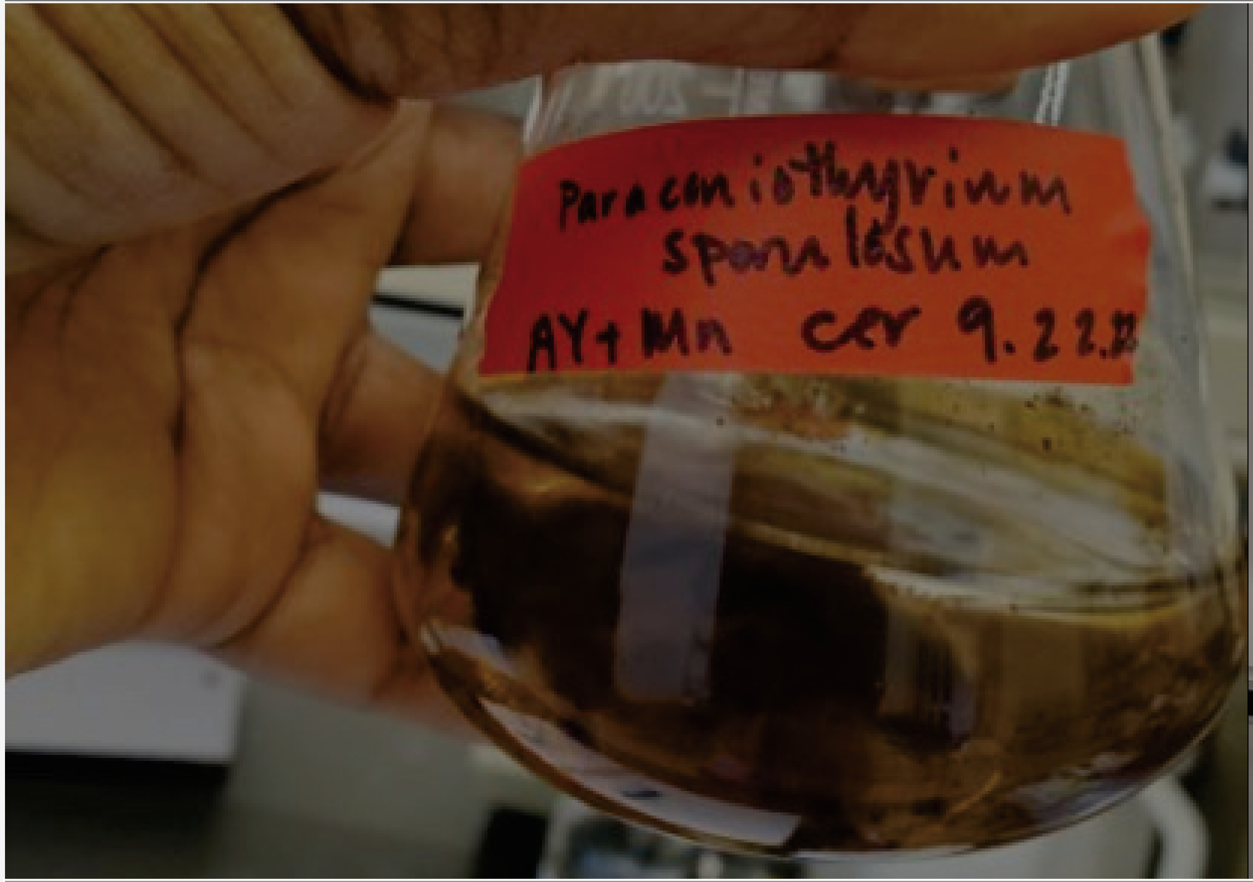
Lab-based assessment of critical metal adsorption by biotic and abiotic hydrous manganese oxides



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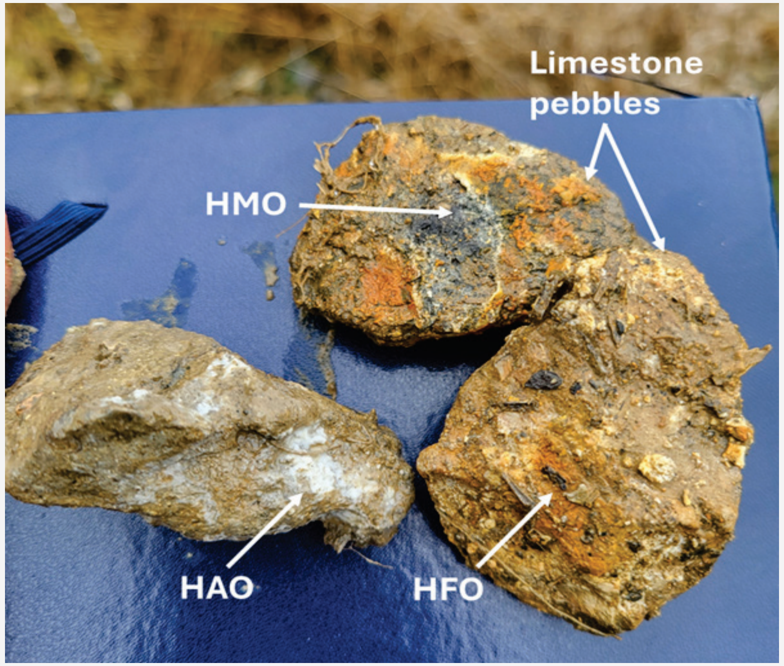
AMD treatment solids: waste or resource?

