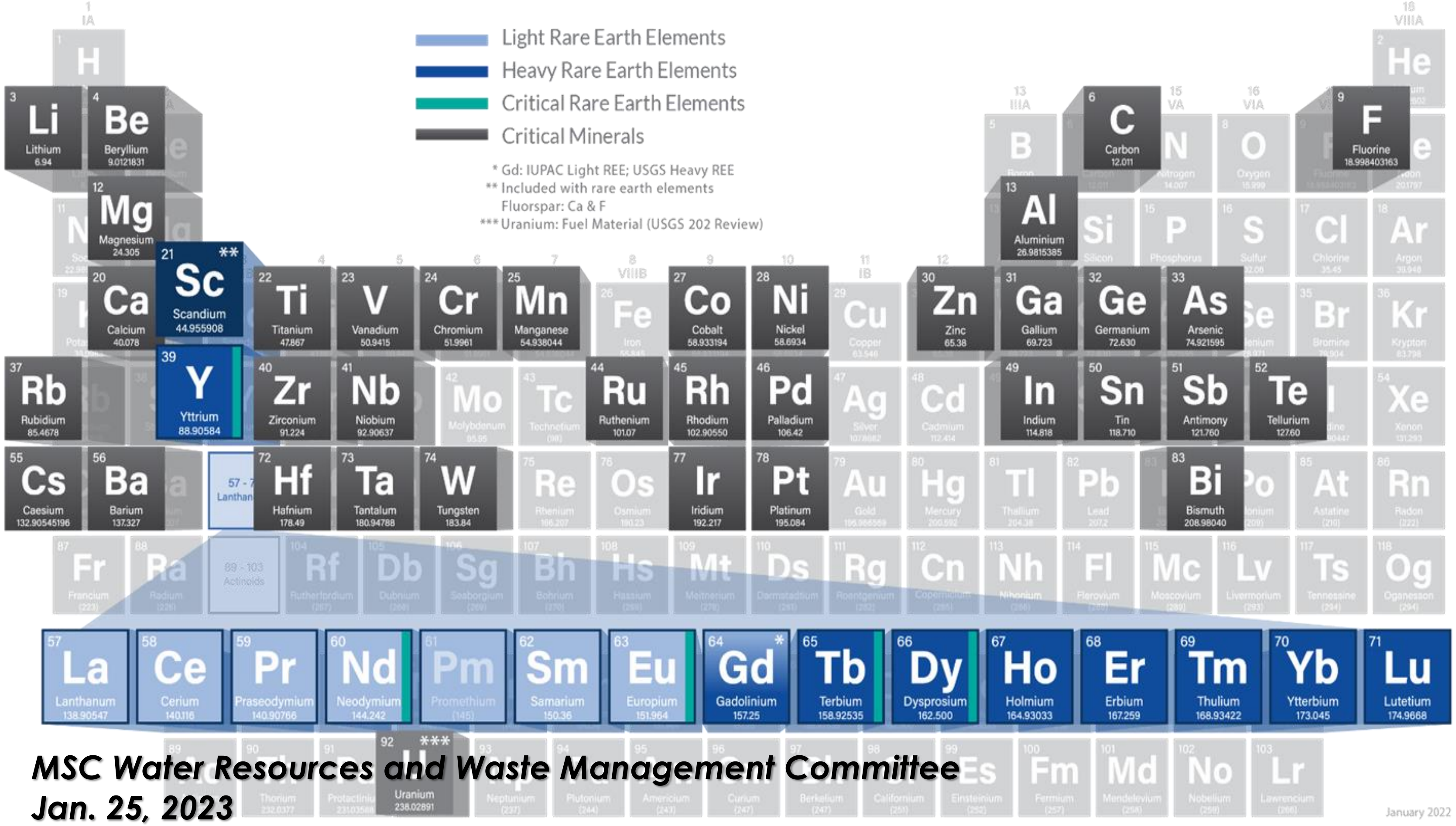
Lithium Resources from Oilfield Produced Water

Justin Mackey
NETL Support Contractor



Produced Water from Marcellus shale and Midland basin.

MSC Water Resources and Waste Management Committee
Jan. 25, 2023

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Lithium Resources

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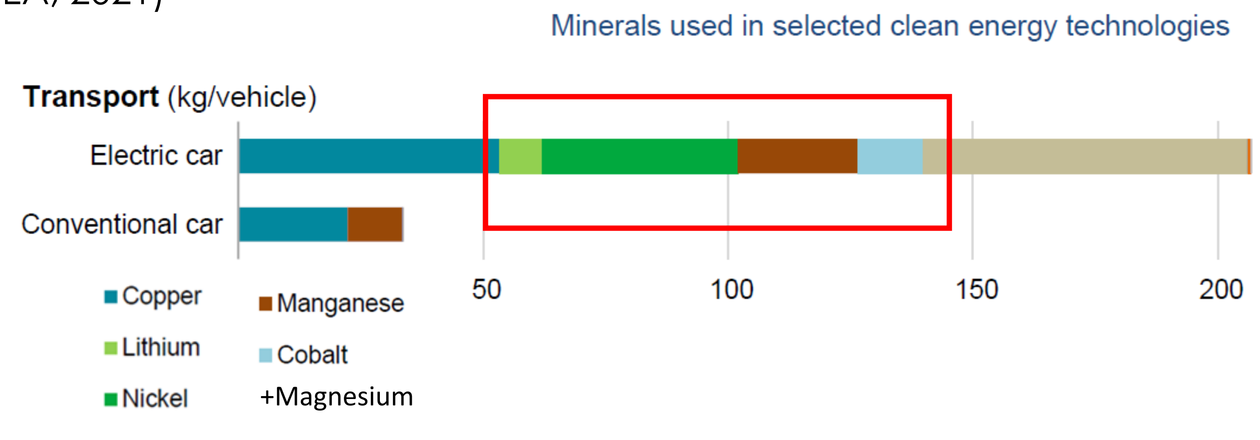
- **U.S. Energy Act 2020 -** Critical minerals are non-fuel mineral or mineral material essential to the economic or national security of the U.S. and which have a supply chain vulnerable to disruption.
- Elements to **fuel future energy technologies.**
- **DOE's Dynamic Dozen** (Co, Dy, Ga, Ge, C, Ir, Li, Mn, Nd, Ni, Pt, Pr).

