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Making Chitin Work in an Electrochemical Environment with Non-Noble, Moderately Electropositive Metals: Production of Sensors and Batteries

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Abstract: Due to adsorption of all metal ions (and some non-metals like As, Sb), metal complexes and metal-rich small (oxide, carbonate, oxalate) particles alike, chitin does remove these M species from a solution or from moist sediments, depleting the solution down to pMol/l levels except for alkali metals, or Mg. Chitin retains substantial metal ions from solutions < 1 nMol/l. Accordingly, there is a (concentration gradient-caused) voltage between two identical pure metal or -alloy electrodes of which one is wrapped by chitin. While 10 min will do to obtain reproducible adsorption on chitin, electrochemical measurements show that the voltage forming between a chitin-surrounded and an identical bare metal electrode keeps on changing for 24 hours except for Ni. Preliminary experiments showed that dried arthropods produce similar results as previously purified chitin(proteins and metal carbonates removed during workup). On chitin exist on-equivalent binding sites the former of which are quickly populated and the metal ions then pass to the latter. However, these latter sites are still located next to the surface of chitin: upon addition of an appropriate ligand, voltage will massively increase within 1 – 2 min which shows that even sizable ligand ions (glycinate, phenolic carboxylic acids like caffeic acid) can still access the metal ions in aq. solution. Chitin does catalyze ligand glycinate oxidation by introduced air oxygen next to cobalt electrodes. Multimetal electrode chitin-modified sensor systems, batteries and designs of fuel cells are discussed. This does agree with results concerning adsorption on surface of living crayfish and crickets and means that the latter can be involved in investigation protocols for environmental pollutants. Except for a longer lag time, electrochemical data are easier to obtain than analyzing metal contents on a chitin interface. Voltage does increase rapidly when there is addition of either a ligand, some species connecting a metal ion to the chitin surface by some molecular or ionic bridge or of an anion which does form hardly soluble salts (e.g., to set M levels in solution similar to those in the open environment) and keeps up for several days until the chitin gets saturated with the metal ion. Oxidation of ligand (glycinate) or reduction of precipitating agent (iodate) both change the voltage but with different signs. Effects of SCN^- addition suggest possible photoactivation of signals, too.

Keywords: chitin; transformation of chemical into electrical signals; sensors; batteries

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1. Introduction

Like other polymeric compounds displaying potential ligand functions, e.g., polyacrylonitrile, polyacrylic acid, bakelite, or organic semiconductor polyaniline, different biopolymers and their thermal or geochemical decomposition products also can retain metal ions. One particularly abundant, easy-to-isolate- and thermally robust such biopolymer is chitin. Chitin (and chitosan) used to be employed in treatment of waste-waters and mine tailing water to withhold heavy metal ions. Whereas an exposition duration of some 10 – 20 minutes was determined to suffice for removal of potential pollutants (in full agreement with our results), it is not yet known whether this does actually

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represent a stable state in thermodynamic terms or metal ions or -complexes will relocate to some other site after adsorption.

It should be noted that "native" chitin mainly is not chitin at all but contains high levels of $CaCO_3$, proteins, and cross-linking quinones [1, 2]. However, the polysaccharide can be extracted from this readily, the purified material (≥ 20% of the original material of obtained from crustaceans) can be purchased, and when we speak of chitin and discuss its properties, we refer to this latter polysaccharide which was employed in both environmental monitoring and electrochemistry by us before. Additionally, the adsorbed amounts of elements at essentially the same site (few cm apart) depend on chitin being exposed to water or to (different kinds of soft) sediment next to each other [3, 4].

Because – as a rule – levels obtained from placing chitin into sediment use to be higher, mechanical extraction of such a sample into the aq. phase will cause desorption of some share of the sorbate given appropriate kinetics. As equilibrium states are available from studies in water, also including effects caused by adding ligands, the respective adsorption timescales allow to estimate the timescale of desorption, too [5]. The latter has drawbacks for vertical transport of elements and sometimes for starting biochemical processes depending on them. Chitin samples previously exposed to sediment can be bared either by muscle activity, e.g., with the leg tips of some crayfish, or simply by periodical erosion, e.g., in surf- or tide areas. Thereafter, certain elements (inter alia, Bi, Eu, and Cd) had been shown to pass for example into an ant, via adsorption to the surface/cuticula and then through pores in the chitin cover rather than by mouth (which holds for other REEs, Zn, Mo, and others) [6]. After erosion or pullout certain biochemical pathways will start next to the water-sediment interface (e.g., employing V in haloperoxydation or N_2 assimilation and LREEs such as La, Ce in oxidation of primary alcohols [7], Mn in photosynthesis in algal mats at bottom of some water pool) or further transport by zooplankton periodic migration takes place.

Both these issues can be addressed by some simple electrochemical experiment (fig.1):

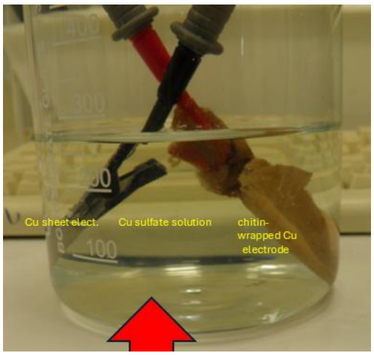

Figure 1. Two identical Cu electrodes are immersed into a dilute aq. Cu nitrate solution. One electrode is located in a mesh bag (right) loosely filled by chitin. Voltage is about 90 mV prior to ligand addition.

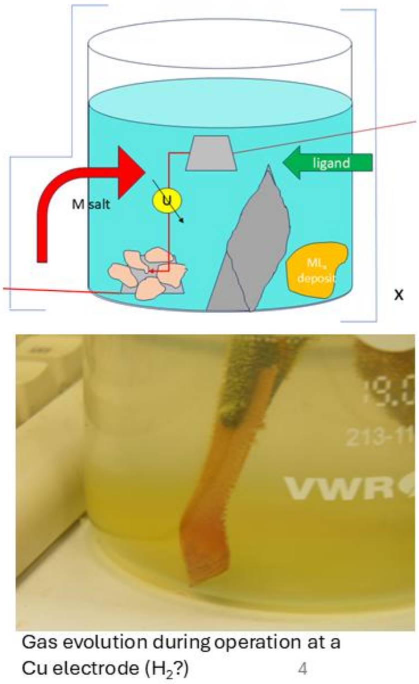

Figure 2. Scheme of cell (top) and gas evolution at more negative bare electrode (bottom).

When the voltage in this setup (and possible responses to ligand additions, including both organic ones and ions like carbonate [REEs, Ga, In], sulfate [REEs], fluoride, or chloride) depends on the kind of metal – which was demonstrated in this work – one can measure even traces of these elements in water, sediment because adsorption may already reach saturation at very low levels, for example 1 nMol/l for Ni^{2+} [3] which is considerably less than the common levels of Ni in freshwater (10 – 70 nMol/l) [8].

Digby (1964) [9] and an Israeli group ([10]; starting in 1991) studied electrochemical and photoelectric/thermoelectric effects related to chitin surface of arthropods (Asian hornet, limpet *Palaemonetes varians*) [fig.3]:

Figure 3. Arthropods chitin layers of which produce electric signals in different non-equilibrium conditions.

It should be noted that

a) intrinsic resistance of chitin is so high that in fact it was used as a dielectric material in capacitors before [11] and

b) the low levels of "embedded" redox-active species (Fe, Ti, quinones, Cu) seen in (native, purified) chitin will not produce any electrochemical signal, probably for the same reasons. This does hold even when chitin samples were dissolved in dimethyl formamide containing Li salts like $LiClO_4$.

