Interpreting Groundwater in Eocene Aquifers by Isotopic Measurements: Piceance Basin, Colorado

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An array of isotope measurements has been used by Shell to refine Piceance Basin hydrologic model inputs. Water-bearing strata between kerogen-rich Eocene Oil Shale layers yield isotopic data that constrain groundwater sources, age of recharge, flow paths, flow velocities and a number of water:rock reactions. A record of mixing of a relatively low volume of water from the upper part of the stratigraphic section (Uinta) to the lower water bearing units (base of Parachute Creek) is recorded by Sr isotope analysis. Oxygen isotope analysis demonstrates that some recharge to deeper units occurred prior to the last ice age or even much earlier. $\delta^{34}S$ values in dissolved sulfate, in combination with $\delta^{13}C$ and oxygen isotope data, increase downgradient in the Parachute Creek, yet the carbon isotopes decrease downgradient in the Uinta – the former likely a result of biogenic sulfate reduction, and the latter a result of carbonate dissolution. These results demonstrate that inclusion of isotopic data significantly augments traditional approaches to basin hydrologic modeling.

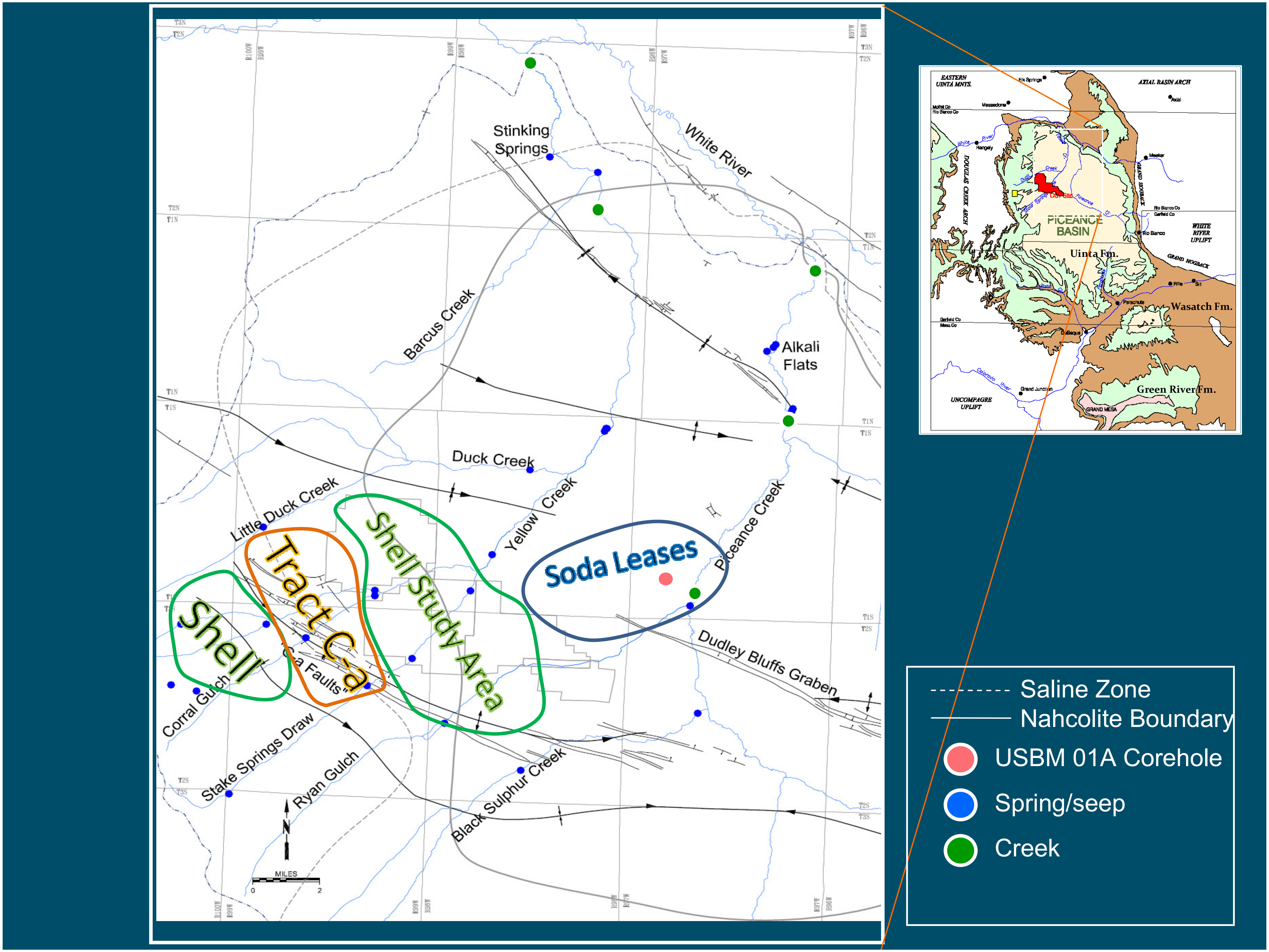
ISOTOPE APPLICATIONS
PICEANCE BASIN

Purpose:

Investigate groundwater age, sources of chemical mass, and nature of geochemical reactions that control the chemistry of ground and surface water.

