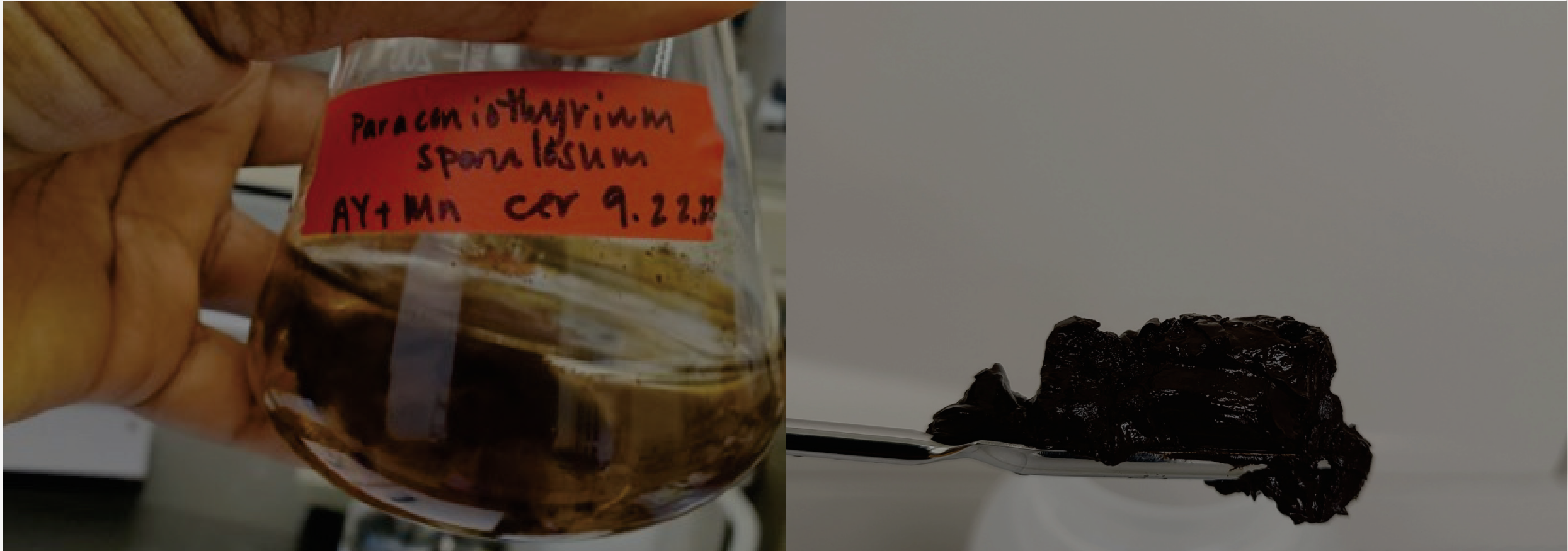


Lab-based assessment of critical metal adsorption by biotic and abiotic hydrous manganese oxides



Tashane Boothe¹, Rosemary Capo¹, Brian Stewart¹, Benjamin C. Hedin², Travis Olds³, Carla Rosenfeld³

¹ Department of Geology and Environmental Science, University of Pittsburgh, Pittsburgh, PA 15260

²Hedin Environmental, 195 Castle Shannon Blvd., Pittsburgh, PA 15228

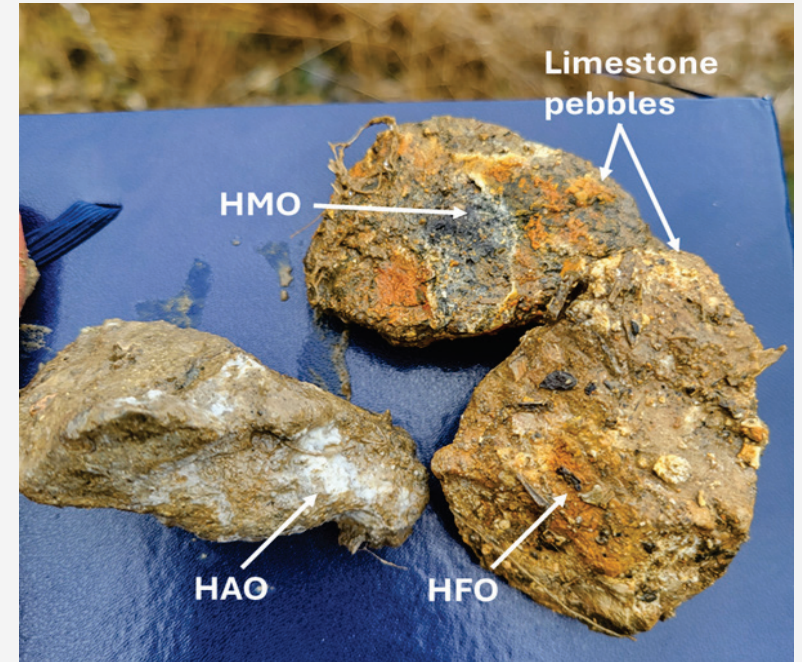
³Carnegie Museum of Natural History, Pittsburgh, PA 15213

AMD treatment solids: waste or resource?



Precipitate by-products from AMD treatment

Source: T. Boothe



Limestone pebble encrusted with major element hydrous oxide

- Over 18,00 tons of treatment solids can be produced per year in Pennsylvania
- Composed of major element oxides and hydroxides, including Fe, Al, and Mn
- Trace metals are associated with hydrous metal oxides

REE: 2000 mg/kg

Co: 5000 mg/kg

Ni: 6700 mg/kg

Hedin et al. (2020)

