



Article Reversible Metal Ion/Complex Binding to Chitin Controlled by Ligand, Redox, and Photochemical Reactions and Active Movement of Chitin on Aquatic Arthropods

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Abstract: There is strong adsorption of metal ions and their complexes to chitin, which depends on both the oxidation and complexation states of many of the said elements (whereas others display chemical reactions detectable via electrochemical methods while being retained by chitin); thus, ad- and desorption at ambient water concentrations (often in the nMol/L range) are controlled by the presence and photochemical properties (concerning Eu and probably U and Ag) of mainly biogenic organic matter (both DOC and POC, and DON). With chitin forming the outer hull of mobile organisms (animals), this biopolymer is expected to take part in metal distribution in aquatic (limnetic and riverine) ecosystems. Having studied the attachment of many different elements to both crayfish and grafted (marine shrimp) chitin, with the highest accumulations observed in Bi, V, Ni, and LREEs, one should consider secondary biochemical transformations which take place at different water and sediment levels. After chitin had been embedded into sediment, methanogenesis (which requires Ni), Bi, and Sb biomethylations and photodesorption in the illuminated water column will occur if there are appropriate organics, causing the vertical separation of Eu from other REEs, at least during the daytime. Eutrophication will enhance both the production and especially the photooxidation rates of organics in water because phosphorylated sugars and lipids are formed quantitatively within min P, which enter water and undergo Eu-mediated photooxidation much more readily. Another biopolymer, gelatin, acts as an inert matrix-enhancing organic photooxidation product via Eu, producing chemical waves, indicating autocatalysis upon light impact. From the redoxrelated photodesorption of metal analytes from chitin, both sensors and devices for (light-assisted) electrochemical energy conversion are being developed by our workgroup. The electrochemical determination of adsorption thermodynamics on chitin is thus directly linked to its applications in environmental monitoring and technology.

Keywords: chitin–metal ion interactions; redox; photoredox desorption of M; daily vertical migration of aquatic arthropods; mineral (catalyst) formation from decaying chitin; Eu photochemistry; devices modeling chitin-related M dynamics on arthropods and their electrochemical readout

1. Introduction

1.1. Introduction

Chitin was previously employed to purify wastewater from HM ions [1,2] and fractionate radionuclides obtained in nuclear technology (produced via the fission and neutron irradiation of ^{235;238}U and HREE nuclides) [3]. Chitin was also demonstrated to act as the site/basis of photoinduced and possibly thermoelectric electric effects [4], concerning wing interspace and egg cocoons of the hornet *Vespa orientalis*. Here, however, photoactivity is not caused by the content/adsorption of metal ions or their complexes, but by that of xanthopterin.

Infrared spectroscopy is used to detect deformation/bond pair bending and vibration along the bond axes of some di- or polyatomic dissymmetrical (otherwise, e.g., in N₂ or CO₂,



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). transitions are "forbidden" and very weak) molecules or ions, including polymers. Certain structural motifs correspond to (that is, can be identified by) certain IR absorption bands which generally are located between some 3 and 40 μ m wavelengths. Hence, chemical reactions that modify such a molecule are likely to cause changes in IR spectra, too, and thus a comparison of IR spectra taken before and after some process can be used to constrain reactions that do or do not take place during interaction with certain reagents. For IR spectra of both chitin and chitosan, see [5]. Possible reagents which might modify chitin in this framework include:

- Hot water, possibly causing the hydrolysis of chitin acetamide groups to yield chitosan or even (N-acetyl-)glucosamine;
- Adsorbed and photoexcited Eu(III);
- Free radicals made from co-adsorbed organic matter attacked by Eu(III)*.

Furthermore, REE ions are known to catalyze the ring-opening polymerization of lactones (with gluconolactone being a product of glucose photooxidation; the ring-opening polymerization method was employed in the preparation of a PLA "biogenic" polymer [6]) and sometimes lactams. In turn, the processes discussed in this paper are unlikely to go on "forever", yet the reactions will likely go on during timescales of zooplankton between molting episodes, given our data on the continuation of photochemical transformations via Eu(III) retained by chitin. Concerning Eu and REEs \neq Eu partitions on and in arthropods, it is likely that different REEs follow different pathways of uptake and release in ambient (illuminated) conditions. The binding capacity of metal ions including Eu(III) on chitin is rather constant [7], with a few exceptions [8].

However, there has been little theoretical or even practical concern for the ecological impacts of this adsorption, e.g., when animals feed on arthropods, lichens covered by chitin and inhabiting areas with high HM (e.g., Pb, Cd, Cu, Zn, Bi, V, and REEs) or toxic LM (Al, Ba, and Be) levels, or the role of chitin in ecosystem-scale element transport. Nor did people consider effects other than pH that might influence adsorption equilibria, such as the presence of ligands or the oxidation state of metal ions. We did so in recent years [9,10]. Now, we are:

- (1) Constructing model devices to study the photochemical effects of chitin's retention of certain ions, especially Eu, with an emphasis on:
- (2) Photo-assisted electrochemical energy conversion [11,12];
- (3) Ecological consequences involving vertical aquatic transport and fractionation by influences of light, O₂, and waterborne ligands [10,13] on metal uptake, release, and sediment deposition by chitin shrouds in mobile aq. microarthropods.

In addition, water flows might bring oxidation or reduction products no longer binding to chitin to remote sites (caves, etc.). The former, especially chromate, is toxic and genotoxic [14], and the latter reductions possibly permit the production of food organics without light or chemical energy sources other than those made available by the movement of chitin or adsorbed items. Different speciation forms of elements binding to chitin differ in binding stability, including complexes [10,15], (pnictogen) biomethylation products [16], and different oxidation states. The interconversion of speciation forms might occur through oxidants, reductants, or even photochemical processes; the latter include:

- Photoredox—(Eu and U, possibly Fe and Cu);
- The cleavage of M-CH₃- (pnictogens, Hg, Sn, and Pb);
- M'-CO bonds, with [M(CO)₆] and [Fe(CO)₅] formed in and vented from landfills [17].

Both the exposition of arthropods, lichens, and animals feeding on either and element cycles in which aq. arthropod mobility is included would change the distribution/partition of elements among chitin, water, and sediment. Concerning REEs, previous data on the abundances of Y, La, Sm, Gd, and Yb in a model tank accommodating daphnia and mussels partly covered by chitin [18] in addition to goldfish, water plants, and sediment can be linked to our previous work on ligand's effects on REE adsorption on chitin surfaces [9,10]. There are photochemical effects of Eu (not studied by Yang) which can be exploited in

the conversion of light and chemical energy [11] and surely will influence the distribution of Eu in such (tank or open-water) ecosystems once there are mobile carriers of chitin, i.e., animals, especially arthropods. The argument will extend to other elements involved in photochemical processes, while chemoclines inducing changes in the redox states of elements should be less important in arthropods as these animals are mostly obligately aerobic. An exception is the dynamics of Mn, which does change oxidation state near the O_2 /water line in the Pourbaix diagram [19], with MnO₂ then catalyzing a multitude of oxidations. Test cells were described to study such effects with an emphasis on Eu, since the latter was previously often used as a redox tracer in geochemistry, often neglecting possible influences of photochemistry. We could show that Eu can be readily photoreduced by quite different organic compounds [11,12], with the Eu²⁺ product then losing the adsorptive grip to chitin. Accordingly, Eu should undergo fractionation from other REEs and trivalent elements in illuminated parts of the biosphere and hydrosphere. Unless there are high ambient concentrations and local enrichments in mine tailing waters, it is hard to study photochemical effects on Eu distribution and Eu dynamics in open fields. In addition, there is just a single site on Earth where Eu-rich particles (in fact, radioactive particles with prevailing ¹⁵²Eu content among radionuclides) have been released into open surface waters: particles (with some 200 in total being isolated) in the River Yenisei near the Zheleznogorsk military nuclear fuel processing plant (formerly called "Krasnoyarsk-26") in which Eu was left over from neutron flow control rods used in Pu production reactors [20]. Here, fortunately, Eu was kept in partly sintered particles in a way that meant leaching and liquid-phase dynamics with or without the involvement of the said photochemistry could not occur and be studied. Additionally, Eu is more mobile than other REEs co-leached from bared lignite when facing illumination [12,13].

Data from test cells filled with chitin, which emulate flows of water and organics over Eu(III)-loaded chitin, illuminated in various aspects and manners, can add important information to our understanding of element cycles in lakes and ponds. This includes exposition estimates for benthic, periodically migrating organisms, and the range of common biogeochemical redox tracers such as Eu, Ce, and Cr can be considerably extended. Here, photochemical contributions and those of oxidations catalyzed by MnO₂ on the chitin adsorption/desorption of different elements needed to be considered. MnO₂ in turn might form [21] when Mn²⁺ is leached from chitin in oxygenated (a precondition to sustain life in most arthropods) and slightly alkalinic conditions, and then oxidizes quite a sizable number of other elements such as Cr, Ce, and Cl.

1.2. Hypothesis

The metal fractionation process promoted by the muscle activity and chitin cover of arthropods is depicted in Figure 1.

Eu(III) adsorption to chitin is known to surpass that of other elements including REEs \neq Ce [8] and depends on the oxidation state; the only ligand that is prone to photooxidation by Eu(III) (11] yet is capable of increasing the adsorption of this ion is glycinate [10]. Formation constants of REE(III) (REE = La, Ce, Pm, and Eu) glycinatocomplexes in water are extremely small (log β < 1) [22], whereas the electrostatic effects of protonated glycine at a negatively charged chitin interface prevail in the enhanced adsorption of La or Eu [10]. Photochemistry mediated by Eu(III) and product patterns for simple carboxylates and the corresponding acids (pH range 1.5–6) were studied by [23], and Mn-mediated oxidation pathways were studied by [24], whereas Eu organic ligand complexes should be of minor importance at the ligand concentrations observed in open waters [25,26].

The release of Eu only occurs if:

- (a) Chitin-covered plankton dwells close to the surface during daylight hours;
- (b) There is sufficient and appropriate C;N_{org} in water.



Figure 1. Daphnias bind (gray arrow) and transport (dark green arrow) metal ions by their diurnal migration patterns. If there is photoactive or especially phosphorylated organic matter, Eu (and U) will be released next to surface. Nighttime contact with sediment possibly transfers some components to the surface of arthropods (bottom). Actual quantitative extent of the depicted process is discussed in this paper.

However, the levels of nitrate/other nutrients control the abundance and growth rates of pico- and phytoplankton; the latter produces and gives away organic matter suitable for photooxidation by Eu (humic acids and certain free and fatty oligosaccharides). The nocturnal presence of chitin-covered animals near the bottom of a water body (Figure 2) allows elements to be taken up directly or indirectly from sediment parts, which can only be released when the above conditions are met.