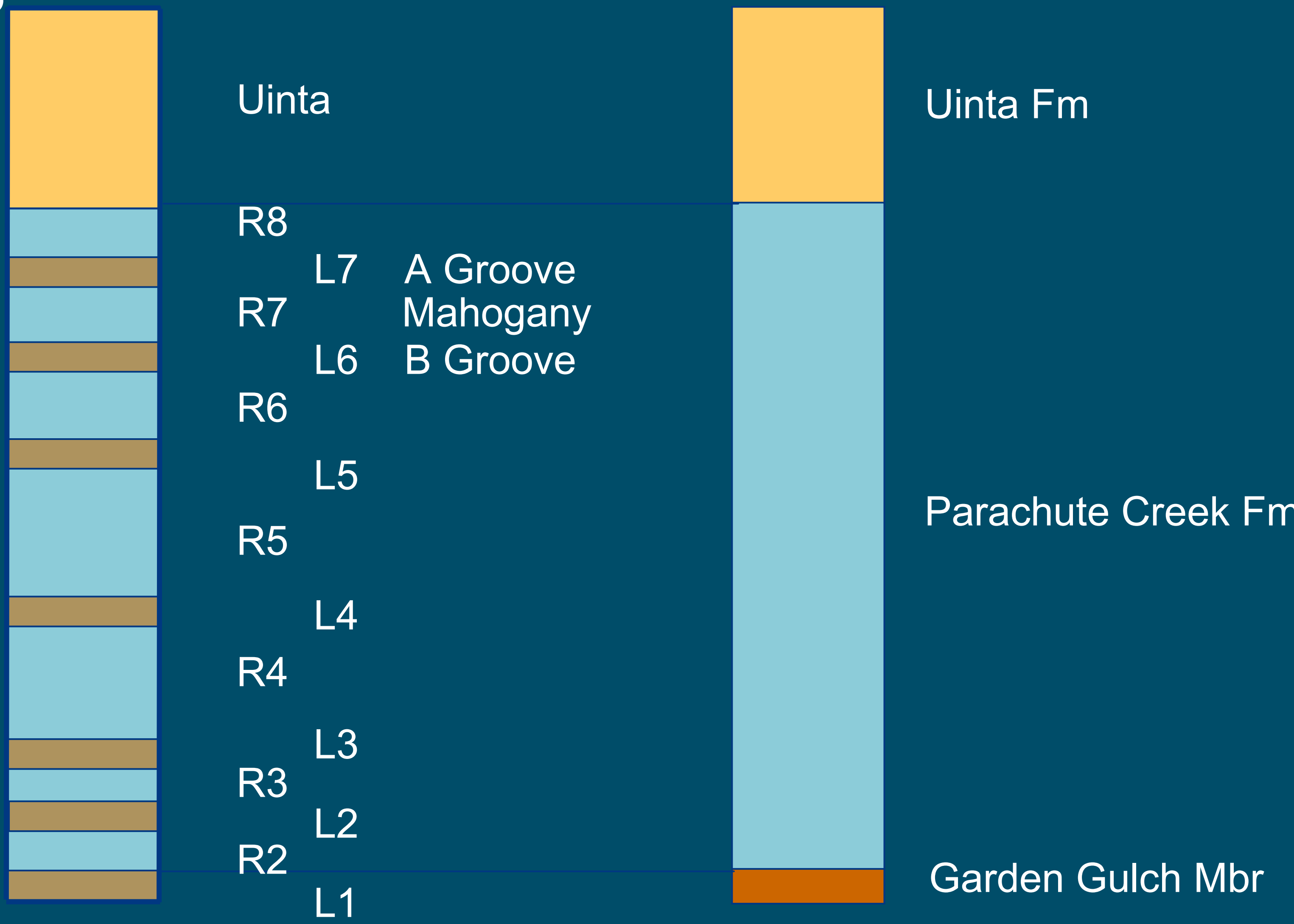
Applications:

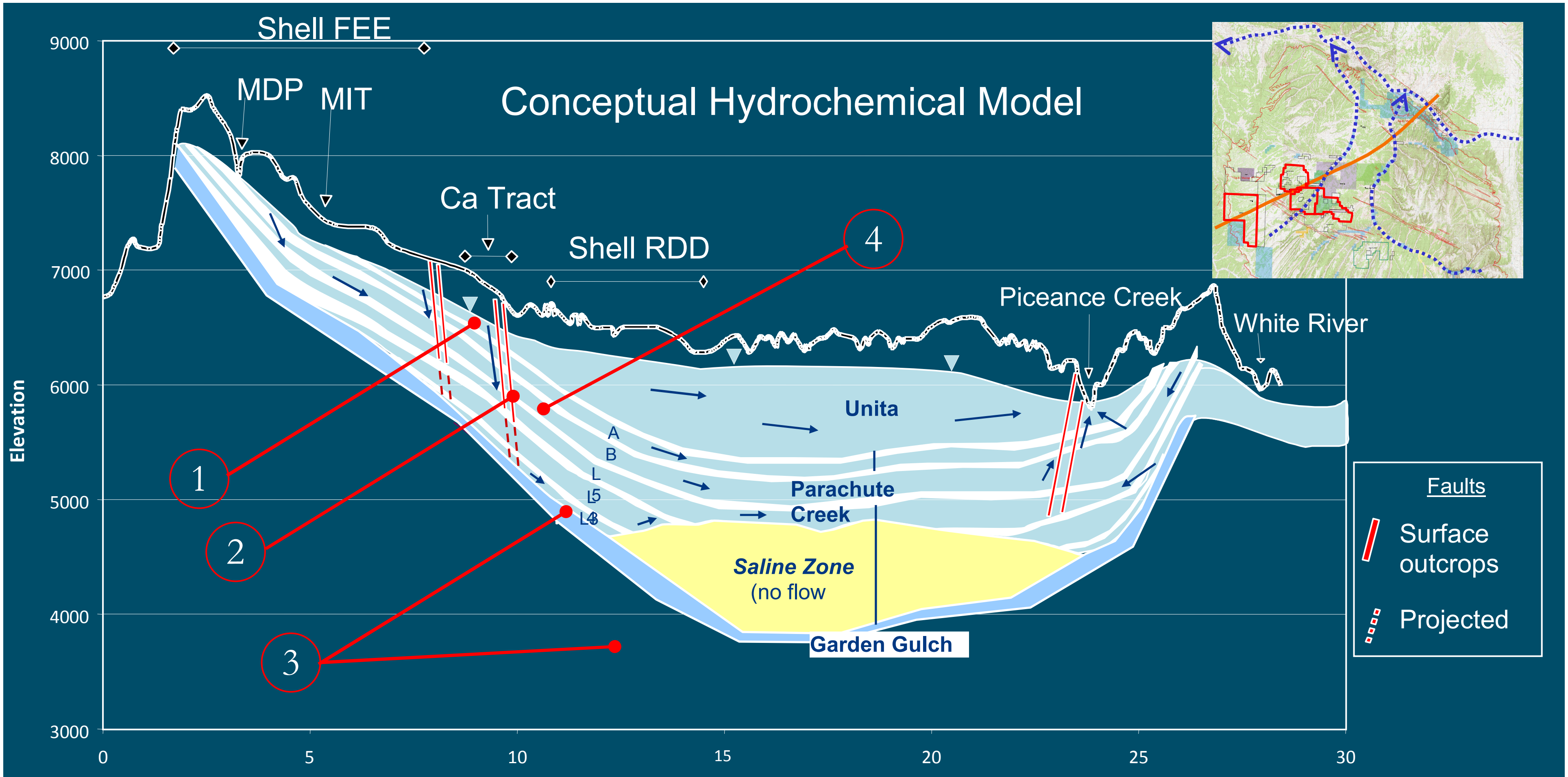
- Source of dissolved constituents
- Geochemical processes (sulfate reduction, fractionation, other)
- Groundwater age
- Flow pathways – recharge / discharge areas