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In terms of electrochemistry this solution is silent unless further ions are added [12] right from the DMF solution. The potential window which can be studied is very large, ranging from < - 2.5 vs SCE (e.g., $Tm^{II/III}$) up to the limits of anodic stability of the DMF solvent near some 1.7 V vs. SCE (chitin itself is much harder to oxidize both at an anode and by even very strong oxidants like Pb(IV) acetate, chromate, periodate [no reaction either unless for previous hydrolysis providing partly chitosan] or RuO_4, MnO_4^-).

c) There is an equivalent solvent (although viscous) which can be used down to almost the same potentials while providing a co-ordinative environment very similar to that in chitin which is why it was used in this work to simulate binding to chitin. This solvent is N-acetyl ethanolamine (N-AEA) [5]

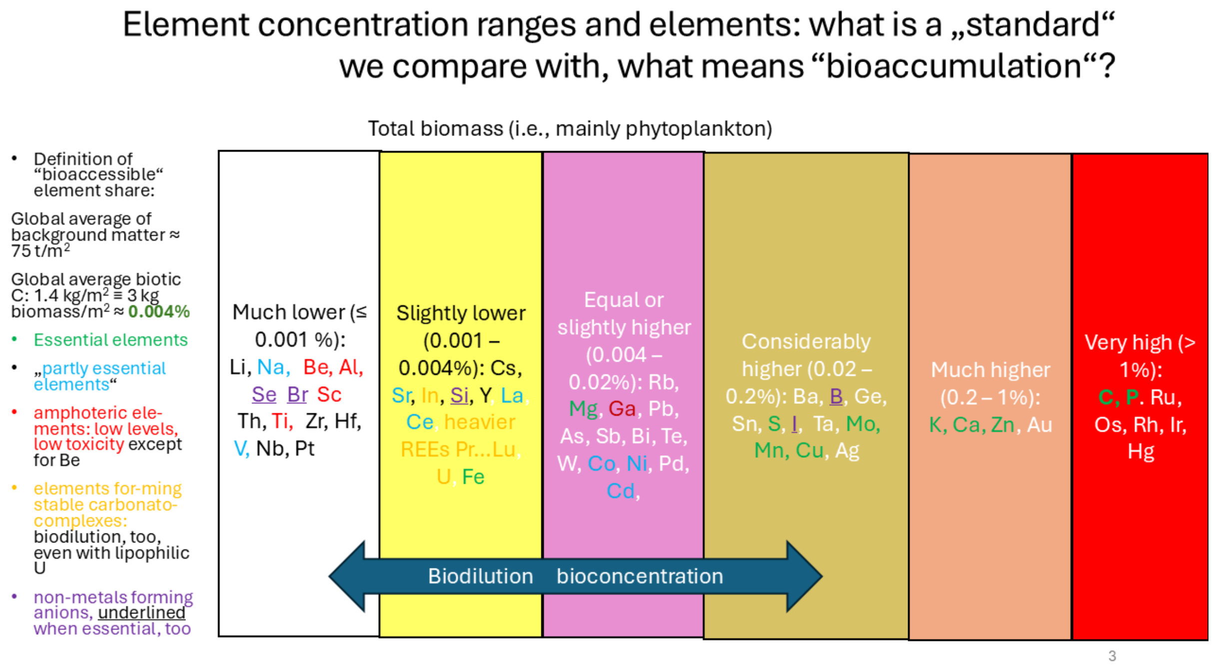
It turned out that a certain region of chitin of *V.orientalis* in between the wings can be caused to produce a ~ 50 mV potential by either illumination or applying some thermal gradient [10]. Similarly, change of salt concentrations around euryhaline shrimp *Palaemon varians* caused potential peaks [9]: although chloride is a rather poor ligand for REEs, at least when compared to bi- or multidentate ones like citrate, oxalate or malate [13], its higher concentration in ocean, salt lakes may compensate for this, and Cl^- is known to invert the sign of the flow potential around chitin at about marine levels, being adsorbed even when pH is >> 4.6, that is, above the isoelectric point of chitin, at an then negatively charged surface due to formation of rather stable hydrogen bonds [14].

Alloys of Ga or In with Al, Fe, REEs were considered in nuclear technology (molten salt moderated reactors) for extraction of REE fission products and separation from fissionable actinoids like ^{233}U or ^{239}Pu [15] which is necessary for continuous operation because e.g., ^{149}Sm, ^{151}Eu, ^{157}Gd, and others are effective neutron poisons [16]. In fact, REEs get extracted at sufficiently high T [18] while U, Pu were shown to be retained in the molten salt phase [15].

In the chitin-based experiment one would dissolve REE metals like La, mixtures thereof or trivalent actinoids in liquid alloys then to achieve selectivity by exchanging the metal cation in the electrolyte, i.e., when one starts with a solution of Auer´s flintstone in Ga_In one can select one redox system by admission of the respective cation towards the electrolyte solution. In a sensor, this can be achieved by either

a) Replacing electrodes placed on one mobile ribbon or
b) Replacing the electrolyte when separating the cations from freshwater, mine tailing waters or the like by passing through one cation exchanger, or
c) adding selective ligands.

The following picture (fig.4) does give the background of environmental concentration/distribution studies referring to chitin (with zooplankton and fungi representing sizable shares of total biomass among opisthoconta). More than of the 20 elements shown in fig.4 were already investigated by us in chitin-based environmental studies (e.g., [3, 6, 8]) and these electrochemical experiments, with amphoteric Be, Al, Sc or Ti most depleted:



Element concentration ranges and elements: what is a „standard“ we compare with, what means “bioaccumulation“?

Total biomass (i.e., mainly phytoplankton)

- Definition of “bioaccessible“ element share:

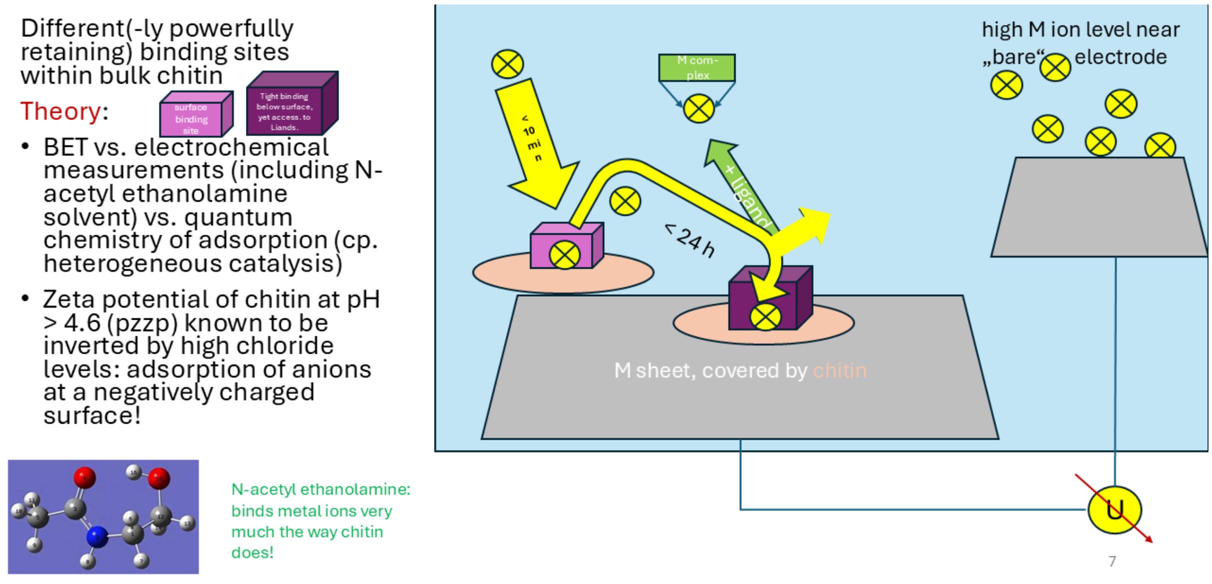
Global average of background matter ≈ 75 t/m^2

Global average biotic C: 1.4 kg/m^2 ≡ 3 kg biomass/m^2 ≈ **0.004%**

- Essential elements
- „partly essential elements“
- amphoteric elements: low levels, low toxicity except for Be
- elements for-ming stable carbonato-complexes: biodilution, too, even with lipophilic U
- non-metals forming anions, underlined when essential, too

Figure 4. Relative element abundances in biomass. More than 20 elements were studied combined with chitin so far. Amphoteric elements Al, Be, Sc, or Ti are considerably depleted in biomass, and REEs somewhat to different extents. Eu is accumulated in illuminated lipids, apparently also in transparent living beings. .

