

Biogenic Approaches To Scarce Element Recovery

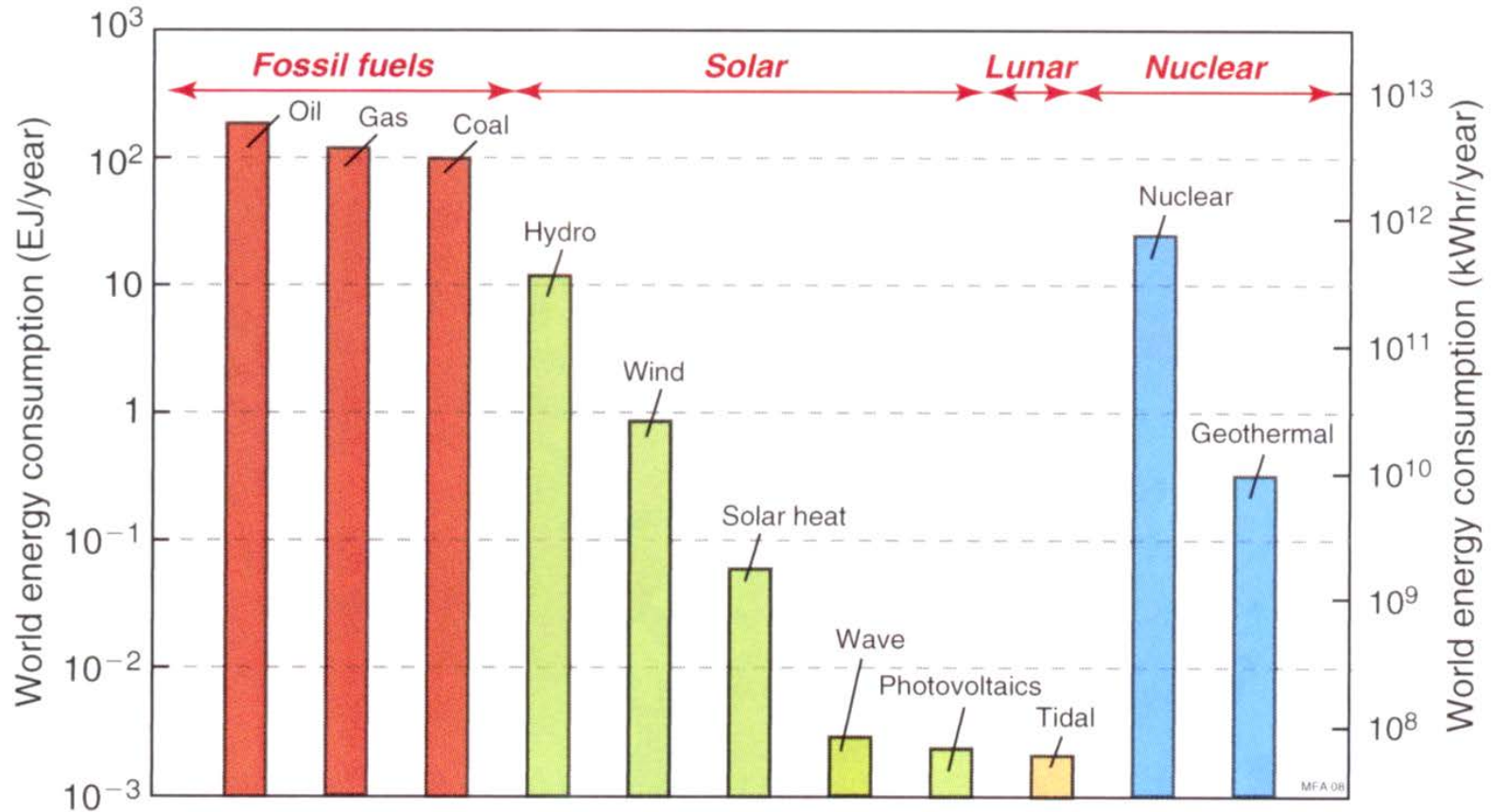
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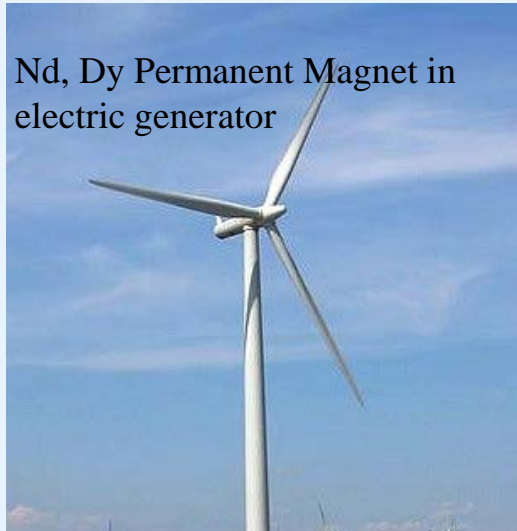
The World's Energy Consumption (2009)



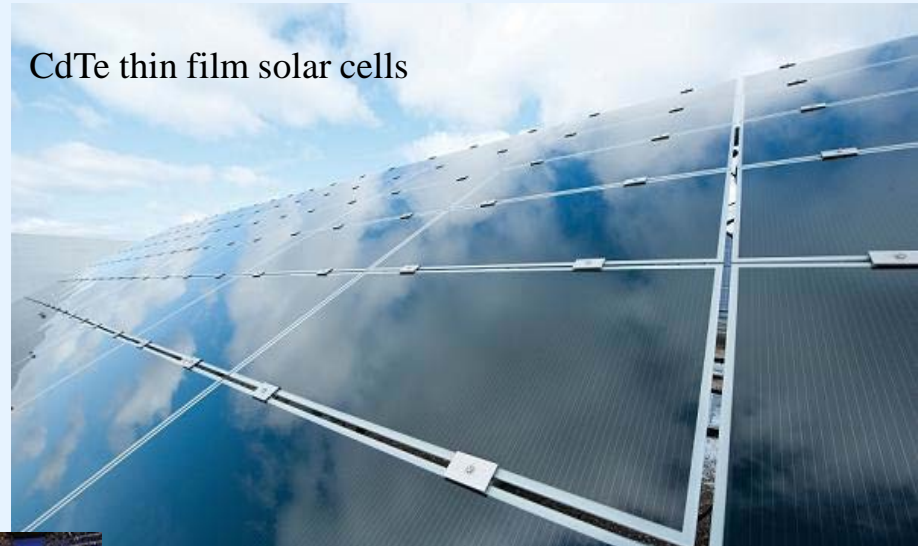
Use of renewables will depend on their cost and availability



Examples of Critical Metals for Renewable Energy Technologies



Nd, Dy Permanent Magnet in electric generator

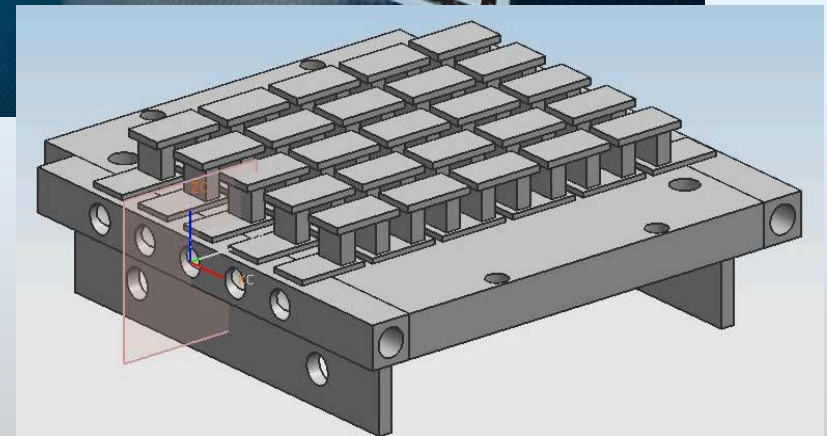


CdTe thin film solar cells



Nd Permanent Magnet in Electric Motor

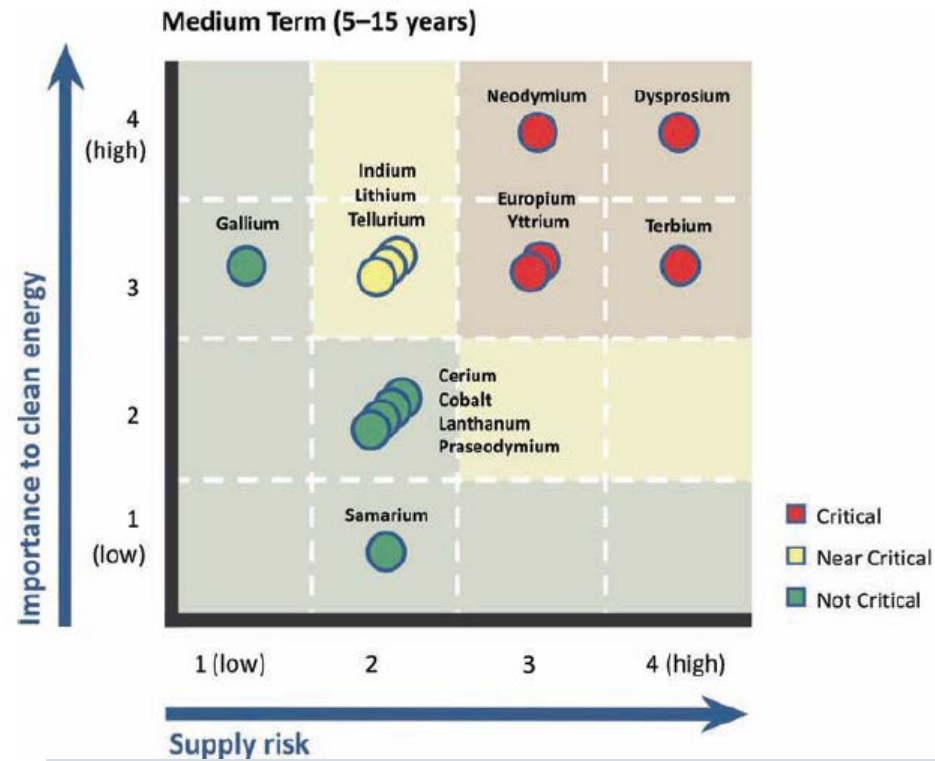
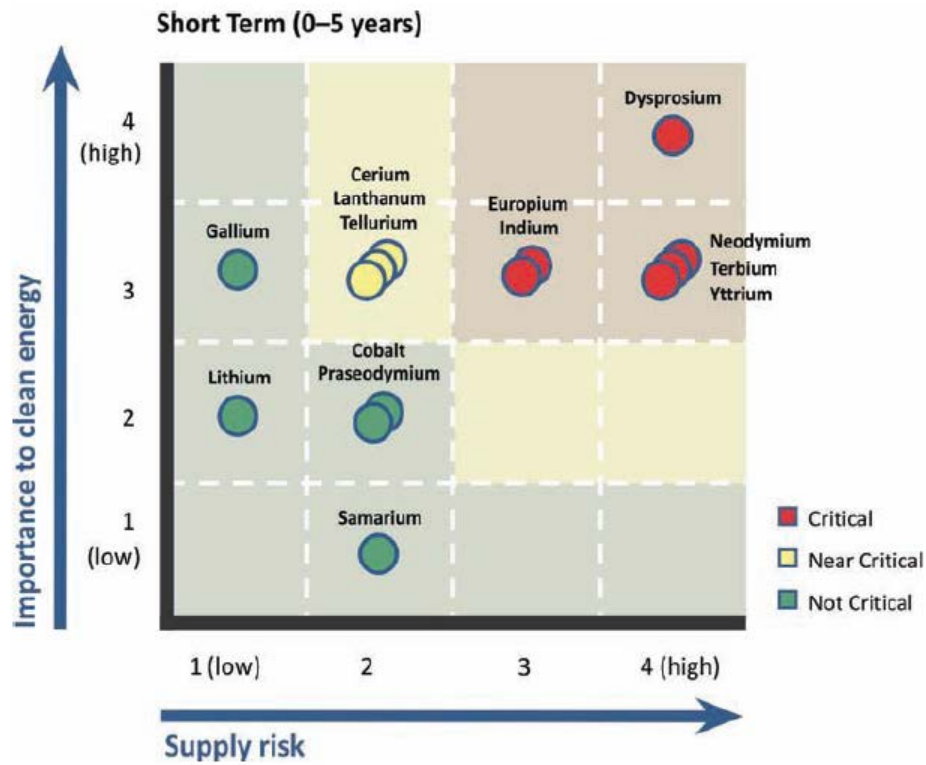
Lithium Batteries



Bi_2Te_3 Thermoelectrics



DOE Assessment of Critical Elements for "Clean" Energy (2010)



Materials Needed for Renewable Energy Technologies (A partial List)

- Wind turbines: Metals for permanent magnet generators
Rare-Earth metals, eg Dy, Nd
- Photovoltaics: Silicon, **CdTe** (First Solar)
- Solid State Lighting: Gallium Nitride, Phosphors
Ga, Eu, Ce, Er
- Fuel Cells: Platinum as catalyst: **Pt**
- Batteries: Lithium **Li**
- Electric cars: Permanent magnet motors
Rare-Earth metals, eg Dy, Nd
- Thermoelectrics: Tellurium, **Te, Bi**
- Smart windows: Glass plus coatings
- Displays: Conducting electrodes **In, Ga, Sn**
- Gas Turbines: Metals for superalloys. **Re, Mo, Ni, Pt**