Stinking Springs
White River
Barcus Creek
Alkali Flats
Duck Creek
Little Duck Creek
Yellow Creek
Piceance Creek
Soda Leases
Tract C-a
Shell Study Area
Shell
"C-a Faults"
Corral Gulch
Dudley Bluffs Graben
Stake Springs Draw
Ryan Gulch
Black Sulphur Creek
MILES
0
2
N
PICEANCE BASIN
Uinta Fm.
Wasatch Fm.
Green River Fm.
EASTERN UINTA MNTS.
AXIAL BASIN ARCH
DOUGLAS CREEK ARCH
GRAND HOGBACK
WHITE RIVER UPLIFT
UNCOMPAGRE UPLIFT
GRAND MESA
Saline Zone
Nahcolite Boundary
USBM 01A Corehole
Spring/seep
Creek

STRATIGRAPHIC UNITS – CASHION AND DONNELL – USGS 1976





1 • Oxidation of sulfide, production of acidity, neutralization by carbonate (calcite/dolomite), ion exchange, dissolution of aluminosilicates(?)

2 • Percolation via enhanced vertical permeability along C-a faults, recharge to WBIs above R5

3 • Methane and CO_2 upwelling both from depth and from R-zones

4
- Microbial sulfate reduction / anaerobic oxidation of methane; greatest at fault; lesser down gradient in a WBI.
- Governs isotopic signal of S, C, O (little);
- Once consumed, mixing with deeper WBI water rules

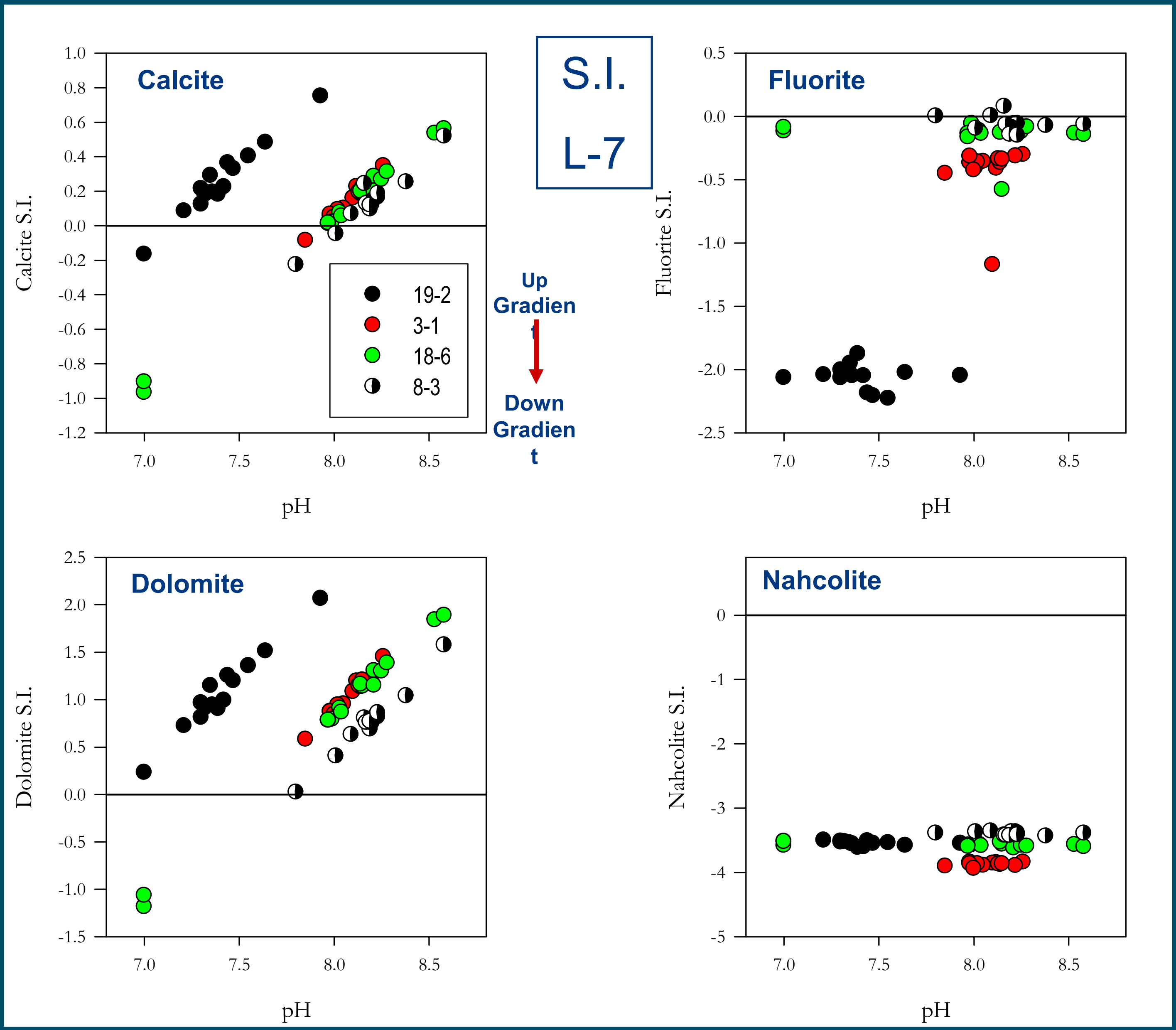
Sulfate Reduction Process in Shallow Uinta Formation