Table 1. 2022 Final List of 50 Critical Minerals from U.S. Geological Survey, Department of the Interior (https://www.federalregister.gov/d/2022-04027)

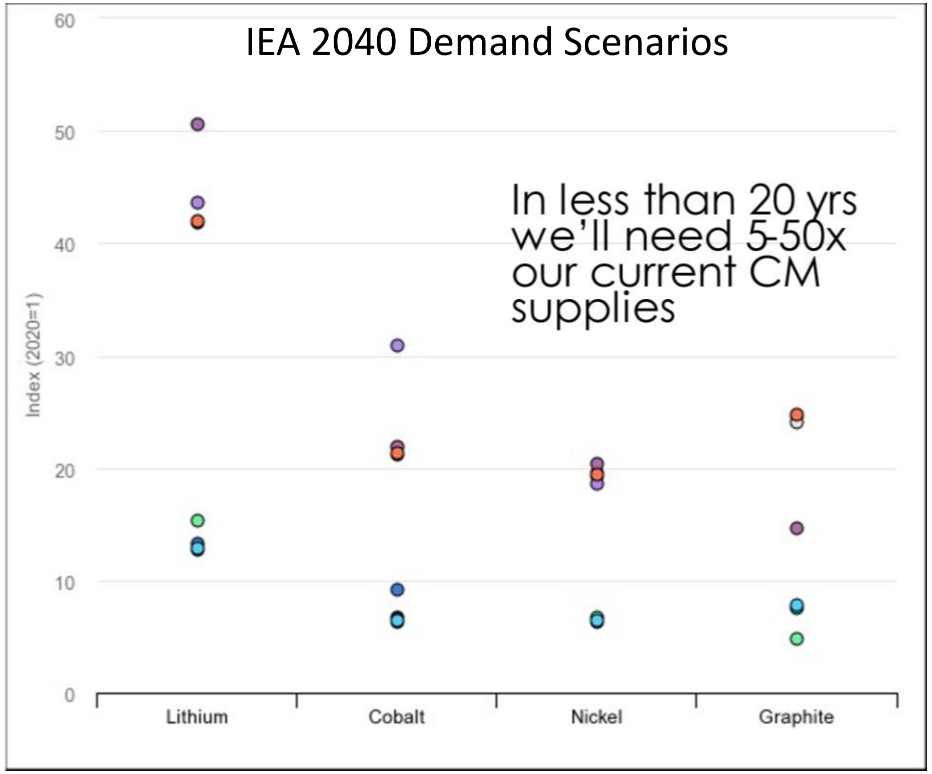
Element name	Element symbol	Element name	Element symbol
Aluminum	Al	Magnesium	Mg
Antimony	Sb	Manganese	Mn
Arsenic	As	Neodymium *	Nd
Barite (barium)	Ba	Nickel	Ni
Beryllium	Be	Niobium	Nb
Bismuth	Bi	Palladium	Pd
Cerium*	Ce	Platinum	Pt
Cesium	Cs	Praseodymium *	Pr
Chromium	Cr	Rhodium	Rh
Cobalt	Co	Rubidium	Rb
Dysprosium *	Dy	Ruthenium	Ru
Erbium *	Er	Samarium *	Sm
Europium *	Eu	Scandium *	Sc
Fluorspar (Fluorite)	CaF_2	Tantalum	Ta
Gadolinium *	Gd	Tellurium	Te
Gallium	Ga	Terbium *	Tb
Germanium	Ge	Thulium *	Tm
Graphite (carbon)	C	Tin	Sn
Hafnium	Hf	Titanium	Ti
Holmium *	Ho	Tungsten	W
Indium	In	Vanadium	V
Iridium	Ir	Ytterbium *	Yb
Lanthanum *	La	Yttrium *	Y
Lithium	Li	Zinc	Zn
Lutetium *	Lu	Zirconium	Zr

Critical Minerals & Produced Water

(IEA, 2021)



(IEA, 2021)



- These elements make up ~50% of batteries for electric vehicles.
    - U.S. automotive supply chains need to transition to domestic sources for battery materials for tax credits.
- Current lithium demand ~2,000 metric tonnes/yr.

IEA (2021), The Role of Critical Minerals in Clean Energy Transitions, IEA, Paris https://www.iea.org/reports/the-role-of-critical-minerals-in-clean-energy-transitions, License: CC BY 4.0

Five-Year Field Samples and New Findings

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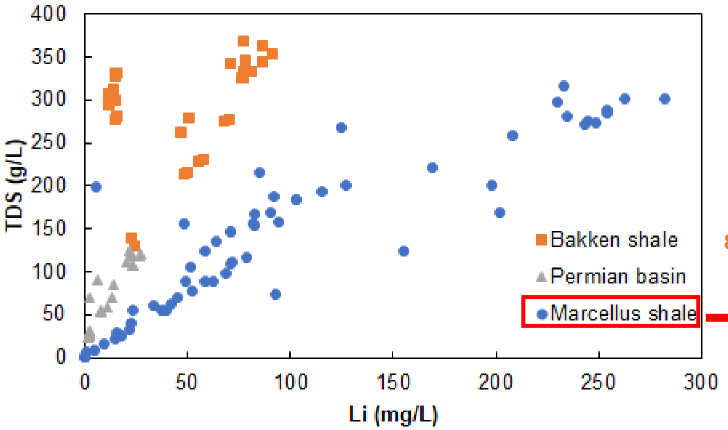
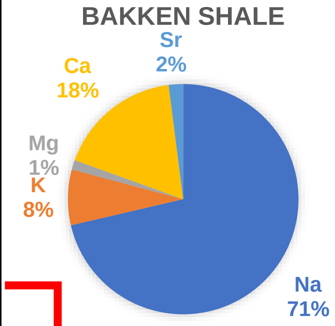
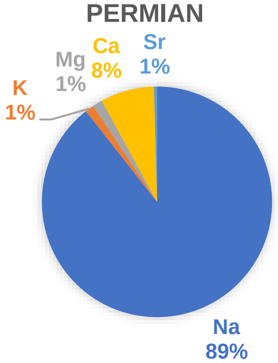
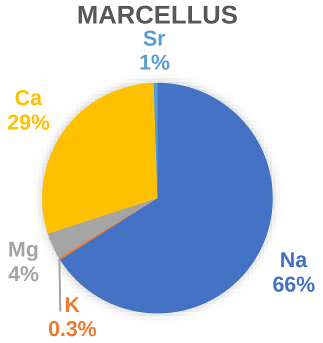
500 Samples: Bakken Shale[1]: ~30/yr; Permian Basin EOR Oil Field[2]: ~30/Yr; Marcellus Shale: ~200[3]

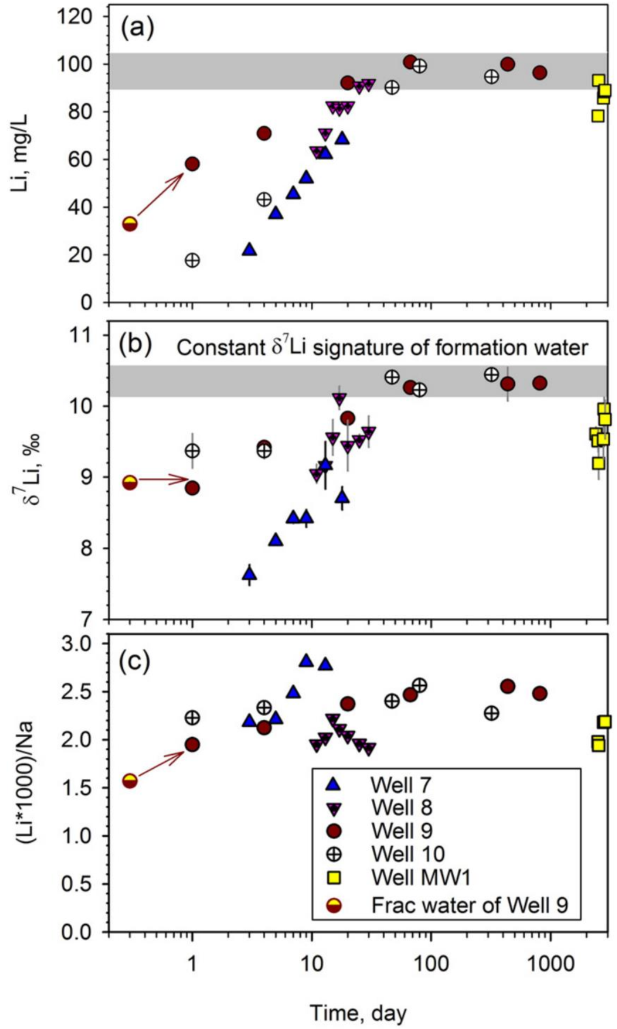
- Up to 300 mg/L Li was found in Marcellus shale produced waters, comparable to the dominant source of Li mining, the brine ponds in Chile (1000 mg/L).
- At the same total dissolved solids (TDS) level, Marcellus shale waters contain more Li compared to Bakken shale and Permian basin waters.
- Marcellus shale brine contain high percentages of Ca and Mg, whereas Permian basin brine contain up to 89% Na.











