Origin of the Kramer Borax Deposit, Boron, CA

A 50 year retrospective

OUTLINE

1. A brief history of borax
2. Kramer borax deposit
   a) Setting and Discovery
   b) Mineralogy of sedimentary borates
   c) Stratigraphy and Lithology
   d) Petrography and implications for geologic setting
   e) Solubility studies and modeling lake characteristics
   f) Comparable modern analogues
3. New evidence
   a) Turkish and Argentinian deposits
   b) Boron isotopic studies
4. *Broader questions – Source water controls (thermal springs), B-As-Sb association, igneous-metamorphic controls on boron in thermal waters*

Why give this talk?

1. Old (but rusty) material to me, new to most of you
2. Desire to see if ideas have changed in the past 50+ years.
3. Citation of my work even today suggests I did something right.
4. Wish to compare Kramer work with evidence from newer borate deposits in Turkey and South America
5. A wish to evaluate these ideas in light of new evidence using tools that weren't available in 1964
6. A chance to ponder broader questions about boron's geochemical cycle.
7. Work done so long ago that if you ask penetrating questions I can always plead a "senior moment"

What was *unique* about my research on the Kramer deposits?

- Used a *combination* of geological tools (Field AND lab work – rare in 1964)
- Stratigraphy, Petrography, and XRD based mineralogy
- Experimental solubility studies of effects of other salts on Na-borate solubilities
- Field studies of other possible borate environments (Borax Lake, Teels and Columbus Marsh, NV, Death Valley, Searles Lake)
- Benefits of discussions with an all-star support team with similar interests (Mary Clark, Blair Jones, G.I. Smith, Sig Muessig, Dick Erd, Ward Smith [USGS], Robert Garrels, Laurie Hardy, Hans Eugster, F.W.Dickson and George Tunell (UCLA), Bill Holser (Chevron Research), ...)

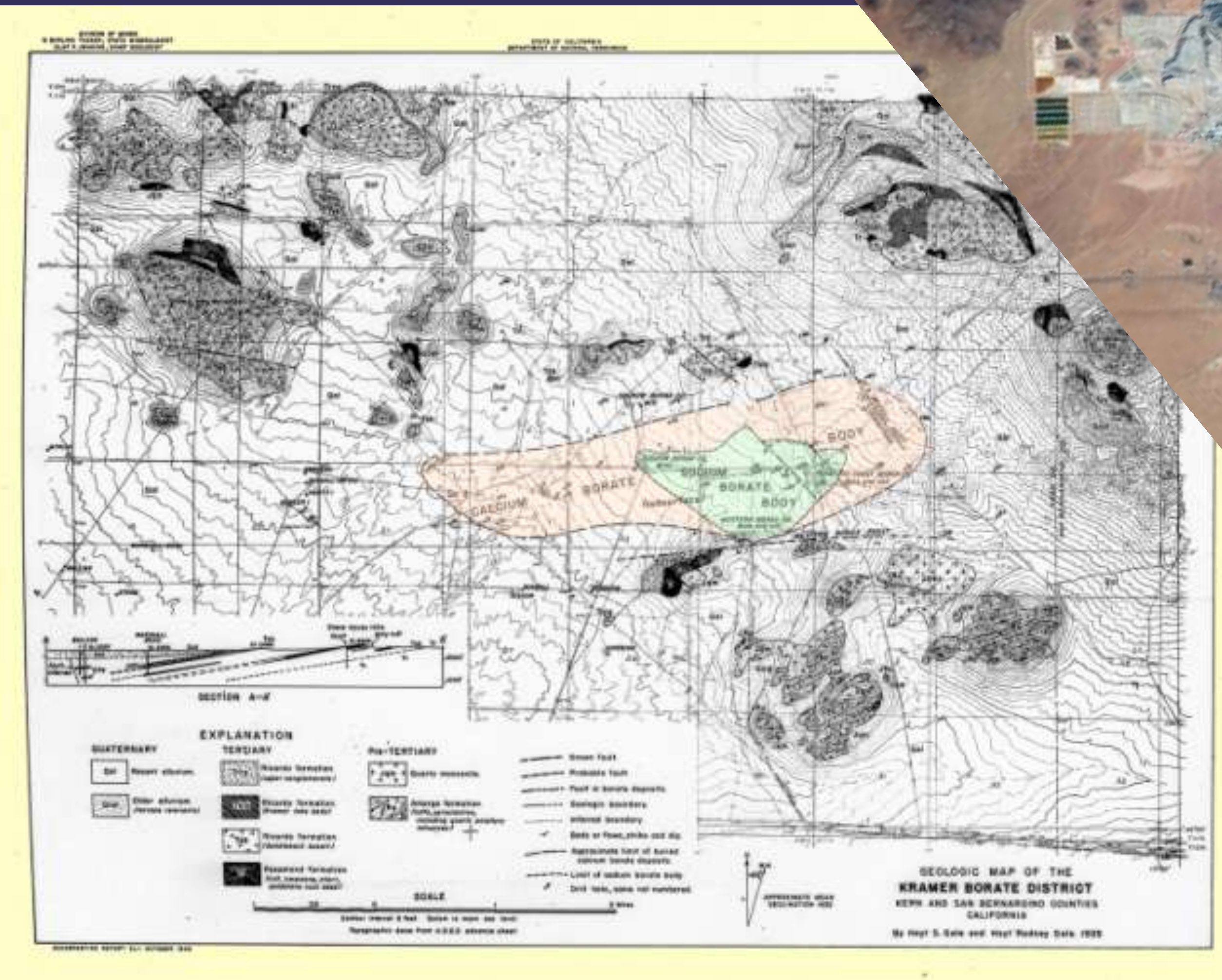
Historical Notes

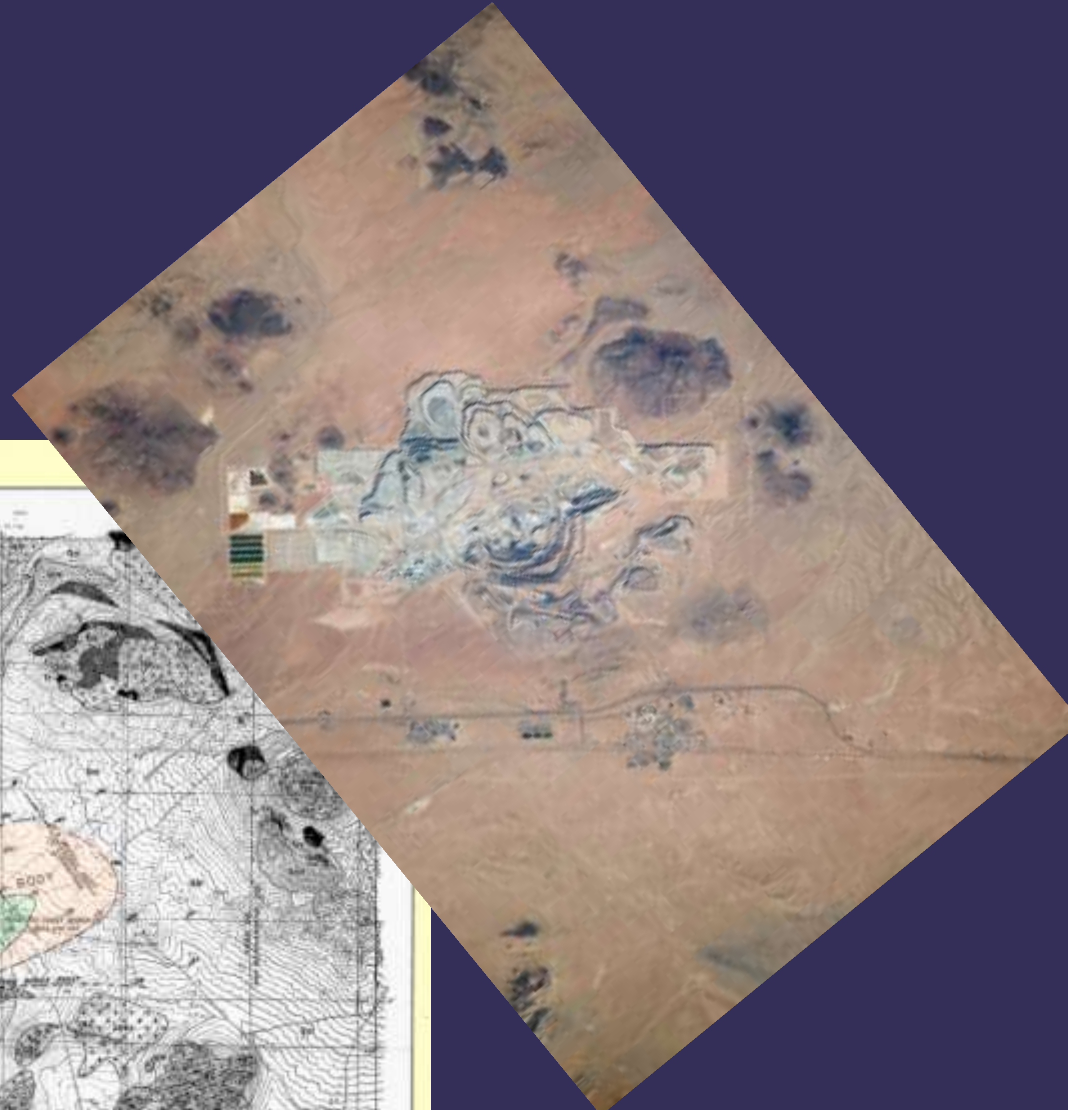
- History of borax – borates (Marco Polo 1294)
- Kublai Kahn – Tibetan lakes
- Buraq (Arabic), Tincal (Sanscrit)
- Known by Chinese for over two millennia (glazes)
- Known by pre-European Indians in Western NA (Borax Lake, CA for soaps)
- Discovered in Death Valley (1882) – Colemanite/Ulexite
- 1912 borates discovered in drilling a water well (Dr. Suckow)
- 1925 drilling discovered massive borax at Kramer site
- 1925-57 Underground Mining -> 1956 Open Pit (U.S. Borax -> Rio Tinto)
- Once virtually only source of borax, now < Turkish & S.A. deposits

Location

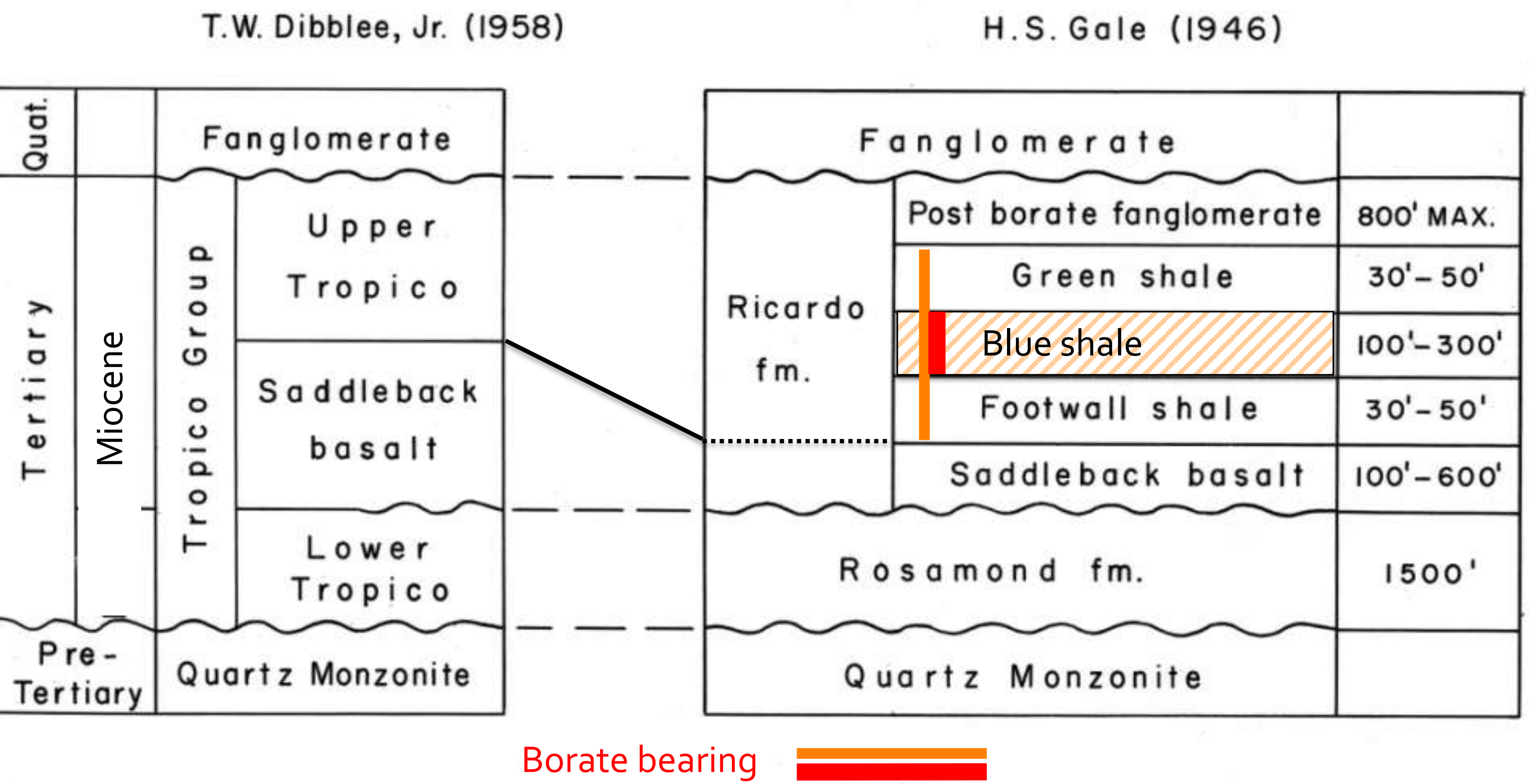
Owens Lake
Southern Sierra Nevadas
Panamint Valley
Death Valley
Las Vegas
Furnace Creek (borates)
Searles Lake
Garlock fault
KRAMER
San Andreas f.

Geologic Setting





Stratigraphy of the Kramer District, California



Borate mineralogy

Na	Na/Ca	Ca	Ca/Mg	Mg	Other
Borax	Ulexite	Inyoite	Inderborite	Inderite	Tunellite
$Na_2B_4O_7 \bullet 10H_2O$ $Na_2B_4O_5(OH)_4 \bullet 8H_2O$	$NaCaB_5O_9 \bullet 8H_2O$ $NaCaB_5O_6(OH)_2 \bullet 5H_2O$	$Ca_2B_6O_4 \bullet 13H_2O$	$CaMg[B3O3(OH)5]_2(H2O)4 \bullet 2H_2O$	$MgB_3O_3(OH)_5 \bullet 5H_2O$	$SrB_6O_9(OH)_2 \bullet 3H_2O$
Tincalconite	Probertite	Meyerhofferite	Hydroboracite	Kurnakovite	Howlite
$Na_2B_4O_7 \bullet 5H_2O$ $Na2B4O5(OH)4 \bullet 5H_2O$	$NaCaB_5O_9 \bullet 5H_2O$ $NaCaB_5O_7(OH)6 \bullet 3H_2O$	$Ca_2B_6O_4 \bullet 7H_2O$	$CaMgB_6O_4 \bullet 6H_2O$	$MgB_3O_3(OH)_5 \bullet 5H_2O$	$Ca_2B_5SiO_9(OH)_5$
Kernite		Colemanite	Priceite		
$Na_2B_4O_7 \bullet 4H_2O$ $Na_2B_4O_5(OH)_2 \bullet 3H_2O$		$Ca_2B_6O_4 \bullet 5H_2O$ $Ca_2B_6O_8(OH)_6 \bullet 2H2O$	$Ca_4B_{10}O_{19}(OH)_5 \bullet 7H_2O$		