Critical metals can become highly concentrated to near ore grade

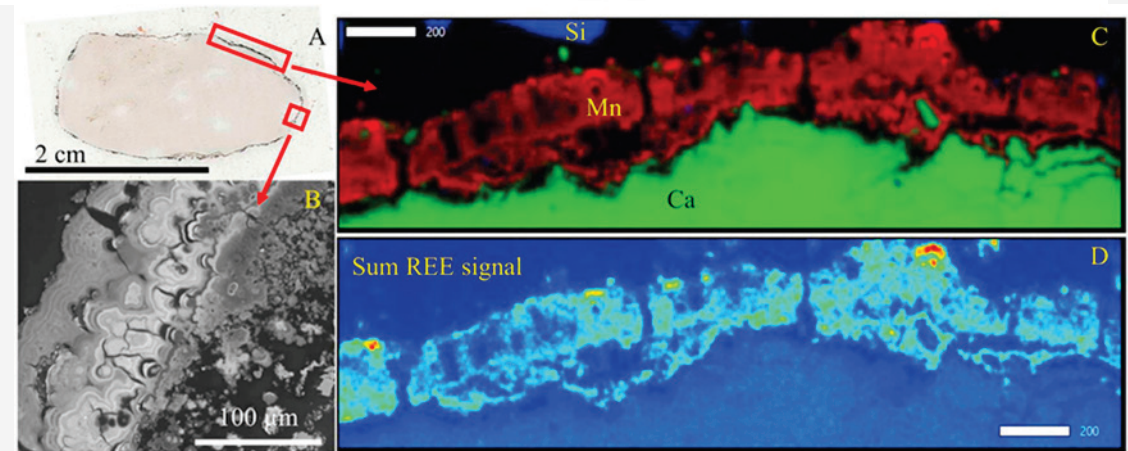
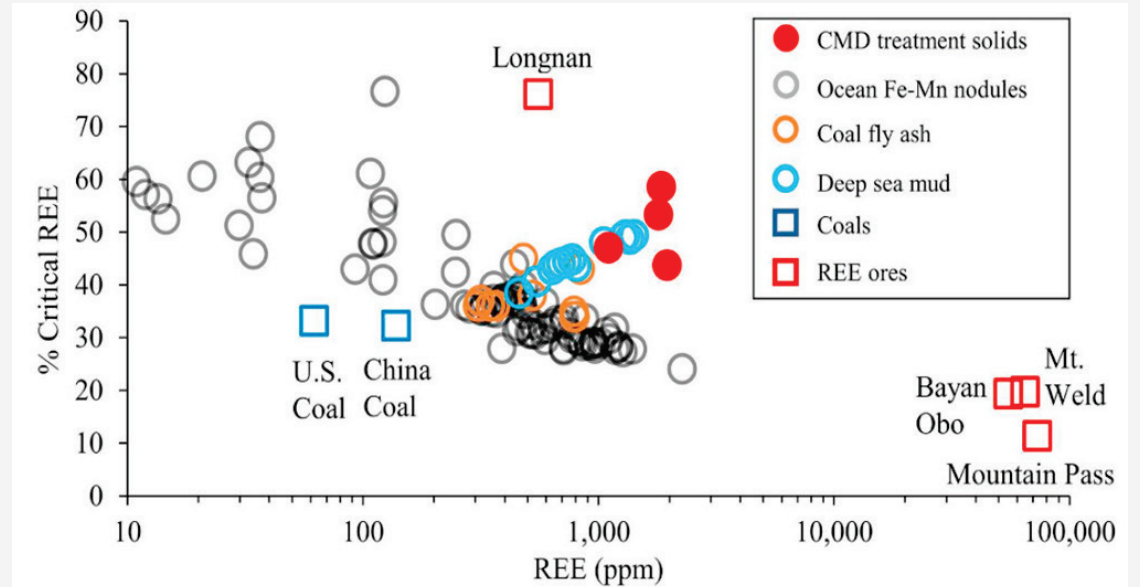
Critical Metals and HMO

Unconventional sources of critical metals

Periodic table of elements highlighting the “critical minerals”

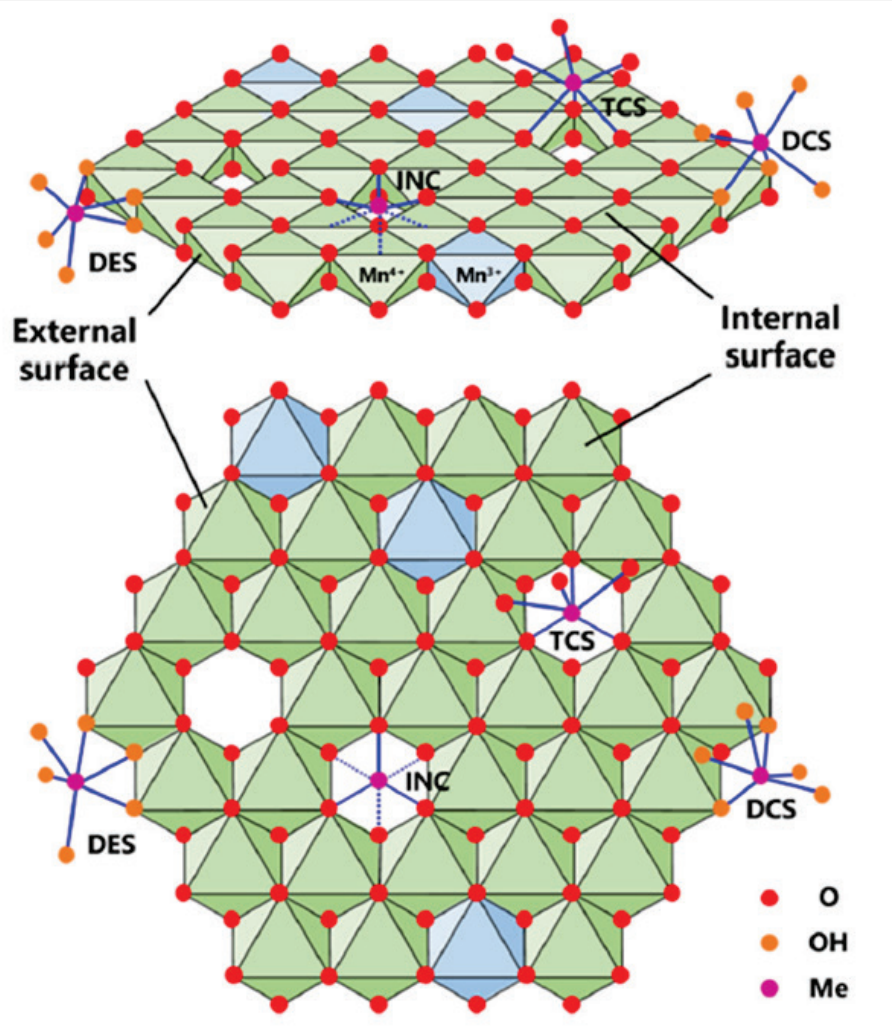
2022 Critical Mineral																		2018 List									
Atomic Number																		Symbol									
Name																		Chemical Group Block									
1 H Hydrogen Nonmetal																		2 He Helium Noble Gas									
3 Li Lithium Alkali Metal	4 Be Beryllium Alkaline Earth Metal																	10 Ne Neon Noble Gas									
11 Na Sodium Alkali Metal	12 Mg Magnesium Alkaline Earth Metal																	18 Ar Argon Noble Gas									
19 K Potassium Alkali Metal	20 Ca Calcium Alkaline Earth Metal	21 Sc Scandium Transition Metal	22 Ti Titanium Transition Metal	23 V Vanadium Transition Metal	24 Cr Chromium Transition Metal	25 Mn Manganese Transition Metal	26 Fe Iron Transition Metal	27 Co Cobalt Transition Metal	28 Ni Nickel Transition Metal	29 Cu Copper Transition Metal	30 Zn Zinc Transition Metal	31 Ga Gallium Post-Transition Metal	32 Ge Germanium Metalloid	33 As Arsenic Metalloid	34 Se Selenium Nonmetal	35 Br Bromine Halogen	36 Kr Krypton Noble Gas										
37 Rb Rubidium Alkali Metal	38 Sr Strontium Alkaline Earth Metal	39 Y Yttrium Transition Metal	40 Zr Zirconium Transition Metal	41 Nb Niobium Transition Metal	42 Mo Molybdenum Transition Metal	43 Tc Technetium Transition Metal	44 Ru Ruthenium Transition Metal	45 Rh Rhodium Transition Metal	46 Pd Palladium Transition Metal	47 Ag Silver Transition Metal	48 Cd Cadmium Transition Metal	49 In Indium Post-Transition Metal	50 Sn Tin Post-Transition Metal	51 Sb Antimony Metalloid	52 Te Tellurium Metalloid	53 I Iodine Halogen	54 Xe Xenon Noble Gas										
55 Cs Cesium Alkali Metal	56 Ba Barium Alkaline Earth Metal	72 Hf Hafnium Transition Metal	73 Ta Tantalum Transition Metal	74 W Tungsten Transition Metal	75 Re Rhenium Transition Metal	76 Os Osmium Transition Metal	77 Ir Iridium Transition Metal	78 Pt Platinum Transition Metal	79 Au Gold Transition Metal	80 Hg Mercury Transition Metal	81 Tl Thallium Post-Transition Metal	82 Pb Lead Post-Transition Metal	83 Bi Bismuth Post-Transition Metal	84 Po Polonium Metalloid	85 At Astatine Halogen	86 Rn Radon Noble Gas											
87 Fr Francium Alkali Metal	88 Ra Radium Alkaline Earth Metal	104 Rf Rutherfordium Transition Metal	105 Db Dubnium Transition Metal	106 Sg Seaborgium Transition Metal	107 Bh Bohrium Transition Metal	108 Hs Hassium Transition Metal	109 Mt Meitnerium Transition Metal	110 Ds Darmstadtium Transition Metal	111 Rg Roentgenium Transition Metal	112 Cn Copernicium Transition Metal	113 Nh Nihonium Post-Transition Metal	114 Fl Flerovium Post-Transition Metal	115 Mc Moscovium Post-Transition Metal	116 Lv Livermorium Post-Transition Metal	117 Ts Tennessine Halogen	118 Og Oganesson Noble Gas											
		57 La Lanthanum Lanthanide	58 Ce Cerium Lanthanide	59 Pr Praseodymium Lanthanide	60 Nd Neodymium Lanthanide	61 Pm Promethium Lanthanide	62 Sm Samarium Lanthanide	63 Eu Europium Lanthanide	64 Gd Gadolinium Lanthanide	65 Tb Terbium Lanthanide	66 Dy Dysprosium Lanthanide	67 Ho Holmium Lanthanide	68 Er Erbium Lanthanide	69 Tm Thulium Lanthanide	70 Yb Ytterbium Lanthanide	71 Lu Lutetium Lanthanide											
		89 Ac Actinium Actinide	90 Th Thorium Actinide	91 Pa Protactinium Actinide	92 U Uranium Actinide	93 Np Neptunium Actinide	94 Pu Plutonium Actinide	95 Am Americium Actinide	96 Cm Curium Actinide	97 Bk Berkelium Actinide	98 Cf Californium Actinide	99 Es Einsteinium Actinide	100 Fm Fermium Actinide	101 Md Mendelevium Actinide	102 No Nobelium Actinide	103 Lr Lawrencium Actinide											