The next fig. does show the relocation processes with time passing by and ligands entering the surface (fig.5):



Different(-ly powerfully retaining) binding sites within bulk chitin

Theory:

- BET vs. electrochemical measurements (including N-acetyl ethanolamine solvent) vs. quantum chemistry of adsorption (cp. heterogeneous catalysis)
- Zeta potential of chitin at pH > 4.6 (pzzp) known to be inverted by high chloride levels: adsorption of anions at a negatively charged surface!

N-acetyl ethanolamine: binds metal ions very much the way chitin does!

Figure 5. By following the voltage over time and comparing it to simple sorptive behavior [6, 8, 21] metal ions can be shown to be mobile after adsorption on chitin yet stay at surface. .

While adsorption to the surface is rather fast, taking some 10 min to provide reproducible results on ion levels in water or inundated sediments (indicating the chance to extract or inject metal ions

2. Materials and Methods

General Remarks on Materials, Setup

Some ligands known [21] to **enhance** binding of REEs like La, Ce, Sm, and Gd to chitin at approximately equimolar amounts were used. This happens though glyc$^-$ [18, 19] or SCN$^-$ [20] form but weak complexes with REEs themselves. This gives additional proof that the entire effect actually is due to scavenging dissolved metal ions by chitin interfaces (which are negatively charged at pH > 4.6 [14]) endowed with some kind of bridge.

Setup

Two identical metal sheet or -drop (Pb, In) electrodes are placed in a solution of a salt of the same element, plus some conductive salt ($NaClO_4$ or $LiClO_4$) when other salt concentrations are small. The standard salt level is 2 mMol/l of the said element. One of the electrodes is placed in a mesh bag the inner volume of which is loosely packed with chitin flakes (about 500 mg DW). After immersion the voltage is recorded with a standard multimeter (2 measurements per s, data being stored in a PC data logger). In the beginning, only such metals were studied which are not too electropositive in order to enable a real equilibrium state of dissolution and deposition at either electrode from aq. solutions at least due to sufficiently large hydrogen overvoltage. Up to now, this included In, Sn, Pb, Bi, V, Co, Ni, Cu, and Cd; thus, both rather toxic (environmental sensoring!) and approvedly innocuous metals (Sn, Bi, In) were studied. In- or Ga-based liquid alloys, e.g., Galinstan, might substitute Hg in polarography-like determinations of more electropositive in an environmentally responsible manner enabling open-field studies, too.

Upon addition of Eu(III) salts and appropriate (ligand- or non-ligand) substrates there are sizable photocurrents which disappear once light is switched off (sacrificial donor: ethanol or $HCOO^-$). Concerning the liquid alloy electrodes, it is obvious that the classical backbone material – mercury – cannot be used in open-field studies or such where living arthropods are used representing chitin surfaces (lichens would be much more robust). Hence Hg was replaced with a liquid Ga_In alloy (24.5 weight-% In, $\varrho = 6.25$ g/cm^3, m.p. = 15.4°C). Auer flintstones (alloys from Ce, La, Fe, Mg, small amounts of other REEs like Pr, Nd), neat La or simply Al foils were shaken with liquid alloy in an Eppendorf vial for a while until there would be saturation [15, 11, 26, 27]. The electrodes were then made using a pipet (1 ml maximum volume) while gently heating the vial and pipet by airstream. Contacts to the electrode were prepared using unprocessed PLA;C_x filaments again. Data were logged by a common voltmeter transferring the measurements to a USB stick once per s.

Additionally, iodate ion is used to realize ”realistic” levels of heavy alkaline earths or REEs, Y as found in open waters because these iodates are almost insoluble [23]. Iodate acts as an oxidant attacking among other species iodide if pH < 6 (the Dushman comproportionation, see Pourbaix diagram [fig.6]),

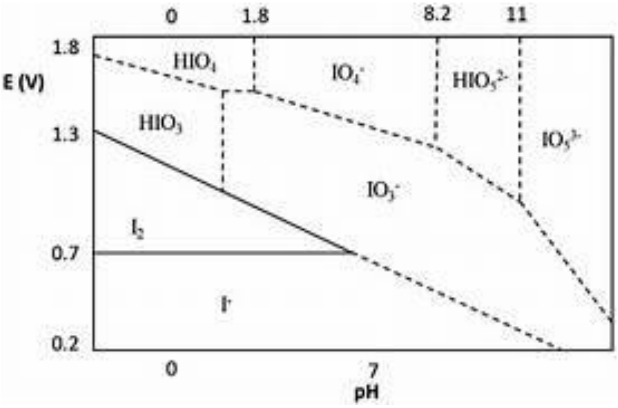


Figure 6. Pourbaix diagram of iodine. At pH < 6 I_2 does separate the stability ranges of iodate/iodic acid (HIO_3) and of I^- whereas at higher pH both may coexist, causing I_2 to undergo disproportionation.

$HCOO^-$ [23], ligands like SCN^- [24], triphenylphosphine, oxalate (the latter only reacts when illuminated), or phosphinate ion $H_2PO_2^-$ [25]. Iodide and Fe(III) do not co-exist in aq. medium whereas $[FeI_4]^-$ can be prepared in other solvents including liquid HI and by applying Me_3SiI. The reaction with thiocyanate affords sulfate, HCN or ICN depending on pH and stoichiometric ratio:

$6\ IO_3^- + 5\ SCN^- + 2\ H_2O \rightarrow$ (irrev.) $3\ I_2 + 5\ SO_4^{2-} + 4\ HCN + CN^-$ (1)

It turns out that by adding SCN^- (KSCN) Fe is extracted from the alloy to provide a bright red front propagating towards the chitin-covered electrode **before** SCN^- is actually oxidized by iodate and brownish Fe_2O_3 does form (the reaction can be taken to be a cyanide-catalyzed oxidation of elemental sulfur to sulfate(VI).

Figure 7. Three electrode pairs using liquid Ga_In alloys (bottom: bare, top: covered with chitin with an electrolyte channel in a polyacrylate support. The black lines are the conductive PLA pieces used to connect the electrodes to a voltmeter (outside of picture) without introducing additional metals. Left: pure Ga_Al, center: with "Auerstein", right: with Al. Note the black dots in the central bare electrode (presumably magnetite). Fe level in chitin does **decrease** during operation, probably because of extraction by SCN^- and oxidation. Final Ce levels in the central setup are some 23 times that of La.

Preparation of Electrodes

Besides common metal sheets or foils, there are two other kinds of electrodes used in these experiments, namely liquid alloys amended with highly electropositive metals and printable polymer electrodes based on polylactic acid (PLA) rather than organic semiconductors. This PLA is made conductive by addition of carbon (soot or graphite) rendering it black without changing the conditions of processing. Experiments showed sufficient conductivity as to obtain useful, highly

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resolved cyclic voltammograms with such working- and counter electrodes successfully replacing such made from Pt. Photoelectrodes are made by heating such printed electrodes until they get sticky and then distribute powdered large-band gap semiconductors (especially Nb_2O_5) on the PLA sheet.

When using an Auer flintstone, tiny black particles would form (presumably Fe_3O_4) from which bright red $[Fe(NCS)]^{2+}$ comes when adding SCN^- to the electrode. Even though there is a second oxidant besides of air (iodate [24]), these multielement electrodes are more stable than the pure Ga_In alloy which obviously even reacts with nitrate ions.

In pure (elemental) metal electrodes, corrosion and sometimes metal deposition from the solution depend on the potential shift caused by the chitin wrapping. As expected, the electrode wrapped by chitin does experience more degradation/corrosion (Co, Ni, In, and other elements), with chitin catalyzing the oxidation of glycine and other organics which causes fast return to the no-ligand voltage data once an oxidant is admitted. Matters are more complicated with the iodate/reductant system (see below). In sensors, one would conclude that the liquid-alloy systems are more tractable, additionally allowing for studying several metals at a time.

