Mineral Resource - Lithium - Recovery from Naturally Occurring Permian Basin Waste Water*

Stephen R. Robichaud[1] and Nicholas W. Robichaud[1]

Search and Discovery Article #42475 (2019)**
Posted December 11, 2019

*Adapted from oral presentation given at 2019 AAPG Rocky Mountain Section Meeting, Cheyenne, Wyoming, September 15-18, 2019
 DOI:10.1306/42475Robichaud2019

[1]Echelon Exploration & Production Company, Inc. Midland, Texas (srrobichaud@alum.rpi.edu)

Abstract

In 1976 the USGS convened a symposium on “Lithium Resources and Requirements by the Year 2000”. This symposium identified oil field waste water as a probable source of recoverable lithium. We are here outlining an exploratory program for the recovery of lithium and other metals from the waste water produced as a secondary product of crude oil and natural gas recovery in the Permian Basin of West Texas and southeast New Mexico. The cumulative crude oil production from the Permian Basin is in excess of 40 billion barrels. Through most of that history the associated water cut has been about 90%. If the dissolved lithium content (an unknown quantity) averages 100 ppm, there would have been a potential recovery of 6.4 million metric tons of Li_2CO_3 from this water. Using a current production of about 3.5 million BOPD and 80% water cut, that would be a potential daily recovery of 787 metric tons of Li_2CO_3, which at currents prices is about $13 million/day. Saller and Steuber (2018) have investigated the origin of Permian Basin interstitial waters and have concluded that the waters are from one of three origins: evaporation of seawater during the Permian; recharge of meteoric water in the New Mexico mountains; recharged meteoric water with dissolution and/or precipitation of rock components and mixture with evaporitic water.

Permian Basin waters have a composition which varies greatly, but some of these waters contain 350,000 ppm TDS, and their dissolved metals are largely unknown. Calcium, sodium, and magnesium are present in large concentrations. Confirmed in some analyses are barium, boron, cadmium, cobalt, lithium, potassium, rubidium and strontium. Other potentially recoverable metals whose presence in Permian Basin waters is unknown are beryllium, copper, molybdenum, nickel, silver, thorium and uranium. Lithium mining in the past has been mostly by way of the hard-rock mining of spodumene (which contains lithium) and the evaporative precipitation of LiCl and Li_2CO_3 from brines. Recent advances in membrane technology have successfully recovered lithium from brines without the need for the broad footprint of an evaporative pan. The exploration for these metals requires a sampling of waters over a broad geography in the Permian Basin, and at a broad spectrum of strata, with analysis by way of atomic emission spectrometry.

References Cited

Galloway, W.E., T.E. Ewing, C.M. Garrett, Noel Tyler, and D.G. Bebout, 1983, Atlas of Major Texas Oil Reservoirs: The University of Texas at Austin, Bureau of Economic Geology, Special Publication, 139 p.

Matchus, E.J., and T.S. Jones, 1984, East-west cross section through Permian Basin of west Texas: Stratigraphic Committee of West Texas Geological Society, cross section.

Saller, A., and A.M. Stueber, 2018, Evolution of formation waters in the Permian Basin, United States: Late Permian evaporated seawater to Neogene meteoric water: AAPG Bulletin, v. 102/3, p. 401-428.

Mineral Resource - Lithium - Recovery From Naturally Occurring Permian Basin Waste Water

Stephen R. Robichaud, PG, CPG
Nicholas W. Robichaud, BS, Chem.
Echelon Exploration & Production Company, Inc.
Midland, Texas
Lakewood, Colorado

Lithium Resources and Requirements by the Year 2000

JAMES D. VINE, Editor

GEOLOGICAL SURVEY PROFESSIONAL PAPER 1005

A collection of papers presented at a symposium held in Golden, Colorado, January 22–24, 1976

