Aqueous Rare Earth Element Patterns and Concentration in Thermal Brines Associated With Oil and Gas Production, Wyoming

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Outline

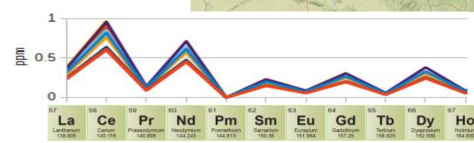
- Why produced waters?

- REE importance

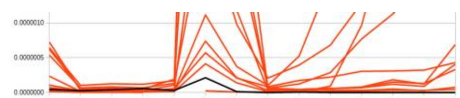
Element	Type	Applications
Ce[1]	REE	Oxidizer and catalyst
Co[1]	Trace	Batteries and alloys

- Study areas: WRB, PRB, Ponds

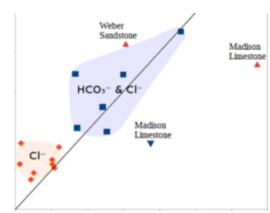
- How REEs are presented



- Data by Basin & Field



- Relationship to possible ligands



Produced waters are perfect

Oil and Gas wells
High Volume,
Pre-developed,
Hot, and **Saline**

Aqueous mining turns salinity into a resource

REE Importance

Element	Type	Applications	Element	Type	Applications
Ce[1]	REE	Oxidizer and catalyst	Mn[1]	Trace	Steel alloys and production
Co[1]	Trace	Batteries and alloys	Nd[1]	REE	Magnets and capacitors
Dy[1]	REE	Magnets and minor alloys additive	Ni[1]	Trace	Multi-purpose metal
Er	REE	Lasers and steel alloys	Pr[1]	REE	Radioactive decay heating
Eu[1]	REE	Lighting and NMR	Sc	REE	Catalyst and lighting
Ga[1]	Trace	Photovoltaics and semiconductors	Sm	REE	Magnets and neutron flux control
Gd	REE	Neutron flux control and many alloys	Tb[1]	REE	Magnets and lasers
Ho	REE	Magnets and lasers	Th	Trace	Fuel and lighting
In[1]	Trace	Photovoltaic film	Tm	REE	Lighting and lasers
La[1]	REE	Catalyst and glass additive	U	Trace	Fuel and ballast
Li[1]	Trace	Flux and batteries	Y[1]	REE	Lasers and steel alloys
Lu	REE	Medical tracer and glass additive	Yb	REE	Reducing agent and steel alloys

[1] DOE identified critical material

Needed for current technology economy

Past Water-Rock interactions

- Offer tracing opportunity
- Sources and authigenic tracking

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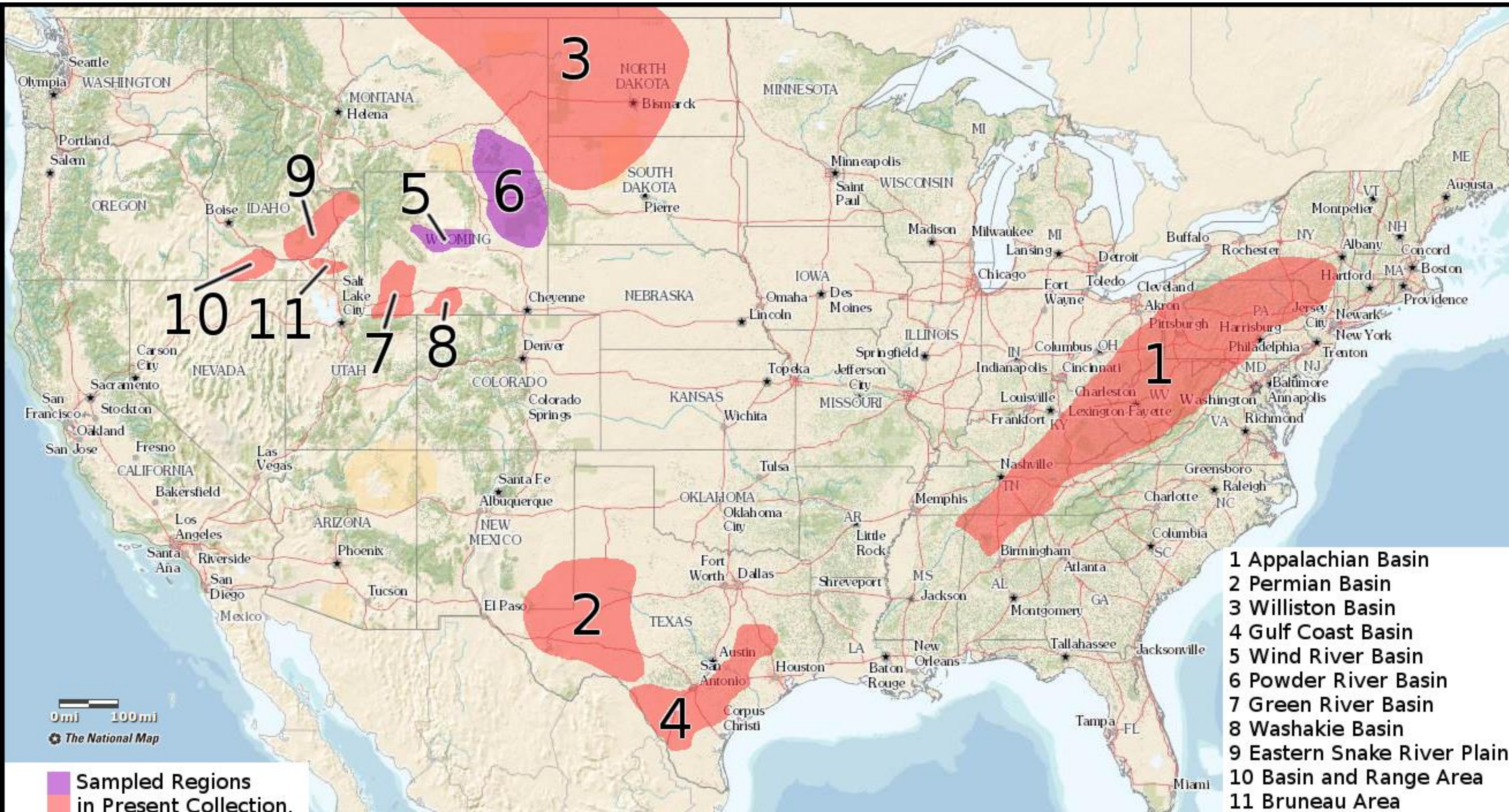
Ongoing REE Work