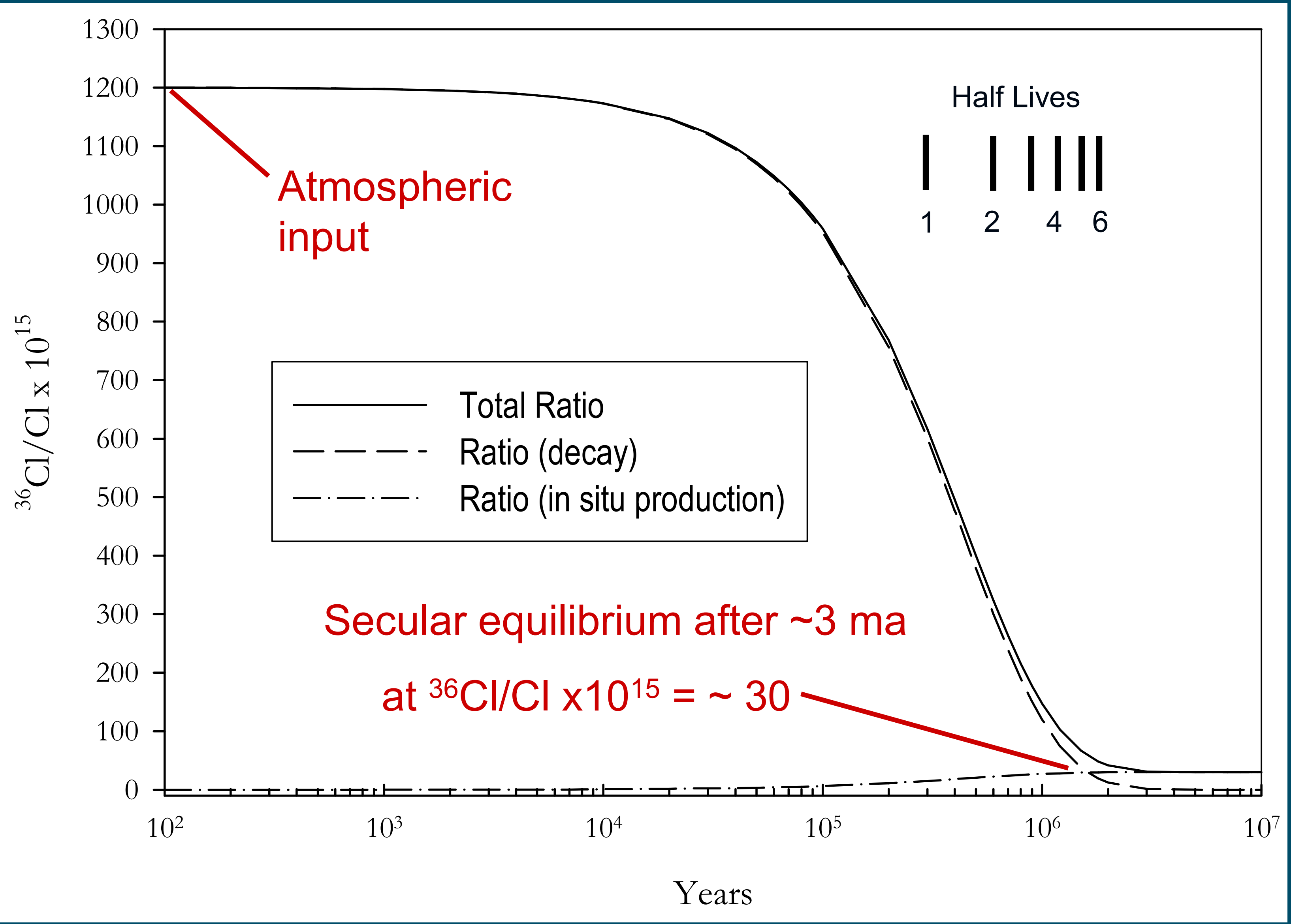
1. Pyrite oxidation in Uinta
2. Anaerobic oxidation of methane
3. Sulfate reduction
4. Recharge of sulfate/sulfide waters does not reach deeper water bearing zones