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1976

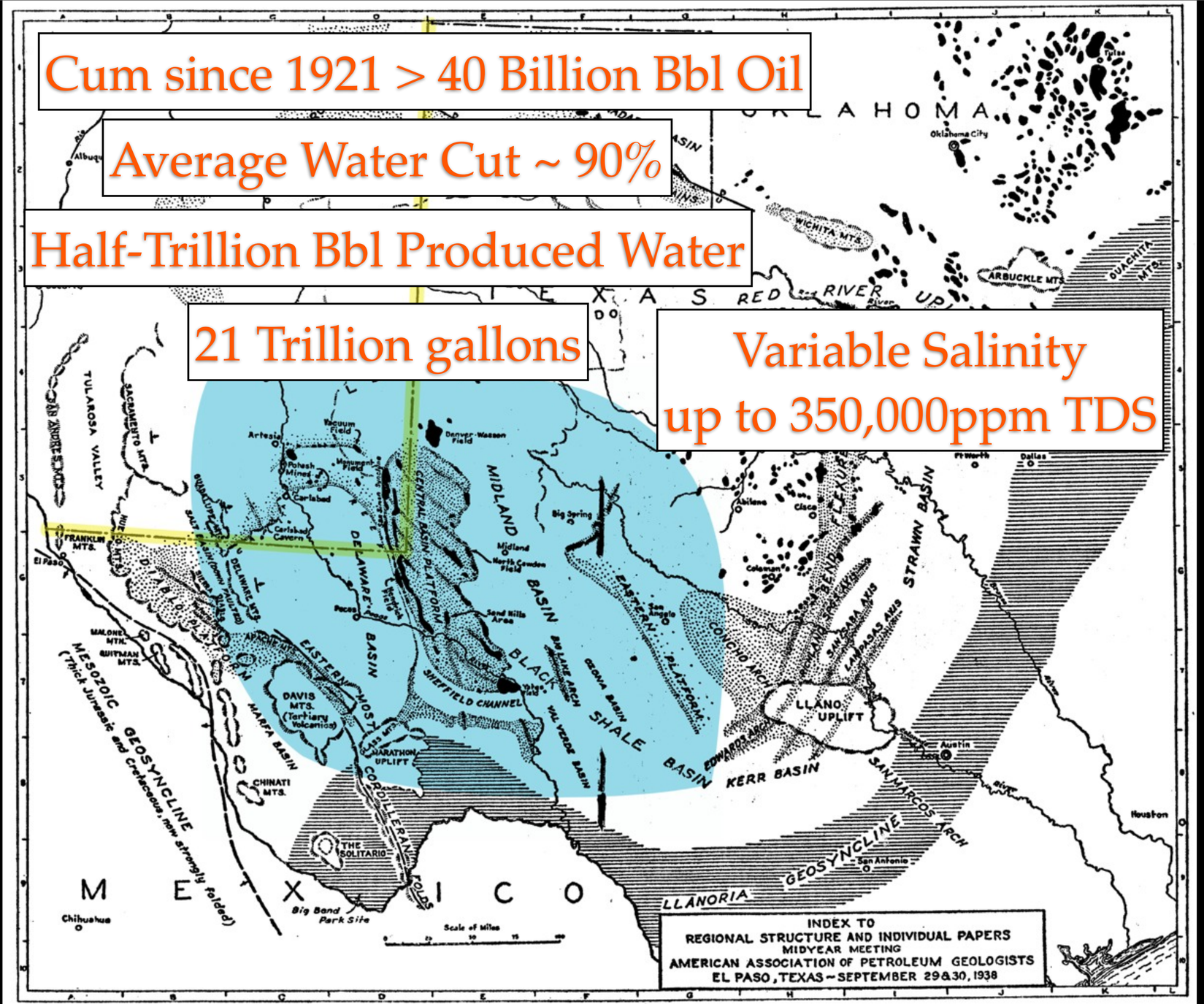
Cum since 1921 > 40 Billion Bbl Oil

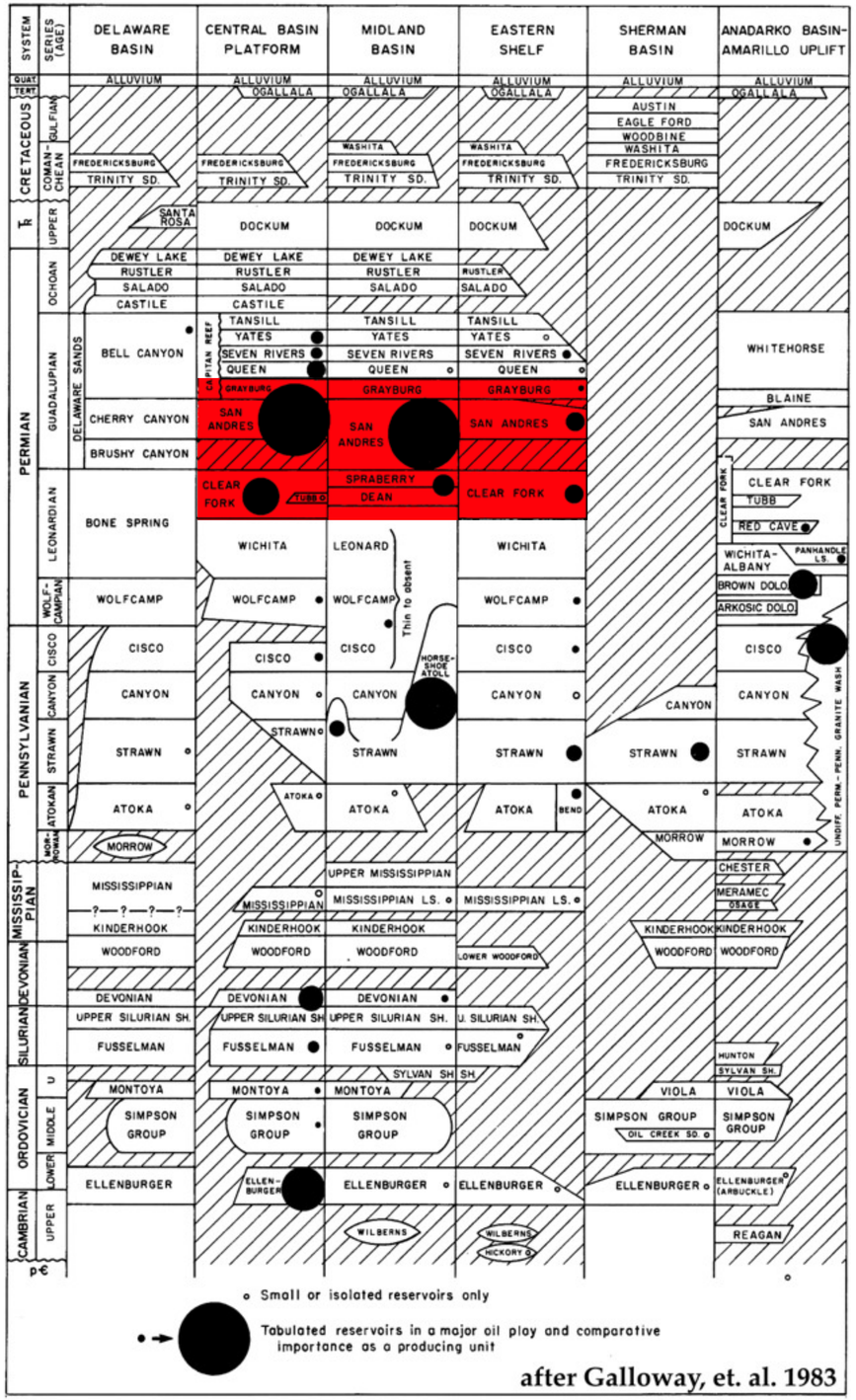
Average Water Cut ~ 90%

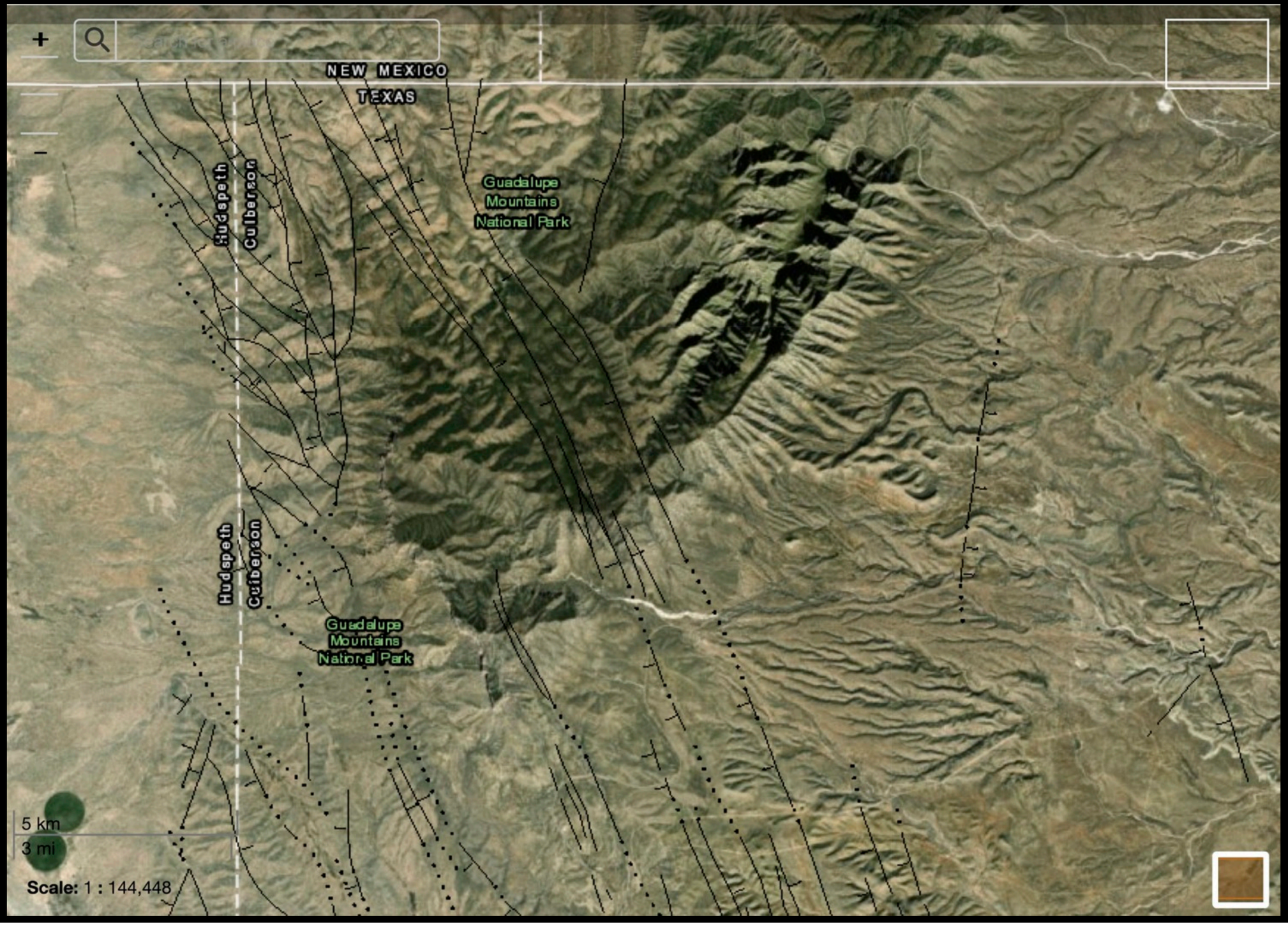
Half-Trillion Bbl Produced Water

21 Trillion gallons

Variable Salinity
up to 350,000ppm TDS




SYSTEM
SERIES (AGE)
DELAWARE BASIN
CENTRAL BASIN PLATFORM
MIDLAND BASIN
EASTERN SHELF
SHERMAN BASIN
ANADARKO BASIN-AMARILLO UPLIFT
QUAT
TERT
ALLUVIUM
OGALLALA
CRETACEOUS
GULFIAN
COMAN-CHEAN
AUSTIN
EAGLE FORD
WOODBINE
WASHITA
FREDERICKSBURG
TRINITY SD.
TR
UPPER
SANTA ROSA
DOCKUM
PERMIAN
OCHOAN
DEWEY LAKE
RUSTLER
SALADO
CASTILE
GUADALUPIAN
DELAWARE SANDS
BELL CANYON
CHERRY CANYON
BRUSHY CANYON
CAPITAN REEF
TANSILL
YATES
SEVEN RIVERS
QUEEN
GRAYBURG
SAN ANDRES
WHITEHORSE
BLAINE
LEONARDIAN
BONE SPRING
SPRABERRY
DEAN
CLEAR FORK
TUBB