N ≈ 150



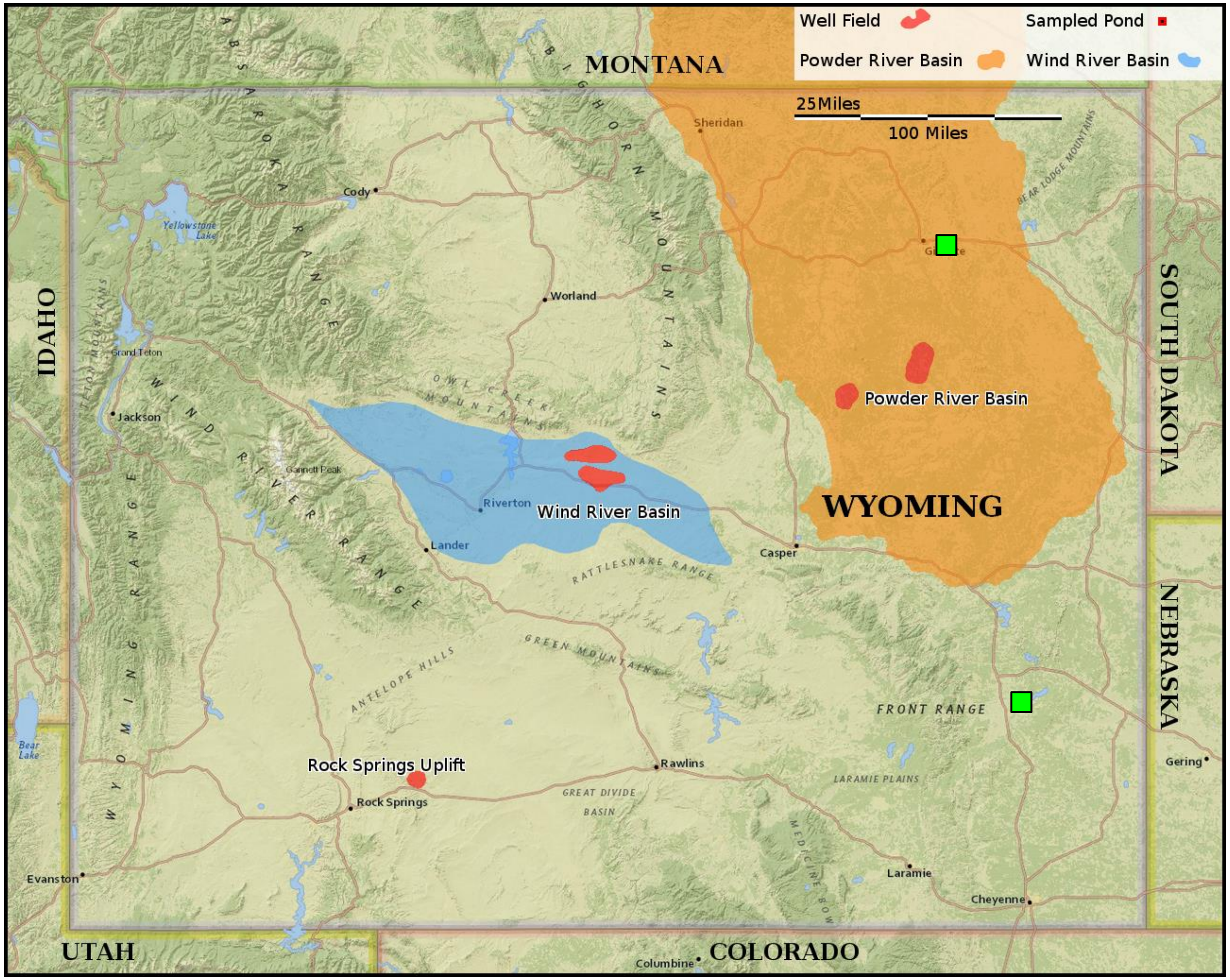
Study Area for this talk

N = 28

Wind River Basin

Powder River Basin

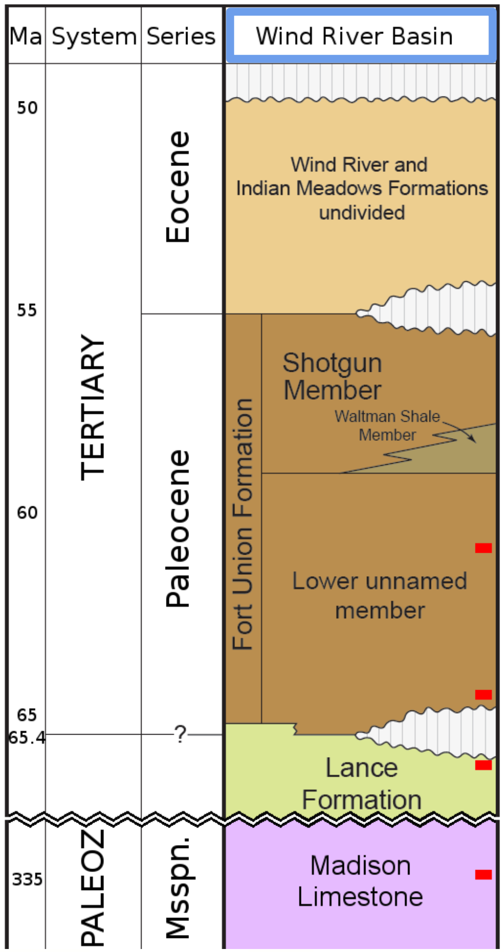
Power Stations

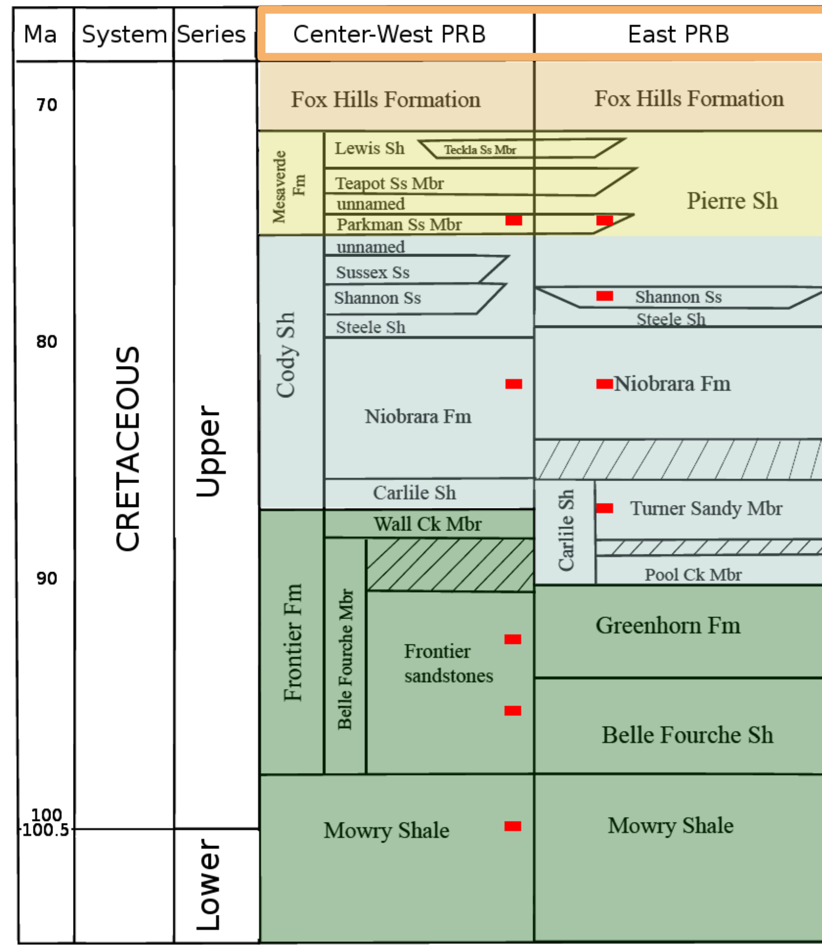


Strata

WRB: Young-Very Old Shallow-Deep

PRB: East-West





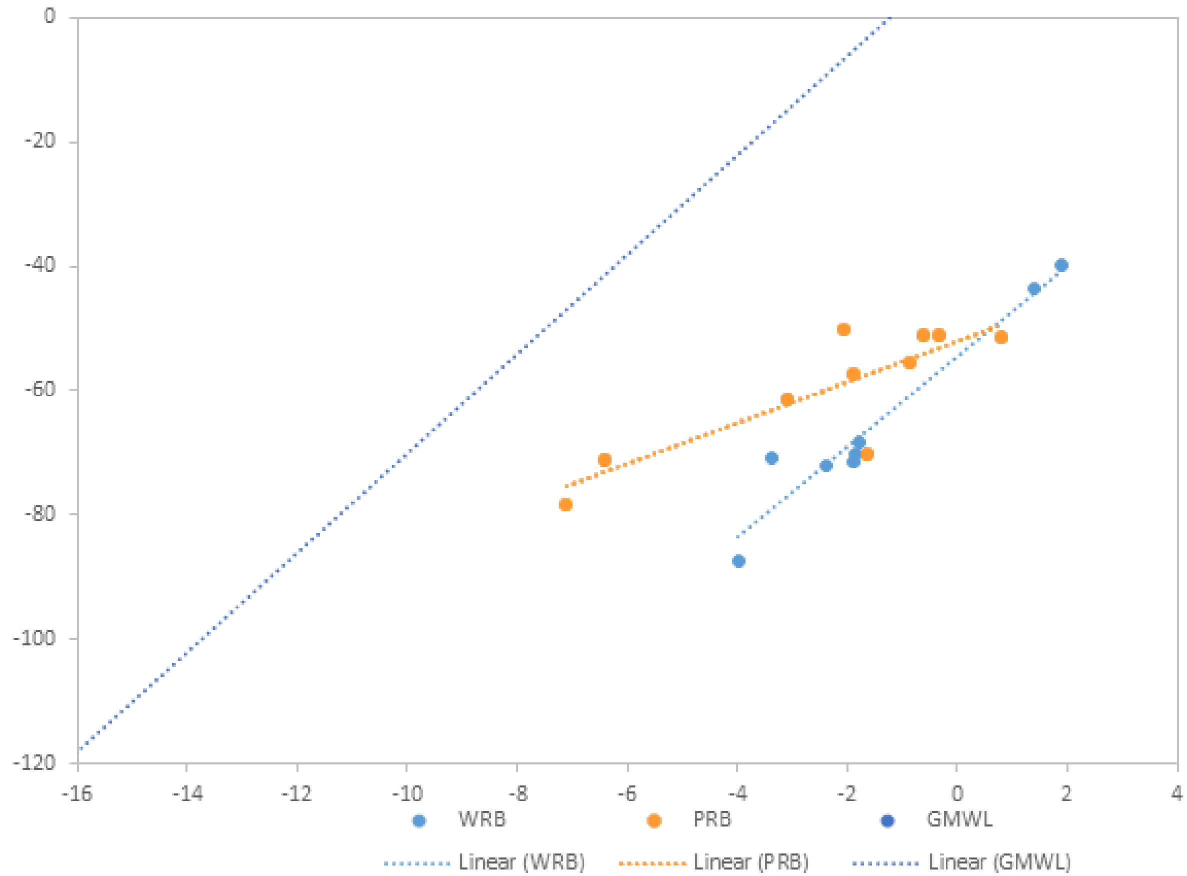
Isotopes: δD, δO18

Right of GMWL

δO18 isotopes heavy enriched