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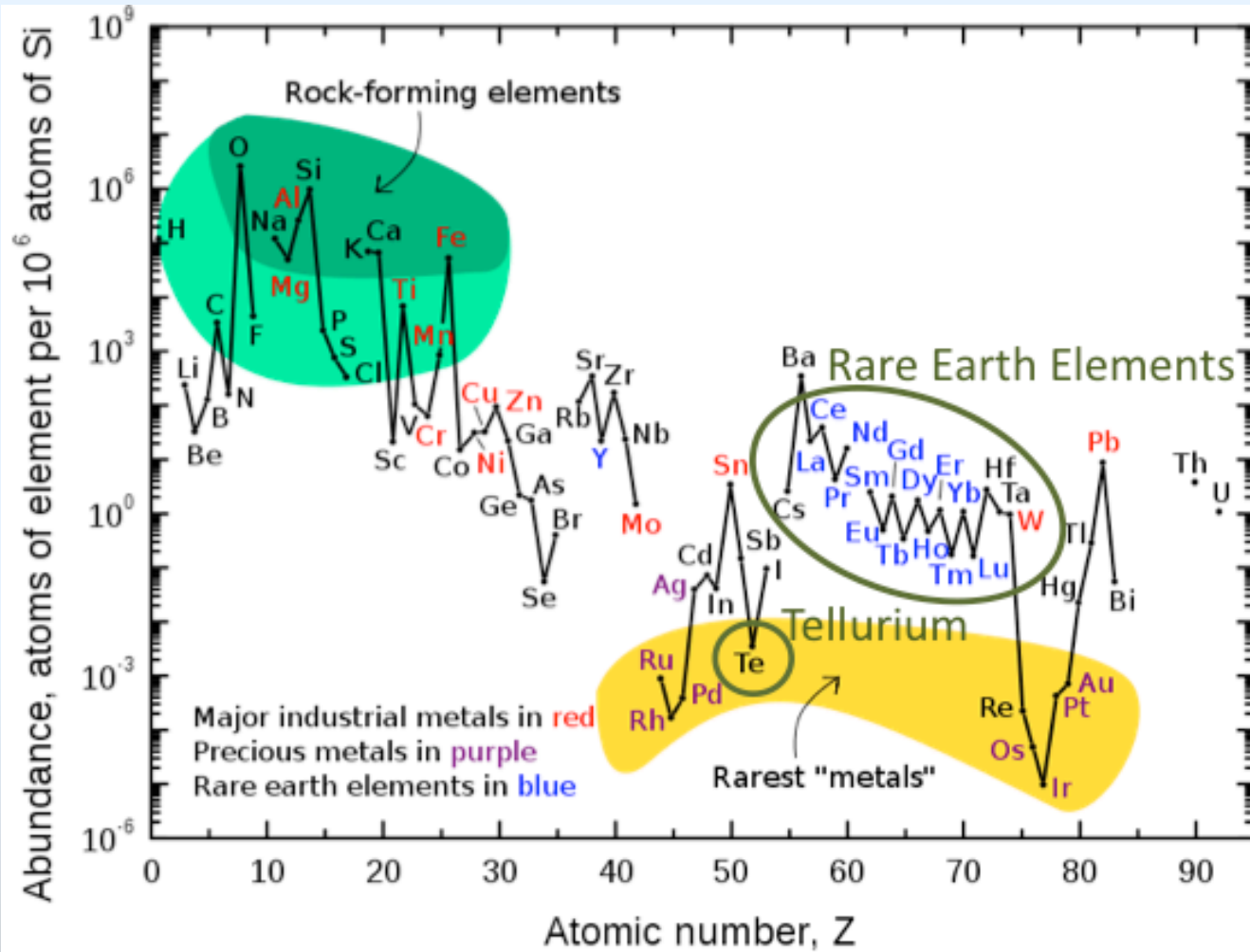
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How Scarce is Scarce ?

- **Natural abundance**
- **Cost**
- **Geopolitics -- China 97% of REE**



Elemental Abundances in the Earth's Crust



Geopolitical Supply Risk

Market concentration quantified using Herfindahl-Hirschman index (HHI)

$$HHI = \sum_i^N s_i^2$$

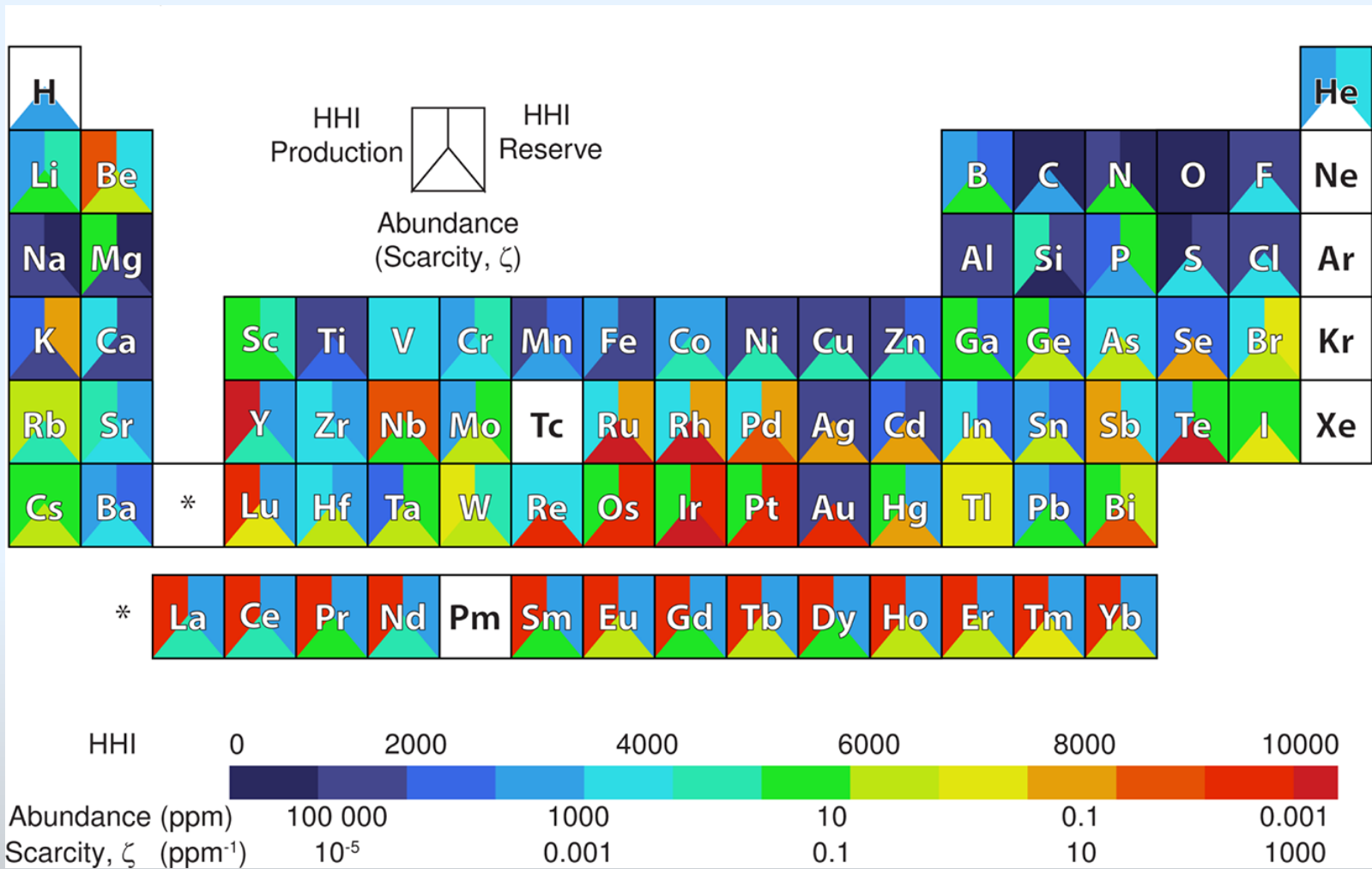
N = number of countries involved
 S = percent market share of country
 i = country

Calculated Herfindahl-Hirschman Indices for select elements' production and reserves

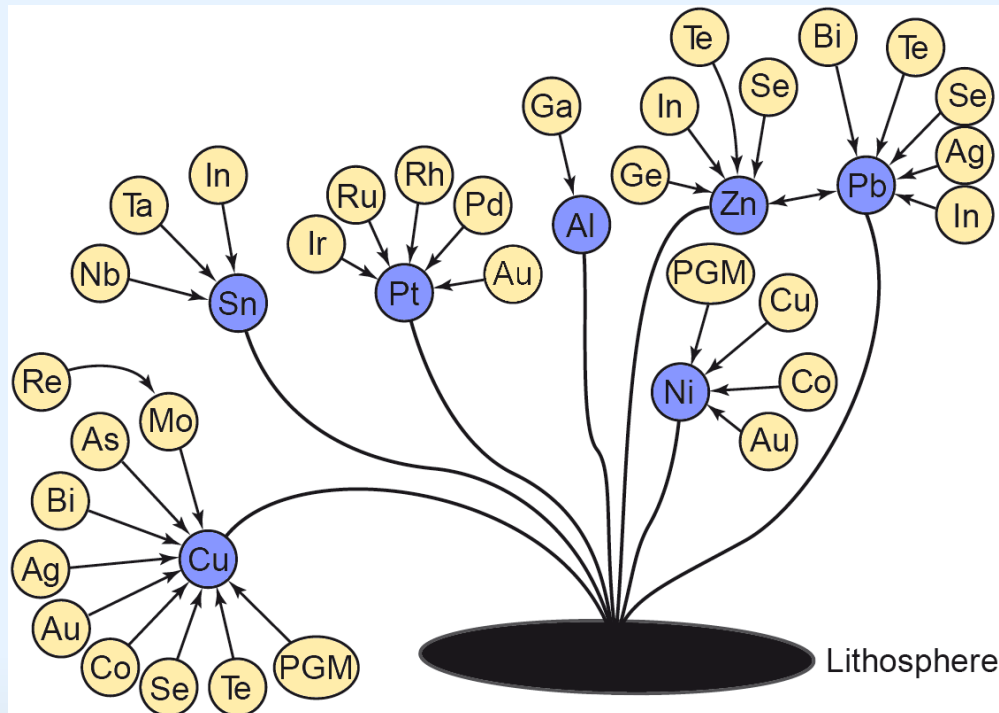
Element	HHI _{Production}	HHI _{Reserve}	Element	HHI _{Production}	HHI _{Reserve}	Element	HHI _{Production}	HHI _{Reserve}	Element	HHI _{Production}	HHI _{Reserve}
Co	3100	2700	Nb	8500	8800	Ba	3000	2300	Yb	9500	3100
Ni	1000	1500	Mo	2400	5300	La	9500	3100	Lu	9500	3100
Cu	1600	1500	Ru	3200*	8000*	Ce	9500	3100	Hf	3400*	2600*
Zn	1600	1900	Rh	3200*	8000*	Pr	9500	3100	Ta	2300	4800
Ga	5500*	1900*	Pd	3200	8000*	Nd	9500	3100	W	7000	4300
Ge	5300	1900*	Ag	1200	1400	Pm	9500	3100	Re	3300	3300
As	3300	4000*	Cd	1700	1300	Sm	9500	3100	Os	5500*	9100*
Se	2200	1900	In	3300	2000*	Eu	9500	3100	Ir	5500*	9100*
Br	3300	6900	Sn	2600	1600	Gd	9500	3100	Pt	5500	9100*
Rb	6000*	6000*	Sb	7900	3400	Tb	9500	3100	Au	1100	1000
Sr	4200	3000*	Te	2900	4900	Dy	9500	3100	Hg	5500	3100
Y	9800	2600	I	4900	4800	Ho	9500	3100	Tl	6500*	6500*
Zr	3400	2600	Cs	6000*	6000*	Er	9500	3100	Pb	2700	1800
						Tm	9500	3100	Bi	5300	6000



Materials Scarcity: Herfindahl-Hirschman Index



Complication: Association of Elements in the Earth's Crust



*Christian Hageluken and Christina Meskers.
Linkages of Sustainability. 2009*

Many scarce metals are “daughter” elements obtained as a by-product of the mining of more commonly mined elements, eg. Te comes from Cu mining and , Ga comes from Al mining.

Consequence: price is highly volatile since depends on availability of smelting activity



Opportunities for Harvesting Elements: Anthropogenic Cycle -- Nickel

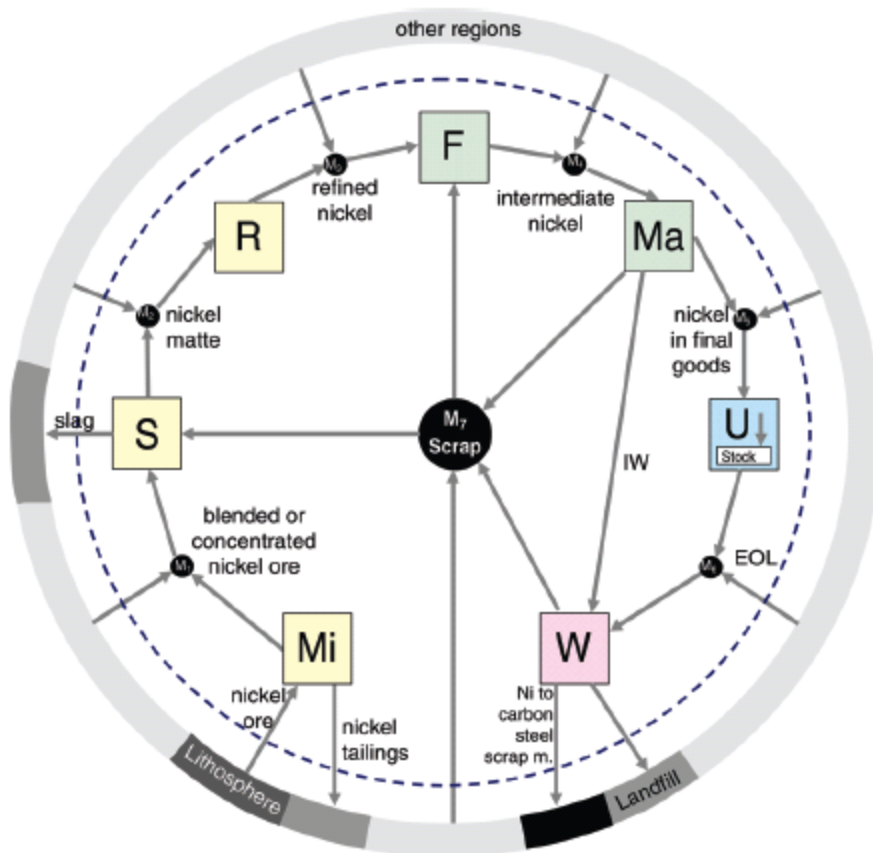


FIGURE 1. (a) Circular diagram for nickel, with the main processes mining/milling (Mi), smelting (S), refining (R), fabrication (F), manufacturing (Ma), use (U), and waste management and recycling (W). The processes are connected through seven markets, each related to other regions through net import flows. "Carbon steel scrap market" stands for "carbon steel and copper scrap markets"; EOL, for end-of-life; IW, for industrial wastes.

TABLE 1. Fabrication In- and Outflows (in Percent)^a

nickel fabrication	fabrication inflows		fabrication outflows		
	primary nickel ^b	scrap	intermediate Ni products ^b	scrap ^c	IW ^c
stainless steel	57	43 ^d	98.9	0.5	0.6
alloy steels	83 ^{b,e}	17 ^{c,e}	98.9	0.5	0.6
nickel (Ni) alloys	92	8 ^c	99	0.5	0.5
copper (Cu) alloys	55	45 ^c	99	0.5	0.5
Ni and Cu alloys (total)	86	14 ^f	99	0.5	0.5
plating	100	0 ^c	97	0	3
foundry	75	25 ^g	99	0.5	0.5
others (total) ^h	100	0 ^c	99.5	0	0.5
total	66	34	98.8	0.4	0.7

How Would Nature Do It ?



Aqueous chemistry, ambient temperature and pressure,
biological processes building on evolutionary developments



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Why Microbial Approaches to Harvesting Scarce Elements ?