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

Critical metals can become highly concentrated to near ore grade

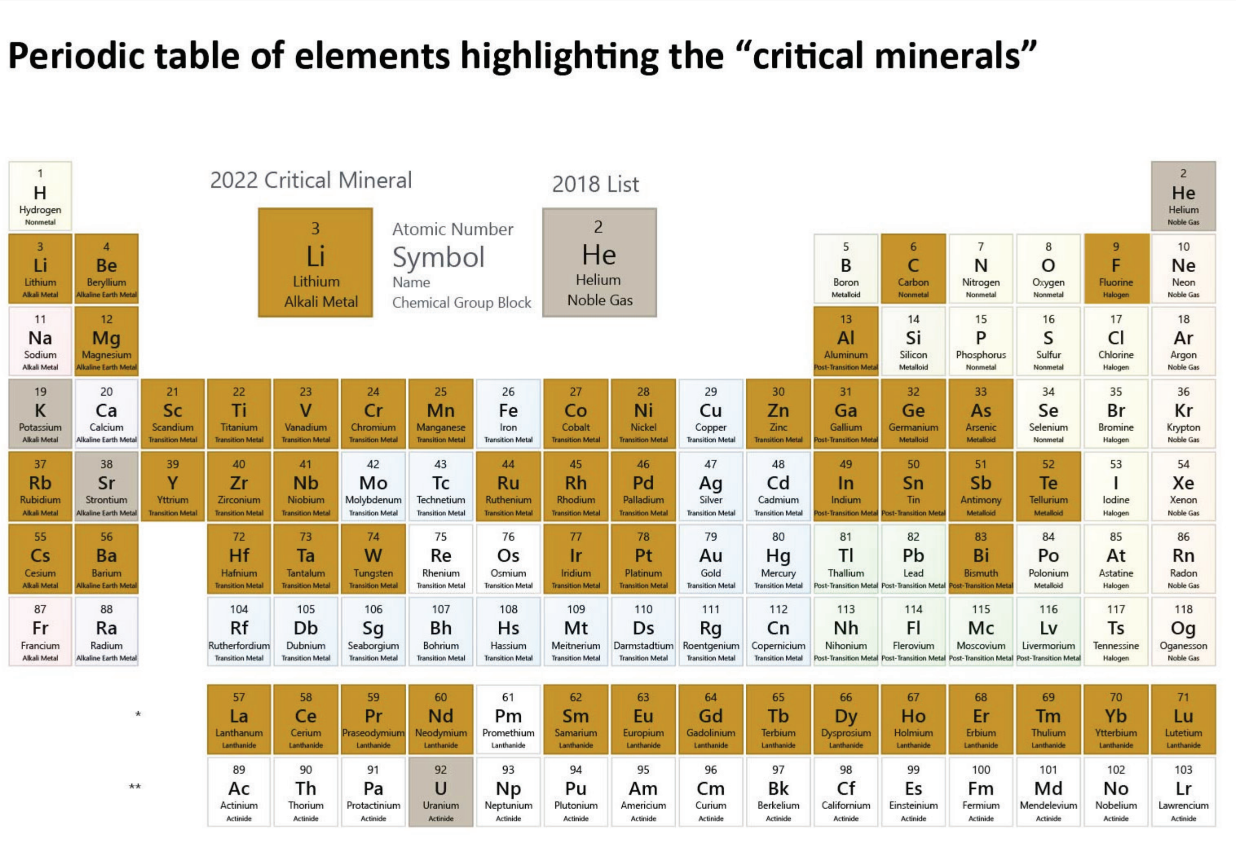
REE: 2000 mg/kg

Co: 5000 mg/kg

Ni: 6700 mg/kg

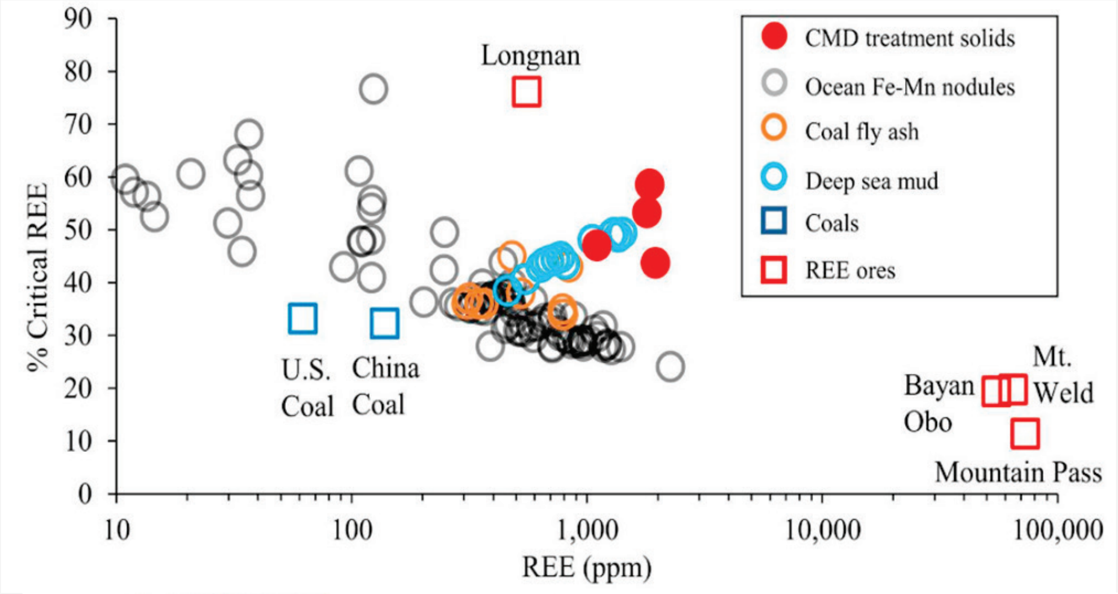
Hedin et al. (2020)