1: Tinker, K., J. et al., (2020). Frontiers in microbiology 11(1781).
2: Gardiner, J., et al. (2020). Applied Geochemistry 121: 104688.
3: Phan, T. T., et al. (2016). Chemical Geology **420**: 162-179.

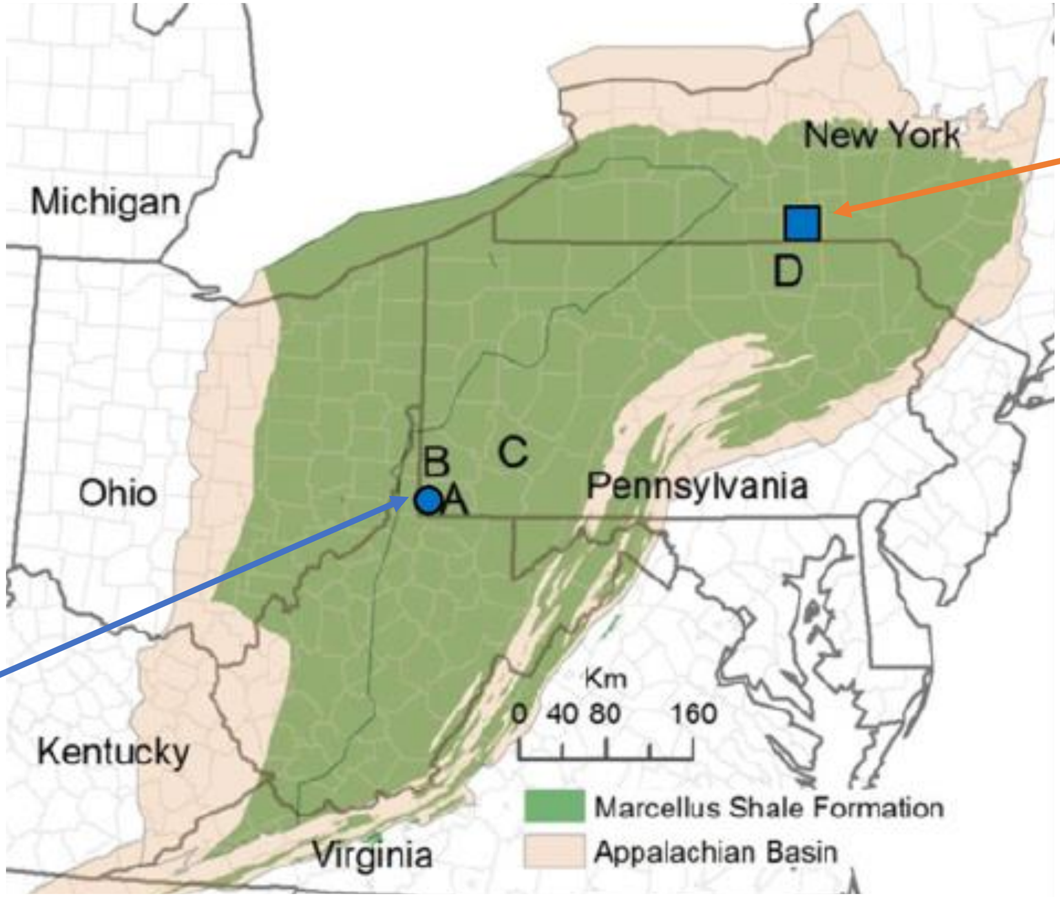
Li Data in Marcellus Shale Produced Waters

Phan, T. T., et al. (2016). Chemical Geology **420**: 162-179

- ***Clay minerals are the main sources of Li in organic-rich shale rock***
- ***Li-rich formation water resulted from long-term alteration of volcanogenic ash***

Southwestern PA

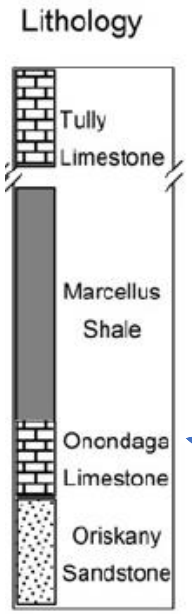
- ***Shale rock Li: 36-48 mg/kg***
- ***Li concentration: 18-233 mg/L***



Produced water samples are from Greene Co., (A),Washington Co. (B), Westmoreland Co. (C), and Tioga Co., PA (D).
Core samples are from Greene Co, PA (blue circle); and dry-drilled rock cuttings from Tioga Co., NY (blue square).

North-Central PA and NY

- ***Shale rock Li: 19-85 mg/kg***
- ***Li concentration: 169-282 mg/L***



Tioga ash layer and other ash layers

Other Influences?

- Depth appears to influence bulk lithium concentration in NY but not in PA.
- Silicate weathering and clay alteration increases lithium concentrations.
- Poor exchangeable affinity due to cation exchange.