In turn, the C/P (dissolved) ratio is known to determine the biodiversity and productivity (in terms of organics released from microorganisms such as all POC, DOC, and DON) of some water volumes. It is thus commonly used as a simple measure of the extent of eutrophication [27]. Previous work showed that even sugars and other organic compounds stable towards Eu(III)-mediated photooxidation, such as ribose or mannose, can be readily processed after phosphorylation [12]. It is unlikely that this effect is related to the complexation of phosphate ester groups because other compounds such as toluene, naphthalene, or chlorobenzene [14] do react with excited Eu(III), although they are not coordinated by Eu(III) or other REEs. It rather is an activation very similar to that seen in biology. The coupled chitin-bound Eu/P/organics cycle inferred from these statements and experiments is shown in the following Figure 2. Rapid transformation of inorg. P getting into water, then some 60% of P become bound to sugars, lipids, amino acids by microbes (red arrow)

Daily vertical migration of daphniae and other microcrustaceans in small ponds, lakes, bogs connects (M in) sediments to surface by chitin adsorption

Photochemical desorption of Eu from chitin near surface *particularly* when organic matter is phosphorylated (blue arrow)

Uptake of elements near sediment top during night

Loss of Mn from chitin in alkalinic, oxygenated conditions, forming pyrolusite (oxidation catalyst; green warped arrow)

Eu²⁺ stays at water surface



Figure 2. Phosphorus (P) cycling in limnetic biotopes interferes with transport of element by Eu because P-ated dissolved organic matter is much more susceptible to photooxidation by Eu(III) (light pink squares on top (insolated) water flea and in solution)) than others. Phosphorylation is accomplished by (cyano-)bacteria within minutes [28] and partly reversed by the said photooxidation and extracellular phosphatases (broken arrow) (cp. [29]), while Eu²⁺ is lost (desorbed, eluted) from Daphnia surface (green square). During night (bottom Daphnia), some part of Mn (rose-colored triangles) is lost in oxidizing conditions to form pyrolusite deposits (black) which in turn oxidize trivalent Cr, Ce, phenols, Cl⁻, etc. Eu is re-adsorbed from both water (the local levels suffice) and near sediment during night and transported to the surface (top Daphnia in morning (at dawn)).

This process is thought to dominate at least in amictic water pools but is also relevant in monomictic water pools. This recapture of Eu on the chitin of some animals is unlikely to happen in small, fast-swimming/moving arthropods such as shrimps, water beetles, and gammarids, while it can and must be considered in big, slow ones (crayfish) and, of course, in cases of water slowly running over extended stationary chitin fields such as the surface of lichens [30]. The performance of the test cell under different illumination conditions permits an estimate of the photo-assisted transport and fractionation of metals in shallow (mono- or amictic) lakes and ponds with a high abundance of microcrustaceans, testing the ideas summarized in Figures 1 and 2.

Dissolved P is rapidly transformed into organic matter by bacteria and cyanobacteria, reducing free HPO_4^{2-} to just picomol/L amounts (moreover, such polysaccharides are known to suspend Eu, Tb, and other REEs [31]). This excludes the precipitation of REE phosphates, while phosphorylated sugars undergo ready photooxidation by Eu(III). Accordingly, once there is eutrophication, Eu released next to a water surface will increase, producing the sizable net upward transport of europium in a- or monomictic waters. Additionally, the ratio of elements such as Eu but also Mn, Cr, and Ce towards a background of strongly accumulating trivalent ions such as Al, La, and Bi [32] should vary with time of day and available C;N_{org}.

2. Materials and Methods

The reported work was carried out using purified chitin from shrimp shells (Sigma-Aldrich; St.Louis, MO, USA) (see Table 1). Grafted chitin was used as supplied (prepurified). The average acetylation extent of natural chitin was some 80–85% ([1,2]), with the remainder being "free" amino groups like in chitosan. The calibration line on partition equilibria [12] was required to determine whether the partition of adsorbed metal ions on chitin introduced into sediment and another sample immersed in water just a few cm distant from each

other [9,32] was "normal" or biased by some subsurface biogeochemical process, as shown in the following graph (Figure 3):

Table 1. Devices and substances used in this study.

Equipment Item/Substance	Precise Denomination	Supplier	Remarks	
Multimeter	Peaktech 3430	Peaktech Ahrensburg, Germany	Recording photocurrents and voltages	
Cyclic voltammetry gear	Radiometer Solartron 402	Tacussel Lyon, France		
FTIR spectrometer	Tensor 27	Bruker Karlsruhe, Germany		
Electrode materials	Cu sheet	unspecified	Electrolytic Cu quality, purchased from local retailer	
	Ta wire	American Elements, Los Angeles, CA, USA	We used Ta wire or sheet electrodes to avoid corrosion observed with Cu wire grids in chitin wraps with a couple of substrates and Eu(III)	
Chitin	Chitin washed	Sigma-Aldrich St.Louis, MO, USA	From marine shrimp Pandalus borealis	
Eu salts	Eu(III) trifluoromethanesulfonate	Sigma-Aldrich St.Louis, MO, USA	Nitrate or perchlorate also worked	
Solvent	Dimethylformamide	VWR Darmstadt, Germany		
Microbes producing substrates	Baker´s yeast	Local retailer	Does convert mannose and others into compounds more reactive towards Eu(III)*, e.g., ethanol	
Organic substrates of photooxidation	Glucose			
	Ethanolamine	Sigma-Aldrich St.Louis, MO, USA		
	Malonic acid	Sigma-Aldrich	Deuterated isotopomers produce far larger photocurrents	
	Ethanediol	St.Louis, MO, USA	Deuterated isotopomers produce far larger photocurrents	
	Glycerol	Sigma-Aldrich	Deuterated isotopomers produce far larger photocurrents	
	Glycine	Laborchemie Apolda, Apolda, Germany Merck, Darmstadt, Germany	Partial photodecomposition (disproportionation) into ethanolamine, CO ₂ , and CN ⁻	
	N-methylglycine	Sigma-Aldrich St.Louis, MO, USA	= sarcosine; does photooxidize only when kept in matrix	
	Mannose	Sigma-Aldrich	Little phototransformation except when in matrix	
	Mannose-1,5-diphosphate	St.Louis, MO, USA		
	Ribose-5-phosphate	Sigma-Aldrich	Unsubstituted ribose is photoinert with Eu(III)	



Figure 3. Partition of element ion sorbates on chitin immersed in water (top) and in wet sediment (bottom). Chitin flakes are located so close to each other that equilibrium (yellow double arrow) can be expected (not implying levels of a given element on flakes in water and in sediment are equal) unless there are subsurface processes absorbing metals into or releasing them from the sediment. Black: anoxic sediment layer where there is sulfate reduction mobilizing Ba, Pb (direction of pink arrow), and Cp. [12].

This bias does report chemical processes either involving this ion or its counterion which occur in sediment, including biochemical transformations or photochemical processes in the water column (Figures 1 and 2) keeping metals from sediment or making them dissolve. The substances were used as supplied, without additional purification measures such as distillation or recrystallization.

FTIR spectroscopy was carried out using a standard spectrometer (Bruker Tensor 27); the analyte was placed as a powder on some planar support (diamond or Ge) and pressed to it. Fourier-transform FT IR spectroscopy draws upon the fact that every curve—including spectra—can be displayed as the sum of several sine functions. Nowadays, it is the standard method of IR spectroscopy. Cyclic voltammetry is used to understand the electrochemical behavior of metal ions and complexes adsorbed and reacting on chitin. Chitin itself is completely silent in CV [12,30] although it contains traces of redox-active elements Fe, Ti, and Cu.

The transport and fractionation processes which take place at an illuminated chitin interface could be simulated using the following simple device in which *photochemical* H_2 production from acidic Eu²⁺ [33] on the second electrode was deliberately precluded by wrapping the flask with Al foil (Figure 4).

The position of either oxidation state of Eu (+II or +III) and thus sites of photoreactions and of possible reoxidations (air, hv [33], or at the counter-electrode) can both be surveyed using fluorescence caused by a colloquial blue LED. The oxidation state of Eu in either the supernatant or at the bottom electrode was checked using its typical (color of) fluorescence (Figure 5).



Figure 4. Illumination of the test system: Eu^{2+} formed via photooxidation of glucose was passed down to the lower cavity with dripping water to give away the "extra" electrons to make (a) H₂ and (b) a negative photocurrent. Illuminating the bottom cavity instead of the upper one produced no photocurrent whatsoever. A Becquerel effect was not observed with metal electrodes but only with illuminated semiconductive electrodes such as Se.



Figure 5. Turquoise fluorescence indicates presence of Eu²⁺ washed down from illuminated upper cavity containing chitin and organic substrate. Eu(III) would appear orange to pinkish if emitted at all in this chemical setting.

Experiments on the metal adsorption on chitin were conductd in a 50/50 by volume mixture of water and DMF [10]. Because adsorption to chitin depends on pH and chitin adsorption does enhance the acidity of protons at the saccharide ring [10,11], we had to find a buffer system which caused neither precipitation nor the excessive complexation of REEs (there is precedence in the published literature concerning the erroneous determination of log β of REE hydroxocomplexes due to using phosphate or carbonate buffers [34]). Inappropriately chosen buffers would either compromise adsorption studies (cp. [10]), or the buffers themselves would experience photooxidation by Eu(III), like acetate [23], or even do both (oxalate/Hox⁻).

The chitin suspension was buffered by adding an equimolar mixture made from aniline and PhNH₃⁺ trifluoroacetate ([10], quintuplicate setups). Ce(IV) is quickly reduced in pure DMFl however (observable by the bleaching of an originally yellow solution), cyclic voltammetry still can be carried out in this medium (Ce(III/IV) \approx 1.62 V vs. SCE, sweep rate \pm 100 mV/s [10,11,35]). Electrochemical data obtained in this manner can then be used to estimate complex stability constants log β by (downward) potential shift. Practical experiments were carried out with arthropods (crayfish *Orconectes limosus*) and compared to results obtained from chitin flakes placed at the same sites [32]. Animals (invertebrates only) were treated according to the published legal regulations. When applying chitin adsorption for environmental analysis, one would take eight times the amount of DMF/1.6 M Li⁺. This does remove the topmost some 15–20 µm of chitin in one step to obtain all the matter adsorbed representing some time range from the last few minutes to several months ago [30,35], taking (small) background into account (for optimization parameters, also see [9,10,12]).