<https://energy.virginia.gov/geology/criticalminerals.shtml>

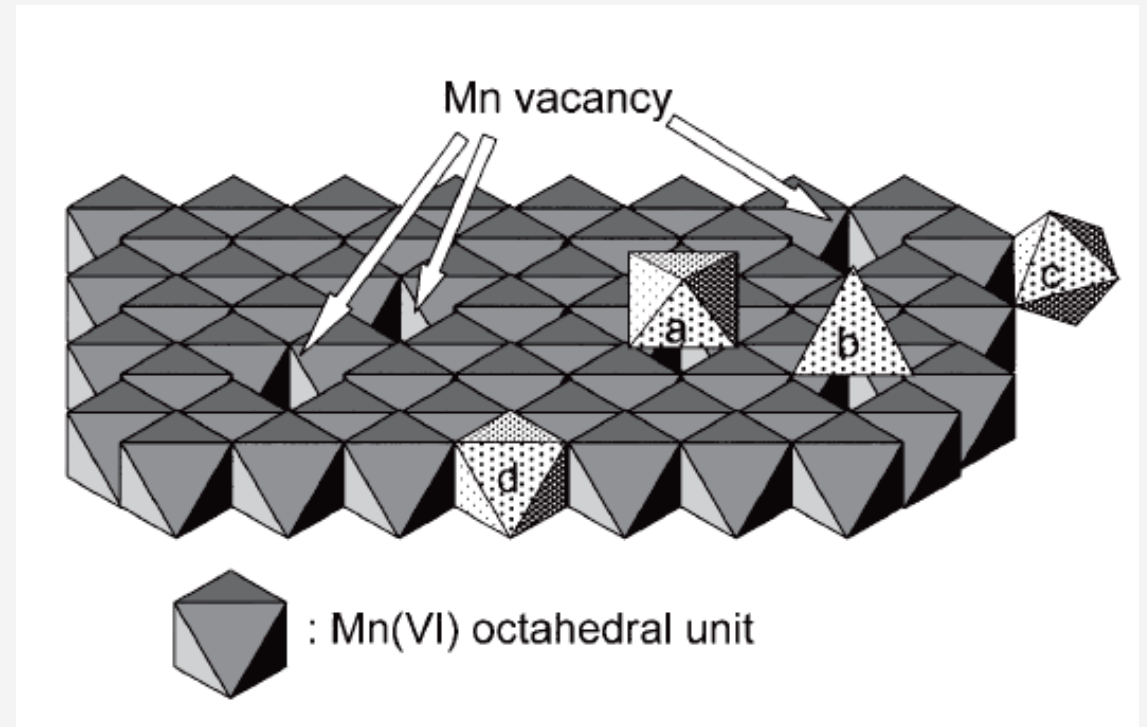


Hedin et al. (2019)

Significance of hydrous manganese oxides (HMO)



Li et al., 2020



Miyata et al., 2007

HMO characteristics

- Overall -ve charge
- Mn +3 in structure
- Missing Mn +4
- High redox potential
- Various sorption site
- Scavenger

HMO applications

- agriculture,
- drinking water purification,
- toxic metal remediation,
- **RECOVERY OF CM FROM AMD SOLIDS**

Aims and objectives



- High concentrations of critical metals typically occurs in passive treatment systems
- This has been attributed to the presence of biotic HMO
- Complex biotic and abiotic processes can occur together in AMD systems

AIM

- To determine relative importance of abiotic and biotic processes occurring in AMD treatment systems
- To understand the sorption behavior of critical metals
- To evaluate is the role of microbial biomass in critical metal sorption