$$2FeS_2 + 2O_2 = 2SO_4^{=} + 2Fe^{+2}$$

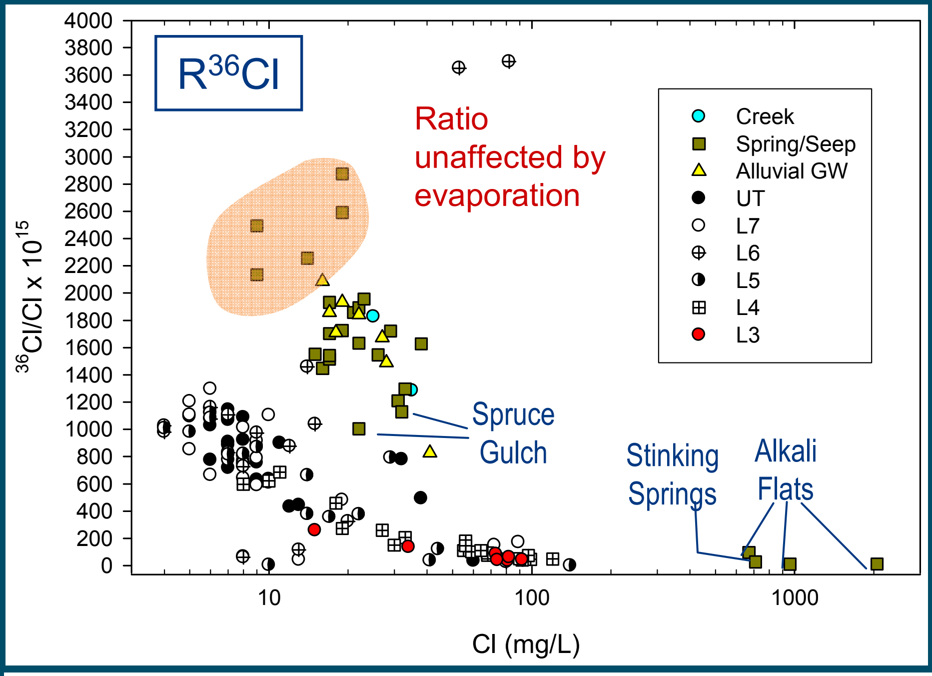
$$CH_4 + 2SO_4^{=} + H^+ = H_2S + HCO_3^- + H_2O$$

5. Nahcolite (halite) dissolution

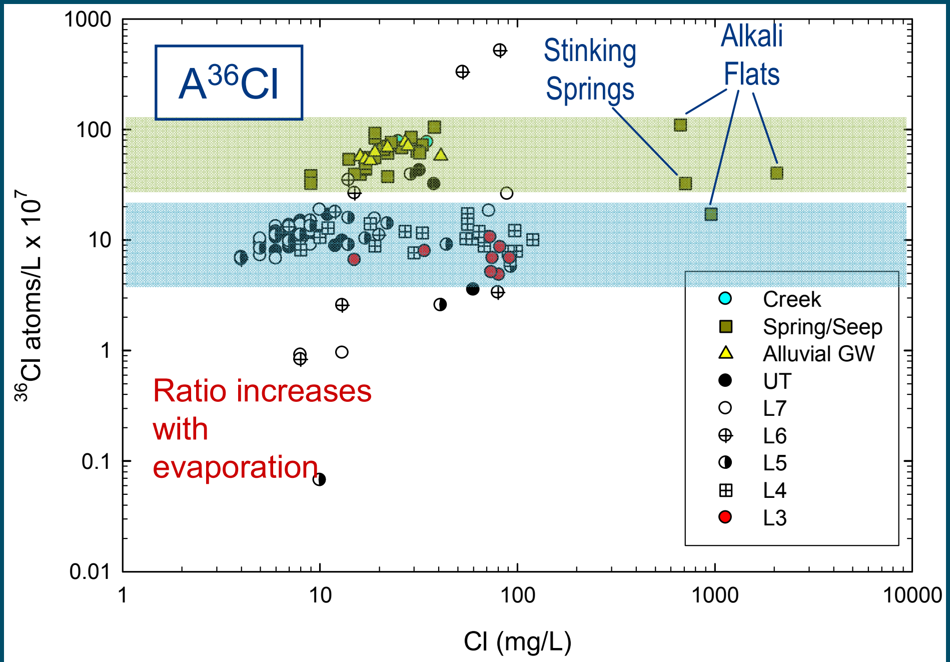

S.I.
L-7
Calcite
Calcite S.I.
pH
19-2
3-1
18-6
8-3
Up
Gradien
t
Down
Gradien
t
Fluorite
Fluorite S.I.
pH
Dolomite
Dolomite S.I.
pH
Nahcolite
Nahcolite S.I.
pH