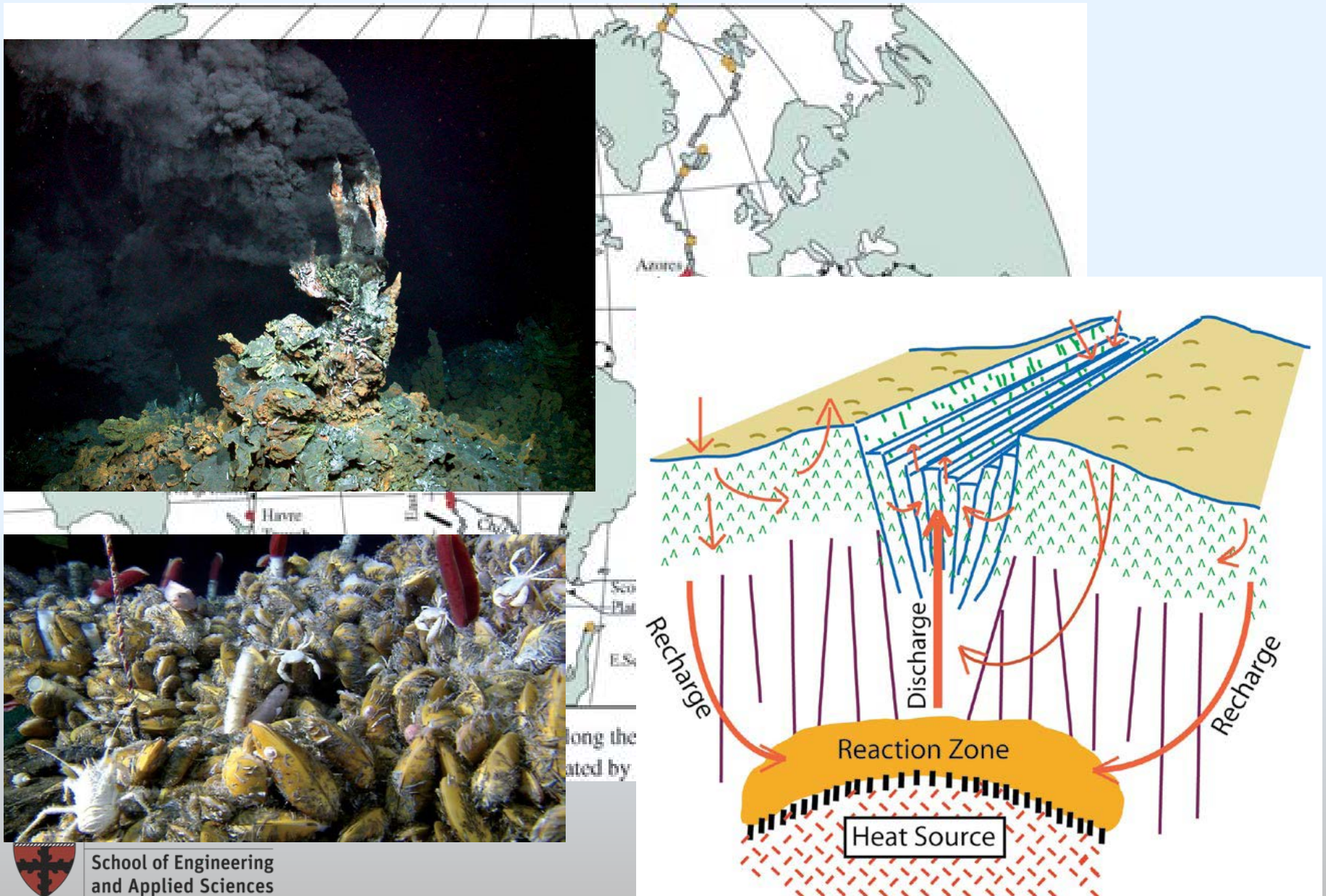
- Potentially cheaper with lower environmental impact
- Potential for recovering scarce metals from low grade ores and tailings
- Can be self-sustaining
- A topic in which we can leverage tremendous advances in micro-biology
- Access to larger pool of scientists and engineers than traditional metallurgy and materials science
- Once candidate microbes that concentrate rare elements have been identified they can be the focus of chemical /biological processes for improving the microbial action as well as identification of optimum concentration conditions.
- If molecular species, eg enzymes can be identified, there is a prospect of identifying gene sequence and generating enzymes by mass production.
- Also, there is the prospect of directed evolution for higher yield harvesting



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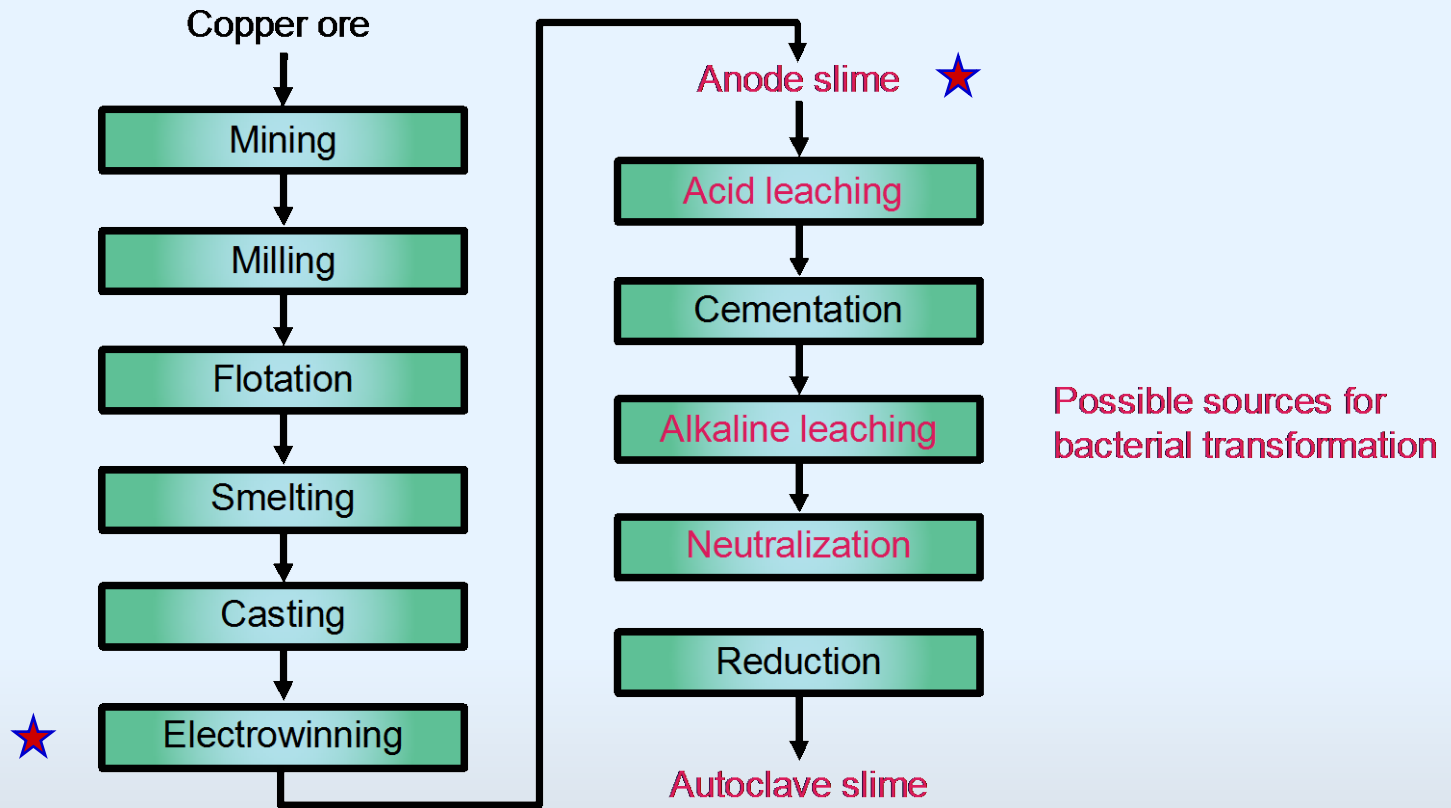
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Hydrothermal Vents: Rich Source of Extremophilic Microbes



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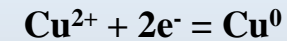
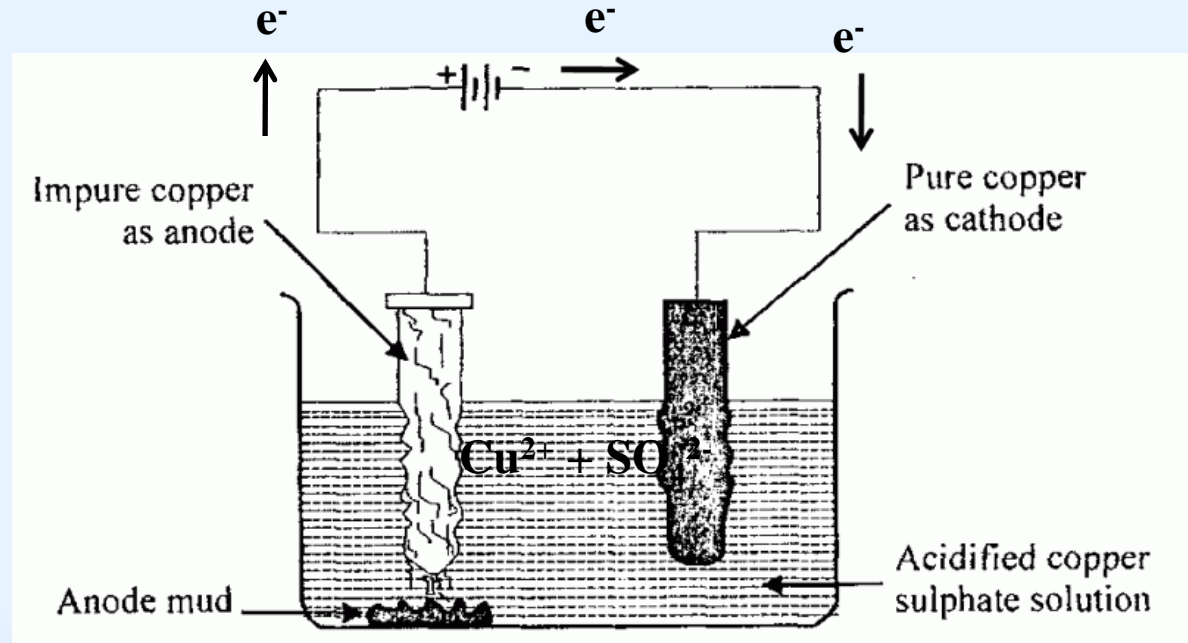
Current Tellurium Processing



80% of initial tellurium is lost during processing



Tellurium Refining by Electrowinning



**Anode contains 200 ppm tellurium,
Anode slime contains 2% tellurium**

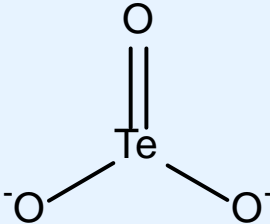
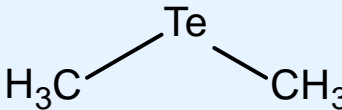
ASARCO, Martin A. Green *Improved Estimates for Te and Se Availability from Cu Anode Slimes and Recent Price Trends*



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Important Forms of Tellurium

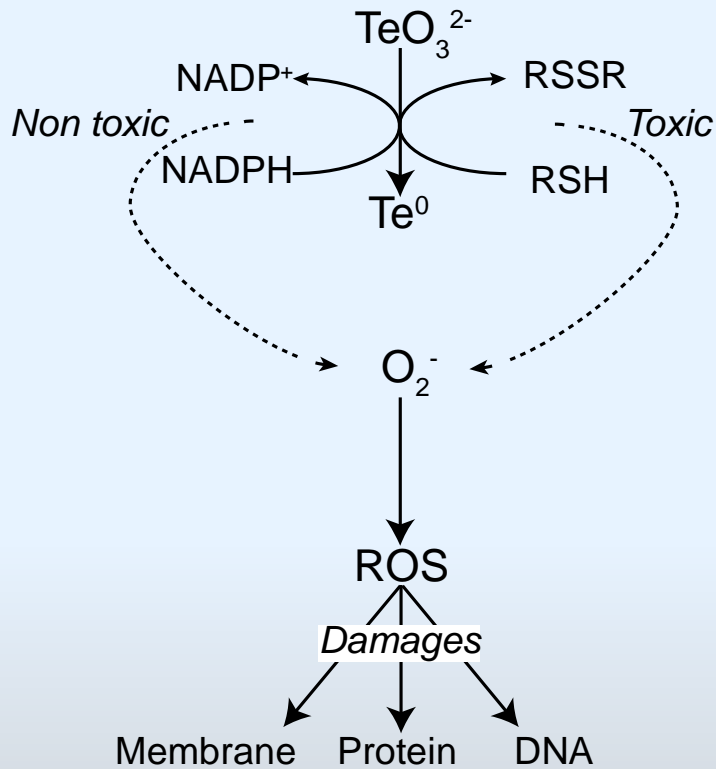
	Name	Formula	Molecule
Biologically relevant	Tellurite	TeO_3^{2-}	
	Metallic tellurium	Te^0	
	Dimethyl telluride	$\text{Te}(\text{CH}_3)_2$	
Industrially relevant	Tellurium Dioxide	TeO_2	$\text{O}=\text{Te}=\text{O}$
	Autoclave Slime	H_2TeO_3 (impure)	
	Bismuth telluride	Bi_2Te_3	
	Cadmium telluride	CdTe	

Tellurite is soluble and accessible by bacteria
Other forms are insoluble/not accessible

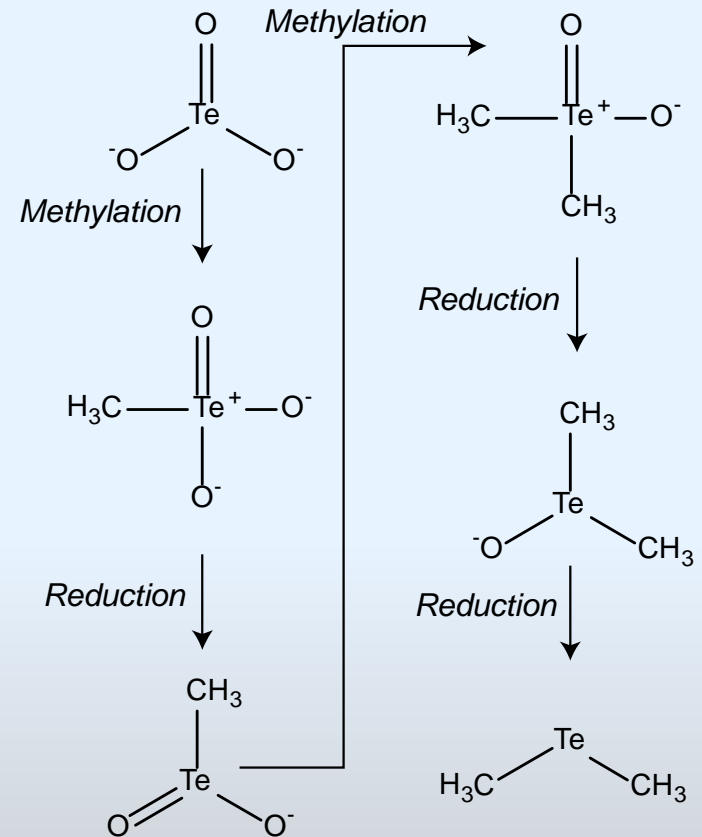


Proposed Tellurium Detoxification Mechanisms in Bacteria

Reduction of Tellurite to metallic tellurium



Tellurite methylation to dimethyl telluride (Challenger mechanism)