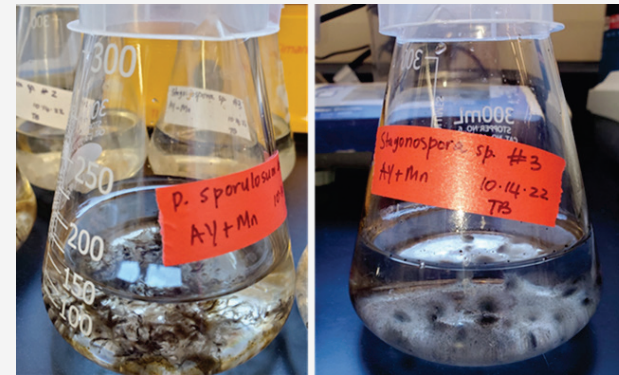
Method

Uptake of 10 Critical Metals

- Co, Ni, La, Ce, Nd, Pr, Gd, Dy, Yb, and Y

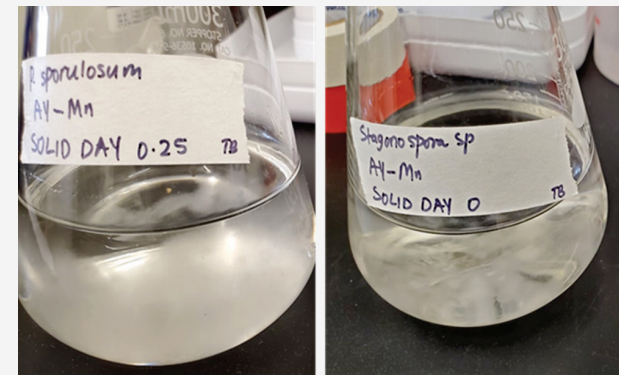
Biotic HMO produced by *Paraphaeosphaeria sporulosa* and *Stagonospora sp.*

Growth media + Fungi
a. *P. sporulosa*
b. *B. Stagonospora sp.* + $MnCl_2$ + Critical metals



Biomass + biotic HMO

Growth media + Fungi
a. *P. sporulosa*
b. *B. Stagonospora sp.* + Critical metals



Biomass only

Method

Uptake of 10 Critical Metals

- Co, Ni, La, Ce, Nd, Pr, Gd, Dy, Yb, and Y

Abiotic HMO, H⁺ birnessite (HB) and δ -MnO₂ (DM), produced by chemical oxidation of MnCl₂ by potassium permanganate

Growth
media

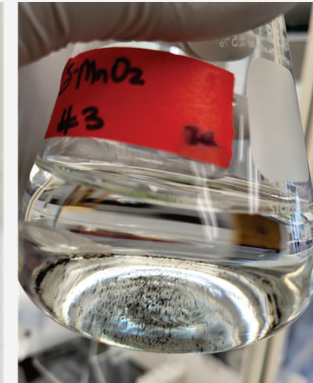


Abiotic HMO

- H⁺ birnessite
- δ -MnO₂



**Critical
metals**



Abiotic HMO

Sampling

- 2 ml aliquot of the critical metals-growth media solution sampled
- 8 time points after the addition of the critical metals: 0 h, 6 h, 1 d, 4 d, 7 d, 10 d, 18 d, and 31 d.
- HMO solids and/or biomass sampled



Sampling

- 2 ml aliquot of the critical metals-growth media solution
- 8 time points after the addition of the critical metals: 0 h, 6 h, 1 d, 4 d, 7 d, 10 d, 18 d, and 31 d.
- HMO solids and/or biomass sampled



Analysis

- time series analyses of dissolved metal concentration over time
 - ICP-MS
- The mineralogy and structure of abiotic and biotic HMO minerals
 - scanning electron microscopy (SEM)
 - X-ray diffraction (XRD)
 - Energy dispersive spectroscopy (EDS)

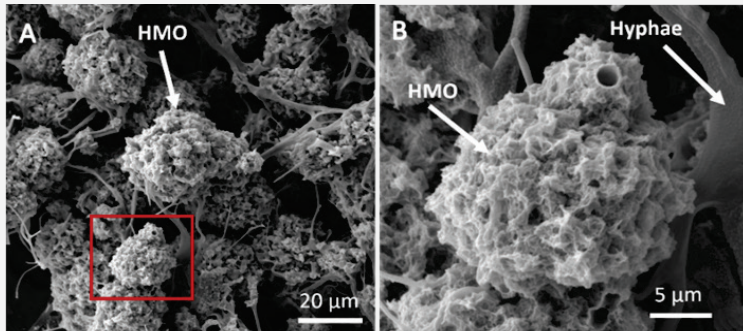
Results- Biotic HMO mineralogy and structure

During the 14-day inoculation period,

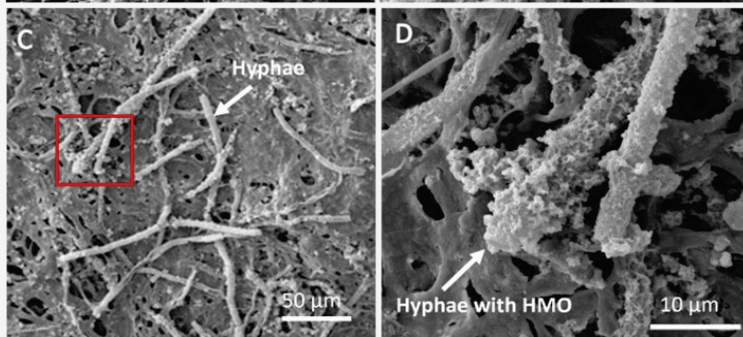
- *Stagonospora* sp. oxidized 99% of Mn(II)
- *P. sporulosa* oxidized 67% of Mn(II)

SEM imagery

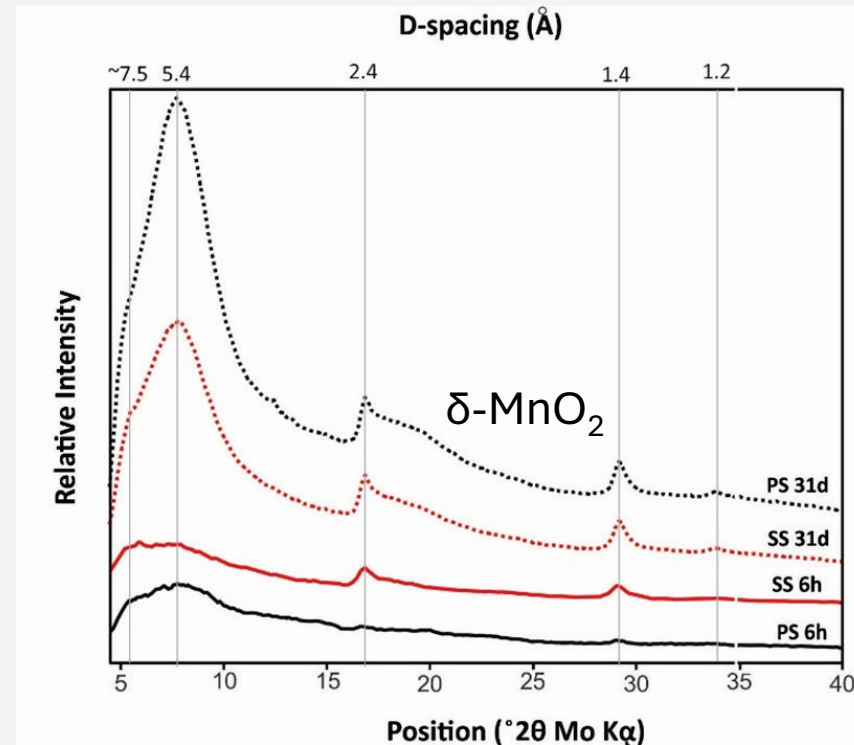
Stagonospora sp.