Steinhoefel et al./ Geochimica et Cosmochimica Acta 295 (2021) 155–177

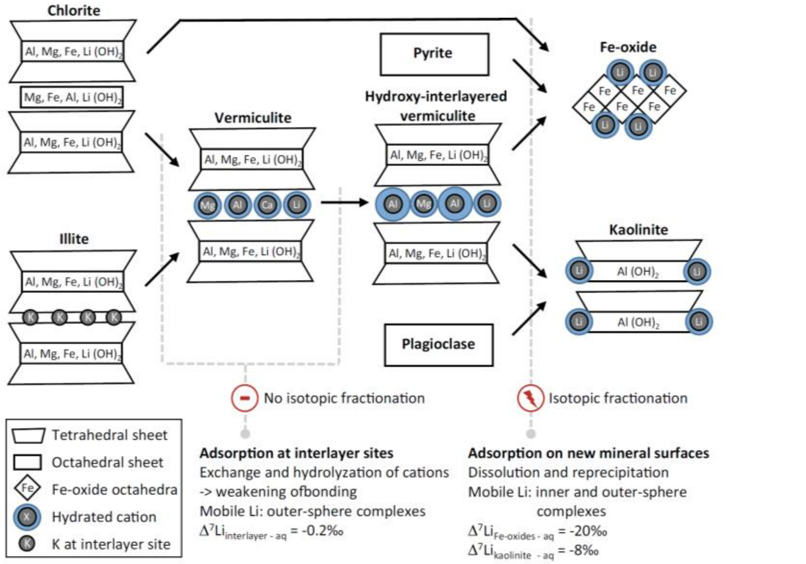
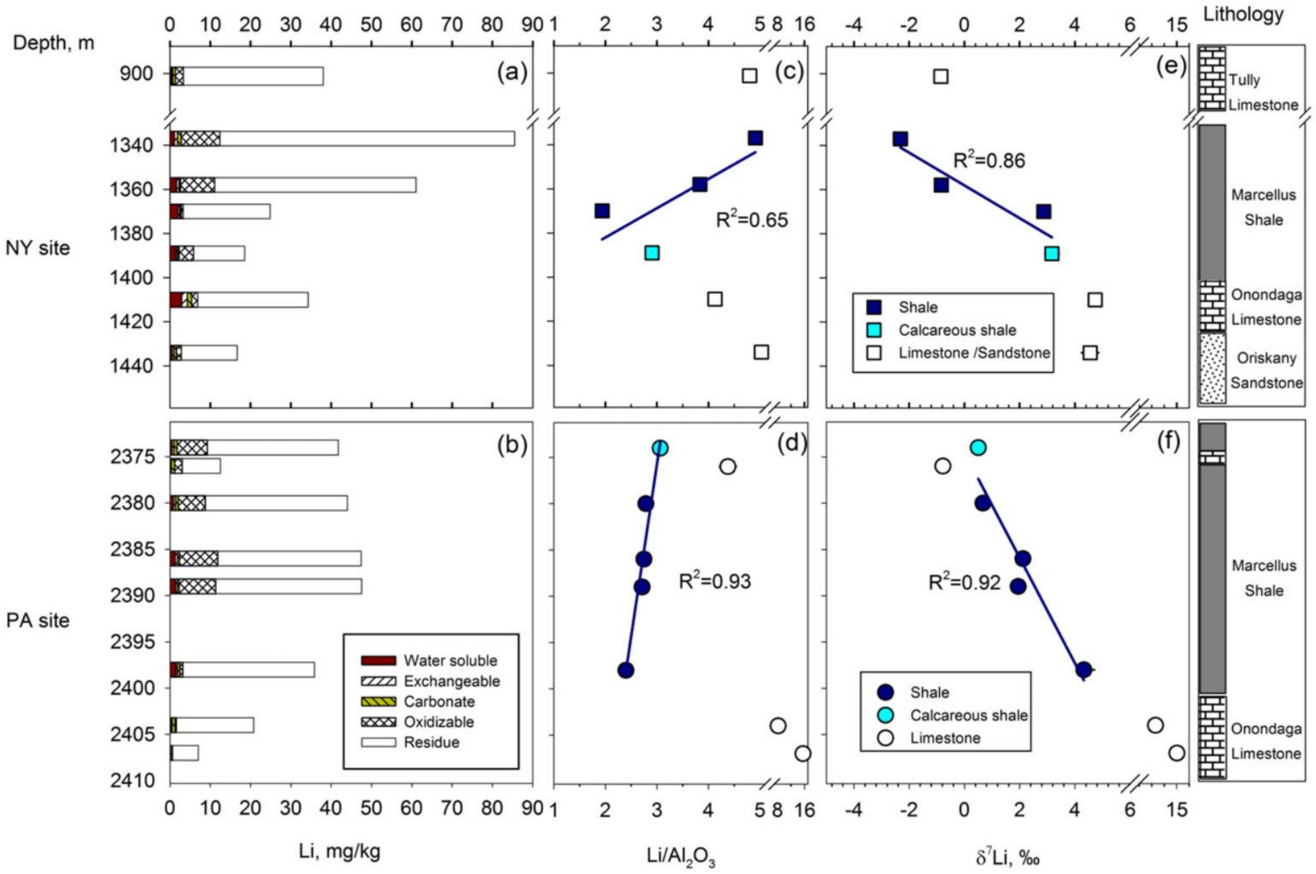


Fig. 5. Schematic illustration of clay transformation and secondary mineral precipitation processes in SSHCZO, which affect Li isotopic fractionation. Isotopic fractionation factors are from Hindshaw et al. (2019a), Li and Liu (2020) and Wimpenny et al. (2010).

T.T. Phan et al. / Chemical Geology 420 (2016) 162–179



Phan, T. T., et al. (2016). Chemical Geology **420**: 162-179

U.S. Produced Water Volumes

U.S. Produces ~2.8 billion gallons of produced water a day[1]

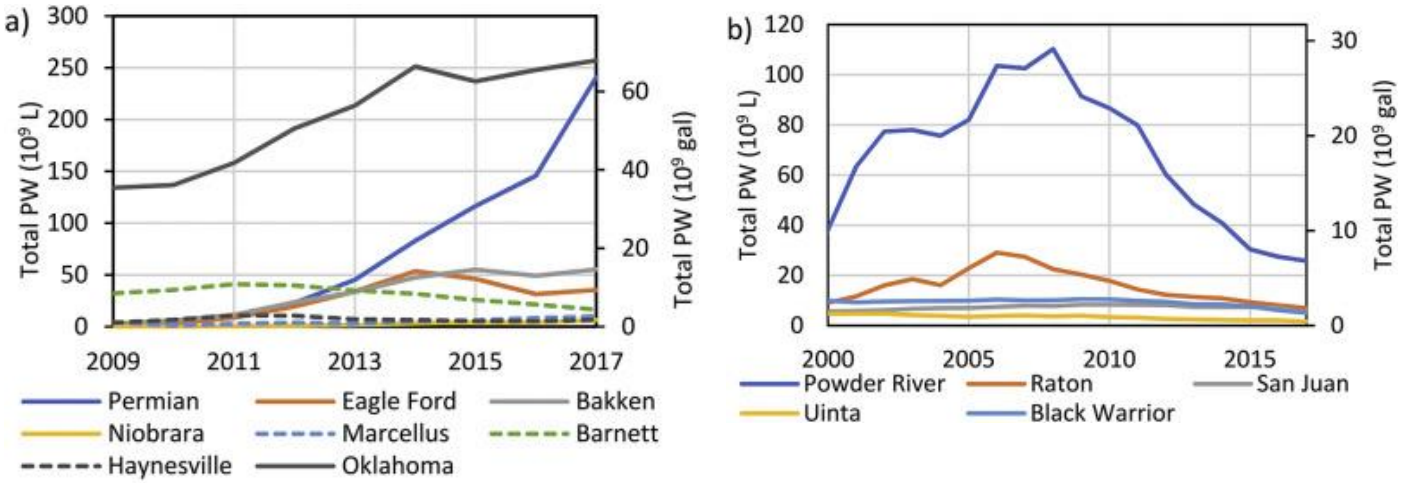


Fig. 1. Time series of produced water (PW) volumes for a) the major tight oil and shale gas plays, and b) the coal bed methane plays. Data for Oklahoma represent statewide values. [2]