Electrochemical studies to understand photochemical effects were carried out using (a) a cyclic voltammograph Radiometer Solartron 402 (Tacussel, France) and (b) homebuilt cells fitted to commercial multimeters (Peaktech, Ahrensburg, Germany). Both reported data to a Dell PC, using either solutions or Petri dishes filled with gelatin containing sets of electrode pairs. For the simulation of biofilms, gelatin (commercial sources (local supermarket retailer)) was doped with Eu(III) (1 mM/L of water used to induce swelling and solidification, with 10% total gelatin content) and organics to be processed by Eu-mediated photochemistry [36]. The matrix effects on Eu-mediated photooxidation were studied by embedding potential substrates of photooxidation which are known to react not at all (aniline and N-methyl glycines) or negligibly fast (mannose, glycine, and cyclohexanol) with excited Eu(III) in gelatin (setup Figure 6). In some experiments, additionally, doped gelatin was incubated with baker's yeast (Saccharomyces cerevisiae) to study the consequences of metabolism, possibly producing (more) photoreactive metabolites, e.g., ethanol from mannose. Saccharomyces cerevisiae (and other fungi such as molds) were shown to be much more robust towards LREEs including Eu [36,37] than any bacteria investigated previously or than archaea (the biodiversity of which is reduced to a remainder of aerobic Thaumarchaeota only in REE mining fields [38]), that is, methanogenesis and anything other than aerobic NH_3 oxidation are suppressed by the addition of REE^{3+} or their solid oxides [38].

In electrochemical experiments, Pt wire was generally replaced with Ta (wire or sheet) as an electrode material to exclude contributions from the heterogeneous catalytic cleavage of CH bonds promoted by PGMs (for a comparison of results, cp. [11]). In addition, unlike Cu or other electrode materials, Ta withstands attack by all the components studied:

- a. Dark, organic matter only;
- b. The addition of Eu(III);
- c. The start of illumination, studying events/changes taking place just after light was admitted (within a few s);
- d. Measuring changes in prolonged irradiation, extending over several days until there was no photoinduced voltage or current left.



Figure 6. Two pairs of electrodes were placed in gelatin in a Petri dish. Gelatin contained 0.9 mM/kg Eu and 5 mM/kg organic substrate. Electrode pairs were used to determine and compare voltages at different sites of lines in Petri dish. The device was isolated from air by a plexiglassTM cover plate through which electrode wires were passed, with glue closing the drilled holes. Upon illumination, slow chemical waves formed, indicated by reversal of sign of voltage at different times at the two pairs of electrodes, e.g., when consuming mannose, sarcosine, or aniline. Period length was about 24 h, and propagation took place at about 1 mm/h. Distance among electrode pairs was 2.8 cm.

The maximum current densities were much higher in this Ta system than when using Cu, too.

The setup for immobilized Eu and substrates is displayed in Figure 6 ([36]; photograph by S.F.):

3. Results and Discussion

3.1. Results in Lab Systems and Using Isolated Chitin

None of the three ions indigenous to chitin in sizable amounts, which undergo redox transitions within the range of biological redox potentials (Fe, Ti, and Cu [7,10]), gave electrochemical signals when dissolved in DMF containing Li⁺ [12]. Moreover, the electrochemical study of adsorbed metal ions was readily feasible in both DMF/Li⁺ solution [10] and solid state (with either causing reduced Eu to leach from chitin surfaces). Though analogous work concerning "real" biofilms has not yet been carried out, information concerning electrochemistry and Eu-mediated photochemistry in gelatin are available. Data on water-exposed parts of crayfish (the antennae and "neck") and on chitin flakes in same media strongly correlate (cp. [12]); so do data obtained from leg tips and sediment-buried chitin flakes.

During our experiments on photo-assisted fuel cells using chitin, we noted that [Eu(OH)]⁺ ions formed by the photooxidation of aq. glucose produce:

- (a) H₂;
- (b) Variable electrochemical signals at a Cu sheet electrode (photograph, Figure 5; screenshot of electrochemical signal over time, Figure 7).

In the lower of the two cavities, while the top electrode is covered/surrounded by chitin flakes. Meanwhile, glucose is rapidly photoconsumed, and lipids (e.g., olive oil) undergo hydrolysis (saponification) catalyzed by REE^{3+} at 25 °C already (own observations); there are thus two different processes occurring at the downstream Cu electrode, that is, H₂ evolution and the formation of an initially negative photocurrent which, however, becomes positive after some time and shows slight additional oscillations (Figure 7).



Figure 7. Development of photocurrent in Figure 4 setup over time.

Thus, some part of the H atoms taken from the photooxidation of glucose (cp. [11]) can be used for both H_2 formation and the reduction of CO_2 , depending on respective overvoltages. Current oscillations are less pronounced with Ta electrodes.

Typical evidence of chemical waves [36] mentioned above included multiple reversals of voltage signs, much like those observed at a given pair of electrodes, while there was some time lag before the same happened at a neighboring pair of electrodes. During ongoing photolysis, sometimes, strange smells and color changes of solution or gelatin (the solvents water, DMF, and gelatin are all inert towards direct photooxidation by Eu) were noticed, usually during the early phases, while some gas bubbles and turbidity were noticed in both solvents and in gelatin systems. Apparently, both the liberation of amines and mineralization down to CO_2 occurred.

The co-adsorption of glycine in addition to REEs to chitin (pzzp = 6.13; $H_0 = 11.0$ in neat DMF [39]) (for the meaning of H_0 , see the list of abbreviations at the end of this paper) was shown to enhance that of LREE, except Sm. A multitude of ligands such as caffeic acid, taken to represent humic acids, malonate, or hydroxamates did so only with Dy and Yb [10]. The calibration line describing the partition of adsorbed metal ions M^{x+} (constant x) on chitin introduced into sediment and another sample immersed in water just a few cm distant from each other [12] was defined as "normal", which was determined like in previous work [12]; a deviation from this expectation indicated chemical processes in sediment or biochemical or photochemical transformation either involving this ion or its counter-ion.

The relative stability of the substrate complexes could be estimated from data on the dissociation of gluconatocomplexes (Pr(III) [40]) and redox potentials for $Eu^{2+/3+}$ and

Eu²⁺/metal in trimethyl phosphate vs. data in water or DMF, CH₃CN [41]. The rather high value of the former potential in TMP [41] indicated the rather weak solvation of Eu(III) in phosphate esters, suggesting that this weak solvation with phosphorylated sugars, alcohols, or ethanolamines does facilitate the attack of Eu(III)* on ester alkyl groups. The said gluconatocomplex and its galactonate, gulonate analogs, all have log $\beta_1 \approx 2.7$ [40], quite comparable to those of glycollato- or lactatocomplexes [25]. Accordingly, the mode of binding should be identical to that of simple 2-hydroxycarboxylate complexes (cp. [25]), omitting the binding of Eu(III) by/at additional hydroxy groups. Whereas glycollate is photochemically inert with Eu(III) and lactate displays little reactivity, glyconitrile, lactonitrile, malate, citrate, and gluconate are all rapidly photooxidized [11]. This emphasizes that there is no relationship whatsoever between complex stability and photochemical lability in this system; accordingly, non-ligating compounds/anions can also be photodehydrogenated by Eu(III)*. Generally speaking, solvents in which this Eu^{2+/3+} photochemistry takes place are distinguished by low potentials (data from [41,42]), that is, there is the pronounced solvation of the trivalent ion (there is no reaction in CH₃CN, for example).

After exploiting its use as a photocatalyst support in the photooxidation of glucose, the following spectra were obtained, now showing the almost irreversible retention of Eu on biopolymers (Figure 8a,b).



Figure 8. Cont.



Figure 8. (a): Native chitin (red) and its degradation after photooxidation mediated by Eu(III); spectral region 1950–1150 cm⁻¹ (\approx 5.1–8.7 µm). (b): Native chitin from *Pandalus borealis* (Sigma-Aldrich) and its photooxidation product; spectral 2600–4000 cm⁻¹. The intermediate range around 2200 cm⁻¹ could not be measured because there were absorption bands of the supporting diamond crystal. Spectra were taken by F.Prasse (Hochschule Zittau-Görlitz, Saxony). "Brennstoffzelle" means fuel cell.

For Fe complexes modeling the transition from slightly brackish water to fungal injections to chitin adsorption, chitin adsorption for energies for corresponding complexes were estimated using data published previously in [12] (Figure 9).



Figure 9. Derivation of chitin adsorption free energies of metal complexes which are likely to occur in soils from electrochemical data. Note that a new reductive peak turns up upon chitin adsorption of (probably Cl⁻ -containing Fe hydroxamatocomplex) at -1.1 V vs. SCE. The lines are inclined to the left, indicating an (uneven) depression of redox potential (determined by CV) upon adsorption to chitin, meaning that the Fe(III) complex (which is very stable in the case of Fe(III) [43]) more strongly adsorbs to chitin than its Fe(II) counterpart. For the CV diagrams, cp. [12]. Picture taken from a conference contribution by S.F.

Even though the solvation energies of trivalent ions in water exceed those measured in DMF (data from [41,44]), about three times more metal ions are transferred from metalliferous slurries in water than to chitin from equally concentrated solutions of the same material in DMF [13].

3.2. Chitin in Organisms, Multilayer Films on Them and Pathways of Metals, Signal Compounds in Eusocial Arthropods: Evidence from Ants

(Some kinds of) ants can live, build nests, and reproduce in areas covered by bared, weathered lignite. In these areas, one might anticipate high environmental levels of such compounds which ants use for intraspecific communication [13], that is, certain long-chain hydrocarbons. The organics released from local lignite (from abandoned and partly flooded Glückauf pit, Zittau/Olbersdorf, SE Saxony, FRG) include benzene, toluene, and valeroor methylated butyrolactone, whereas C_{22} alkane, 1-eicosene n- $C_{18}H_{37}CH=CH_2$, and a C_{13} -amine [13] were isolated from the waxy cuticle overlying chitin in these small animals. Accordingly, they do not interfere with ant communication (Figure 10 (left side)):



Figure 10. Left: cross-section of an ant showing the waxy cuticle absorbing non-polar organics and the underlying chitin layer with arrows indicating matter exchange equilibria. Inner organs of an ant were exposed to hemolymph liquid percolating the body freely, without blood vessels, while there was a heart, glands, and other organs (sketch by S.F.). Cu levels are very high due to hemocyanin transporting dioxygen in most arthropods, while Zn is very common in enzymes. Actual levels on chitin were 1–2 μ g/g DM each. Ants shown in right photo (S.F.; [13,45]) were about 4 mm long.

In ants which inhabit degrading lignite, there is evidence of effects which might even enhance fractionation against Eu via photochemistry: La, Ce, Sm, or Dy enter ants mainly via the mouth, whereas a sizable percentage of total Eu is observed to be absorbed in/at the surface chitin layer [13]. When organic matter is available from the environment, Eu²⁺ formed by its photoreduction will be transported on top of the chitin layer. There is an analogous separation between Zn and Cd [13], which are taken up in different ways. It is an open issue as to whether the difference among (Eu vs. other REEs) pathways is related to Eu-mediated photochemistry, with Eu²⁺ possibly following Ca²⁺ ion channels in the chitin layer (Figure 10 left). If the effect seen in lignite-dwelling ants also holds for limnetic zooplankton, the larger contribution at the outer chitin surface (which in ants even is covered by an additionally waxy cuticle almost completely free of any metal ions) should enhance the extent of chitin-related transport and fractionation in upper, euphotic water layers, too (cp. Figures 2 and 11).