P. sporulosa



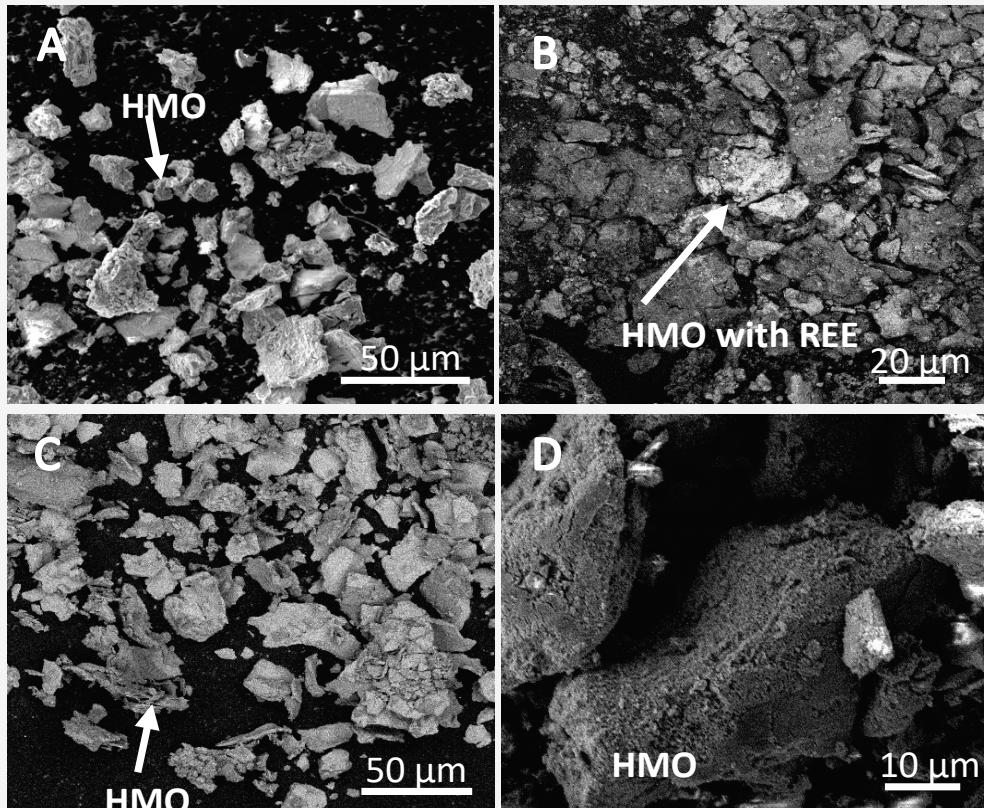
XRD analysis



- 1.4 \AA : layer (310)/(020)
- 2.4 \AA : layer (200)/(110)