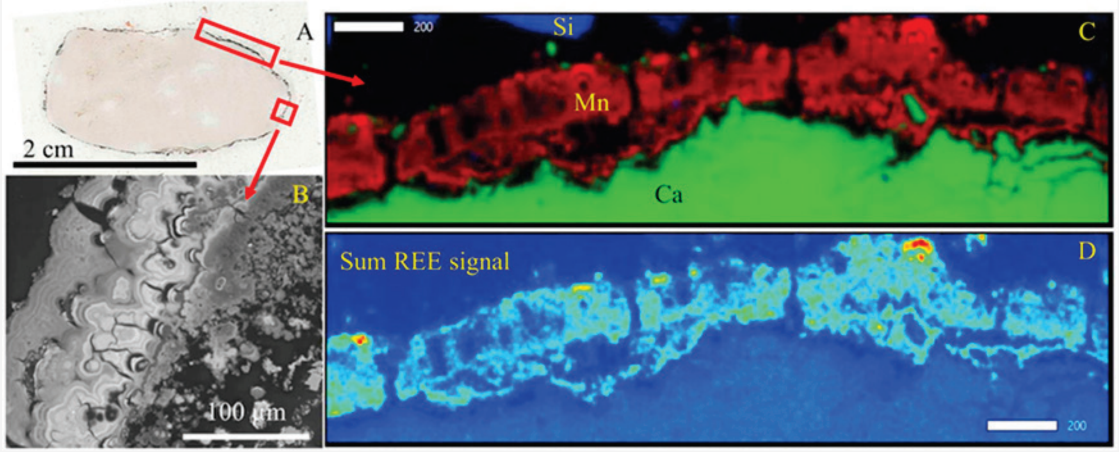
Critical Metals and HMO



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

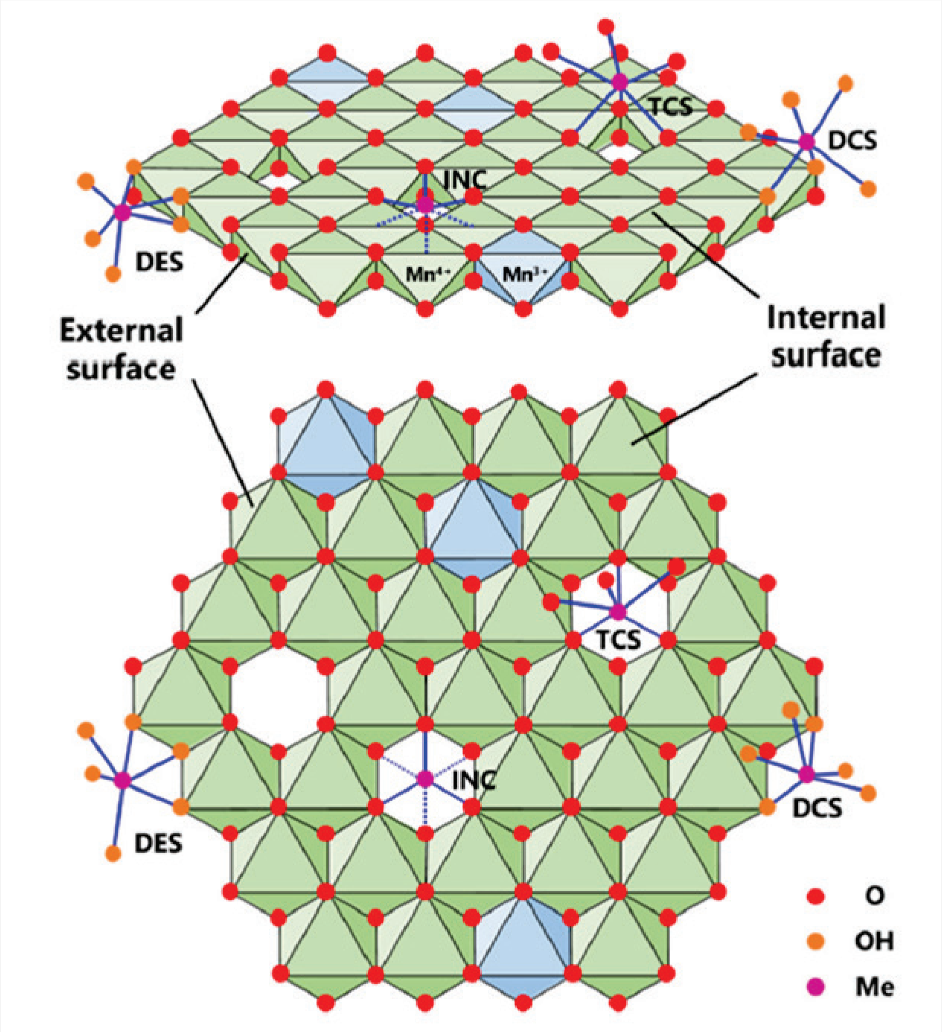
Unconventional sources of critical metals



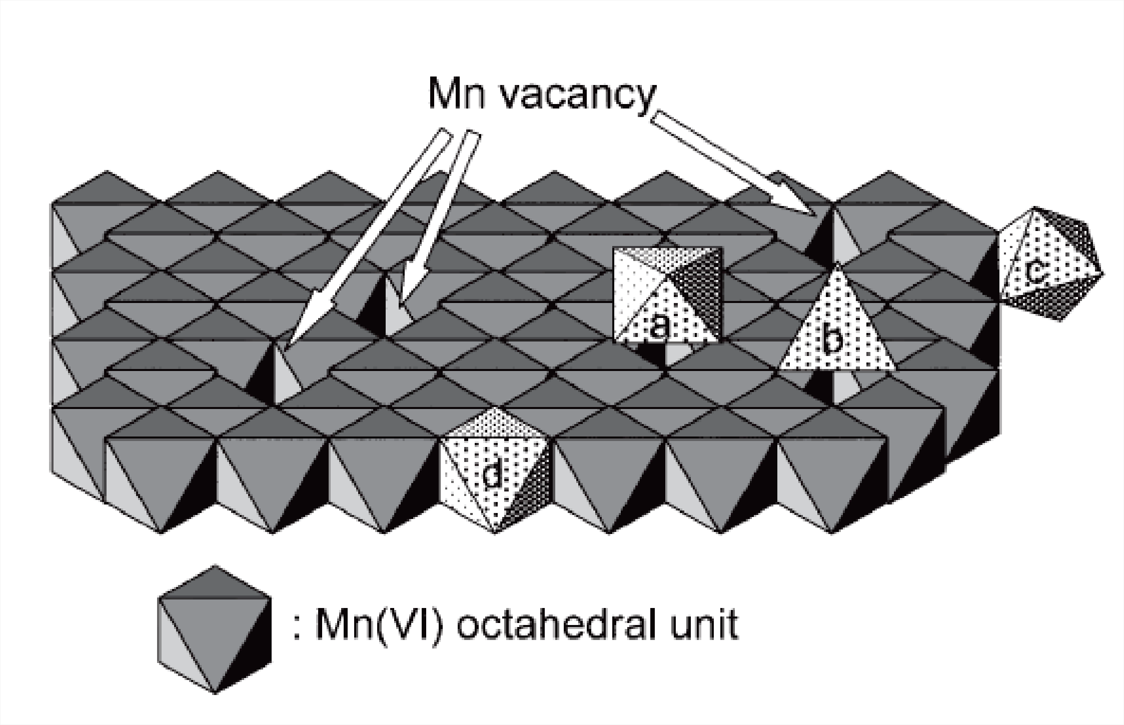


Hedin et al. (2019)