Budelmann [32] studied element concentrations in water and on different parts of crayfish *Orconectes limosus* which were or were not (leg tips and telson) exclusively exposed to water (this animal does not dig into sediment) rather than sediment. This changed the adsorption on grafted chitin dislocated in water and in sediment, both dislocated next to the traps the crayfish were caught in. The effects in a real outdoor system—representing several water bodies, including ponds, a creek, and a flooded quarry in upper Lusatia studied in August, 2020—are summarized in the following Table 2. The upper limits for mixing ratios of Eu in water could only be given owing to the lesser sensitivity of ICP-MS-based analytical determination and probably lower contents than for La and even-Z REE Sm. Animals were caught during the night, thus excluding the said photochemistry associated with Eu. Hence, the ratios observed on chitin should represent the upper limits reached over a day. The pH of all four water bodies was similar, about 7.5. Nevertheless, the Eu/La, Eu/Sm, and Eu/Bi ratios in chitin were rather high (black number are ratios by weight, and red ones are by stoichiometry) (Table 2):



Figure 11. Different polysaccharides are involved in retention of M ions in limnetic environments, including biofilms (mainly glucan, left) and chitin actively (diurnal migration of copepods and water fleas) and passively (deposition of dead arthropods), switching among water depth levels. Upon illumination along appropriate organic matter, Eu—hitherto firmly adsorbed to chitin to an exceptional extent—photooxidizes the latter by CH bond photocleavage. Transport by animal movement (cp. Figures 1 and 2) competes well with that caused by annual circulation.

Some elements thus deposited after downward transport on chitin might be critical in sediment-located biochemical pathways, such as Ni and Co in methanogenesis, which require certain minimum levels of either metal. The same holds for La and other LREEs in methanol oxidation. In turbid waters or those rich in humic acids, Eu²⁺ will only be released close to the surface. Chlorophyll (Mg porphyrine) undergoes rapid M exchange with REEs including Eu, and Eu porphyrines are thus formed as much superior photocatalysts compared to simple Eu(III) salts or complexes in terms of photocurrent [45]. The same process should occur in phytoplankton including phototrophic cyanobacteria. Apparently, Eu is lost from photosynthetic organs due to photoreduction, as shown by its depletion from pine needles or birch or whortleberry leaves relative to the BCF levels of other LREEs at these light-exposed sites (calculated from data in [46,47]).

If this holds for phytoplankton, too, the oral uptake of Eu by zooplankton in turn should also be reduced, whereas the chitin shells of, e.g., water fleas are partly transparent. The behavior of Mn^{2+} on chitin (although at fixed (buffered) pH (aniline/PhNH₃⁺ in water/DMF)) alone and in combination with REEs as a result of ligand addition was studied in our workgroup by M.Erler [10]. This concerned ligands known or likely to exist in groundwaters derived from all plant roots, fungi, soil, such as hydroxypolycarboxylates, glycine, and hydroxamates, plus humic matter, models thereof (caffeic acid), and SCN⁻ (for comparison). He found the rather high retention of Mn^{2+} to chitin in all samples in the mixture, indicating that the loss of Mn from chitin to aerated alkaline waters as MnO_2 will not occur readily. In turn, the MnO_2 -catalyzed transformations of both metals and ligands [19,21,24] on chitin and in free water will only occur with already existing pyrolusite deposits, rather than forming such deposits to any significant extent.

Table 2. Relative metal adsorption by chitin (grafted or in different parts of *O. limosus*) in several water bodies in Upper Lusatia (Saxony, FR Germany). Blanks denote missing data (too little for analytical determination), and the upper limits in water are due to all Eu levels in water itself being below determination limit (90 ng/L or \approx 600 pMol/L, that is, much higher than for other REEs or Bi or Cr).

Site, Element Ratios	Water	Antennae	Carapace	Mandi-bles	Leg Tips (Usually Immersed into Sediment)	Telson (Lower Part)	Branching Ratio on (Grafted) Chitin for Eu, M' (Sedim/Water-Exposed Chitin)
Irmerteich ("Irmer´s pond"), former lignite open pit, 6.3 m deep							Eu: no data
Eu/La	<2.9 <2.65	5.19 4.74	0.78 0.71	5.51 5.04	4.2 3.84	12.7 11.6	La 0.39
Eu/Sm	<3.46 <3.42	16.2 16.0	5.8 5.74				Sm: no data
Eu/Bi	<0.75 <1.03	6.3 8.66	11.6 15.95	20.3 27.9	12.2 16.8	1.03 1.41	Bi 1.65
Hartauer Lache ("shallow pond located at Zi-Hartau"); shallow pool rich in SO4 ²⁻ ; bottom covered by clay							Eu: no data
Eu/La	<0.8 <0.7		2.56 2.34				La 10.9
Eu/Sm	<1.64 <1.62		4.82 4.77				Sm
Eu/Bi	<3.4 <4.7		3.76 5.17				Bi 1.9
Landwasser creek							Eu: data for sedim. Only
Eu/La	<0.94 <0.86	59.7 54.6	10.4 9.51	25.5 23.3	11.8 10.8		La 10
Eu/Sm	<1.35 <1.34		39.1 38.7				Sm: data for sedim. Only
Eu/Bi	<90 <124	1.42 1.95	6.14 8.44	7.4 10.2	6.20 8.53		Bi 2.2
Ostritz flooded quarry; chitin was treated with boiling water prior to analysis							Eu
Eu/La	<2.5 <2.3	14.5 13.25		4.61 4.21		14.2 13.0	La 4.5
Eu/Sm	<4.8 <4.75	80.0 79.2		9.6 9.5		36.5 36.1	Sm 9.2
Eu/Bi	<22.5 <30.9	11.7 16.1		7.1 9.8		9.6 13.2	Bi 1.13

The release of other metals rather abundant in chitin such as Fe, Ti, Al (10–20 μ g/g each), and Zn [7,10] by the bacterial degradation of "dead" chitin in sediment [48] and subsequent reactions by inference are unlikely to produce significant amounts of photosemiconductors such as TiO₂, CaTiO₃ (aerated top-zone of sediment), ZnS, CuFeS₂ just (about 0.5 mm [28]) below, or of Fe oxides such as magnetite. This estimate renders photoelectrochemistry related to the chitin-based shuttling of metals unlikely. An example would be the Dhar-Mukherjee (1934) preparation of amino acids from polyalcohols, sugars, and nitrate mediated by TiO₂ (unspecified crystal structure) [49] occurring at the bottom/shore of a water body.

3.3. Discussion

Chitin adsorption kinetics and the method to investigate them were described in previous papers [9,11,31]; adsorption is essentially completed within 10 min [7,9,10,34], with few ligands slowing down the pathway to equilibrium, such as citrate with Fe(III) [10]. Understanding element (Pb, Cu, Zn, Cd, and As) fractionations by binding to chitin the way it was depicted in Figures 1 and 2 calls for electrochemical studies on isolated (suspended and dissolved) polysaccharide strands which can be amended with arbitrary amounts and kinds of metal ions or complexes. The progression of metal(-oid) diffusion through thick chitin layers [35] can be measured through the repeated dissolution of plane layers $2-3 \mu m$ thick using DMF/Li⁺ and analyzing the fractions one by one [10,35]. However, as mentioned before, there are also irreversible effects which require consideration: Figure 8a,b show substantial changes in either part of the FTIR spectrum (blue ("spent" chitin retaining Eu) vs. red (native state)]). The final spectrum differs considerably from that of chitosan (Figure 1 in introduction) and of acetamide (not shown here), especially in the 1400–1500 $\rm cm^{-1}$ region, arguing against simple photoinduced acetamide hydrolysis in chitin. However, the corresponding spectral features introduced by Eu-mediated photochemistry are also present in 2-oxopropanol (hydroxyacetone) (Figure 12).



Figure 12. FTIR spectrum of hydroxyacetone [50].

Hence, it is more likely that the photocatalytic passivation ("poisoning") of Eu(III) bound to chitin is related to the oxidation of the neighbor -CH(OH)- structural motif than to hydrolysis. Given the results with amines, the deprotection of the glucosamine moiety would also explain the decrease in photoactivity, but this is not compatible with the shown spectra. The fact that both glucuronic acid and hyaluronic acid readily undergo photooxidation in this system [11], producing sizable photocurrents, argues against the alternative assumption that the exocyclic -CH₂OH group is involved in the process. The oxidation of a ring similar to oxidizing propylene glycol into hydroxyacetone thus appears to outcompete hydrolysis; it is not yet possible to distinguish between the two pathways of photooxidation of the polysaccharide by Eu(III), i.e., either direct or indirect using free radicals.

The numeric method was described previously, too [7,10]. It is used to calculate element fractionation on chitin exposed to (a) different ambient ligands and (b) a water–

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flakes (or benthic animals partly penetrating the interface, while other parts covered by chitin are kept clear to be exposed to water only) In open waters, chitin and biofilms will have some negative charges due to pzzp values (3.5; [51]) and thus preferentially adsorb cations (both Na⁺ and the like and organic ones derived from amines and amino acids, e.g., H_3N^+ -CH₂COOH). Unlike Li⁺ or Na⁺, organic cations provide **bridges** and (charged) anchor groups at chitinous interfaces to enhance the adsorption of ions (cp. ion exchange and complexation chromatography). However, this must be studied for every single kind of ion because even different REEs differ considerably with respect to causing either increases or decreases in adsorption [10]. The sugar complex stabilities of REEs are unknown, with a few exceptions for certain hexose uronic acids (log $\beta \approx 2.7$; [40]), that is, they are quite similar to simple lactate and glycolate complexes [25,26,34,44]. Published examples of carbohydrate photochemical transformations [52] include photooxidations of glucose, mannose, and galactose by TiCl₄ in methanol to yield pentodialdoses [53,54]), or those of glucose, mannose, and arabinose by FeCl₃ (causing C_1/C_2 photocleavage) or C_2/C_3 photocleavage in fructose in water [53]. Accordingly, biofilms should be inert towards photochemical attack by transition metal ions except when there are very high levels of Fe(III) or of Eu(III) after enrichment in biofilm. We found that lignite and chitin are inert towards illuminated FeCl₃ [13], while Eu(III)* particularly attacks lignite [13].