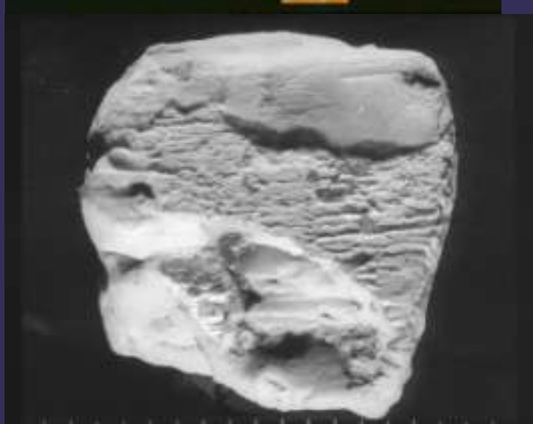
Decreasing water content

Sodium Borate Minerals

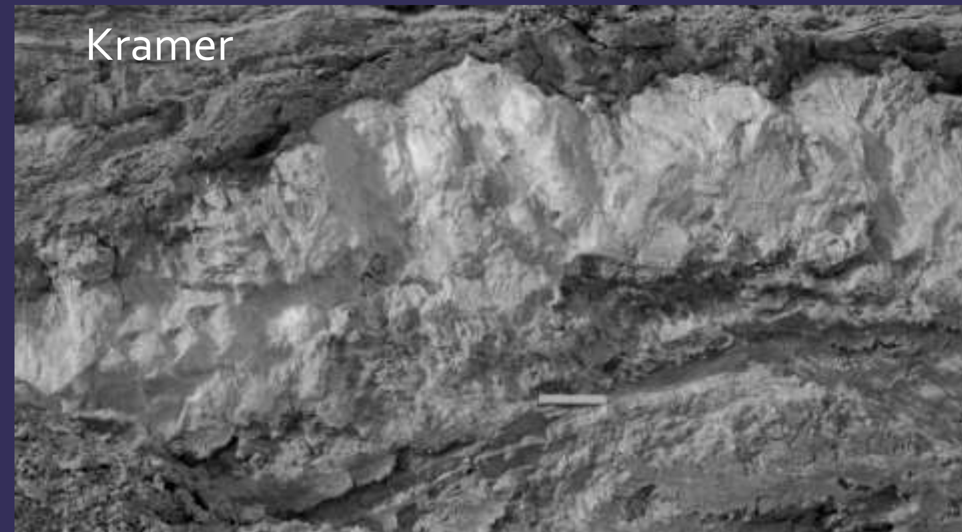
Borax

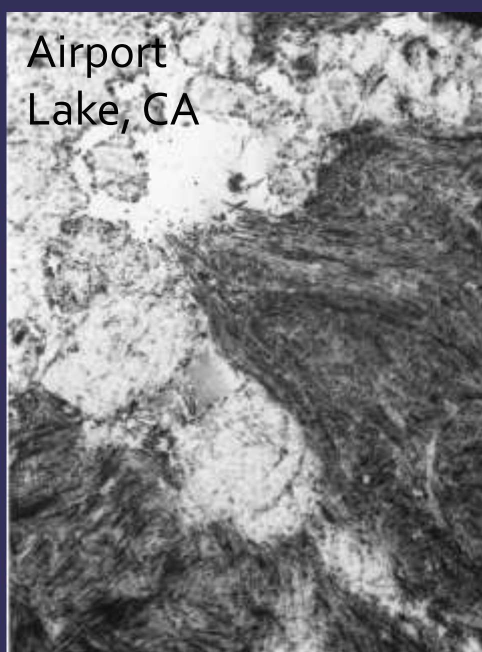
Tincalconite

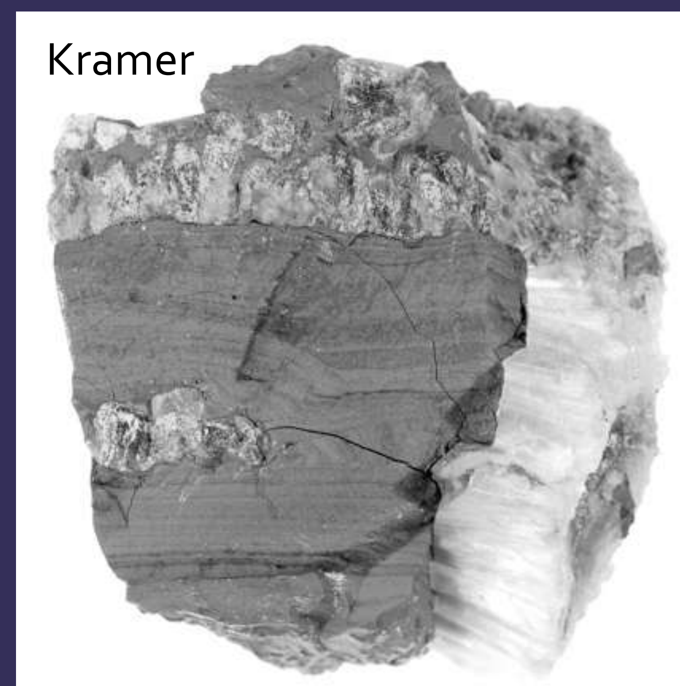
Kernite

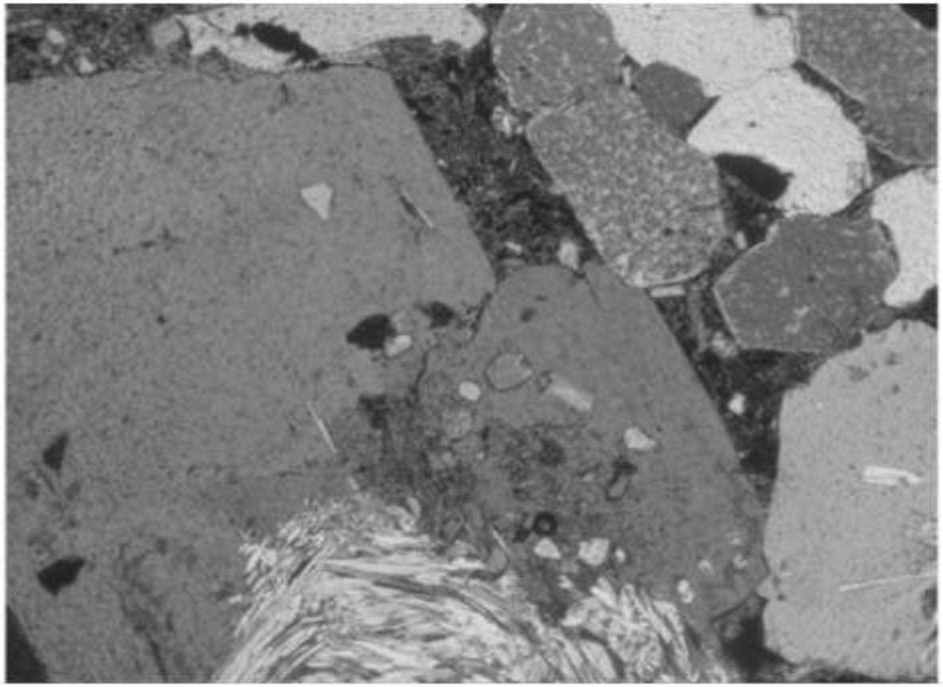


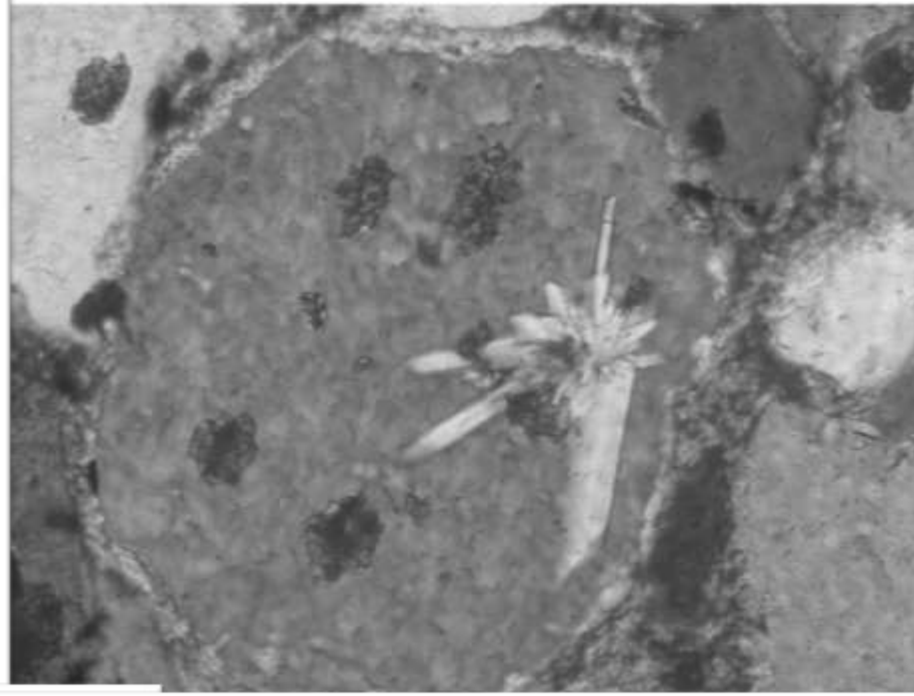
Ulexite (Na-Ca)

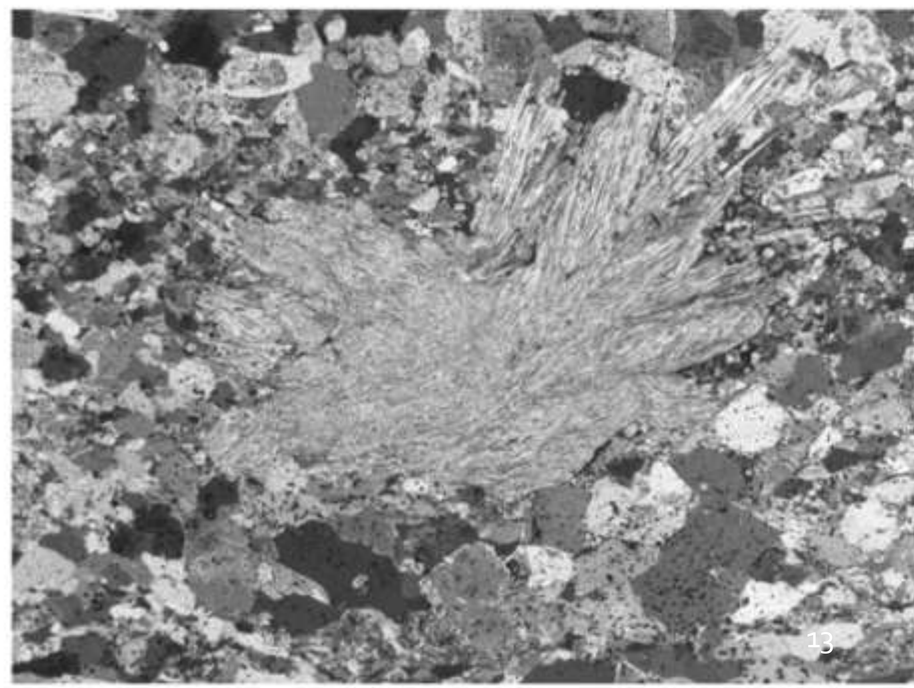




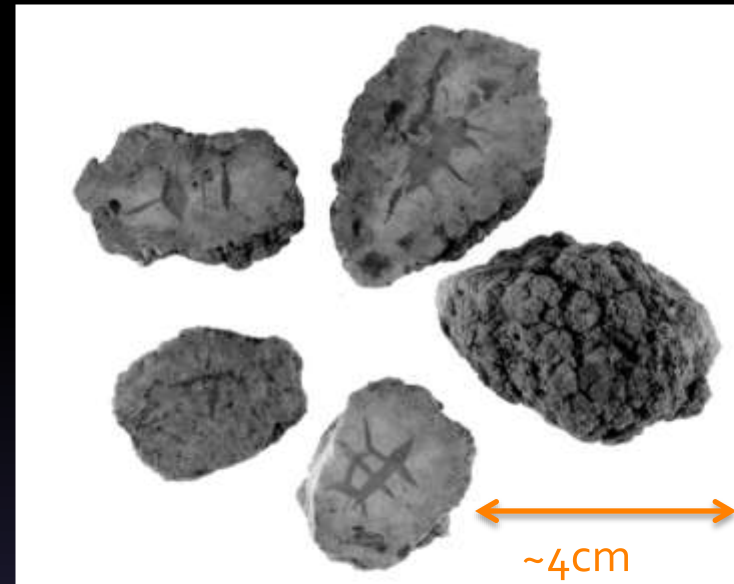


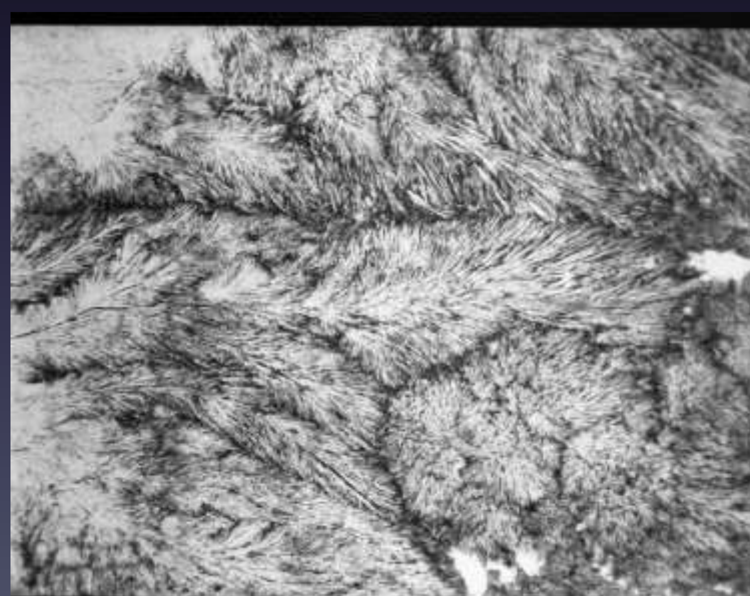






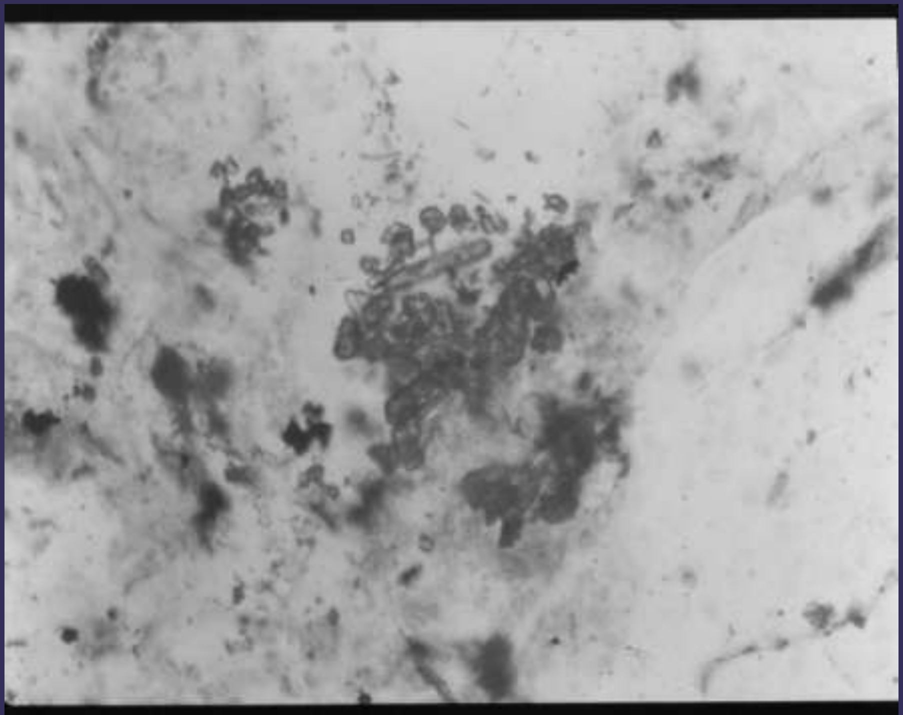
Colemanite (Ca)



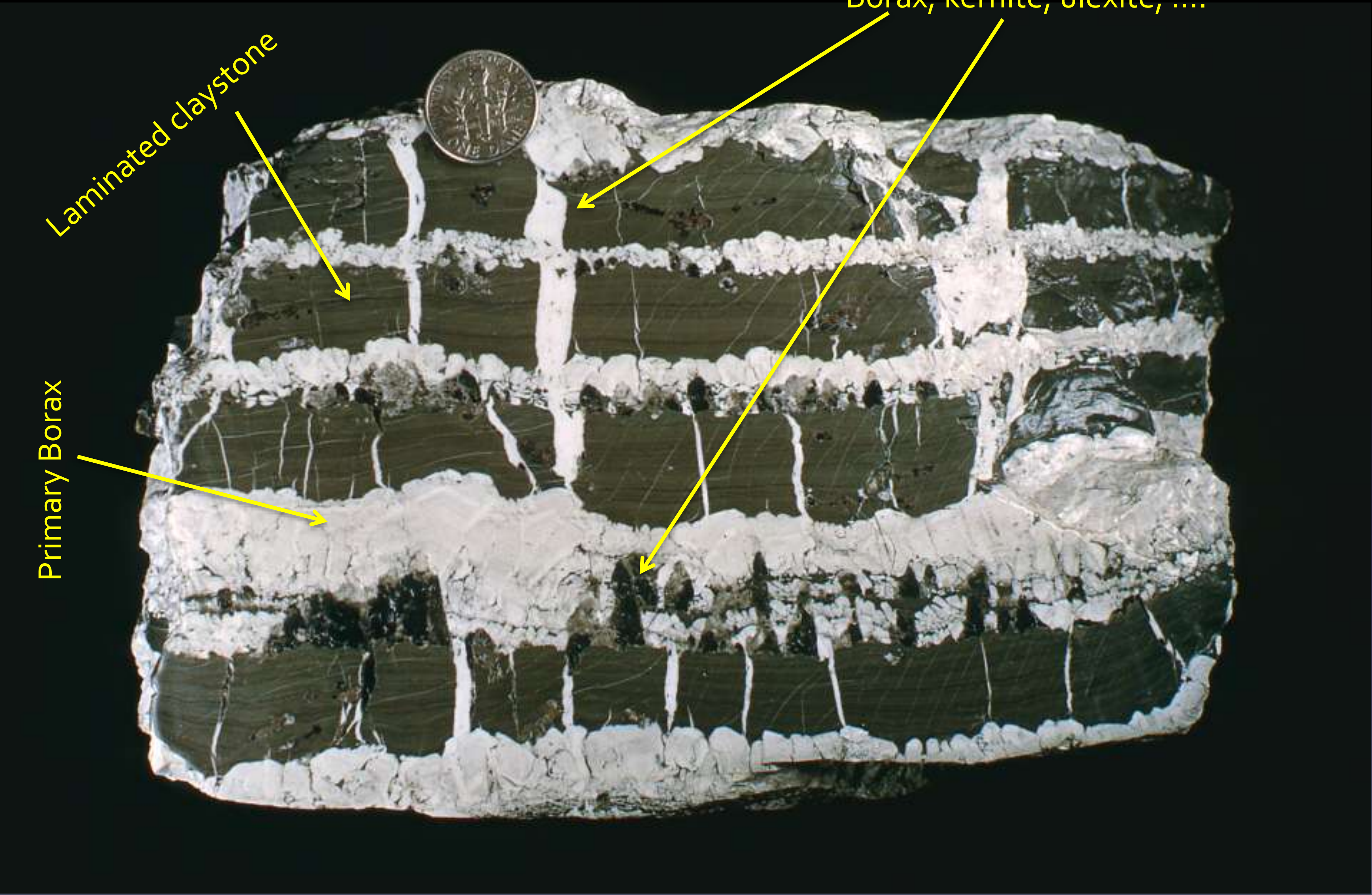


Kurnakovite (Mg)

Realgar-orpiment in radiating spray of ulexite



The whole story in one specimen



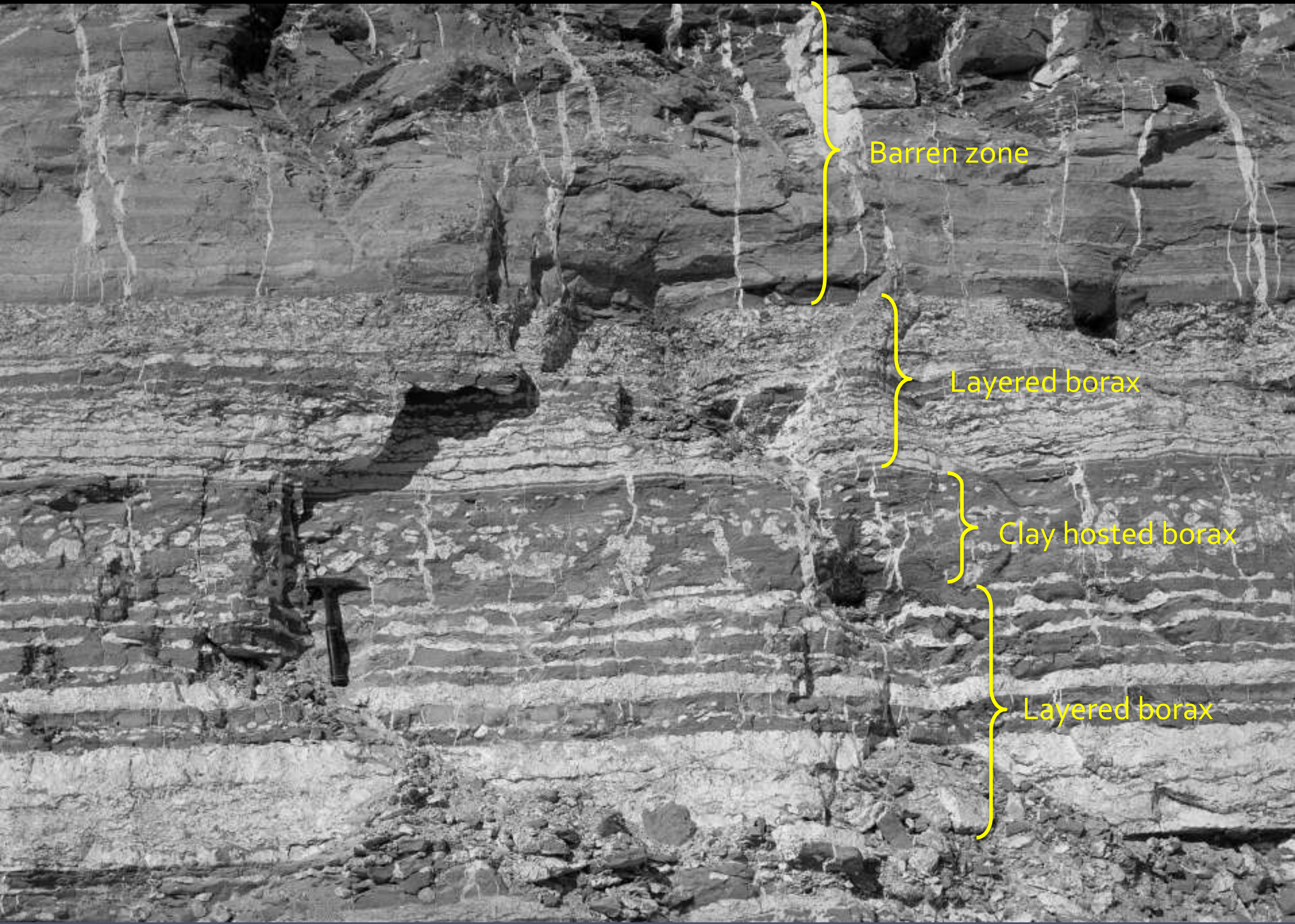
The story in two parts:

1- Depositional ***

- Thermal spring fed, closed basin – fault bounded
- Close association with volcanism (flows, tuffs)
- Alternating mudstone – borax series (>300’) 65% Borax
- Lateral zonation (Ca -> Na-Ca -> Na) edge to core
- Evaporation >> total fluid inflow

2- Post-depositional

- Burial
- Thermal diagenesis (>65°C) & dewatering, clay compaction
- High pH (mobile Si,Al, metals)
- Continued hydrothermal inputs??