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

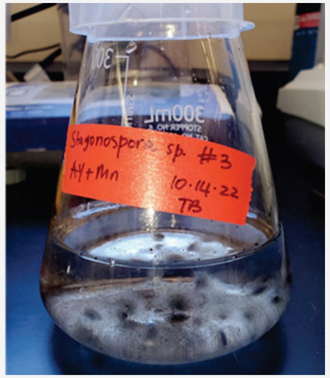
Method

Uptake of 10 Critical Metals

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

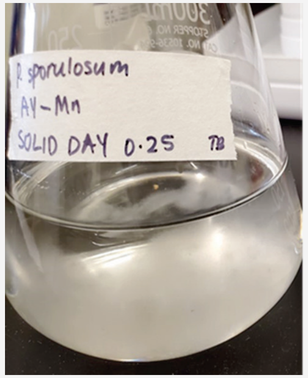
Biotic HMO produced by *Paraphaeosphaeria sporulosa and Stagonospora sp.*

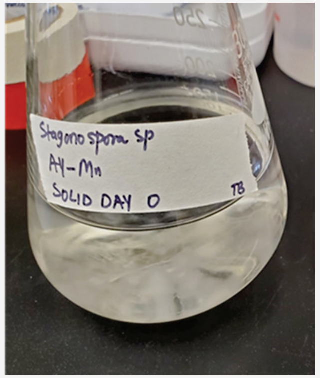
Growth media + Fungi a. P. sporulosa b. B. Stagonospora sp. + $MnCl_2$ + Critical metals



Biomass + biotic HMO

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





Biomass only

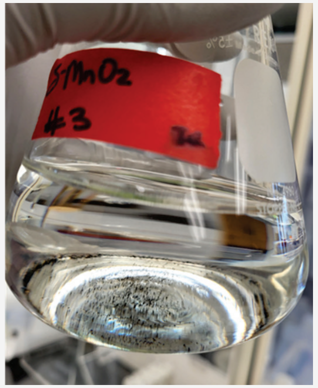
Method

Uptake of 10 Critical Metals

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

Abiotic HMO, H+ birnessite (HB) and δ-MnO_2 (DM), produced by chemical oxidation of $MnCl_2$ by potassium permanganate

Growth media **+** **Abiotic HMO**
a. H+ birnessite
b. 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

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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

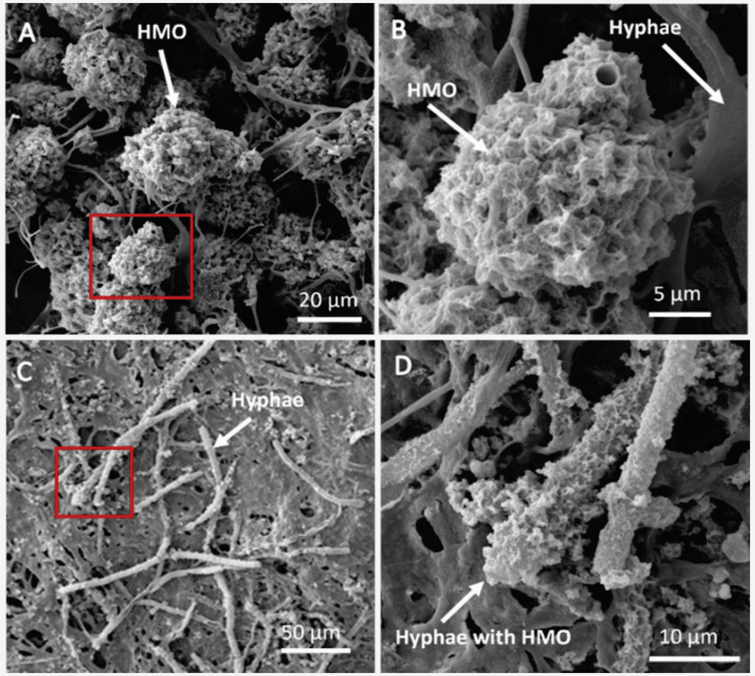
During the 14-day inoculation period,

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

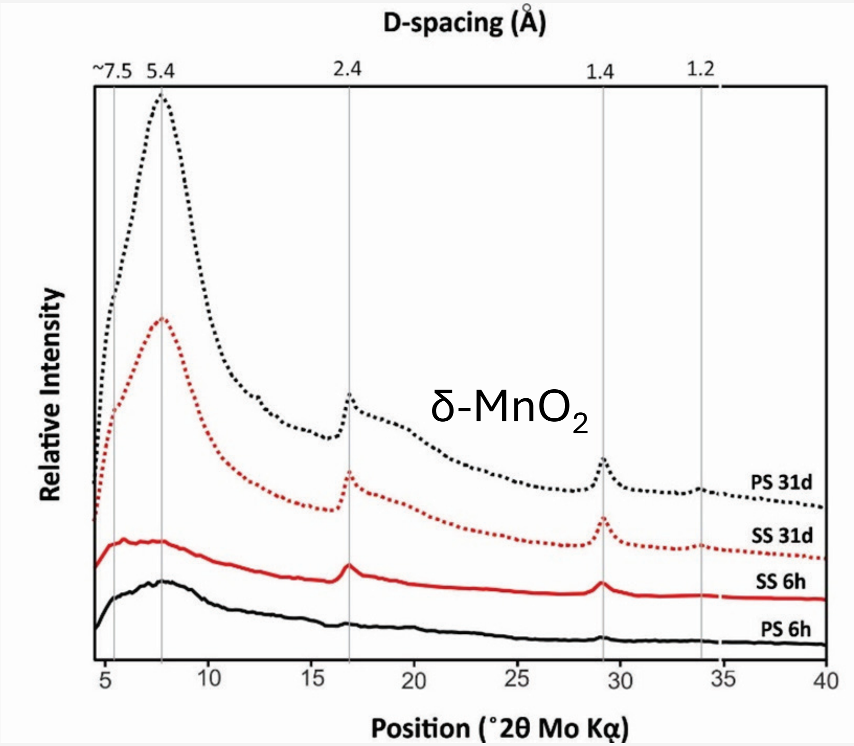
SEM imagery

Stagonospora sp.