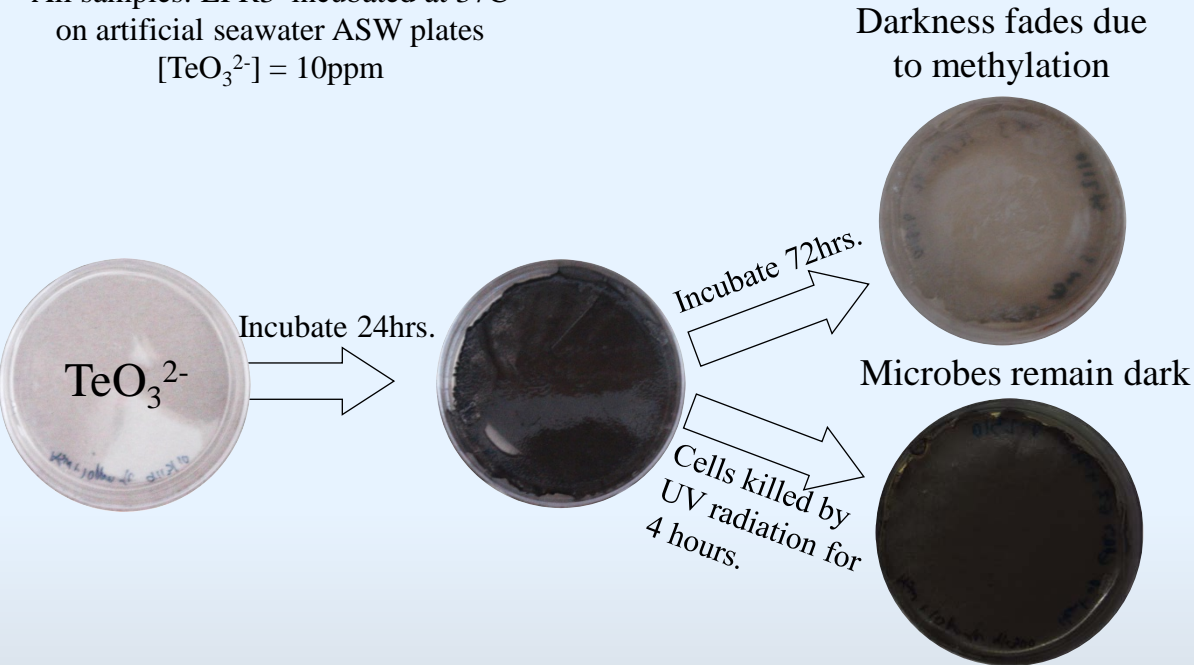


- Reduction to insoluble metallic tellurium
- Volatilization to dimethyl telluride vapor

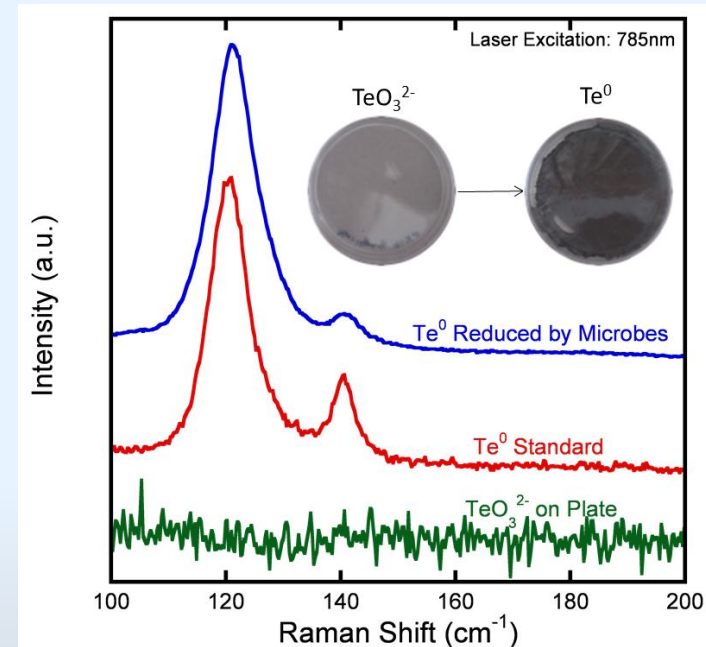


EPR3 Bacteria Reduces and Methylates Tellurite

All samples: EPR3 incubated at 37C
on artificial seawater ASW plates
[TeO₃²⁻] = 10ppm



Verification by Raman

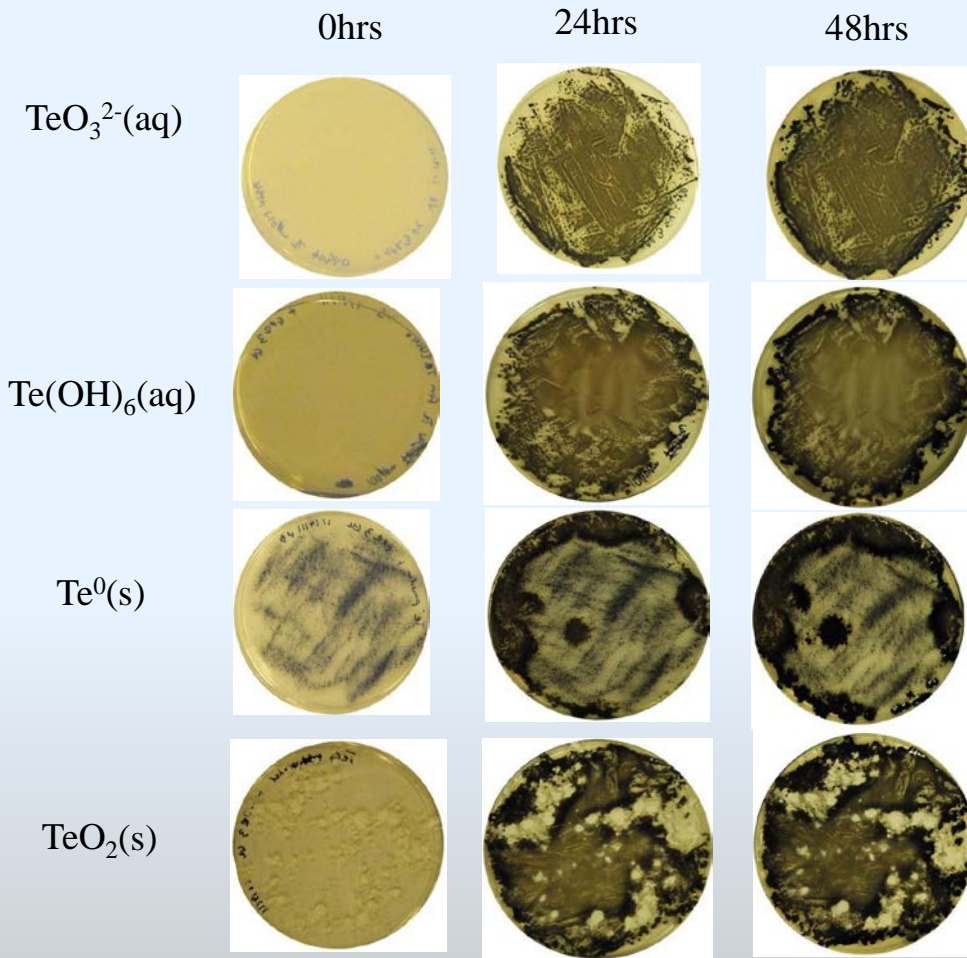


EPR3 converts TeO₃²⁻ to Te⁰ and to Te(CH₃)₂.



EPR3 converts a variety of tellurium species

Pseudoalteromonas sp. EPR3 from deep sea vents



- Darkening due to precipitation of Te metal.
- Garlic odor
- Important intermediates in Te purification
- Solid and aqueous species transformed
- 4+, 6+, 0 oxidation states transformed
- Reduction and methylation processes

All samples: EPR3 incubated at 37C on artificial seawater agar plates

$[\text{TeO}_3^{2-}] = 10\text{ppm}$

$[\text{Te}(\text{OH})_6] = 100\text{ppm}$

$\text{Te}^0 = 0.025\text{g}$

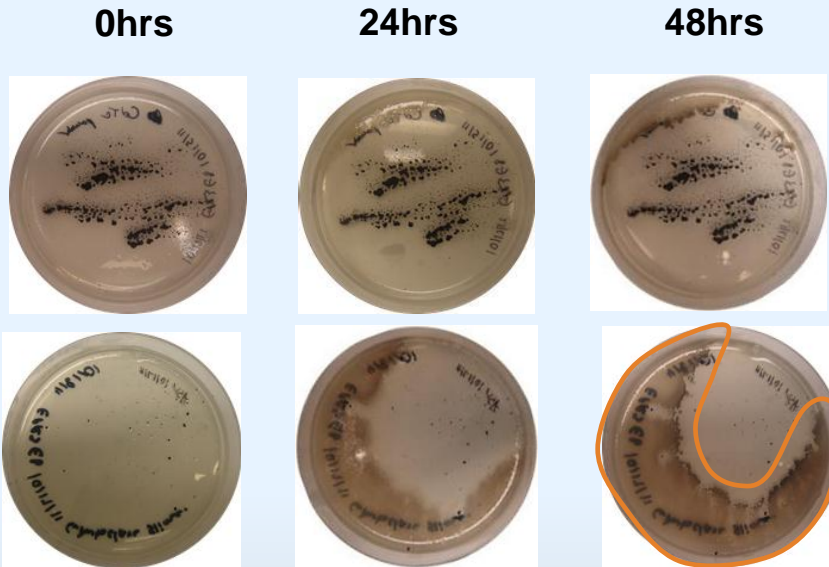
$\text{TeO}_2 = 0.025\text{g}$



Tellurium Precipitation from Leach Slime and CdTe

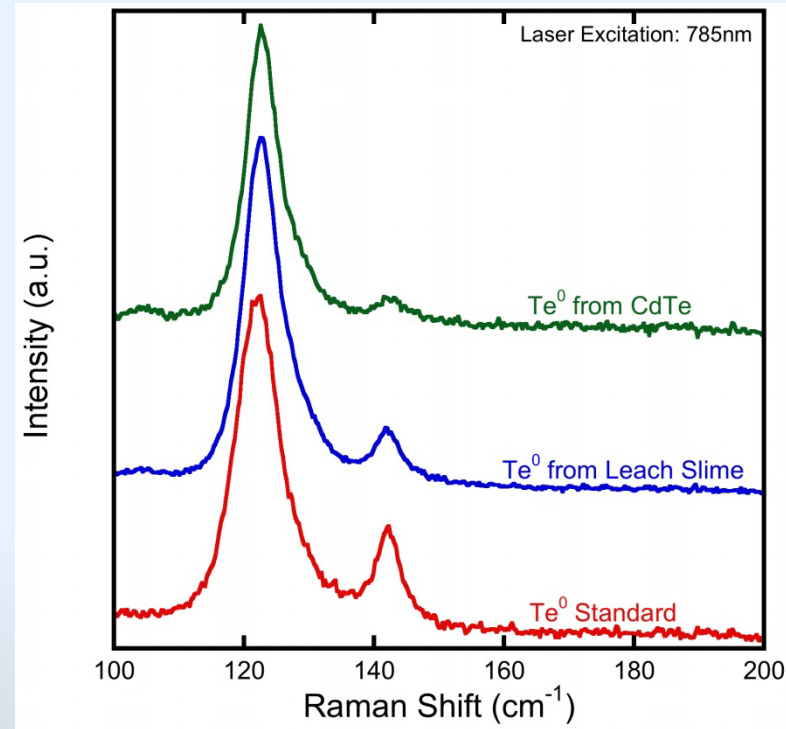
Copper
Leach
Slime
(Rio Tinto)

CdTe



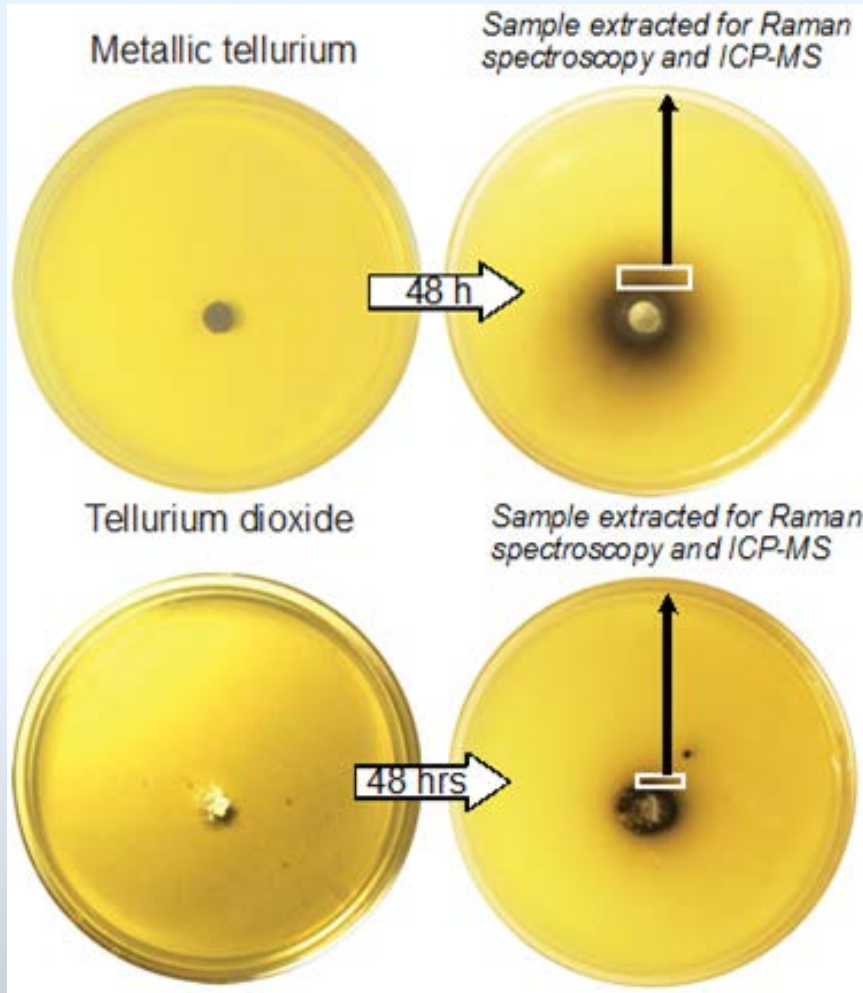
EPR3 microbes reduce/methylate Te from both leach slime and CdTe