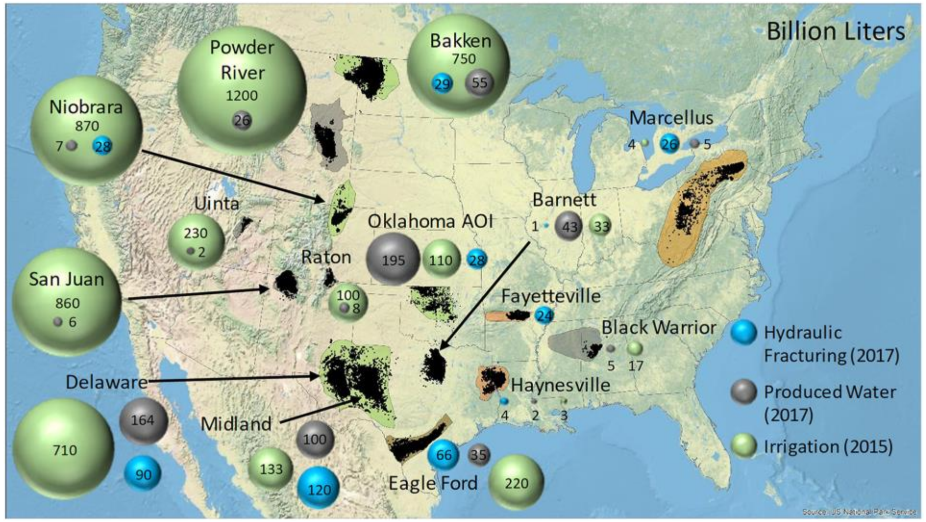


Fig. 2. Comparison of water demand for irrigation (2015), produced water volumes and hydraulic fracturing water demand (2017) for shale oil and gas reservoirs and coal bed methane reservoirs. [2]

Table 1. Formation types[2], PW volumes (2017)[2], projected PW volume[2] and TDS range[3] for samples assessed in current study

Formation	Bakken	Eagle Ford	Permian (Midland)	Permian (Delaware)	Marcellus	Niobrara	Haynesville	Oklahoma AOI	Powder River	San Juan	Black Warrior	Raton	Uinta
Type	Tight oil	Tight oil	Tight oil	Tight oil	Shale gas	Tight oil	Shale gas	Tight oil	Coal bed methane	Coal bed methane	Coal bed methane	Coal bed methane	Coal bed methane
PW Volume 2017 (10^9 L) [2]	54.6	35.1	100.3	164.2	5.3	6.7	2.2	195.3	26.1	5.7	4.9	7.8	1.7
Projected PW volume (10^9 L) (& remaining years) [2]	2,500 (64)	1,100 (26)	9,900 (47)	39,400 (80)	2,200 (73)	-	-	-	-	-	-	-	-
TDS range (calc), mg/L [3]	106,000-313,000	85,000-97,000	69,000-175,000	118,000-261,000	55,000-162,000	13,400-51,300	154,000-254,000	106,000-214,000	700-1600	6,000-22,000	2,800-52,000	500-3,000	5,000-27,000

1. Veil, John. "US produced water volumes and management practices in 2017." *Groundwater Protection Council* (2020).
2.: Scanlon, B.R., Reedy, R.C., Xu, P., Engle, M., Nicot, J.P., Yoxtheimer, D., Yang, Q., Ikonnikova, S., 2020. Can we beneficially reuse produced water from oil and gas extraction in the U.S.? Science of The Total Environment 717, 137085.
3. TDS Calculated from: Blondes, M.S., Gans, K.D., Engle, M.A., Kharaka, Y.K., Reidy, M.E., Saraswathula, V., Thordsen, J.J., Rowan, E.L., and Morrissey, E.A., 2018. U.S. Geological Survey National Produced Waters Geochemical Database (ver. 2.3, January 2018), U.S. Geological Survey data release.

Critical Mineral Concentration in U.S. PW

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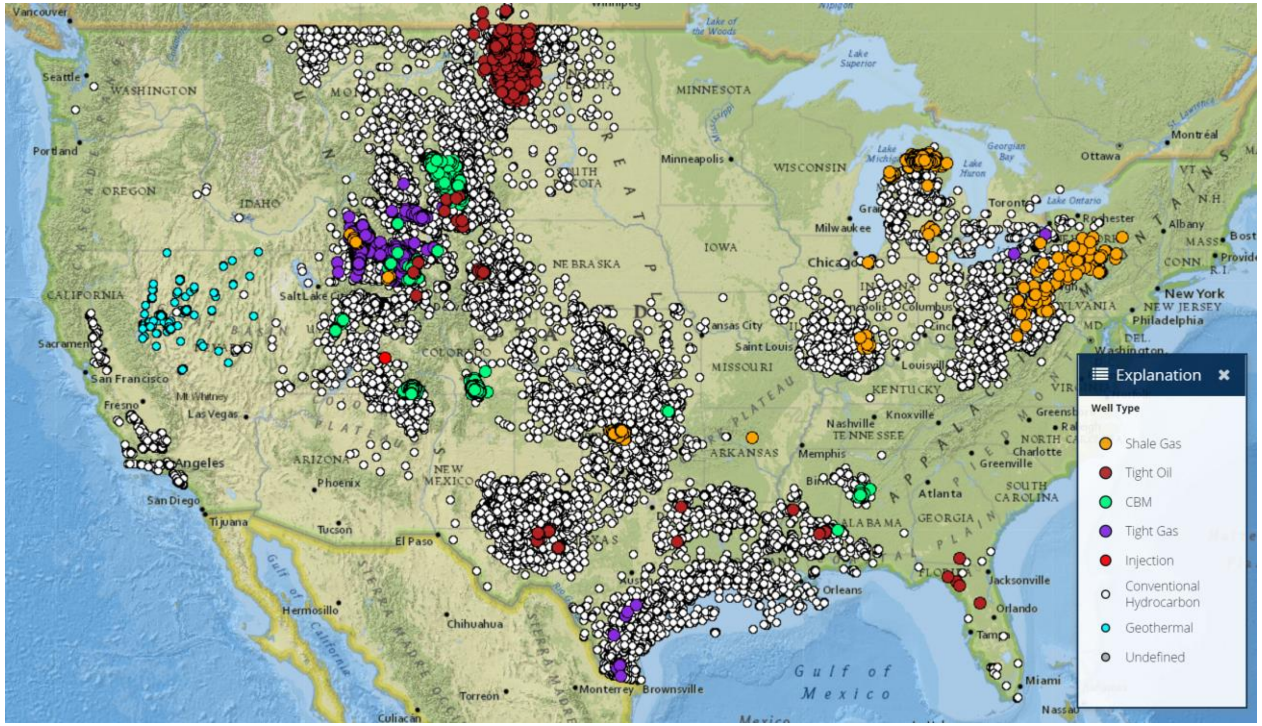
Compile critical mineral (CM) concentration data with production water volumes to **quantify critical mineral resource potential across U.S. regions**.

Identify **opportunities** and **highlight limitations/data gaps** for the development of produced water as a source of critical minerals.