P. sporulosa



XRD analysis

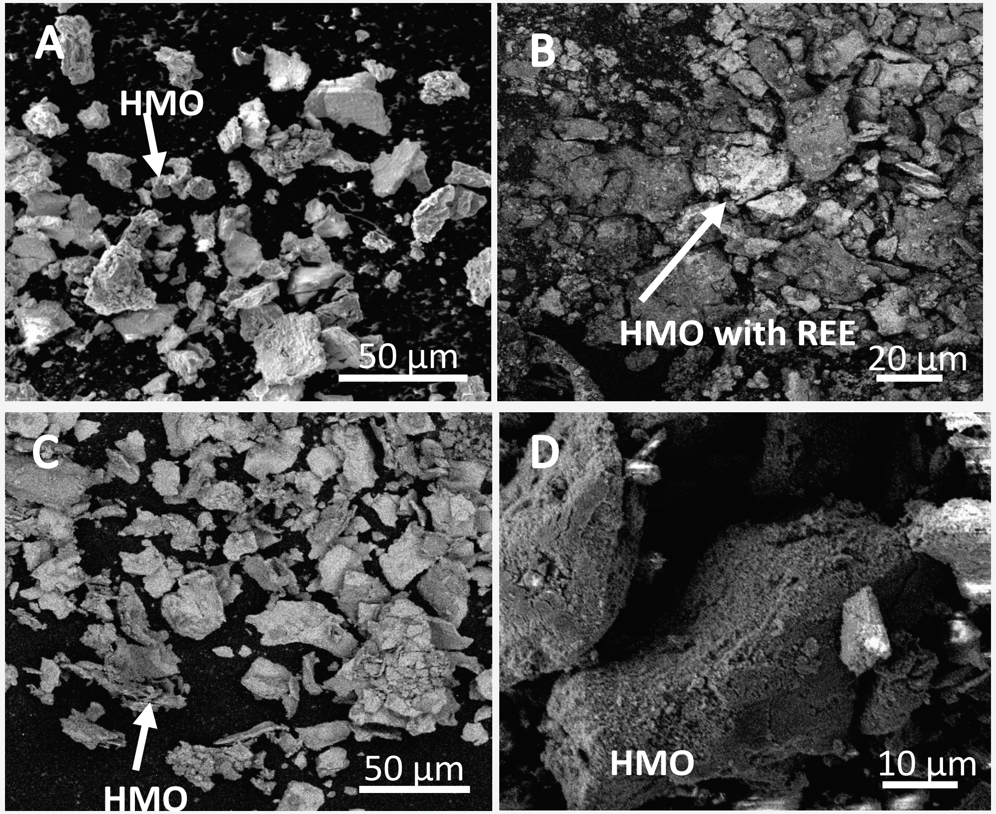


- 1.4Å: layer (310)/(020)
- 2.4Å: layer (200)/(110)