Raman spectra confirms tellurium precipitation



All samples: EPR3 incubated at 37C on artificial seawater agar nutrient plates
Leach Slime = 0.025g
CdTe = 0.005g

Conversion Extends Spatially



0.1 g of various tellurium compounds in liquid ASW after 48 hrs at 37°C

Tellurium source ^a	Soluble tellurium concentration ^b (mmol l ⁻¹)
Metallic tellurium	0.038
Tellurium dioxide	0.063

^aIncubated in the absence of EPR3

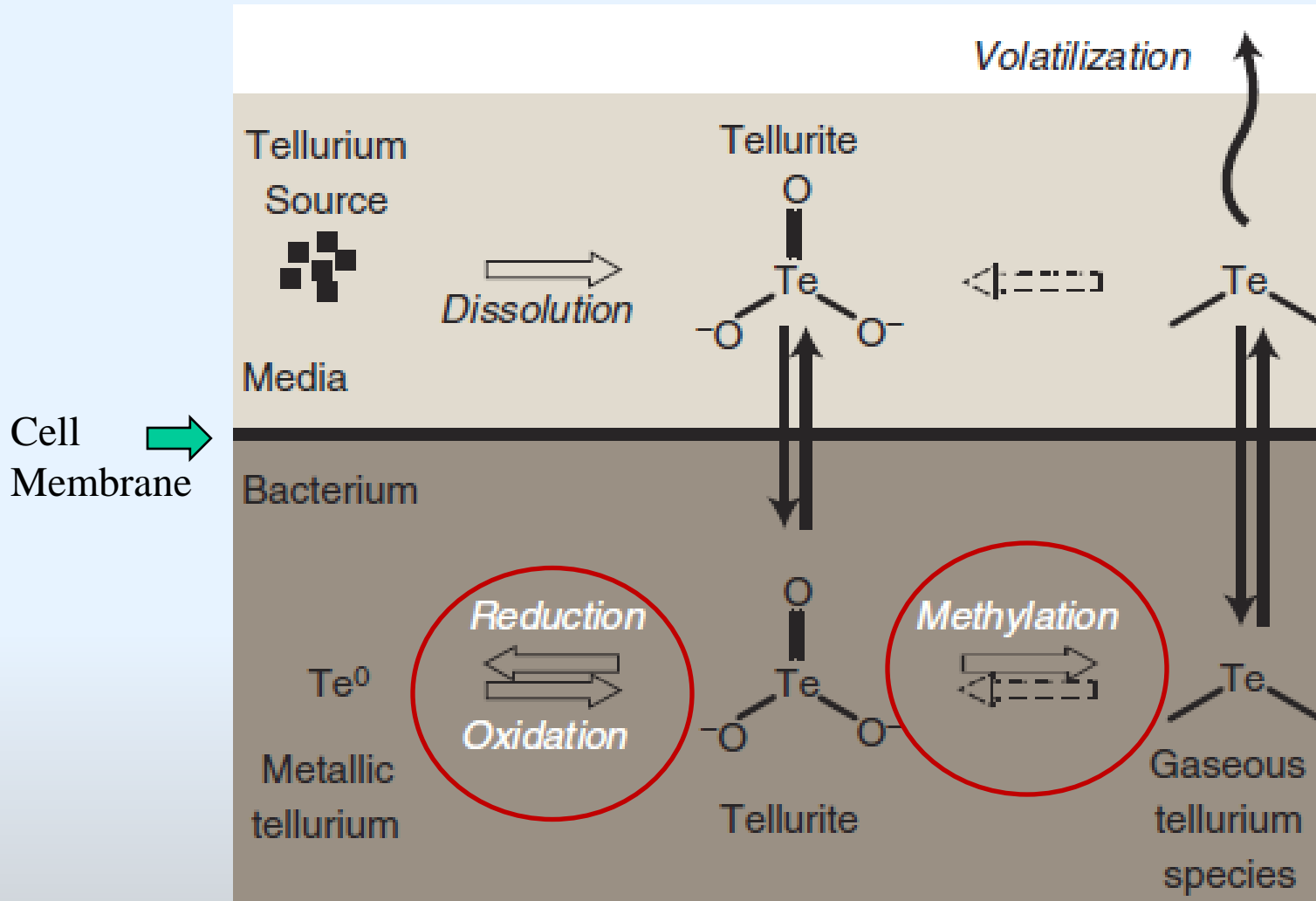
^bICP-MS sensitive to 20 nmol l⁻¹

- Tellurium compounds are all slightly soluble
- Precipitation of metallic tellurium occurs at a distance from source
- Volatilization of gaseous tellurium species also occurs

Therefore, there is a diffusing diffuses involved



Tellurium Processing by EPR3 Bacteria



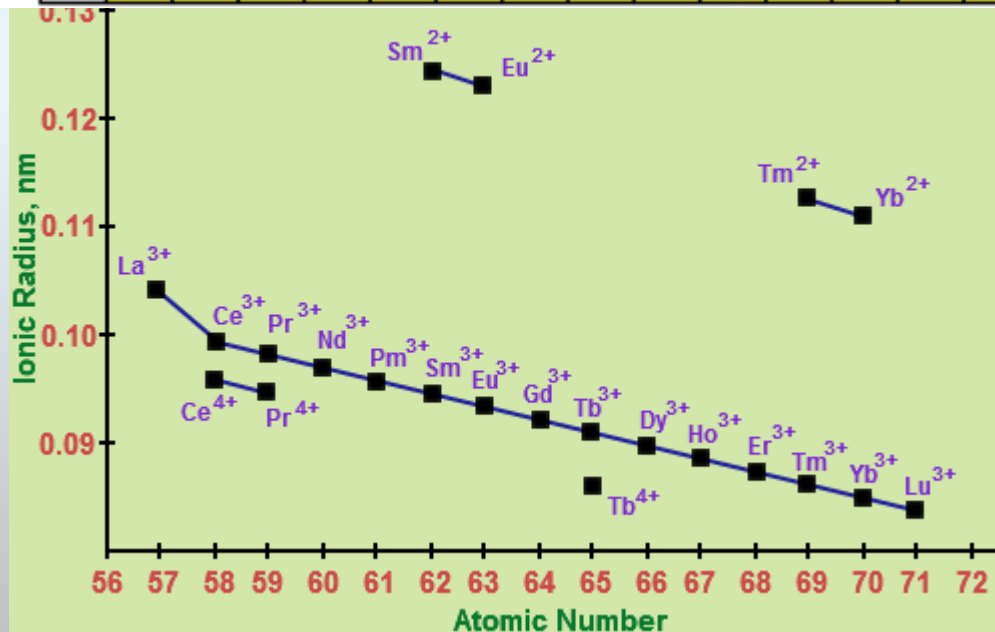
The EPR3 bacteria consumes the tellurium source through a soluble Te anion intermediate

The Rare-Earth Elements

1												18							
1	H	2											13	14	15	16	17	18	He
2	Li	Be											B	C	N	O	F	Ne	
3	Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar	
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
6	Cs	Ba	Lan- thi- des	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
7	Fr	Ra	Acti- nides																

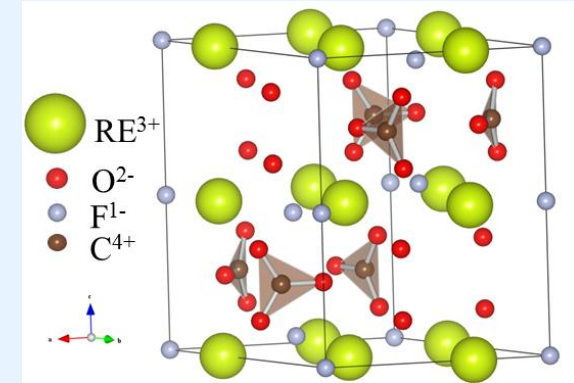
Lan- thi- des	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

Lanthanide contraction

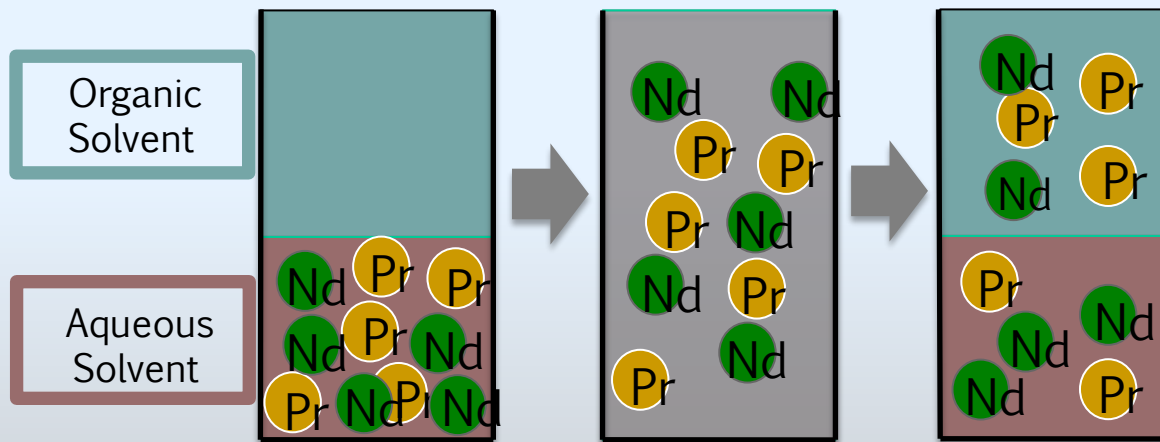


Current Status of REE Separation

- REE chemistry is very similar (trivalent and similar size)
- Typical mineral refining, which is based on varying oxidation states and/or size, cannot be used
- In ores, the REEs occupy the same crystallographic sites
- Separation by liquid-liquid solvent extraction (toxic)



Bastnaesite (REE ore)



$$\text{Separation Factor (Pr/Nd)} = \frac{D_{\text{Pr}}}{D_{\text{Nd}}} \quad D_{\text{Pr}} = \frac{[\text{Pr}]_{\text{Organic Phase}}}{[\text{Pr}]_{\text{Aqueous Phase}}}$$

Biosorption

- Physiochemical process of absorbing ions to the surface of bacteria
- Used in environmental remediation, absorbing toxic metals from waste water

Table 4: Examples of Toxic Heavy Metals Accumulating Microorganisms

Organism	Element
Citrobacter sp.	Lead, Cadmium
Thiobacillus ferrooxidans	Silver
Bacillus cereus	Cadmium
Bacillus subtilis	Chromium
Pseudomonas aeruginosa	Uranium
Micrococcus luteus	Strontium
Rhisopus arrhizus	Mercury
Aspergillus niger	Thorium
Saccharomyces cerevisiae	Uranium

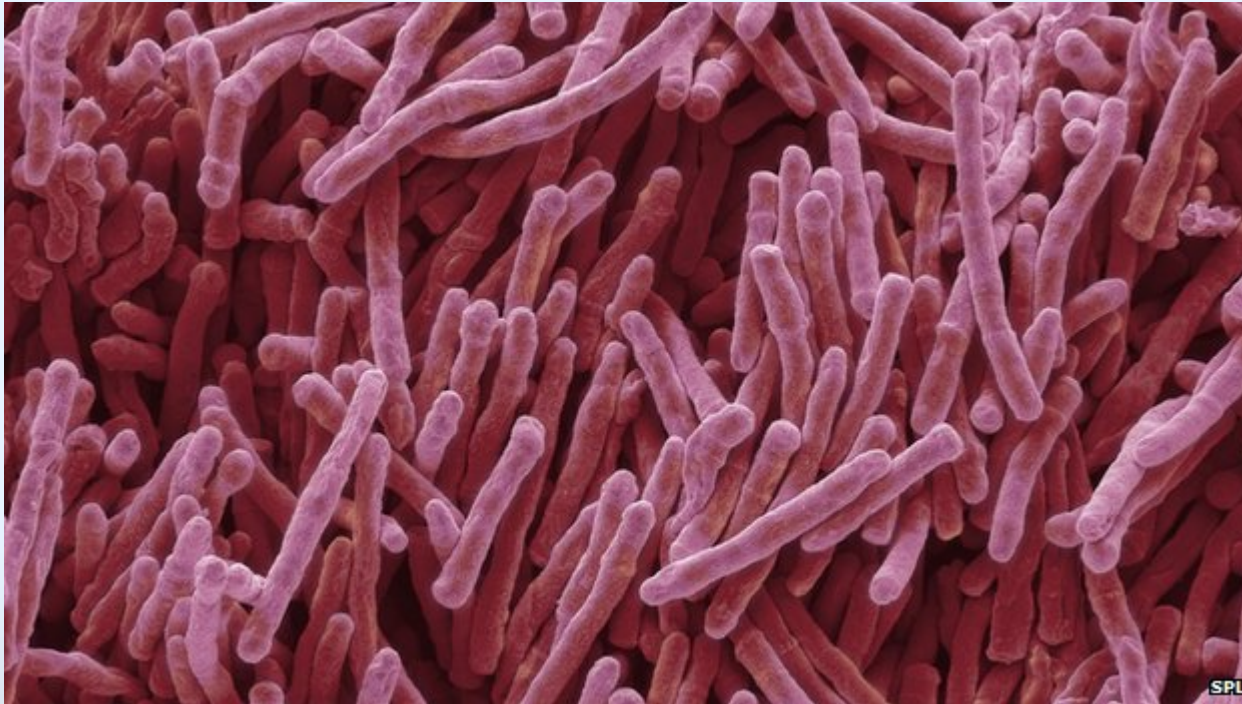


What is known about Lanthanide Biosorption

- Individual lanthanides absorption to archetypal biomass
- No evidence for any bioactivity
- Absorption occurs rapidly
- No apparent distinction between the few lanthanides studied
- Absorption studied in batch reactions
- Absorption consistent with Langmuir absorption



Typical Microbe Morphology

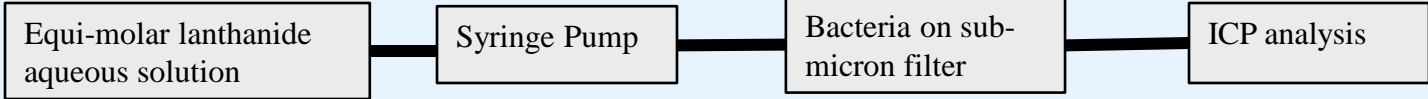


Nature, Jan 2015

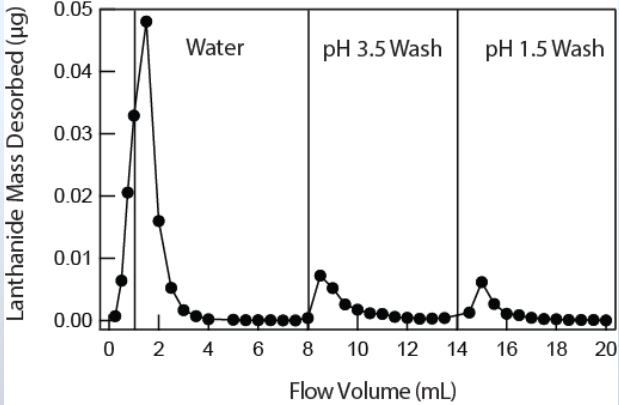
Very large surface area, multitude of different surface sites