- U.S. Geological Survey National Produced Waters Geochemical Database (ver. 2.3, January 2018)[1]
  - Data filtered for basin/formation of interest
  - Excluded data with charge balance greater than ±20%
  - Excluded top and lower quartiles of TDS data for each formation/basin
- [CM] x annual PW volume = {CM} metric tonne/yr



Spatial map of USGS NPWGD sample locations (https://eerscmap.usgs.gov/pwapp/)

1. Blondes, M.S., Gans, K.D., Engle, M.A., Kharaka, Y.K., Reidy, M.E., Saraswathula, V., Thordsen, J.J., Rowan, E.L., and Morrissey, E.A., 2018. U.S. Geological Survey National Produced Waters Geochemical Database (ver. 2.3, January 2018), U.S. Geological Survey data release.

This analysis is for **domestic raw material supply**. Some U.S. supply chain sensitivity is because of CM refinement, which is not addressed in this study.

Resource Abundance Estimate

Compounding this effort - We need more statistically robust figures to make these estimates.

		Alk	Al	NH_4	Ba	Br	Ca	Cl	Fe	Fe(dis)	Li	Mg	Mn	K	Na	Sr	SO_4	TDS	pH
	26r data (mg/L)																		
n=457	mean	71	1	113	7531	753	11676	89033	127	83	189	918	8	982	34498	3698	9	162802	5.89
	1st quartile	45	0	79	5270	435	6020	56200	89	67	142	500	5	978	23100	2123	5	104000	5.70
	3rd quartile	107	2	188	11800	1320	25200	148000	175	117	265	1863	12	986	54100	6748	7	263000	6.20
	USGS data (mg/L)																		
n=183	mean	107	115	0	1109	770	9269	71709	55		73	878	5	217	29372	1659	43	120634	6.27
	1st quartile	66	71	0	583	498	6136	51900	33		52	603	3	222	21400	1118	33	87800	5.90
	3rd quartile	190	215	1	3386	1166	14800	102000	128		98	1490	9	440	39810	2890	62	169000	6.60

Estimates calculated from waste reports would yield ~2.5 times the resources in place than calculated with existing published data.

Measurement Matters!

Lithium, Li

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Import Sources (2017-2020): Argentina, 54%; Chile, 37%; China, 5%; Russia, 3%; and other, 1%

Li Uses: Electric vehicles, battery storage, ceramics, glass

2021 Consumption : 2,000 metric tonne/yr

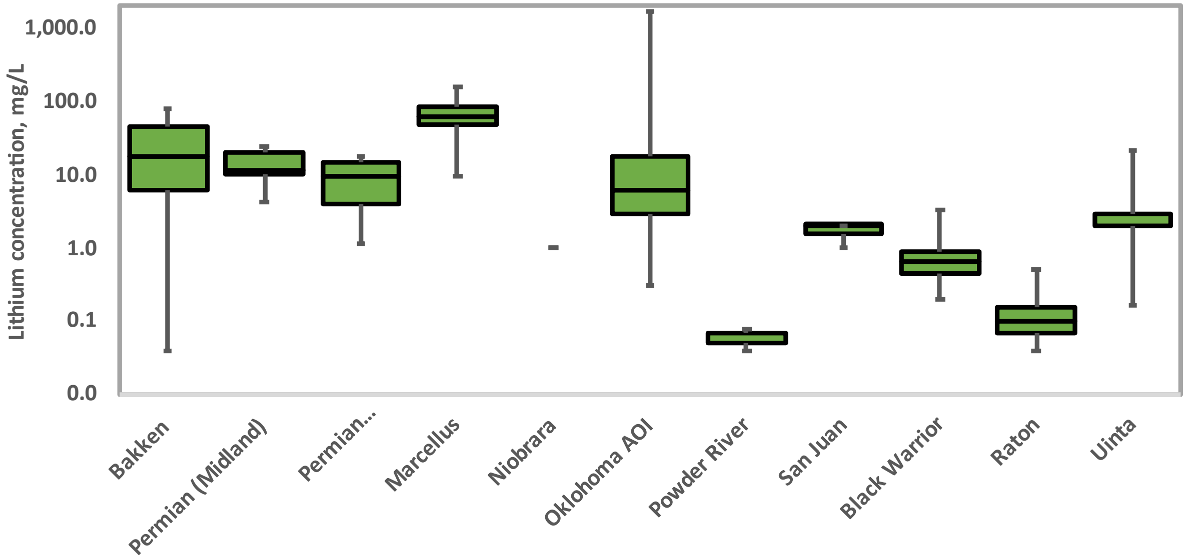


Fig. 1. Lithium concentration in U.S. major oil and gas formations and coal bed methane basins calculated from USGS Produced waters database (Blondes et al.. 2018).

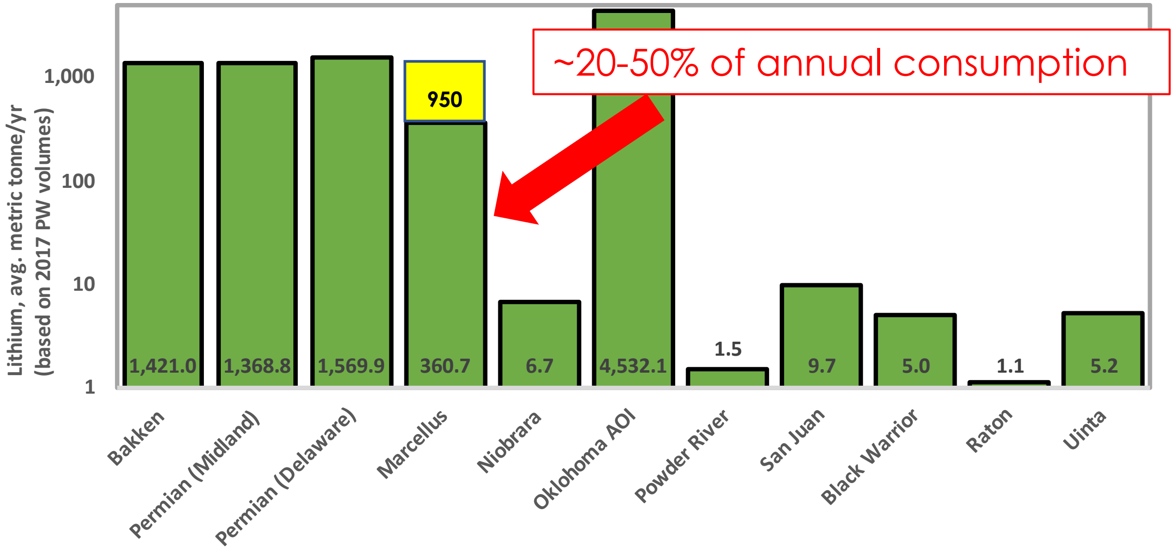


Fig. 2. Lithium resource potential from U.S. major oil and gas formations and coal bed methane basins. Resource potential in tonne/year was calculated using 2017 PW volumes from Scanlon et al. (2020) and average Li concentration (mg/L) calculated from USGS Produced waters database (Blondes et al., 2018).