The following materials were used in the work (tab.1):

Required material	Formula	Source	Remarks, Purposes
Lanthanum nitrate	$La(NO_3)_3$	Merck	
Cerium nitrate	$Ce(NO_3)_3$	Sigma-Aldrich	Trivalent cerium, undergoes air oxidation on dry chitin; reversed when wet
Europium(III) triflate	$Eu(CF_3SO_3)_3$	Sigma-Aldrich	Used to identify response/possible perturbations of electrochemical signals by Eu-mediated photochemistry making radicals from ligands, other organics or changing oxidation state of dissolved ions bridging “bare” and chitin-covered electrodes
Liquid Ga_In alloy		Merck/Goodfellow	Eutectic mixture; by weight 75.5% Ga, 24.5% In
Auer flintstone	approximate composition: main components are Ce, La, Fe, and Mg	Local retailer	Surroundings of Ga_In + Auer stone alloy gets bright red several hours after SCN^- was added, oxidation of thiocyanate occurring only later
La metal			
Na iodate	$NaIO_3$	Sigma-Aldrich	does react with thiocyanate, formate and other reductants [24]
La iodate	$La(IO_3)_3$	Prepared in lab by wet reaction	
Ce iodate	$Ce(IO_3)_3$	same	

Na bicarbonate	$NaHCO_3$		Source of carbonate ions complexing all Ga, In [28], or REYs ≠ Y, Tm…Lu [29], added ion simulates respiration of arthropods or fungi introducing chitin into the system
K thiocyanate	KSCN		
glycine	$H_2N\text{-}CH_2\text{-}COOH$	Laborchemie Apolda	
Protease enzyme (papain etc.)		Raw, freshly-cut papaya slice; flesh and pressed juice taken as such	Local food retailer, papaya (ripe, yellow skin) from Brazil
chitin		Purified, protein-free	For residual metal contents see [21]
chitin (arthropods)	dried *Daphnia*, sandhoppers and grasshoppers	Local pet shop	Preliminary comparisons using La in liquid alloy show that chitin behaves like pure chitin, movement away from the bare electrode does increase voltage and amino acids can be released by (plant-derived mixture of) proteases
differently shaped objects made from various metal foils, acting as electrodes		Merck, Goodfellow or local retailers (Cu, Sn)	Selected according to toxic relevance (Pb, Cd, Ni, V), possible cathodic reduction of CO_2 on the material (In, Sn, Pb, Bi) [30] or the chance to deposit the very metal from water on a cathode (all)
Conductive PLA	Polylactate plastics amended with soot		Non-metal electrode link to liquid alloy electrodes

3. Results and Discussion

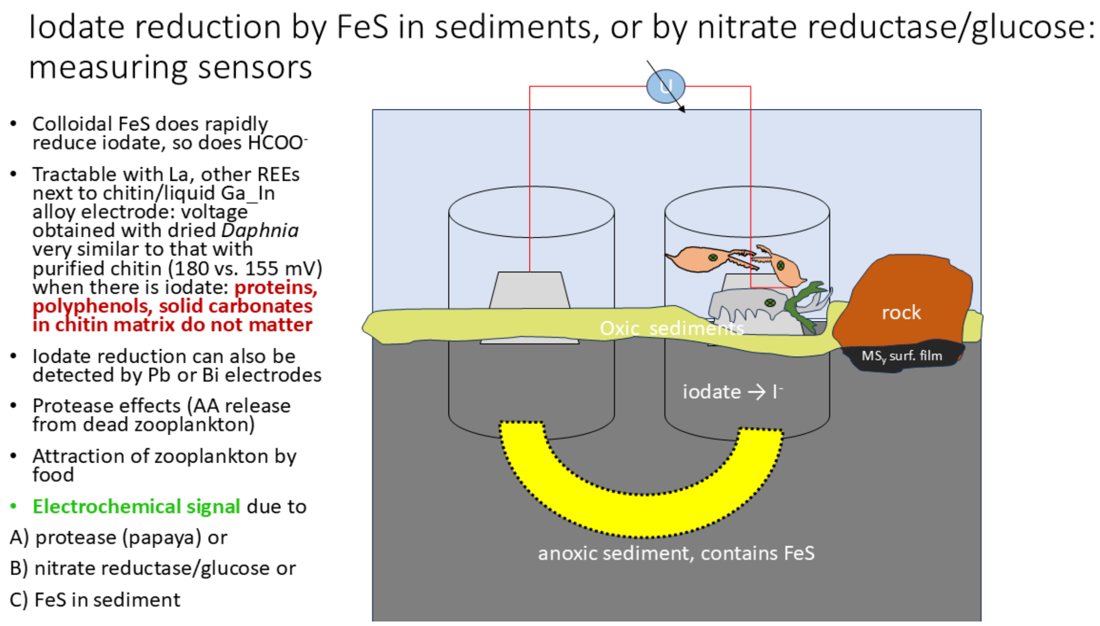
While most metal ions reach comparable levels on chitin once there is saturation indicated by breakdown of the voltage, Ga (if combined with In and REEs, some 165 µmol/g), Ce (in same system, about 122) and Bi (554 µmol/g, > 10 times “normal” concentration) are far better adsorbed. In contrast to previous reports [31], there are no exceptionally high levels of Pb or Eu bound on chitin. The accumulation of Ce apparently depends on its being oxidized by air (it cannot be oxidized by IO_3^- at any pH), unlike La (the amount of Ce retained on chitin around the electrode is about 23 times that of La although Ce/La ≈ 1 in both liquid alloy and the added salts). During this process, “extremely high” voltages near one V are obtained while black particles hitherto present at the bare liquid-alloy electrode (presumably Fe_3O_4) will disappear.

However, once a papaya slice (representing a broad range of proteases/peptidases [32] including textile washing detergents, snake venoms) or free glycine was added right in between the electrodes, the voltage would increase considerably. Action of papaya slices produced similar signals as adding glycine, suggesting that proteases work as expected. Analyses of papaya juice show that there are few potent ligands with respect to REE binding, in particular, essentially no citrate or oxalate (salicylate, tartrate and adipate do prevail [33]). After continuous action of both enzyme and iodate the voltage would reduce to about 20 mV but increase again to 300 mV upon squeezing the papaya slice or replacing it with a fresh one. After some 30 min the value decreased to some 70 mV again. On next morning, after adding some water, it was about 100 mV, increasing to 180 mV (the original value) upon addition of fresh daphnia. Then solid KSCN was added and dissolved with a few drops of water. The voltage increased from 155 to 473 mV within 40 min and then to a maximum of 638 mV. After six hours it was 520 mV; squeezing the papaya slice caused another increase to 670 mV. Meanwhile the surroundings of the bare electrode had turned bright red, indicating formation of Fe thiocyanatocomplexes rather than direct oxidation by iodate. Overnight the surface of the La iodate turned yellowish-brown without substantial further changes of voltage; that is, the reaction between iodate and thiocyanate according to

$$6\,IO_3^- + 5\,SCN^- + 2\,H_2O \rightarrow \text{(irrev.)}\ 3\,I_2 + 5\,SO_4^{2-} + 4\,HCN + CN^- \qquad (2)$$

Will not directly change the potential at either electrode nor consume (adsorbed) SCN^- to an extent that there are no more bridges to chitin. However, a second addition of KSCN will rise the voltage from 416 to 650 mV immediately and two min later even to 743 mV.