Prolonged Rxn with Rock

Non-Meteoric water



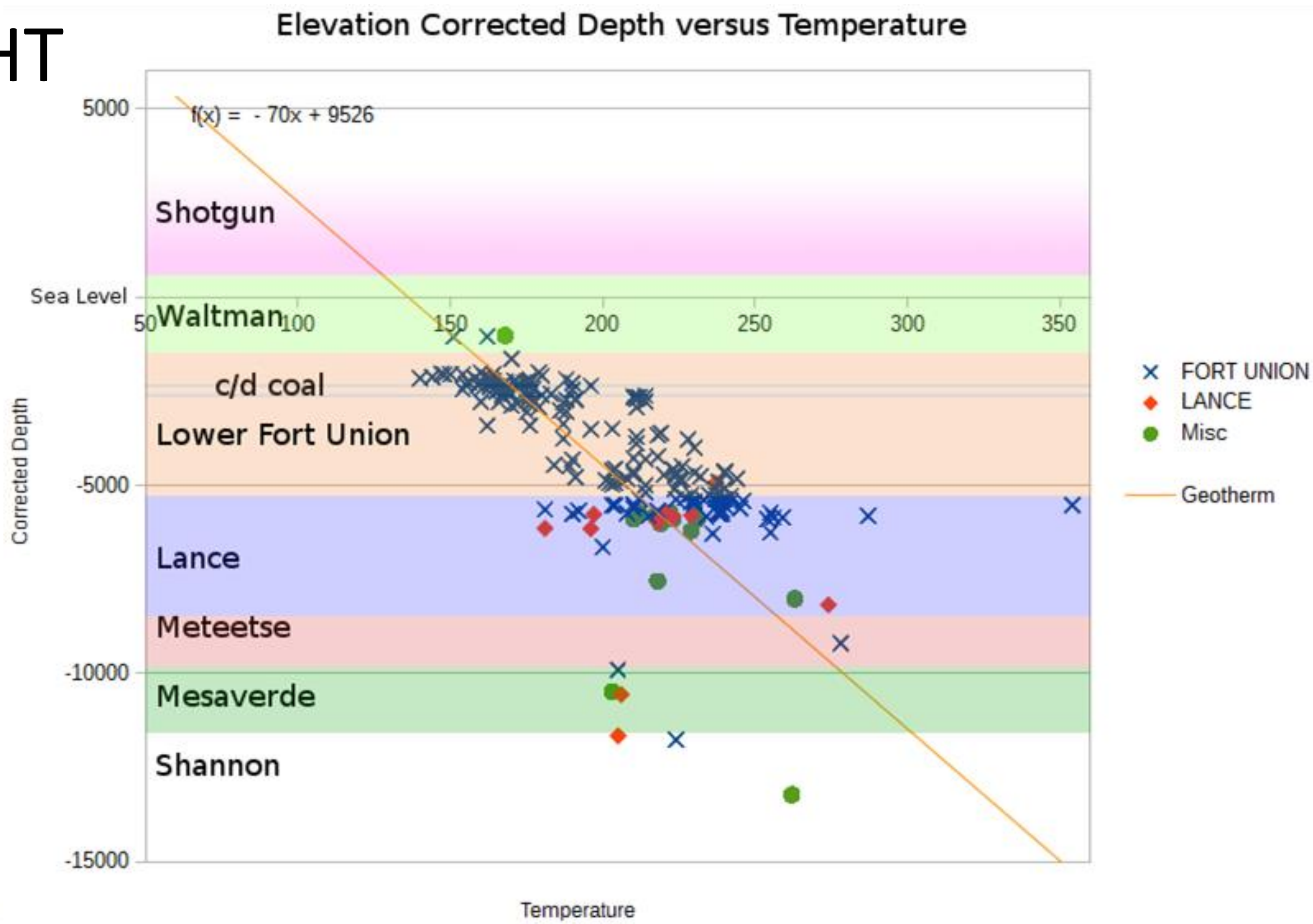
Heat in WRB

English BHT records

1°F/ 70ft

2 groups

Coal

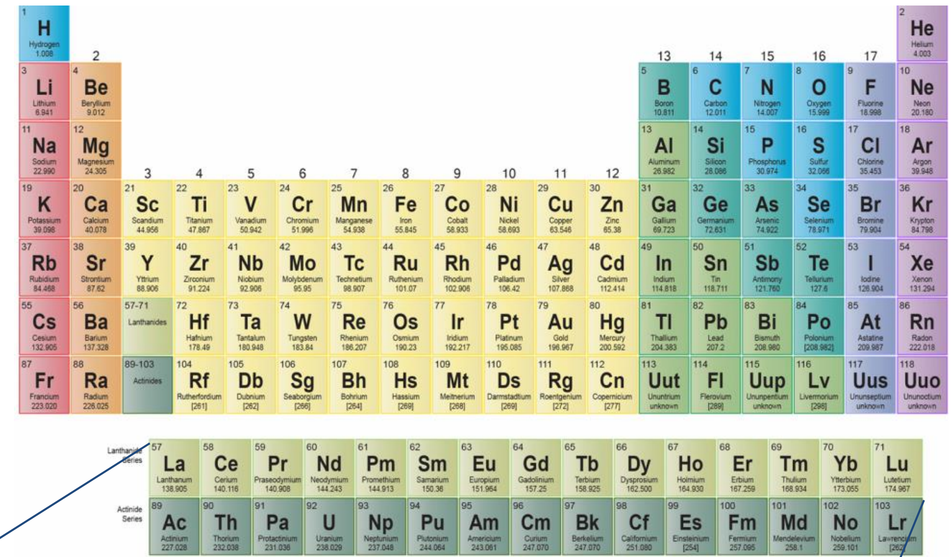


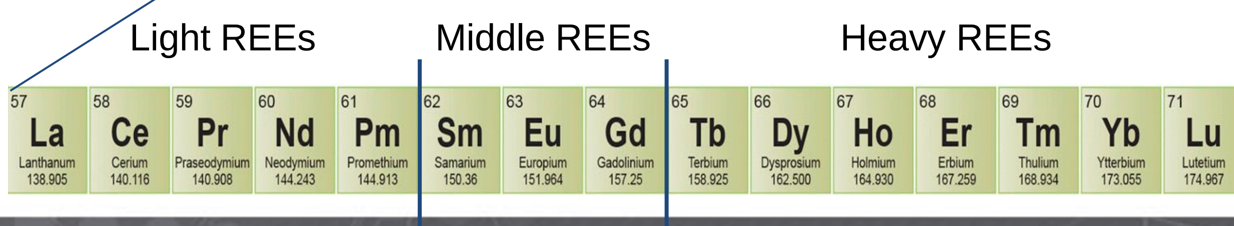
How REE data are presented

Plot in F-block order

Saw-tooth

Normalize





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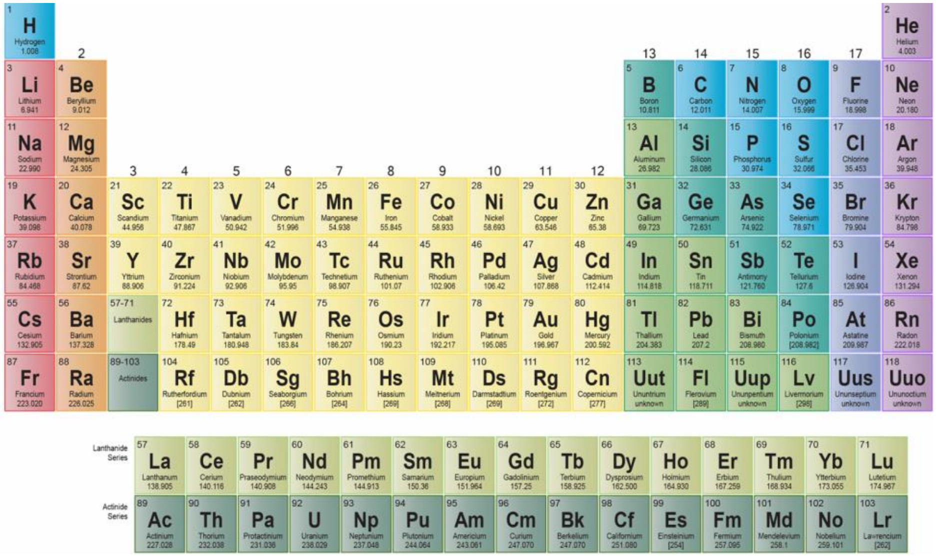