RED CAVE
WICHITA
LEONARD
WOLFCAMP
WICHITA-ALBANY
PANHANDLE LS.
BROWN DOLO
ARKOSIC DOLO
Thin to absent
PENNSYLVANIAN
CISCO
CANYON
STRAWN
ATOKAN
ATOKA
BEND
MORROWAN
MORROW
HORSE-SHOE ATOLL
UNDIFF. PERM. - PENN. GRANITE WASH
MISSISSIPPIAN
UPPER MISSISSIPPIAN
MISSISSIPPIAN LS.
CHESTER
MERAMEC
OSAGE
KINDERHOOK
WOODFORD
LOWER WOODFORD
DEVONIAN
SILURIAN
UPPER SILURIAN SH.
U. SILURIAN SH.
FUSSELMAN
HUNTON
SYLVAN SH.
ORDOVICIAN
U
MIDDLE
LOWER
MONTOYA
VIOLA
SIMPSON GROUP
OIL CREEK SD.
ELLENBURGER
ELLEN-BURGER
ELLENBURGER (ARBUCKLE)
CAMBRIAN
UPPER
REAGAN
p€
WILBERNS
HICKORY
o Small or isolated reservoirs only
Tabulated reservoirs in a major oil play and comparative importance as a producing unit
after Galloway, et. al. 1983


NEW MEXICO
TEXAS
Hudspeth
Culberson
Guadalupe
Mountains
National Park
Hudspeth
Culberson
Guadalupe
Mountains
National Park
5 km
3 mi
Scale: 1 : 144,448