Hence the sensor responds to all SCN^-, hydrolysis of proteins while signs of effect differ. Except for volcano fumaroles, SCN^- is not a common component of natural water whereas glycine can be produced e.g., by grass roots or decay of soil, aquatic organisms. Yet, iodate does also react with FeS or H_2S as indicated in the following drawing (fig.8) [34]:



Iodate reduction by FeS in sediments, or by nitrate reductase/glucose: measuring sensors

- Colloidal FeS does rapidly reduce iodate, so does $HCOO^-$
- Tractable with La, other REEs next to chitin/liquid Ga_In alloy electrode: voltage obtained with dried *Daphnia* very similar to that with purified chitin (180 vs. 155 mV) when there is iodate: **proteins, polyphenols, solid carbonates in chitin matrix do not matter**
- Iodate reduction can also be detected by Pb or Bi electrodes
- Protease effects (AA release from dead zooplankton)
- Attraction of zooplankton by food
- **Electrochemical signal** due to

A) protease (papaya) or

B) nitrate reductase/glucose or

C) FeS in sediment

Figure 8. Extrapolation from dead to living aquatic arthropods and from SCN^- to FeS reductant: when iodate is added, the voltage between the two electrodes with and without chitin/zooplankton is about 170 mV. When adding/admitting (like in the above picture) some reductant or adding glycine (as such or provided via protease activity) the voltage would increase even further. Accordingly, the local biogeochemical conditions and M ion activities can be measured in a most simple way. The F value [4, 8, 21] can be measured by the change of this voltage especially for M = REEs, Bi or Pb. Small fishes or crustaceans can tolerate substantial iodate levels [35], while the setup works with insoluble La or Ce iodates in between Ga_In liquid alloy electrodes containing (metallic) solutes from an Auer flintstone.

Upon addition of protease derived from papaya slices or of thiocyanate ions the sensor will respond differently: hydrolysis of proteins included in the dried water fleas (proteins constituting most of its nutritional value to pet fishes) does cause a sizable reduction (after a brief upward excursion) of voltage to almost zero (170 mV when water was added again) sometimes even inversion of voltage whereas adding SCN^- does cause a steady increase of voltage to > 500 mV; known products of the reaction include iodine, ICN, I^-/I_3^-, HCN, and sulfate [24]. Presumably H_2S or FeS would produce similar results (above)

Even though both glycinate or especially the glycine zwitterion or SCN^- form but very weak complexes with REEs in water [19 – 21], Erler [21] could show previously that either does increase REE ion adsorption to chitin even if applied in sub-stoichiometric amounts. Whereas it is obvious that an ammonio group binds to the negatively charged chitin via its H bonds and to REEs via the carboxylate terminus of the amino acid zwitterion form, the case of SCN^- needs more consideration. Unlike Fe(III), Bi(III), Cu, or PGMs the more stable (if only isolable) form of thiocyanatocomplexes of REEs binds via N; yet nitrogen is much more capable of forming H bridges with the polysaccharide support than the S terminus. Fe becomes extracted from the liquid alloy by adding SCN^- as a complex only slowly and successively getting oxidized by iodate.

The behavior of the going-to-be electrochemical sensor (addressing all M content, enzyme activity and ligand-derived reactions) was studied with twice addition of thiocyanate, meanwhile allowing for an oxidation of SCN^- by (solid La) iodate. During this process the voltage will rise to some 700 mV, with still 460 mV after five hours. Accordingly, the concentration of La ions among the chitin flakes or dried daphnia will be even smaller than otherwise, with the carboxylate termini (i.e., $\log \beta \approx 2 – 2.5$ for REEs [13]) or one end of SCN^- withholding the ions. Some other ions like NCO^-, aminomalonodinitrile anion or nitrocyanoacetate are likely to perform even better. It was demonstrated that mechanically shifting away electrolyte-immersed daphnia from the bare electrode does immediately increase the voltage.

Replacing Purified Chitin with "Complete" Arthropods

For La at least, it could be shown that the final potentials (voltages) are the same whether one takes purified chitin or dried Daphnia, and effects of adding ligands, their precursors, and iodate are similar, too. Hence e.g., polyphenols will not interfere with M ion interaction for REEs at least; it is likely different for Fe, V (caffeic acid was applied with a V metal/chitin-electrode array), actinoids and some other elements. Given that native chitin from aquatic arthropods consists of sizable shares of all proteins, polyphenols, different metal carbonates (Ca, Zn, and others) fortifying the material and sometimes other components which may or may not interact with adsorbed metal ions to further decrease their activity, it is important to compare purified chitin to authentic (just dried) arthropods or lichens, respectively with respect to potential changes at some electrode. Both the pure-chitin- and the dried-*Daphnia* covered Ga_In; Ce, La, Fe electrodes produced a voltage of about 170 mV with no additives over $La(IO_3)_3$.

Data on Ga/In fractionation depending on the presence of yet other metals, ligands are given in the following table 2:

Table 2. Ga/In partition on chitin, contents of other metals after voltage-producing reaction terminates.

Sample ID	Ga content of chitin after saturation [μg/g]	Ga [μmol/g]	In content of chitin after saturation [μg/g]	In (μmol/g]	Stoichiometric ratio on chitin [-]	remarks	Contents of other metals [μmol/g]
No (alloy)		1082.86		213.38	5.075	No chitin added	No
Pure chitin (background values)							Al 0.32 μmol/g, Cu 0.21, Fe 0.36; that is, Σ ≤ 2 % of saturation
Ga, In		66.263		21.295	3.112	Substantial relative Ga depletion on	

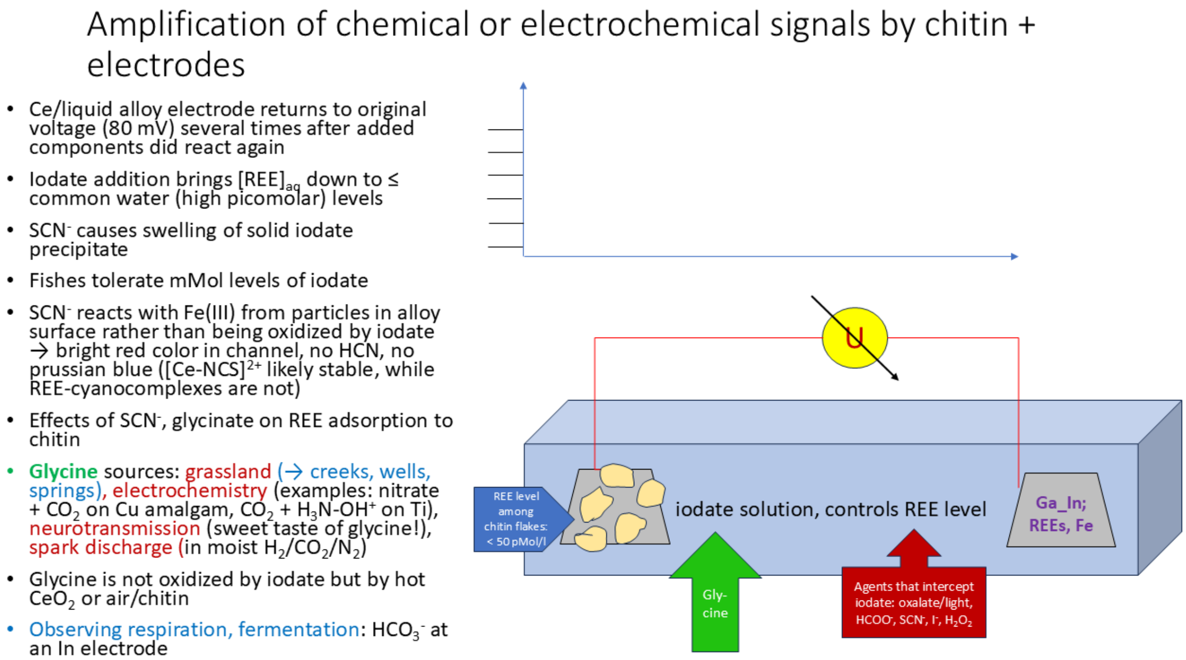
				chitin when there are no additives other than HCO$_3^-$; Ga about “common” saturation level in chitin	
Al, Ga, In	35.503	2.4306	14.61	Al mainly reduces In retention by chitin, less so of Ga	
Ga, In, Fe, La, Ce	165.18	31.2	5.294	Fe, La, Ce from “auerstein“; Ga/In ratio close to that of alloy; very high potentials obtained upon adding SCN$^-$	Ce (about 120 µmol/g)/La ≈ 23, probably due to air oxidation of Ce on drying chitin while free [REE(III)]aq. is limited by iodate precip.; Fe rather low (12.6 µg/g) but extractable from alloy

In photoredox systems Eu is taken up by chitin next to a metal electrode to grossly varying amounts: very little with V (the initially green [V(III)] solution turns blue during the process even though there is V metal; possible photooxidation of ligand caffeic acid), comparable amounts with Al or Pb (nine or 5.5 µmols/g), and much more with Ni which taints the chitin dark-olive to black (13.5 µmol/g Eu, almost 24 µmol/g Ni [a rather low saturation value]).