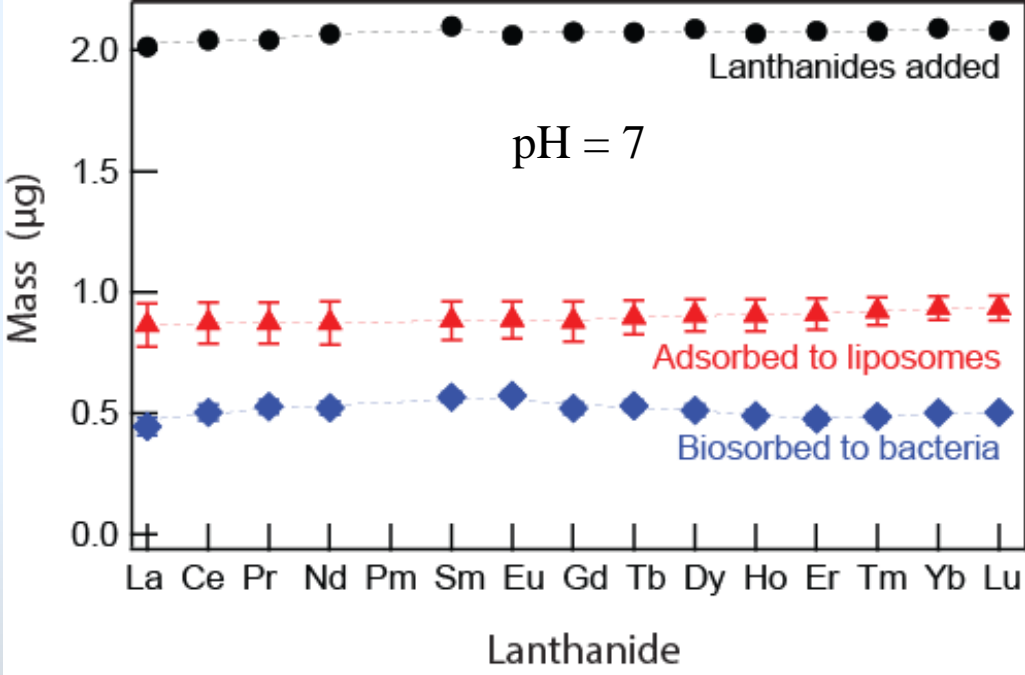
Lanthanide Biosorption Under Continuous Flow



Cultivated *Roseobacter* sp. AzwK-3b
 2 µg/mL of individual RE ions
 0.2 micron Hydrophilic filter

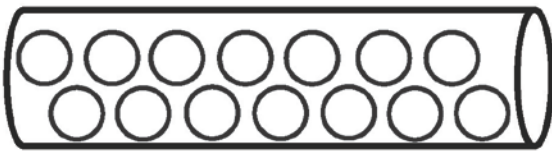


Flow rate: 2.5 mL/min

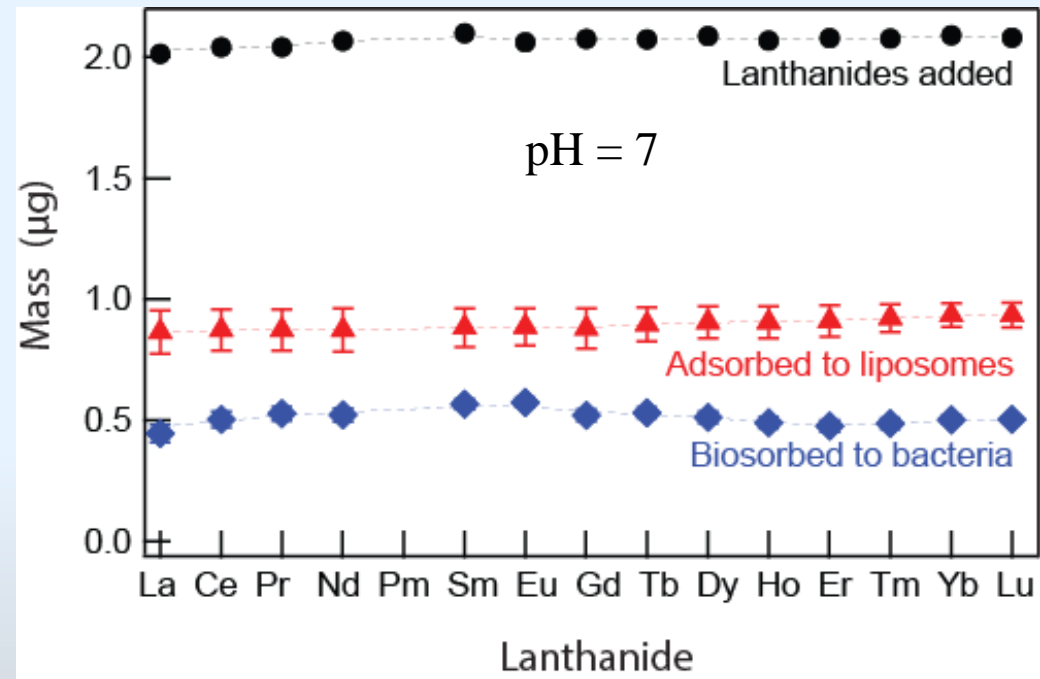


Biosorption of Lanthanides to Surface Sites

Initial condition - unbound surface sites



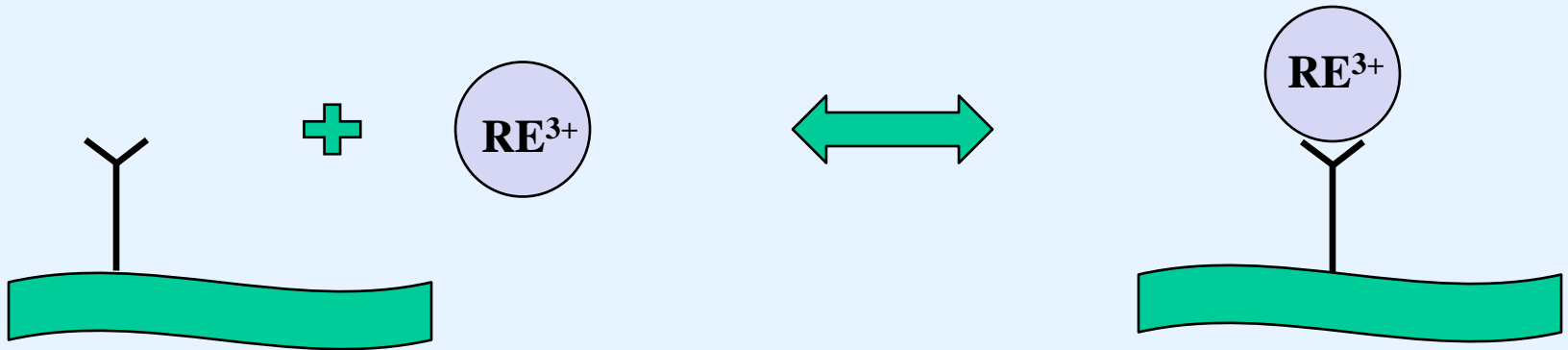
Biosorption - washing with lanthanide ions



Roseobacter sp. AzwK-3b

phosphatidic acid liposomes

Equilibrium Biosorption: Single Site, Single Ion



Equilibrium dissociation constant depends on binding energy, ΔG_i , of the individual lanthanide, i

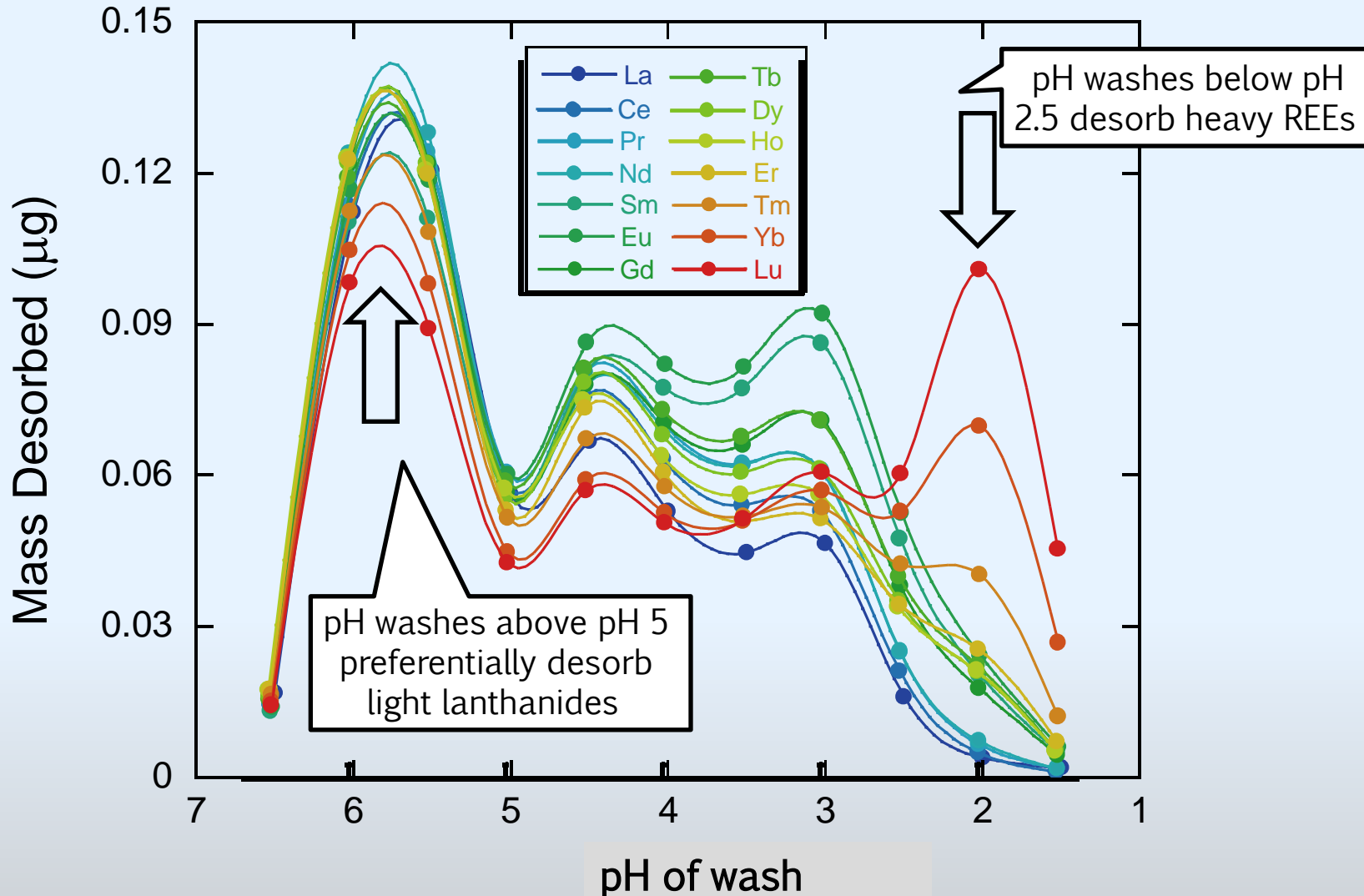
$$K_D = \exp\left(\frac{\Delta G_i^o}{RT}\right)$$

Binding energy should depend on pH: desorption depends on pH

Approach: can we selectively desorb different lanthanides by changing pH ?



Lanthanide Desorption With pH



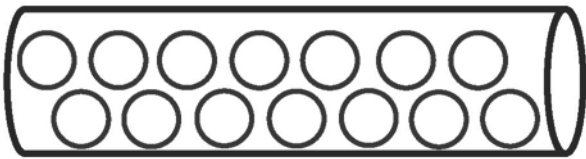
- Similar but distinctive titration curves for each rare earth
- REEs biosorb to bacterial surface sites based on atomic number



REE Separation By Sequential Biosorption and Titrated Desorption.

- Wash bacteria with REEs solution for biosorption to occur
- Wash with progressively lower pH solutions
- Different REEs selectively desorb as a function of the pH

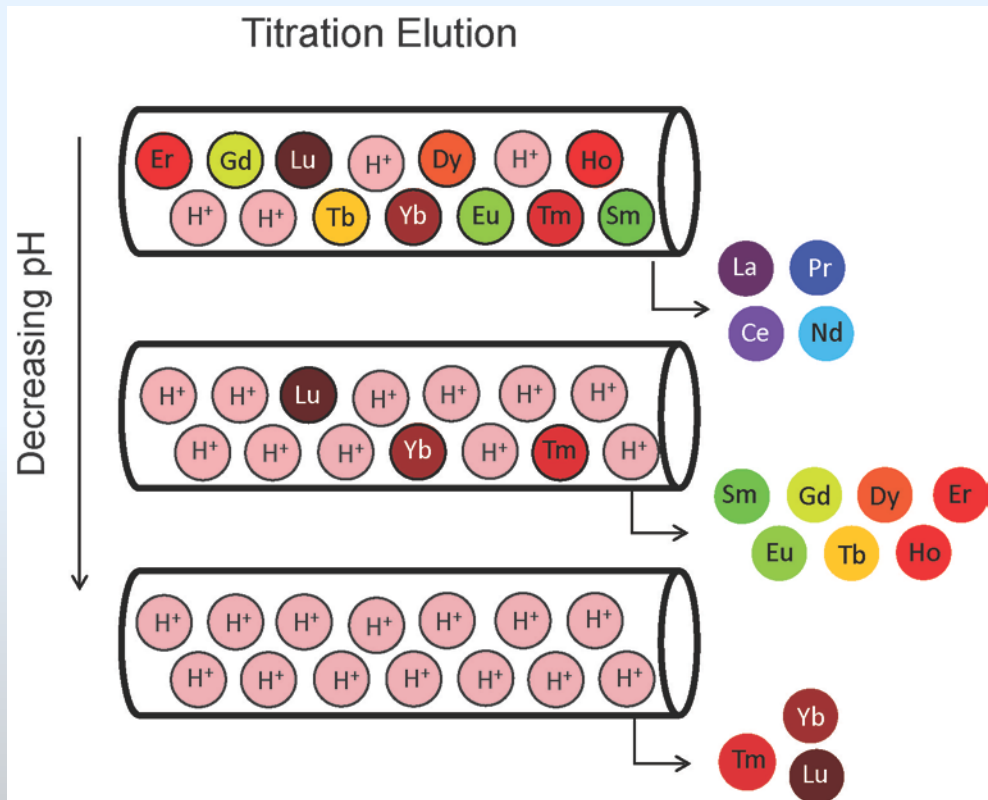
Initial condition - unbound surface sites



