Chlorine isotopes in arid interior basins: how can we explain the large fractionations?

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Outline

- Laboratory intercomparisons

- Examples of extreme $\delta^{37}Cl$ in continental settings
  - Chatham group sediments, North Carolina, USA
  - Salt occurrences, Atacama Desert, Chile
  - China Lake, California, USA
  - Chinese basins Jurassic and recent
  - Safford Basin, Arizona, USA

- Fractionation and separation mechanisms

Homework

Become familiar with the graph of δD (δ^2H) versus $\delta^{18}O$ as applied to hydrology.
Understand the terms

1. **Global Meteoric Water Line**
2. **Local Meteoric Water Line**
3. **Evaporation trend**
4. **Annual amount-weighted mean**
5. **Altitude effect**
6. **Amount effect**

Applied Geochemistry 74 (2016) 1–12

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Stable chlorine isotopes in arid non-marine basins: Instances and possible fractionation mechanisms

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A R T I C L E   I N F O

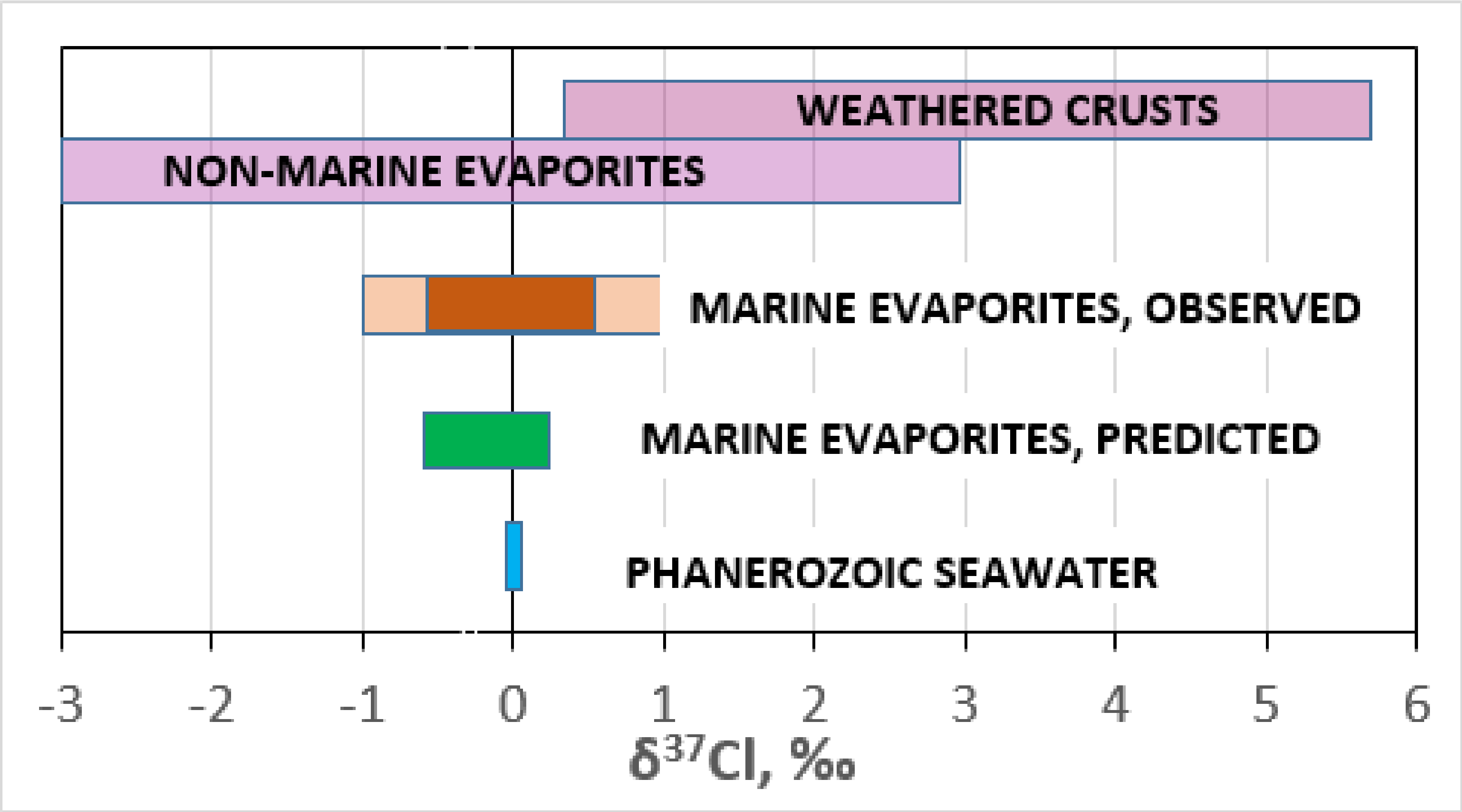
Article history:
Received 29 February 2016
Received in revised form
16 August 2016
Accepted 26 August 2016
Available online 27 August 2016

Keywords:
Chlorine isotopes
Halite
Groundwater
Playas
Diffusion
Halophytes

A B S T R A C T

Stable chlorine isotopes are useful geochemical tracers in processes involving the formation and evolution of evaporitic halite. Halite and dissolved chloride in groundwater that has interacted with halite in arid non-marine basins has a δ^{37}Cl range of 0 ± 3‰, far greater than the range for marine evaporites. Basins characterized by high positive (+1 to +3‰), near-0‰, and negative (−0.3 to −2.6‰) are documented. Halite in weathered crusts of sedimentary rocks has δ^{37}Cl values as high as +5.6‰. Salt-excluding halophyte plants excrete salt with a δ^{37}Cl range of −2.1 to −0.8‰. Differentiated rock chloride sources exist, e.g. in granitoid micas, but cannot provide sufficient chloride to account for the observed data. Single-pass application of known fractionating mechanisms, equilibrium salt-crystal interaction and disequilibrium diffusive transport, cannot account for the large ranges of δ^{37}Cl. Cumulative fractionation as a result of multiple wetting-drying cycles in vadose playas that produce halite crusts can produce observed positive δ^{37}Cl values in hundreds to thousands of cycles. Diffusive isotope fractionation as a result of multiple wetting-drying cycles operating at a spatial scale of 1–10 cm can produce high δ^{37}Cl values in residual halite. Chloride in rainwater is subject to complex fractionation, but develops negative δ^{37}Cl values in certain situations; such may explain halite deposits with bulk negative δ^{37}Cl values. Future field studies will benefit from a better understanding of hydrology and rainwater chemistry, and systematic collection of data for both Cl and Br.

THE PROBLEM



WEATHERED CRUSTS
NON-MARINE EVAPORITES
MARINE EVAPORITES, OBSERVED
MARINE EVAPORITES, PREDICTED
PHANEROZOIC SEAWATER
-3
-2
-1
0
1
2
3
4
5
6
δ37Cl, ‰

Acknowledgements unpublished data:

North Carolina: State of NC, hydrologic investigation of Wake-Chatham low-level nuclear waste disposal site

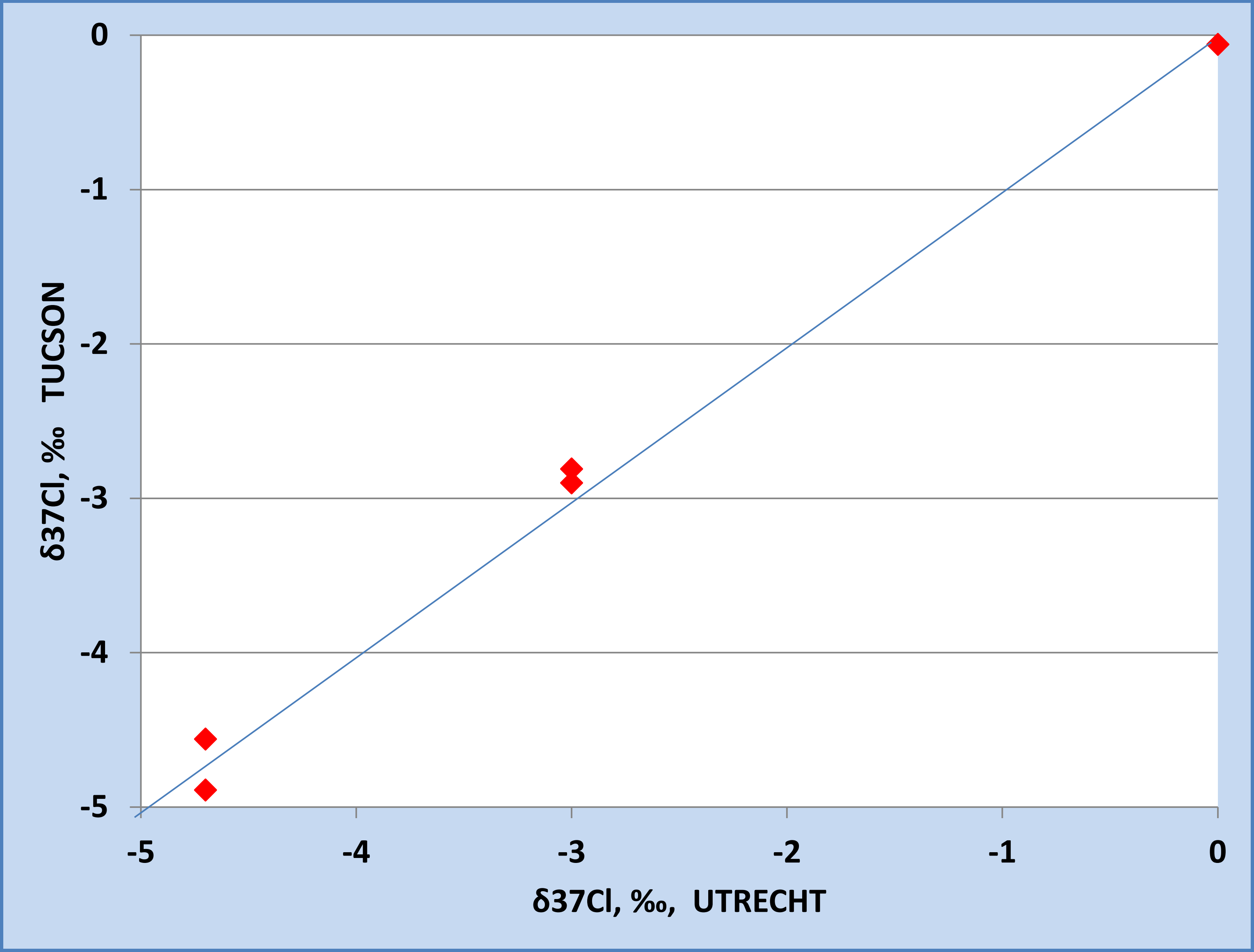
Mixing of different fluid types

California: Department of Defense, hydrologic investigation of China Lake Naval Weapons storage site

Arizona: Ray Harris, Arizona Geological Survey, study of Safford Basin for legal case

Arizona: Other basins – my own research

Tucson-Utrecht Intercomparison



ISL 354 COMPARED WITH NIST SRM 975 (Xiao et al, 2002)

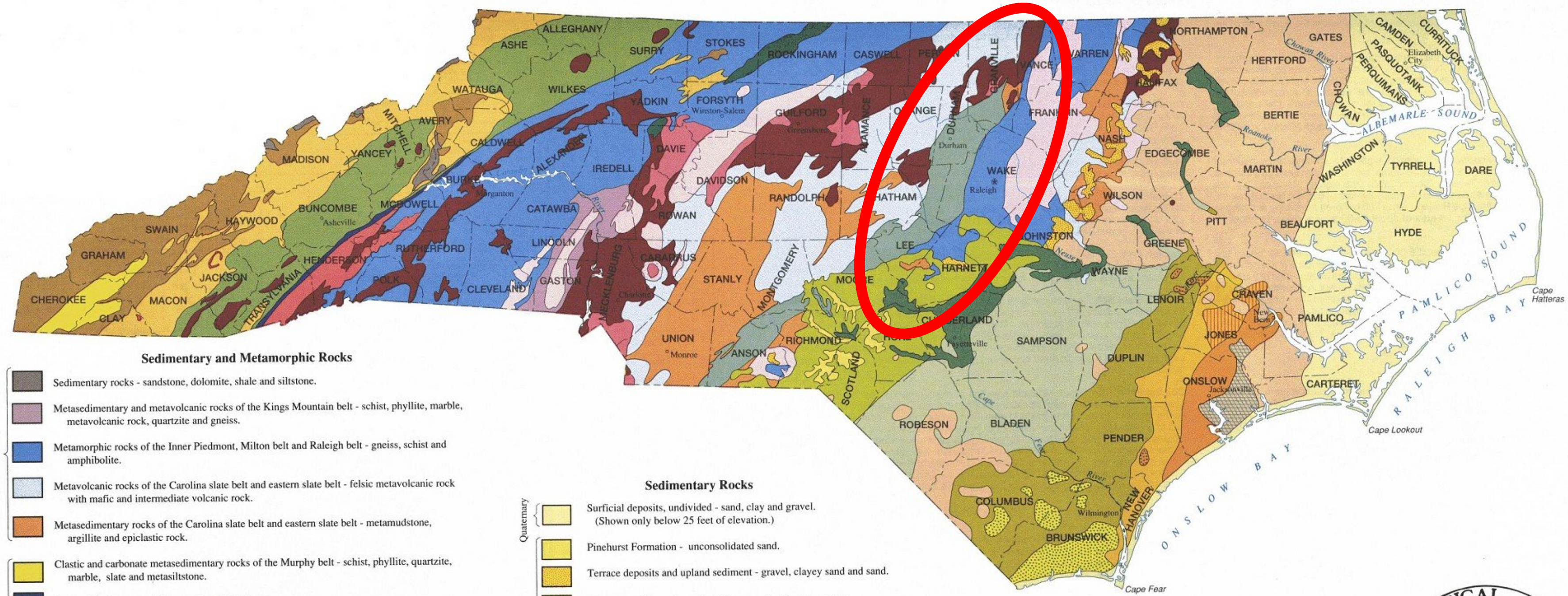
Difference in $\delta^{37}Cl$, ‰ (2σ errors):