The activity of La in the alloy [17] is further decreased by adding proteases. Although neither glycine [18] nor SCN$^-$ [20] do form particularly stable complexes with La or Ce, they apparently provide a kind of bridge between the adsorbed metal ion and chitin. Thus, the effective activity of the metal ion on chitin will decrease even further unless the bridging species is removed by oxidation some time afterwards (SCN$^-$ by iodate [24], glycine by Ce(IV) [36] or air/Co^{2+}); only then the voltage which can be well larger than 500 mV will decrease again. Thus, it can be anticipated that SCN$^-$ from other sources, like reduction of (SCN)$_2$ or photolysis (LF bands [37]) of ions like reineckate cis-[Cr(NCS)$_4$(NH$_3$)$_2$]$^-$ will also produce a similarly strong signal.

Previous studies [21] had shown that polyphenol (-derivatives) caffeic and ferulic acids will hardly influence REE metal ion adsorption to purified chitin (fractionated uptake from mixed Ce/Sm- and Ce/Gd oxides, La/Sr/Co ferrite). Carbonate ions acting as a potent complexing agent for Ga, In, REEs ≠ Y, Yb, Lu [13, 28, 29] in fact do change the electrochemical signals associated with In, Ce, or La next to chitin. In (or Pb) embedded into chitin flakes may be pushed to so low potentials that reduction of CO$_2$ or HCO$_3^-$ - of course also influencing the current flow – becomes feasible [30]. This holds the more if Ga_In contains electropositive metals, forming bridging species such as glycine (with added nitrate) or dicarboxylates oxalate, malonate, especially when SCN$^-$ was added to the bridging solution besides of Al, REEs. In contrast polyphenols from outside (aq. phase) will not change chitin performance [22]. Things are different with metals forming very stable polyphenol complexes like vanadium. The redox reaction between (solid lanthanum- or cerium) iodate and thiocyanate (both salts of strong acids) [24, 25] will produce hydroxide or cyanide ions after turnover, and La, Ce hydroxides are way less soluble than the iodates. This could be the reason for parts of the increase of voltage. Native chitin and daphnia behave almost identical, again differing from the findings with crayfish [4, 38, 39].

There is considerable recent literature discussing both semiconductor properties (band gap about 4 eV, type of conduction not specified) and non-linear optical features of REE triiodates [41] or mixed iodate-fluorides. The size of the bandgap argues against simple transistor property but it is not clear whether redox processes at the surface of the iodate would make the band-gap much smaller. In addition, chitin is well-known to behave as a semiconductor itself [9], probably related to its photo- and thermoelectric properties [10] if it also contains xanthopterin and to the electric response to changes of salt concentration or pH in the surrounding waters. Even though, the similarity of the setup to a metal(-oxide film)/SC/SC device, namely, a transistor (fig.9) is striking and intriguing.



Amplification of chemical or electrochemical signals by chitin + electrodes

- Ce/liquid alloy electrode returns to original voltage (80 mV) several times after added components did react again
- Iodate addition brings $[REE]_{aq}$ down to ≤ common water (high picomolar) levels
- SCN^- causes swelling of solid iodate precipitate
- Fishes tolerate mMol levels of iodate
- SCN^- reacts with Fe(III) from particles in alloy surface rather than being oxidized by iodate → bright red color in channel, no HCN, no prussian blue ($[Ce\text{-}NCS]^{2+}$ likely stable, while REE-cyanocomplexes are not)
- Effects of SCN^-, glycinate on REE adsorption to chitin
- Glycine sources: grassland (→ creeks, wells, springs), electrochemistry (examples: nitrate + CO_2 on Cu amalgam, CO_2 + $H_3N\text{-}OH^+$ on Ti), neurotransmission (sweet taste of glycine!), spark discharge (in moist $H_2/CO_2/N_2$)
- Glycine is not oxidized by iodate but by hot CeO_2 or air/chitin
- Observing respiration, fermentation: HCO_3^- at an In electrode

Figure 9. Thiocyanate does increase the voltage in Ga_In; La, La(III) system considerably before undergoing slow reaction with iodate. Fe is extracted from liquid alloy and withhold from getting into chitin. The entire system resembles a transistor superficially but the total voltage is far smaller than the band gap of either chitin or La iodate.

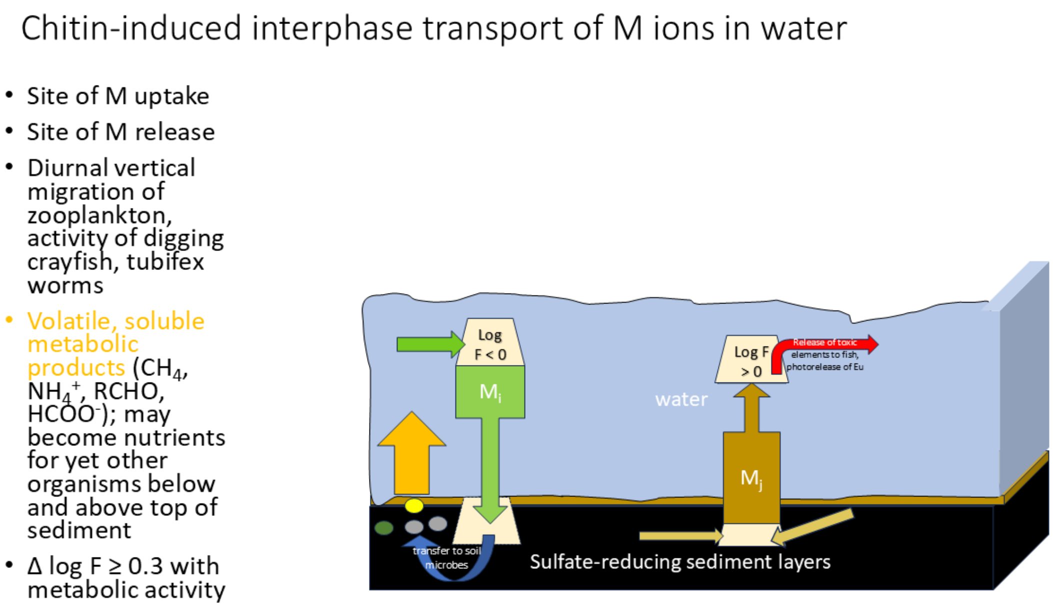
The voltage in-between the electrodes (bare and chitin-covered) is much smaller than the band gap of a typical REE iodate (note that sizable crystals do form) [40] which precludes the systems from acting as a real transistor even after adding some reductant to the region where there is solid REE iodate connecting the electrodes. In the latter case, the original 170 mV for REE = La (much less for Ce) increase to ≥ 550 mV (as compared to some 260 – 300 mV when only papaya is applied and almost zero after extended enzymatic proteolysis), meaning the potential of the chitin-/Daphnia-covered electrode (both behave very similarly) gets considerably lower than that of

$La + 3\ IO_3^-/La(IO_3)_3 + 3\ e^-$ (3) or

$Ga\_In;\ La + 3\ IO_3^-/La(IO_3)_3 + 3\ e^-$ (4)

which both can be calculated from the known (tiny) activity of La saturated in cold (RT) Ga_In [17] and the known solubility product of La iodate [22].