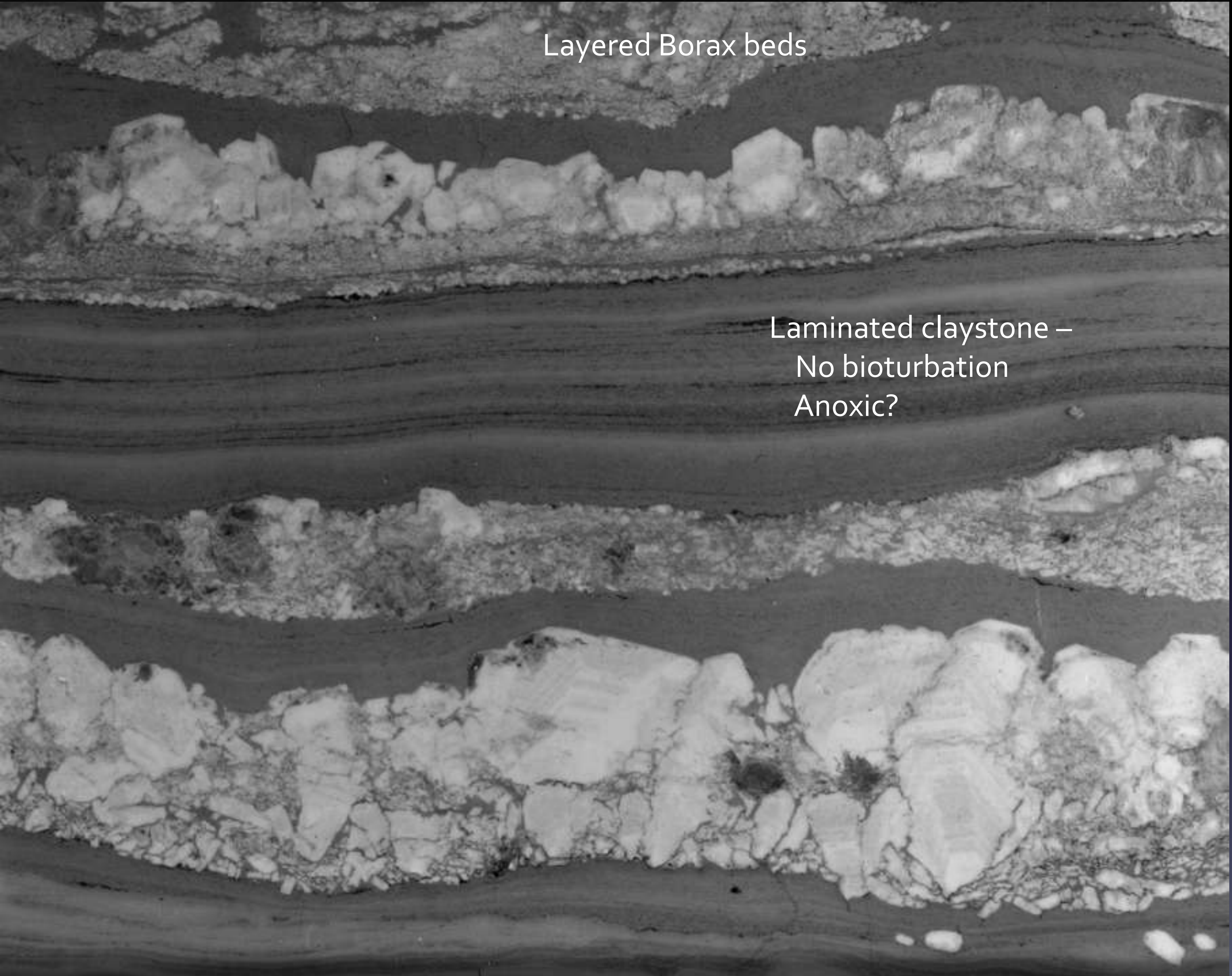

Barren zone
Layered borax
Clay hosted borax
Layered borax

Clay hosted borax

- Single borax crystals with internal clay "inclusions"
- Oxidized, iron-rich laminae.
- Growth *in muds* – playa conditions
- How?
    - Clay – ion exchange
    - slow growth
    - silicate dissolution?

Veatch, 1878, Borax Lake, CA, Playa conditions

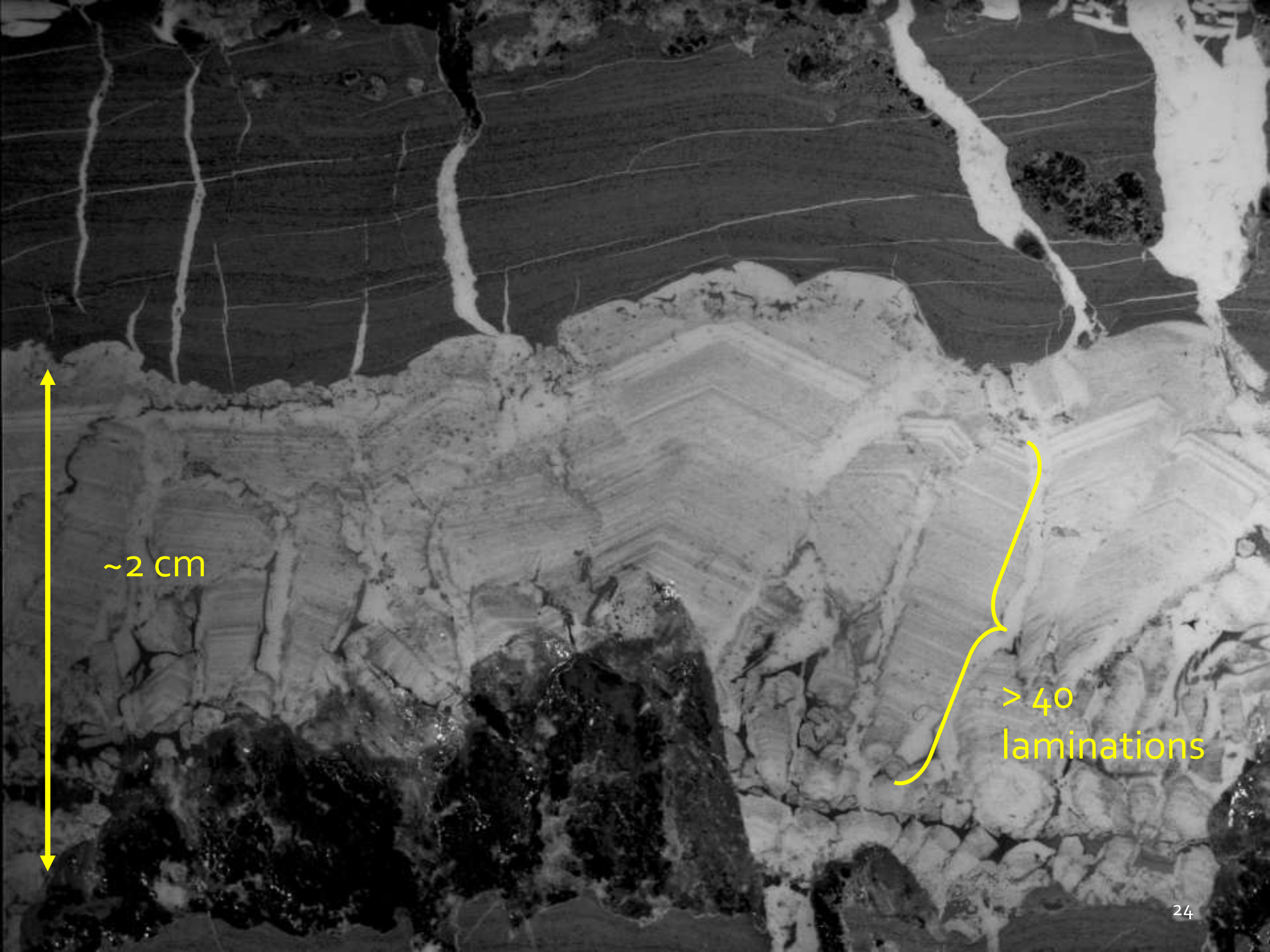
Clay hosted borax and replacement ulexite

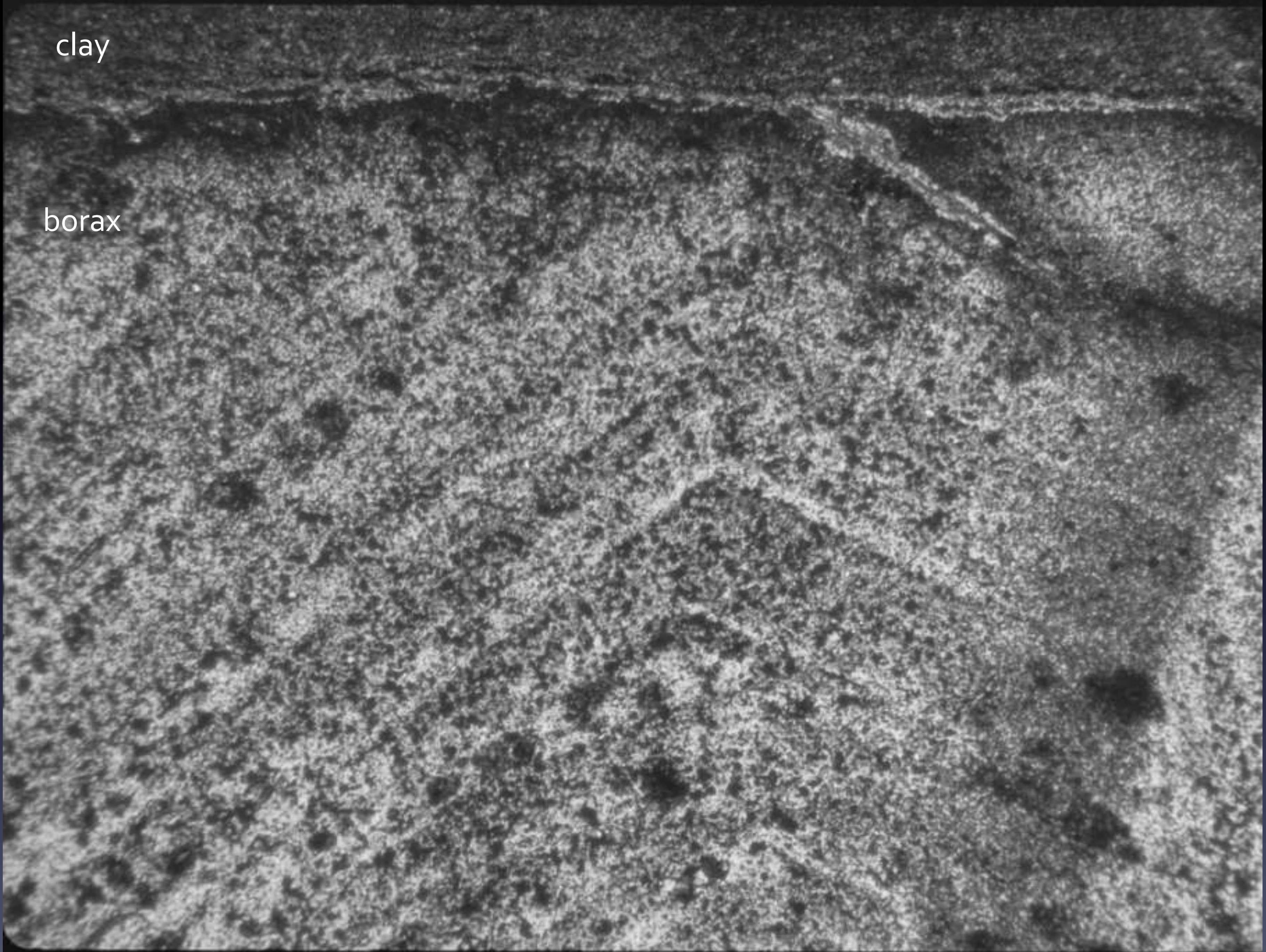

Layered Borax beds
Laminated claystone –
No bioturbation
Anoxic?

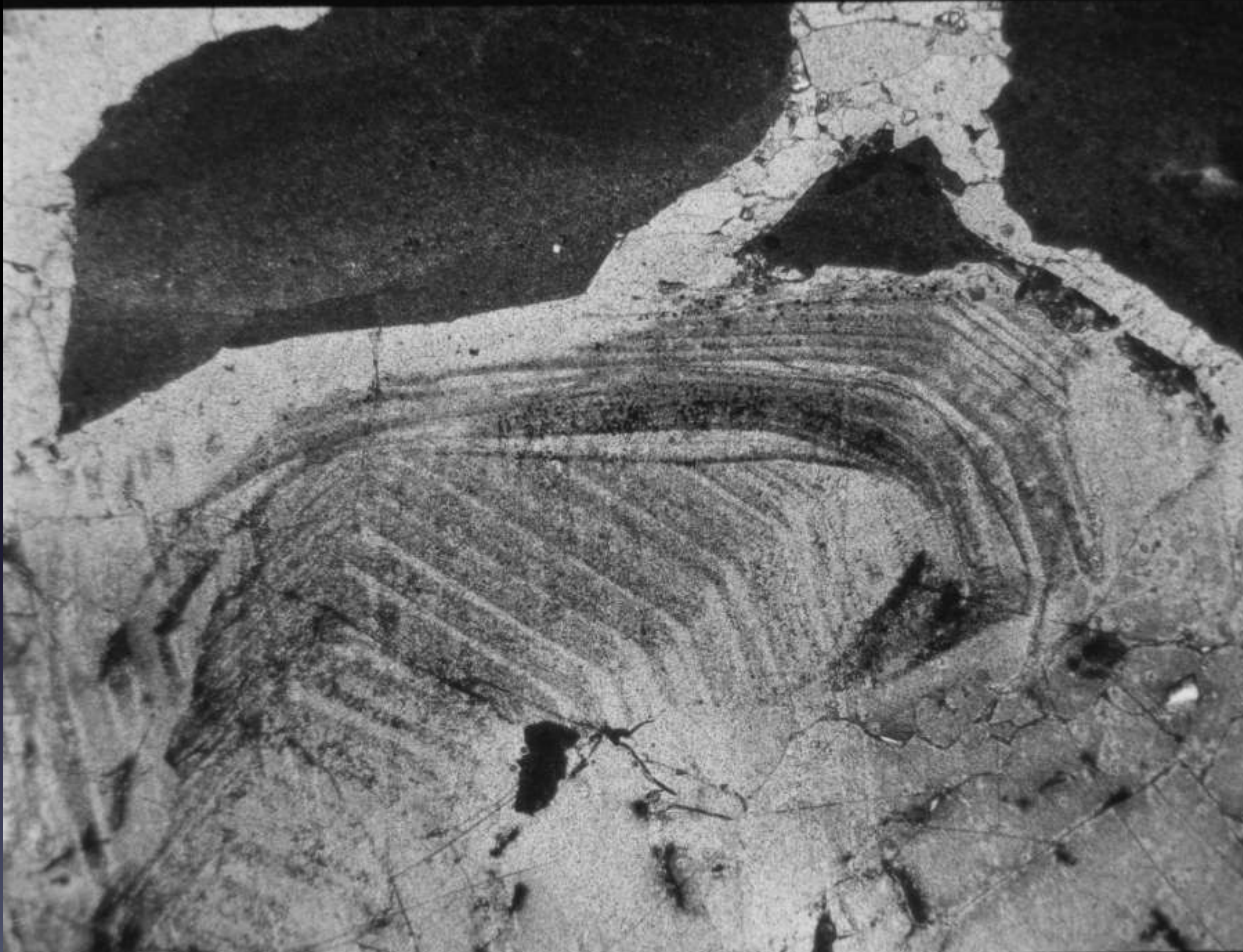
Top and bottom of single primary borax bed

