH}_4$  or  $\text{CO}_2$  or  $\text{HCO}_3^-$  plus some isolated, C-free speciation form of N. Likely rates of these “unmixing” processes are limited by limited availability of catalysts whereas only few elements are controlled with respect to their transport into and inside cells by chaperons, such as Cu, Ni, or Sb. We are left with the conclusion that the others which might possibly cause “uncoupling” reactions are rare enough to avoid these processes in common conditions.

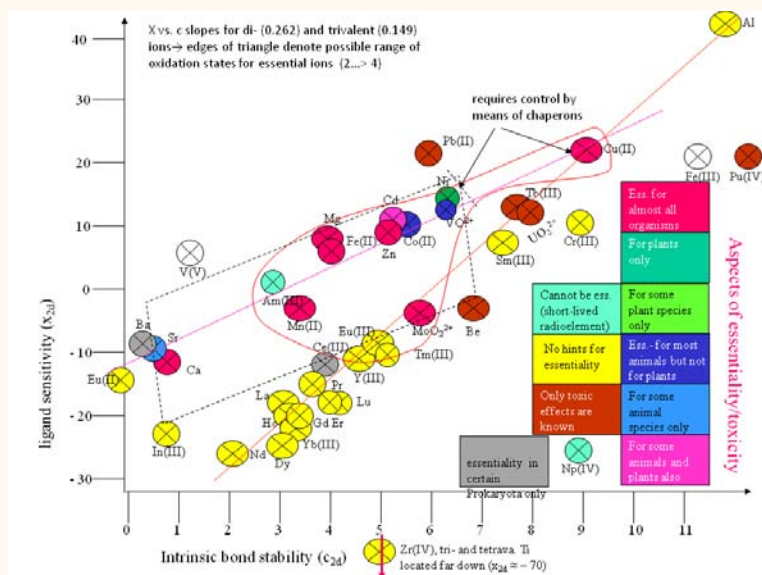
O get a first idea to which extent elements which possibly catalyze reactions critical to N content of biomass get withhold by it reconsider distribution of elements in biomass [4]. In this study the region where photosynthesis might take place or influence soil chemistry by root activity was considered to be “accessible” (column 6 in tab. 3), which amounts to the top 100 m of ocean and top 3 m of soil (forest rhizosphere). X and c [17,28] denote quantitative features of metal ions in complexation (Figure 6) by which a certain parameter range is distinguished by being apparently favorable for biological purposes (“window of essentiality”). Positive values of  $x_{2d}$  [28] (Table 3), optical representation see Figure (6) denote a bias towards N donors (amino acids, carboxamides, nitriles, heterocycles alike), while negative  $x_{2d}$  means preferred binding via O donors (e.g. carboxylate). Accordingly, within and around the “window of essentiality” different [C/N] in biomass will influence the

extent of retention of certain metal ions by biomass. In some metabolic processes mutual relationships of two metals must be balanced, e.g. [Mg/Mn] in photosynthesis for an efficient coupling of water photo oxidation and electron consumption to reduce carboxysugar phosphate. Conversely the effective electrochemical ligand parameter controls bioaffinity of metals which can be involved in either C-N uncoupling or transformation of biomass into either  $\text{CH}_4$  or  $\text{CO}_2$ .

$$-\log k_{\text{diss}} = x^* E_L(L) + c [17,28]$$

Where  $E_L(L)$  is electrochemical ligand parameter, being an empirical measure of ligand/metal ion covalent interaction on orbital energies (of di-/trivalent Ru but likewise applying to other coordination compounds). Almost identical average BCF for couples Sr/Mg, Mn/Ni and Cu/Zn  $\rightarrow E_L(L)_{\text{eff}} - 0.20, -0.18$  or  $-0.29$  V, Y/Cr gives  $-0.17$  V<sup>4</sup>  $\rightarrow$  less than average terrestrial green plant, indicating an even larger [C/N] ratio of  $\geq 40$  (low share of amino acid, carboxamides [peptide bond] or N heterocycles [purine, pyrimidine, porphyrine, histidine side chains] ligand functions). The Irving-Williams series is maintained only within

<sup>4</sup> Possibly, this fractionation effect among “bimetals” can be observed in some peculiar populations/new species of Loricifera which dwell in anaerobic (sulfate reduction occurring, hydrogenosomes replacing mitochondria in these animals) hyper saline deep-ocean sediment near Crete Island [29,30]: although there are lots of Mg (0.4 M/l) in the overlying brine, there is virtually no Mg in the organisms, while levels of Cu and Zn also differ from those observed in “normal”, aerobic Loricifera populations outside the Mediterranean Sea.