REE iodates are reported to cause protein degradation and corresponding activities against both bacteria and hulled viruses [41], while glutathione is implied in iodate reduction in vertebrates. Yet, it is feasible to produce sizable voltage excursions. The known [42] potential oscillations in the scn-/solid In system are negligibly small (few mV) and occur only upon anodic forcing.


Chitin-induced interphase transport of M ions in water

- Site of M uptake
- Site of M release
- Diurnal vertical migration of zooplankton, activity of digging crayfish, tubifex worms
- Volatile, soluble metabolic products (CH_4, NH_4^+, RCHO, $HCOO^-$); may become nutrients for yet other organisms below and above top of sediment
- Δ log F ≥ 0.3 with metabolic activity

Figure 10. Mechanical extraction or input into of metal-loaded chitin can cause secondary biochemical reactions once the critical (minimum) level of some essential element is exceeded. Conversely, local biochemical activity will increase F as to enhance the chance of mechanical extraction and possibly alter the electrochemical signal.

Using the data by Budelmann (2021) [8], one can estimate from the behavior of metals on chitin in a) water and b) sediment (two different flooded lignite open pits without appreciable inflow, one clay pit) whether some depletion on chitin put into sediment, and thus delivery/transport of elements from water into sediment (left part of fig.11) is realistic (table 3):

Table 3. comparison of F differences over organic-rich and loamy sediments to investigate the range of metals to be extracted on chitin from sediments by some mechanical baring.

Metal ions, oxidation state	**Set of elements**	**Regression equation (F2 – F1)**	**Critical value of a for log F < 0, lignite pits only**	**Regression equation (F3 – F1)**	**Critical value of a for log F < 0, clay pit vs. lignite pools**	**Remarks**
+II	Mn, Co, Ni, Cu, Zn, Pb	0.1261 a + 0.433 $r^2 = 0.66$	-3.43 smaller than critical for Pb, Cu only	0.0559 a + 0.478 Poor correlation (r = 0.163) only	-8.55 (unrealistic)	Ba omitted, transition metals and Pb only;
+III	Al, La, Ce	0.4583 – 0.0276 a, r^2 = 0.8876	16.6	0.0490 a – 0.816	16.65	No a value known for Bi, incomplete data for Cr. Critical values include all trivalent M

save Al, incl.
all REEs

As a result, animal activity will enrich water with M^{xy+} from sediment, not *vice versa*, except for few cases. There are ecological consequences.

Ecological meaning of the measurements

Retschke (2016) [3] and Fränzle et al. (2019) [4] could show that biogeochemical activity in the sediment related to some metal (e.g., Ni associated with methanogenesis) brings about and can be determined an increased factor F, allowing to "look" deep into the sediment by means of pairs of chitin flakes located next to each other in water and directly underneath sediment. This effect was corroborated by lab experiments showing the behavior of Mo on chitin [45] when there are nitrate-reducing bacteria in sediment and glucose, nitrate in water [34]. Nitrate reductases can also reduce iodate [34]. The increased F value due to biogeochemical activity would produce another (different) electrochemical signal. Judging from preliminary results, there is no substantial difference between purified chitin (originally obtained from Arctic shrimp *Pandalus borealis*; Sigma-Aldrich) and actual organisms which might be arranged as follows (fig. 11):

3D-printed housing for chitin-modified electrodes, animals, or lichens next to electrodes

- Conductive PLA (black) forms electrode connections and the cage arthropods are trapped in (made by 3D-printing)
- Different electrodes placed on a strip which is moved (yellow), producing different active electrodes consecutively (grey, colored circles, liquid Ga_In; M´alloy in blue jar)
- Animals (zooplankton [right], caddisfly larva or hermit crab) attracted to electrodes by food or light (no photopotentials even when there is Eu/sub-strate)
- Ga_In liquid electrodes permit additional measurements of Al, REEs, etc.
- Additional electrode with chitin placed in sediment (brownish-grey, to the right) studies M-related biochemical activity (connections not shown)

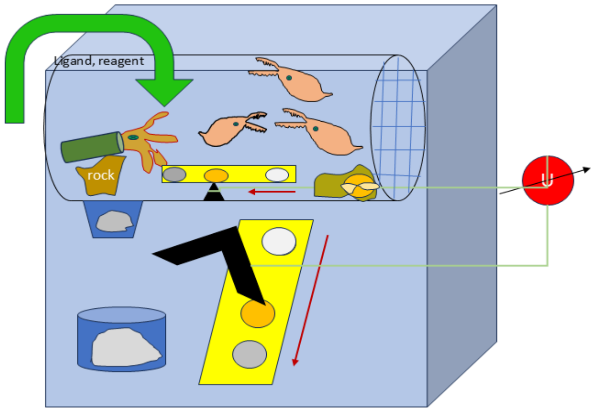


Figure 11. Multiple electrodes are fixed to some ribbon, with conductive PLA (black) producing a metal-free conductive site. Living arthropods kept next to an electrode by the cage (and possibly by something attracting them, such as food or light) will produce an electrochemical signal at the very electrodes most similar to that of dried chitin. the liquid alloy Ga_In; M, M´ electrode is included in the blue sink at left.

Around some multielectrode system in a cage (top) or spontaneously gather there for food or light (below), providing the chitin cover of one electrode (fig. above)

Role of chitin-based cross-interface M transport in limnetic chemical ecology

- Mn transport to plants (PS II), enhanced photosynthesis produces oxygen bubbles to oxidize rocks (much less Mn retained on leg tips than on crayfish antennae)
- REE transport to proteobacteria (primary alcohol oxidation) [blue arrow]
- As-containing schwertmannite-, Na jarosite/FeAsS equilibria
- Ni-rich particles adhere to chitin and then support hydrogenases
- Eu(II) produced by photochemical reduction of Eu(III) by C-; N^{org}_{ads} (both violet) is extracted into (non-polar) inundated sediments, like with transfer into toluene (> 200-fold enrichment upon rather weak illumination)
- Ligands are both photochemical substrates and can modify transfer of elements
- Possible agents: crayfish, *Tubifex*, midge- and dragonfly larvae, ostracods

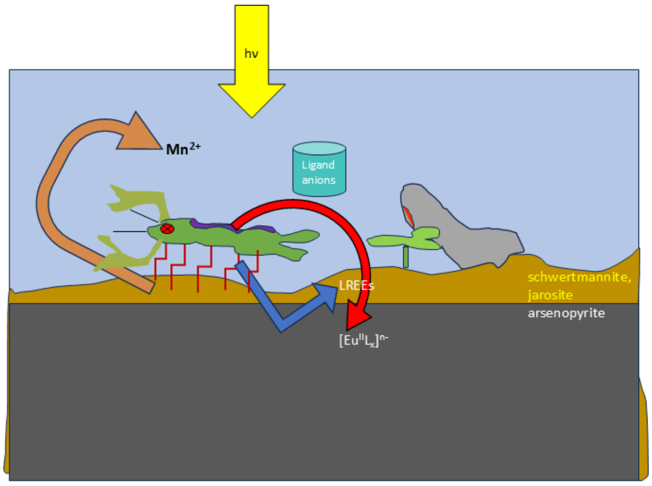


Figure 12. mechanical element transfers and photoeffects in a realistic setting (oxidation of ferrous rock by ascending O_2 from photosynthesis [pink] was observed in the region), and Eu does bind/remain bound to chitin to considerably varying extents depending on interactions with other ions.

This can be addressed simply by comparing electrochemical data from pure chitin to those obtained samples of dried arthropods or lichens, that is, replacing the purified chitin in the mesh bag around some electrode by (dead) arthropods. However, then you do introduce some other compounds into the setup, including proteins or peptides.