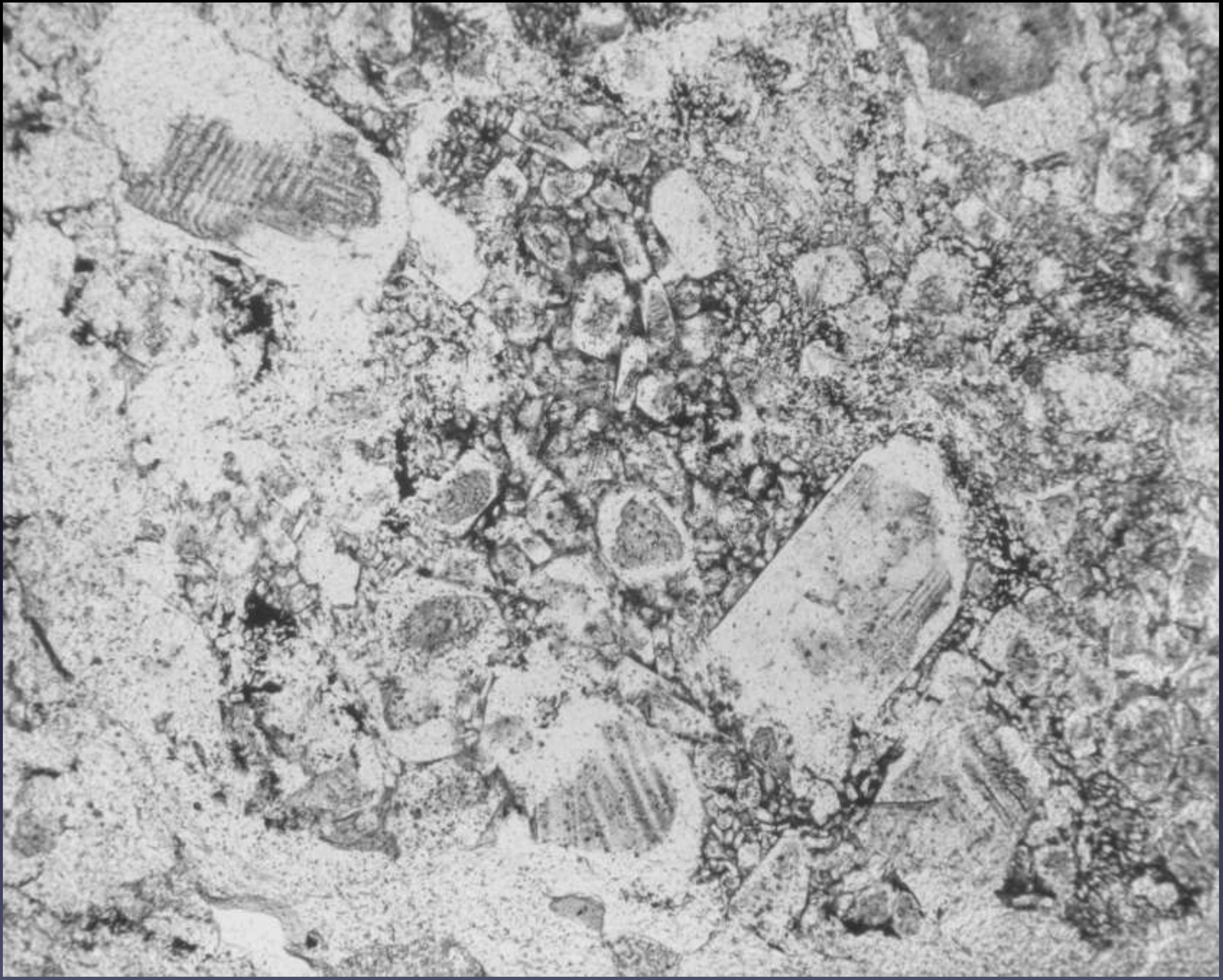
Top

Bottom

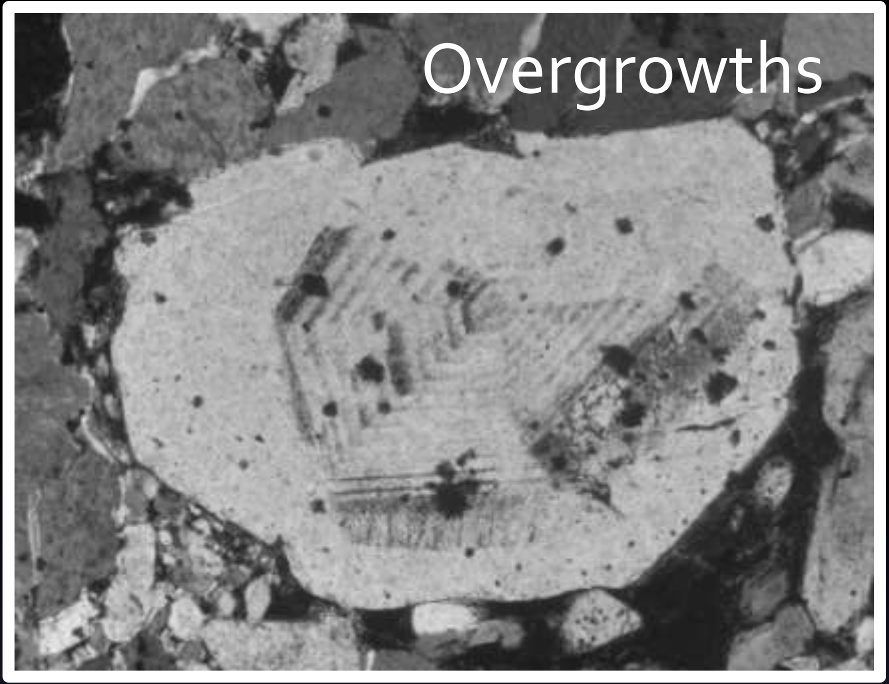

~2 cm
> 40
laminations

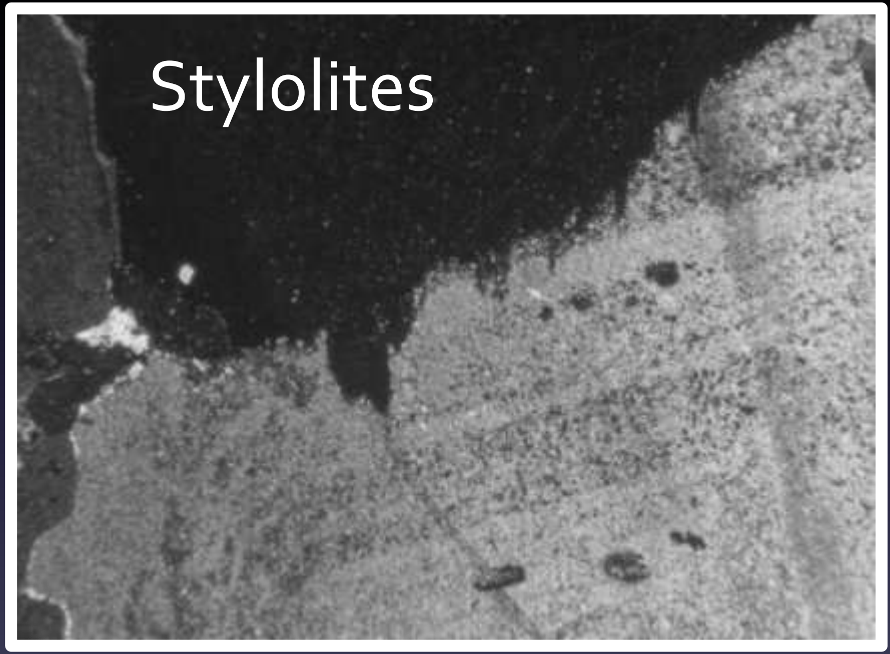

clay
borax



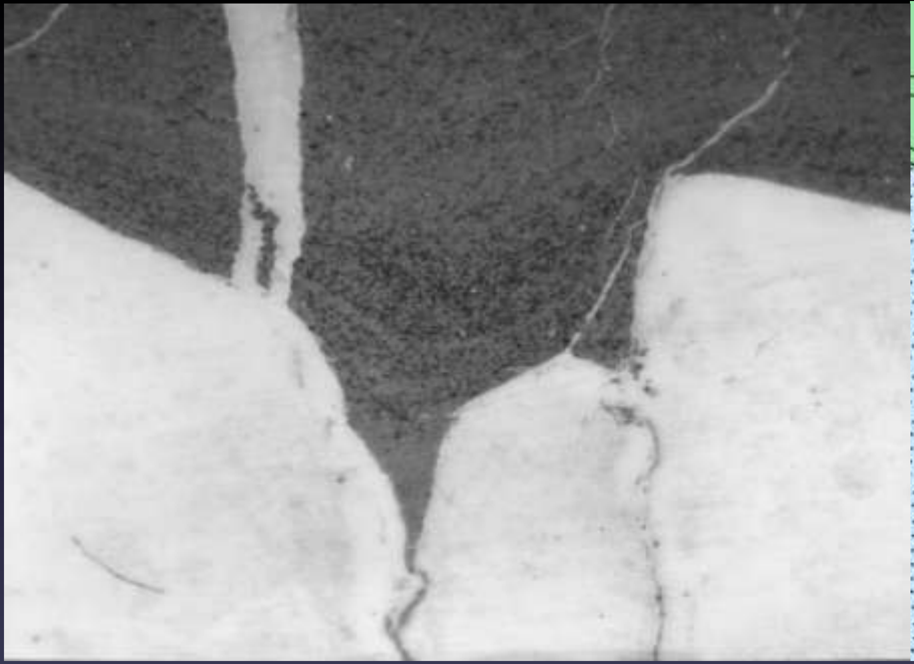


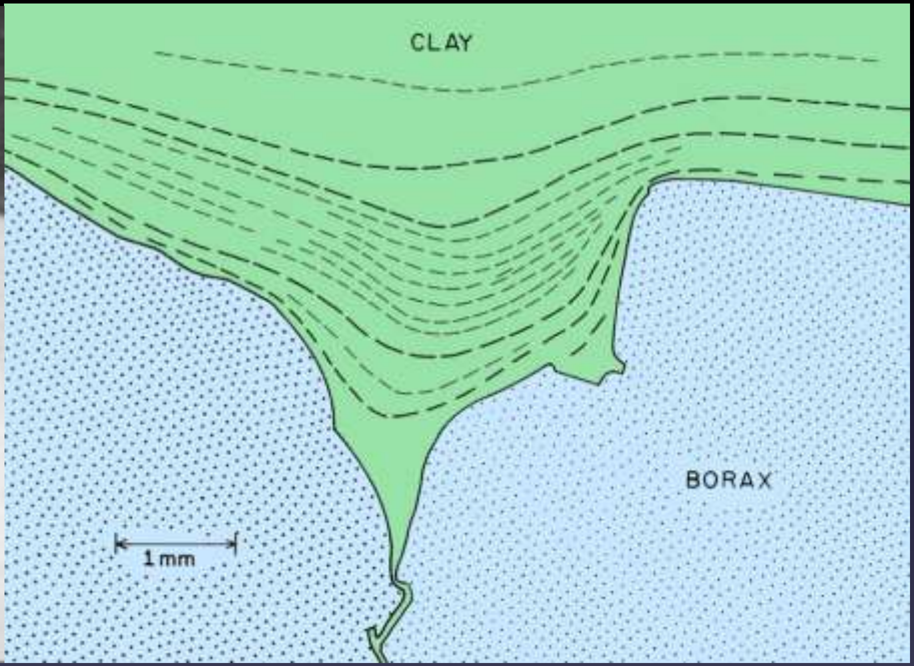
Synsedimentary and post-deposition al textures



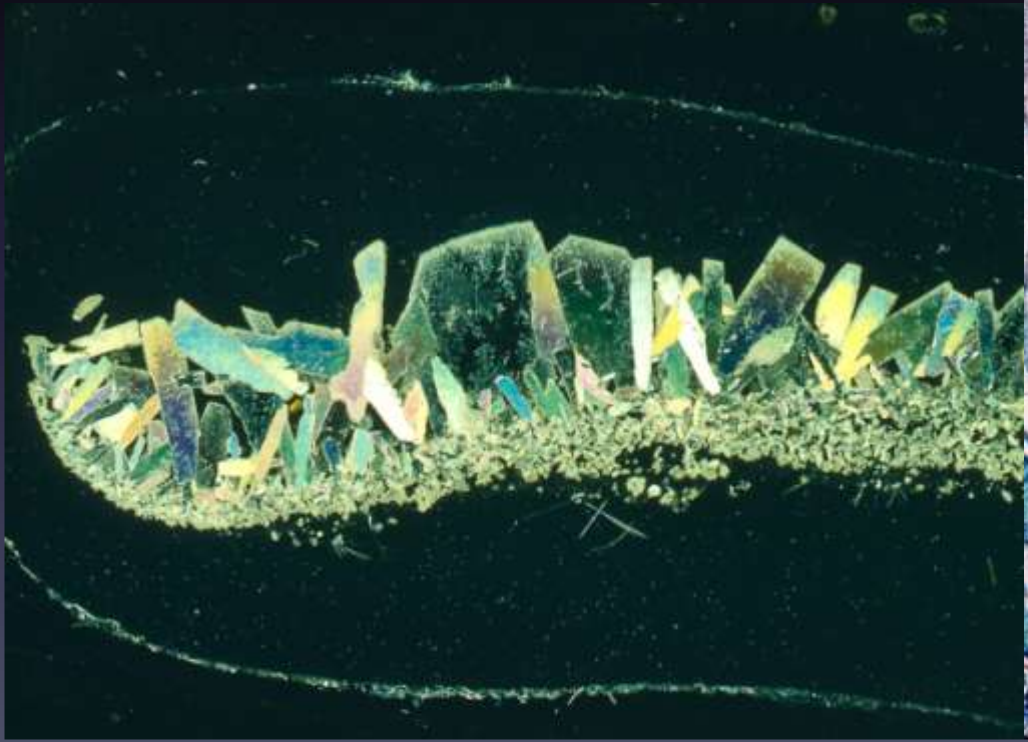


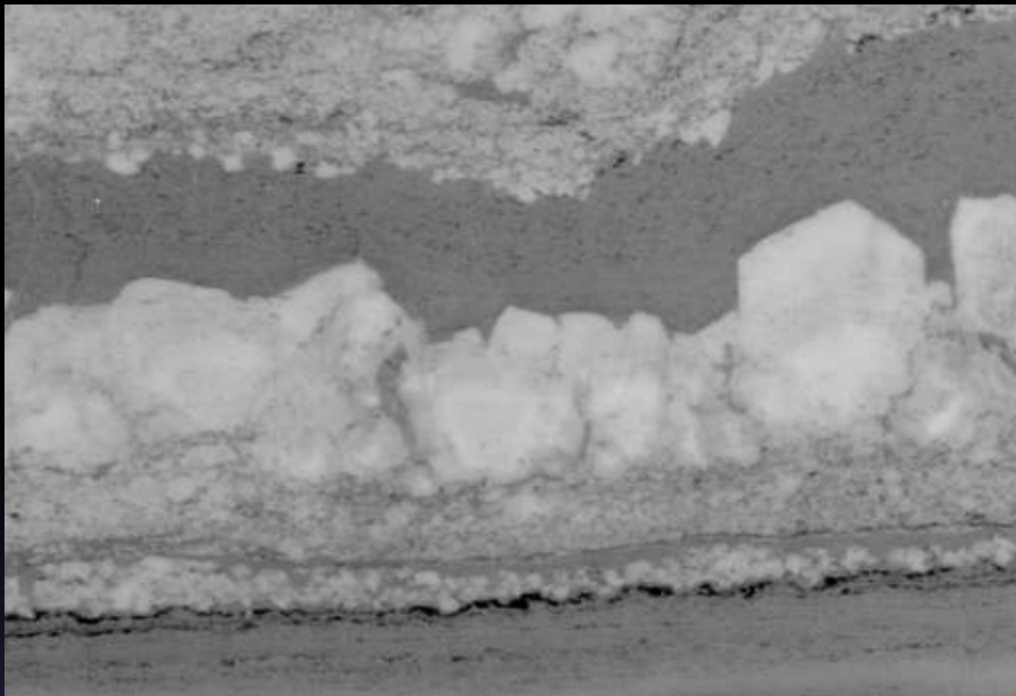
Clay deposited after underlying borax

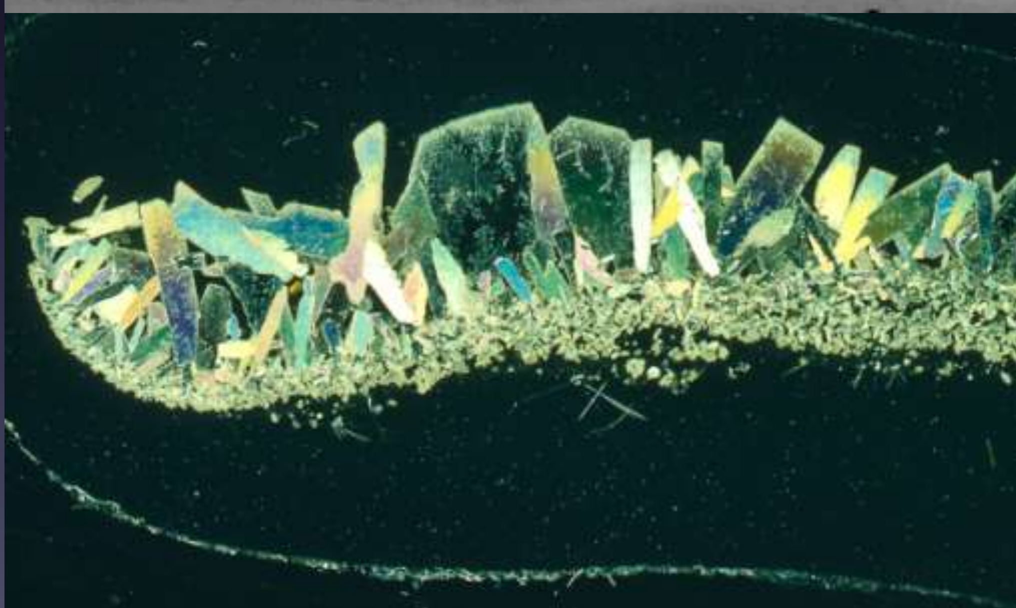


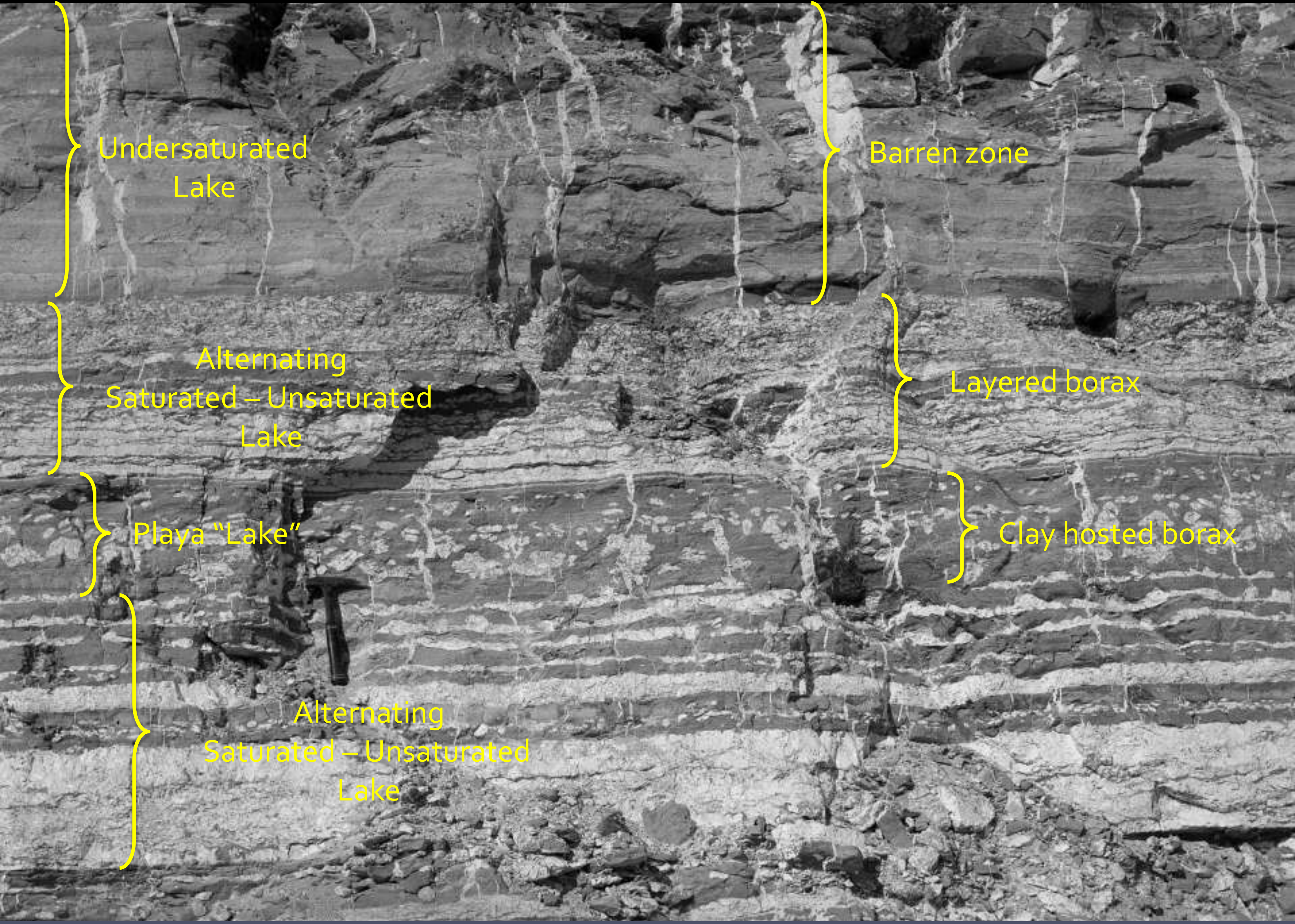


Kramer in a beaker








Undersaturated Lake
Barren zone
Alternating Saturated – Unsaturated Lake
Layered borax
Playa "Lake"
Clay hosted borax
Alternating Saturated – Unsaturated Lake

Implications of laminae:

1- Growth in alternatively clear and cloudy brine

2- Sharpness of transitions imply rapid changes in lake clarity

3- "Cyclical" alternations (clear – cloudy)

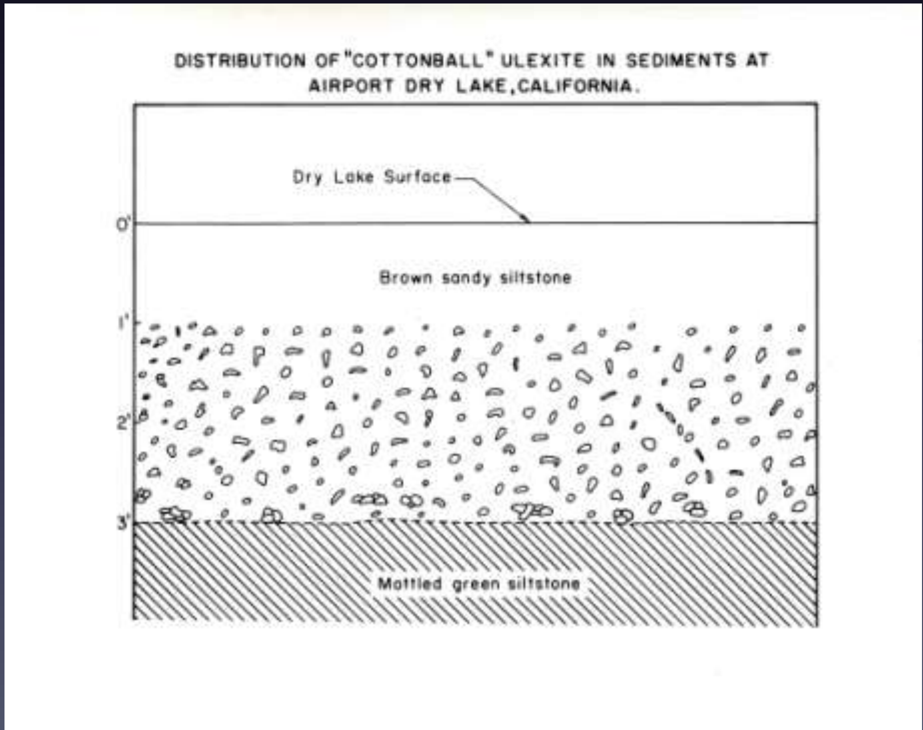
4- Growth rate variations?