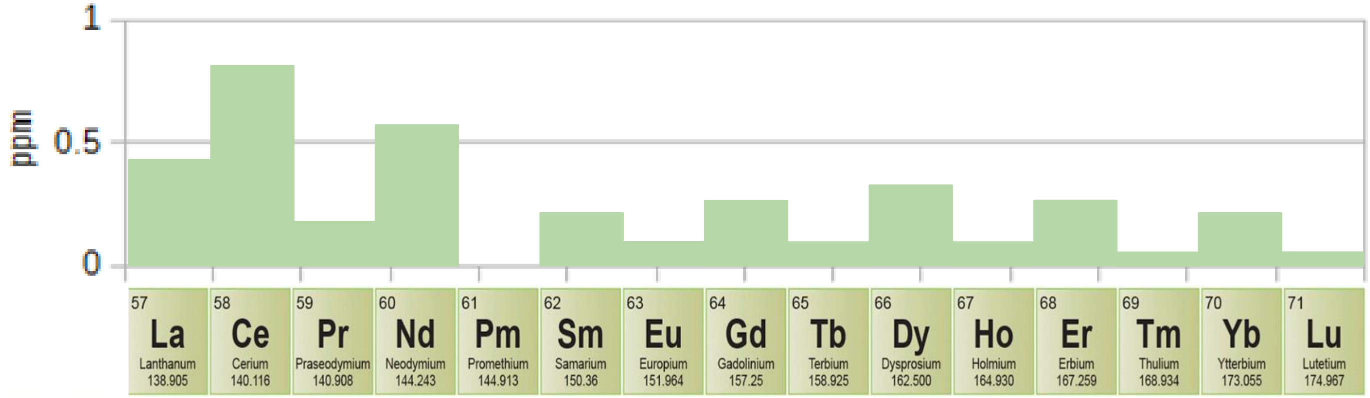

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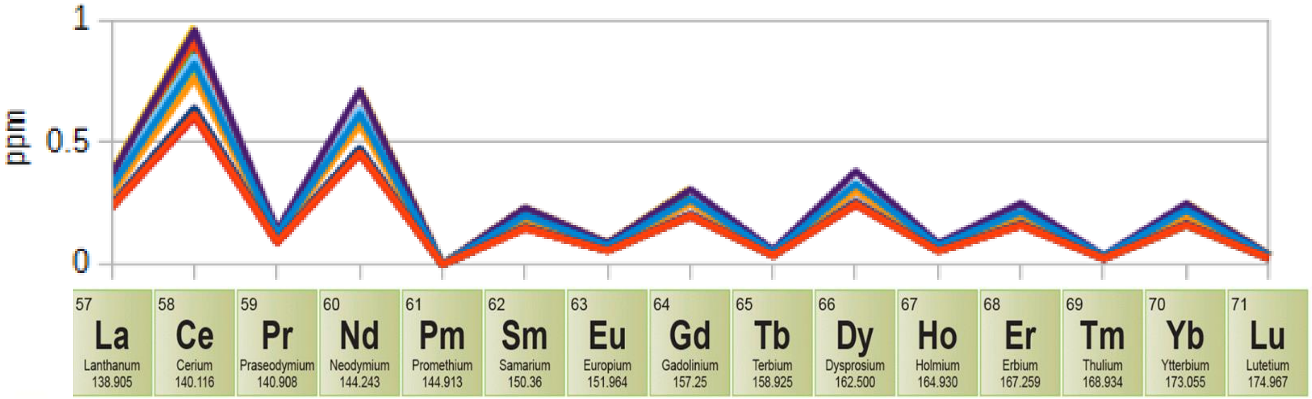

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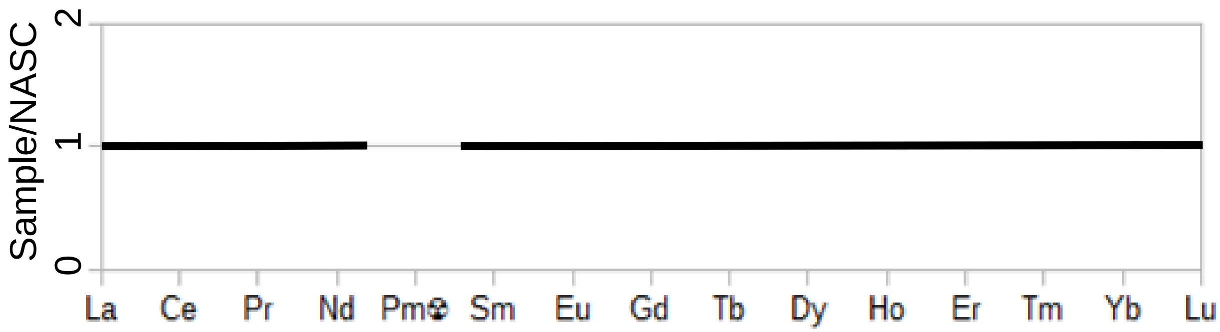

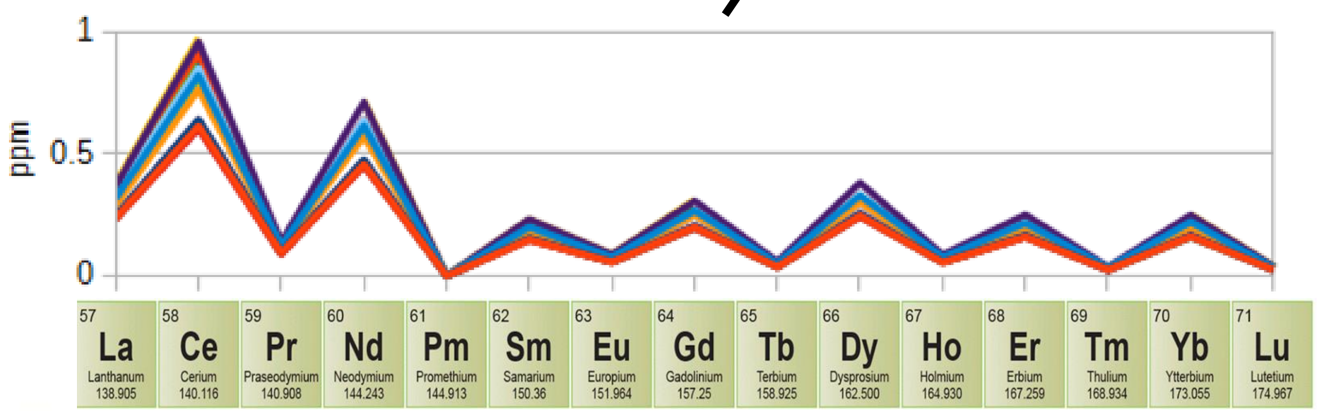

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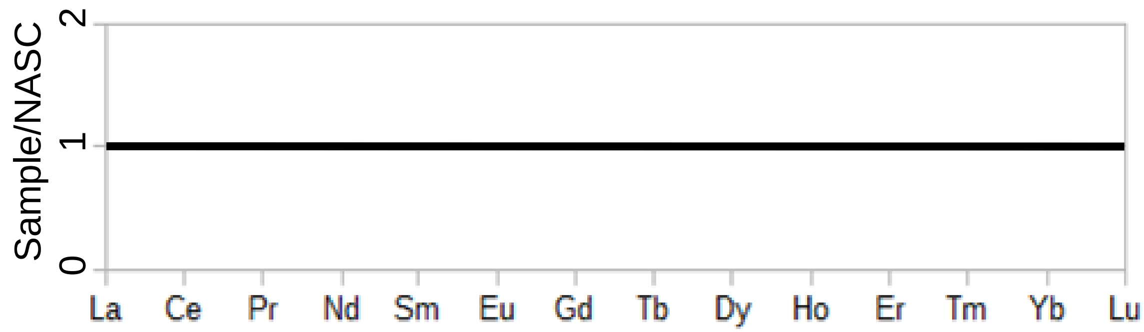
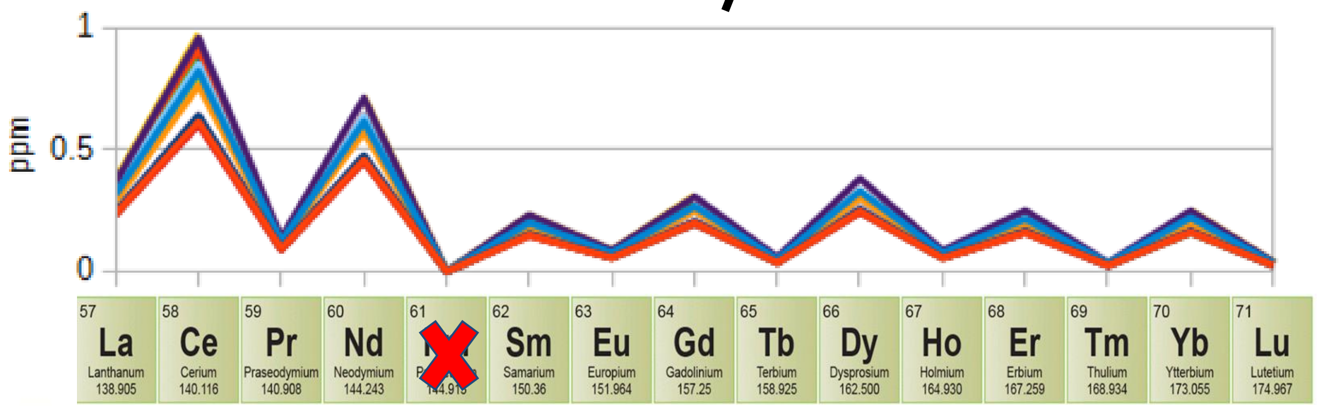
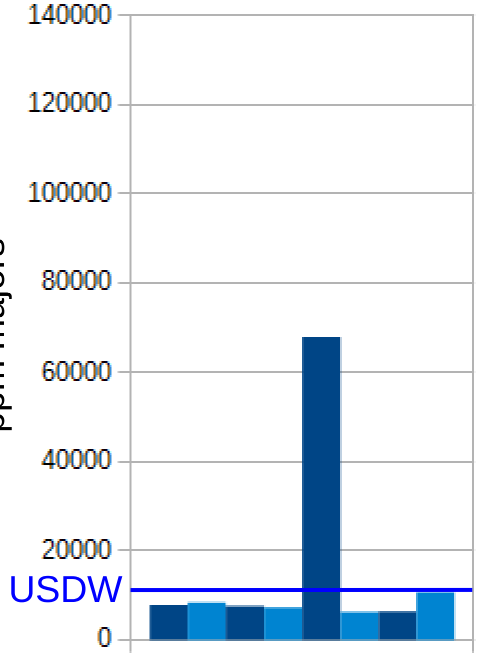
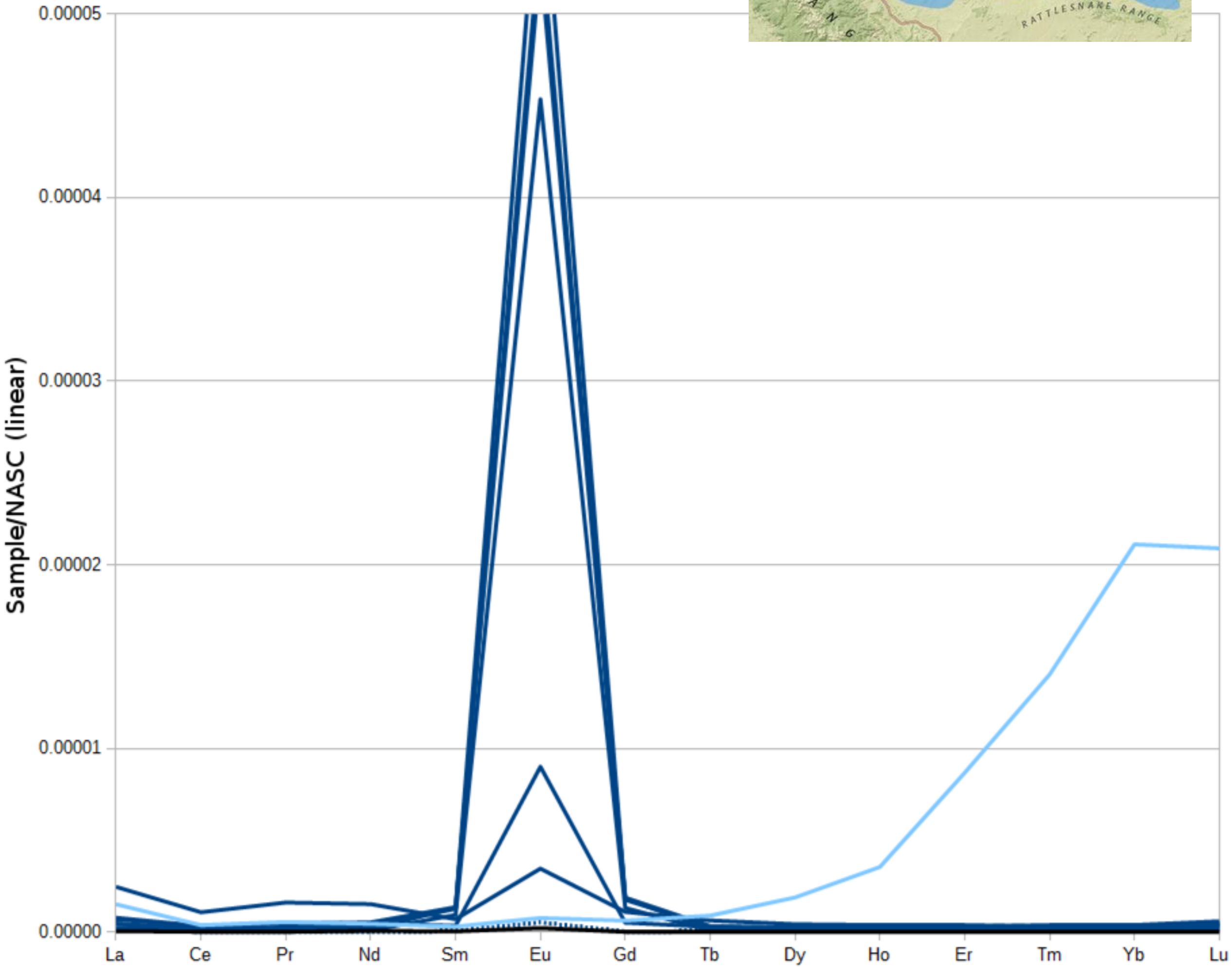