Biosorption - washing with lanthanide ions



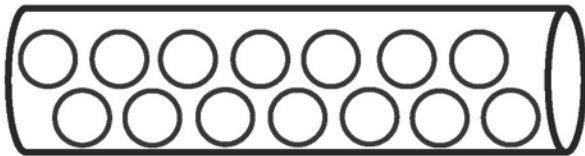
Titration Elution



Altering the Surface Binding By Pre-Protonation

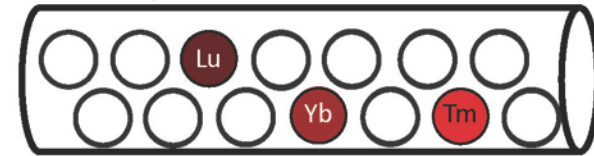
- Wash bacteria with acid solution to protonate higher pKa binding sites
- Wash with REEs and only heavy REEs biosorb (bind pKa sites lower than 2.5)
- Washing with lower pH releases remaining REEs

Initial condition - unbound surface sites

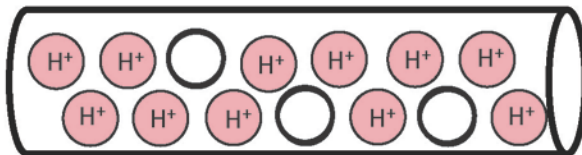


Wash with lanthanide ions

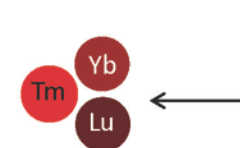
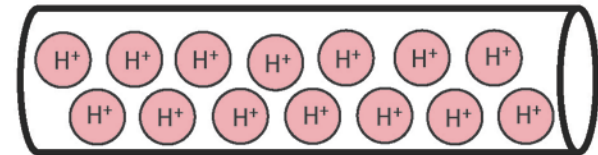
only Tm, Yb and Lu biosorb



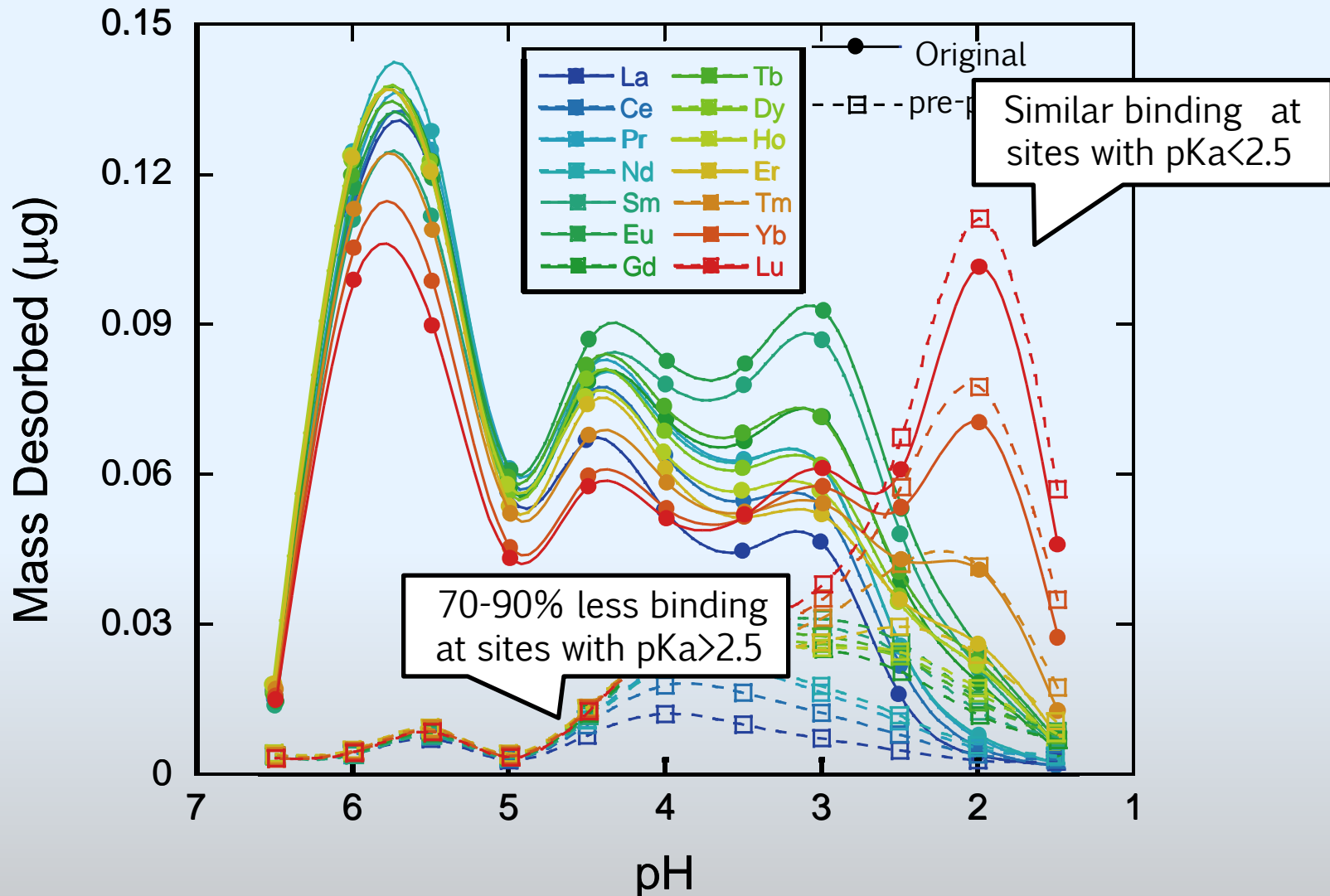
Wash with pH 2.5 acid



Wash with pH 1.5 acid



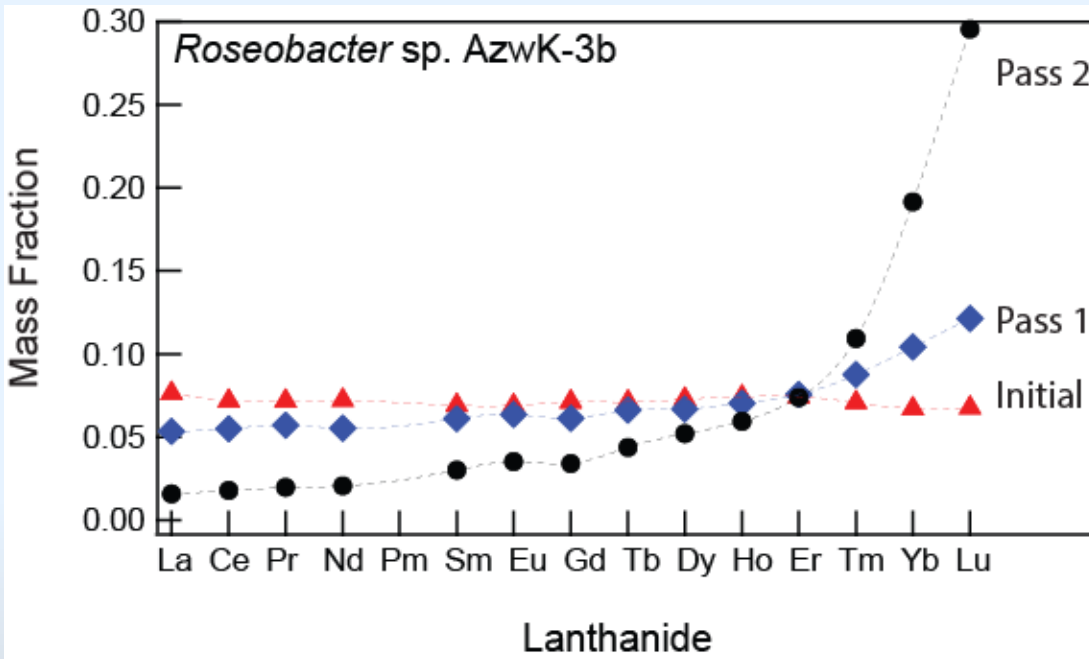
Desorption (Elution) After Pre-Protonation



Pre-protonation at pH 2.5 enhances heavy lanthanide separation

Enhanced Heavy REE Recovery By Multiple Washes

REE solution passed successively over pre-protonated *Roseobacter*

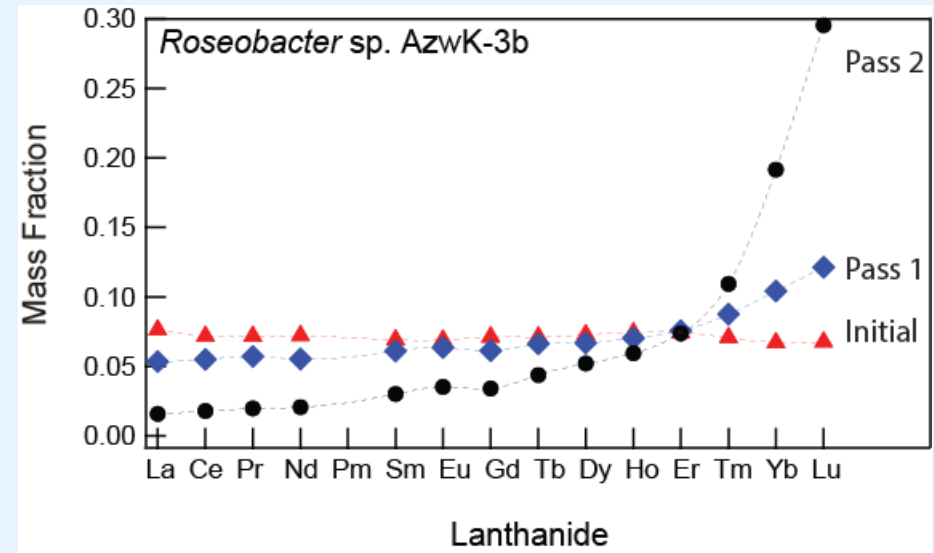
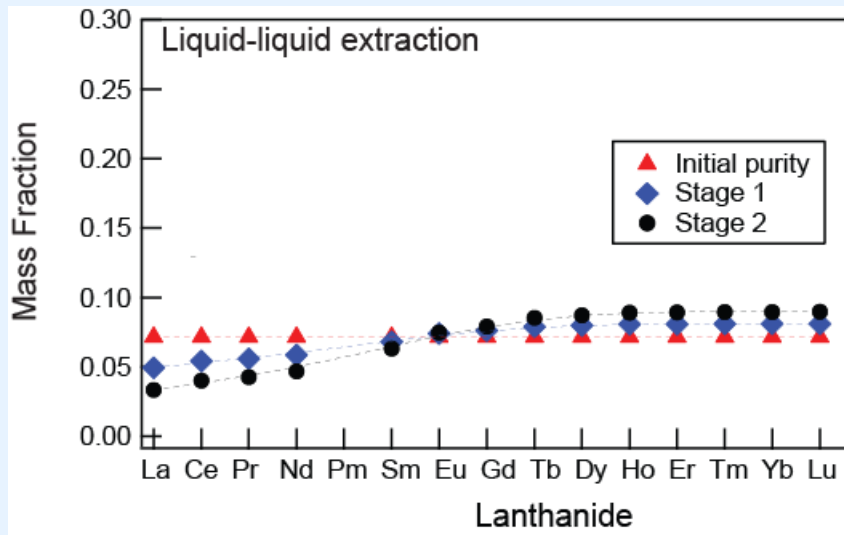


Lanthanide	Initial mass fraction	Final mass fraction
La	0.08	0.02
Ce	0.08	0.02
Pr	0.08	0.02
Nd	0.07	0.02
Sm	0.07	0.03
Eu	0.07	0.04
Gd	0.07	0.03
Tb	0.07	0.04
Dy	0.07	0.05
Ho	0.07	0.06
Er	0.07	0.07
Tm	0.07	0.11
Yb	0.06	0.19
Lu	0.07	0.30

- Technique concentrates Tm, Lu, and Yb from a near equal concentration REE solution
- 50% of final solution is Yb and Lu. Very effective separation



Separation of Heavy Lanthanides: Comparison with Solvent Extraction



Solvent extraction process
using HCl/EHEHPA

Bacterial continuous flow process

(2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester)



Bacteria Studied So Far

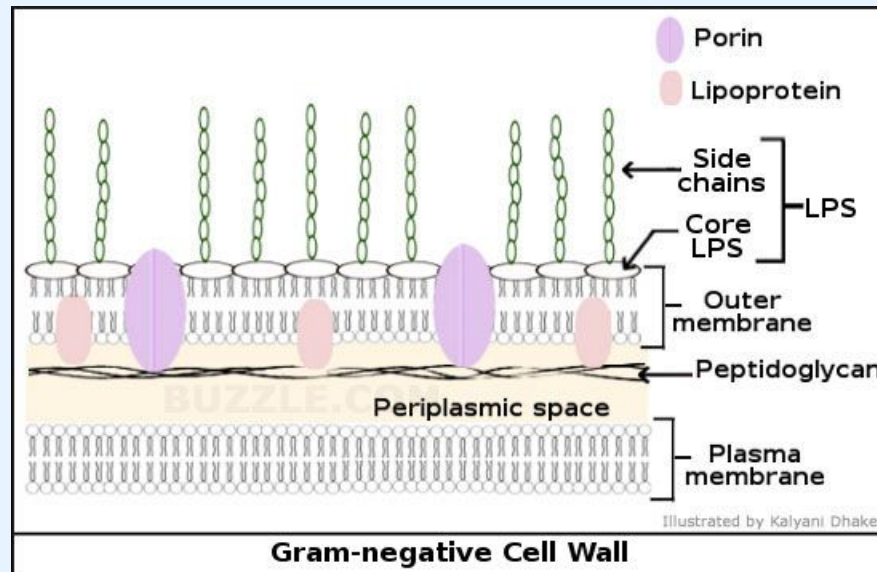
Bacterial strains used in filtration assay for lanthanide recovery

Bacterial Strain	Reason for Selection
Pseudoalteromonas sp. EPR3	Hydrothermal vent microbe with high levels of polysaccharides, tellurium resistant
Pseudoalteromonas sp. RD1	A different strain of Pseudoalteromonas
Roseobacter sp. AzwK-3b	Marine microbe that may produce superoxide on surface, high capacity for metals
Sphingomonas sp. RD1	Marine microbe that produces sphingophospho lipids on membrane
Halomonas sp. RD1	Extremely halophilic marine bacteria, tolerant to wide range of metals
Alcanivorax sp. EPR7	Hydrothermal vent oil-degrading bacteria, contains unique surface glycolipids
Acinetobacter sp. EPR174	Hydrothermal vent bacteria with metabolic diversity, high resistance to metals
Escherichia Coli P8	Archetypal gram-negative bacterial strain
Shewanella Oneidensis MR-1	Bacteria capable of reducing many metals