DELAWARE BASIN

CENTRAL BASIN PLATFORM

MIDLAND BASIN

West

East

OCHOAN

GUADALUPIAN

PERMIAN

LEONARDIAN

PENNSYLVANIAN

WOLFCAMP

SILURIAN

ORDOVICIAN

PRECAMBRIAN

1000 m

3000 ft

10 MILES
~16 KM

TANSILL

SEVEN RIVERS

YATES

SAN ANDRES

CLEAR FORK

WICHITA-ABO

MISSISSIPPIAN

WOODFORD

SILURIAN

ELLENBURGER

PRECAMBRIAN

PERMIAN

WOLFCAMP

PENNSYLVANIAN

DEVONIAN

SILURIAN

ORDOVICIAN

10 MILES
~16 KM

SALT

ANHYDRITE

SAND/SILTSTONE

MUDSTONE WITH SAND & CARBONATE

SHALE

CONGLOMERATIC

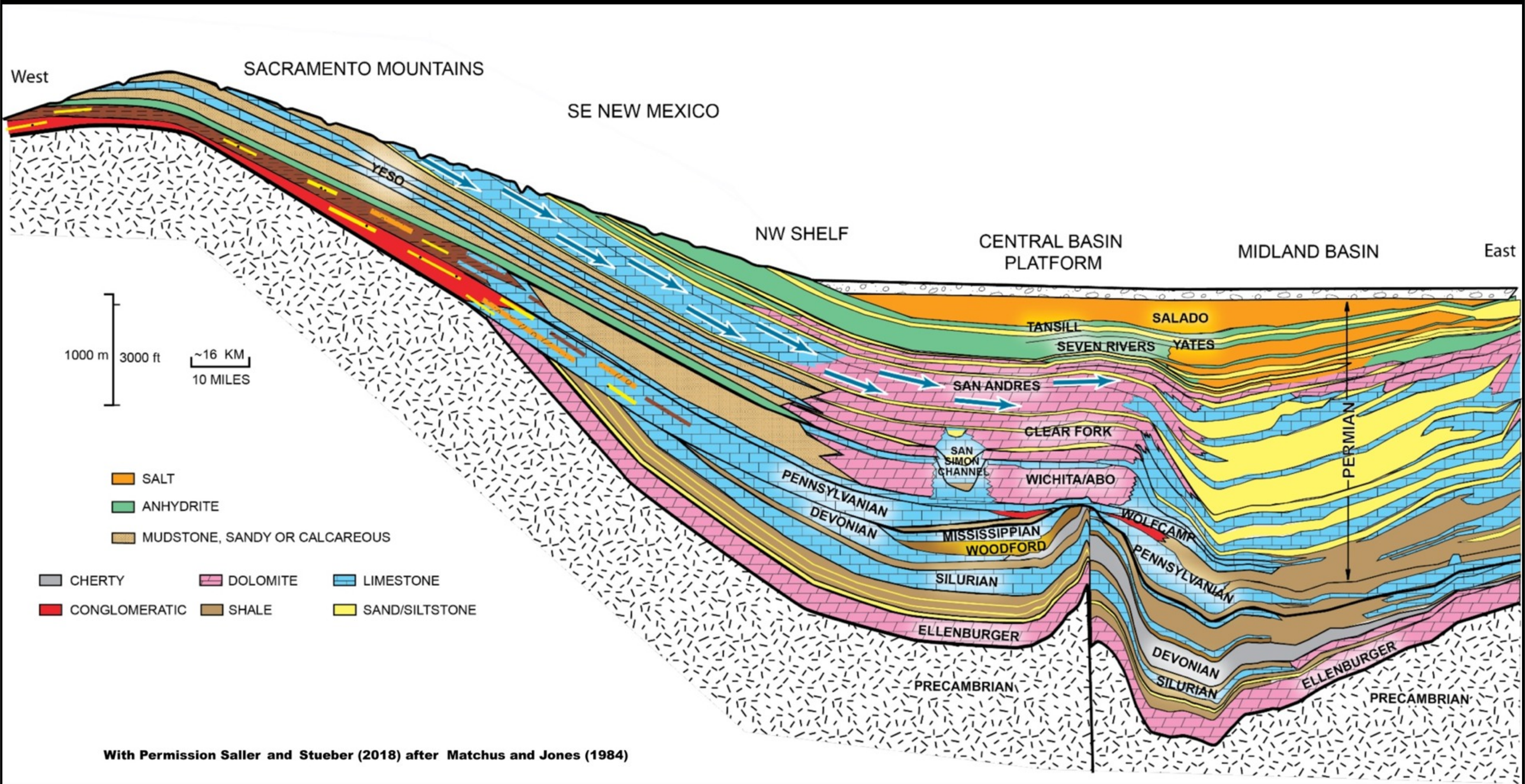
DOLOMITE

BLACK SHALE

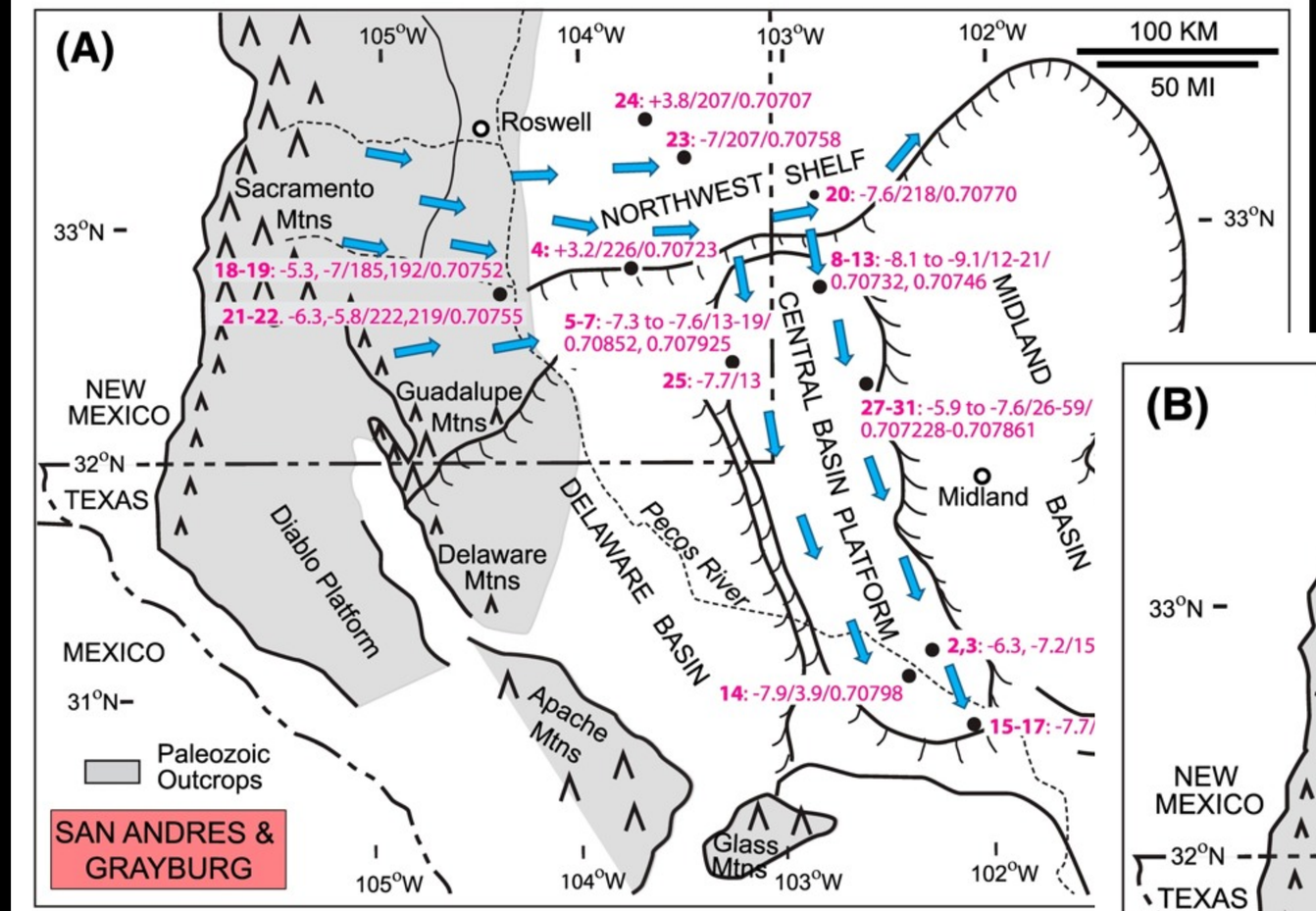
LIMESTONE

CHERTY

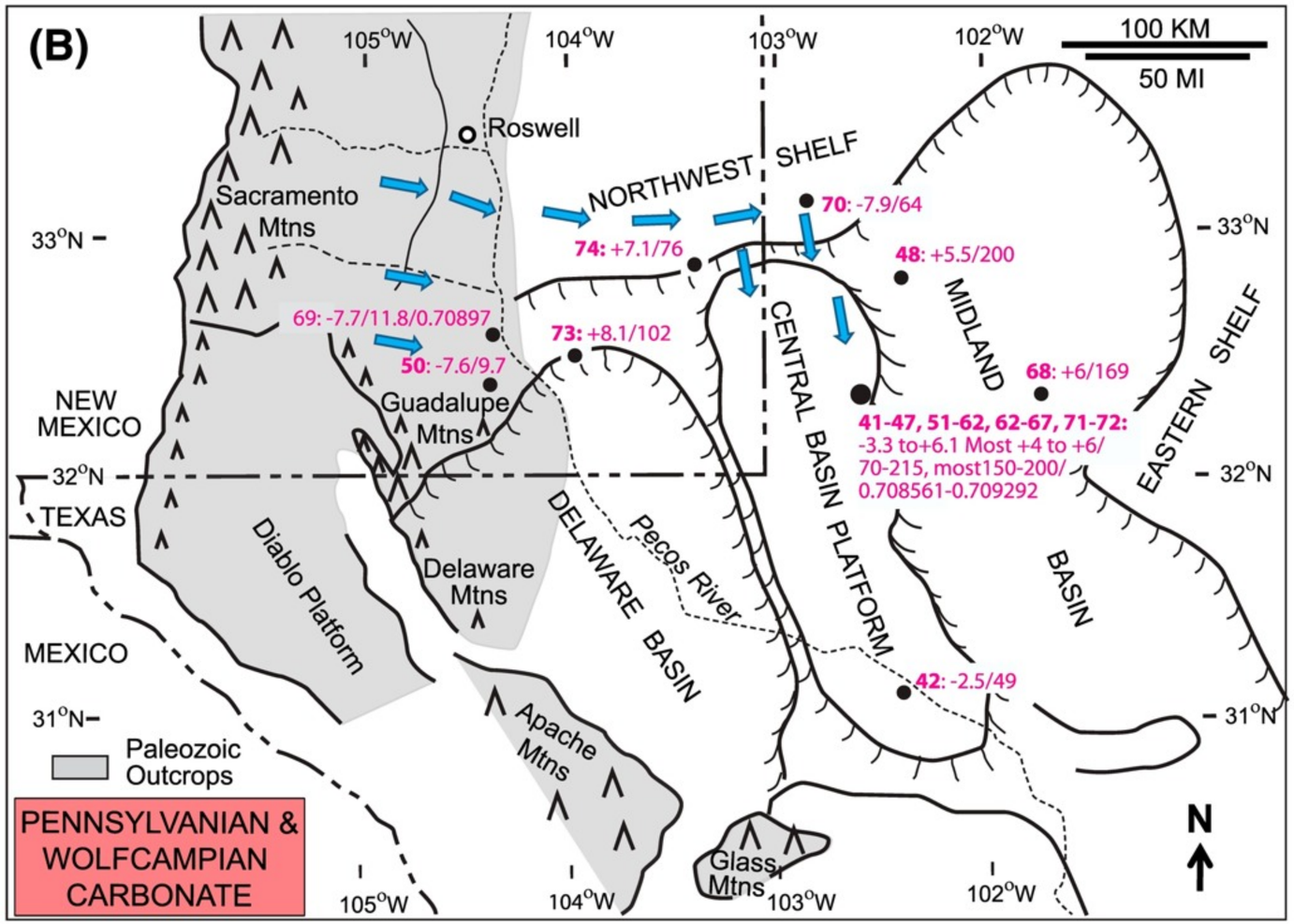
With Permission Saller and Stueber (2018) after Matchus and Jones (1984)



With Permission Saller and Stueber (2018) after Matchus and Jones (1984)



With Permission Saller A



With Permission Saller AND Stueber (2018)

Chemistry of Lithium Carbonate Recovery

1. Evaporation of solute.
   -Concentrate the solution
   -Saturation: ~820 ppm (5.90×10^{-2} M)

Chemistry of Lithium Carbonate Recovery

1. Evaporation of solute.
   -Concentrate the solution
   -Saturation: ~820 ppm (5.90×10^{-2} M)

2. Removal of other salts.
   -Variable to source
   -$CaCO_3$
   -$MgCl_2$

Chemistry of Lithium Carbonate Recovery

1. Evaporation of solute.
   - -Concentrate the solution
   - -Saturation: ~820 ppm (5.90×10^{-2} M)

2. Removal of other salts.
   - -Variable to source
   - -$CaCO_3$
   - -$MgCl_2$

3. Precipitation of Lithium Carbonate.
   - -Addition of Carbonate
   - -Alternatives: Extraction, Reverse Osmosis

Solubility Product (K_{sp})

General : $CA_{(s)} \xrightleftharpoons{H_2O} C^+_{(aq)} + A^-_{(aq)}$

$$K_{sp} = [C^+][A^-]$$

Solubility Product (K_{sp})