**Figure 6** The implications of complex binding properties for biological roles of elements. Metals whose complexes are “too stable” regardless of ligand-derived modulating effects tend to be highly toxic (Be, Pb, U and heavier elements). Note essential functions of Ce and Ba in prokaryotes. X is related to complex stability by empirical relationship.

**Table 3:** elements of Irving-Williams series (and some trivalent ones) in their sequence of common stability of bidentate ligand complexes (Irving & Williams 1953) vs. share in biota, BCF from soil urease is specifically mentioned for its role in controlling [C/N] in an organism.

Element ( $M^{2+}$ )	x	c	Share in soil (ppb)	Log share + 9	Share in biota (% of accessible M)	Log share + 9	Essential?	Relative BCF; remarks
Ba	-8.0	0.45	500,000	5.70	0.02	5.30	For desmid microalgae	0.40
Sr	-9.0	0.55	200,000	5.30	$2.1 \cdot 10^{-3}$	4.32	For stony corals	0.10
Ca	-10	0.73	$15 \cdot 10^6$	7.18	0.7	6.85	almost universal	0.5
Mg	8.24	3.94	$10^6$	6.00	$7.5 \cdot 10^{-3}$	4.87	universal	0.075
Mn	-5.32	3.01	440,000	5.65	0.1	6.00	almost universal (urease, malate enzyme in animals)	2.3
Fe	6.05	4.20	About $3 \cdot 10^7$	7.48	$10^{-3}$	4.00	Almost universal	$3 \cdot 10^{-4}$ biological share similar to REEs, commonly divalent in biomass
Co	3.93	5.48	8,000	3.90	$5.5 \cdot 10^{-3}$	4.73	Nitrile hydratase, C backbone rearrangement, $CH_3$ transfer, $N_2$ assimil.	7
Ni	13.33	6.41	50,000	4.70	$7 \cdot 10^{-3}$	4.85	methanogenesis, plant ureases	1.4
Cu	21.84	9.04	20,000	4.30	0.11	6.04	Many redox enzymes, e.g. arene hydroxylation	55
Zn	8.69	5.15	50,000	4.70	0.22	6.34	universal	44
Pb	11.8	5.7	23,000	4.36	0.01	5.00	None known	4.3
Cd	11.30	5.29	1,000	3.00	0.012	5.07	“backup” carboanhydrases	120
Trivalent ( $M^{3+}$ )								
Al			About $4 \cdot 10^7$	Some 7.60	$4 \cdot 10^{-4}$	3.60	None known	$10^{-4}$
Cr	13.9	8.90	50,000	4.70	$6.5 \cdot 10^{-3}$	4.82	(contested)	1.30
Y	-11.0	4.71	23,000	4.36	$1.9 \cdot 10^{-3}$	4.27		0.8 Does accumulate in apples, catalyzes lactam $\rightarrow$ polyamide conversions, next to “window of essentiality”
Ce			50,000	4.70	$2.2 \cdot 10^{-3}$	4.32	Methanol oxidase of some methylotrophic bacteria	0.44



some narrow range of electrochemical ligand parameter; else “permutations” in ranking will be observed [17] (Table 3).

Soil bacteria are as rich in N as animals or fungi whereas sediment tends to get depleted by fractionation/partition after introduction of N into some covalent framework. This partition, e.g. brought about when some organic matter next to surface of an inundated sediment happens to be in an area of sediment column where nitrate undergoes reduction by either  $H_2S$  or  $CH_4$  (Figure 7) will mean N-enriched organic matter gets extracted into water by decrease of  $\log k_{ow}$  while “plain” organics will be partitioned into the (fairly non-polar deeper sediment (Figure 2 above). The same is going to happen next to the (either lipid or [in Archaeans] long-chain ether) membrane of a cell, in favor of withholding N inside it (Figure 4). The effect will be more pronounced if the cell or larger organism dwells within sediment. During evolution many metabolic pathways developed which were capable of changing both [C/N]- and [C/P] ratios (Table 4).