Results- Abiotic HMO mineralogy and structure

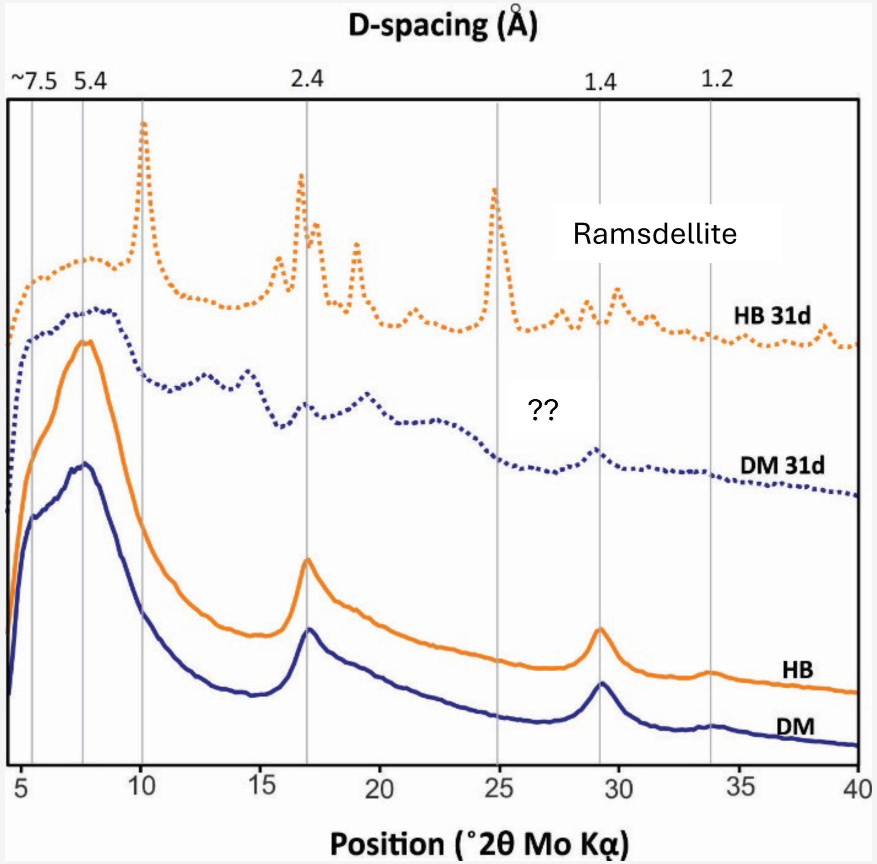
XRD analysis

SEM imagery



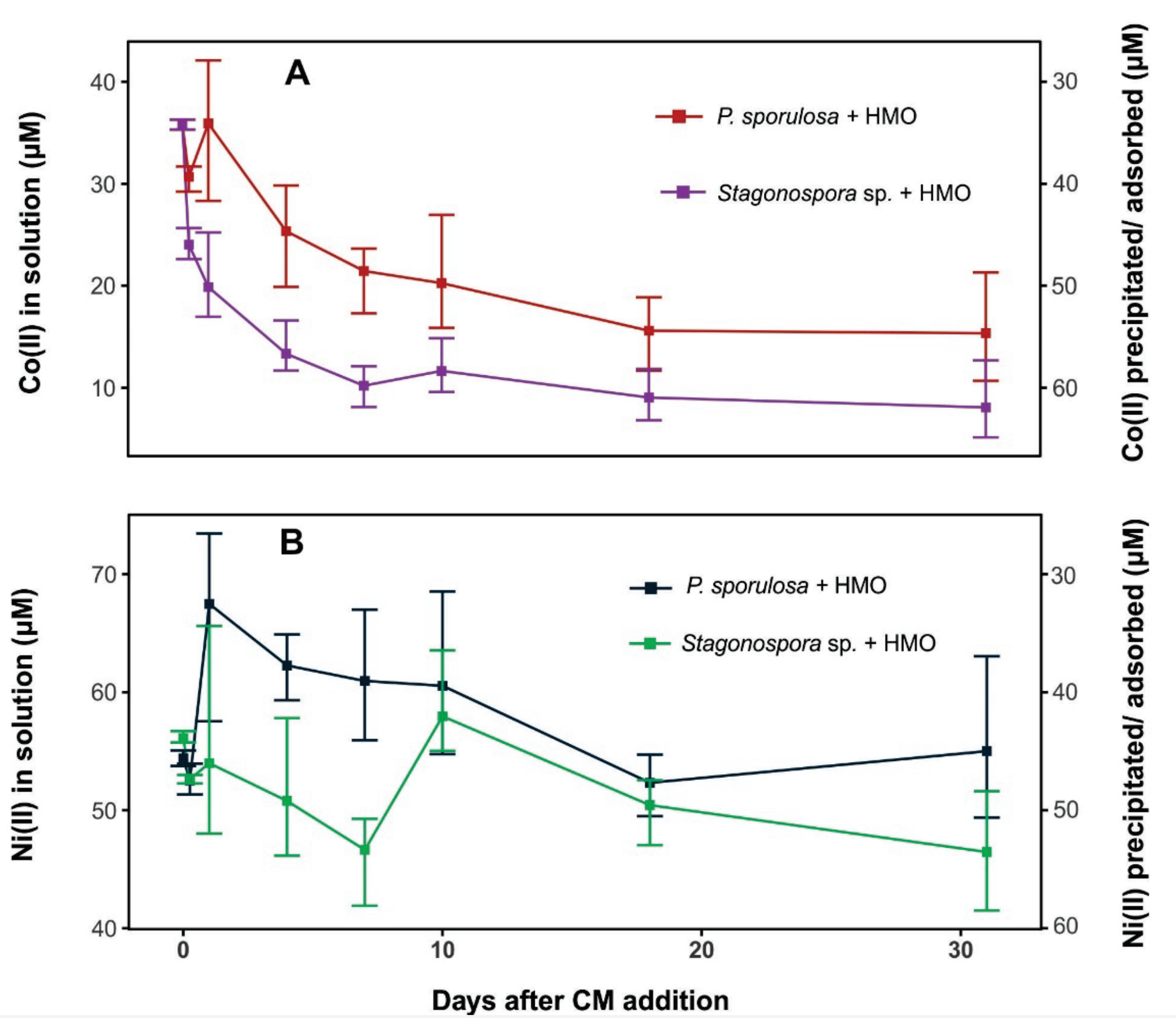
δ-MnO_2

H+ birnessite



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

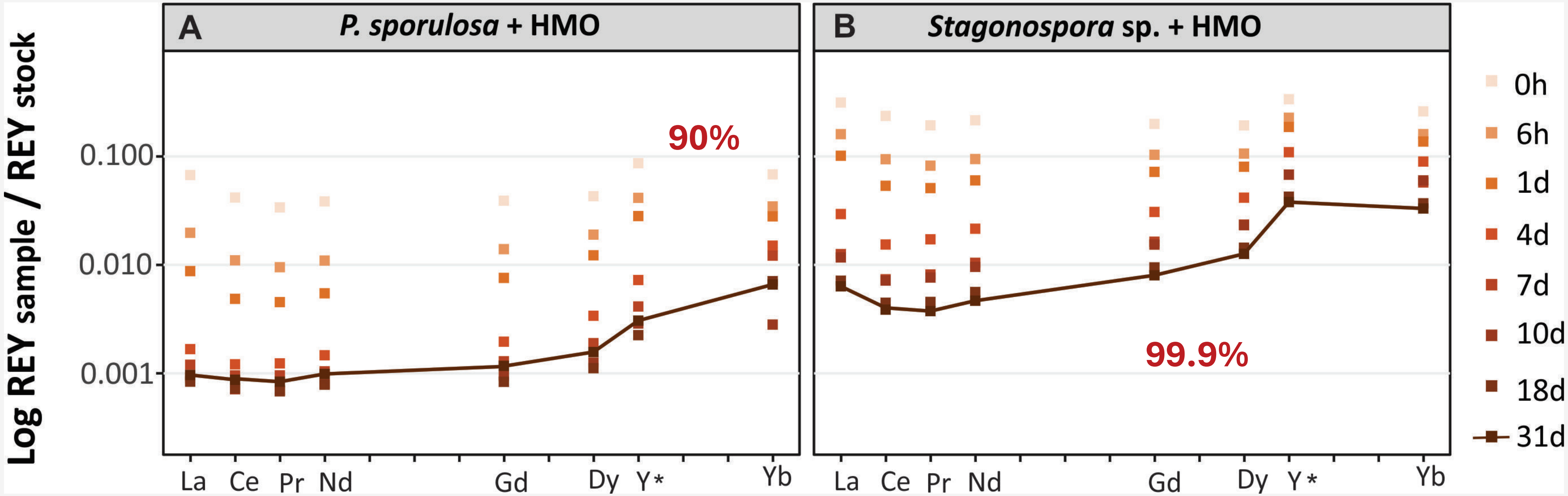
80-90% adsorption

Nickel Adsorption

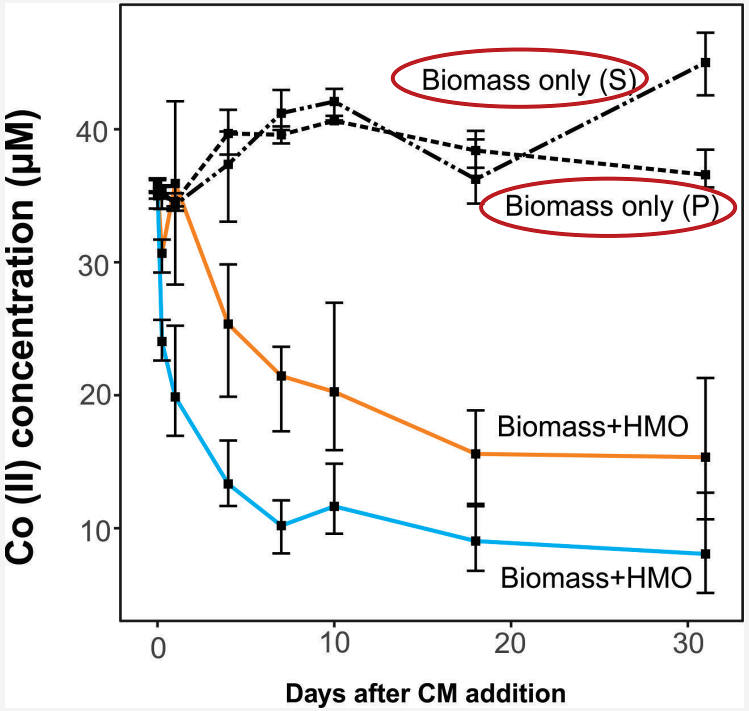