Biofilms leak phosphatases to open water [27–29], possibly controlling photochemical turnover rates by Eu(III) in shallow waters according to Figure 2. Accordingly, one needs more pieces of information on kinds of organic matter in photic stagnant waters to estimate photoreactivity before and after phosphorylation, because groups of organic compounds differ considerably with respect to rates of photooxidation by Eu(III). The photooxidation sensitivity of various substrates towards Eu(III) varies with the content of other elements, especially that of N, P, and S, which are most important in biogenic organic compounds. The typical abundance ranges of photoreactive and other organic and heteroorganic compounds in freshwater biotopes can be found in [28]. The transformation of alcohols or sugars into phosphate esters generally increases the rates and yields of photooxidation, while the introduction of S blocks this process [9,11,12], and that of N causes quite different changes. These effects can be both significant activation (ethanolamine vs. ethanediol, glycine vs. glycolic acid, and HOCH₂CN vs. ethanol) to partial (glycinate vs. propionate) or even total inactivation (aniline vs. toluene); amines usually do not react, unlike the respective quaternary ammonium salts [12]. The actual effect seems to be related to the IP of the said organics [45].

P contents in biomass (that is, (C/P)) are directly correlated with the rates of reproduction/cell budding and other metabolic activity, given the compositions of ATP, nucleic acids, and of CO_2 acceptors in both photo- and chemolithoautotrophs [55]. These processes in turn afford matter that can undergo photooxidation by Eu(III), with phosphorylated organics being much more reactive. When phyto- or zooplankton does grow, $CO_2 + NO_3^{-}$, phosphates, or N-poor foods, respectively, are transformed into organics parts which are described by the above empirical rules on photooxidation rates, and the latter in turn are related to the ecological stoichiometry of local organisms [11,12]. Among the sugars mainly producing plant tissues and wood, glucose, xylose, and oligomers are photooxidized by Eu(III), although without the permanent lowering of pH because there is CH homolytic bond cleavage by Eu(III)* rather than electron transfer from organic ligands like in LMCT photochemistry [53], whereas, unlike the corresponding phosphorylated compounds, mannose hardly reacts and ribose does not react at all. Phyto- and zooplankton bacterial cells are destroyed by surf to produce peculiar kinds of foam near shores, while dead matter sinks down as detritus. Phytoplankton (and higher plants, macroalgae) and cyano- and thiophotobacteria (which photosynthesize using H_2S as a hydrogen/electron source) all contain relatively little N and P, yet both elements are essential for making more reactive (towards Eu(III)*) sugars, carboxylates, lipids, and certain amino acids by biological processes. Photosynthetic net productivity will control production-, wave- and

surf-related mechanical activity, which causes the release of organics which then undergo photooxidation. Of course, the organics previously contained in the cells or plankton organisms then are exposed to photooxidation, with the net outcome likely controlled by ecological stoichiometry [55]. There are two principal kinds of biomass, namely heterotrophs (animals, fungi (Opisthoconta), and most bacteria) rather rich in N and P and autotrophs such as plants and phytoplankton distinguished by much lower (and more variable) N- and P-contents. Chitin only exists in the former *Opisthoconta*, except for in lichen symbiosis (for a list, see [56]). Since (most) animals are mobile, aquatic animals can contribute to the vertical transport of chemical elements in pools and lakes, and Eu desorption by photochemical processes on chitin will become a dominant process during the daytime, changing the distribution of water columns. The next drawing (Figure 13) shows the likely results, including our own works [32] insofar as the measured levels that suffice for analysis (cp. Table 2).

Glycine betaine in mangrove-, salt pond sediments: dominant ion, only becomes active when undergoing CH_3^+ abstraction and transport to sediment surface by methyl transferases (\rightarrow glycine, CH_3OH , CH_3SH , dimethyl sulfide, etc.), same with cholin \rightarrow ethanolamines: activation for photooxidation \rightarrow Eu/M'_{chitin} ratio signals Methyl transferases operate on Co; no Zn, Cu, or Ni present

Eu at illuminated sediment surface or on benthic organisms (violet)

Methyl transferase controls photochemistry of Eu(III)+organics on top of sediment

Eu leaching from chitin after photoreduction (does not work indefinitely)

Possible perturbations of Eu/M[']_{chitin} signals by in-sediment processes (activ. [red] or reducing Eu phototurnover [blue])



Figure 13. Activities of methyl transferases; CH_4 -making Ni proteins control conversion of methyl compounds CH_3Z including acetate by $Eu(III)^*$ (violet) on top of sediment (adsorption of Eu, e.g., to chitin litter, Ti-rich sand, and benthic organisms).

Phosphorylation by bacteria and cyanobacteria is rapid, but extracellular phosphatases might return parts of the material into P_{inorg} ($H_2PO_4^-/HPO_4^{2-}$, depending on local pH and pyrophosphate) again [27,29]. Organic P amounts to some 60% of total phosphorus in lakes [57], suggesting the phosphorylated species will control the extent of C;N^{org} photooxidation by Eu(III) and thus that of Eu²⁺ formation next to the surface. Amino acids and oligosaccharides are reported to be main components of DOM at levels of 5–50 µMol C/l total DOM in Lake Constance (Überlingen "fjord") top waters.

H₂ evolution in this process is an interesting phenomenon given the sizable overpotential for this process observed on a Cu electrode (some 0.5 V, [58]). In fact, $Eu^{2+/3+}$ transition in water occurs at a potential which does not permit H₂ production at nearly neutral pH (between pH 6 and 9). Meanwhile, the Pourbaix diagram of Eu [19] shows that there will be no H₂ evolution at an 0.3 V overpotential-electrode between pH 1 and 10.5. However, the formation of carbonato- or sulfatocomplexes of Eu(III) reduces the potential in ocean or limnetic waters significantly, in favor of H₂ evolution. Both the photodetachment of Eu²⁺ during the photooxidation of organics [32,35] and the "stripping"/partition of adsorbed ions to biofilms or ion-exchanging minerals and biopolymers (such as rotting wood) in top sediment layers will decrease concentrations of M^{x+}, M^{·y+}, ... adfilms on chitin, inevitably producing even more negative potential. The difference may be in the order of 100 mV when changing from 0.2 M NaCl to freshwater (see Figure 1 in [59]). Formula (1) was derived for the estimation of complex stabilities [11]:

$$Log \beta = a \times \Sigma \sigma + b \tag{1}$$

and now can be applied to calculate the relative absorption strengths (thermodynamic, not optical) of metal ions in biofilms (consisting mainly of polysaccharides [37], using $\sigma_{OH} = -0.37$ [60]) or other polymers given that the binding functional groups are known; $\sigma \approx -0.44$ holds for chitin in pure water. In slightly alkalinic freshwaters containing other complexing ions such as sulfate [32,34], polysaccharides [28], humic-, or amino acids [12], effective σ values are somewhat lower than -0.44. The retention of traces of dissolved ions from water or soil liquids or water films on ground minerals [7,9,15] thus depend on the polymeric nature of the ligand, with

$$\log \beta' \approx \log \beta_{\text{monomer ligand}} + \log n \tag{2}$$

where n is the extent of polymerization/polycondensation (while there will be significant complexation at monomer only if $[M] \ge 1/\beta$; in a kilomer (i.e., n = 1000), just one binding site of 1000 rings would need to be occupied, meaning the equilibrium concentration $[M]^*$ would be $10^{-3}/\beta$ to sustain this state). For chitin, n is about 1500 [61]. Previous experiments showed [15] that native chitin reached saturation concerning Ni²⁺_{aq} already at 1 nM/L, while it was only reached at much higher levels for insoluble salts including Ni minerals and for some complexes placed next to a chitin surface. Here, $\Sigma \sigma = -0.74$ as these materials are essentially free of N, or -0.54 for pectin (higher σ of methoxy groups [60]).

Data concerning the comparison of binding of Eu(III) to polysaccharides cellulose, chitin, and chitosan can be obtained from the literature [62]. Certain amino acids and peptides made thereof are involved in cross-linking chitin strands in arthropod chitin [63]. They readily undergo consumption by bacteria when stored moist and produce typical residues of H transfer upon pyrolysis, including benzene, toluene, and indole (from aromatic amino acids), way before the typical degradation products of polysaccharides, namely 3-acetamidofurane and its rearrangement products acetylpyrrole, and pyridine is formed (i.e., at 300 °C or less) [63]. TLRFS data show that whereas with the adsorption of this metal ion to cellulose or chitosan only \approx two water molecules in the coordination polyhedron of Eu(III) are replaced vs. the aquaion; binding to chitin replaces six or more water molecules from the Eu coordination polyhedron. Accordingly, the binding of Eu will link two parallel chitin strands in both native biomass and solution. Cp. Figure 14 (from [64]).



Figure 14. From [64]. pH between 6.5 and 7.9; highest pH means least replacement of H_2O by polysaccharide. Accordingly, Eu will stick much better to arthropods or lichens than to plant leaves, influencing rates of photooxidation of embedded substrates (sugars and amino acids) as well as increasing leaching rates of Eu²⁺.

There is a linear correlation between the σ of the sidechain and the number of Eu binding positions occupied by something other than water molecules, combining data from [60] and [64] (Table 3):

Table 3. Sidechain electron acceptor activity (Hammett's constant vs. replacement of water ligands from Eu(III) by polysaccharides.

Substance (Biopolymer)	L	σ _{sidechain}	$\Delta n_{\rm H2O}$
cellulose, alkalinic conditions	O ⁻	-0.8	≤ 2
chitosan	NH ₂	-0.66	about 2
cellulose	ОН	-0.37	3–3.5
chitin	NH-COCH ₃	0	6–6.5

Accordingly, pectin ($\sigma_{OCH3} = -0.27$) should display Eu(III) retention properties in between those of cellulose (in acidic conditions) and of chitin; the haloacetate treatment of chitosan would provide yet another intermediate-strength sorbent. Eu(III) photochemistry modifies chitin in the long run, also meaning that some structural motifs might be turned into radicals. The observed modification of chitin rendering Eu(III) retention almost irreversible indicates that $\sigma_{sidechain}$ is even higher than zero. The value for chitin indicates, in accordance with another suggestion by Ozaki et al. (2010) [62], that part of Eu(III) becomes locked away in some "cavity" between parallel chitin strands, replacing an accordingly larger number of water molecules.