Except for methanogenesis and plant-related processes, there is some “trend” in evolution to decrease both [C/N] and [C/P], that is, “in favor” of higher enzyme levels (see below) and metabolic activities while shares of (N-free) storage compounds get reduced. Both C/Mg- and C/Ni ratios are likely to change during late chemical evolution as from the primary to later steps complexation properties of intermediates will alter and “improve” (in terms of both complex formation constants and selectivity) during chemical evolution [4,17]. Among the mentioned metals, Mg tends to bind to (hydroxyl-) carboxylic acids, while Ni “prefers” cyanide and amino acids and Zn is somewhat more flexible in terms of ligation, also including binding to S donors (Figure 6).

Most of  $CH_4$  (also cp. Figure (2)) and an unknown part of  $N_2O$  are re-processed in topsoil limiting the effects of volatile formation on [C/N] in a given topsoil biota. The same holds for [C/P] as most of phosphane formed remains adsorbed to matrix [27]. Once methane or nitrous oxide made it to the atmosphere, they are lost for a given ecosystem or westward of it; matters are different for  $PH_3$  due to its short troposphere lifetime of a few hours. Yet there was some period in early evolution [10] when there was methanogenesis but not yet methylotrophic biochemistry or  $N_2$  fixation<sup>5</sup>, meaning that [C/N] was going to

5 <sup>7</sup>These values relate the fractionation behavior of some (assumed to be) biden-

increase in early sediments. These sediments are distinguished by high levels of magnetite and siderite ( $FeCO_3$ ) [11]. These might have influenced C feedback in late chemical evolution on Earth also. With no  $O_2$  around, estimated lifetimes of  $CH_4$  in the troposphere (now about 10 years; [23]) may have been much longer some 4 bio. years ago, thus ensuring global dispersion of fully reduced C almost from biogenesis onwards. Yet the data on Martian  $CH_4$  strongly suggest there are effective sinks not yet understood or appreciated, such as adsorptions to clays or possibly photo electrochemistry in Ti-containing mineral phases [31-34]; most of  $CH_4 \rightarrow CO_2$ , little formation of CN bonds with co-substrates). As nutrient feedback within an ecosystem is a crucial feature of ecological stoichiometry and ecosystems dynamics, topsoil bio- and atmospheric chemistry of C-, N-, S-, etc [35]. Compounds gained importance once biota “fragmented” into different ecosystems, probably even before  $O_2$  became a major component of the atmosphere. By now it is impossible to estimate the size of such effects some 3 – 2.3 bio. years ago.

### [C/N] IN DIFFERENT KINDS OF PROTEINS

The optimum [C/N] depends on function of some protein, the following diagram also including „exotic“ ones such as self-replicating peptides which might have had some more significant role in very early forms of life (yet, genetic dating [36-38] does extend some 4 bio. years ago indicating that such a phase predating “modern” forms of life and of organizing inheritance must have been short at most (Figure 7, Table 5).

### CONCLUSIONS

Biomass is unstable not only ever after the Great Oxygenation Event but was so from the very beginnings. Its constant existence on Earth, especially given the fact that yields of “prebiotic” energetized chemical transformations are fairly poor in realistic geochemical settings, is likely due to the fact that elements which promote covalent uncoupling of C and N use to be rare, some of them (or even reactions like in the nitrile/primary amine equilibrium) additionally requiring kinds of ligands uncommon to biology, such as phosphanes or arsanes. Organisms which yet

tate ligand including biomass (by all experience, one entire organ of a plant or animal behaves in a homogeneous fashion);  $E_{(L)} = -0.17$  V e.g. corresponds to oxalato ligand [17]. Common values for photosynthetic organs of land plants are somewhat higher whereas in aquatic plants  $E_{(L)} \leq -0.3$  V which is required for sufficient uptake of Mn from trace levels in ocean water