Xining Lab: 0.39 ± 0.05

Tucson lab: 0.38 ± 0.06

Tucson analytical precision, 1σ 0.075‰ for natural samples

GENERALIZED GEOLOGIC MAP OF NORTH CAROLINA



Sedimentary and Metamorphic Rocks

Late Proterozoic to Early Paleozoic

- Sedimentary rocks - sandstone, dolomite, shale and siltstone.
- Metasedimentary and metavolcanic rocks of the Kings Mountain belt - schist, phyllite, marble, metavolcanic rock, quartzite and gneiss.
- Metamorphic rocks of the Inner Piedmont, Milton belt and Raleigh belt - gneiss, schist and amphibolite.
- Metavolcanic rocks of the Carolina slate belt and eastern slate belt - felsic metavolcanic rock with mafic and intermediate volcanic rock.
- Metasedimentary rocks of the Carolina slate belt and eastern slate belt - metamudstone, argillite and epiclastic rock.

Late Proterozoic

- Clastic and carbonate metasedimentary rocks of the Murphy belt - schist, phyllite, quartzite, marble, slate and metasiltstone.
- Brevard fault zone - schist, marble and phyllonite.
- Clastic metasedimentary and metavolcanic rocks of the Ocoee Supergroup, Grandfather Mountain Formation, Mount Rogers Formation and quartzite of the Sauratown Mountains anticlinorium - slate, metasiltstone, schist, metagraywacke, calc-silicate granofels, quartzite and felsic metavolcanic rock.
- Clastic metasedimentary rock and mafic and felsic metavolcanic rock of the Ashe Metamorphic Suite, Tallulah Falls Formation and Alligator Back Formation - gneiss, schist, metagraywacke, amphibolite and calc-silicate granofels.

Middle Proterozoic

- Felsic gneiss derived from sedimentary and igneous rocks in the northern outcrop area; biotite gneiss in the southern outcrop area; locally migmatitic and mylonitic. Locally and variably interlayered with amphibolite, calc-silicate granofels and rare marble. Intruded by Late Proterozoic mafic and felsic plutons.

Intrusive Rocks

Middle Paleozoic to Late Paleozoic

- Granitic rocks - unfoliated to weakly foliated.
- Syenite - Concord ring dike.

Late Proterozoic to Middle Paleozoic

- Metamorphosed gabbro and diorite - foliated to weakly foliated.
- Metamorphosed granitic rocks - foliated to weakly foliated; locally migmatitic.
- Henderson Gneiss - uneven-grained monzonitic to granodioritic.
- Meta-ultramafic rocks.

Sedimentary Rocks

Quaternary

- Surficial deposits, undivided - sand, clay and gravel. (Shown only below 25 feet of elevation.)

Tertiary

- Pinehurst Formation - unconsolidated sand.
- Terrace deposits and upland sediment - gravel, clayey sand and sand.
- Waccamaw Formation - fossiliferous sand with silt and clay.
- Yorktown Formation and Duplin Formation, undivided - Yorktown Formation- fossiliferous clay and sand. Duplin Formation- shelly sand, sandy marl and limestone.
- Belgrade Formation, undivided - Pollocksville Member- oyster-shell mounds in sand matrix. Haywood Landing Member- fossiliferous clayey sand.
- River Bend Formation - sandy, molluscan-mold limestone.
- Castle Hayne Formation - Spring Garden Member- molluscan-mold limestone.
- Comfort Member and New Hanover Member, undivided - Comfort Member - limestone with bryozoan and echinoid skeletons. New Hanover Member - phosphate-pebble conglomerate.
- Beaufort Formation, undivided - Unnamed upper member - glauconitic, fossiliferous sand and silty clay. Jericho Run Member - siliceous mudstone with sandstone lenses.

Cretaceous

- Peedee Formation - marine sand, clayey sand and clay.
- Black Creek Formation - lignitic sand and clay.
- Middendorf Formation - sand, sandstone and clay.
- Cape Fear Formation - sandstone and sandy mudstone.

Triassic

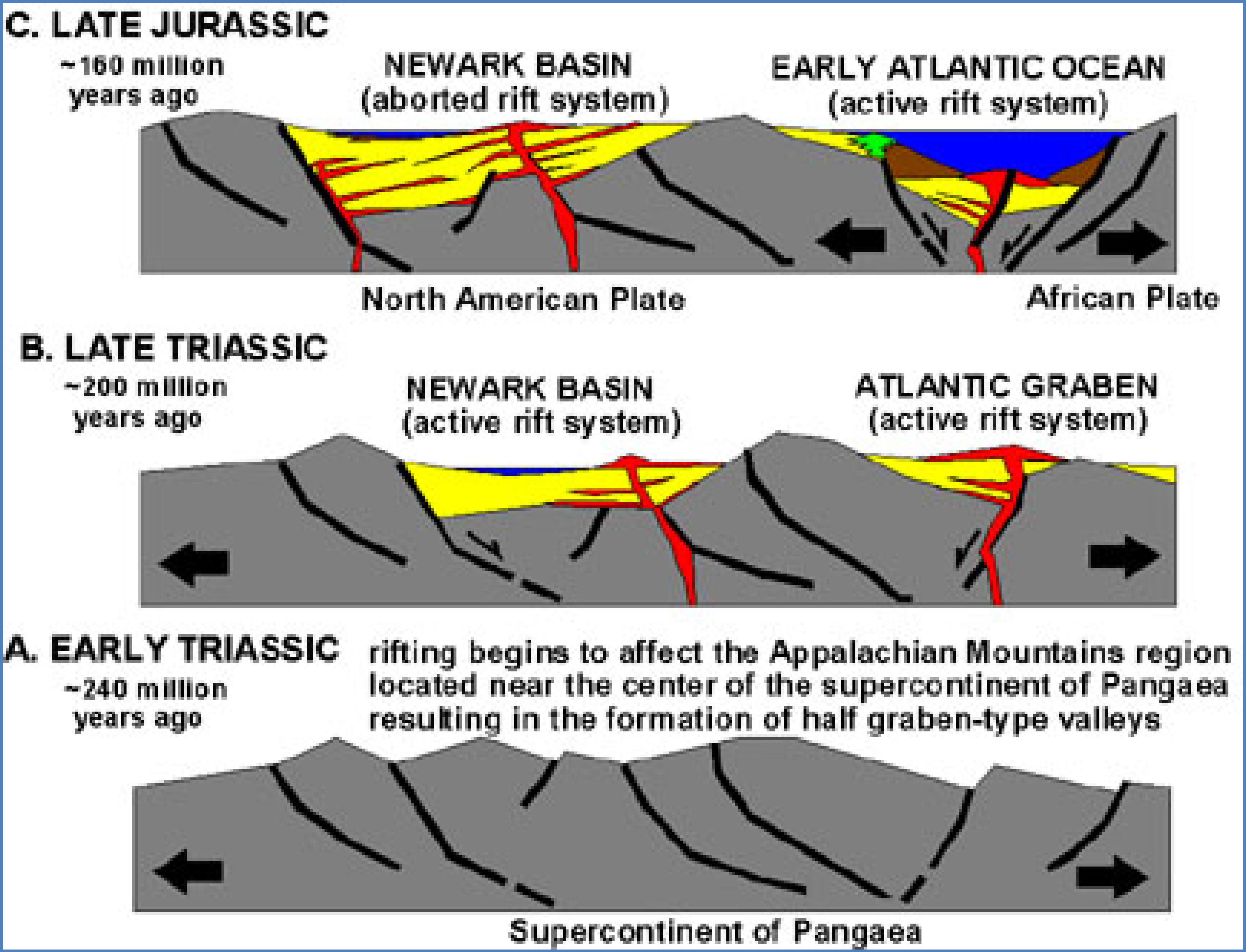
- Dan River Group, undivided - Stoneville Formation - conglomerate, sandstone and mudstone. Cow Branch Formation - mudstone. Pine Hall Formation - sandstone, mudstone and conglomerate.
- Chatham Group, undivided - Sanford Formation - conglomerate, sandstone and mudstone. Cumnock Formation - sandstone and mudstone. Pekin Formation - conglomerate, sandstone and mudstone.

GEOLOGICAL SURVEY N.C. 1823

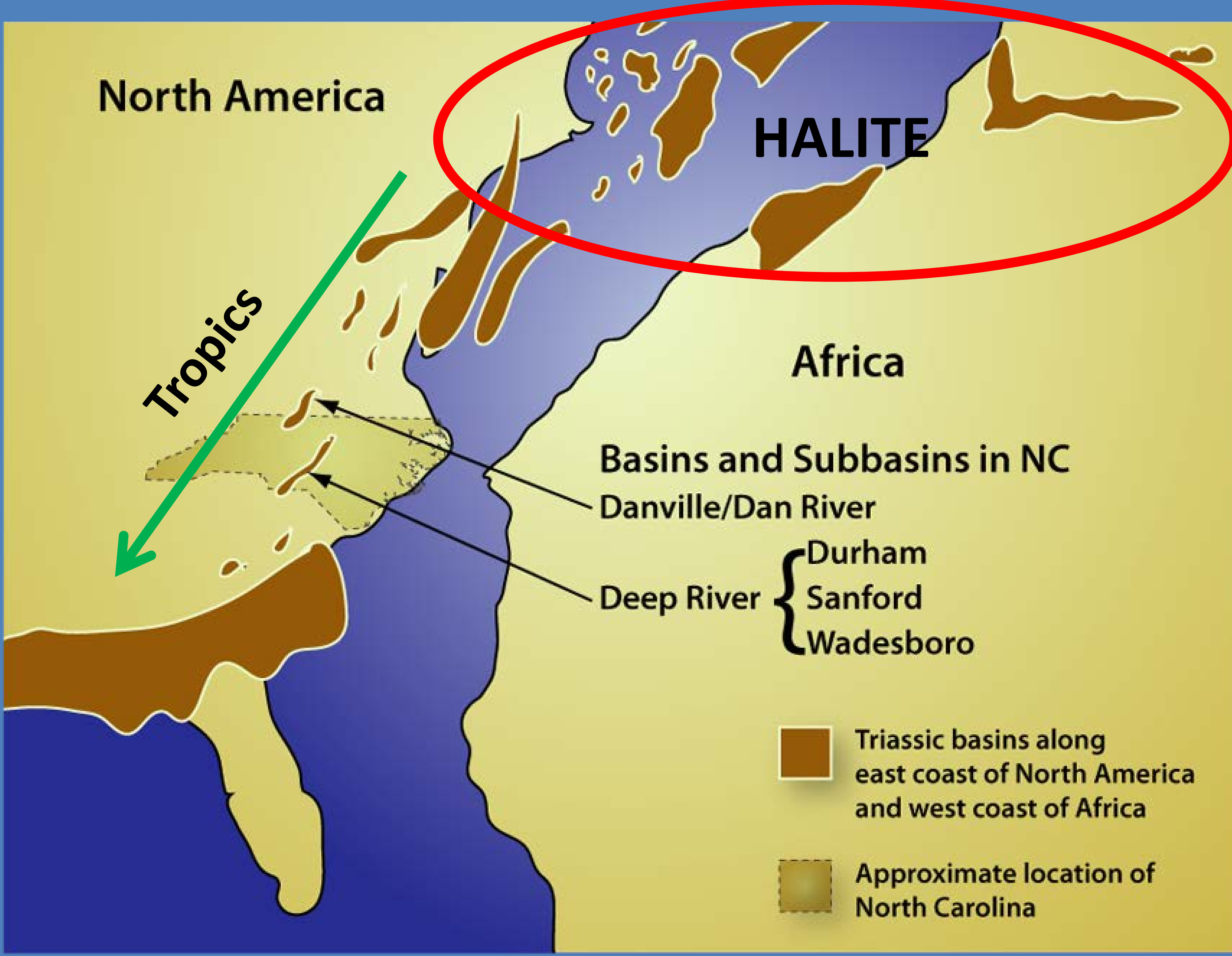
50 Miles

1991

Reprinted, 1996



3dparks.wr.usgs.gov



Generalized map of the major exposed and buried Triassic rift basins of the Newark Supergroup in North America and similar aged basins in Africa. (Modified from Ralph Lewis, Connecticut Geological Survey, www.wesleyan.edu/ctgeology/CtLandscapes/).