Unlike other metals, the preheating of chitin by immersion into boiling *aqua dest*. does reduce the retrieval of REEs such as Gd and La [32]. An alternative would be the formation of some oxidation products of the acetamido group increasing Eu complexation, too, such as conversion into hydroxamic acid. σ for hydroxamates or ethylideneamines is not given in the literature, but it is for -NH(OH) [-0.34], benzylideneamines, or hexafluoroisopropylideneamine [60]. However, using Equation (1) and its formal rearrangement to yield:

$$\sigma_{\text{Lig}} = (\log \beta_{\text{MLig}} - b_{\text{M}}x^{+})/a_{\text{M}}x^{+} \text{ [bidentate binding]}$$
(3)

and data for acetohydroxamatocomplexes of Nd(III) and Eu(III) [65], namely log $\beta_{Nd} \approx 5.17$ and log $\beta_{Eu(III)} = 4.332$ irrespective of nitrate- or perchlorate-based ionic media, yields $\sigma_{CH3CO-N(H)O} \approx -0.2$ for acetohydroxamate, that is, a value which is much lower than for acetamido or formamido groups. Similar considerations hold for other plausible photooxidation products. Accordingly, Eu(III) at high concentrations and illumination intensities tends to migrate to some position "below" the surface where neither CH bond cleavage from co-adsorbed or dissolved organics nor Eu²⁺ release can readily occur (if chitin thus "spent up" is dissolved in DMF/Li⁺, however, some Eu²⁺ gets into the liquid phase, which can be extracted by filtration and displays green–turquoise fluorescence when excited by blue/violet LED light). However, it is unlikely that this state of matters is ever reached with arthropods or lichens in ambient conditions, except perhaps when there is strong pollution such as in mine-tailing waters. There are few larger water bodies distinguished by $[Eu]_{aq} \ge 20$ nMol/L, such as Baikal (Siberia), Masurian lakes (Poland), or Lake Michigan (Figure 15):



Figure 15. REE levels omitting Pm for many larger waterbodies around the globe [46]. Levels in ocean are much lower (<1 [odd-Z-REEs Tb–Lu] ... \approx 50 [La, Ce, Nd] ng/L), similar to blue dots in this diagram [66].

With respect to non-electrode processes related to photoproduct Eu^{2+} , kinetics were studied for just few among the sizable number of inorganic species which might be reduced by Eu^{2+} , noting that reductions of I_3^- and V^{3+} , V(III) complexes and of $[Co^{III}L(NH_3)_5]^{2+}$ (L = simple anions, acrylate, NCS⁻, N₃⁻) are rather fast, while that of CIO_4^- is rather slow and that of Cr^{3+} is even reversible [67,68]. Apparently, electron transfer or H-H coupling next to electrodes involving surface hydroxide and $[Eu^{II}(OH)]^+$ prevails over electron transfer even on Cu with its sizable H₂ formation overpotential [58], as H₂ is formed both in gelatin (Figure 6) and in the bottom part of test cells (Figure 4). Accordingly, arthropods displaying the above effect should be almost "silent" towards predators in command of electroreceptors, such as sharks or platypuses [69], except of course for signals betraying nerve or muscle activity.

The DOC/DIC ratio is closely correlated in quite diverse lakes from China except for Karst waters [70]. Whereas the DIC levels were comparable among oligotrophic (100–300 μ M/L) and eutrophic waters (60–200 μ M/L, respectively), DOC—and by inference the level of substrates for photooxidation then causing Eu mobilization from chitinous interfaces—behave in a different way:

$$\text{Log DIC}_{\text{oligotr}} = \log \text{DOC} + 1.13$$
, that is, $\text{DOC} \approx \text{DIC}/13$ (4)

and

$$Log DIC_{eutroph} = 0.63 \log DOC + 0.81$$
(5)

There is no such correlation for sulfate, which likewise forms rather stable REE(III) complexes [26,34], meaning that at rather high pH and water hardness, the availability of both non-chitin Eu and its substrates grow with carbonate content due to the solubility of

 $[Eu(CO_3)]^+$. For both this ion and its excited state, log $\beta \approx 6.6$ [71], while log $\beta = 3.64$ for sulfatocomplex [34].

Irmerteich and Hartauer Lache are eutrophic waters, and additionally, at some spots in either pond, lignite is locally exposed, thus being subject to direct photooxidations. Accordingly, Eu/M´ ratios observed on chitin are lower than in "pure" (i.e., oligo- or mesotrophic) waters. Even though (estimated) Eu/M´ ratios in water are not that different in the four waterbodies, the re-uptake of Eu by the chitin interface during the night cannot compensate for enhanced photochemically induced desorption. Sampling was conducted in the morning at dawn, meaning that the Eu levels observed on crayfish chitin (all data are given where it was possible to detect and quantify Eu) should have been close to the maximum, as shown in the following graph (Figure 16).



Figure 16. Predicted variation of Eu bound to chitin with and without glycine, potential substrates of Eu-mediated photooxidation over daytime. Sampling was conducted int the morning at dawn [32].

The high partition ratios of La for grafted chitin placed on either site of the water–sediment transition (Table 2) might indicate La use by methanol oxidases in sediment [72,73].

The general statements hold for all water volumes inhabited by arthropods or their larvae (insects, crabs, spiders, and water scorpions) provided there is a significant P level, available organic matter, and sufficient light influx. Sizes might range from phytotelmata like those of pitcher plants or bog pools up to sizable lakes and shallow rivers. The diurnal vertical migration of arthropods is typical in all of them, while living plant tissue or peat (providing citrate, malate, and humic acids) are substrates readily photooxidized by Eu(III) [11,74] and are involved in the supply or exchange of organic matter acting as ion exchangers. Main contribution would be from phytogenic glucose in addition to the organics mentioned before. Phytotelmata or bog pools are distinguished by very high levels of bacteria involved in P dynamics, whereas there are no larger predators feeding on the arthropods, except sometimes for frogs (tadpoles are herbivorous in common circumstances) [75]; particularly, fishes are absent. LREEs are—in addition to Bi, Ni, and V among the elements producing the largest transport effects associated with chitin. Like Ni, LREEs are involved in the metabolism of (here: aerobic) microorganisms [72,73], while Eu undergoes selective bioaccumulation, too [76], without becoming a phototoxic agent [9,36]. Insofar, the hypothesis summarized in Figures 1, 2 and 12 can be considered tested and reaffirmed in order to understand the actual behavior of Eu in eutrophic conditions which

M contents on grafted chitin placed in water for 10 min and on crayfish indicate kinetics: La, Sm, others match well, Al is slow \rightarrow excluded from comparison

La, Sm, Bi (likely) do not change over daytime (orange bottom line, Eu/M' >> 1 except for Irmerteich)

glycine from surrounding grasslands: increases chitin binding of La and Eu, but not of Sm (green line at top)

oligotrophic water: little variation of Eu level on chitin, higher background minimum

eutrophic water: strong variation of Eu caused by photochemistry, very low background values after night (often undetectable) tend to prevail both with time and increasing human and agricultural activities around them [28]. Phosphate levels and P speciation thus become significant in the biomonitoring of ponds and lakes by this method at least insofar as biomonitoring employing chitin is concerned.

4. Conclusions

Understanding processes which occur in chitin in ambient conditions is important for planning its use in biomining as well as estimating its role in the transport of elements on mobile animals in aquatic environments. The results obtained from both grafted chitin and different interfaces of arthropods (crayfish and ants) and the electrochemical data on the behavior of free and adsorbed ions/complexes on chitin agree that metal transport on mobile chitin (i.e., animals partly or completely covered by it) can produce significant effects with regard to metal distribution in ecosystems, whether the animals move in a periodic manner or chitin parts are discarded during or after life. Thus, eutrophication in the water bodies populated by chitin-covered organisms such as water fleas, crayfish, shrimps, or gammarids will change Eu dynamics by producing a higher share and level of phosphorylated compounds and in turn speed up their photooxidation. The extended illumination of such substrates along with Eu(III) will not cause EuPO₄ to precipitate. Specific reactions of certain elements, such as the photochemical reduction of Eu(III) or the biomethylation of elements [77] accumulating on chitin (especially Bi) then cause fractionation across the water column. Animals predating [28,78] aquatic or semi-aquatic arthropods (larvae and submerging water insects) thus are exposed to a different "cocktail" of metals when feeding at different sites from surface to benthos.

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Abbreviations

- β complex formation constant. Depends on T and solvent for a given complex such as $[LaCl]^{2+}$ or $[Fe(glyc]^{2+}$
- DMF solvent N,N-dimethyl formamide. Fully miscible with water and aromatics but not with aliphatic hydrocarbons, perfluorinated organics, or long-chain ethers. Best solvent for performing photoreduction of Eu(III) when combined with organic matter.
- DOC Dissolved organic carbon. Usually < 10% of total limnetic C content. Main component is polysaccharide
- DON dissolved organic nitrogen. Can be both highly reactive in biological terms (amino acids) or persist over centuries.
- ε Redox potential vs. some standard electrode, often \rightarrow SCE.

- $\begin{array}{ll} H_0 & \mbox{Chemical potential of solvated proton in non-aq. media. Concerning fully dissociated acids such as HClO_4 or HSO_3CF_3 in CH_3CN or <math display="inline">\rightarrow$ DMF, H_0 = 0 for a 1 M solution. The most acidic solutions which can be prepared (H_0 < -20) correspond to almost bare protons, with species such as H_2F^+, HCO^+, H_2SO_3F^+, or even H_4O^{2+}, H_3^+ just weakly interacting with anions such as SbF_6^- and its SO_3 solvates in such (viscous, highly associated) media, such as "magic acid" or HF/SbF_5 (the main problems in making such solutions are their corrosive properties and the fact that few strong fluoride acceptors do readily dissolve in either HF_{liq} or HSO_3F [79]). In water, H_0 = pH. Buffer systems in non-aq. solutions will have a H_0 value different from pH in water, e.g., glycine in DMF (11.0 [39] rather than 6.1) \\ \end{array}
- HM heavy metals. Here, denominating metals have an elemental density $\rho \ge 6 \text{ g/cm}^3$, thus deliberately excluding elements which differ massively from "typical" HM in their chemical properties while their densities are 5–6 g/cm³, like Eu (unlike all other REEs), Ra, Ga, and V. Some non-metals sometimes are mis-labeled as HM for their toxic properties, especially As, Sb, and Te.
- LM Light metals. All metal-forming elements with low(-er) densities (see HM).
- LREE Light rare-earth elements. Unprecise definition but often used to summarize elements Z = 57-63 (La-Eu).
- POC Particulate organic carbon. In lakes, POC sometimes forms "lake snow". Consists of suspended biopolymers (chitin, cellulose, and insoluble salts with organic anions) and dead plankton.
- REE Rare-earth elements. All the metals with Z = 57–71 (La–Lu), sometimes including yttrium. Highly reactive, electropositive metals (Eu and Yb even dissolve in liquid ammonia [80], like alkali metals and heavy alkaline earths) among which, Eu has unique photochemical properties. Mostly trivalent, while Eu, and to a lesser extent Yb (also in water), Sm, Tm, Nd, and Dy (in solvents such as THF, series of decreasing stability) form M²⁺ ions and M(IV) can be prepared for Ce (various media), Pr, Nd, Tb, and Dy (in solvents HF, BrF₅, or solid state only). Peculiar spectroscopic properties due to partly vacant f orbitals are used in solid-state lasers and fluorescent agents. REE alloys (Nd, Sm, and Dy with Fe or Co) form the most powerful ferromagnetic materials known.
- σ L.P. Hammett's (1893–1987) substituent constant which originally described changes in the reactivity of benzene or benzoic acid towards electrophiles; oxidantsor side chain reactants are observed when the aromatic ring is endowed with some substituent \neq H, COO⁻. The Hammett parameter can also be used to define binding in and electrochemical properties of metal complexes, with σ describing binding centers in the ligand [12].
- SCE saturated (6 M KCl solution) calomel electrode; redox couple