General : $CA_{(s)} \xrightleftharpoons{H_2O} C^+_{(aq)} + A^-_{(aq)}$

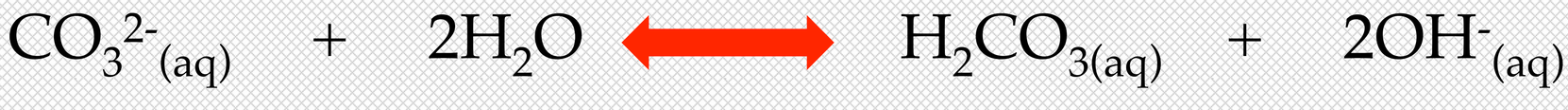
$$K_{sp} = [C^+][A^-]$$

Lithium Carbonate : $Li_2CO_{3(s)} \xrightleftharpoons{H_2O} 2\,Li^+_{(aq)} + CO_3^{2-}{}_{(aq)}$

$$K_{sp} = [Li^+]^2[CO_3^{2-}] = 8.15 \times 10^{-4}$$

Precipitation with Sodium Carbonate

Precipitation with Sodium Carbonate



Precipitation with Sodium Carbonate

$$Na_2CO_{3(s)} \xrightarrow{H_2O} 2Na^+_{(aq)} + CO_3^{2-}{}_{(aq)}$$

$$CO_3^{2-}{}_{(aq)} + 2H_2O \rightleftharpoons H_2CO_{3(aq)} + 2OH^-_{(aq)}$$

$$H_2CO_{3(aq)} \xrightarrow{OH^-} 2H_2O + CO_3^{2-}{}_{(aq)}$$

Precipitation with Sodium Carbonate

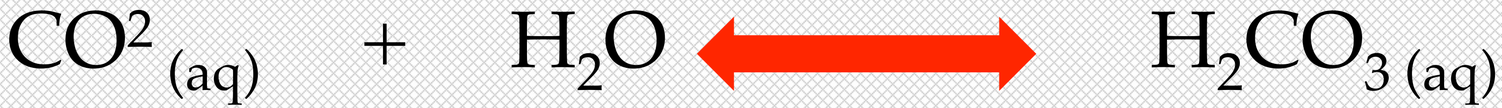
$$Na_2CO_{3(s)} \xrightarrow{H_2O} 2Na^+_{(aq)} + CO_3^{2-}{}_{(aq)}$$

$$CO_3^{2-}{}_{(aq)} + 2H_2O \rightleftharpoons H_2CO_{3(aq)} + 2OH^-_{(aq)}$$

$$H_2CO_{3(aq)} \xrightarrow{OH^-} 2H_2O + CO_3^{2-}{}_{(aq)}$$

$$2Li^+_{(aq)} + CO_3^{2-}{}_{(aq)} \xrightarrow{OH^-/CO_3^{2-}} Li_2CO_{3(s)}$$

Precipitation with Carbon Dioxide



Precipitation with Carbon Dioxide

$$CO^2_{(aq)} + H_2O \rightleftharpoons H_2CO_{3\,(aq)}$$

$$H_2CO_{3(aq)} \xrightarrow{OH^-} 2H_2O + CO_3^{2-}{}_{(aq)}$$

Precipitation with Carbon Dioxide

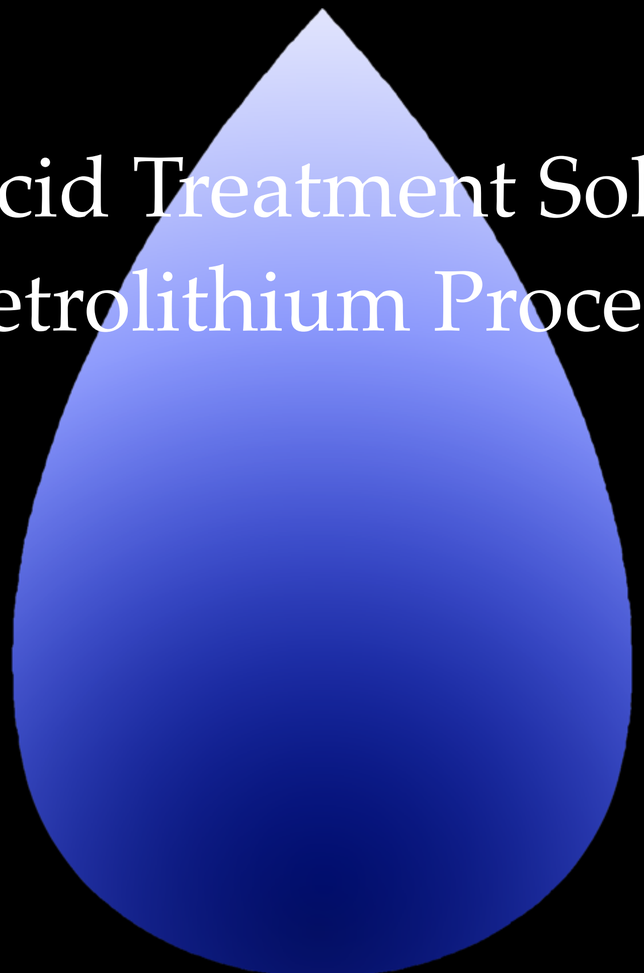
$$CO^{2}_{(aq)} + H_2O \rightleftharpoons H_2CO_{3\,(aq)}$$