Table1: Li concentration (average) and number of samples

Formation	Bakken	Eagle Ford	Permian (Midland)	Permian (Delaware)	Marcellus	Niobrara	Haynesville	Oklahoma AOI	Powder River	San Juan	Black Warrior	Raton	Uinta
Avg. Li concentration, mg/L	26.0	n/a	13.6	9.6	68.1	1.0	n/a	23.2	0.1	1.7	1.0	0.15	3.1
# Li samples	22	0	16	10	106	2	0	172	9	3	6	6	109

Lithium, Li

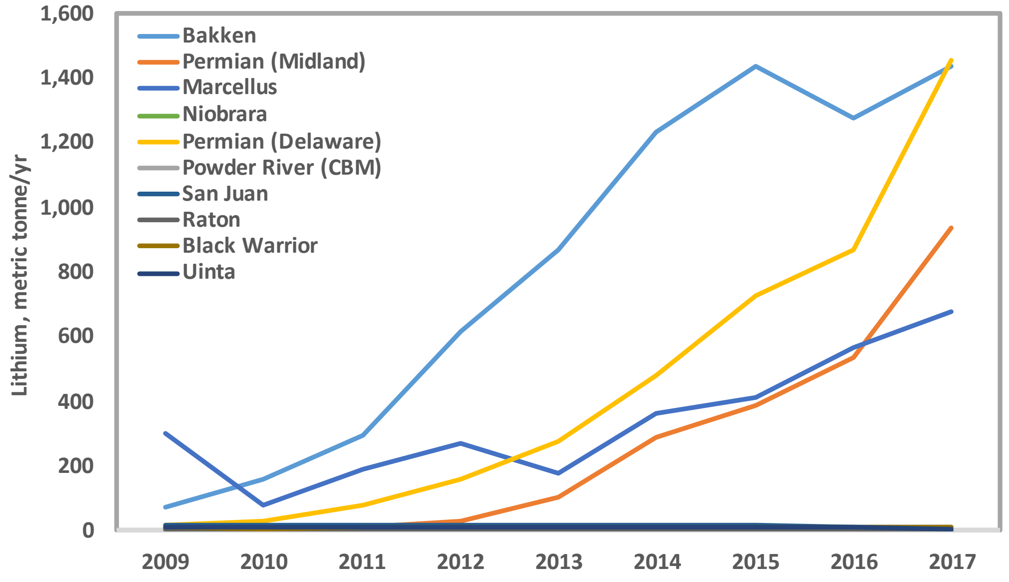


Fig. 1. Time series of lithium resource potential calculated from PW volumes presented by Scanlon et al. (2020) and average Li concentration from USGS PW database (Blondes et al., 2018).

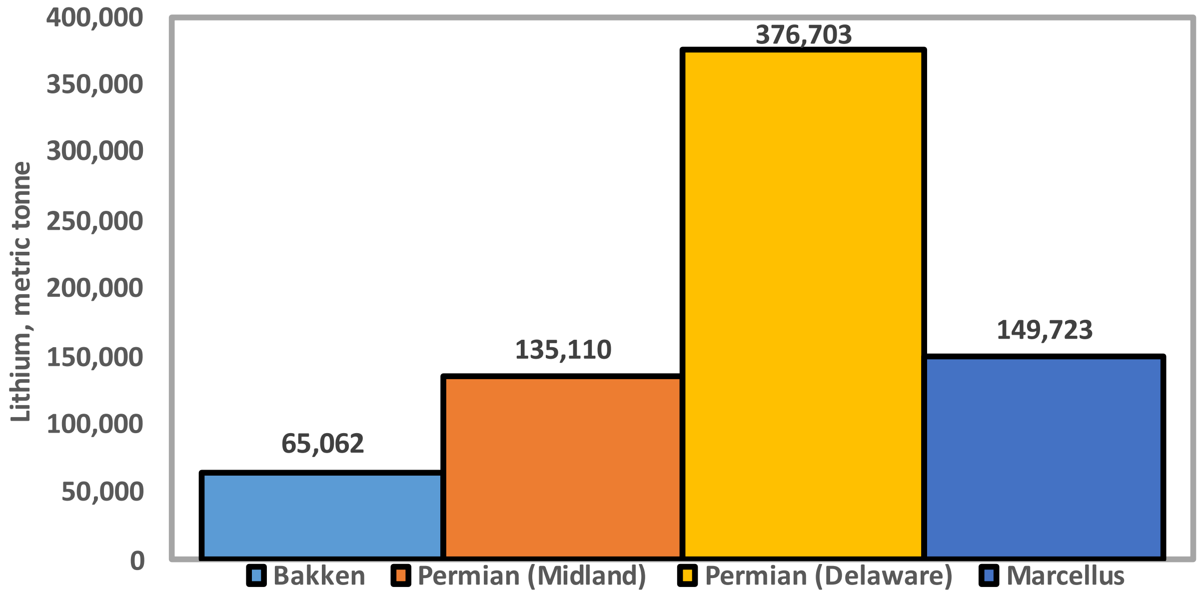


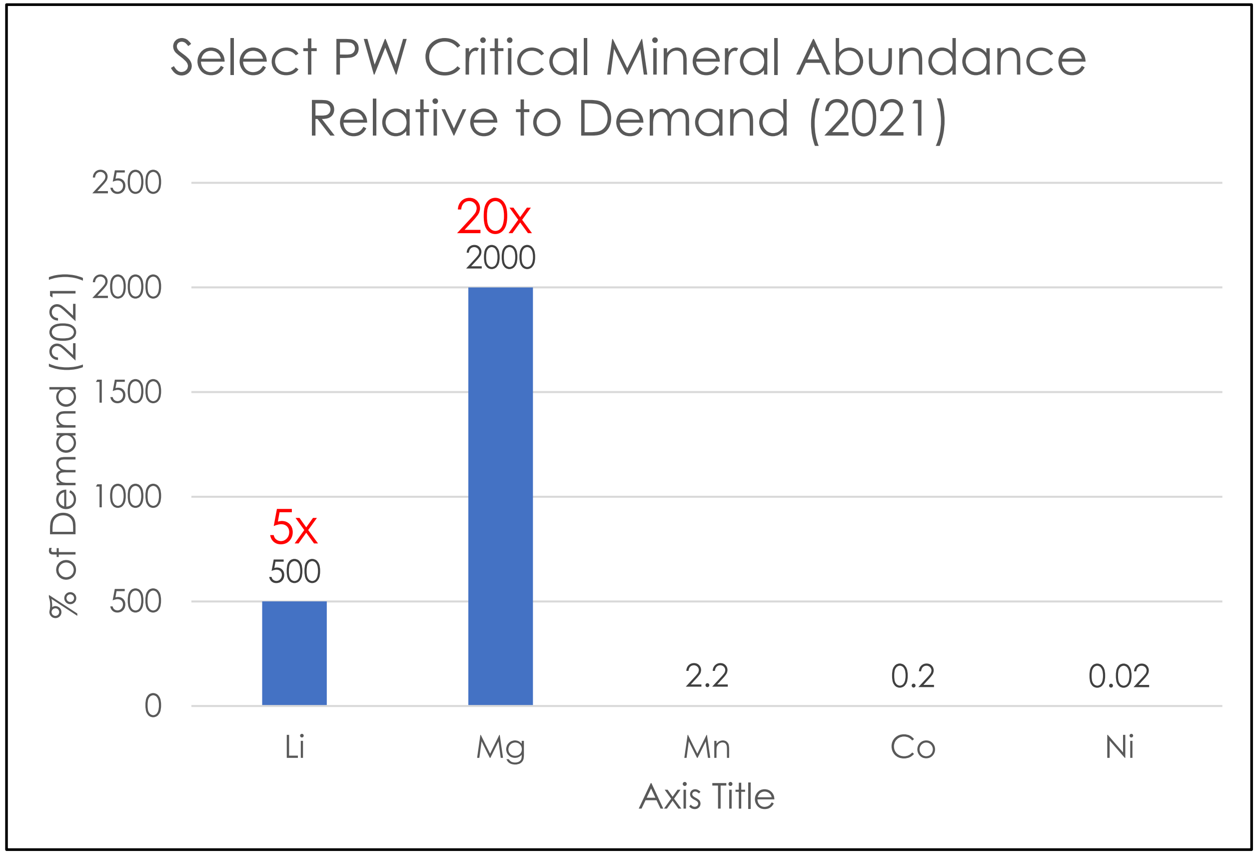
Fig. 2. Projected lithium resource potential calculated from projected remaining PW volumes (Scanlon et al., 2020) and average Li concentration in each formation.