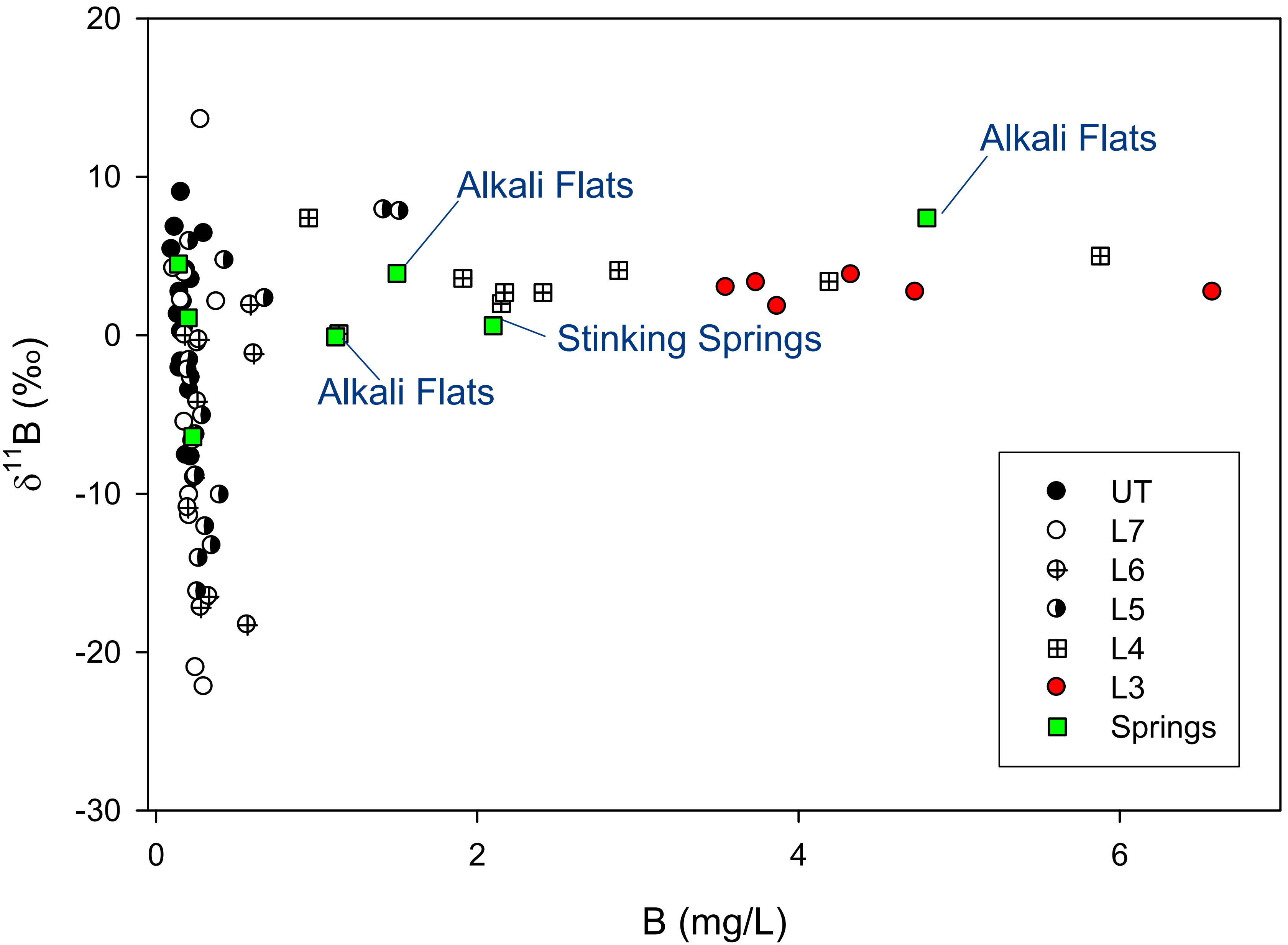
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
$^{36}Cl/Cl \times 10^{15}$
10^2
10^3
10^4
10^5
10^6
10^7
Years
Atmospheric input
Half Lives
1
2
4
6
Total Ratio
Ratio (decay)
Ratio (in situ production)
Secular equilibrium after ~3 ma
at $^{36}Cl/Cl \times 10^{15}$ = ~ 30



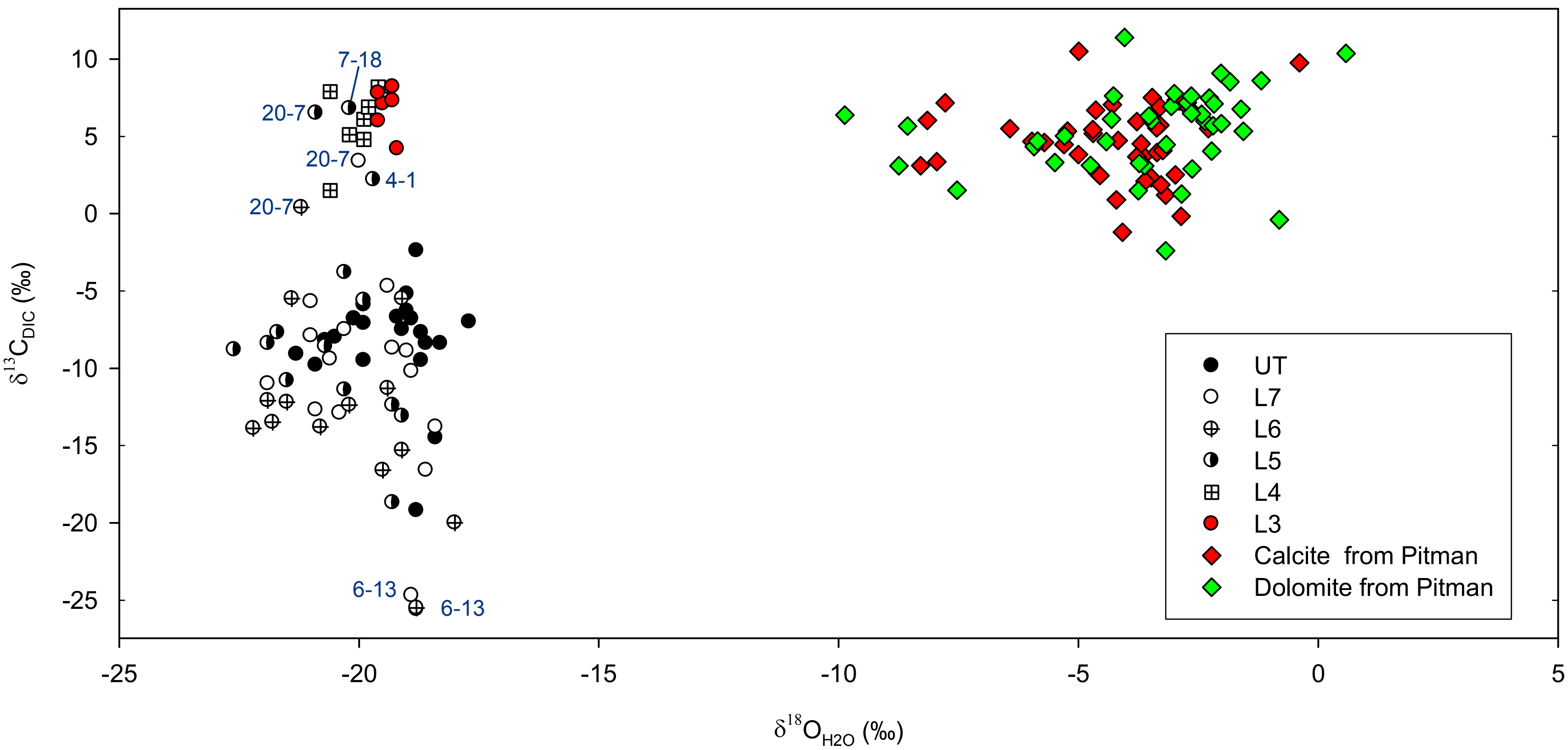
R36Cl
Ratio unaffected by evaporation
Creek
Spring/Seep
Alluvial GW
UT
L7
L6
L5
L4
L3
Spruce Gulch
Stinking Springs
Alkali Flats
36Cl/Cl x 10^15
Cl (mg/L)