5- Related to variations in growth rate and/or wind velocity, not changes in river inputs

6- Unstratified – evaporation is the driving mechanism

7- Implies a ***shallow lake*** that responds quickly to wind stress and evaporation, but remains saturated w.r.t. borax

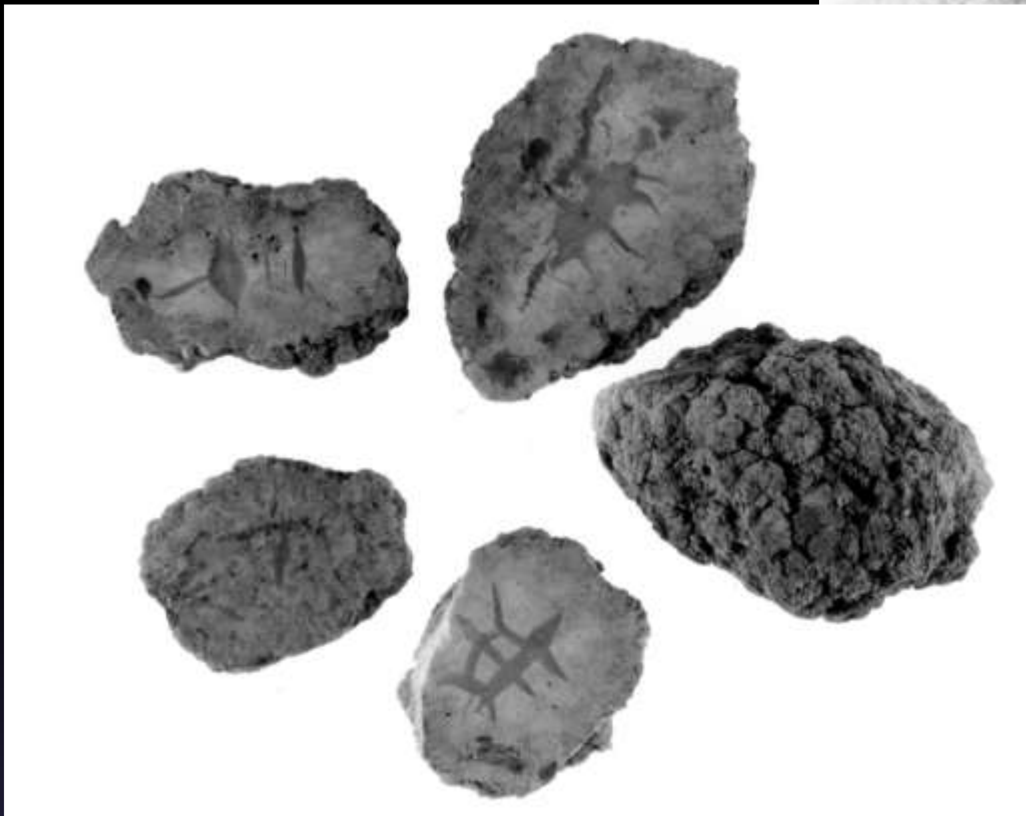
Airport Dry Lake
"cottonball" ulexite



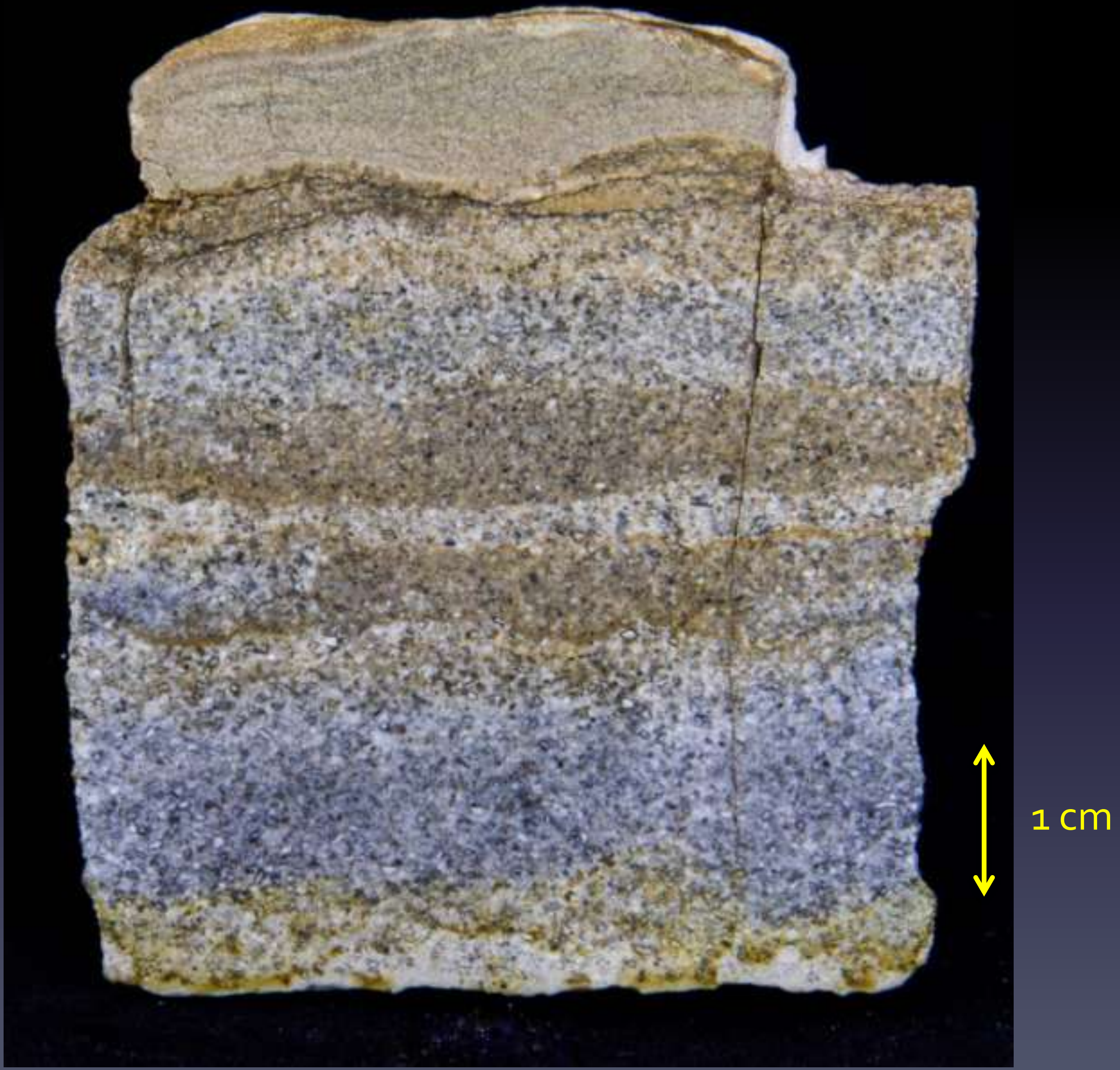
Septarian nodules

Carbonate

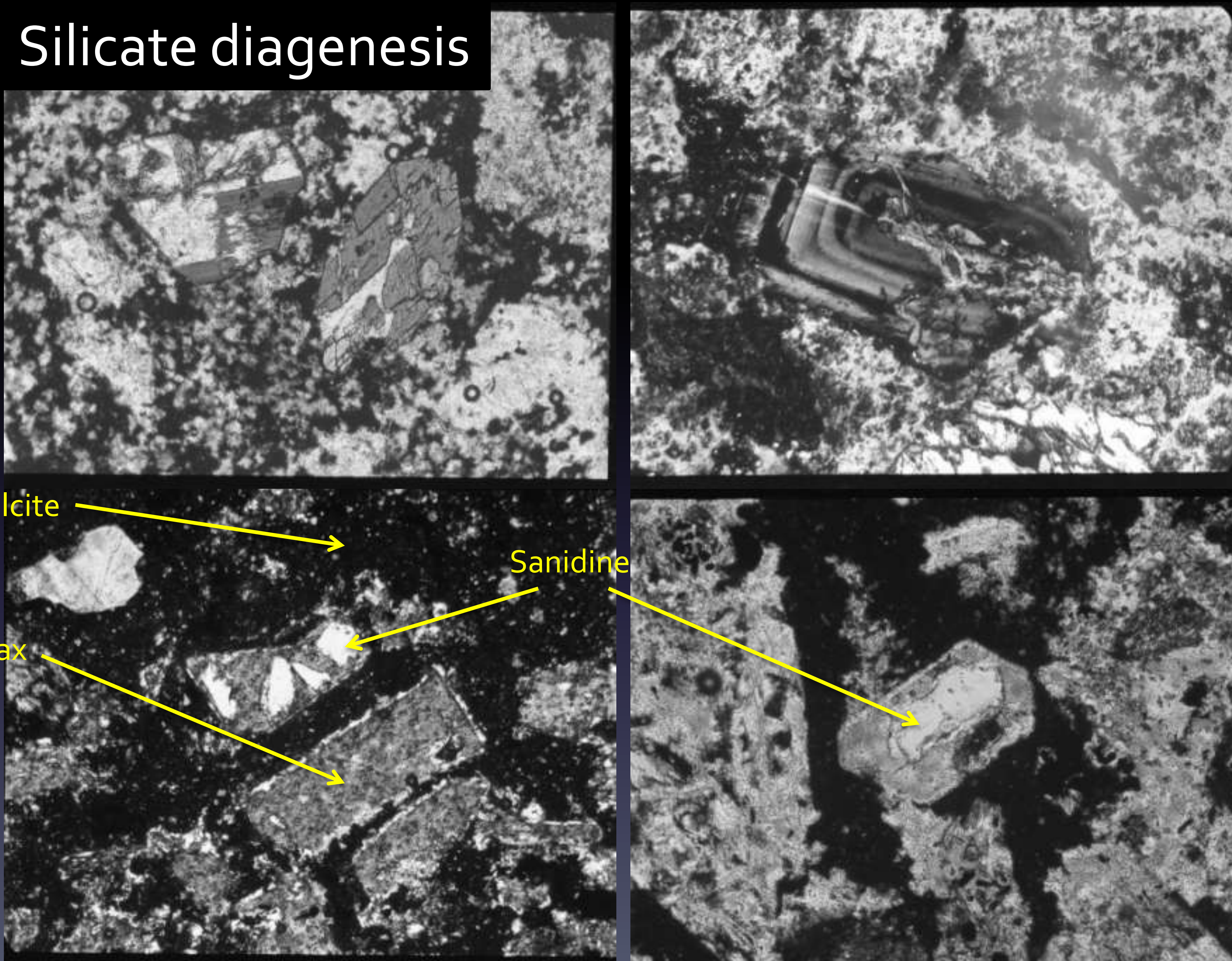
Colemanite




Tuff bed – “barren zone”



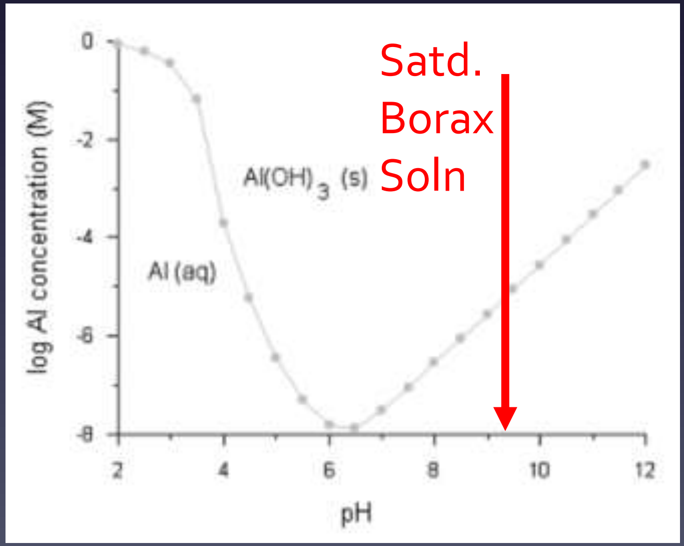
Silicate diagenesis

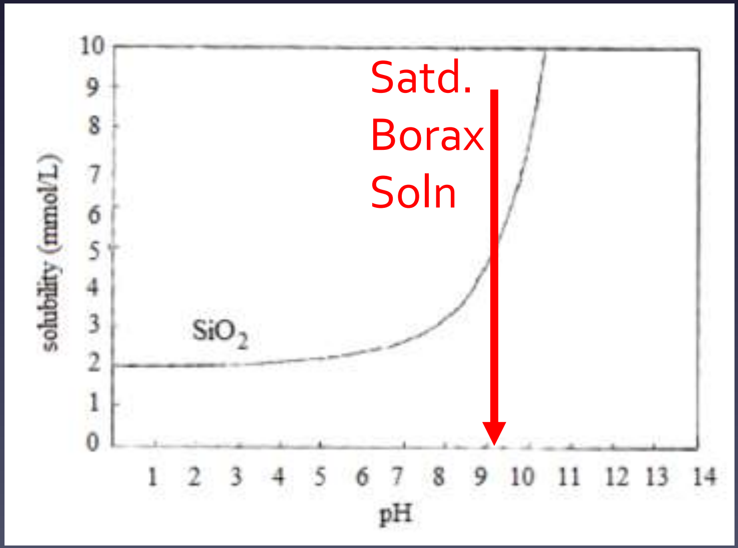


Reaction

- Plagioclase, amphibole, quartz + Aqueous-B
- -> Borax + Analcime + Si, Al, Ca, Na, K, Fe, Mg

Sodic alteration – loss of Fe, Mg, Ca, K





Precipitation Mechanisms

① Air-Water interface (“hopper halite”, crystalline “mush”)

② Lake bottom (solid substrate) ***

   a) Growth into the overlying fluid medium on *solid substrate*

   b) Selective growth of oriented crystals able to out compete others in a less favorable orientation

   c) Growth rates on order of mm/day with incorporation of clays marking the growth lines

③ Growth within lake muds *** (ala Borax Lake, Airport Dry Lake, etc)

   a) chemical (replacive) ***

   b) Mechanical (displacive)

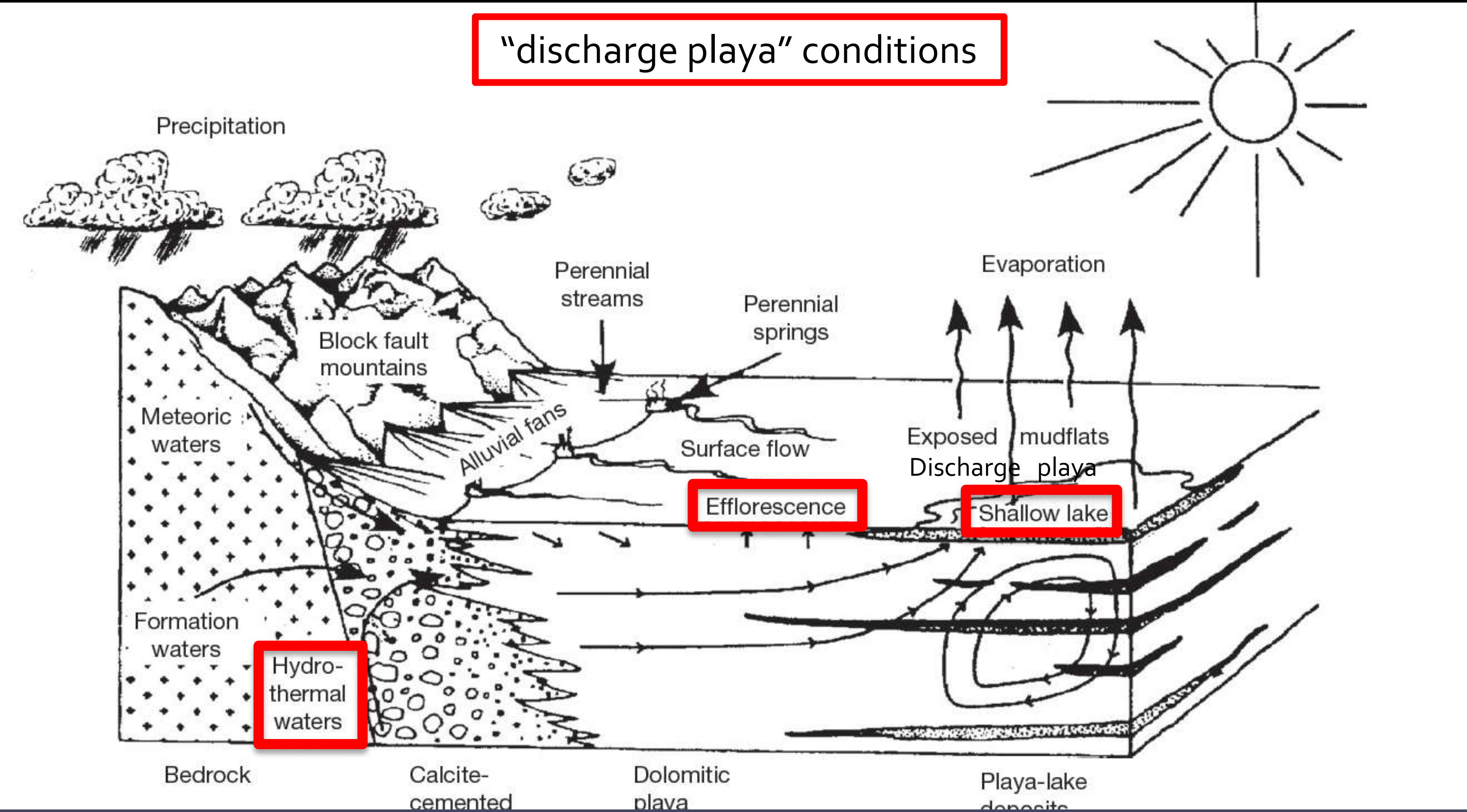
Setting the stage
What kind of lake is this?

1) Monomineralogic precipitation of borax on lake bottom or in muds (Primary borax)
2) Alternating lake saturation/undersaturation and corrosive dissolution of tops of primary borax beds.
3) Occasional playa lake conditions leading to mud hosted primary borax (see: Borax Lake)
4) Lateral "facies" of Na-Ca borate (ulexite) and Ca-borate (colemanite)
5) No "room" for other evaporite minerals in primary borax beds, such as halite, gypsum, etc. [the crux of the arguments about source waters]

Controls on Lake Water Chemistry

- Generalized hydrologic cycle for playa lakes
- Mineral/rock control on cationic and anionic composition of waters
- Mineral precipitation and controls on the evolution of evaporating waters
- Uniqueness of sodium borate lakes and restrictions on their compositions.