Results- Abiotic HMO mineralogy and structure

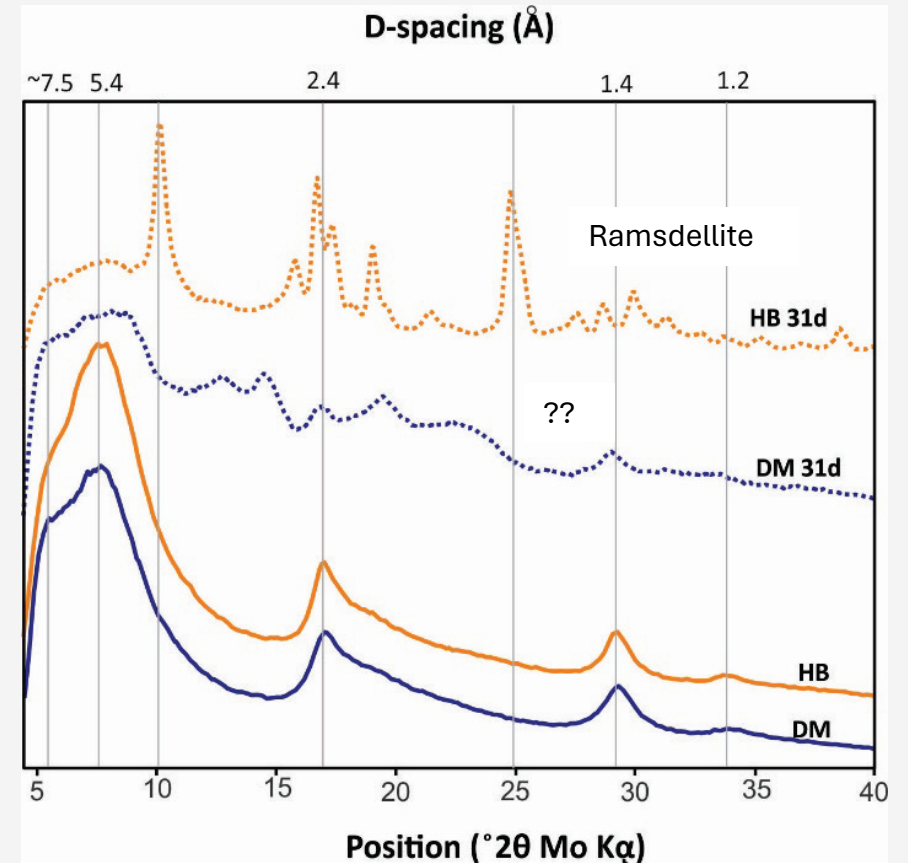
SEM imagery



δ -MnO₂

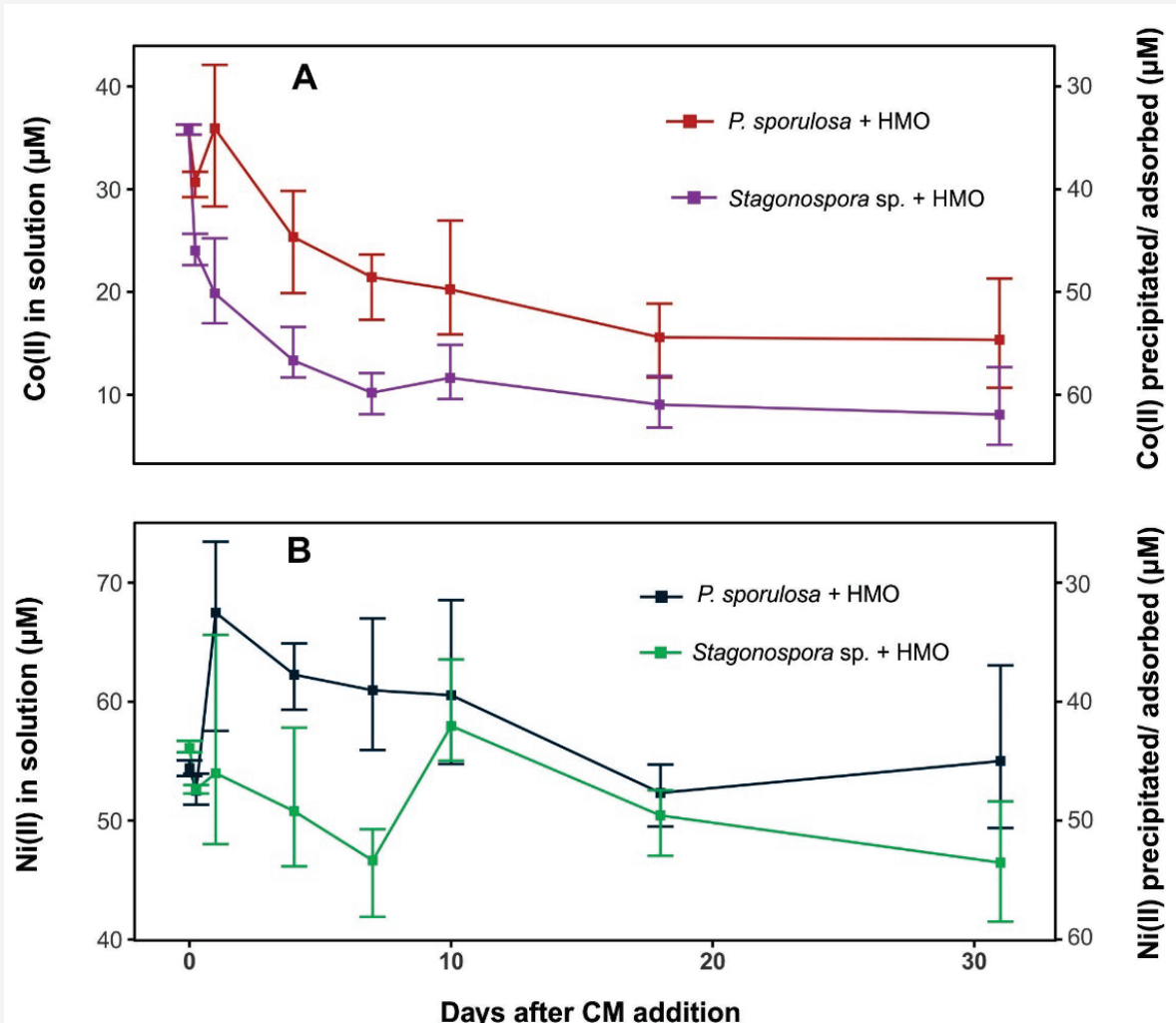
H+ birnessite

XRD analysis



The 002 peak at 3.6 Å which distinguishes H+ birnessite is absent which speaks to random stacking of sheets and high levels of disorder

Results- Co and Ni adsorption by biotic HMO



Cobalt Adsorption

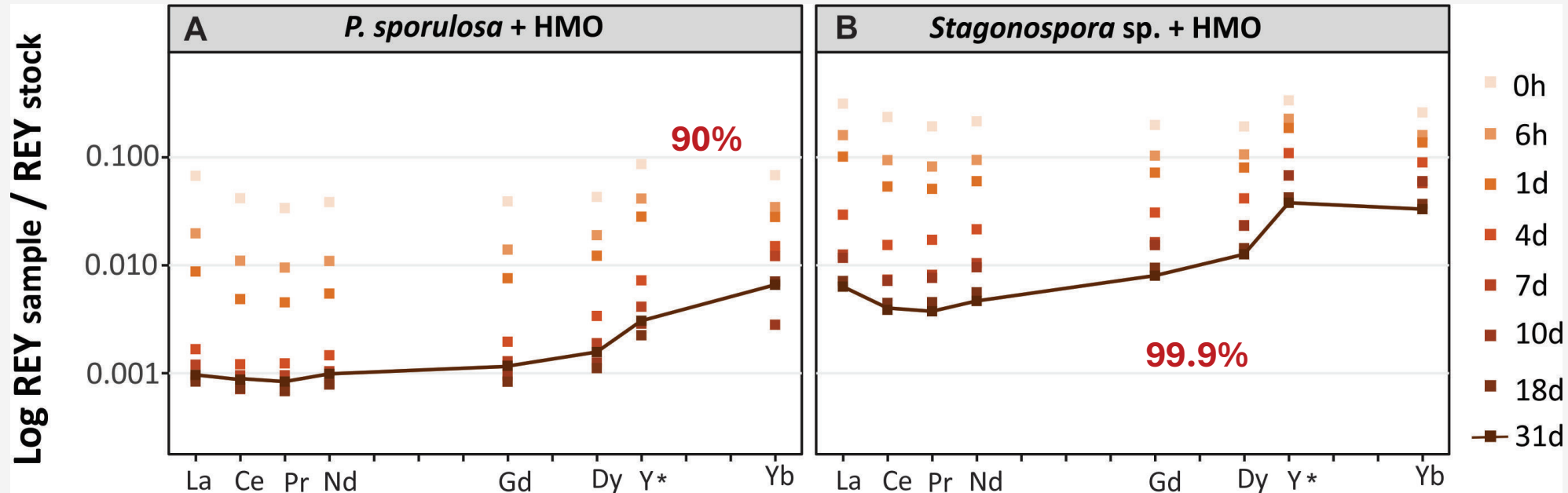
80-90% adsorption

- Co more readily oxidized by HMO
- Co can be sorbed, then oxidized
- Ni does not compete for sorption sites