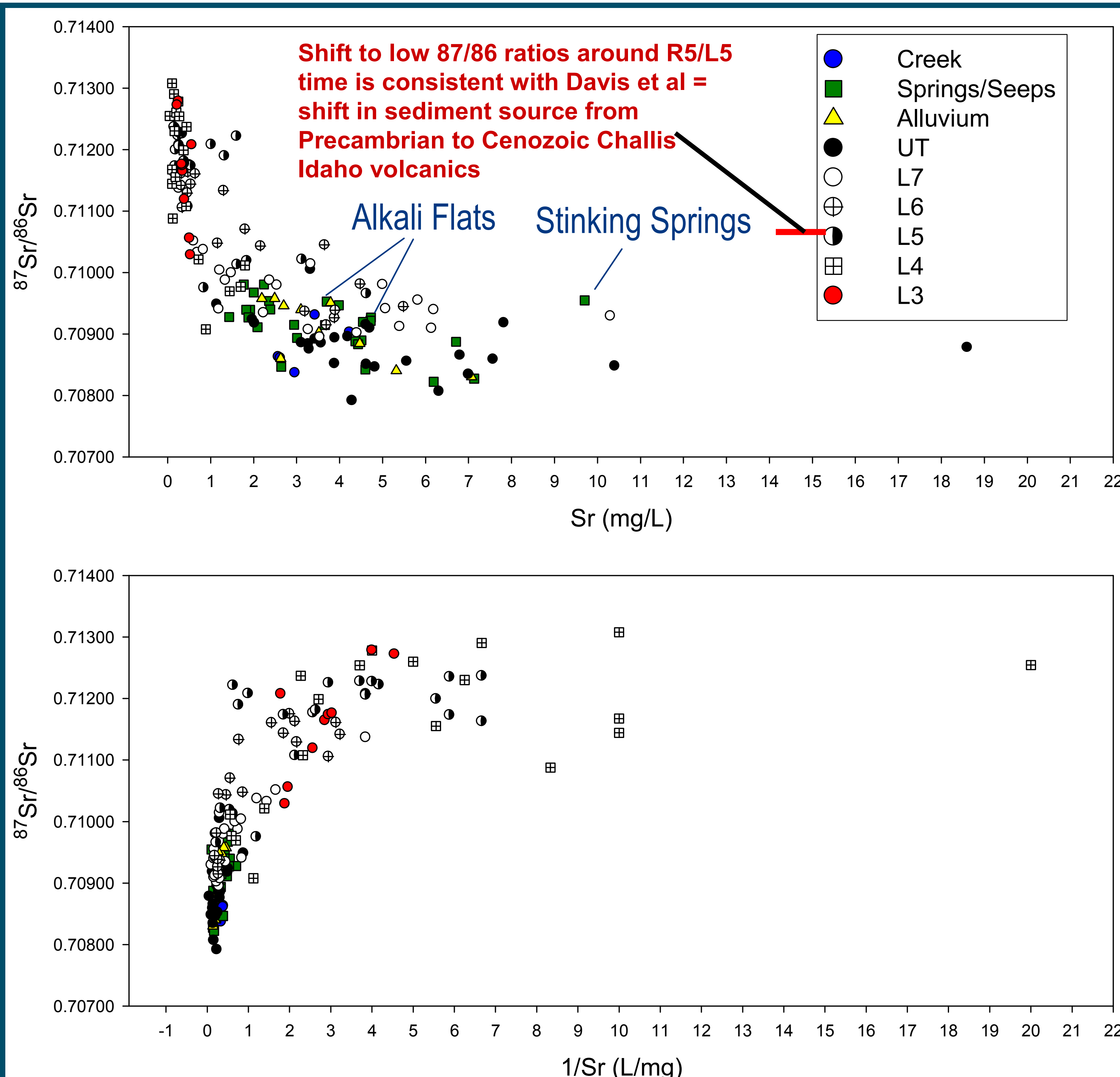
A36Cl
Stinking Springs
Alkali Flats
Ratio increases with evaporation
Creek
Spring/Seep
Alluvial GW
UT
L7
L6
L5
L4
L3
36Cl atoms/L x 10^7
Cl (mg/L)