Hydrologic elements of closed-basin evaporative lakes (after Eugster and Hardie, 1975)

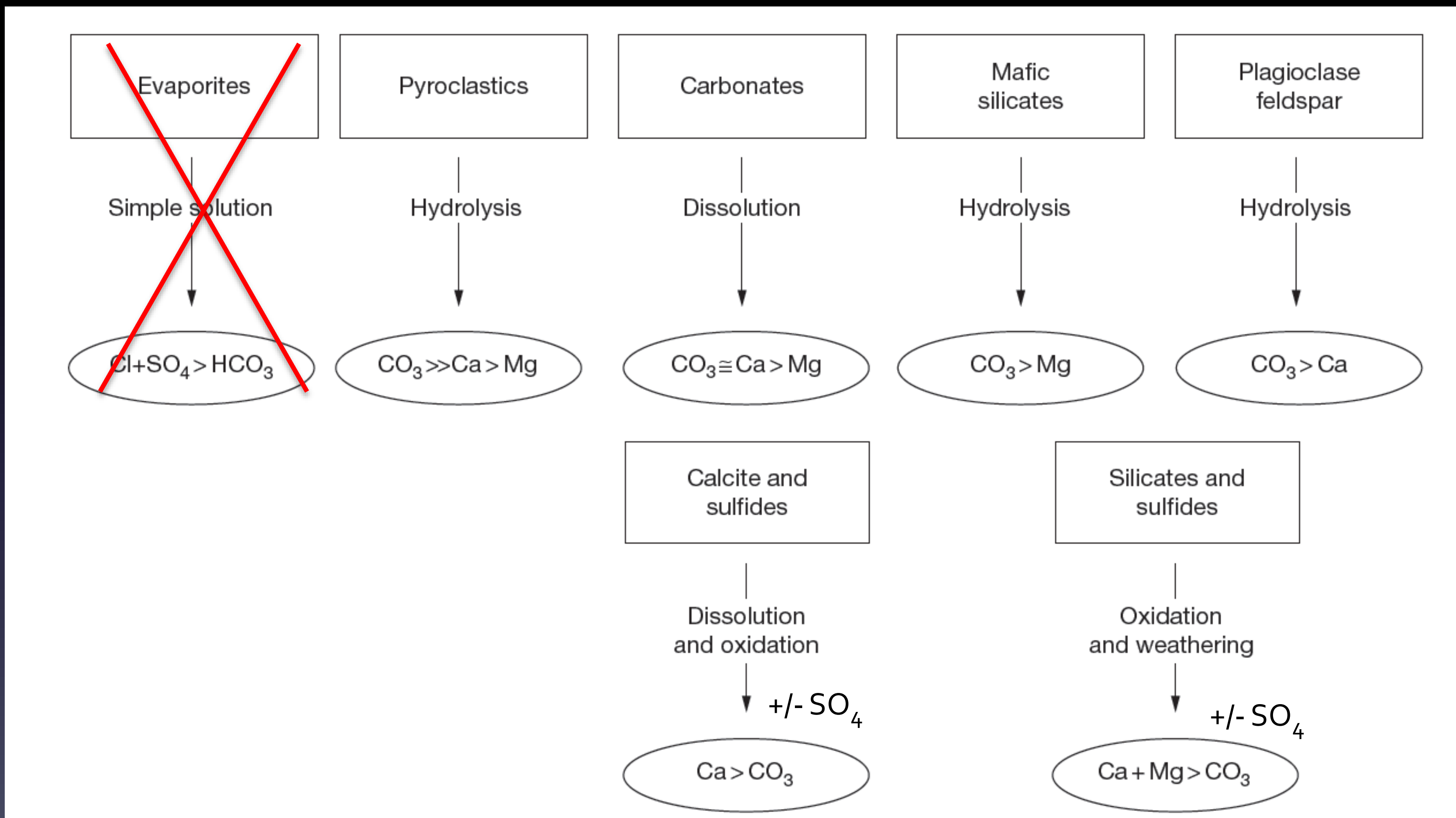


It's all about the anions

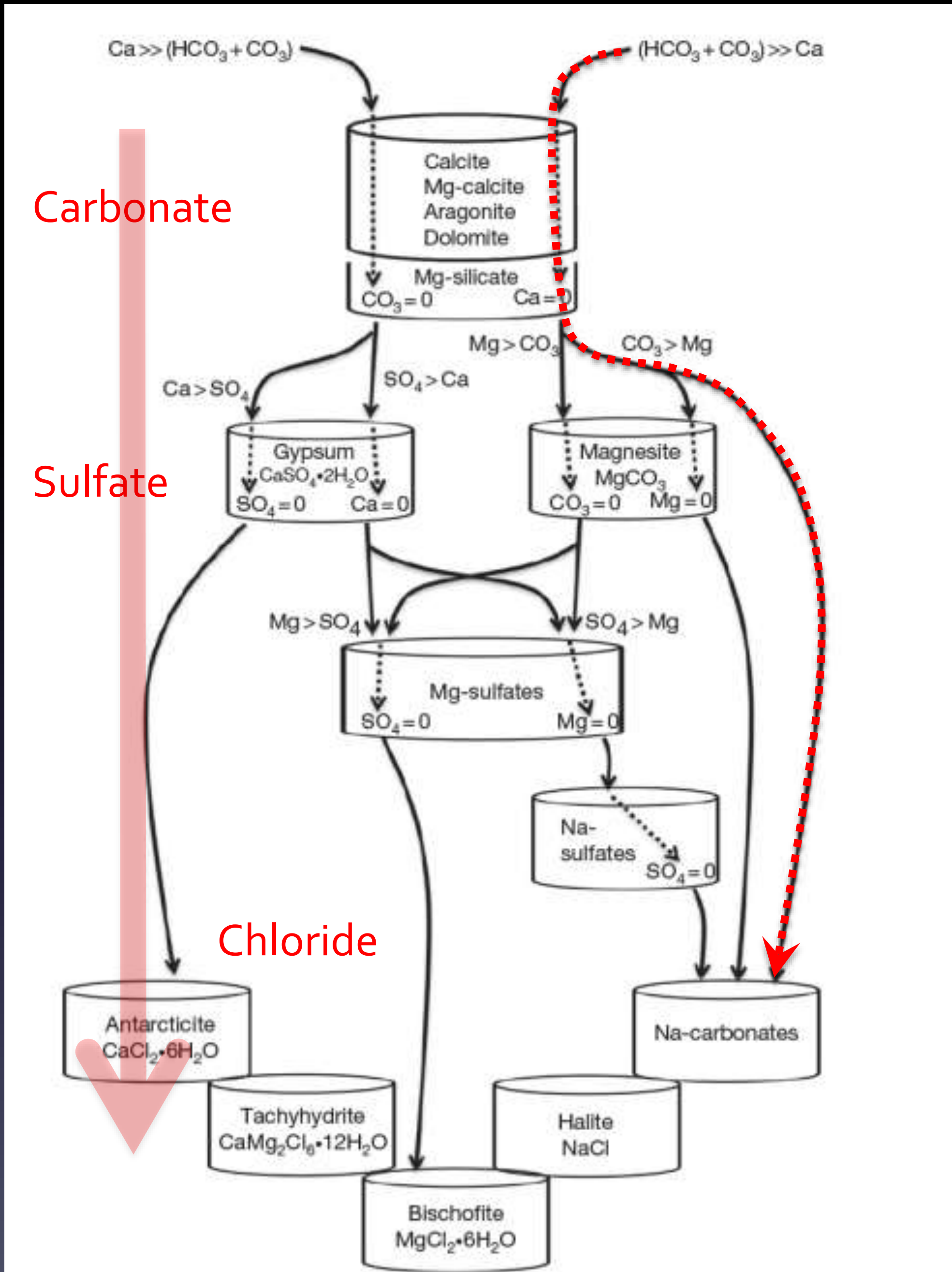
- Why no chloride salts? (Halite)
- Why no sulfate salts? (Gypsum)
- Why no major alkali carbonates (trona, hanksite, etc.)
- Non-marine evaporites (heterogeneous waters)
- Marine evaporites (quasi homogeneous waters)

Suggested sources of major *anions* in weathering and dissolution/hydrolysis environments.

$CaSiO_3 + 2CO_2 \rightarrow Ca^{++} + SiO_2 + 2HCO_3^-$



Diocampo and Jones, 2014



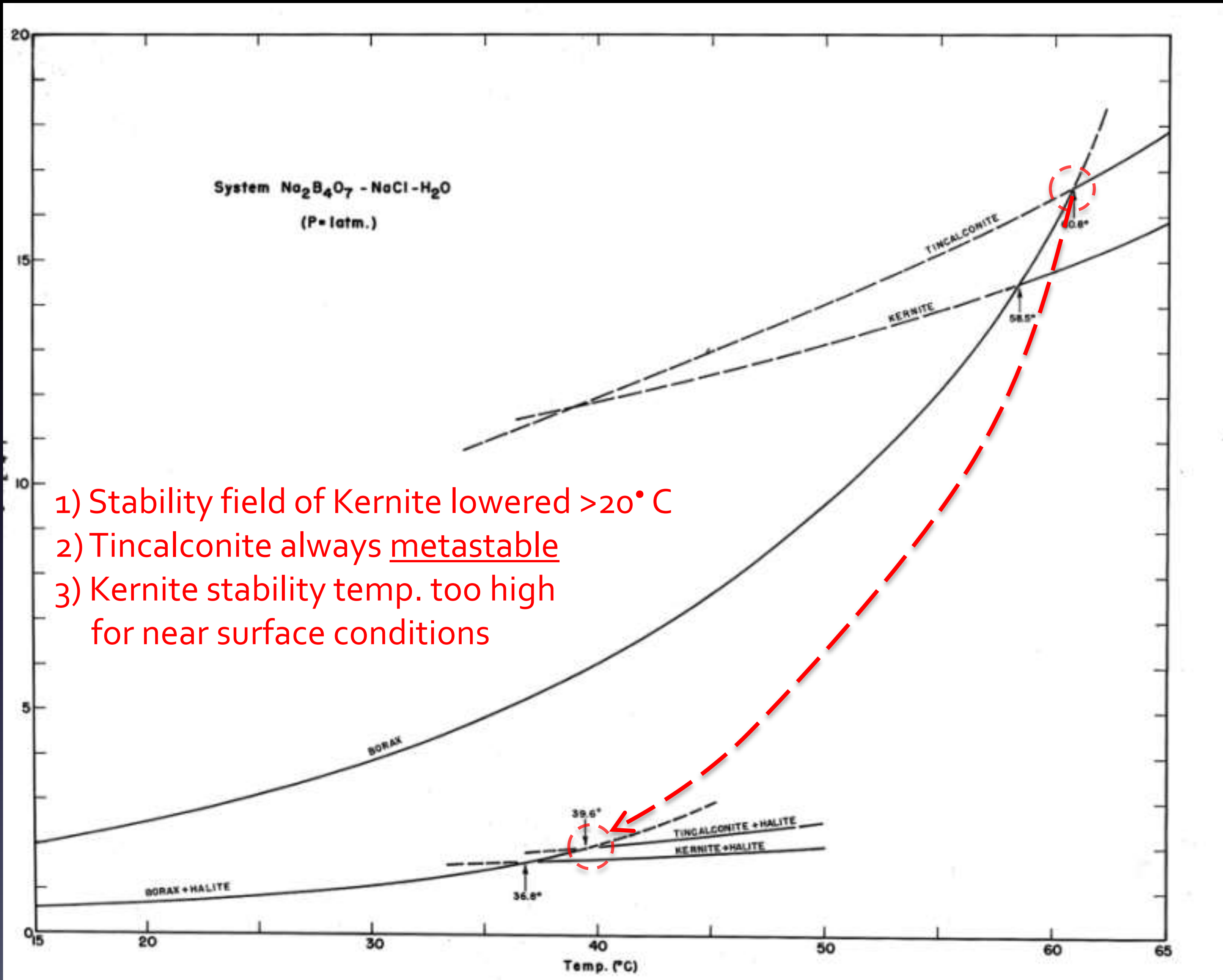
Modified version of "geochemical watershed" concept of Eugster, Jones, and Hardie

Sulfate and chloride free waters at Kramer derived from HCO_3/CO_3 dominated waters with added borate from thermal springs.

Red line is suggested evolutionary path for a low Cl and SO_4 waters.

Sulfate reduction in anoxic lake to remove sulfate?

The system $Na_2B_4O_7$-NaCl-H_2O



1) Stability field of Kernite lowered >20° C
2) Tincalconite always <u>metastable</u>
3) Kernite stability temp. too high for near surface conditions

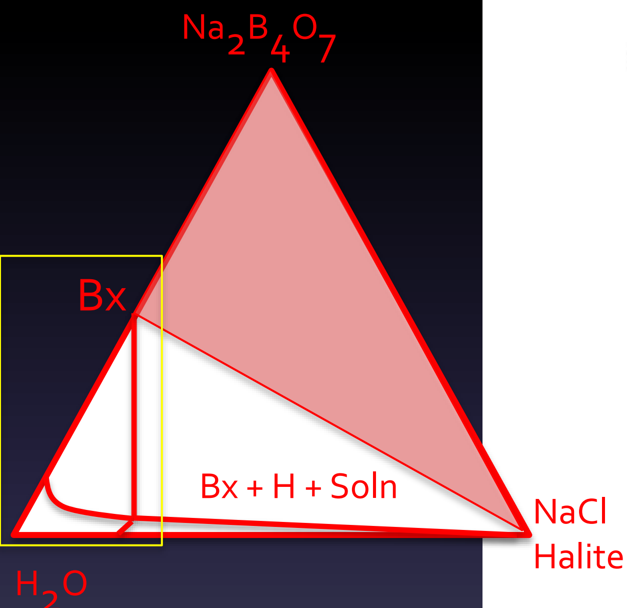
Controls on lake chemistry

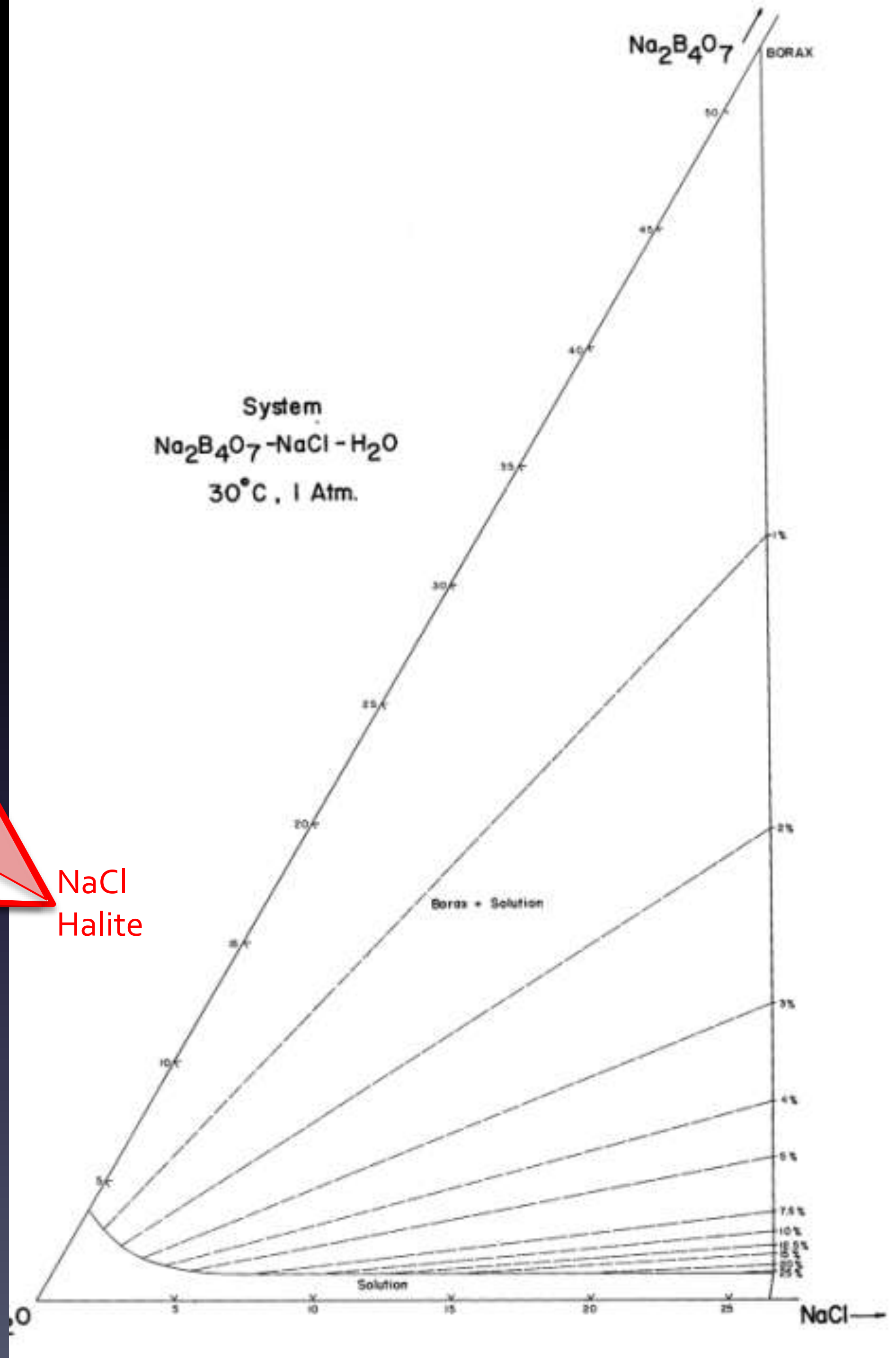
Limits on other anionic species (esp. Cl and SO_4)

No halite or gypsum precipitation in over 300′ of seds.