References

- Pinto, P.X.; Al-Abed, S.R.; Reisman, D.J. Biosorption of heavy metals from mining influenced water onto chitin products. *Chem. Eng. J.* 2011, *166*, 1002–1009. [CrossRef]
- Anastopoulos, I.; Bhatnagar, A.; Bikiaris, D.N.; Kyzas, G.Z. Chitin adsorbents for toxic metals: A review. Int. J. Mol. Sci. 2017, 18, 114. [CrossRef]
- 3. Muzzarelli, R.A.A.; Rocchetti, R.; Marangio, G. Separation of zirconium, niobium, cerium and ruthenium on chitin and chitosan columns for the determination of cesium in nuclear fuel solutions. *J. Radioanal. Chem.* **1972**, *10*, 17–25. [CrossRef]
- Ishay, J.S.; Benshalom-Shimony, T.; Ben-Shalom, A.; Kristianpoller, N. Photovoltaic effects in the Oriental hornet, *Vespa orientalis*. J. Insect Physiol. 1992, 38, 37–48. [CrossRef]
- 5. Dahmane, E.M.; Taourirte, M.; Eladlani, N.; Rhazi, M. Extraction and characterization of chitin and chitosan from *Parapenaeus longirostris* from Moroccan local sources. *Int. J. Polym. Anal. Charact.* **2014**, *19*, 342–351. [CrossRef]
- 6. Agarwal, S.; Mast, C.; Dehnicke, K.; Greiner, A. Rare earth metal initiated ring-opening polymerization of lactones. *Macromol. Rapid Commun.* **2000**, *21*, 195–198. [CrossRef]
- Bauer, A. Orientierende Untersuchungen zur Bindung von Metallionen an Chitin und zur Davon Abhängigen Eignung von Arthropoden zur Bestimmung von Metallionenkonzentrationen in der Umwelt. Master's Thesis, IHI Zittau/TU Dresden, Zittau, Germany, 2014.
- 8. Vijayaraghavan, K.; Balasubramanian, R. Single and binary biosorption of cerium and europium onto crab shell particles. *Chem. Engin. J.* **2010**, *163*, 337–343. [CrossRef]
- 9. Fränzle, S.; Erler, M.; Blind, F.; Ariuntsetseg, L.; Narangarvuu, D. Chitin adsorption in environmental monitoring: Not an alternative to moss monitoring but a method providing (lots of) bonus information. *J. Sci. Arts Univ.* **2019**, *19*, 659–674.

- 10. Erler, M. Untersuchung des Bindungsverhaltens Ausgewählter Elemente und Ihrer Bodenrelevanten Komplexe an Chitin. Master's Thesis, IHI Zittau/TU Dresden, Zittau, Germany, 2020.
- 11. Blind, F. Orientierende Untersuchungen zur Platinmetall Freien Aktivierung von CH-Bindungen für Europium Basierte Brennstoffzellenanwendungen. Master's Thesis, IHI Zittau/TU Dresden, Zittau, Germany, 2018.
- 12. Blind, F.; Fränzle, S. Chitin as a sorbent superior to other biopolymers: Features and applications in environmental research, energy conversion, and understanding evolution of animals. *Polysaccharides* **2021**, *2*, 773–794. [CrossRef]
- 13. Luoga, Y.F. Potential Influence of Exposed Lignite on Local Biota and Biodiversity. Master's Thesis, IHI Zittau/TU Dresden, Zittau, Germany, 2020.
- Nickens, K.P.; Patierno, S.R.; Ceryak, S. Chromium genotoxicity: A double-edged sword. Chem. Biol. Interact. 2010, 188, 276–288. [CrossRef]
- Retschke, D. Orientierende Untersuchungen zur Adsorption von Schwermetallen (Nickel) unter dem Einfluss Ausgewählter Komplexliganden Sowie in Arealen Potenzieller und Manifester Methanogenese. Master's Thesis, IHI Zittau/TU Dresden, Zittau, Germany, 2017.
- 16. Schieritz, R. (IHI (International Institute) Zittau, TU Dresden, Zittau, Germany); Fränzle, S. (IHI (International Institute) Zittau, TU Dresden, Zittau, Germany). Investigation into adsorption of neutral biogenic organometal entities (pnictogen trimethyls, Fe, Mo, and W carbonyls) on chitin and chemical (I2, dioxygen complexes) photochemical modification of sorbate films thus produced. unpublished results. 2015.
- 17. Feldmann, J.; Cullen, W.R. Occurrence of volatile transition metal compounds in landfill gas: Synthesis of molybdenum and tungsten carbonyls in the environment. *Environ. Sci. Technol.* **1997**, *31*, 2125–2129. [CrossRef]
- Yang, X.; Yin, D.; Sun, H.; Wang, X.; Dai, L.; Chen, Y.; Cao, M. Distribution and bioavailability of rare earth elements in aquatic microcosm. *Chemosphere* 1999, 39, 2443–2450. [CrossRef]
- 19. Takeno, N. Atlas of Eh-pH diagrams: Intercomparison of thermodynamic databases. Geol. Surv. Jpn. Open File Rep. 2005, 419, 102.
- 20. Bolsunovsky, A.; Melgunov, M.; Chuguevskii, A.; Lind, O.C.; Salbu, B. Unique diversity of radioactive particles found in the Yenisei River floodplain. *Sci. Rep.* **2017**, *7*, 11132. [CrossRef] [PubMed]
- Curragh, E.F.; Henbest, H.B.; Thomas, A. Amine oxidation. Part VII. Cleavage of tetra-N-substituted 1,2-diamines by manganese dioxide. J. Chem. Soc. 1960, 3559–3565. [CrossRef]
- 22. Tanner, S.P.; Choppin, G.R. Lanthanide and actinide complexes of glycine. Inorg. Chem. 1968, 7, 1268–1271.
- Matsumoto, A.; Azuma, N. Photodecomposition of europium(III) acetate and formate in aqueous solutions. J. Phys. Chem. 1988, 92, 1830–1835. [CrossRef]
- 24. Jiang, J.; Gao, Y.; Pang, S.-Y.; Lu, X.-T.; Zhou, Y.; Ma, J.; Wang, Q. Understanding the role of manganese dioxide in the oxidation of phenolic compounds by aqueous permanganate. *Env. Sci. Technol.* **2015**, *49*, 520–528. [CrossRef] [PubMed]
- 25. Karraker, R.H. Stability Constants of Some Rare-Earth Metal Chelates. Ph.D. Thesis, Iowa State University of Science and Technology, Ames, IA, USA, 1961.
- 26. Moeller, T.; Martin, D.F.; Thompson, L.C.; Ferrus, R.; Feistel, G.R.; Randall, W.J. The coordination chemistry of yttrium and the rare earth metal ions. *Chem. Rev.* **1965**, *65*, 1–50. [CrossRef]
- 27. Sinsabaugh, R.L.; van Horn, D.J.; Shah, J.J.F.; Findlay, S. Ecoenzymatic stoichiometry in relation to productivity for freshwater biofilm and plankton communities. *Microb. Ecol.* 2010, *60*, 885–893. [CrossRef] [PubMed]
- 28. Schwoerbel, J.; Brendelberger, H. Einführung in die Limnologie, 10th ed.; Springer: Berlin, Germany, 2013.
- 29. Thompson, A.J.; Sinsabaugh, R.L. Matrix- and particulate phosphatase and aminopeptidase activity in limnetic biofilms. *Aquat. Microb. Ecol.* **2000**, *21*, 151–159. [CrossRef]
- 30. Loppi, S.; Vannini, A.; Monaci, F.; Dagodzo, D.; Blind, F.; Erler, M.; Fränzle, S. Can chitin and chitosan replace the lichen *Evernia prunastri* for environmental biomonitoring of Cu and Zn air contamination? *Biology* **2020**, *9*, 301. [CrossRef]
- Jurkowski, W.; Paper, M.; Brück, T.B. Isolation and Investigation of natural rare earth metal chelating agents from *Calothrix* brevissima-A Step Towards Unraveling the Mechanisms of Metal Biosorption. Front. Bioeng. Biotechnol. 2022, 10, 833112. [CrossRef] [PubMed]
- Budelmann, P. Verbreitung der Flusskrebse (Decapoda) in der Südlichen Oberlausitz und die Eignung des Invasiven Kamberkrebses (Orconectes Limosus) für Chitin-Basiertes Monitoring von Schwermetallen in Limnischen Ökosystemen. Master's Thesis, IHI Zittau/TU Dresden, Zittau, Germany, 2021.
- 33. Brandys, M.; Stein, G. Photochemical evolution of hydrogen from aqueous solutions of europium ions at lambda > 310 nm. The role of europium(II). *J. Phys. Chem.* **1978**, *82*, 852–854. [CrossRef]
- 34. Wood, S.A. The aqueous geochemistry of the rare-earth elements and yttrium. 2. Theoretical predictions of speciation in hydrothermal solutions to 350 °C at saturation water vapor pressure. *Chem. Geol.* **1990**, *88*, 99–125. [CrossRef]
- 35. Gebauer, T. Methodische Optimierung des Übertrags von Metallionen aus Umweltprobenmodellen auf Chitinoberflächen und von Diesen zu Zwecken Analytischen Biomonitorings sowie Untersuchungen zur Diffusion/Ausbreitung von Analyten in Chitinproben. Master's Thesis, IHI Zittau/TU Dresden, Zittau, Germany, 2016.
- 36. Pulsfort, J. Biopolymere Als Potenzielle Substrate der Photooxidation Durch f-Block-Metalle. Master's Thesis, IHI Zittau/TU Dresden, Zittau, Germany, 2021.
- Malhotra, N.; Hsu, H.-S.; Liang, S.-T.; Jmelou, M.; Roldan, M.; Lee, J.-S.; Ger, T.-R.; Hsiao, C.-D. An Updated Review of Toxicity Effect of the Rare Earth Elements (REEs) on Aquatic Organisms. *Animals* 2020, 10, 1663. [CrossRef] [PubMed]