$$H_2CO_{3(aq)} \xrightarrow{OH^-} 2H_2O + CO_3^{2-}{}_{(aq)}$$

$$2Li^+_{(aq)} + CO^{2-}_{3(aq)} \xrightarrow{OH^-/CO_3^{2-}} Li_2CO_{3(s)}$$

Membrane Technology

PurLucid Treatment Solutions
Petrolithium Process

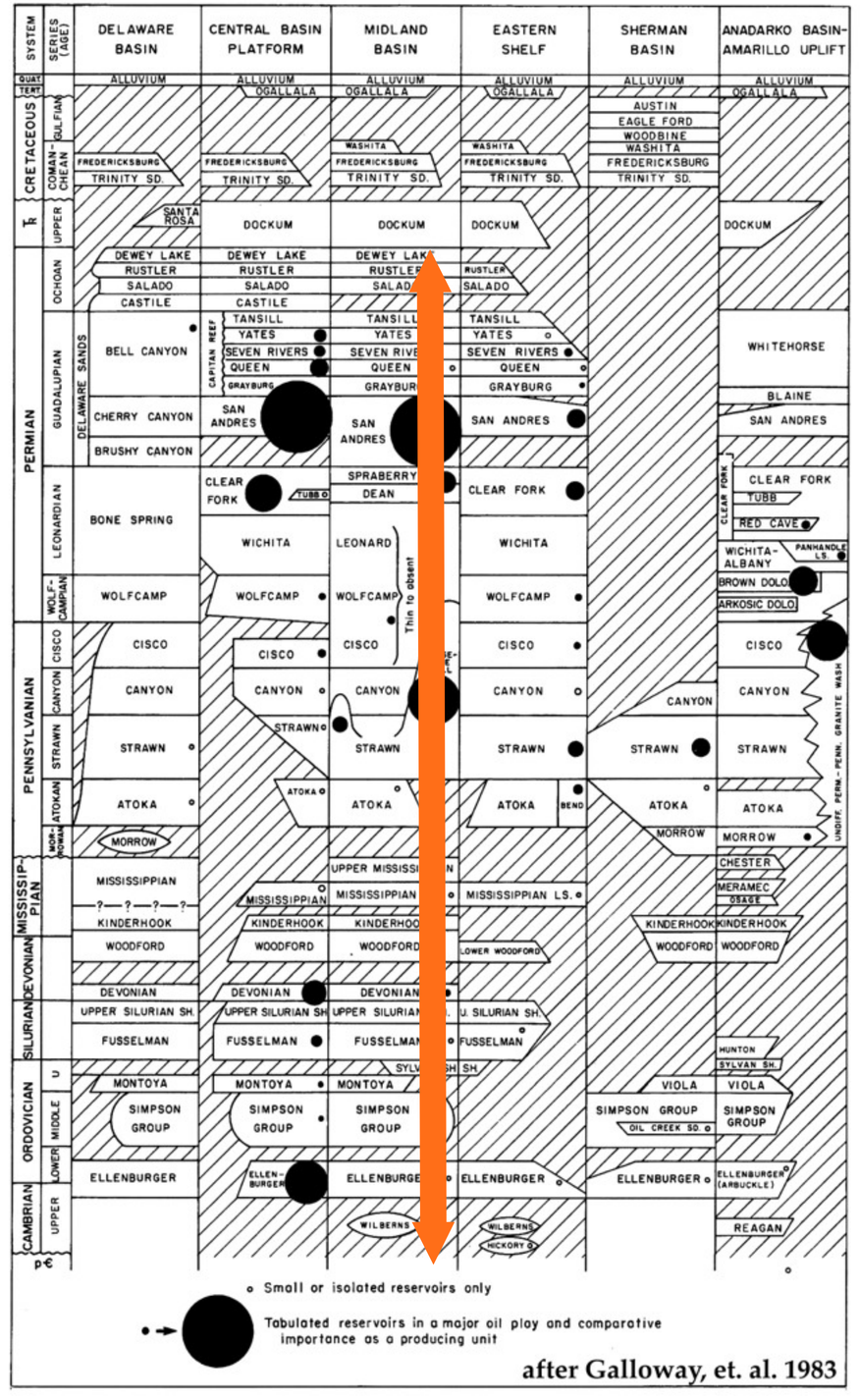


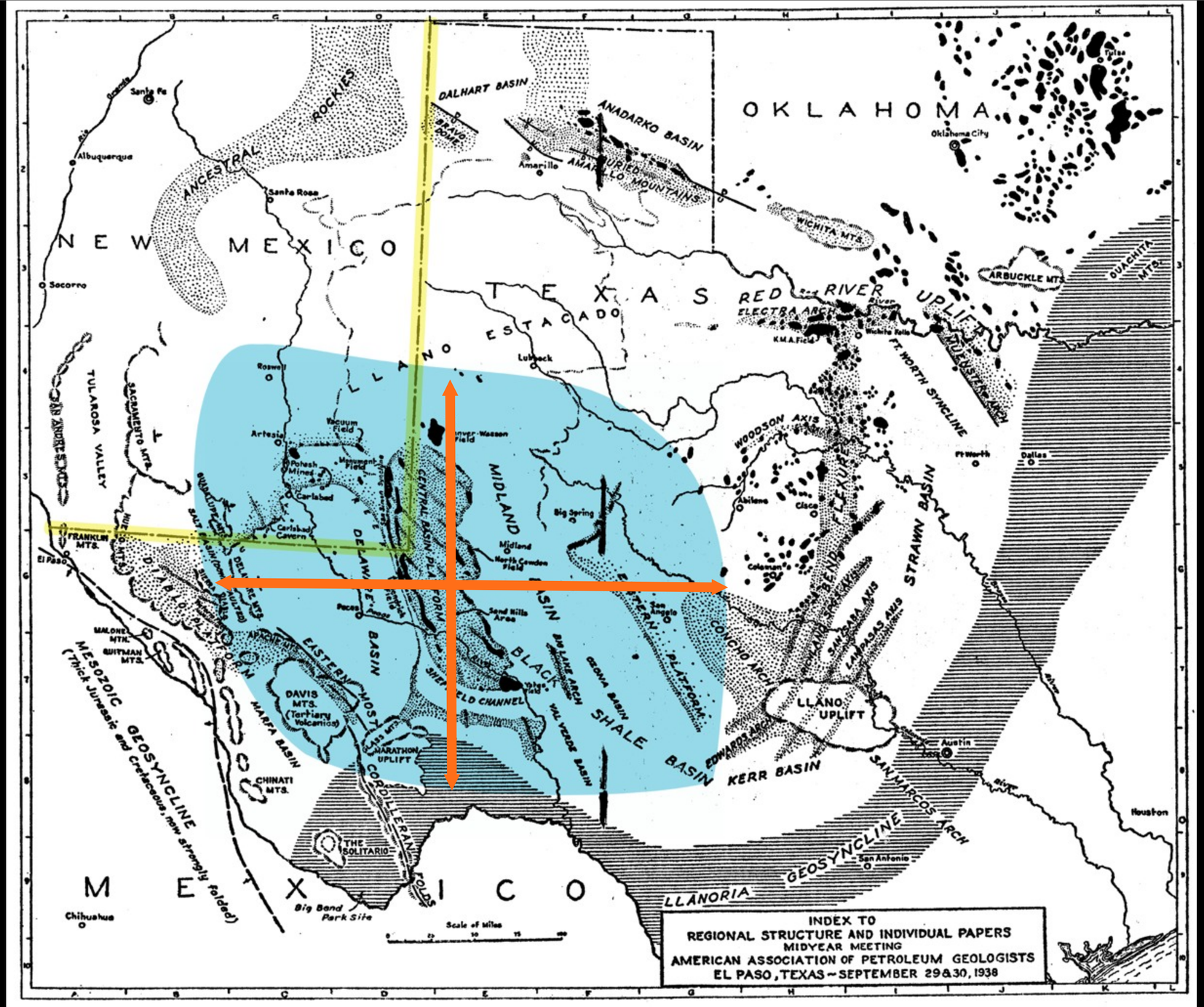
Periodic Table of the Elements

1 1IA 11A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 H Hydrogen 1.0079												5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.998403	2 He Helium 4.00260
3 Li Lithium 6.941	4 Be Beryllium 9.01218																10 Ne Neon 20.1797
11 Na Sodium 22.989768	12 Mg Magnesium 24.305											13 Al Aluminum 26.981539	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.95591	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938	26 Fe Iron 55.847	27 Co Cobalt 58.9332	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.64	33 As Arsenic 74.92159	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium 98.9072	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.9055	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.90447	54 Xe Xenon 131.29
55 Cs Cesium 132.90543	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.9665	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98037	84 Po Polonium [208.9824]	85 At Astatine 209.9871	86 Rn Radon 222.0176
87 Fr Francium 223.0197	88 Ra Radium 226.0254	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Uuq Ununquadium [289]	115 Uup Ununpentium unknown	116 Uuh Ununhexium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