40-45% adsorption

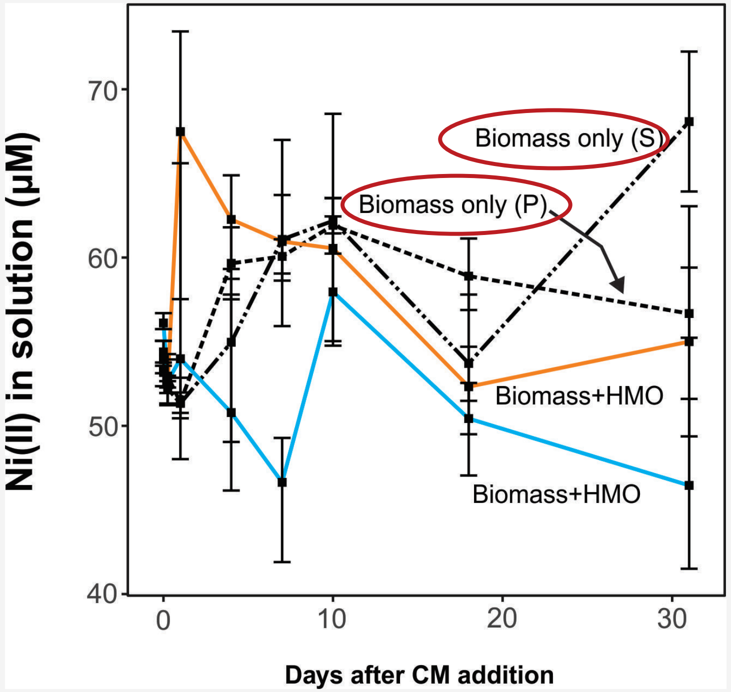
- Co more readily oxidized by HMO
- Co can be sorbed, then oxidized
- Ni does not compete for sorption sites

Results- REE adsorption by biotic HMO

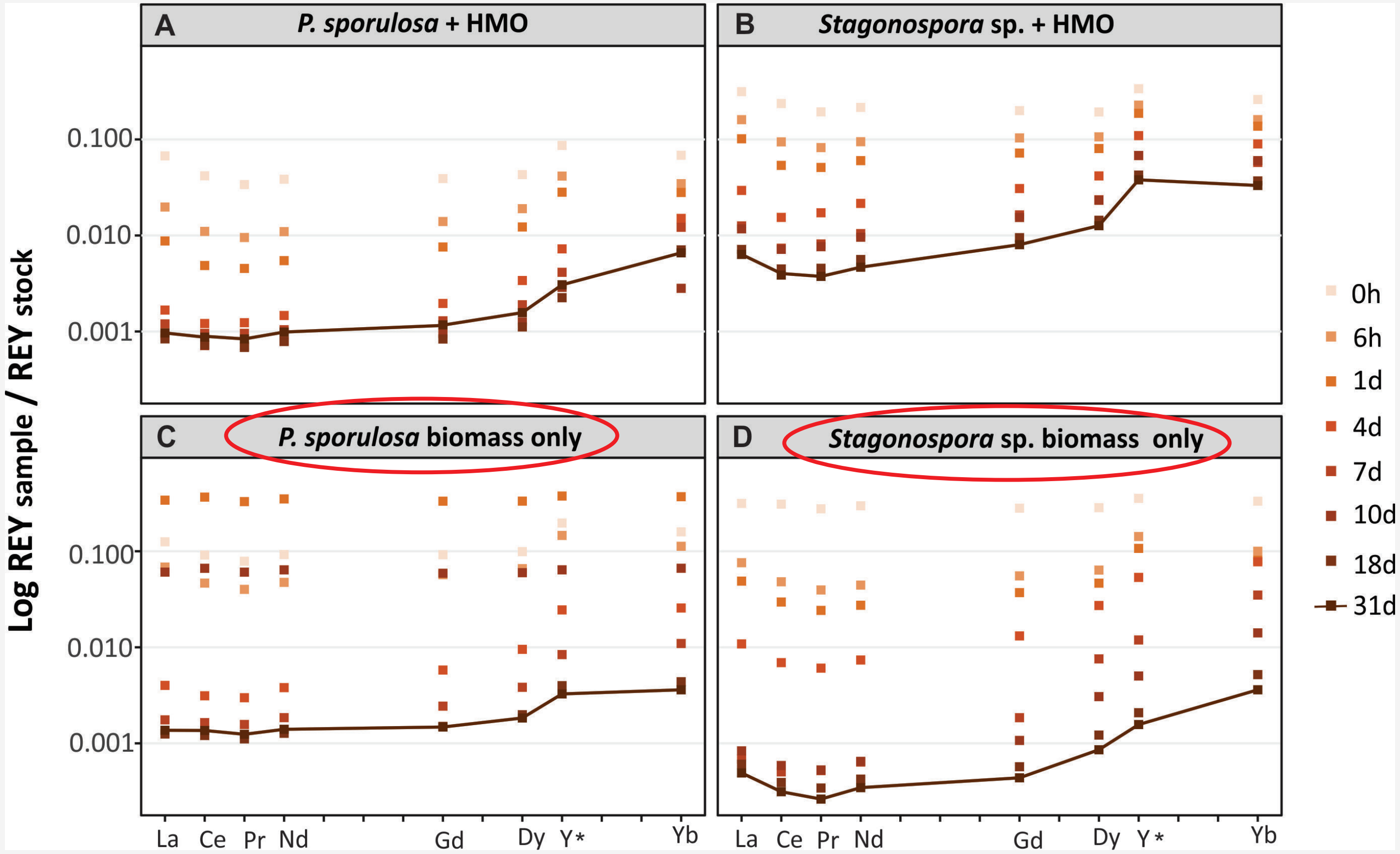


- Ce(III) can be oxidized to Ce(IV) by HMO
- REE forms complexes with OH^-, H_2O which then bond with Mn(IV)