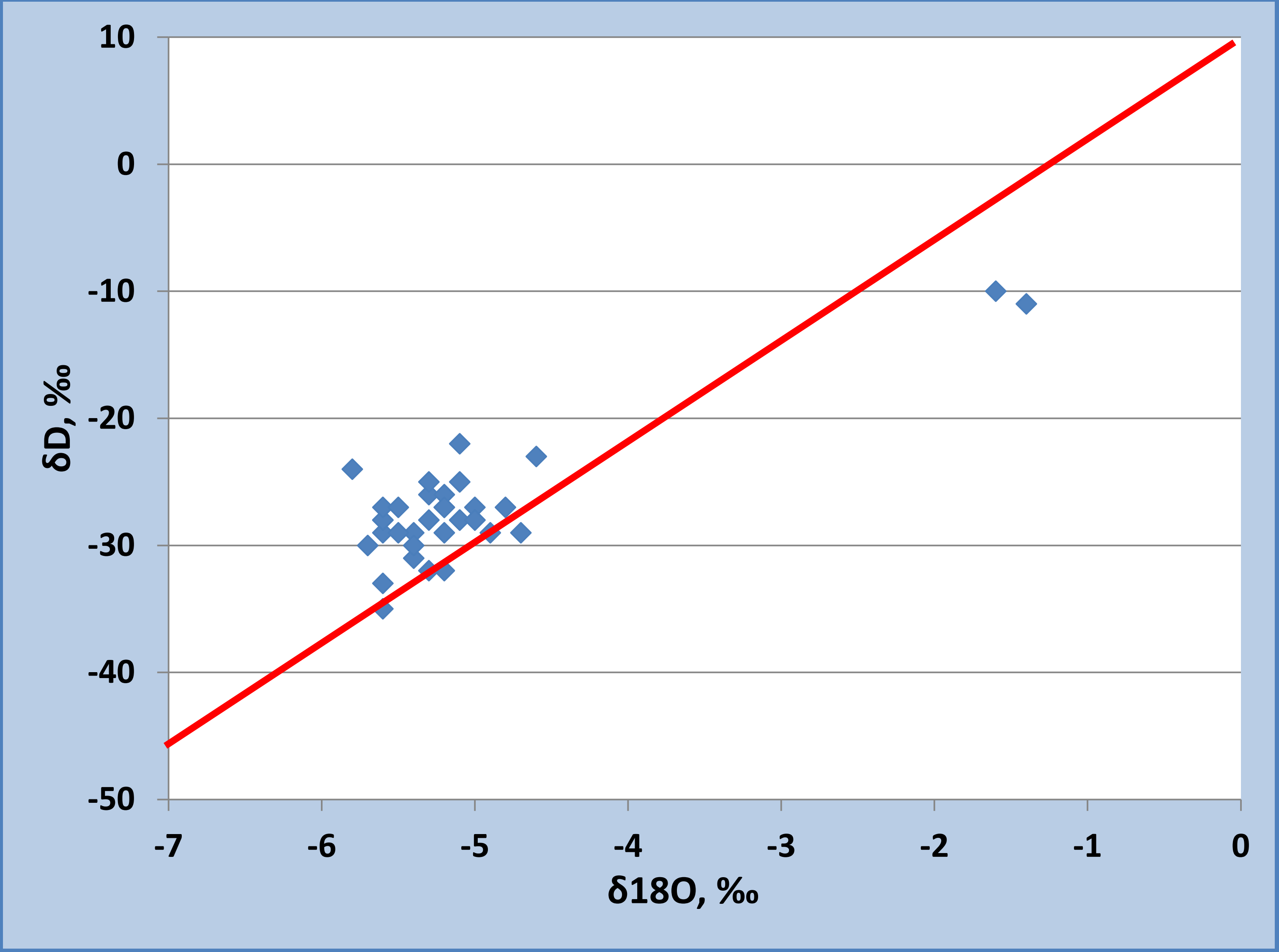
Chatham Group environment

- Fluvial and lacustrine, thousands of meters of sediment
- In Deep River basin, red bed sandstone and conglomerate, with intervining limestone and mudstone. In other areas, coal.
- Tropical latitude
- In nearby basins, evidence of drying: evaporite casts, mud cracks, caliche, gypsum beds (50-60 km south)
- Intruded by diabase

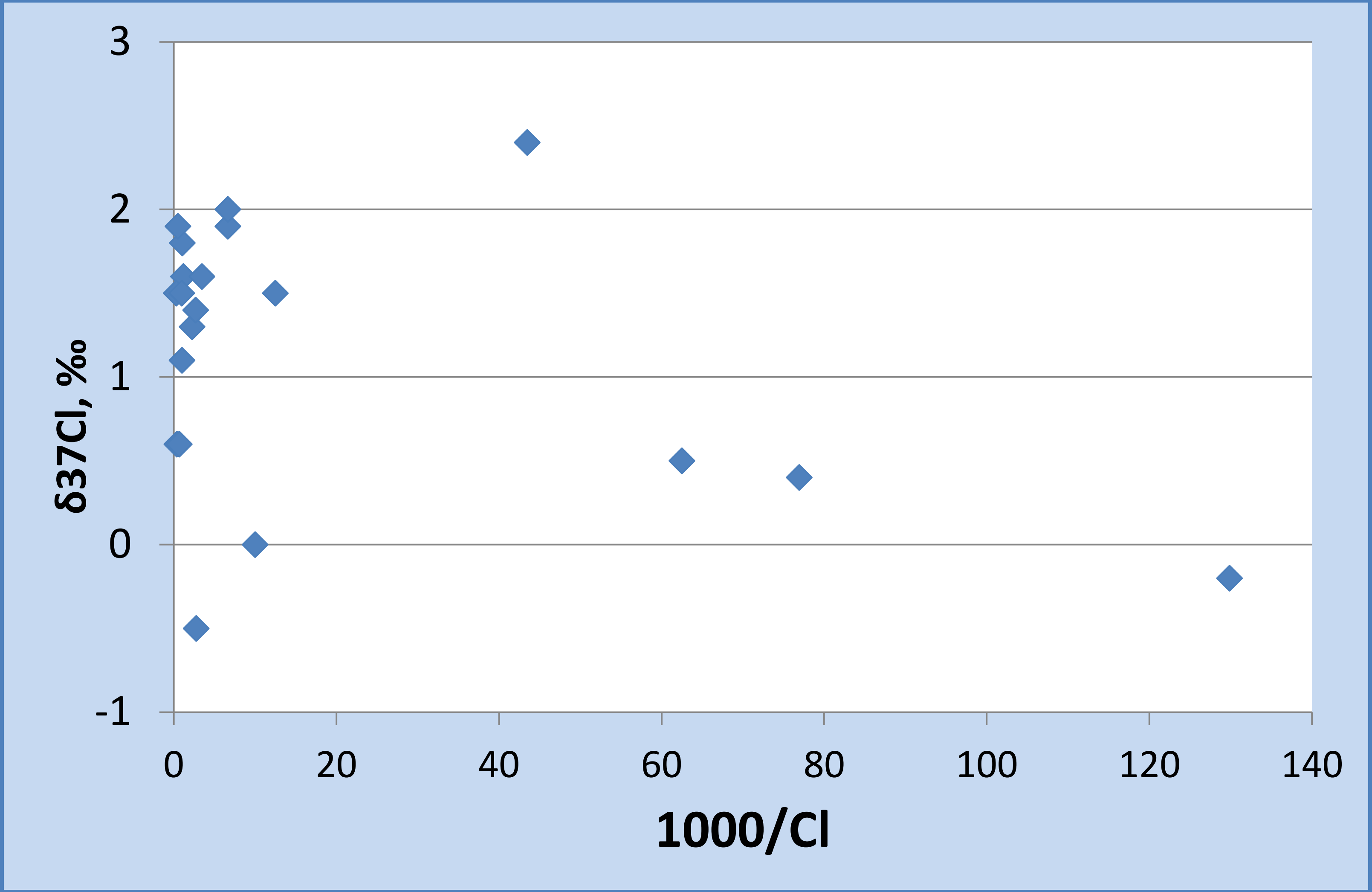
Olsen, P.E., Froelich, A.J., Daniels, D.L., Smoot, J.P. and Gore, P.J.W., 1991,   Rift basins of early Mesozoic age, in Horton, J.W. Jr. and Zullo,V.A., eds., The Geology of the Carolinas, Carolina Geological Society 50th Anniversary volume. Knoxville, Univ. of Tennessee Press, p. 142-170

Smoot, J.P. and Olsen, P.E., 1988, Massive mudstones in basin analysis and paleoclimatic interpretation of the Newark Supergroup, in Manspeizer, W., ed., Developments in Geotectonics 22: Triassic-Jurassic rifting. Amsterdam, Elsevier, p. 249-274.

Wake-Chatham OH isotopes groundwater



Wake Chatham Cl isotopes




Google earth

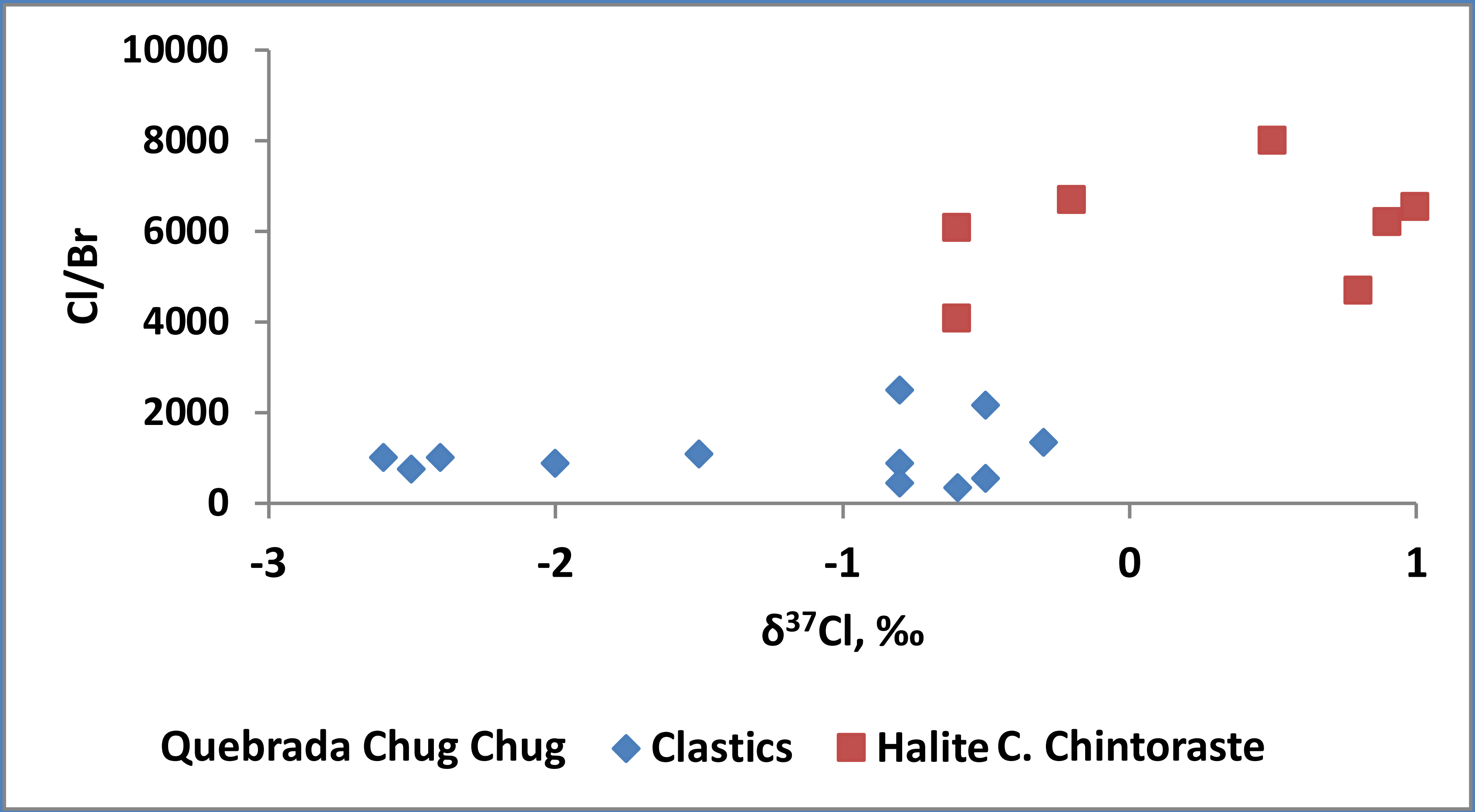

CHUG
CHUG
Radomiro Tomic mine
Chuquicamata mine
Calama
CHINTORASTE
25
23
10 km
21.9 km
Image Landsat
© 2015 Mapcity
Google earth
Imagery Date: 4/9/2013 lat -22.446112° lon -68.938166° elev 2395 m eye alt 95.53 km