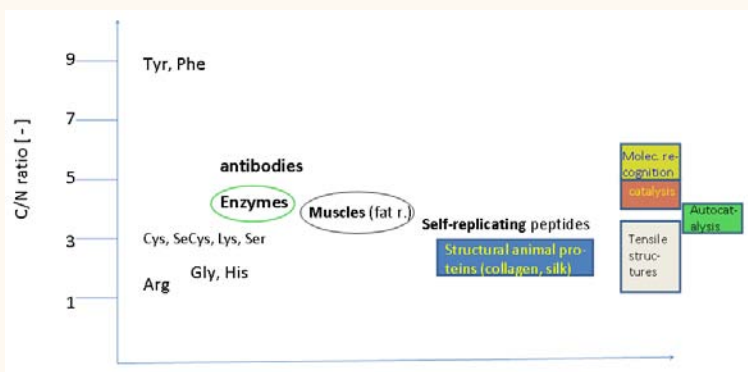


Figure 7 [C/N] vs. protein function. “tensile structures” include tendons, silk fibers and the like while molecular recognition refers to antibodies.

**Table 4:** sequence of steps/"innovations" in evolution and drawbacks for ES [C/N]- and [C/P] ratios (timescale according to Battistuzzi et al. 2004).

Process	Approximate beginning (Ga ago)	Metals catalyzing	Effect of pathway on [C/N] in biomass product	Effect of pathway on [C/P] in biomass product	Preference to "prebiotic-formed" ligands (which?)	Remarks
0 (starting conditions)	< 4.55	Not applicable	[C/N] probably < 10 <sup>-2</sup> in primeval atmosphere	Not applicable		[C/N] about 30 on Venus, Mars now
1 chemical evolution	4.4 – 4.3 ?	Several (experiments are non-specific, employing metal ion mixtures)	↑↑ (does define starting level, likely large, between 3 – 50)	? (prebiotic pathways into "activated phosphate" use Fe/(CN <sup>-</sup> , hv) and Mg)		In prebiotic simulation experiments, yields of RCH(OH)COOH, simple carboxylic acids (mainly formate, acetate) and benzene each use to be higher than those of RCH(NH <sub>2</sub> )COOH (most of the latter uses to be glycine, sometimes alanine) [Miller & Urey 1959], that is [C/N] ≈ 10 – 15 among combined products other than "tar"
2 methano-genesis	Between 4.1 and 3.78	Ni (first step: Mo or W for O abstraction from carbamate <sup>1</sup> ). Depends on species: W may replace Mo but not vice versa	↑	↓ (phosphorylation by exothermic process, most of used C vented as CH <sub>4</sub> )		[C/N] in methanofuran, methanopterin and Ni-F <sub>430</sub> ; about 5 (carbamate, formamide intermediates)
3 methylotrophy	About 3.6	Ni ("classical") Ce and other REEs	↓	↓	Ni: amino acids, thiolates; REEs: hydroxy-carboxyl-ates	
4 chemolitho-autotrophy	> 3		± (depends on parallel N fixation capability)	↑ (energy storage in C compounds [saccharides, lipids] rather than via NTPs)		
5 N <sub>2</sub> assimilation	3.2		↓	↓		
6 sulfate reduction	About 3		↓ (does consume organic matter thus not available for biomass buildup)	Probably ↓		Exceptions: reduction of H <sub>2</sub> (if p <sub>H2</sub> > 1 mbar), inversion of sulfate reduction near 100°C (fumaroles, black smokers)
7 oxygenic photosynthesis	Close to 3		↑ (no direct coupling to N fixation; [C/N] ≈ 30 – 40 in photosynthetic organs of green plants)	↑ (energy storage by plants, algae in C compounds [saccharides, lipids] rather than via NTPs); [C/P] ≈ 1,000 in photosynthetic organs of green plants		Oldest samples giving proof of oxidizing surface conditions (U(VI), Cr(VI)) are 2.96 bio. y old
8 nitrate respiration	? (requires presence/stability of N <sup>ox</sup> )	Mo	↓ (C loss, N uptake)	↓ (C loss, prolific ATP production)		
9 formation of heterotrophic multicellular organisms	1.5 ? (prior to separation of fungi, animals and non-algal green plants)		↓ ([C/N] usually < 12 in multicellular heterotrophs)	↓ (O <sub>2</sub> oxidation of C substrates provides much ATP)		
10 oxidative degradation of lignified aromatics, polysaccharides	0.298	Mn + Fe-haem, with aromatics: Cu or V	↑ (wood is almost nitrogen-free)	↓		