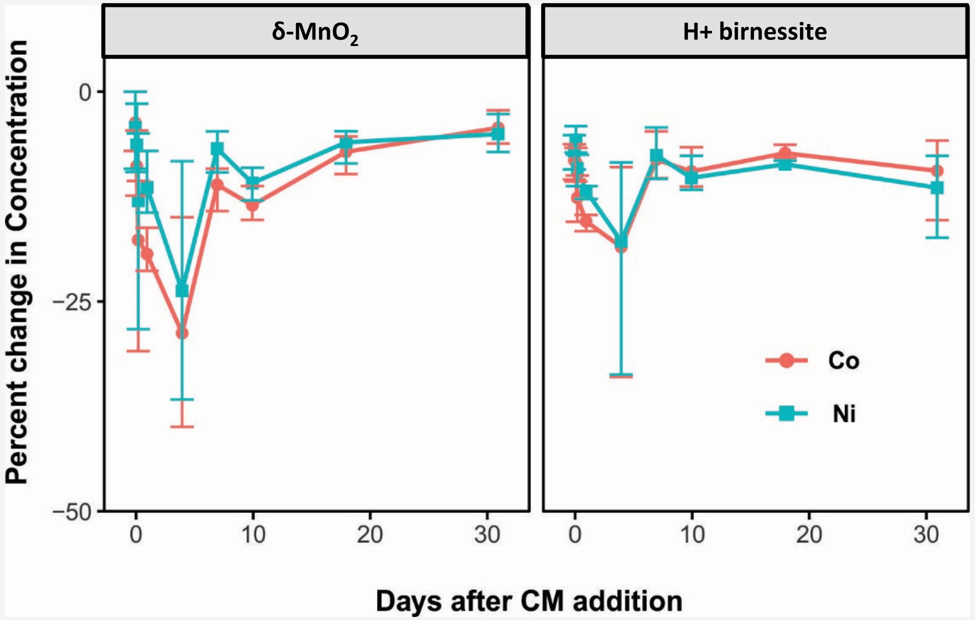
Results- Biomass only experiments



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

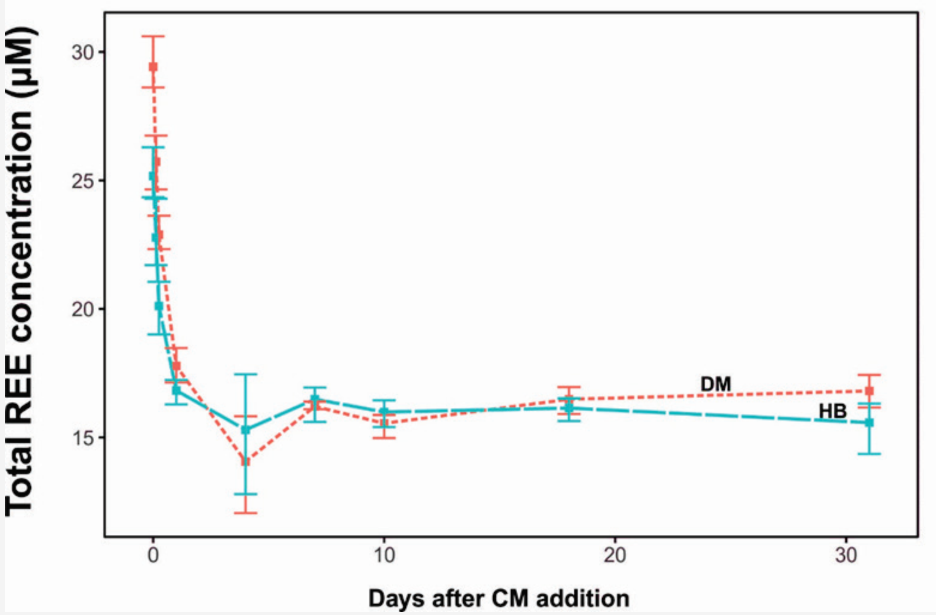
Results- Co, Ni, and REE adsorption by abiotic HMO

Ni and Co sorption by abiotic HMOs

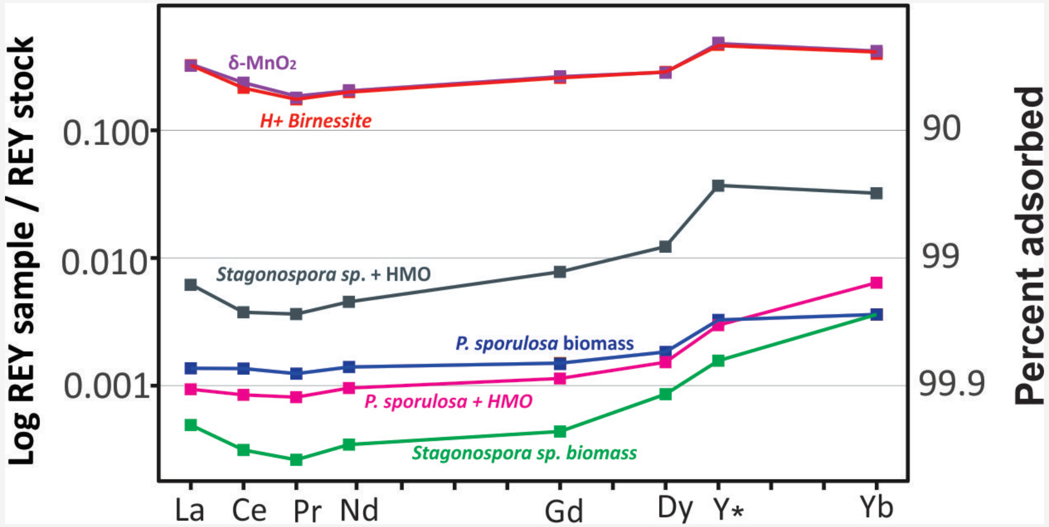


- Sorption rate slower than biotic HMO
- Lower sorption may be due to lower surface area and higher crystallinity
- Desorption may be due to HMO dissolution

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

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- Carnegie Museum of Natural History

THANK YOU.