Atacama desert

Cerro Chintoraste Halite

T. Arcuri

Atacama Salt



Data from Arcuri and Brimhall, *Econ. Geol*. 2003

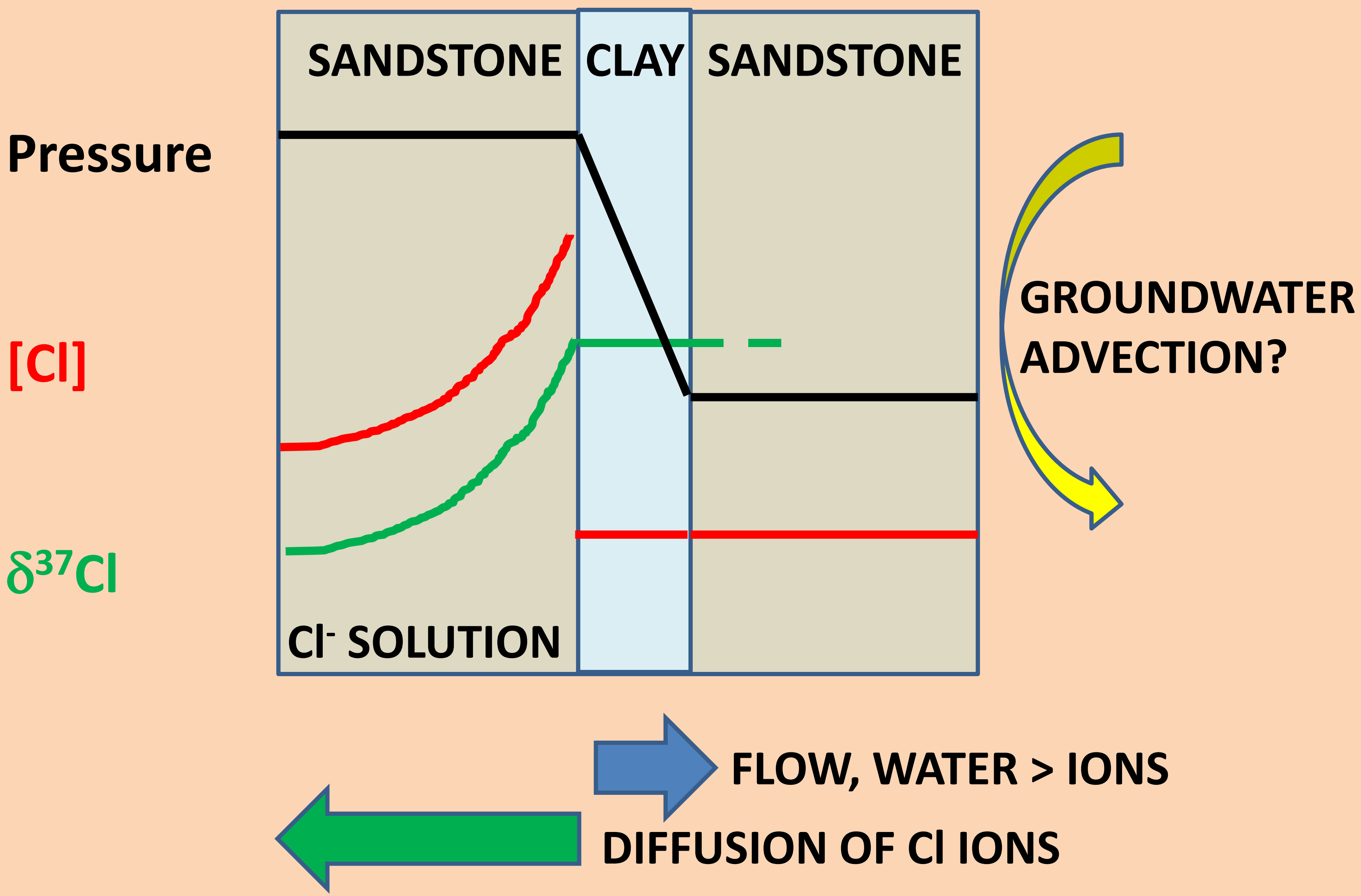
Mechanism for negative $\delta^{37}Cl$

Diffusion? (suggested by Arcuri and Brimhall, 2003)

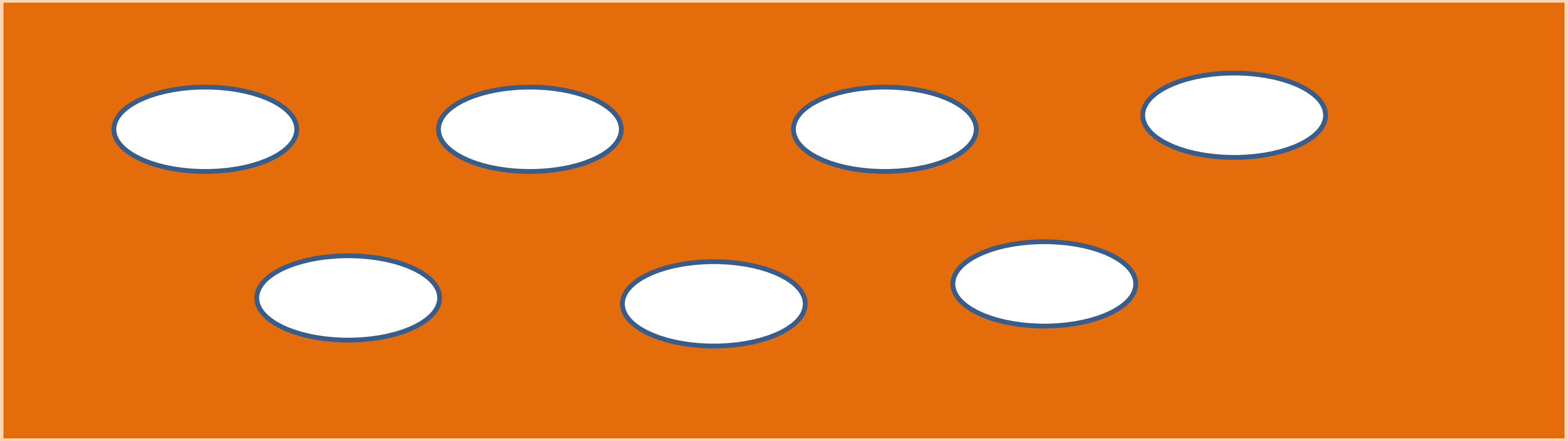
Ion filtration?

Original $\delta^{37}Cl$ values?

ION FILTRATION THROUGH MEMBRANE



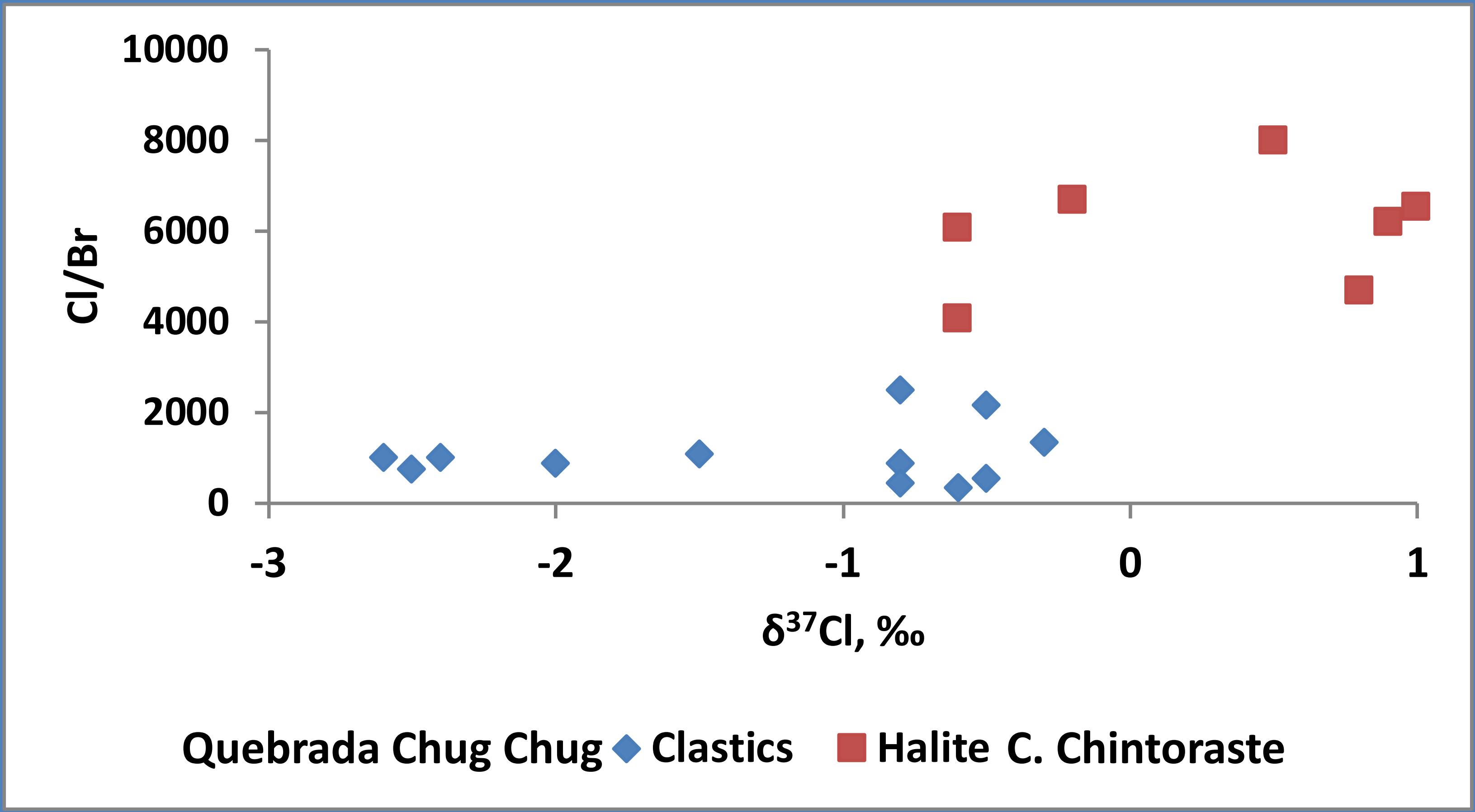
ION FILTRATION IN COMPACTING MUDSTONE?