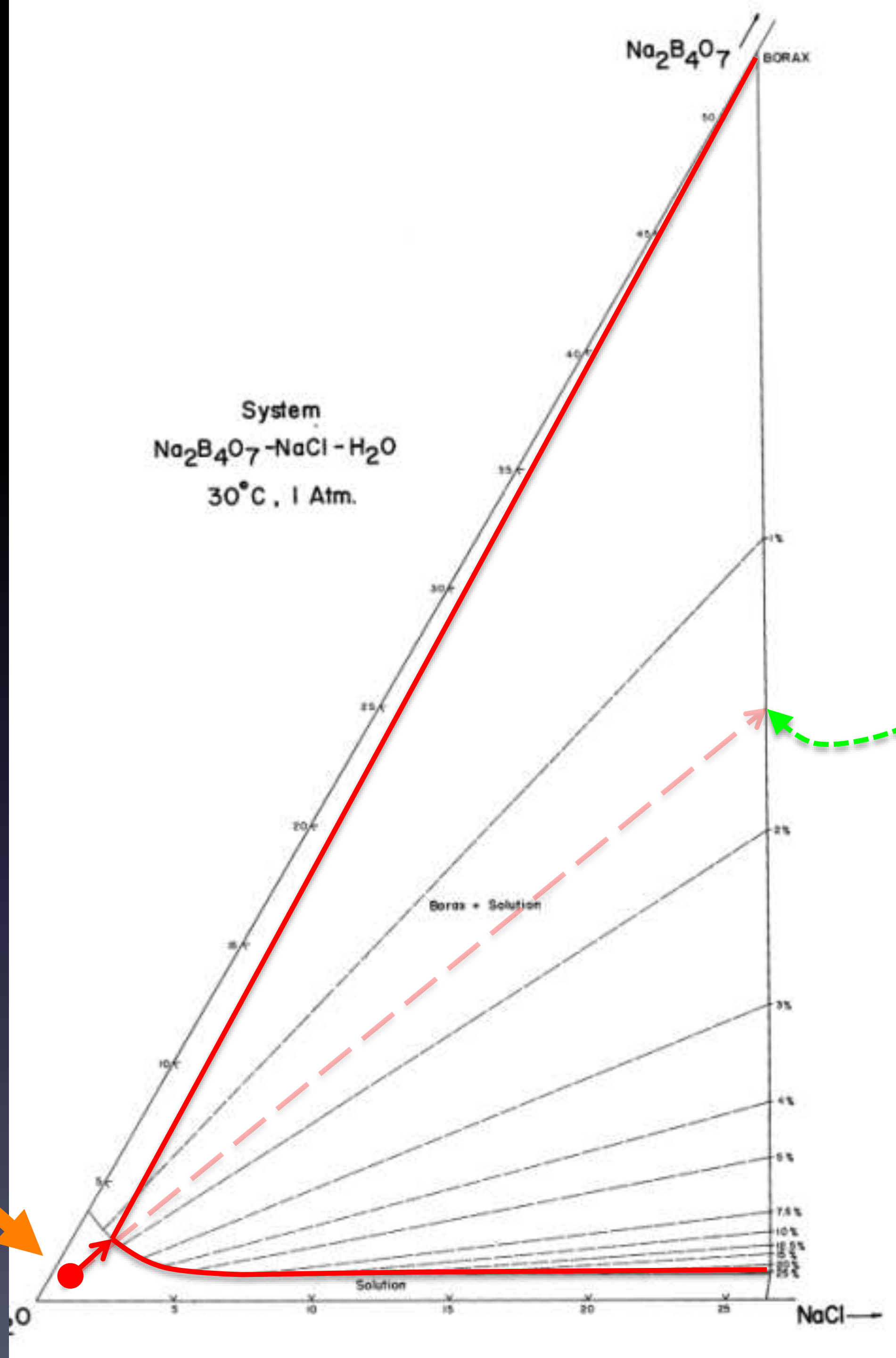
Comparison with other lake systems

Thermal spring water compositions


Na2B4O7
Bx
Bx + H + Soln
NaCl
Halite
H2O

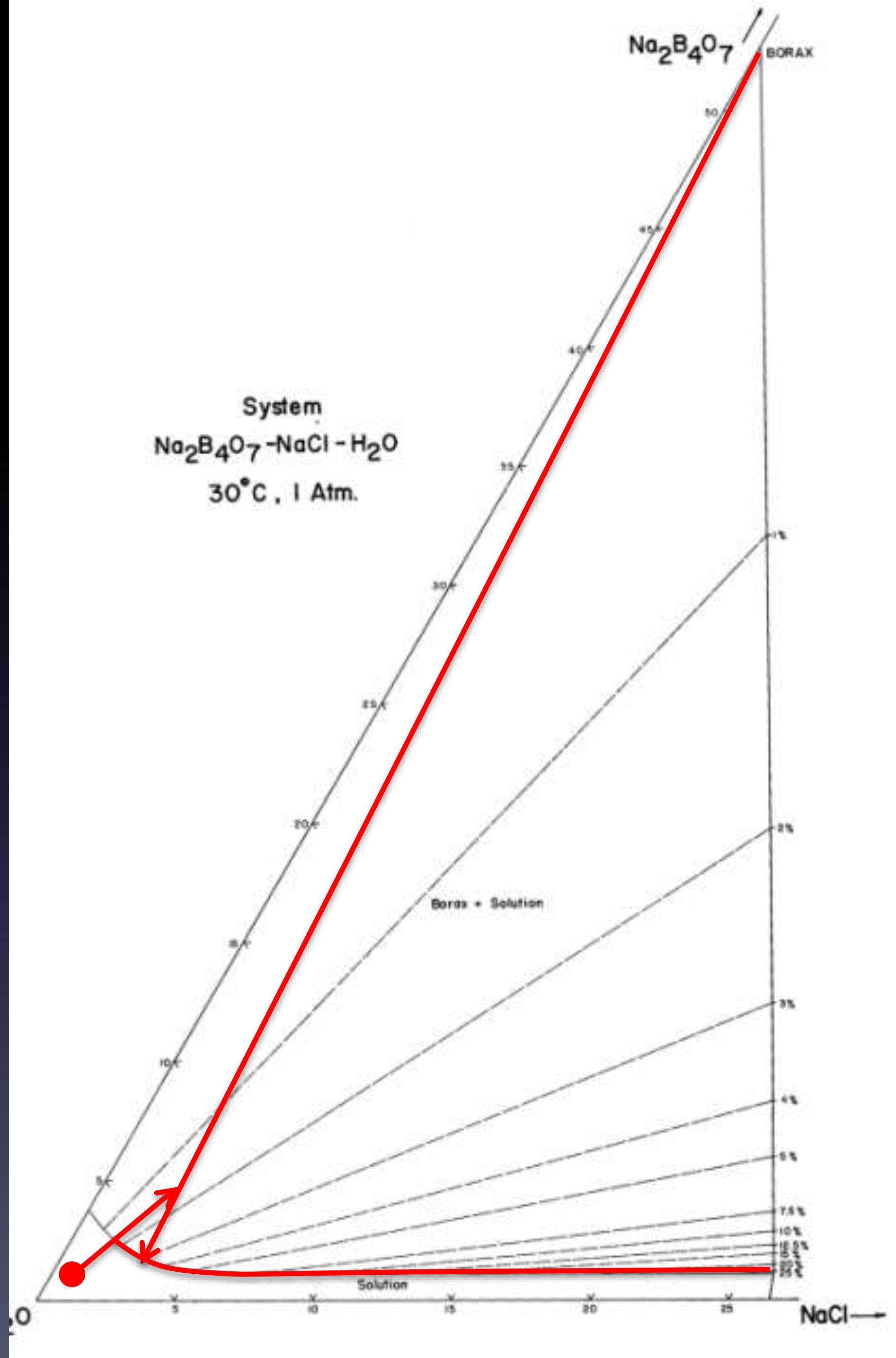

Na2B4O7
BORAX
System
Na2B4O7-NaCl-H2O
30°C, 1 Atm.
Borax + Solution
Solution
NaCl

Isothermal Evaporation with variable "starting" NaCl concentrations

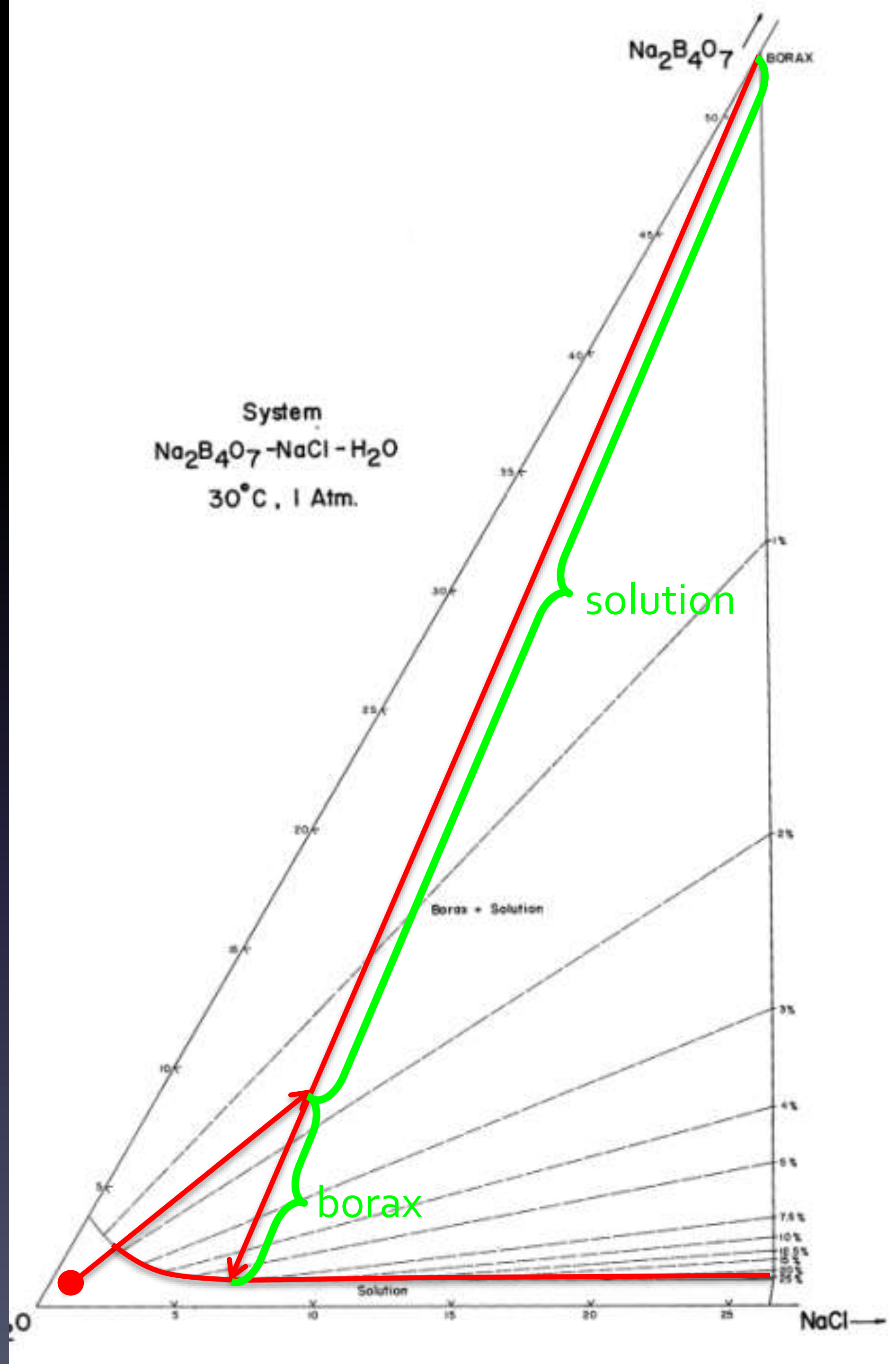


"Starting NaCl Concentration"
=
NaCl concentration at the point of borax saturation

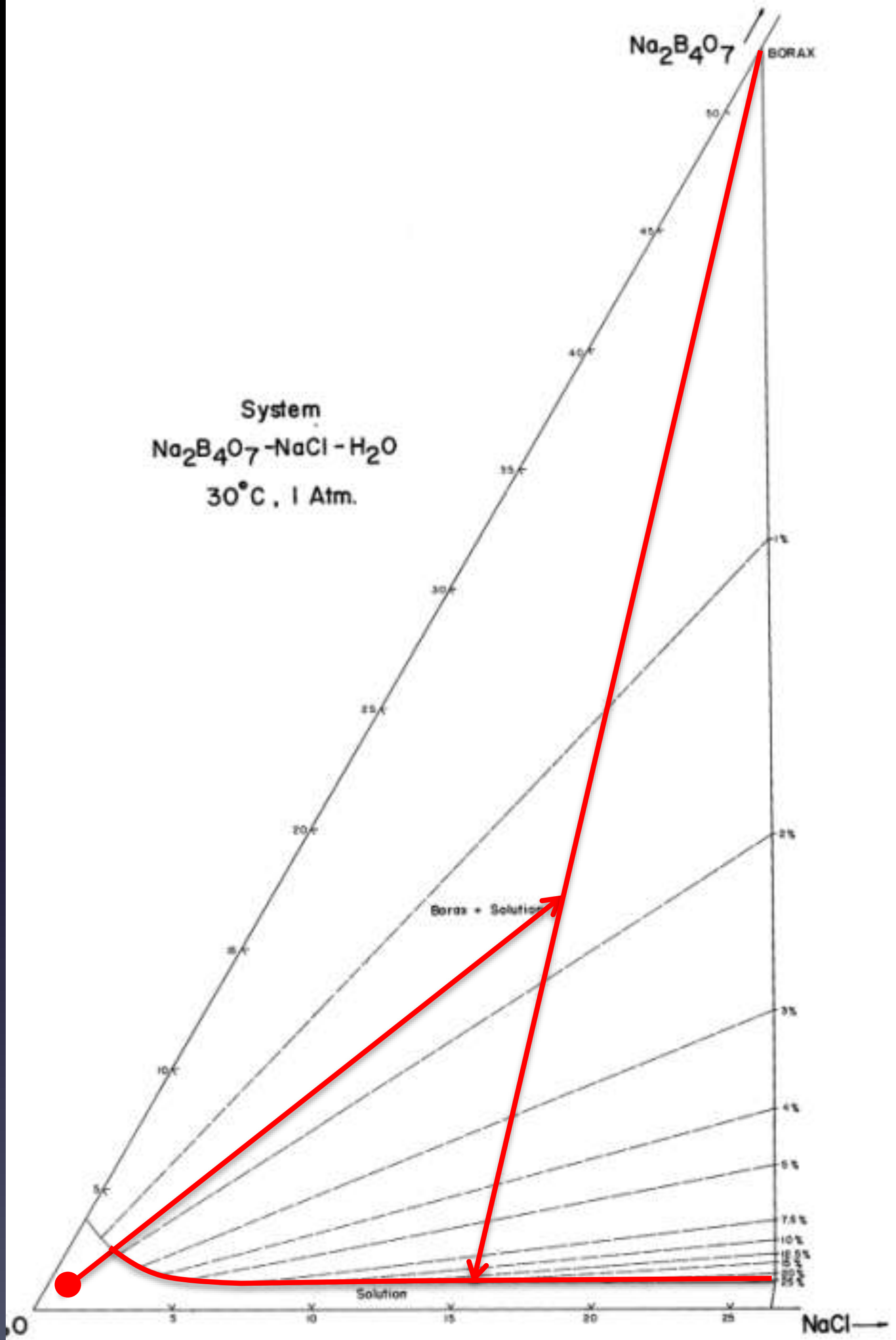
Isothermal Evaporation with variable “starting” NaCl concentrations



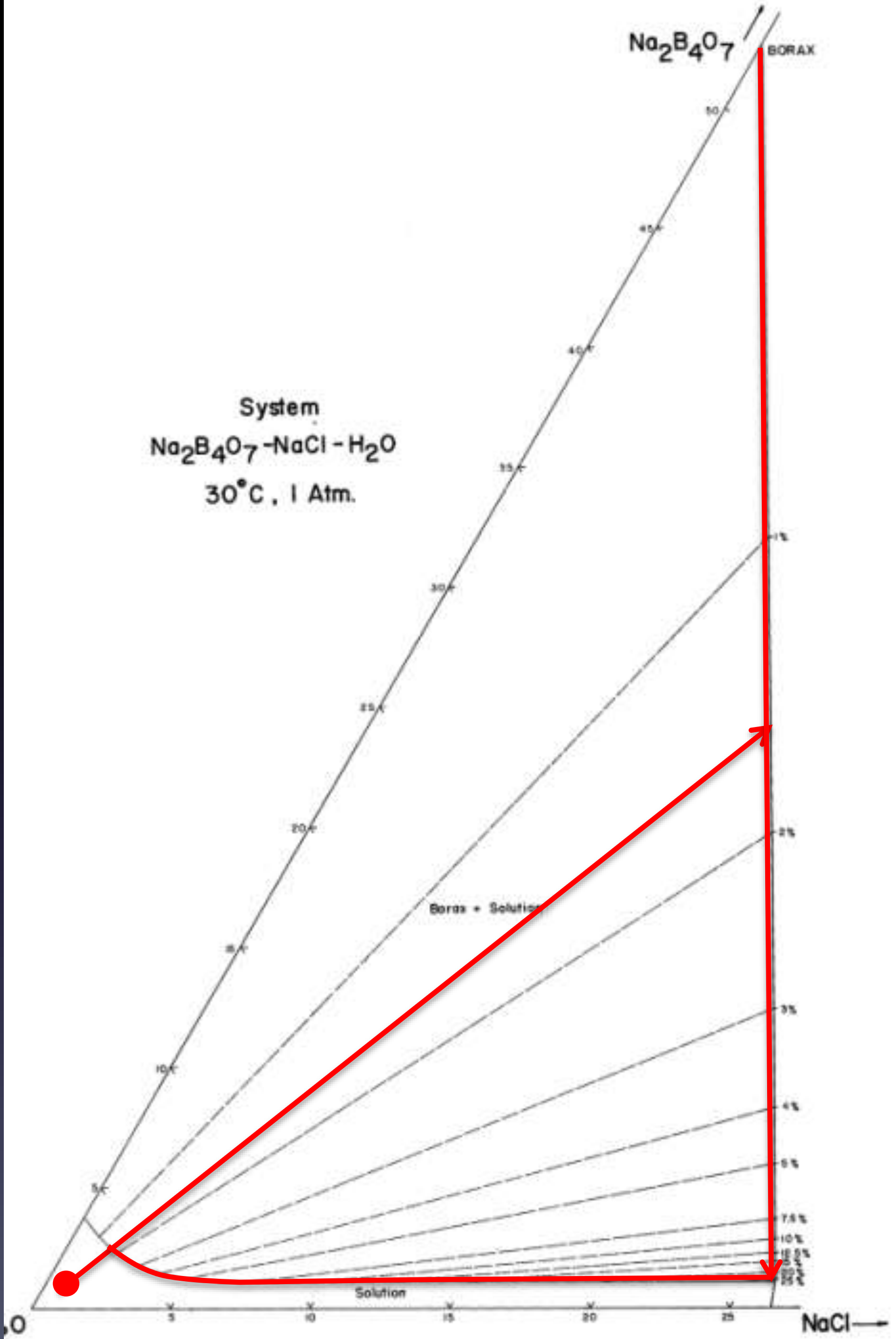
Isothermal Evaporation with variable “starting” NaCl concentrations



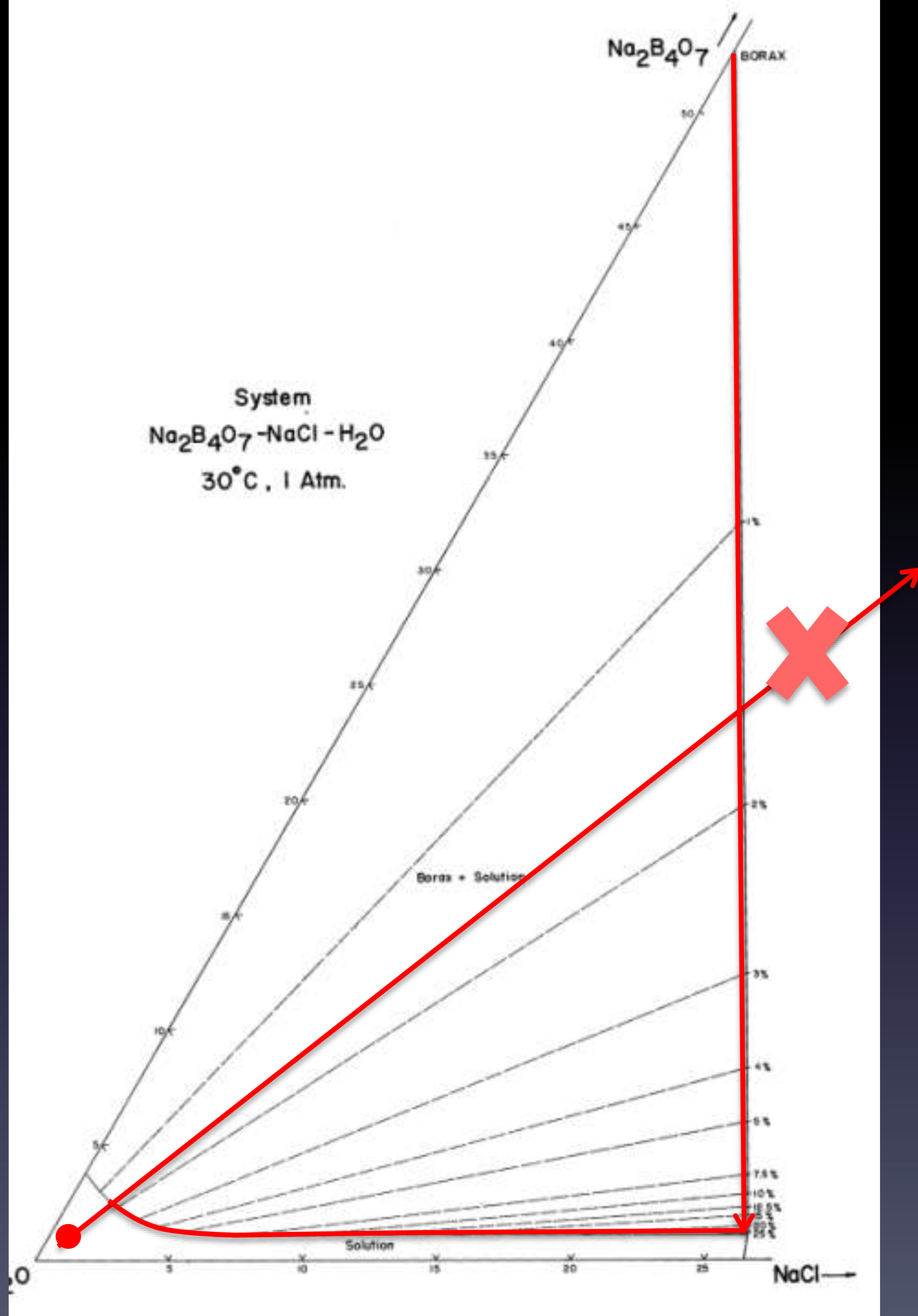
Isothermal Evaporation with variable "starting" NaCl concentrations