Lanthanide Series	57 La Lanthanum 138.9055	58 Ce Cerium 140.115	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium 144.9127	62 Sm Samarium 150.36	63 Eu Europium 151.9655	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.0278	90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium 237.0482	94 Pu Plutonium 244.0642	95 Am Americium 243.0614	96 Cm Curium 247.0703	97 Bk Berkelium 247.0703	98 Cf Californium 251.0796	99 Es Einsteinium [254]	100 Fm Fermium 257.0951	101 Md Mendelevium 258.1	102 No Nobelium 259.1009	103 Lr Lawrencium [262]

Alkali Metal | Alkaline Earth | Transition Metal | Basic Metal | Semimetals | Nonmetals | Halogens | Noble Gas | Lanthanides | Actinides


SYSTEM
SERIES (AGE)
DELAWARE BASIN
CENTRAL BASIN PLATFORM
MIDLAND BASIN
EASTERN SHELF
SHERMAN BASIN
ANADARKO BASIN-AMARILLO UPLIFT
QUAT
TERT
ALLUVIUM
OGALLALA
CRETACEOUS
GULFIAN
COMAN-CHEAN
AUSTIN
EAGLE FORD
WOODBINE
WASHITA
FREDERICKSBURG
TRINITY SD.
TR
UPPER
SANTA ROSA
DOCKUM
PERMIAN
OCHOAN
DEWEY LAKE
RUSTLER
SALADO
CASTILE
GUADALUPIAN
DELAWARE SANDS
CAPITAN REEF
TANSILL
YATES
SEVEN RIVERS
QUEEN
GRAYBURG
BELL CANYON
CHERRY CANYON
BRUSHY CANYON
SAN ANDRES
WHITEHORSE
BLAINE
LEONARDIAN
BONE SPRING
SPRABERRY
DEAN
CLEAR FORK
TUBB
RED CAVE
WICHITA
LEONARD
WICHITA-ALBANY
PANHANDLE LS.
BROWN DOLO
ARKOSIC DOLO
WOLF-CAMPIAN
WOLFCAMP
Thin to absent
PENNSYLVANIAN
CISCO
CANYON
STRAWN
ATOKA
BEND
MORROW
UNDIFF. PERM.-PENN. GRANITE WASH
MISSISSIP-PIAN
MISSISSIPPIAN
MISSISSIPPIAN LS.
KINDERHOOK
CHESTER
MERAMEC
OSAGE
DEVONIAN
WOODFORD
LOWER WOODFORD
UPPER SILURIAN SH.
FUSSELMAN
HUNTON
SYLVAN SH.
ORDOVICIAN
U
MIDDLE
LOWER
MONTOYA
SIMPSON GROUP
OIL CREEK SD.
VIOLA
ELLENBURGER
ELLEN-BURGER
ELLENBURGER (ARBUCKLE)
CAMBRIAN
UPPER
WILBERNS
WILBERNS
HICKORY
REAGAN
p€
o Small or isolated reservoirs only
Tabulated reservoirs in a major oil play and comparative importance as a producing unit
after Galloway, et. al. 1983


NEW MEXICO
TEXAS
OKLAHOMA
ROCKIES
ANCESTRAL
DALHART BASIN
ANADARKO BASIN
AMARILLO MOUNTAINS
WICHITA MTS.
ARBUCKLE MTS.
OUACHITA MTS.
RED RIVER UPLIFT
ELECTRA ARCH
KMA Field
Wichita Falls
Ft. WORTH SYNCLINE
WOODSON AXIS
Ft. Worth
Dallas
Abilene
Cisco
BEND FLEXURE
STRAWN BASIN
LLANO ESTACADO
Lubbock
Roswell
Artesia
Vacuum Field
Wasson Field
Potash Mined
Monument Field
Carlsbad
Carlsbad Cavern
Big Spring
Midland
North Cowden Field
Sand Hills Area
Pecos
Santa Fe
Albuquerque
Santa Rosa
Socorro
Amarillo
Oklahoma City
Tulsa
TULAROSA VALLEY
SACRAMENTO MTS.
SAN ANDRES MTS.
FRANKLIN MTS.
El Paso
DIABLO PLATFORM
DELAWARE BASIN
CENTRAL BASIN PLATFORM
MIDLAND
EASTERN SHELF
EASTERN PLATFORM
BASIN
BLACK
SHALE
DELAWARE MTS.
GLASS MTS.
APACHE MTS.
DAVIS MTS. (Tertiary volcanics)
MARFA BASIN
MARATHON UPLIFT
CORDILLERAN FOLDS
VAL VERDE BASIN
DEVILS RIVER UPLIFT
CONCHO ARCH
SAN ANGELO
PLATFORM
CROSS BASIN
EDWARDS ARCH
LLANO UPLIFT
KERR BASIN
SAN MARCOS ARCH
Austin
San Antonio
Houston
GEOSYNCLINE
LLANORIA
MALONE MTN.
GUITMAN MTS.
MESOZOIC GEOSYNCLINE (Thick Jurassic and Cretaceous, now strongly folded)
CHINATI MTS.
THE SOLITARIO
Big Bend Park Site
Chihuahua
MEXICO
Scale of Miles
INDEX TO
REGIONAL STRUCTURE AND INDIVIDUAL PAPERS
MIDYEAR MEETING
AMERICAN ASSOCIATION OF PETROLEUM GEOLOGISTS
EL PASO, TEXAS ~ SEPTEMBER 29&30, 1938

32

33

Summary

- Abundant and Accessible Permian Waste Water
- Very High Salinity
- Lithium and Other Metals are Known to be Present
- Technology Exists for the Recovery of these Metals
- Unknowns: Geographic and Stratigraphic Distribution
- Execution: Permission and Funding