Problems:

Isolated pores filled with fluid
Little pressure change between pores
No room for back-diffusion
Ion filtration in one pore cancels back-diffusion in next pore

Atacama Salt

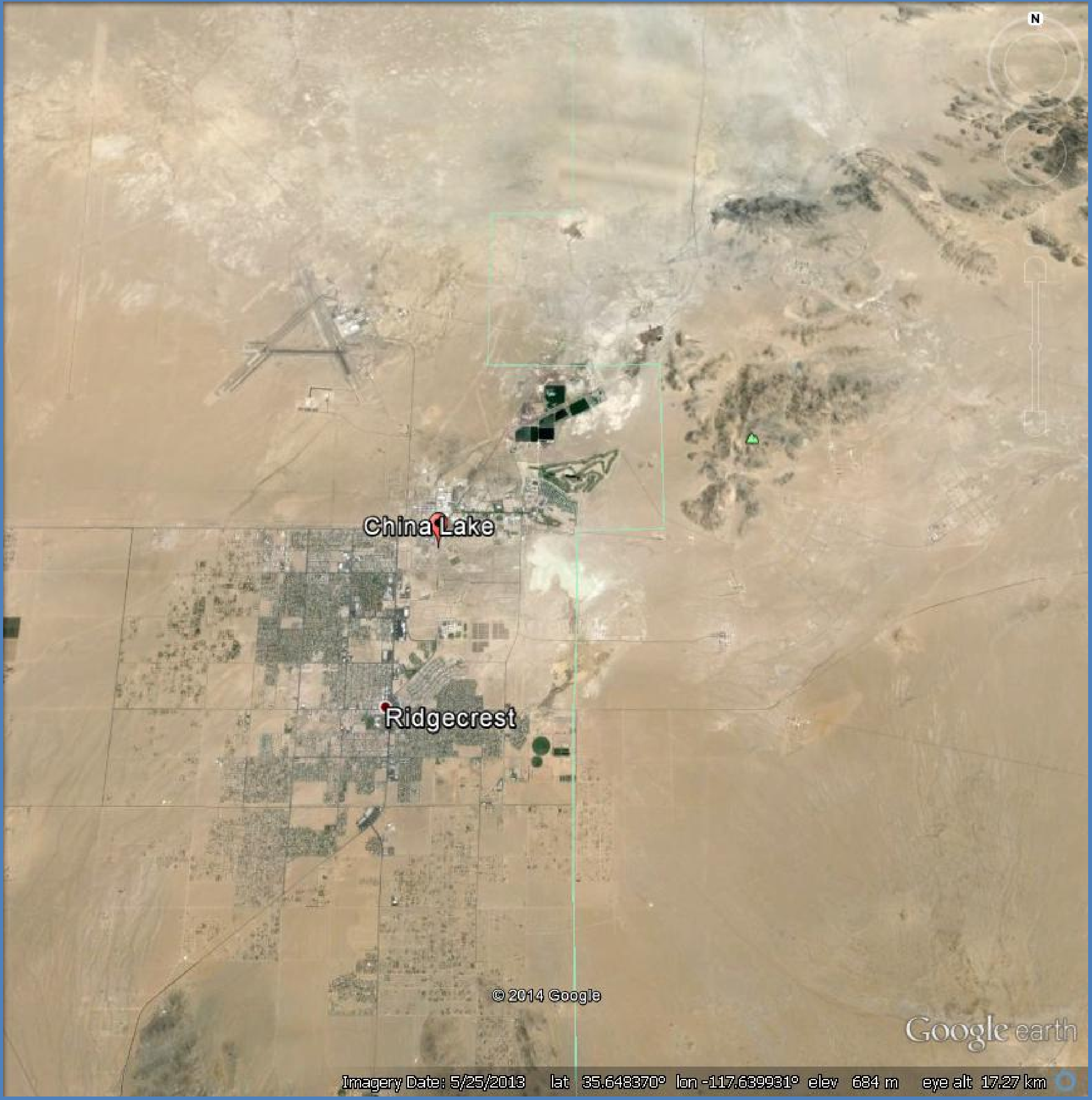


Not diffusion out of mudstone – this would leave + δ^{37}Cl

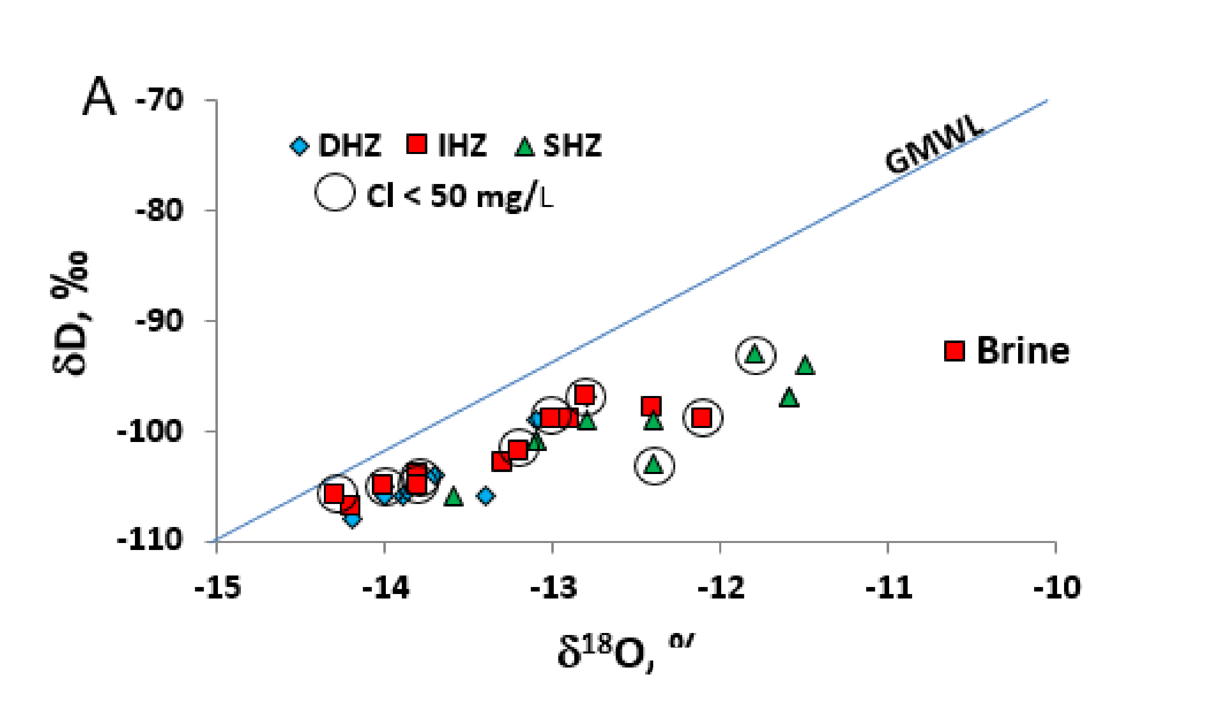
Not ion filtration

Therefore a depositional δ^{37}Cl signature?


Other Nearby Points of Interest
• Mount Whitney
• Kern River Valley
• Red Rock Canyon State Park
• Pinnacles National Natural Landmark
San Francisco
398 miles
Yosemite
Mammoth
Nevada
Monterey
Sequoia
National Park
Las Vegas
240 miles
Death Valley
Lake Meade
Hoover Dam
Bakersfield
China Lake
Santa Barbara
170 miles
Palmdale
Point Mugu
Los Angeles
160 miles
Lake Havasu
Channel Islands
Joshua
Tree
National Momument
Santa
Catalina
San Diego
255 miles
Arizona


China Lake
Ridgecrest
© 2014 Google
Google earth
Imagery Date: 5/25/2013 lat 35.648370° lon -117.639931° elev 684 m eye alt 17.27 km
N

China Lake California



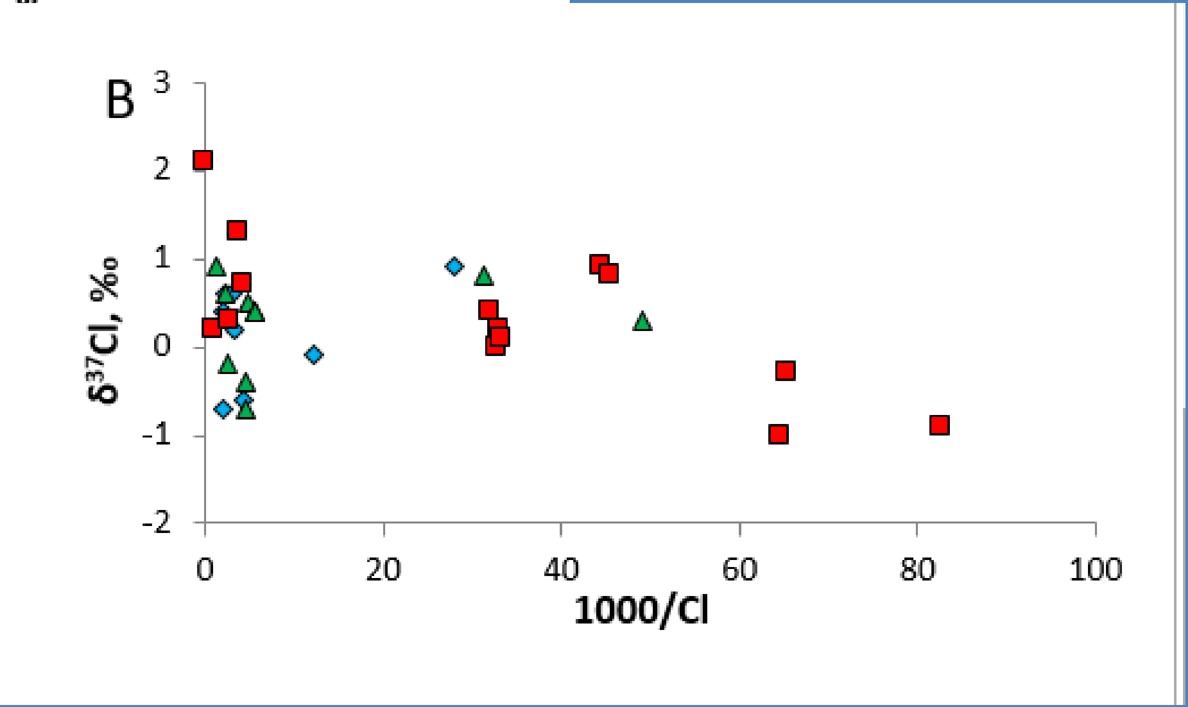
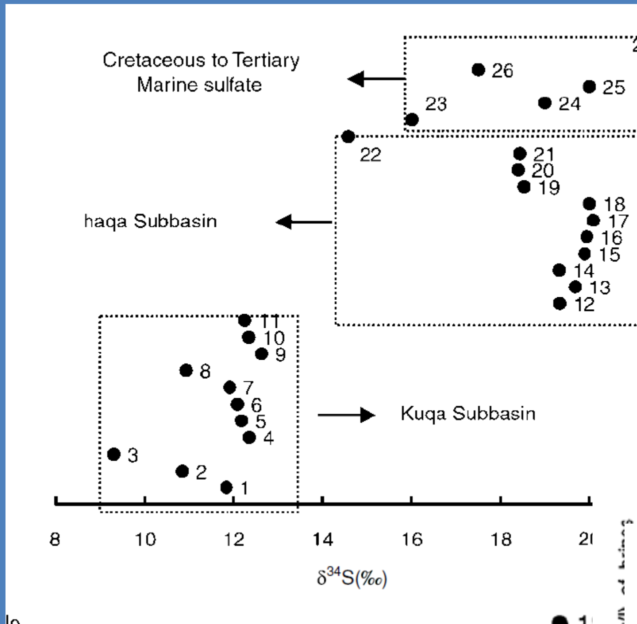
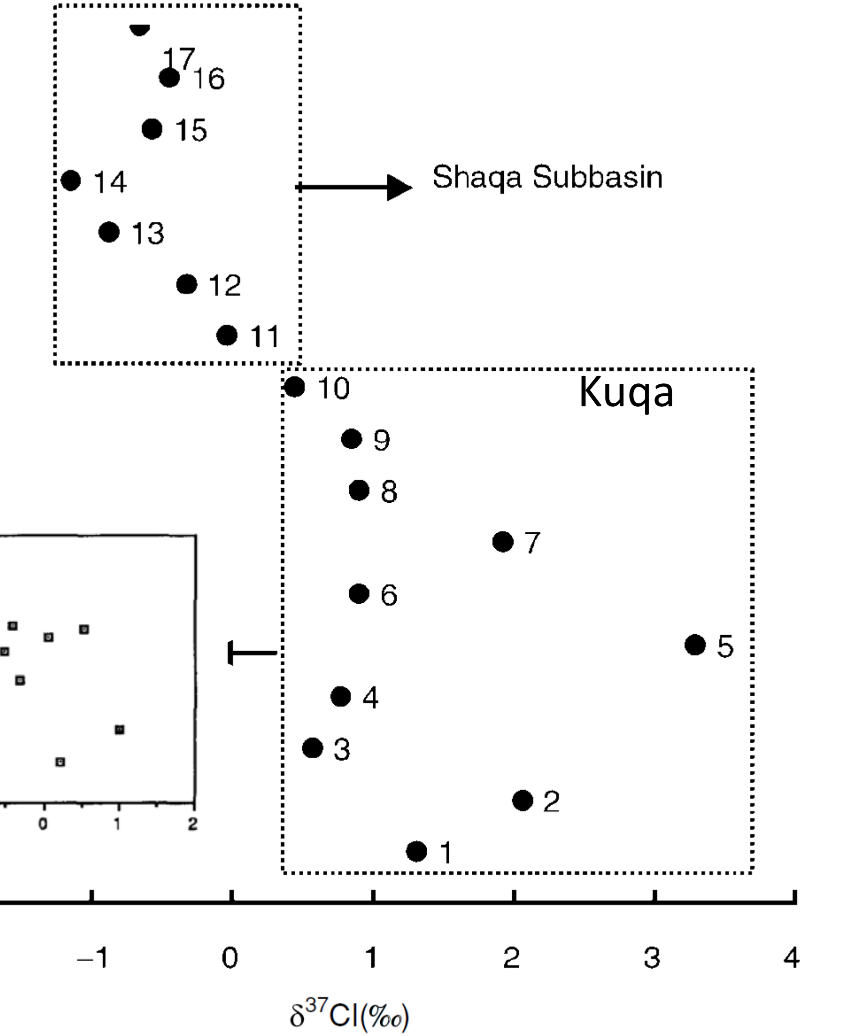


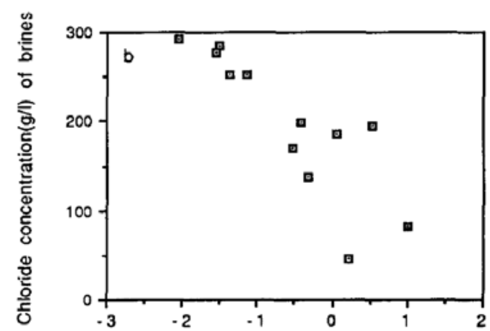
Table 3
Chlorine isotope and chlorine, bromine, and boron contents of middle–late Eocene halite from the Yunying depression.