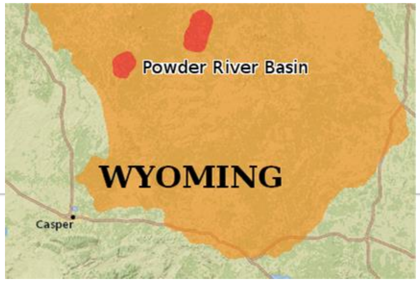
Basin REE

WRB:
175°C & 215°C

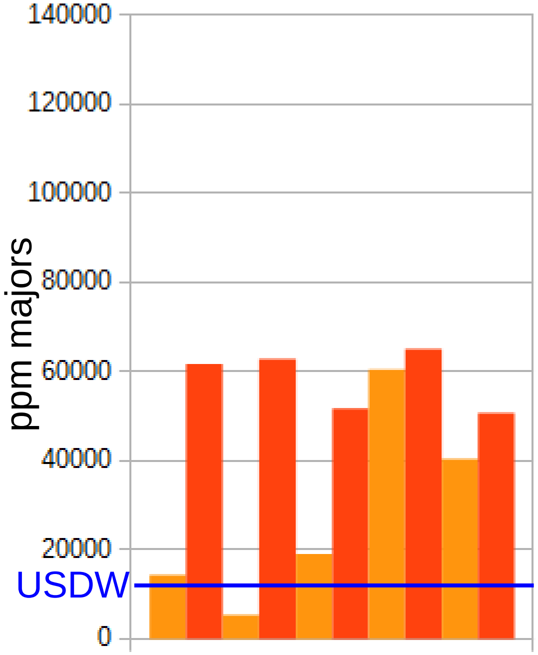


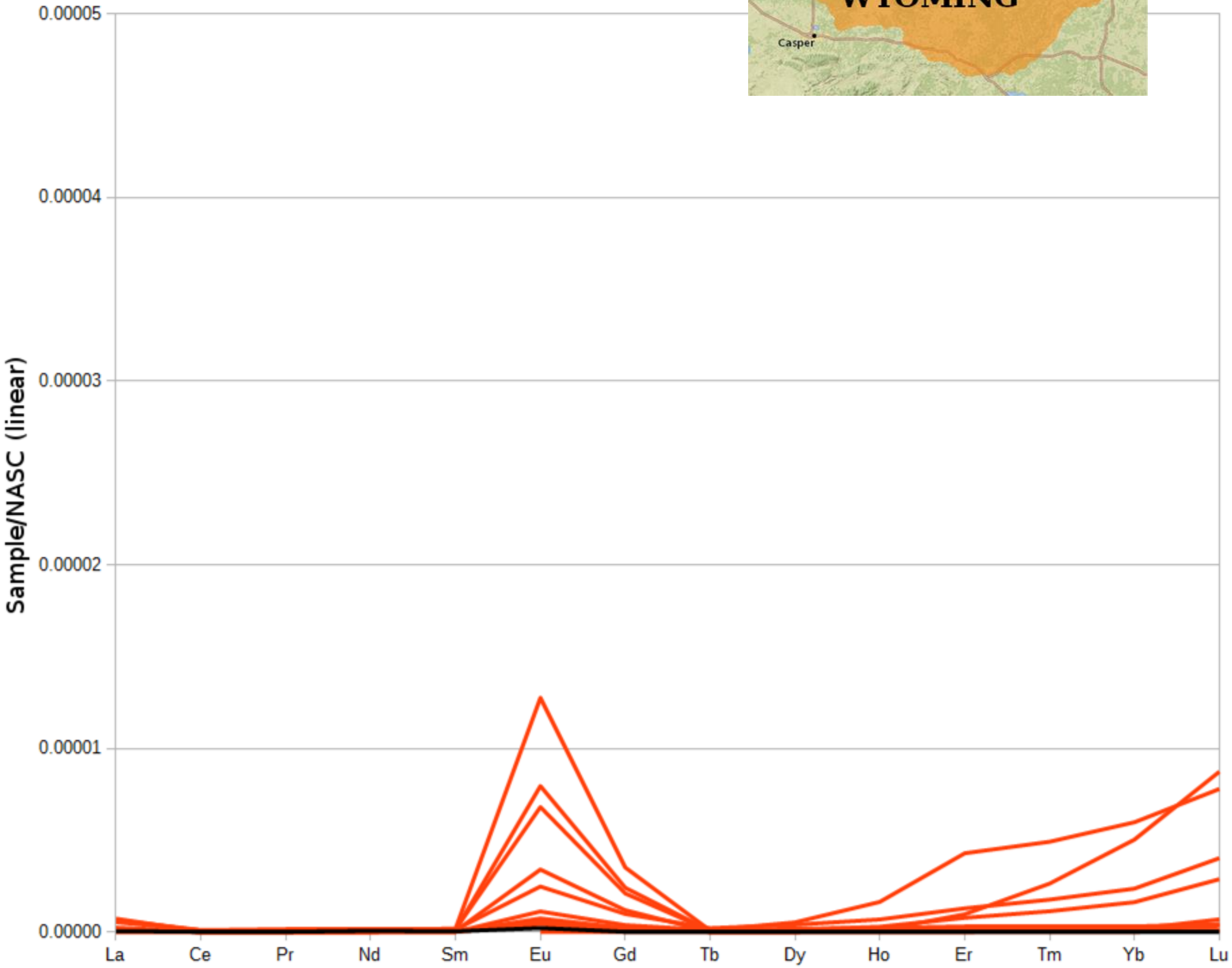


Basin REE



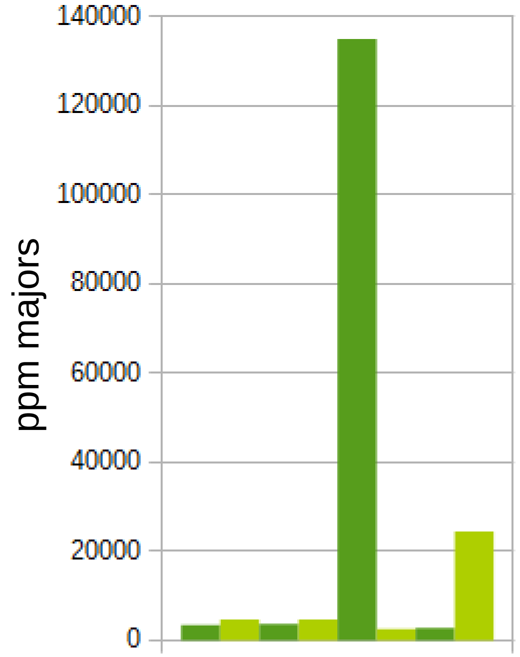
PRB:
115°C

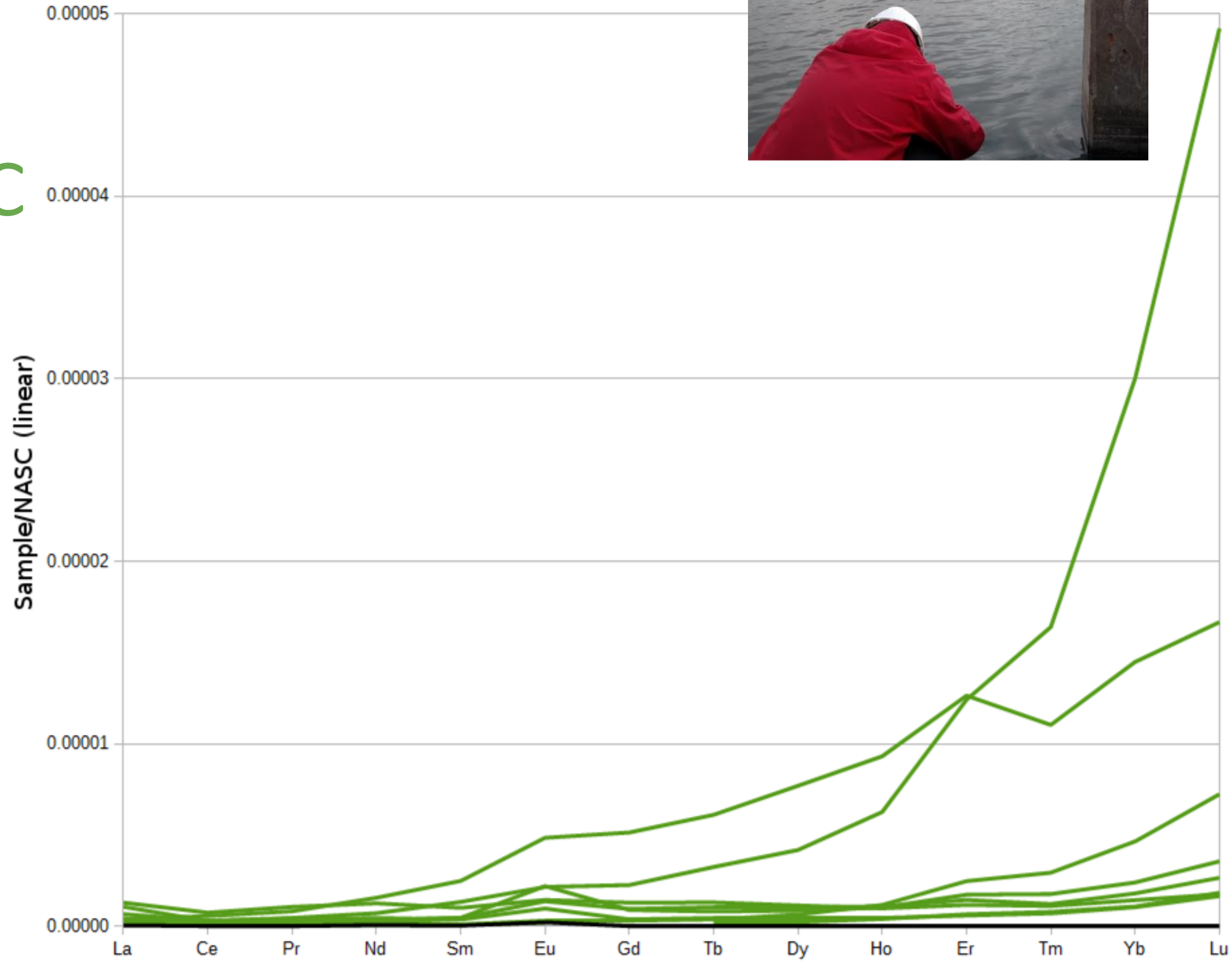




Basin REE

Ash-Ponds:
1270→300→20°C





Ligands

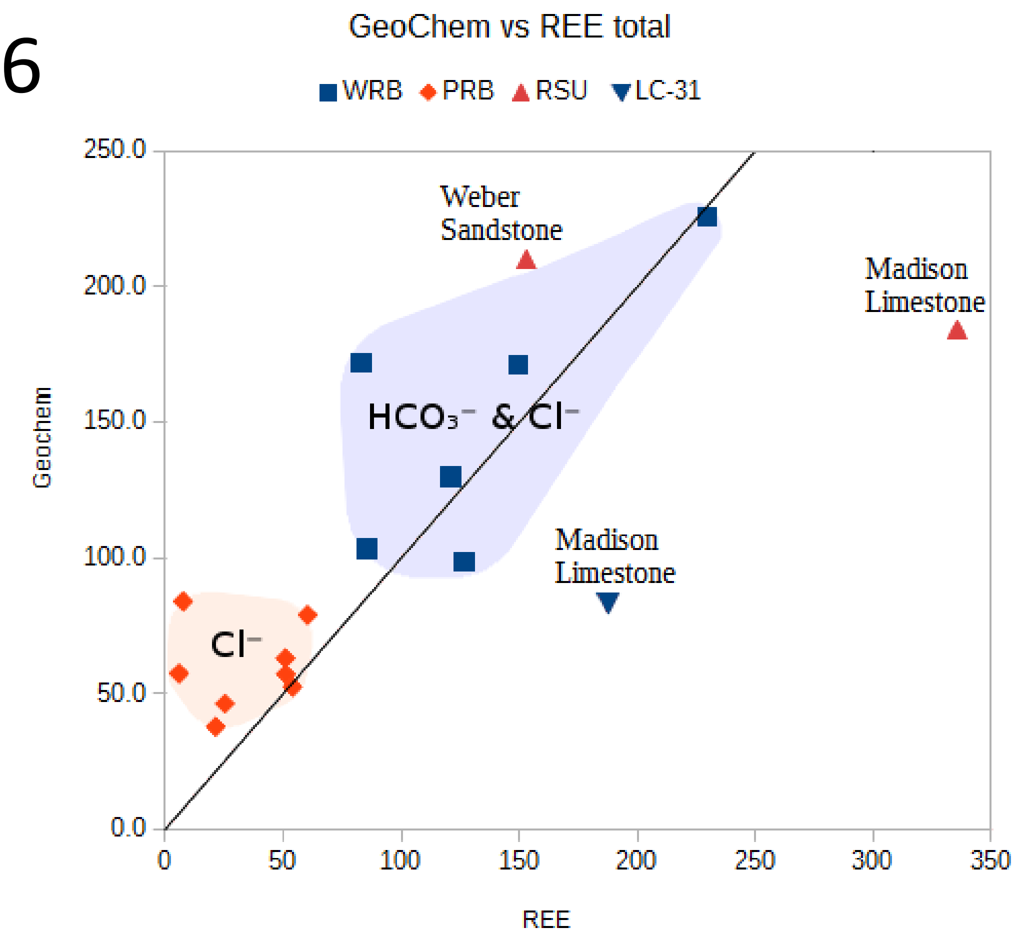
Migdisov et al 2016

ppm of:

Cl^- Br^- HCO_3^-

ppt of:

total REE



$$(0.05 \bullet Alk) + (0.01 \bullet Br) + (0.001 \bullet Cl) = R$$

Conclusions

REE exist in solution and can be measured

δO^{18} isotopes show prolonged rock interaction

Geothermal gradient may be high due to coal

Each study area has a unique signature:

Eu - WRB, Gd - PRB, HREE - Ash Ponds

Produced water have local HREE behavior

Total REE in wells may relate to ligands

Role of depositional environment

Acknowledgements

Funding sources:

DOE: EERE

State of Wyoming

Team Members:

THE UNIVERSITY OF WYOMING EQUALITY 1886

USGS science for a changing world

Carbon Management Institute

INL Idaho National Laboratory

Questions? Comments?

New project

More data collection

Guidance?