Nickel Adsorption

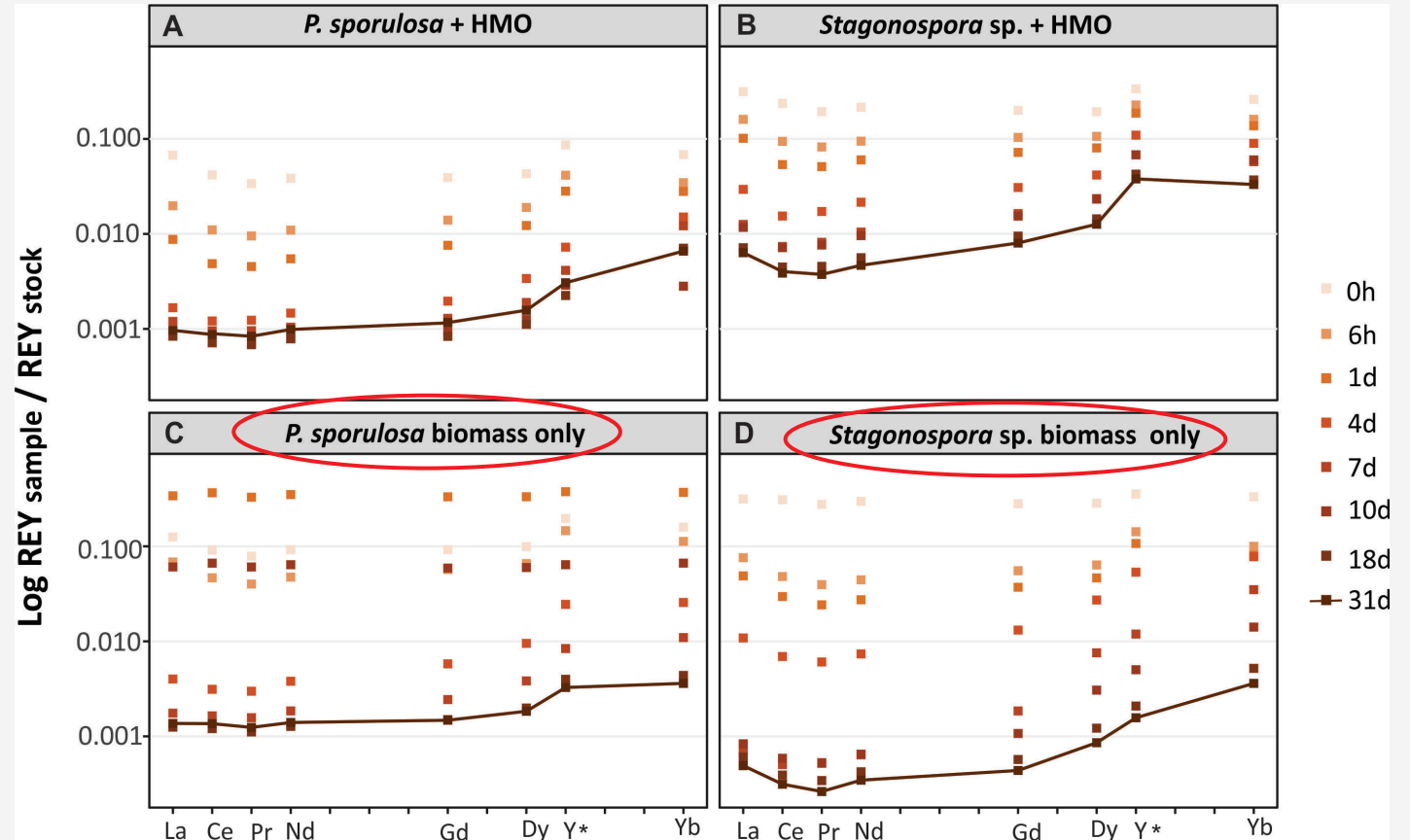
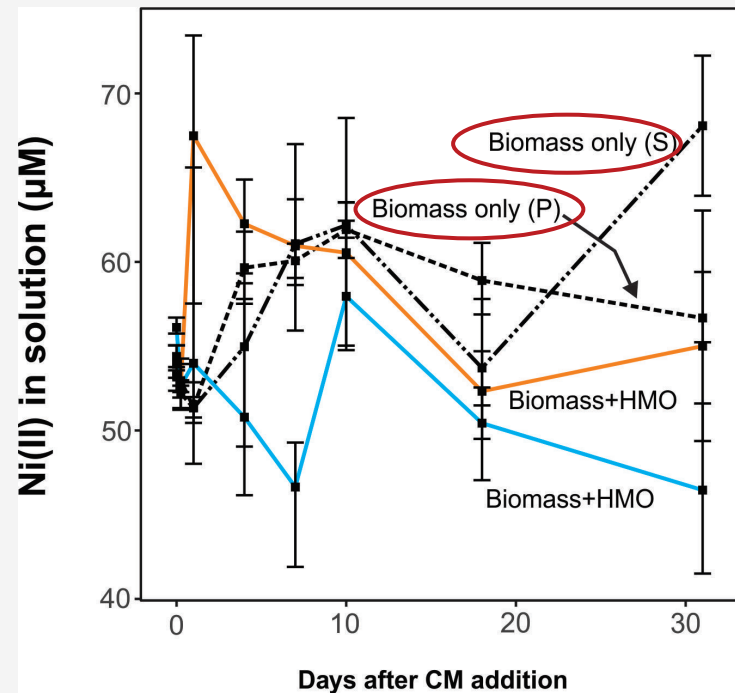
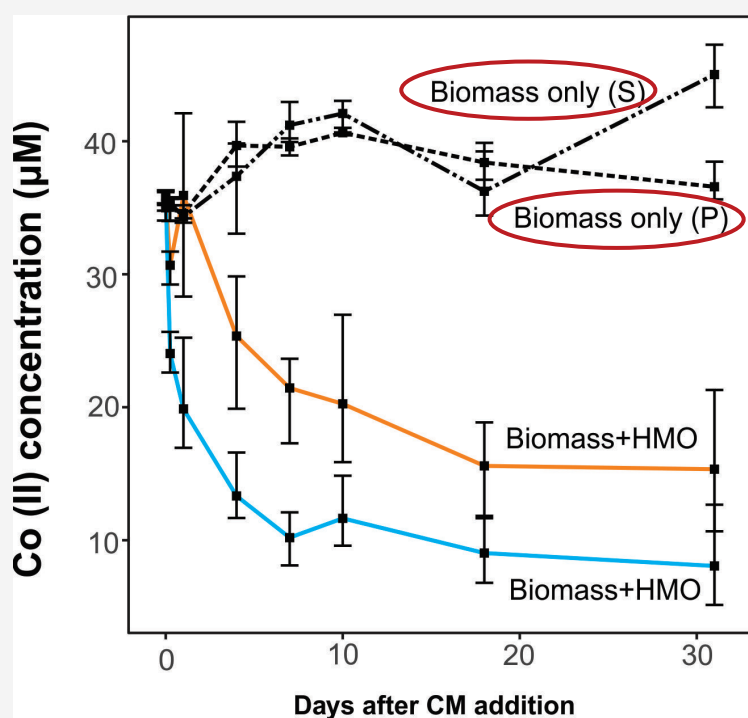
40-45% adsorption

Results- REE adsorption by biotic HMO



- Ce(III) can be oxidized to Ce(IV) by HMO
- REE forms complexes with OH^- , H_2O which then bond with Mn(IV)