Similar elution separation behavior with pH observed with different bacteria but not identical



Structure of Bacterial Surface (Too simple but useful)



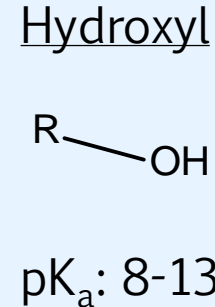
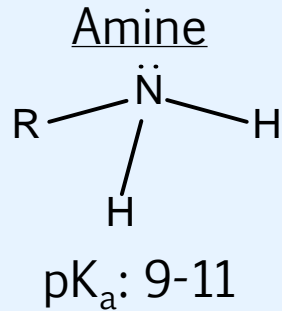
On the surface:

Possible binding molecule	Groups
Phospholipids	Phosphate
Proteins	Amine
Polysaccharides	Carboxyl and hydroxyl
Extracellular polymeric substances	All of the above
DNA, sugars, other organics	

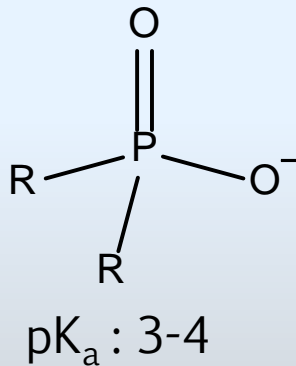


Surface Groups Have Distinctive pKa's

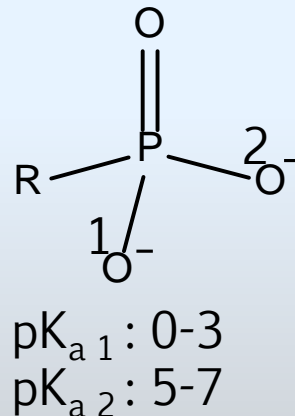
NB. pK_a is the pH at which half of the sites are protonated



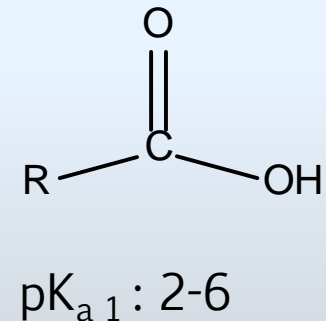
Phosphate diester



Phosphate monoester



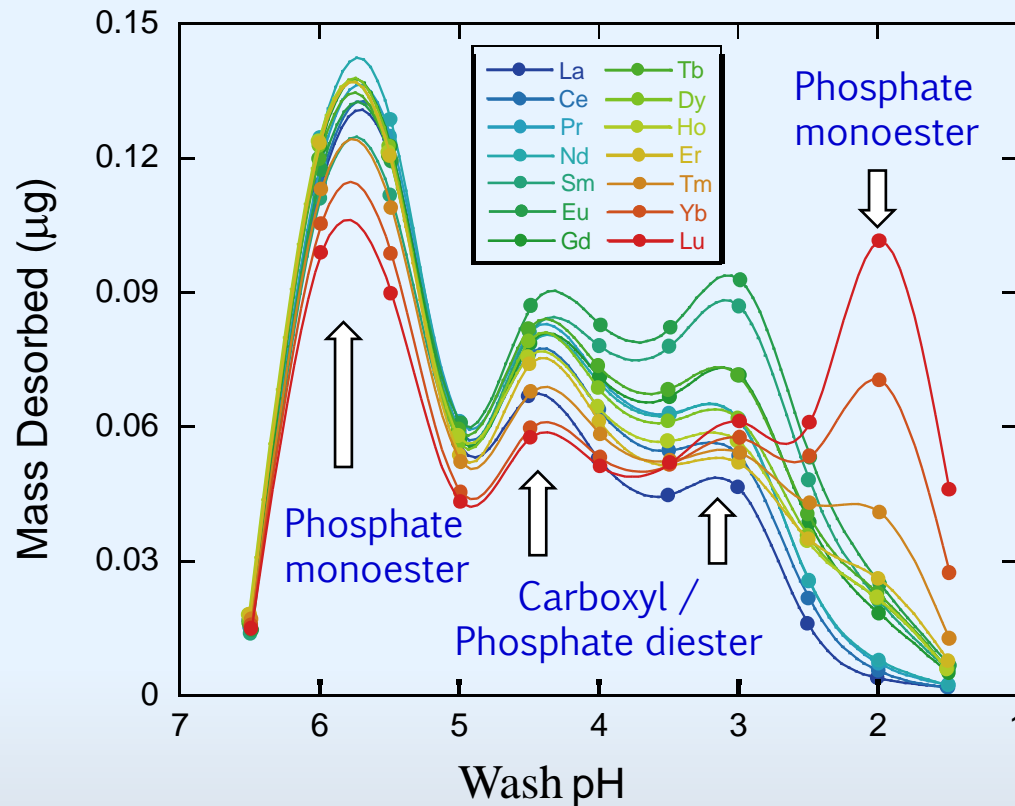
Carboxyl



Carboxyl and phosphate sites generally responsible for cation adsorption



Interpretation: More Acidic Lanthanides Bind to Lower pKa Sites

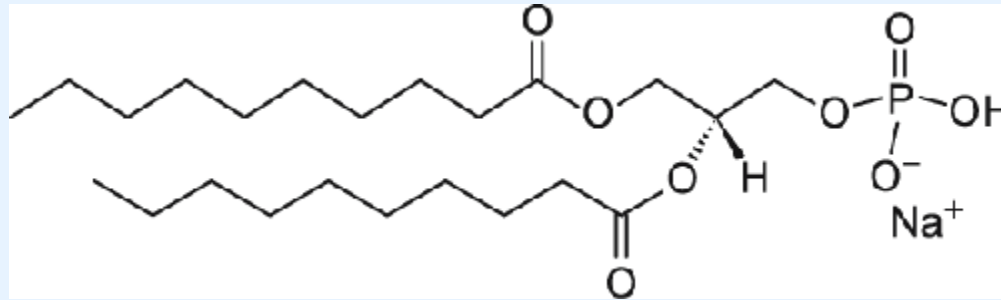


- Appear to be 3-4 broad pK_a surface sites
- Lanthanides increase in acidity with atomic number: $La < Gd < Lu$
- Lanthanides bind as a function of pK_a



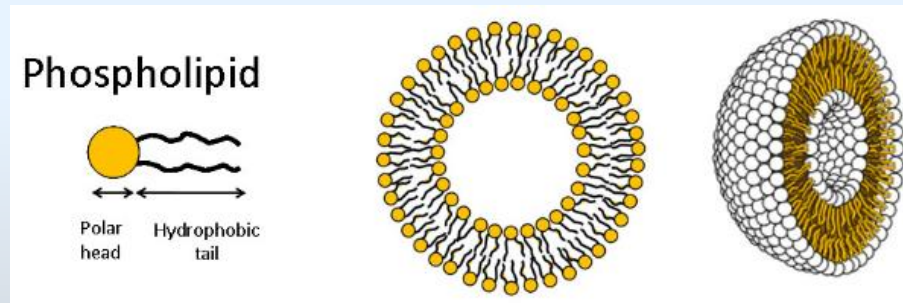
Synthetic Absorbers: Liposomes with Phosphatidic Acid

Prepare liposomes using phosphatidic acid (PA) lipids



Published pK_a : 3.0

Liposomes are 'synthetic' cell with single surface group

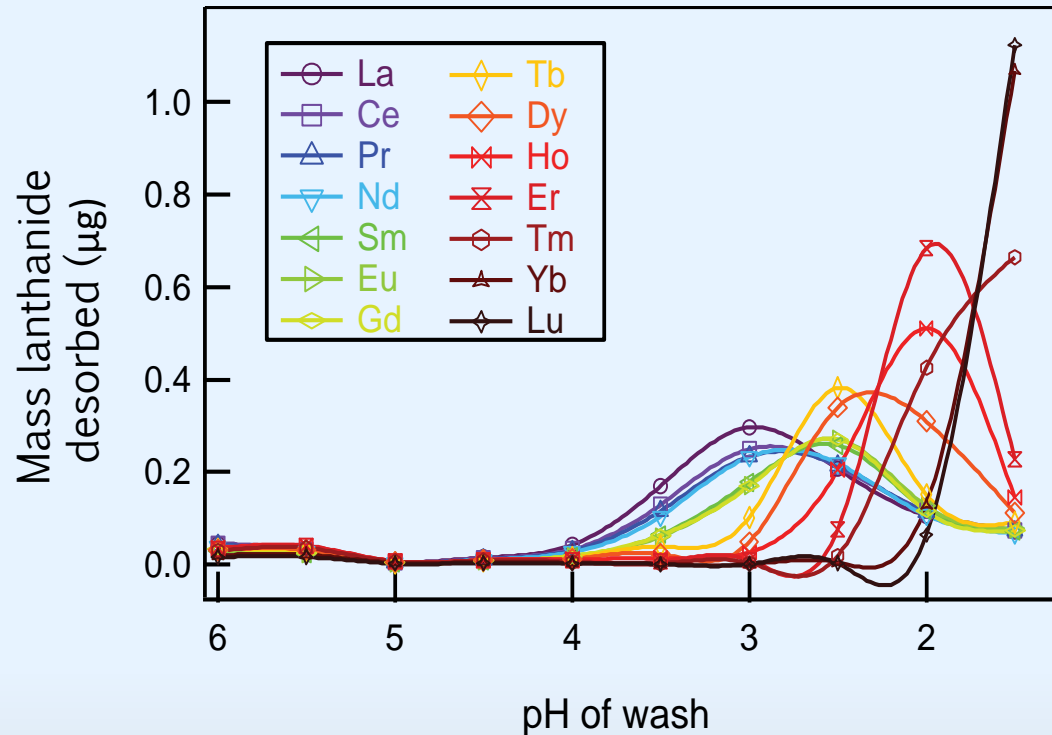


Liposome

Sizes ranged from 0.2 – 10 μm



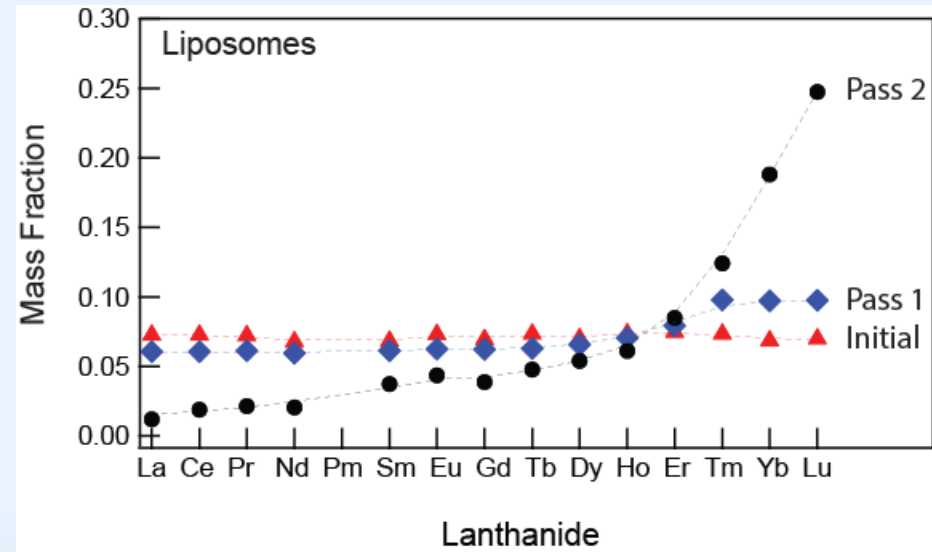
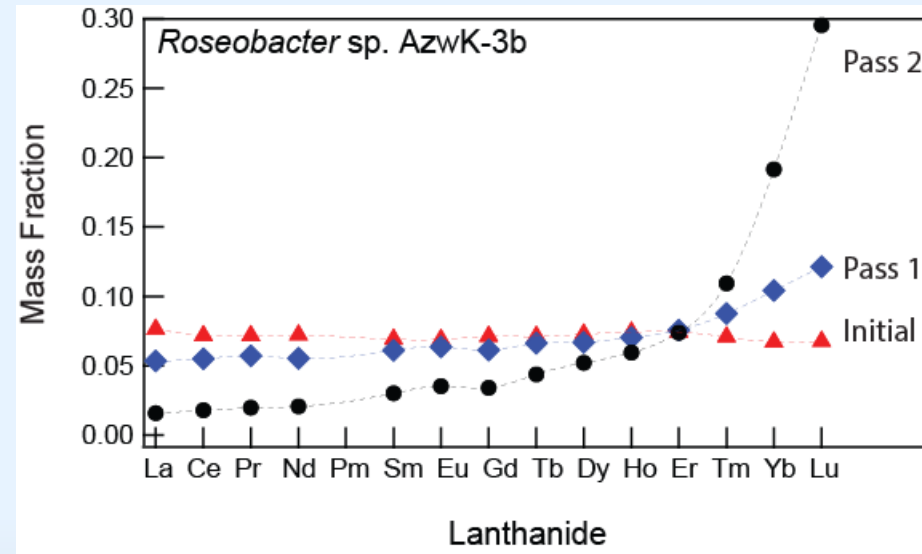
Elution Desorption From Phosphatidic Acid Liposome



- Published pK_a of ~ 3
- Desorption pH varies with atomic number
- Suggests there is a coordination/size effect and possibly curvature effect
- Larger ions exhibit higher pK_a
- Smaller ions, exhibit lower pK_a and possibly more highly coordination



Heavy Lanthanide Separation



Very similar separation possible with both *Roseobacter* microbes and phosphate-terminated liposomes

Summary: Microbial Processing for Harvesting Scarce metals

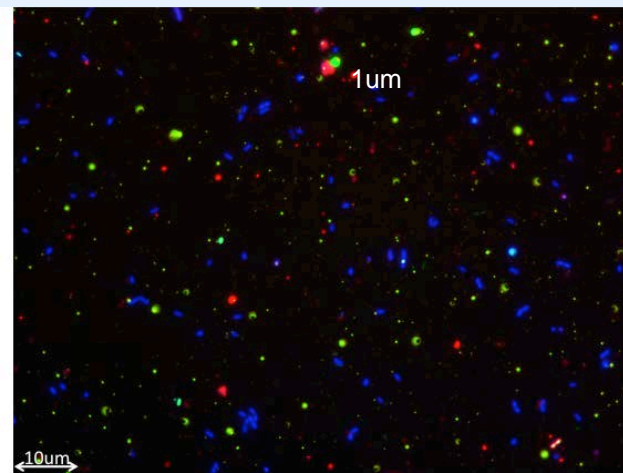
Benefits of using microbes:

- Can be highly specific and selective
- Microbes can overcome some kinetic and thermodynamic barriers
- Extremophiles are robust and stable
- Cleaner, more benign processing as based on aqueous solutions.
- Potential for genetic engineering and optimization

Disadvantages

- Low metal concentrations
- Low throughput at present
- No processing expertise in place

Potential for paradigm shift in metal harvesting and in education



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