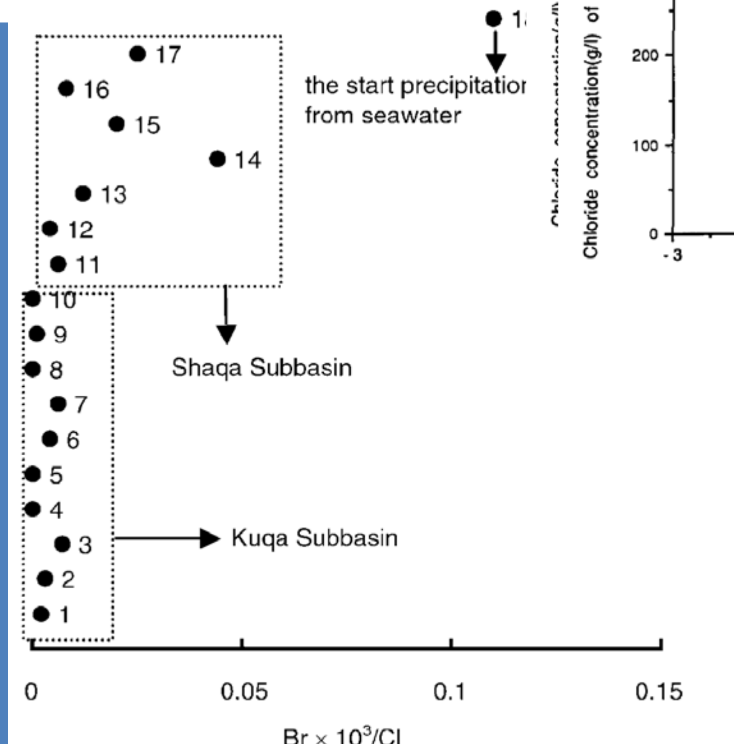
Samples	$\delta^{37}Cl$	Error SD (n = 3)	Cl^- (%)	Br^- (ppm)	B_2O_3 (%)
YC-1	1.70	0.03	60.31	<2	<0.0006
YC-2	2.49	0.01	60.23	<2	<0.0006
YC-3	1.82	0.10	60.26	<2	0.0023
YC-4	0.89	0.14	60.41	<2	<0.0006
YC-5	2.04	0.11	58.87	<2	<0.0006
YC-6	−0.11	0.14	60.36	<2	<0.0006
YC-7	0.14	0.22	60.20	<2	0.0009
YC-8	2.09	0.16	60.25	<2	<0.0006

Meng et al., 2014, Jianghan Basin, China



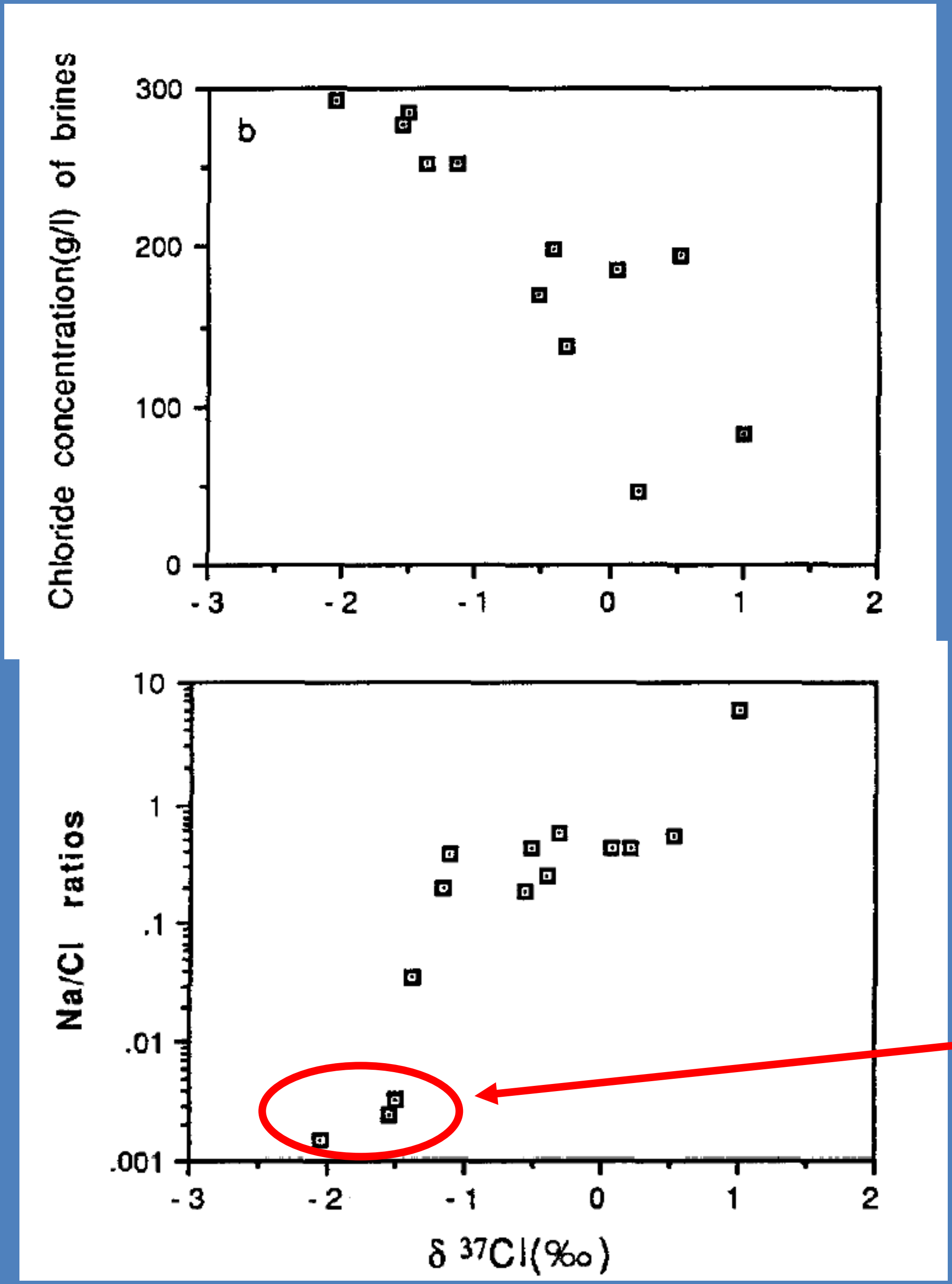






Tarim Basin

Tan et al, 2006



Liu et al, 1997

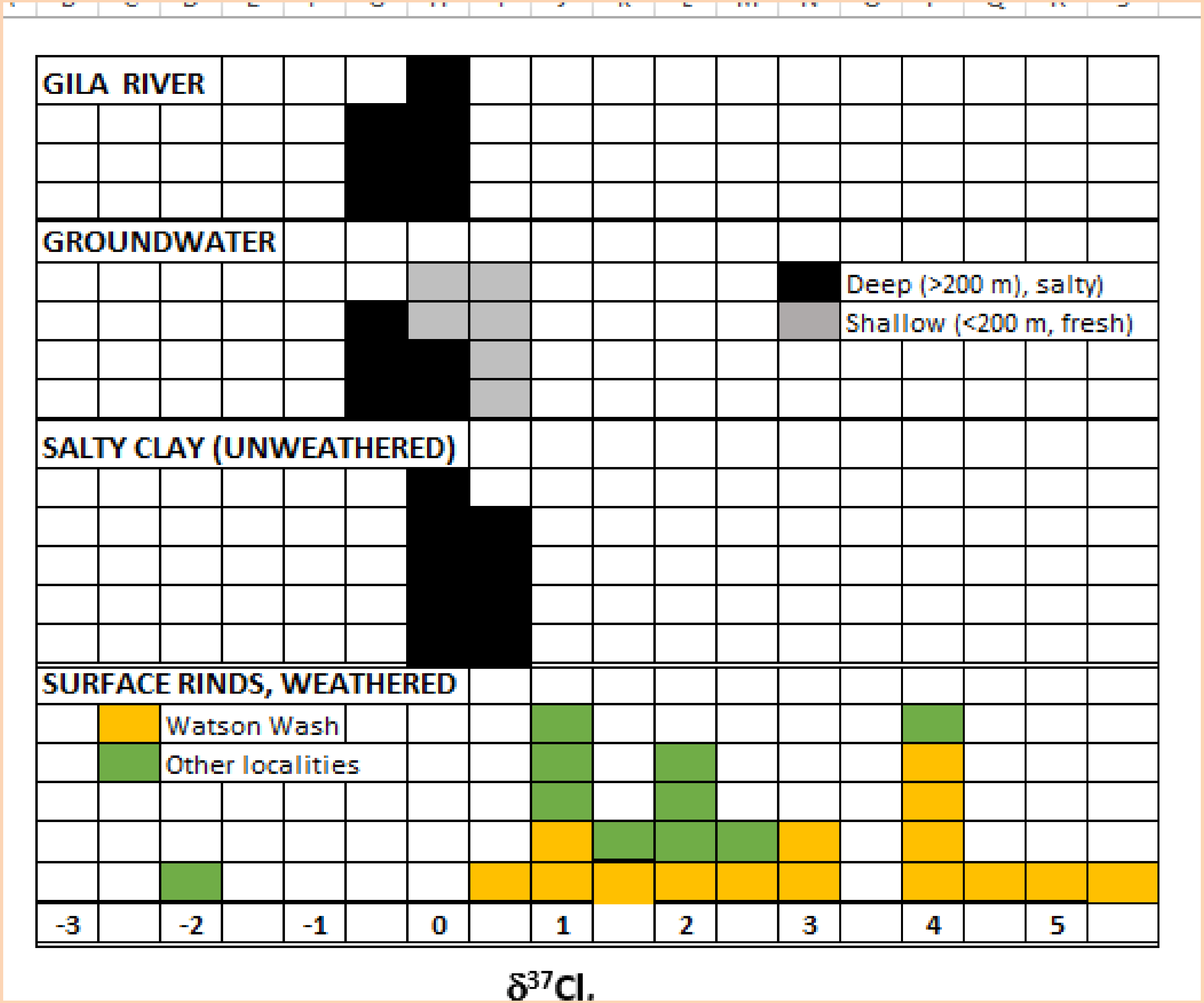
Qaidam Basin salt lakes

Oilfield Ca-Cl brines

Fig. 1: Location Map


N
Safford, AZ
11.5 km
Google earth
Imagery Date: 5/9/2014 lat 32.819533° lon -109.680204° elev 900 m eye alt 49.73 km