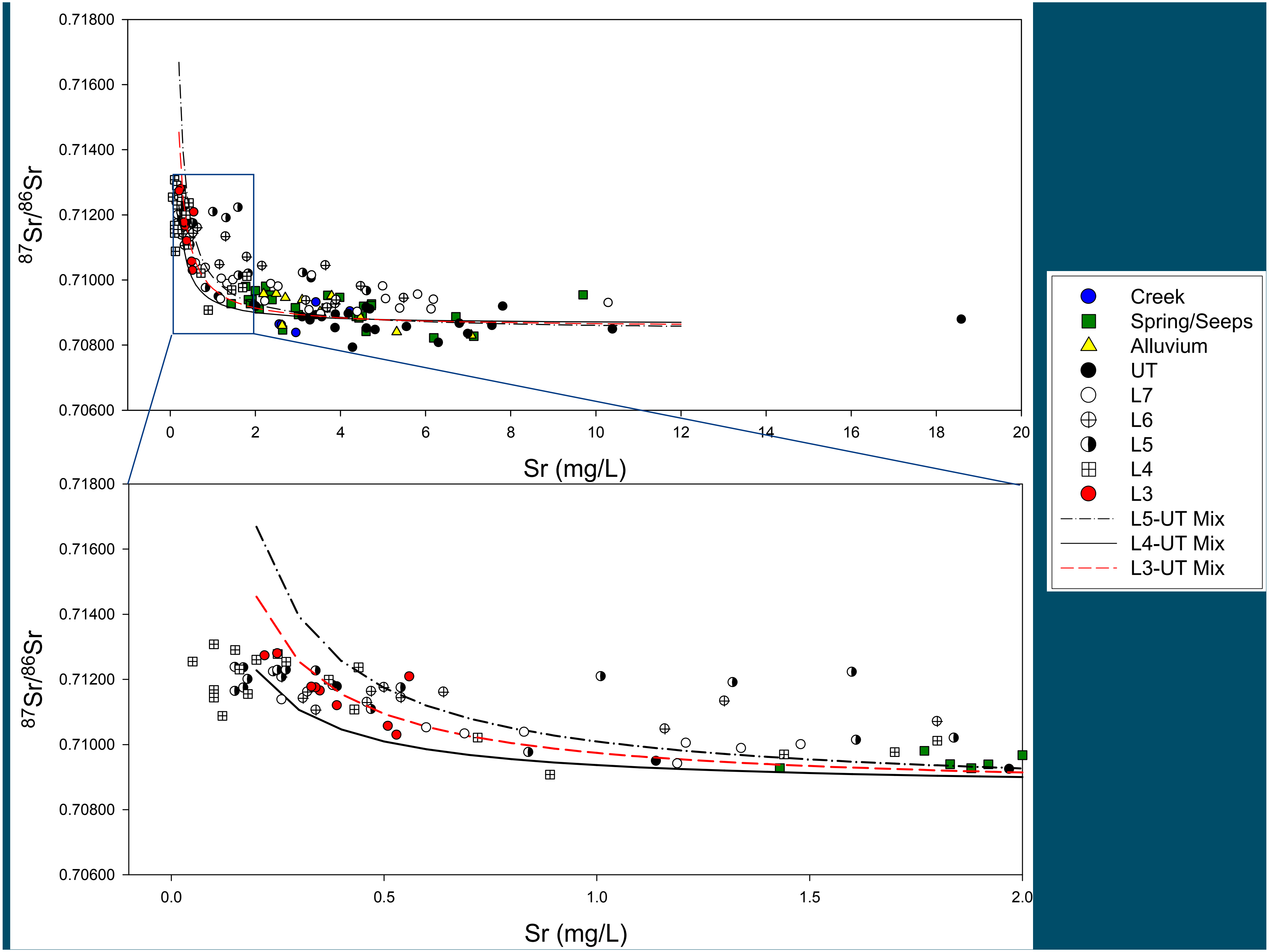


Alkali Flats
Alkali Flats
Stinking Springs
Alkali Flats
UT
L7
L6
L5
L4
L3
Springs
$\delta^{11}B$ (‰)
B (mg/L)
20
10
0
-10
-20
-30
0
2
4
6



10
5
0
-5
-10
-15
-20
-25
-25
-20
-15
-10
-5
0
5
δ13CDIC (‰)
δ18OH2O (‰)
7-18
20-7
20-7
4-1
20-7
6-13
6-13
UT
L7
L6
L5
L4
L3
Calcite from Pitman
Dolomite from Pitman


Shift to low 87/86 ratios around R5/L5
time is consistent with Davis et al =
shift in sediment source from
Precambrian to Cenozoic Challis
Idaho volcanics
Alkali Flats
Stinking Springs
Creek
Springs/Seeps
Alluvium
UT
L7
L6
L5
L4
L3
$^{87}Sr/^{86}Sr$
Sr (mg/L)
1/Sr (L/mg)
0.71400
0.71300
0.71200
0.71100
0.71000
0.70900
0.70800
0.70700



0.71800
0.71600
0.71400
0.71200
0.71000
0.70800
0.70600
$^{87}Sr/^{86}Sr$
0
2
4
6
8
10
12
14
16
18
20
Sr (mg/L)
0.0
0.5
1.0
1.5
2.0
Creek
Spring/Seeps
Alluvium
UT
L7
L6
L5
L4
L3
L5-UT Mix
L4-UT Mix
L3-UT Mix

Conclusions

- Meteoric recharge to upper intervals causes pyrite oxidation. Anaerobic oxidation of methane accompanies sulfate reduction, but only above R5.
- Boron isotopes: Indicate hydrologic isolation of upper from lower intervals. Different B sources for upper and lower intervals. Generally, L3/4 and UT have values more reflective of carbonates; other values reflective of silicates.
- Carbon isotopes: Distribution in dissolved inorganic carbon reflects fractionation assoc w AOM. Source C = carbonates. Methane generated from CO_2 reduction = biogenic process.
- ^{36}Cl: Bomb waters present in shallow units. Rapid recharge & discharge through the Uinta. Active recharge reaches into L6 L7; but L3/L4 << active recharge. Very old ages in L3/L4. Very slow flow.
- Sr concentration and isotopes: Two possible processes: Either cross flow from deeper to shallower formations, or carbonate precipitation or dissolution reactions that sequester or release Sr.
- Strontium Isotopes: Support Davis et al: Sr isotopic shift indicates a change in primary sediment composition from more radiogenic Precambrian source to less radiogenic source from young Challis Idaho volcanics around L5/R5 time.

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