- Sjöberg, S.; Callac, N.; Allard, B.; Smittenberg, R.H.; Dupraz, C. Microbial communities inhabiting a rare earth element enriched birnessite-type manganese deposit in the Ytterby Mine, Sweden. *Geomicrobiol. J.* 2018, 35, 657–674. [CrossRef]
- Junold, M. Untersuchung der Eignung von Bipolartransistor und MOSFET (Metall-Oxid-Feldeffekttransistor) zur Identifikation von Kurzkettigen Carbonsäuren. Master's Thesis, IHI Zittau/TU Dresden, Zittau, Germany, 2021.
- 40. Giroux, S.; Rubini, P.; Aury, S. Complexes of praseodymium(III) with d-gluconic acid. Polyhedron 2000, 17, 422–428. [CrossRef]
- 41. Gutmann, V.; Peychal-Heiling, G. Das polarographische Verhalten von Europium in Abhängigkeit vom Lösungsmittel und Leitsalz. *Mon. Chem.* **1969**, *100*, 1423–1433. [CrossRef]
- 42. Couffin, F. Potentiels d 'Oxydo-Reduction des Elements Lanthanides et Actinides dans les Solvants Organiques; CEA-BIB 233; 1980.
- Farkas, E.; Enyedy, E.A.; Zekany, L.; Deak, G. Fe hydroxamatocomplexes, natural: Interaction between iron(II) and hydroxamic acids: Oxidation of iron(II) to iron(III) by desferrioxamine B under anaerobic conditions. *J. Inorg. Biochem.* 2001, *83*, 107–114. [CrossRef]
- 44. Holleck, L. Zur Komplexchemie der seltenen Erden. Die polarographischen Strompotentialkurven des Europiums als Nachweismittel komplexer Bindung. Z. für Naturf. B 1947, 2, 81–89. [CrossRef]
- 45. Blind, F. (IHI (International Institute) Zittau, TU Dresden, Zittau, Germany); Fränzle, S. (IHI (International Institute) Zittau, TU Dresden, Zittau, Germany). Influence of CH bond energies and substrate ionization potentials, orbital sequences on the chance to accomplish photooxidation by Eu(III). Unpublished results. 2019.
- Adeel, M.; Lee, J.Y.; Zain, M.; Rizwan, M.; Nawab, A.; Ahmad, M.A.; Shafiq, M.; Yi, H.; Jilani, G.; Javed, R.; et al. Cryptic footprints of rare earth elements on natural resources and living organisms. *Environ. Int.* 2019, 127, 785–800. [CrossRef]
- 47. Markert, B.; de Li, Z. Natural background concentrations of rare-earth elements in a forest ecosystem. *Sci. Total Environ.* **1991**, *103*, 27–35. [CrossRef]
- 48. Köllner, K.E.; Carstens, D.; Keller, E.; Vazquez, F.; Schubert, C.J.; Zeyer, J.; Bürgmann, H. Bacterial chitin hydrolysis in two lakes with contrasting trophic statuses. *Appl. Environ. Microbiol.* **2012**, *78*, 695–704. [CrossRef] [PubMed]
- 49. Dhar, N.R.; Mukherjee, S.K. Photosynthesis of amino acids in vitro. Nature 1934, 134, 499. [CrossRef]
- 50. Anonymous. NIST Table of Chemicals Properties. Available online: https://webbook.nist.gov/cgi/cbook.cgi?ID=116-09-6 (accessed on 15 January 2022).
- Klapiszewski, Ł.; Wysokowski, M.; Majchrzak, I.; Szatkowski, T.; Nowacka, M.; Siwińska-Stefańska, K.; Szwarc-Rzepka, K.; Bartczak, P.; Ehrlich, H.; Jesionowski, T. Preparation and Characterization of Multifunctional Chitin/Lignin Materials. *J. Nanomat.* 2013, 2013, 425726. [CrossRef]
- Hennig, H.; Rehorek, D. Photochemische und Photophysikalische Reaktionen von Koordinationsverbindungen; Deutscher Verlag der Wissenschaften: Berlin, Germany, 1987.
- 53. Horvath, O.; Stevenson, K.L. Charge Transfer Photochemistry of Coordination Compounds; VCH: New York, NY, USA; Weinheim, Germany, 1993.
- Araki, K.; Sakuma, M.; Shiraishi, S. Photooxidation of d-fructose with iron(III) chloride under aerobic conditions. *Chem. Lett.* 1983, 665–666. [CrossRef]
- 55. Sterner, R.W.; Elser, J.J. Ecological Stoichiometry: The Biology of Elements from Molecules to the Biosphere; Princeton Univ. Press: Princeton, NJ, USA, 2002.
- 56. Wagner, G.P.; Lo, J.; Laine, R.; Almeder, M. Chitin in the epidermal cuticle of a vertebrate (*Paralipophrys trigloides, Blenniidae, Teleostei*). *Experientia* **1993**, 49, 317–319. [CrossRef]
- 57. Weiss, M.; Simon, M. Consumption of labile dissolved organic matter by limnetic bacterioplankton: The relative significance of amino acids and carbohydrates. *Aquat. Microb. Ecol.* **1999**, *17*, 1–12.
- 58. Ruetschi, P.; Delahay, P. Hydrogen overvoltage and electrode material. A theoretical analysis. *J. Chem. Phys.* **1955**, *23*, 195–199. [CrossRef]
- 59. Digby, P.S.B. Semi-conduction and electrode processes in biological material. Proc. Royal Soc. B 1964, 161, 504–525.
- Hansch, C.; Leo, A.; Taft, R.W. A Survey of Hammett Substituent Constants and Resonance and Field Parameters. *Chem. Rev.* 1991, 97, 165–195. [CrossRef]
- 61. Funahashi, R.; Ono, Y.; Qi, Z.-D.; Saito, T.; Isogai, A. Molar Masses and Molar Mass Distributions of Chitin and Acid-Hydrolyzed Chitin. *Biomacromolecules* **2017**, *18*, 4357–4363. [CrossRef]
- 62. Ozaki, T.; Kimura, T.; Yoshida, Z.; Francis, A.J. Speciation study of actinides and lanthanides by time-resolved laser-induced fluorescence spectroscopy. *Chem. Lett.* **2003**, *32*, 560–561. [CrossRef]
- 63. Stankiewicz, B.A.; Mastalerz, M.; Hof, C.H.J.; Bierstedt, A.; Flannery, M.B.; Briggs, D.E.G.; Evershed, R.P. Biodegradation of the chitin-protein complex in crustacean cuticle. *J. Org. Geochem.* **1998**, *28*, 67–76. [CrossRef]
- 64. Ozaki, T.; Kimura, T.; Ohnuki, T.; Kirishima, A.; Yoshida, T.; Isobe, H.; Francis, A.J. Association of europium(III), americium(III), and curium(III) with cellulose, chitin, and chitosan. *Environm. Toxicol. Chem.* **2006**, *25*, 2051–2058. [CrossRef] [PubMed]
- 65. Pati, A.; Bhattacharyya, A.; Pujari, P.K.; Pal, S.; Kundu, T.K. Investigation of lanthanide complexation with acetohydroxamic acid in nitrate medium: Experimental and DFT studies. *J. Chem. Sci.* 2021, 133, 60. [CrossRef]
- 66. Nozaki, Y. A Fresh Look at Element Distribution in the North Pacific. EOS Trans. 1997, 78, 221–226.
- 67. Adin, A.; Sykes, A.G. The Kinetics of the oxidation of europium(II) with vanadium(III) and chromium(III) in aqueous perchloric acid solutions. *J. Chem. Soc.* **1966**, 1230–1236. [CrossRef]

- 68. AAdegite; Egboh, H. Kinetics and Mechanism of the Oxidation of Europium(II) by Aqueous Solution of Iodine and Triiodide. *Inorg. Chim. Acta* **1977**, *21*, 1–4. [CrossRef]
- 69. Scheich, H.; Langner, G.; Tidemann, C.; Coles, R.B.; Guppy, A. Electroreception and electrolocation in platypus. *Nature* **1986**, *319*, 401–402. [CrossRef] [PubMed]
- 70. Song, K.; Wen, Z.; Xu, Y.; Yang, H.; Lyu, L.; Zhao, Y.; Fang, C.; Shang, Y.; Du, J. Dissolved carbon in a large variety of lakes across five limnetic regions in China. *J. Hydrol.* **2018**, *563*, 143–154. [CrossRef]
- 71. Kim, J.I.; Klenze, R.; Wimmer, H.; Runde, W.; Hauser, W. A study of the carbonate complexation of Cm(III) and Eu(III) by time-resolved laser fluorescence spectroscopy. *J. Alloy. Compd.* **1994**, *213*, 333–340. [CrossRef]
- 72. Pol, A.; Barends, T.R.M.; Dietl, A.; Khadem, A.F.; Eygensteyn, J.; Jetten, M.S.M.; den Camp, H.J.M.O. Rare earth metals are essential for methanotrophic life in volcanic mudpots. *Environ. Microbiol.* **2014**, *16*, 255–261. [CrossRef]
- 73. Cook, E.C.; Featherston, E.R.; Showalter, S.A.; Cotruvo, J.A., Jr. Structural basis for rare earth element recognition by *Methylobacterium extorquens* lanmodulin. *Biochemistry* **2019**, *58*, 120–125. [CrossRef]
- 74. Monsallier, J.-M.; Scherbaum, F.J.; Buckau, G.; Frimmel, F.H. Influence of photochemical reactions on the complexation of humic acid with europium(III). J. Photochem. Photobiol. A Chem. 2001, 138, 55–56. [CrossRef]
- 75. Kitching, R.L. Food webs in phytotelmata: "bottom-up" and "top-down" explanations for community structure. *Annu. Rev. Entomol.* **2001**, *46*, 729–760. [CrossRef]
- Maleke, M.; Valverde, A.; Vermeulen, J.-G.; Cason, E.; Gomez-Arias, A.; Moloantoa, K.; Coetsee-Hugo, L.; Swart, H.; van Heerden, E.; Castillo, J. Biomineralization and bioaccumulation of europium by a thermophilic metal resistant bacterium. *Front. Microbiol.* 2019, *10*, 81–88. [CrossRef]
- 77. Ridley, W.P.; Dizikes, L.; Cheh, A.; Wood, J.M. Recent studies on biomethylation and demethylation of toxic elements. *Environ. Health Perspect.* **1977**, *19*, 43–46. [CrossRef]
- Michalke, K.; Schmidt, A.; Huber, B.; Meyer, J.; Sulkowski, M.; Hirner, A.V.; Boertz, J.; Mosel, F.; Dammann, P.; Hilken, G. Role of intestinal microbiota in transformation of bismuth and other metals and metalloids into volatile methyl and hydride derivatives in humans and mice. *Appl. Environ. Microbiol.* 2008, 74, 3069–3075. [CrossRef] [PubMed]
- 79. Waddington, N.C. Nichtwässrige Lösungsmittel; utb: Heidelberg, Germany, 1972.
- 80. Golub, A.A.; Köhler, H. Pseudohalogenide; Deutscher Verlag der Wissenschaften: Berlin, Germany, 1978.