## (Footnotes)

1 In synthetic organic chemistry carbamate esters are reduced using LiAlH<sub>4</sub> to directly yield methyl amines, but often with rearrangement of carbon backbone

**Table 5:** Key steps of evolution and their ramifications for [C/N]- and [C/P]-ratios in (going-to-be and present) biota.

	substrate	metals involved	first intermediate(s) after fixation steps	kinds of organisms, evolutionary estimated age	minimum level of crucial metal (s), co-substrates; remarks
Pathway of C fixation into (proto-) biomass					
methanogenesis	CO <sub>2</sub>	Ni (methyl group transfer from cobalamine, methanol, acetate, eventual reduction by coenzyme M thiolate); Mo or W (starting step of carbamate reduction)	Primary carbamate	Methanogenic Archaea, 3.8 – 4.11 Ga	Ni > 12 µg/g substrate, Co ≥ 0.5 µg/g, p <sub>H2</sub> > 5 mbar
	acetate trimethyl amine	Ni (CN bond cleavage in TMA also caused by Ni corrinoids)	CH <sub>3</sub> -Ni compounds		
methylotrophy	CH <sub>4</sub> primary alcohols	Ni, sometimes REEs like Ce		Various bacteria, yeasts	REE-based methylotrophy takes exceptional levels of Ce etc. in water, sludge
Heterotrophic nutrition	Complex organic compounds (AAs, TCA acids, lipids)	Peptidases: Zn Transamination: no TCA (Krebs cycle): Mg, Zn, Mn Rearrangement of carbon backbones: Co	TCA species, acetyl CoA		
Pathway of N fixation into (proto-) biomass					
prebiotic	N <sub>2</sub> or NH <sub>3</sub> , spark discharge, catalytic reduction or photo-semiconductor		Spark discharge: HCN, other: NH <sub>4</sub> <sup>+</sup>		
N <sub>2</sub> assimilation	N <sub>2</sub> , isocyanides		NH <sub>4</sub> <sup>+</sup>		Also cleavage of C≡N bonds (isocyanides faster than nitriles) to produce CH <sub>4</sub> besides of NH <sub>3</sub> , amines Requires much ATP although reactions are exothermic
Nitrate reduction	NO <sub>3</sub> <sup>-</sup>	Mo	NO <sub>2</sub> <sup>-</sup>		
Nitrile-, carboxamide hydrolysis	RCN, RCONHR'	Co	One-step		
urease	urea	Ni in green plants, Mn in animals	One-step		
transamination	Amino acids	none	2-oxo acids, pyridoxamine		most metals inhibit activity of pyridoxal phosphate to some extent → indirect control of [C/N] by metal serum level

effect either of these transformations, e.g. making HCN or NH<sub>4</sub><sup>+</sup> from glycine do so only in very protected, contrived conditions or at particular redox potentials. Any finite [C/N] other than 1 is unstable hence it is remarkable that this key parameter of ecological stoichiometry is almost constant among heterotrophic organisms. Functional proteins use to have [C/N] ≈ 4, values for compounds involved in electron transfer like flavines or porphyrins are similar. Processes which revealed limits of stability of C compounds started already at the very beginnings of biological evolution (methanogenesis) [39-43].

Later events in evolution were likely to decrease both [C/N]

and [C/P] step by step, except for onset of oxygenic photosynthesis and possibly of certain kinds of chemolithoautotrophy [44,45]. The decreased log *k*<sub>ow</sub>, increased hydrophilicity of N organics vs. isotopological C frameworks permits to maintain finite [C/N] inside a cell surrounded by unpolar (lipid or long-chain ether) membranes, sediment while it causes both N enrichment and transport of metals forming stable amino acid- or amine complexes from sediment to overhead water column [46,47]. The latter processes can be observed by proper placement of chitin plates which adsorb metals mobilized by this and other biochemical processes occurring at or below the sediment top.

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