Ref

Chu, Steven.: Critical Materials Strategy, Department of Energy, Office of International Affairs, Washington, DC (2011). Accessed from: https://energy.gov/sites/prod/files/DOE_CMS2011_FINAL_Full.pdf (December, 2016)

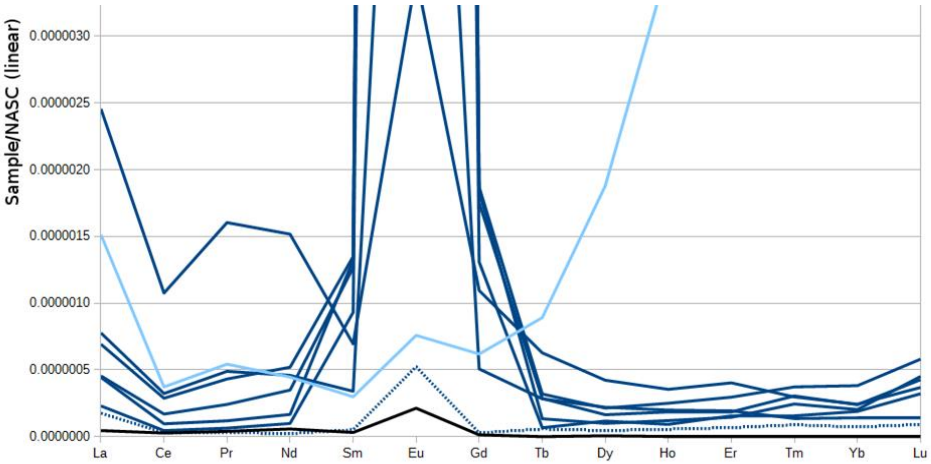
Clark, Ian, and Peter Fritz, 1997, Environmental isotopes in hydrogeology: Boca Raton, Fla., Lewis Publishers.

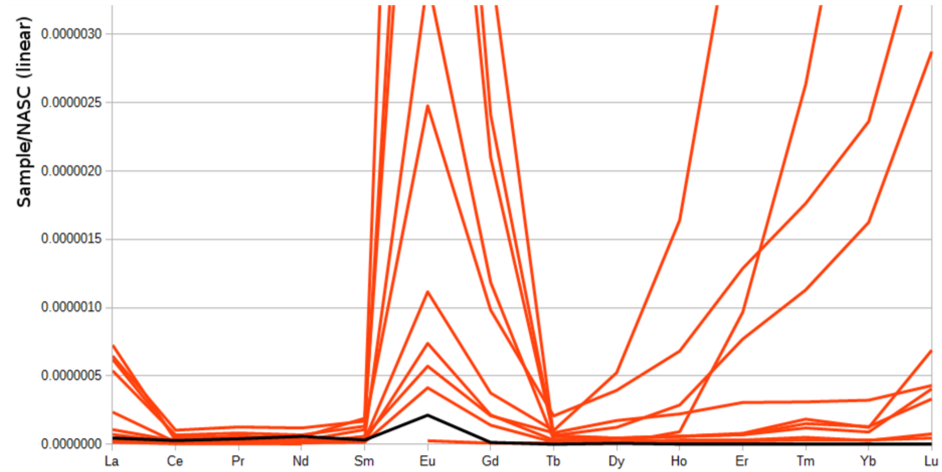
Hatje, Vanessa, Bruland K., and Flegal A. R.“Increases in Anthropogenic Gadolinium Anomalies and Rare Earth Element Concentrations in San Francisco Bay over a 20 Year Record” Environmental Science & Technology 2016 50 (8), 4159-4168 DOI: 10.1021/acs.est.5b04322

McLennan, S. M. (2001), Relationships between the trace element composition of sedimentary rocks and upper continental crust, Geochem. Geophys. Geosyst., 2, 1021, doi:10.1029/2000GC000109.

Migdisov A., A.E. Williams-Jones, J. Brugger, F.A. Caporuscio. (2016) Hydrothermal transport, deposition, and fractionation of the REE: experimental data and thermodynamic calculations. Chemical Geology, 439, pages 13–42. http://dx.doi.org/10.1016/j.chemgeo.2016.06.005