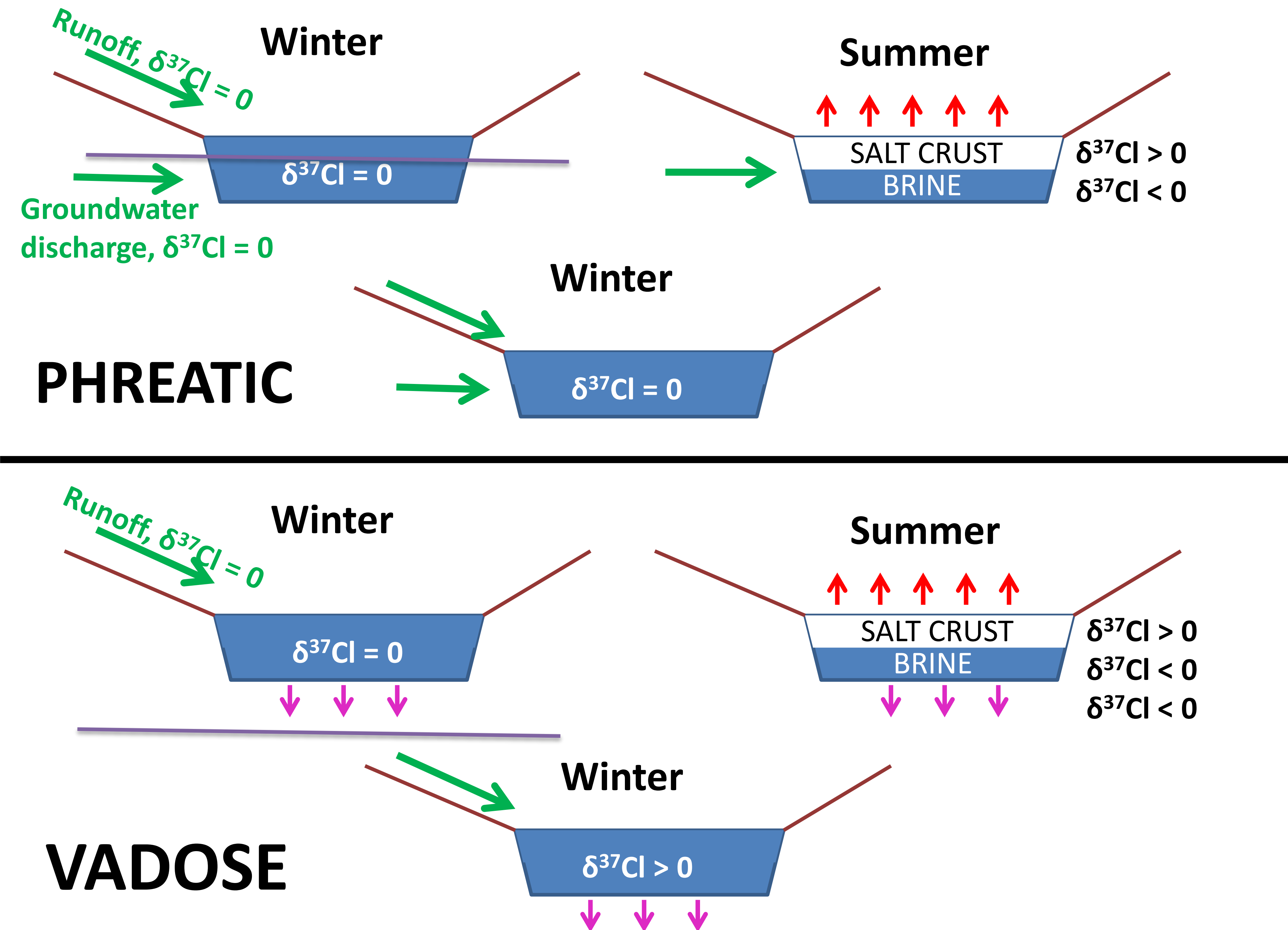
SAFFORD BASIN



Safford Basin
Watson Wash

FRACTIONATION MECHANISMS

- We need to generate a large change (at least 2‰)
- We need fractionation in both positive and negative directions
- Mechanism is acceptable only if it also keeps the fractions of chloride separate in the long term
- Diffusion, halite crystallization can operate


Runoff, δ37Cl = 0
Winter
Summer
δ37Cl = 0
Groundwater
discharge, δ37Cl = 0
SALT CRUST
BRINE
δ37Cl > 0
δ37Cl < 0
Winter
δ37Cl = 0
PHREATIC
Runoff, δ37Cl = 0
Winter
Summer
δ37Cl = 0
SALT CRUST
BRINE
δ37Cl > 0
δ37Cl < 0
δ37Cl < 0
Winter
δ37Cl > 0
VADOSE

Cl isotope fractionation in a vadose playa

Winter:

playa receives runoff

all halite dissolves

small net gain of NaCl (otherwise playa salt would eventually disappear)

bulk δ^{37}Cl doesn't change

Summer:

no runoff

halite crust forms, with brine beneath

small net loss of NaCl to groundwater in brine

bulk δ^{37}Cl increases in playa

Cl isotope fractionation in a vadose playa

$b^0 = \delta^{37}Cl$ of initial brine = 0.0‰

a = net fraction of initial Cl gained during winter, 0.0‰

f = fraction of total NaCl in salt crust

$h = \delta^{37}Cl$ of bulk halite crust

$B = \delta^{37}Cl$ of brine below halite crust

$= hf/(f+1)$ (Rayleigh fractionation; isotope balance)

$b' = \delta^{37}Cl$ of brine at end of winter after one evap. cycle

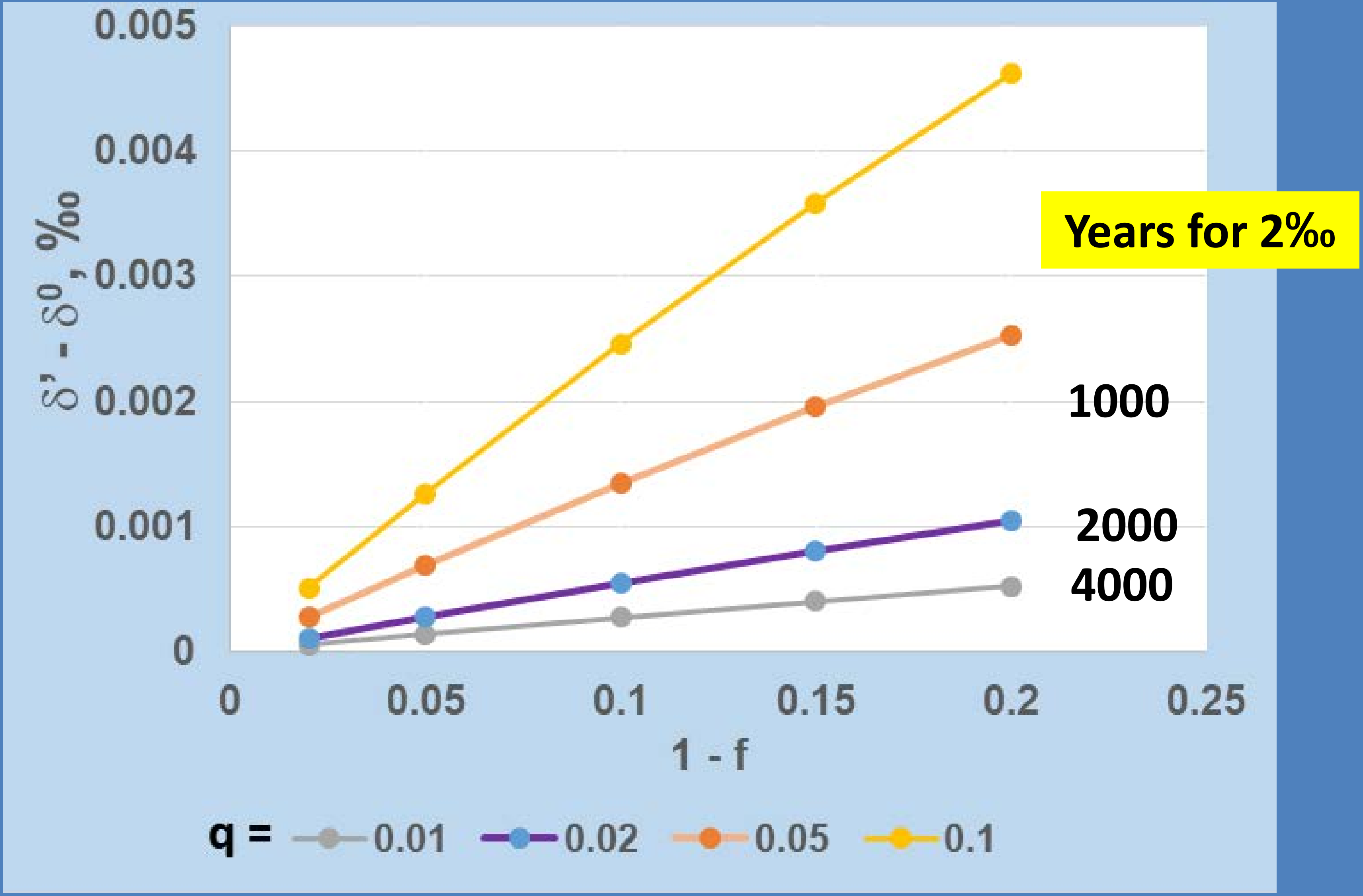
q = fraction of brine discharged each summer

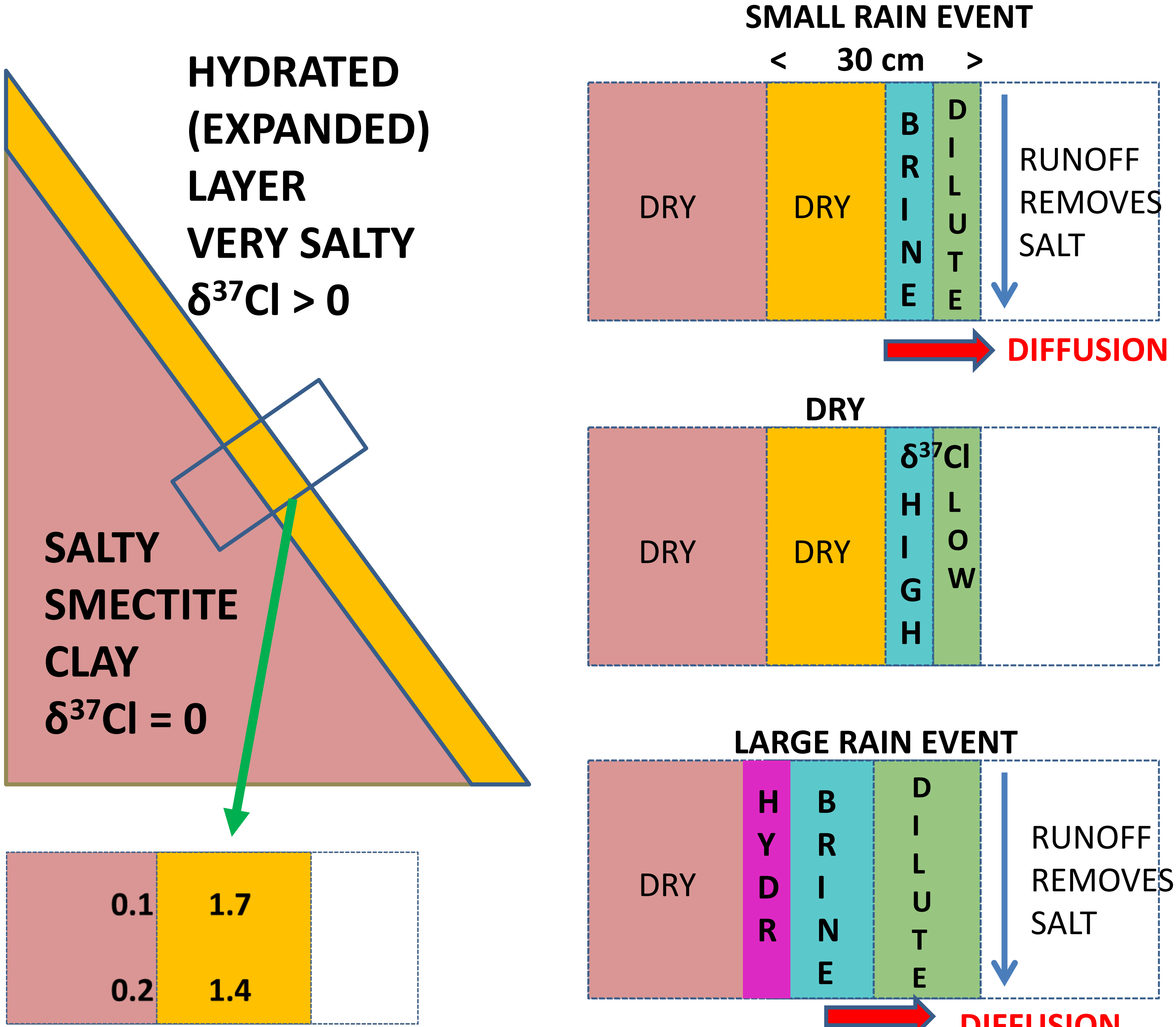
ISOTOPE BALANCE GIVES:

$$b' [(1-f)(1-q) + f + a] = (1-f)(1-q) B + fh + a(0)$$

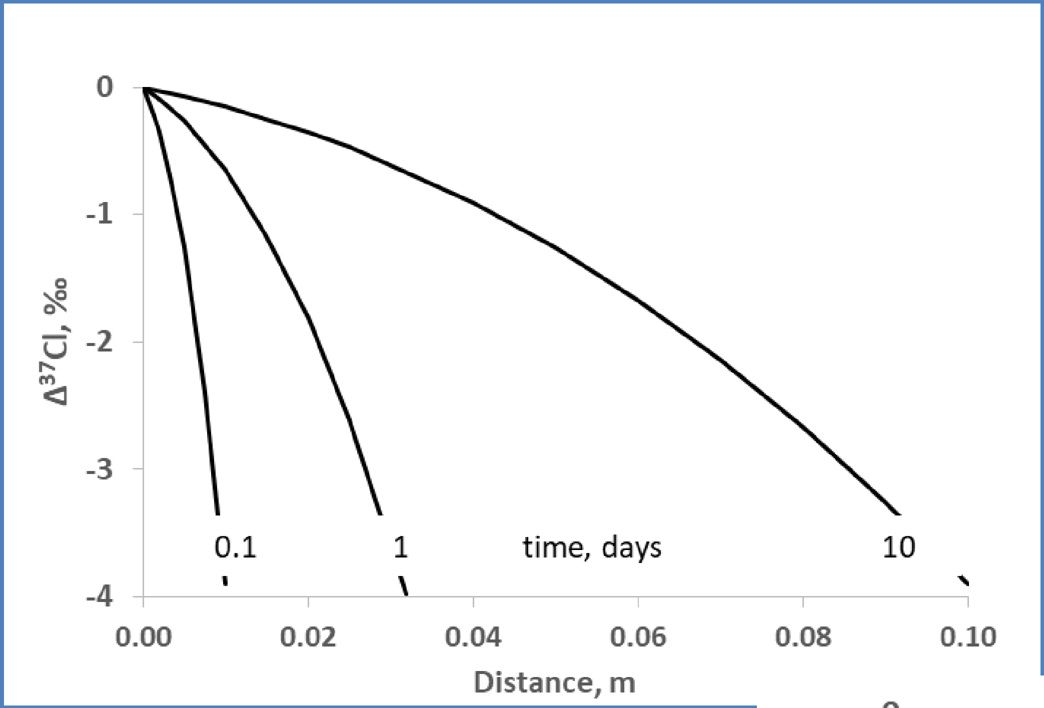
brine crust new NaCl

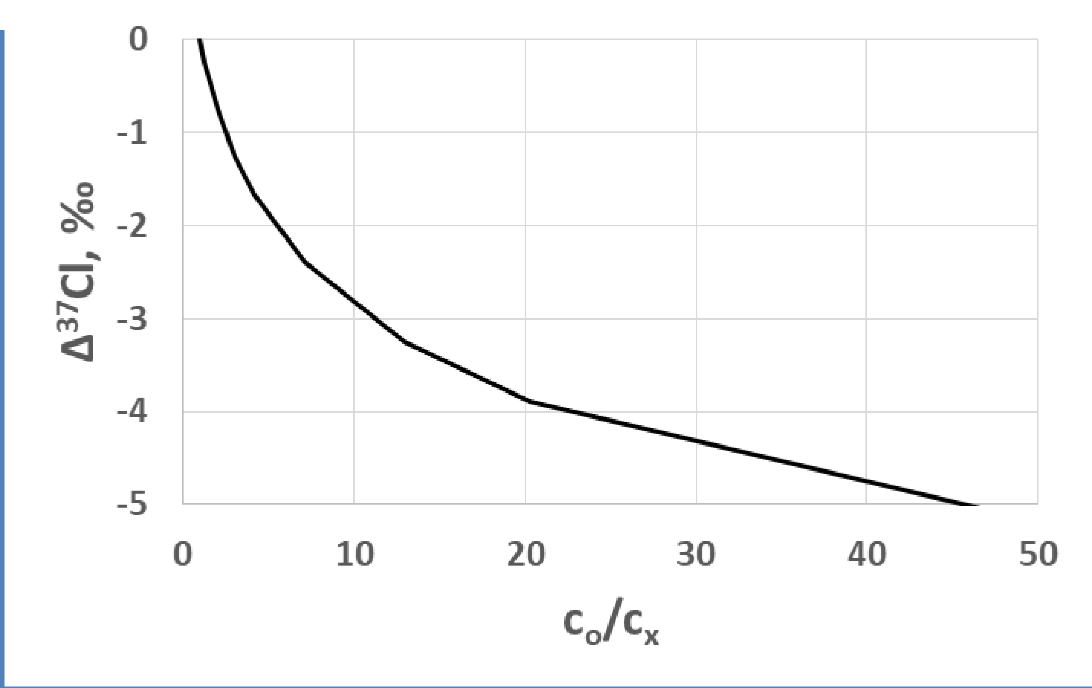
Cl isotope fractionation in a vadose playa




HYDRATED
(EXPANDED)
LAYER
VERY SALTY
$\delta^{37}Cl > 0$
SALTY
SMECTITE
CLAY
$\delta^{37}Cl = 0$
0.1
1.7
0.2
1.4
SMALL RAIN EVENT
< 30 cm >
DRY
DRY
BRINE
DILUTE
RUNOFF
REMOVES
SALT
DIFFUSION
DRY
DRY
DRY
$\delta^{37}Cl$
HIGH
LOW
LARGE RAIN EVENT
DRY
HYDR
BRINE
DILUTE
RUNOFF
REMOVES
SALT
DIFFUSION

Fick's Law diffusion





Playas with negative $\delta^{37}Cl$

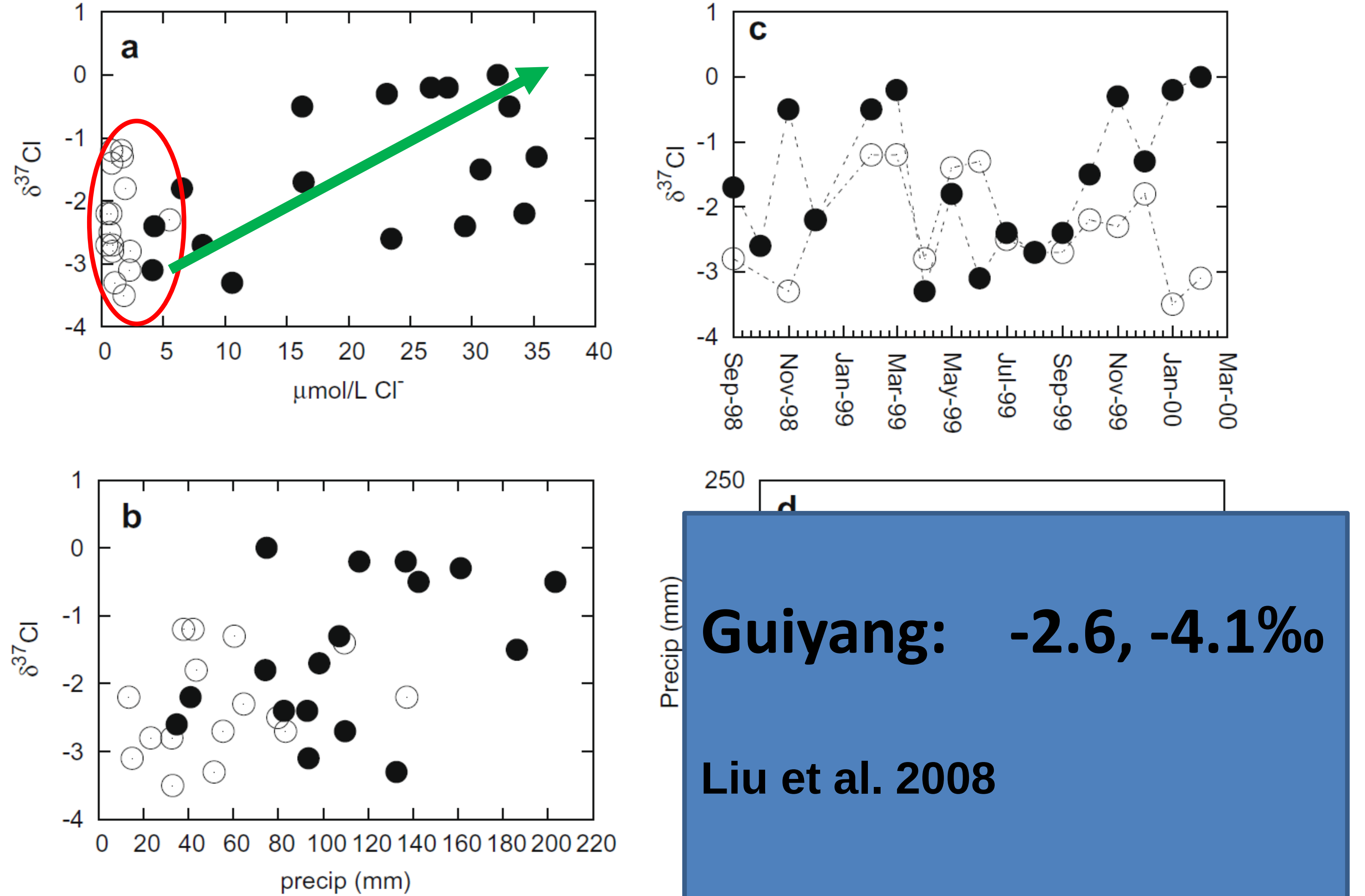
- $\delta^{37}Cl$ values -1.5 to -2.7 ‰

- Can’t be explained by halite crystallization

- Unlikely to be caused by diffusion, because negative $\delta^{37}Cl$ would correspond with low Cl concentration

- Fractionated chloride source, rather than fractionation in basin

RAINWATER, CANADA



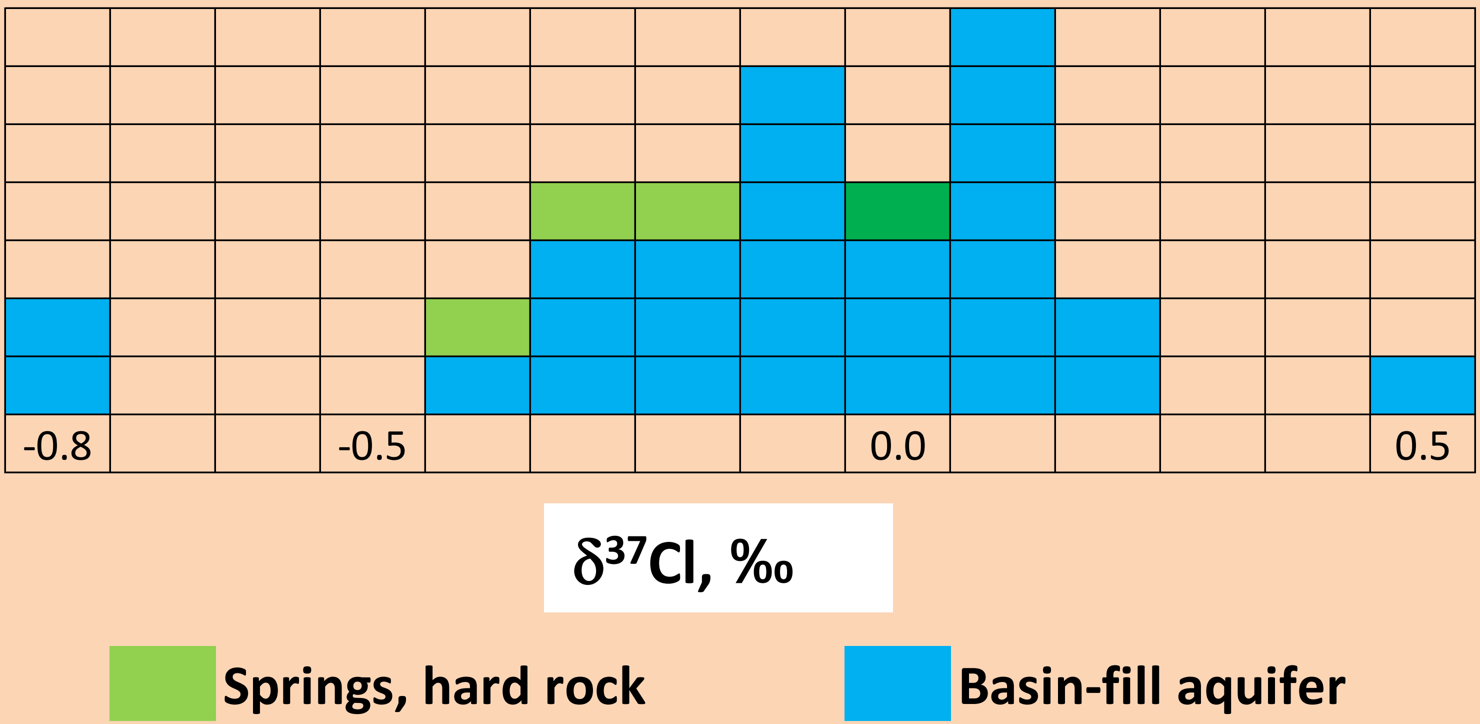
Guiyang: -2.6, -4.1‰

Liu et al. 2008

Fig. 2. Variability of $\delta^{37}Cl$ values of dissolved Cl^- in rainwater with respect to Cl^- concentrations (a), amount of precipitation (b), and collection date (c). The relationship between precipitation amount and date is shown in (d). Open and closed circles represent samples from Bonner Lake and Bay D'Espoir, respectively.

Koehler and Wassenaar, 2010

Tucson Basin Groundwater, Histogram



Conclusions

- Salt found in many arid/semiarid basins has a wide range of $\delta^{37}Cl$, -3 to +5 ‰
- $\delta^{37}Cl$ range +1 to 2 ‰ is common, and found in lacustrine halite or brine.
- Positive $\delta^{37}Cl$: halite crystallization + vadose playa processes
- Near-0 $\delta^{37}Cl$: phreatic playa processes
- Negative $\delta^{37}Cl$: uncertain source of chloride fractionation; rainwater?
- Fractionation due to diffusion in weathered smectite cannot keep different chloride fractions separate.

Fig. 2: Map of Safford Basin

Fig 2.cdr