Summary of Analysis

- **Significant lithium resources** to meet current and conservative future demands.

- **Magnesium exceeds** current consumption.
  - Future EV demand is unclear.

- **Mn, Co, and Ni** have negligible impact on import reliance but could offset costs of treatment.



Commercializing CM Recovery from PW

CM Extraction Technologies

- Extraction technologies need to accommodate varying PW quality.
  - PW can be highly saline (Bakken play TDS ~ 255 g/L which is ~7 x greater than seawater).
  - Substantial variability in PW compositions, including TDS between different PW sources (TDS also varies by depth within a play).
- Extraction processes will mainly depend on PW composition.
  - Options include: electrocoagulation, chemical precipitation, thermal distillation, adsorption, advanced oxidation, membrane filtration (mechanical vapor compression, forward osmosis, reverse osmosis, membrane distillation, electrodialysis, etc.), flotation, solvent extraction, biological technologies…
  - Multi-stage, modular processes likely required to achieve desired throughput, recovery, and purity of CM.
- Environmental/carbon footprint of process needs to be considered.
  - E.g., higher temperature PW may also contain heat that can be used to drive extraction technologies.
- Economic needs to be assessed.
  - Value of critical minerals could offset costs of treatment and reuse.

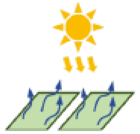
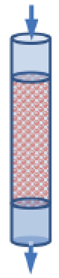
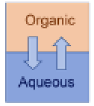
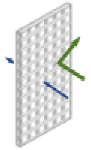
Technology	Mechanism	Developer
Solar evaporation	 Lithium-containing solutions in ponds are concentrated by solar heating; lithium carbonate precipitated on addition of soda ash (sodium carbonate). $2LiCl + Na_2CO_3 \rightarrow Li_2CO_3 + 2NaCl$	Conventional
Phosphate precipitation	Lithium phosphate precipitated on addition of phosphoric acid. $3LiCl + H_3PO_4 \rightarrow Li_3PO_4 + 3HCl$	POSCO[8-10]
Ion exchange resin	 Lithium ions intercalated into layers of aluminum hydroxide on ion exchange resins. $LiCl{+}NaCl \cdot 2Al(OH)_3 \cdot nH_2O \rightarrow NaCl{+}LiCl \cdot 2Al(OH)_3 \cdot nH_2O$	Dow[11-13]
Aluminum based adsorbent	Lithium ions adsorbed onto aluminum hydroxide with the almost same mechanism as ion exchange resin above.	FMC[14-16] Simbol[17,18] Eramet[19]
Manganese based adsorbent	Lithium ions adsorbed within layers of manganese oxide such as $H_{1.6}Mn_{1.6}O_4$ and λ-MnO_2.	JOGMEC[20]
Titanium based adsorbent	Lithium ions adsorbed into layers of titanium oxide such as H_2TiO_3.	Neometals[21]
Solvent extraction	 Lithium ions extracted from water phase by oil phase. $R\text{-}H_{sol} + LiCl_{aq} \rightarrow R\text{-}Li_{sol} + HCl_{aq}$	Tenova[22,23]
Nanofiltration	 Lithium ions concentrated through differences in ion rejection ratios and water flow rejection by membrane	MGX[24,25]

Table 1. Examples of lithium extraction technologies[1]

1. Kumar, A., Fukuda, H., Hatton, T.A., Lienhard, J.H., 2019. Lithium Recovery from Oil and Gas Produced Water: A Need for a Growing Energy Industry. ACS Energy Letters 4, 1471-1474.

Commercializing CM Recovery from PW

- NETL recently patented a non-sorbent base direct lithium extraction process.
  - Currently in licensing discussions and have a CRADA partner for testing.

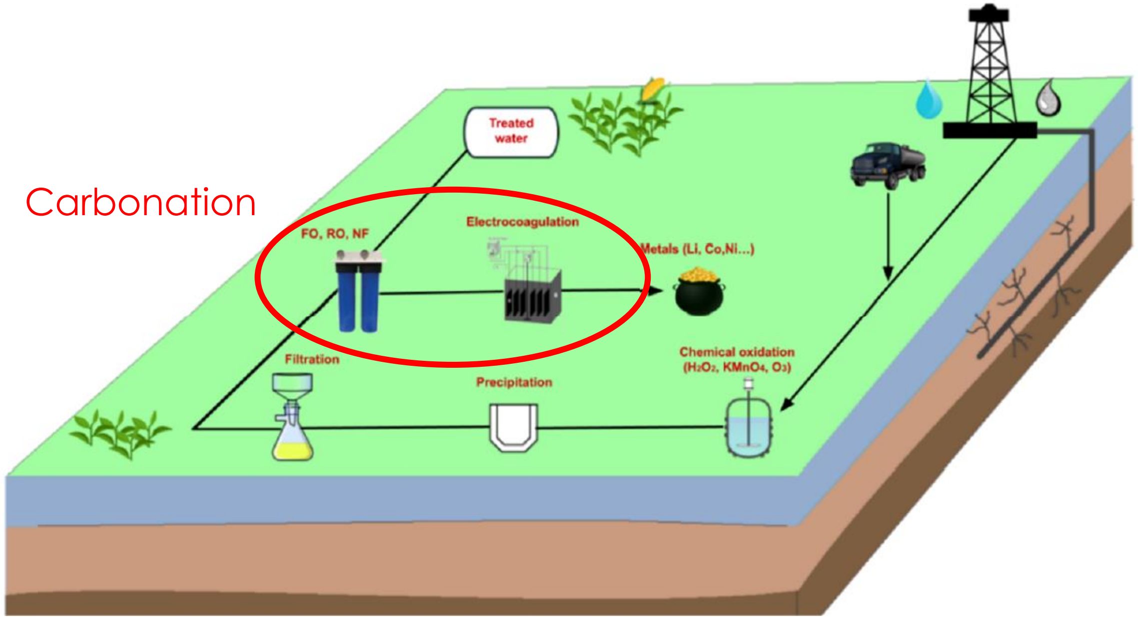


Figure showing process path of produced water valorization. Modified from Sanchez-Rosario and Hildenbrand, 2022.

Sanchez-Rosario, R., & Hildenbrand, Z. L. (2022). Produced Water Treatment and Valorization: A Techno-Economical Review. *Energies*, *15*(13), 4619.

Acknowledgement

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