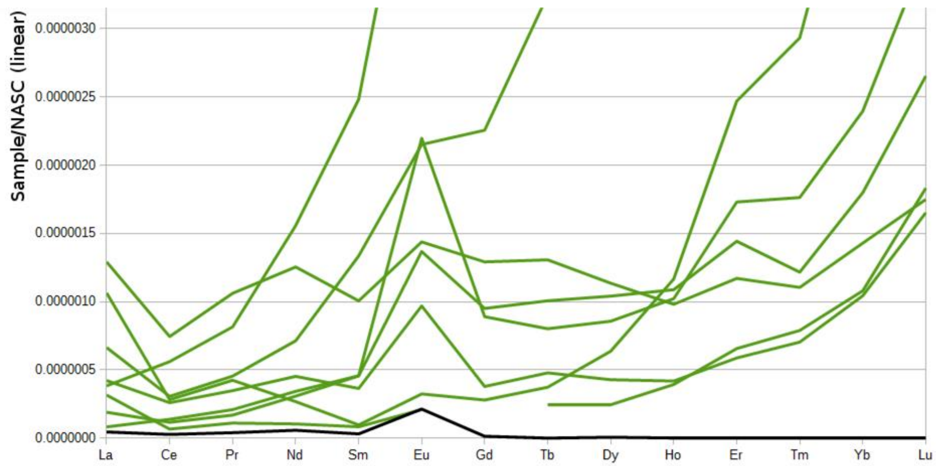
Detection Above Blank





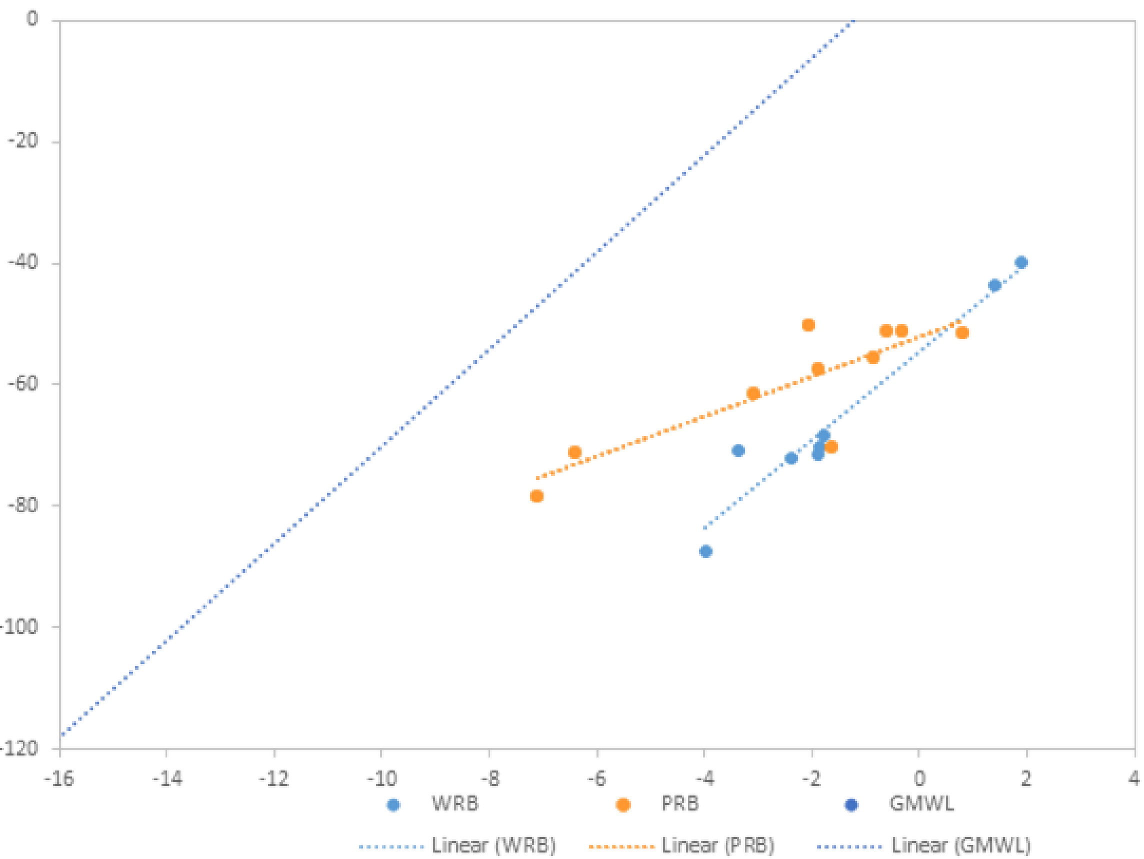
WRB

PRB



Power Stations

Isotopes from Water-Rock



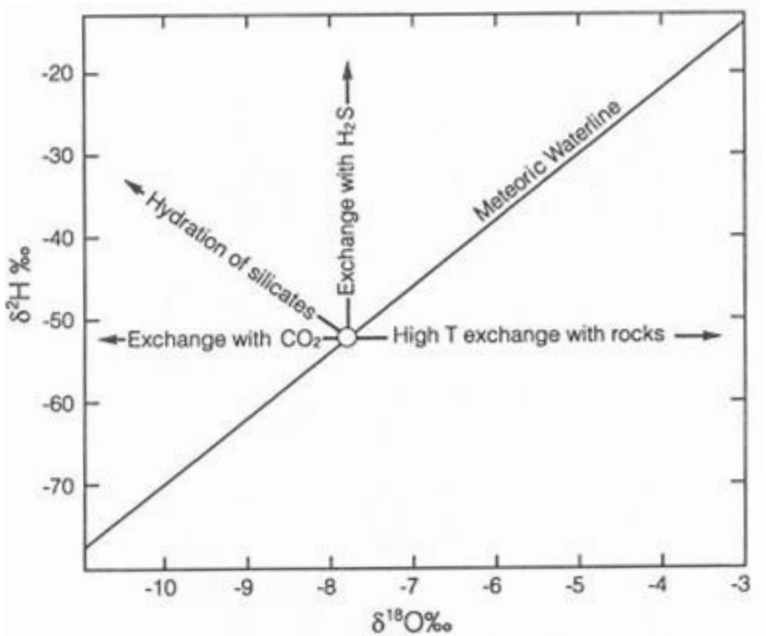
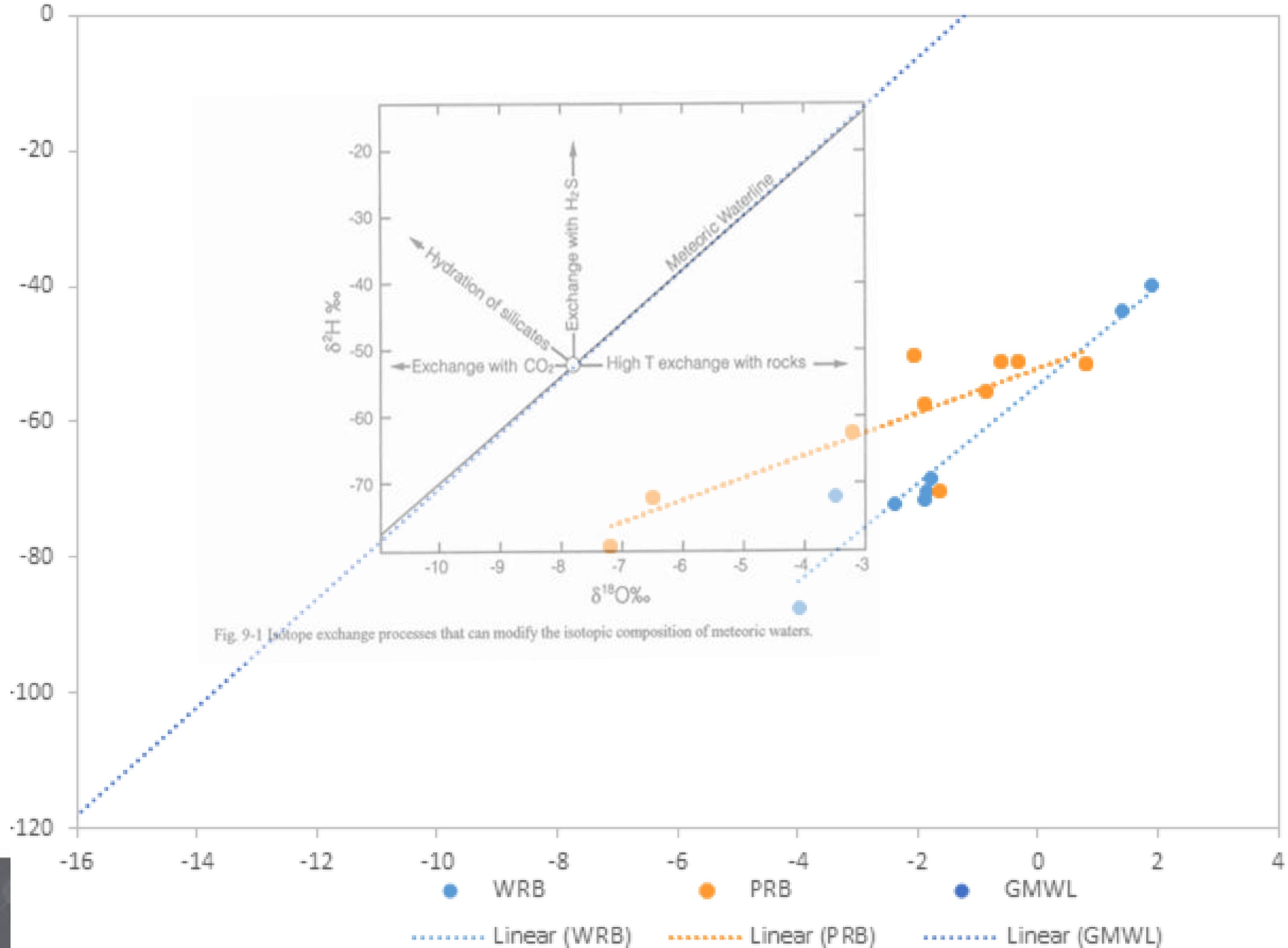


Fig. 9-1 Isotope exchange processes that can modify the isotopic composition of meteoric waters.

Isotopes from Water-Rock



Complex Transport

In Power stations the REEs may move with SO4 or OH? (basic)

In Produced waters the REEs may move with Cl or (Bi)Carbonate (neutral acid)

LOW TDS Brine
[<4.5 g/L]

AG 50W-X8 Resin

Column (Re)generation
Water, Concentrated Acid, Water

Sample Chromatography
Gravity flow

Elution of Mono/dia-valent Cations
Dilute acid wash, Water rinse

Elution of REEs
Concentrated acid wash

Analysis by ICP-MS

High TDS Brine
[4.5-300 g/L]

Chelex-100

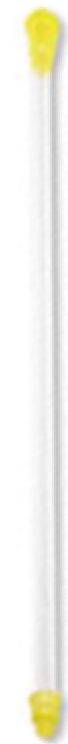
Column (Re)generation (for 25 mL Chelex)
Water, Acid, Water, Ammonia

Sample Chromatography
pH adjustment, Gravity flow

Elution of Mono/dia-valent cations
Multi-stage water and ammonia washes

Elution of REEs
Multi-stage acid wash

Analysis by ICP-MS



Brine Sample

LOW TDS Brine
[<4.5 g/L]

AG 50W-X8 Resin
[200-400 mesh, volume based on sample size, TDS, and major cations]

Column (Re)generation
[50 mL nano-pure water, 8 M Optima HNO_3 (5 x resin volume), 50 mL nanopure (NP, 18 MOhm-cm) water]