Thus, muscle activity or simple erosion give rise to the following transport processes causing secondary biochemical activity next to the water/sediment interface (fig. 13):

Chitin-based export of metals from sediment

- Slow (~ 24 h) processes only except for Mn, Ni, V (essential) and Al, Ba, Cr (Ba is removed subsequent to sulfate reduction)
- Essential metals transported by chitin (digging arthropods which regularly return to upper benthos or even swim) into water: depends on kind of sediment

muddy, C-rich, containing lignite: La, Ce, V

Sandy: Mo, Mn, Co, Cu, Ni (Zn) → local methanogenesis (bubbles) does increase Ni export, nitrate reduction that of Mo,

→ Co export next to/by chitin causes oxidation of amino acids in water column, thus increases toxicity of Cu, Ni

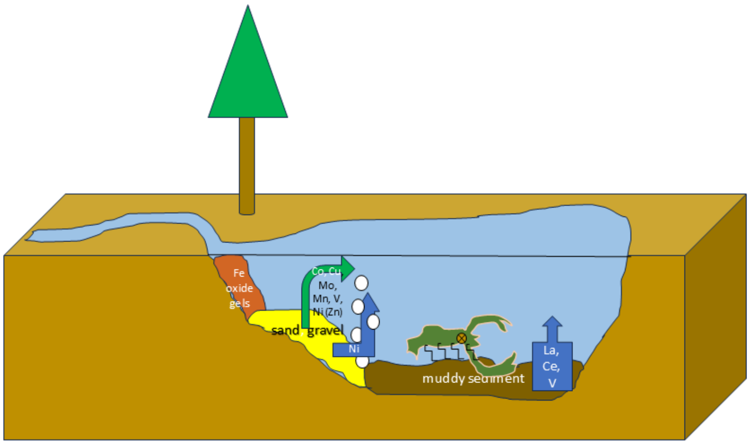


Figure 13. when metals adsorbed to chitin within sediment are released upon contact with water, they can start typical biogeochemical processes. The white bubbles symbolize methane, related to spatial dynamics of nickel.

There are sizable differences between metal ion adsorption in/on loamy sediments and soft, organic-rich ones while arthropods are known to approach even the most remote sites of partly inundated caves like Krubera/Voronya cave (Abkhazia/Georgia, > 2100 m deep from entrance, with springtails living at farthest dry points from surface entrance) [46] and display a very peculiar social behavior next to hydrothermal springs in deep ocean [38] which presumably causes both exchange and horizontal transport of metal ions. In fact, arthropods outcompete all other animals save nematodes in the harshest and most remote [46, 47] cave biotope conditions, indicating that these animals might once again benefit from the adsorption of metal ions on chitin.

REE contents of phyto- and zooplankton use to be low with respect to soil, also when compared to levels in local waters while benthic organisms accumulate REEs in chitin, as does purified chitin [8, 43, 44]. Thus, detritus and organic-rich sediments formed from this and bacteria will be very low in REEs. In stark contrast, erosion of ″normal″ sediments in some creek or river or leaching of lignite causes an input of high-REE matter (at least insofar as La, Ce, Y, and Nd are concerned, to lesser amounts also Pr, Sm, Yb and in some cases which need further discussion also Eu) and thus the total levels in sediment should much higher. Both Irmer´s Pond and Lake Olbersdorf formed fairly recently (former lignite open pits flooded during 1990s), are distinguished by being almost closed water volumes (i.e., evaporation/hypogeic inflow >> in- and outflow by surface creeks), and with very little contribution of possibly eroded materials. Accordingly, the REE levels in sediment may even be lower than those in water (cp. [8]). Yet, the behavior of electrodes covered with chitin does prove that corresponding metal contents do vary and realistic water levels bring about a sizable electrochemical signal. They strongly depend on redox, photoredox behavior of REEs, other metals while Eu(III)/organic H photodonor/hν does not alter the measured the voltage. Here, analytics and electrochemistry produce different pieces of information.

The indium metal/SCN^--system does display potential oscillations on its own if exposed to rather negative potentials at a hanging-drop mercury electrode and high $[SCN^-]$ (5 M/l) [43]. The potential amplitude is a few mV at an outer potential of – 0.95 V. There are indications for similar reactions in the full-scale system while indium itself and Ga_In without electropositive additions show severe corrosion when embedded by chitin [5]. Neither would obscure the signals seen with chitin.

4. Conclusions

While it is straightforward to operate such a device “amplifying” chemical signals from ligand admission on metals (and their subsequent removal by some chemical reaction) which can be deposited from water, too, like Cu, Bi, Cd, Pb, Ni and others, both the classical polarographic setting and chlorine-alkali electrolysis demonstrate that very electropositive elements can also be extracted from water by a suitable, i.e., liquid cathode. However, the application of elemental mercury cannot be accepted in systems which may get or even (sensors) are meant to get into direct contact with the open environment. Here, Hg must be replaced by another liquid alloy which is non- or little toxic. There are medical applications for Ga and its alloys with mp. ≤ 30°C [28]. Accordingly, experiments are run which introduce other electropositive elements such as Al, LREEs La, Ce, Pr, Nd (and Fe, Mg) into such alloys and see whether a similar reversible electrochemical behavior and response to ligand addition like with say Ni or Bi is obtained. The most simple amino acid glycine was tested with many of the metals to study changes of voltage (which may become larger or smaller then) before while it was anticipated that a common protease would liberate amino acids from the other components of a dried water flea or sandhopper, for example. Biosensors inspired by the famous bananatrode (effecting polyphenol oxidations by enzymes in bananas) were thus tried, starting with the protease mix from papaya.

Thiocyanate does produce a sizable electrochemical signal with either La or Ce ions levels of which are controlled by iodate before the redox reactions described by Gauguin (1949) [24] take place. Thiocyanate can also be released from thiocyanato(N)-complexes by ligand field excitation at long wavelengths and high quantum yields (e.g., $\varphi = 0.26$ at $\lambda = 600$ nm for $[Cr(NCS)_6]^{3-}$ [36], indicating the chance of an electrical detection of SCN^- after photolysis, that is, starting optical reactions. Other photochemical or enzyme-based processes like hydrolysis of peptides, photoaquation of fluoroligands would also give rise to ligands shown to be active in the chitin/metal (-alloy) system. After alloying with liquids, some of the resulting quaternary alloys have interesting properties which can be exploited in determination of Mn or Co in solution. The Heusler alloys $MM^{13}M^{coin}_2$ where M is Mn or Co, M^{13} = Al, Ga or In and M^{coin} = Cu or Ag are ferromagnetic at RT, which means that a magnetic field will exert some force on a copper wire (to be measured by a balance or causing it to move) which is immersed into Ga_In in reducing conditions (that is, next to chitin) if there is either Mn or Co in the solution.

Possible application of chitin adsorption and ligand-based reactions in processing information was discussed in a previous paper by these authors [48]. A sensor might be constructed as an inverted electrode, too (fig. 15):

Fieldwork sensor using liquid alloys

- Ga_In (non-toxic, grey) can replace Hg
- Meaningful signals with very electropositive elements like Al, La
- Metal ion injections (top right) after accumulation by cation exchanger resin
- Chitin flakes (apricot) make the dfference between electrodes
- Simple correlation of voltage change with log β → indirect verification of metal ion identity
- Mixing by tilting entire device to the right → inverted electrode (electroactive solution percolating liquid-metal electrode)

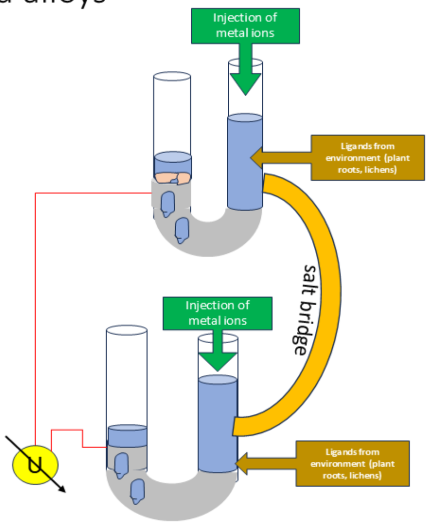


Figure 15. inverted electrode sensor (electroactive liquid solution inside the likewise liquid electrode).

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Conflicts of Interest: The authors declare no conflict of interest.

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