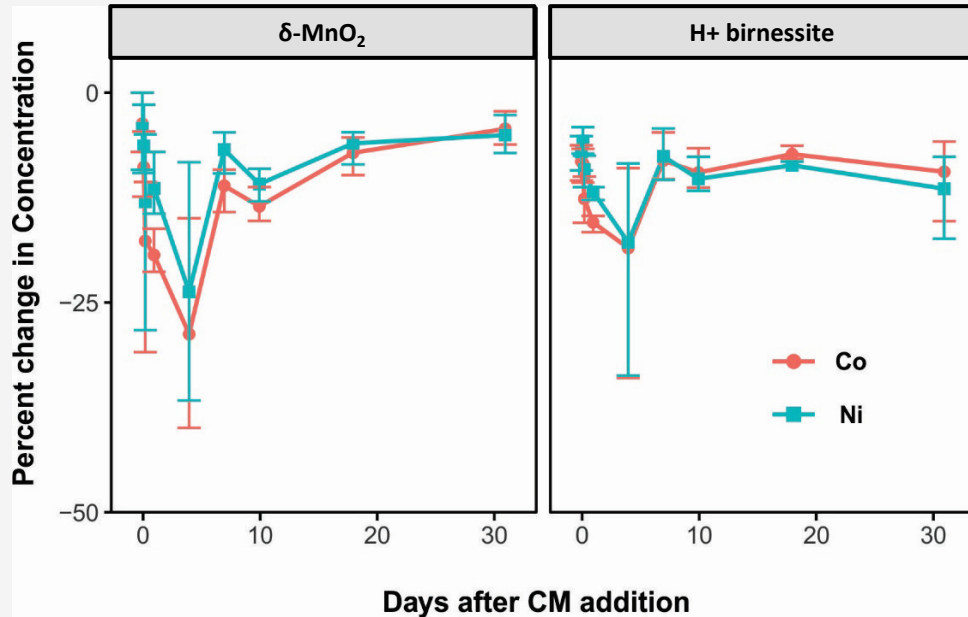
Results- Biomass only experiments



- Functional groups(phosphate, carboxyl) on fungal cell wall forms complexes with ions
- No oxidation occurs
- REE preferentially sorbed by limited sorption sites?

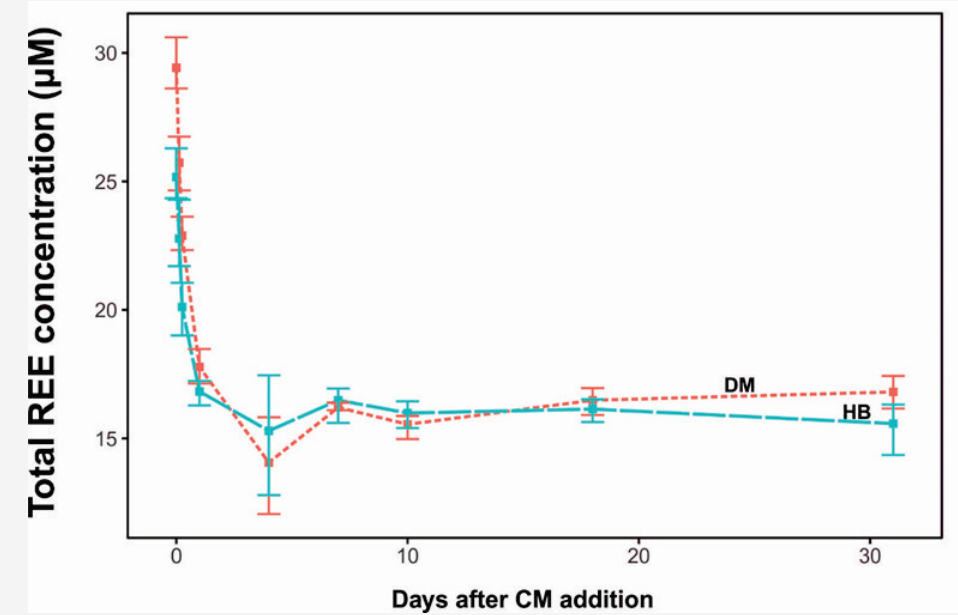
Results- Co, Ni, and REE adsorption by abiotic HMO

Ni and Co sorption by abiotic HMOs

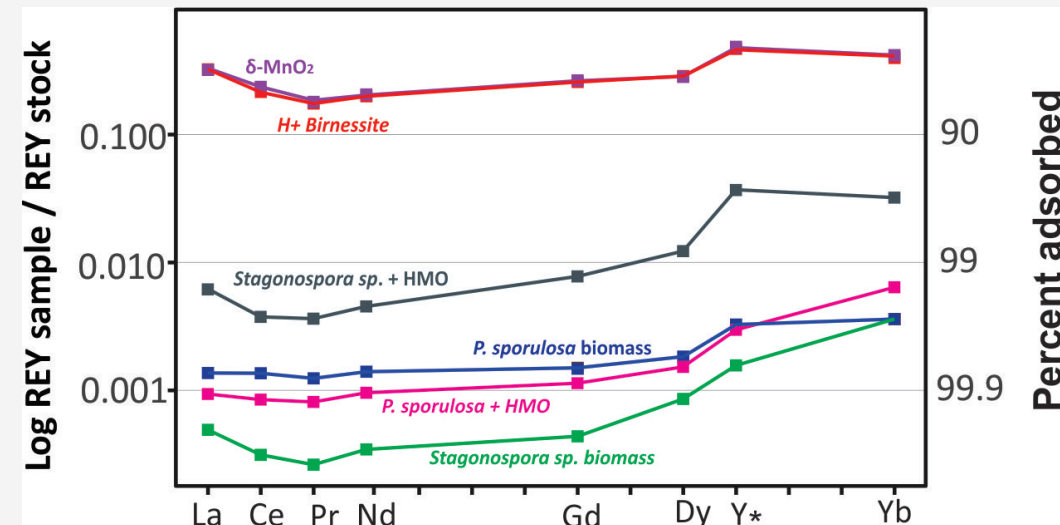


- Sorption rate slower than biotic HMO
- Lower sorption may be due to lower surface area and higher crystallinity
- Desorption may be due to HMO dissolution

Total REE adsorption by abiotic HMO



REE pattern for all experiments after 31d



Key take aways

- Biotic HMO are more important for CM sorption, particularly for REE and Co
- Biosorption is very effective in sorbing REE compared to Co and Ni
- Abiotic HMO are efficient at REE sorption compared to Co and Ni
- Low crystallinity, high surface area, and greater stability in biotic HMO
- Treatment systems that promote biotic oxidation of Mn should be targeted for CM recovery

Acknowledgement

- ❖ Geological Society of America Graduate Student Research Grant
- ❖ DOI-Office of Surface Mining Applied Science award
- ❖ Carnegie Museum of Natural History

THANK YOU.