Sample Chromatography
[sample passed through column, gravity flow]

Elution of Mono/dia-valent Cations
[2.5 M HNO_3 (8 x resin volume), 50 mL nano-pure water]

Elution of REEs
[8.0 M HNO_3 (4 x resin volume), 25 mL nano-pure water]

Evaporation to Dryness
[on a 100 deg C hot plate]

Dissolution
[5 mL 1% HNO_3]

Analysis by ICP-MS

High TDS Brine
[4.5-300 g/L]

Chelex-100
[200-400 mesh, volume based on sample size and TDS]

Column (Re)generation (for 25 mL Chelex)
[50 mL NP water, 25 then 50 mL 2.5 M HNO_3, 25 then 50 mL NP water, 25 then 50 mL 2.0 M Optima ammonia, NP water until effluent pH is near neutral (7-8)

Sample Chromatography
[ammonium acetate added (@0.985 g/100 mL) sampleadjusted to pH 5.3-5.4 (with ammonia and HNO_3), gravity flow]

Elution of Mono/dia-valent cations
[50 then 25 mL NP water, two 50 then one 100 mL 1.0 M ammonia, 50 mL then 25 mL NP water]

Elution of REEs
[One 50 mL then two 5 mL 2.5 M HNO_3, 25 mL NP water]

Evaporation to Dryness
[on a 100 deg C hot plate]

Dissolution
[5 mL 1% HNO_3]

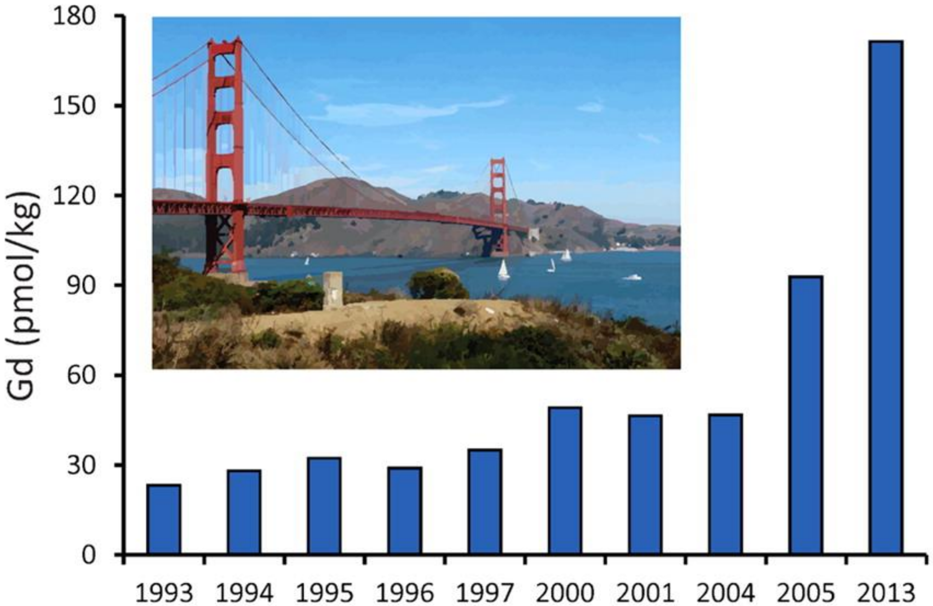
Analysis by ICP-MS

Isotopes: δC^{13}

Show Formation even though REEs don't

Gd and MRI

Gd in near-city waters can indicate Hospitals with MRIs …. but….



No hospitals 75ma (rock) nor even ~2ka (water)

Recycled frac/mud?