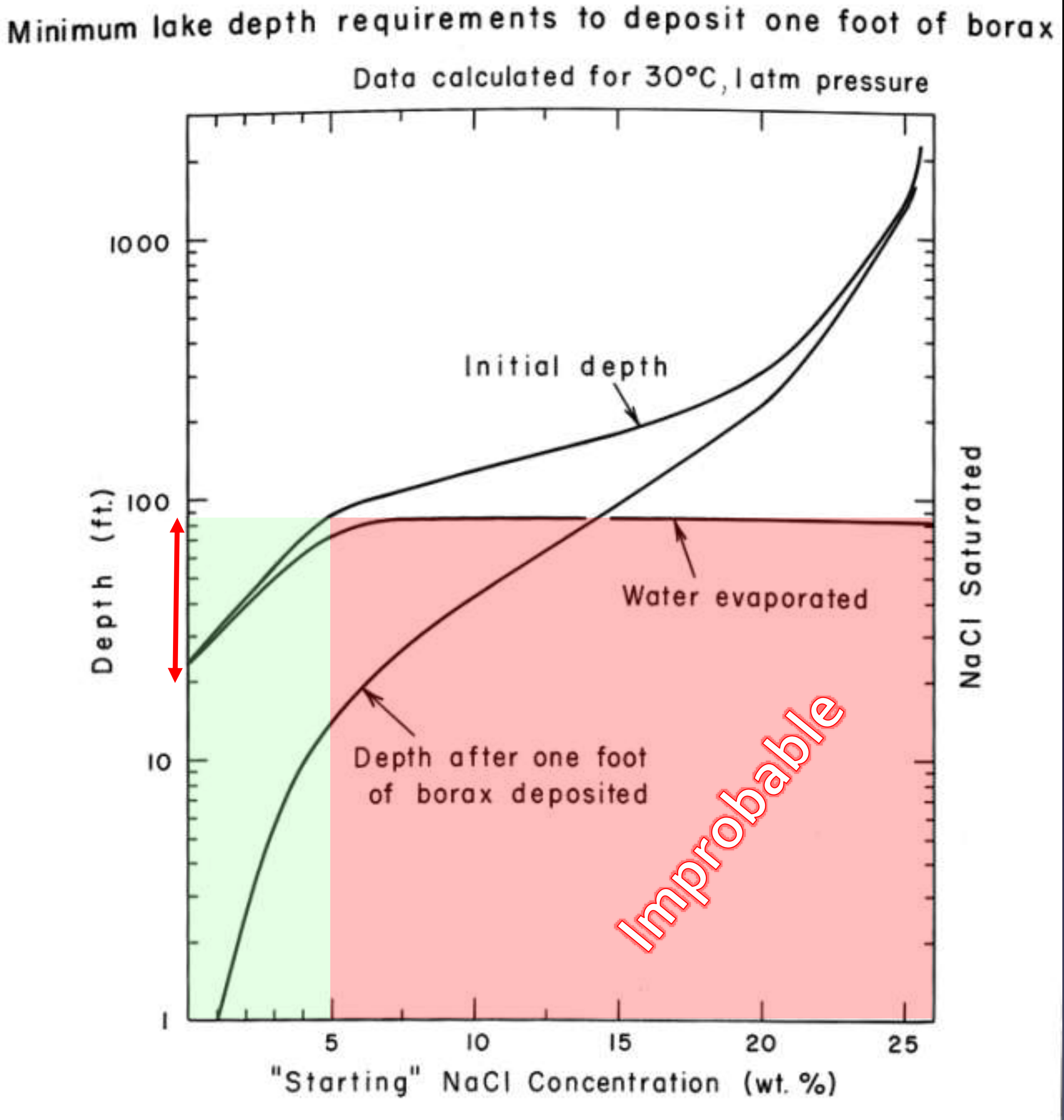


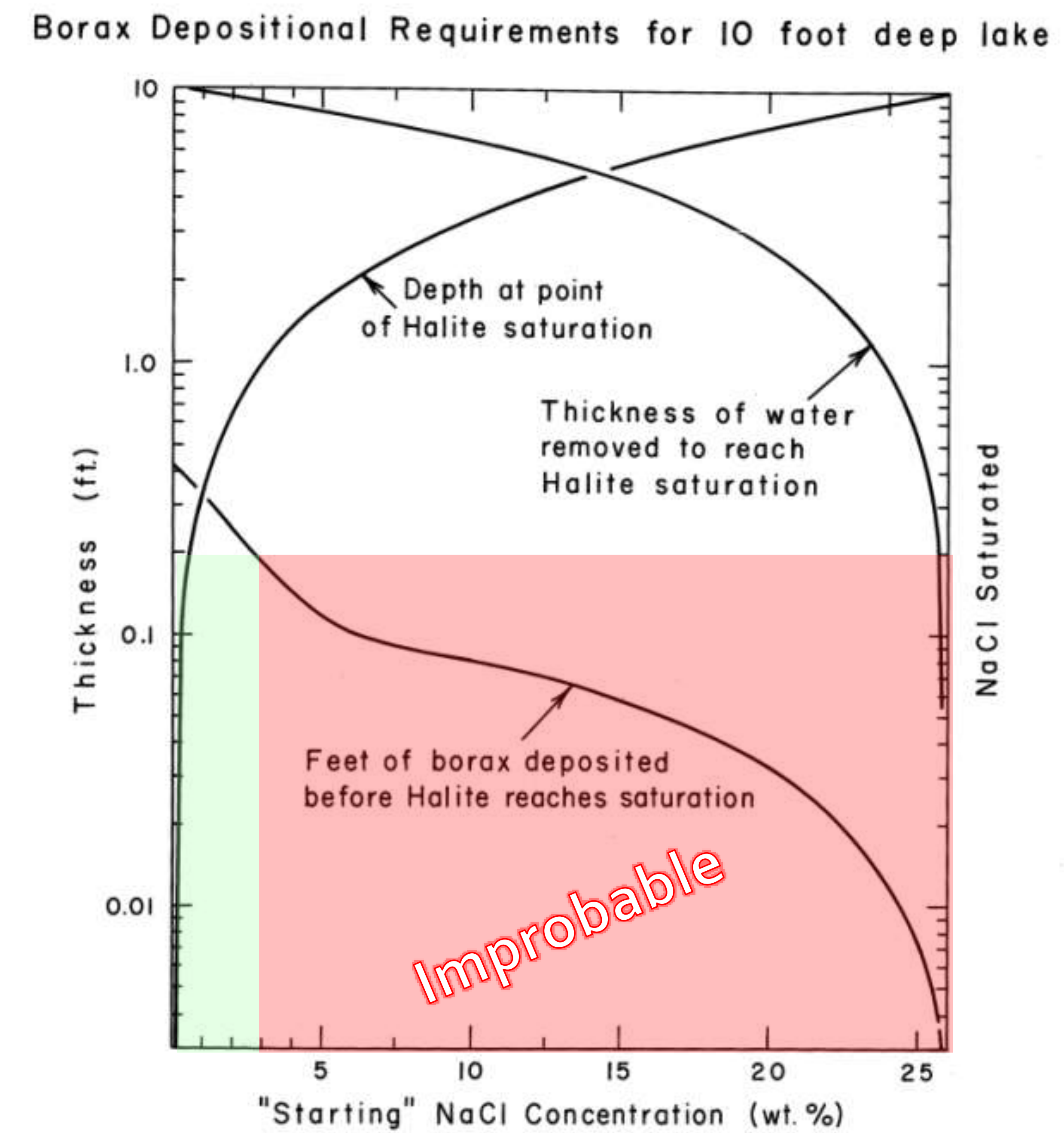
Isothermal Evaporation with variable "starting" NaCl concentrations



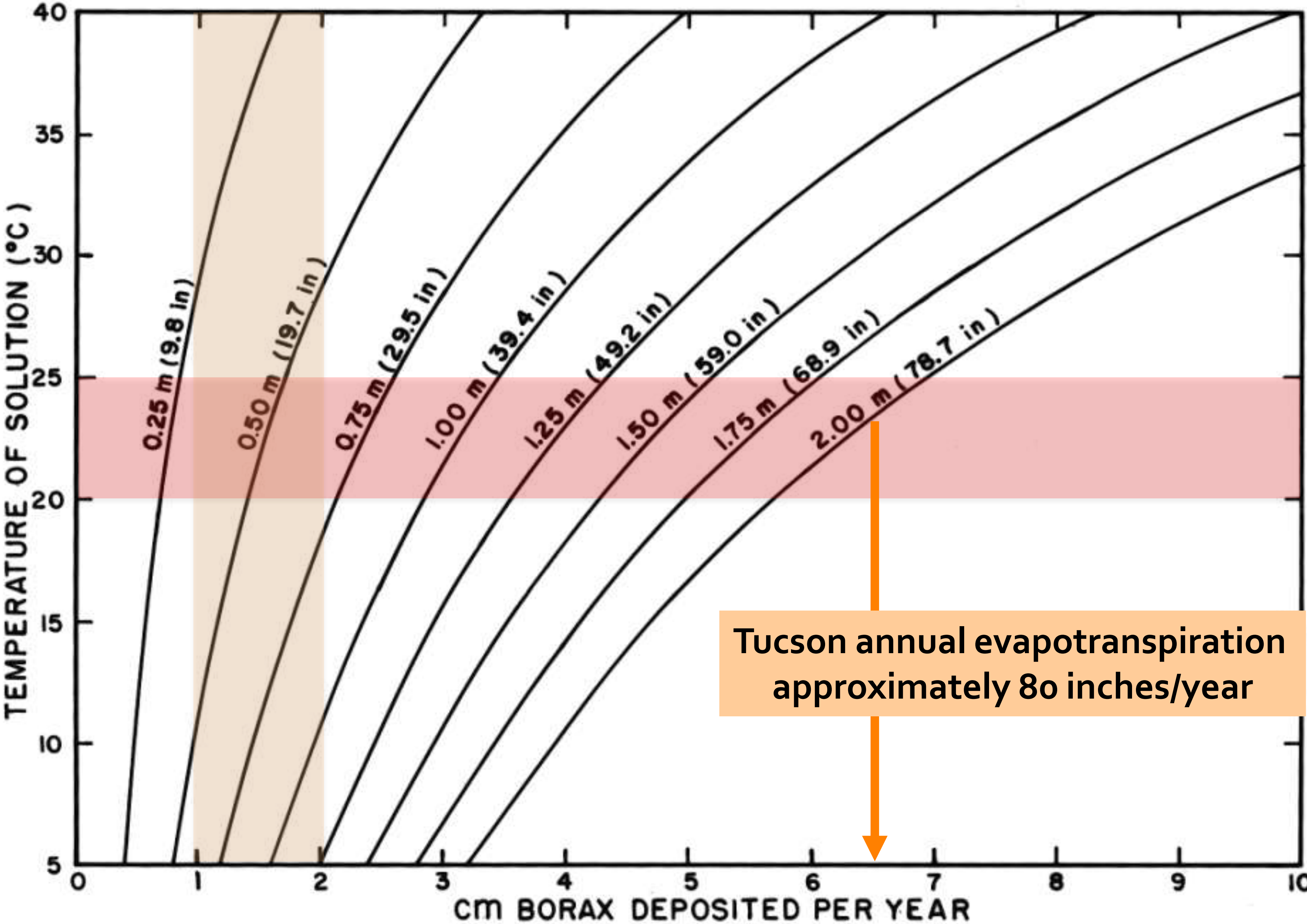
Isothermal Evaporation with variable “starting” NaCl concentrations




Minimum lake depth requirements to deposit one foot of borax
Data calculated for 30°C, 1 atm pressure
Depth (ft.)
1000
100
10
1
5
10
15
20
25
"Starting" NaCl Concentration (wt. %)
NaCl Saturated
Initial depth
Water evaporated
Depth after one foot of borax deposited
Improbable



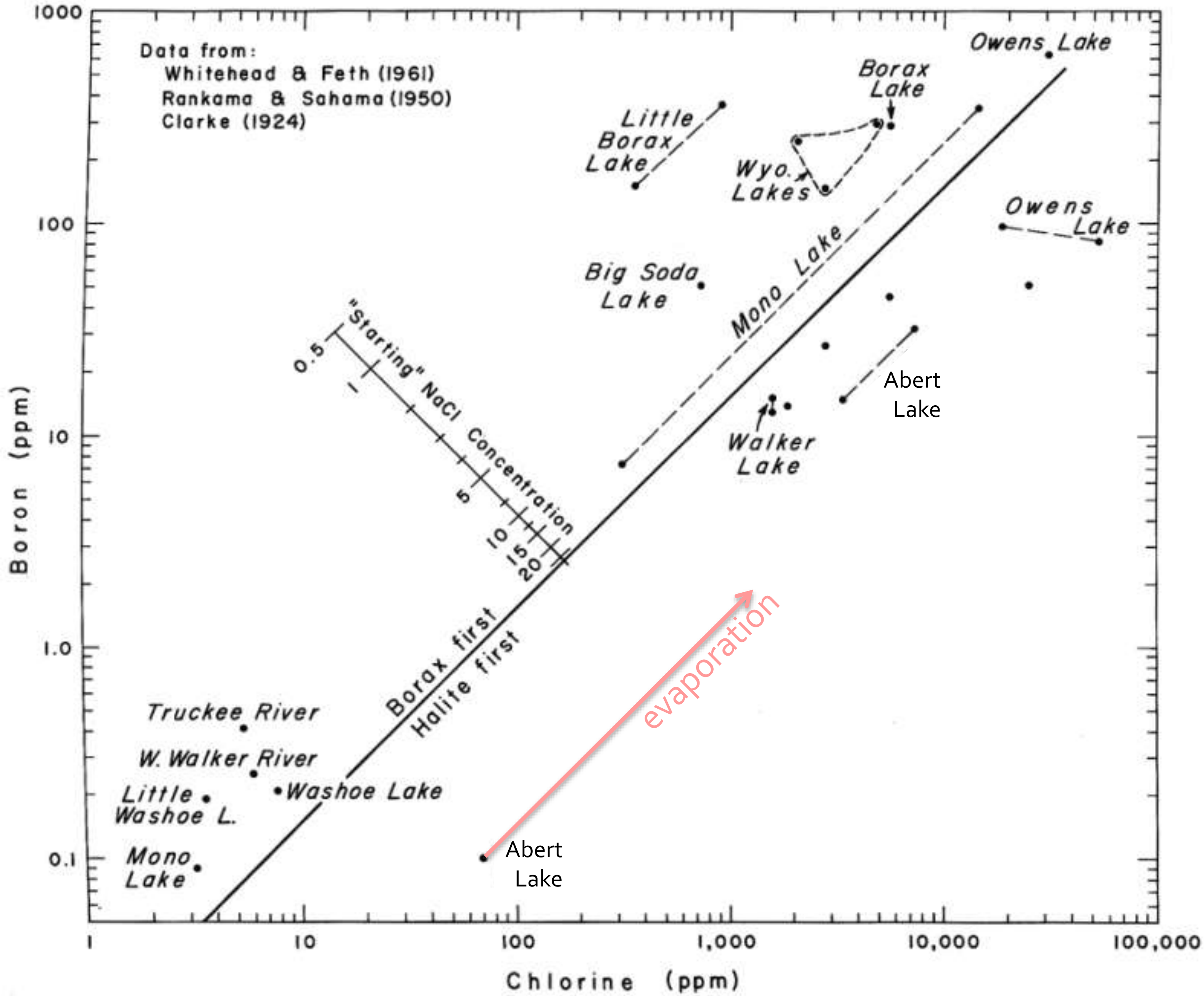
Borax Depositional Requirements for 10 foot deep lake
10
1.0
0.1
0.01
Thickness (ft.)
Depth at point of Halite saturation
Thickness of water removed to reach Halite saturation
Feet of borax deposited before Halite reaches saturation
Improbable
NaCl Saturated
5
10
15
20
25
"Starting" NaCl Concentration (wt. %)


TEMPERATURE OF SOLUTION (°C)
CM BORAX DEPOSITED PER YEAR
0.25 m (9.8 in)
0.50 m (19.7 in)
0.75 m (29.5 in)
1.00 m (39.4 in)
1.25 m (49.2 in)
1.50 m (59.0 in)
1.75 m (68.9 in)
2.00 m (78.7 in)
Tucson annual evapotranspiration
approximately 80 inches/year

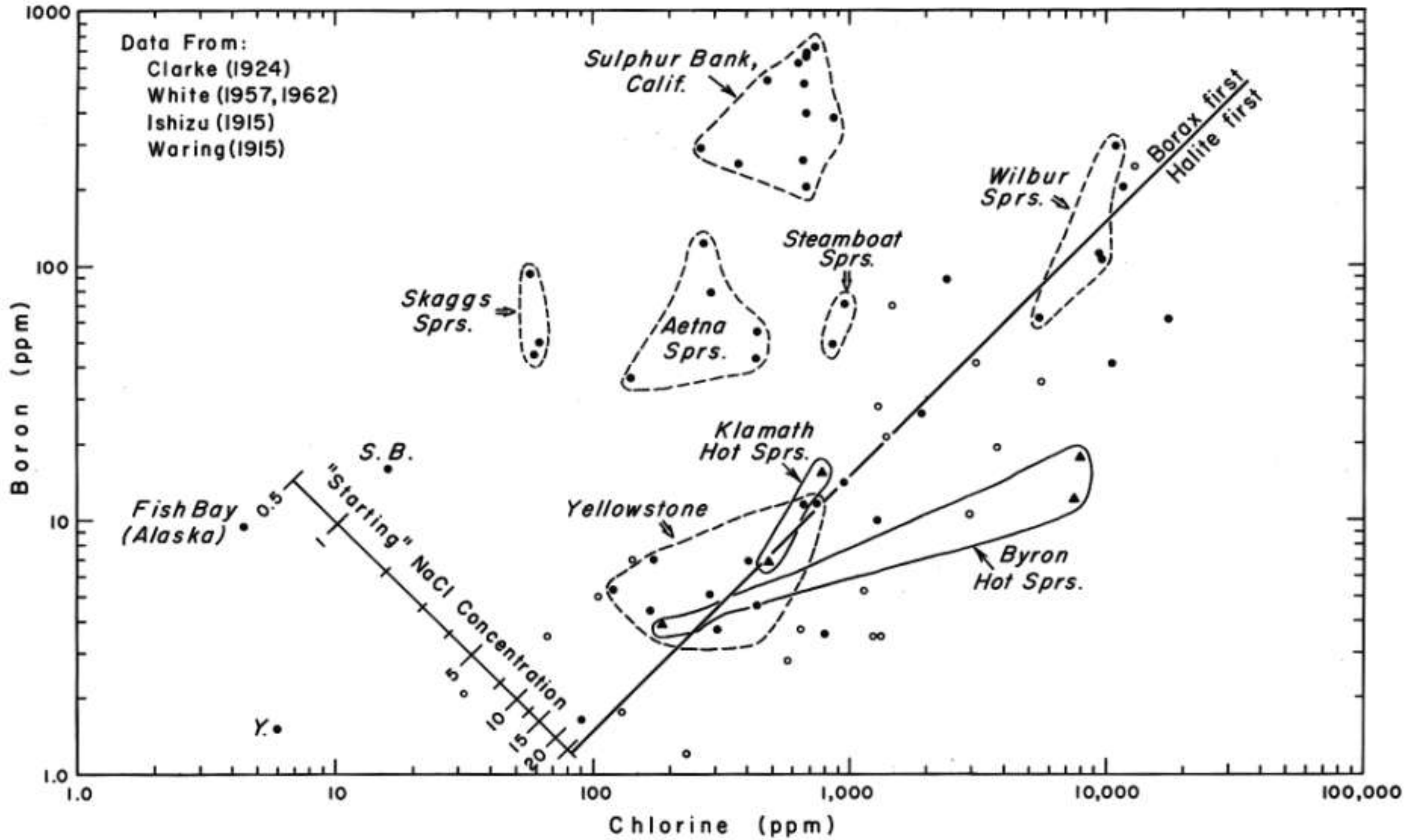
Consequences

1) Lake deposited only borax through 300 ft. of sediment accumulation
2) Most of the time the lake existed as an undersaturated (meromictic) lake
3) If lake never "flushed" or overflowed the Cl^- concentration must have been very low
4) If the lake DID overflow: [two consequences]
   - Sizeable amount of borate solution was carried into other downstream basins (exploration possibility?)
   - The incoming spring-fed fluids must have had a high enough B/Cl ratio to swamp out the effect of accumulating chloride in the lake brine.

Boron vs chlorine in lakes

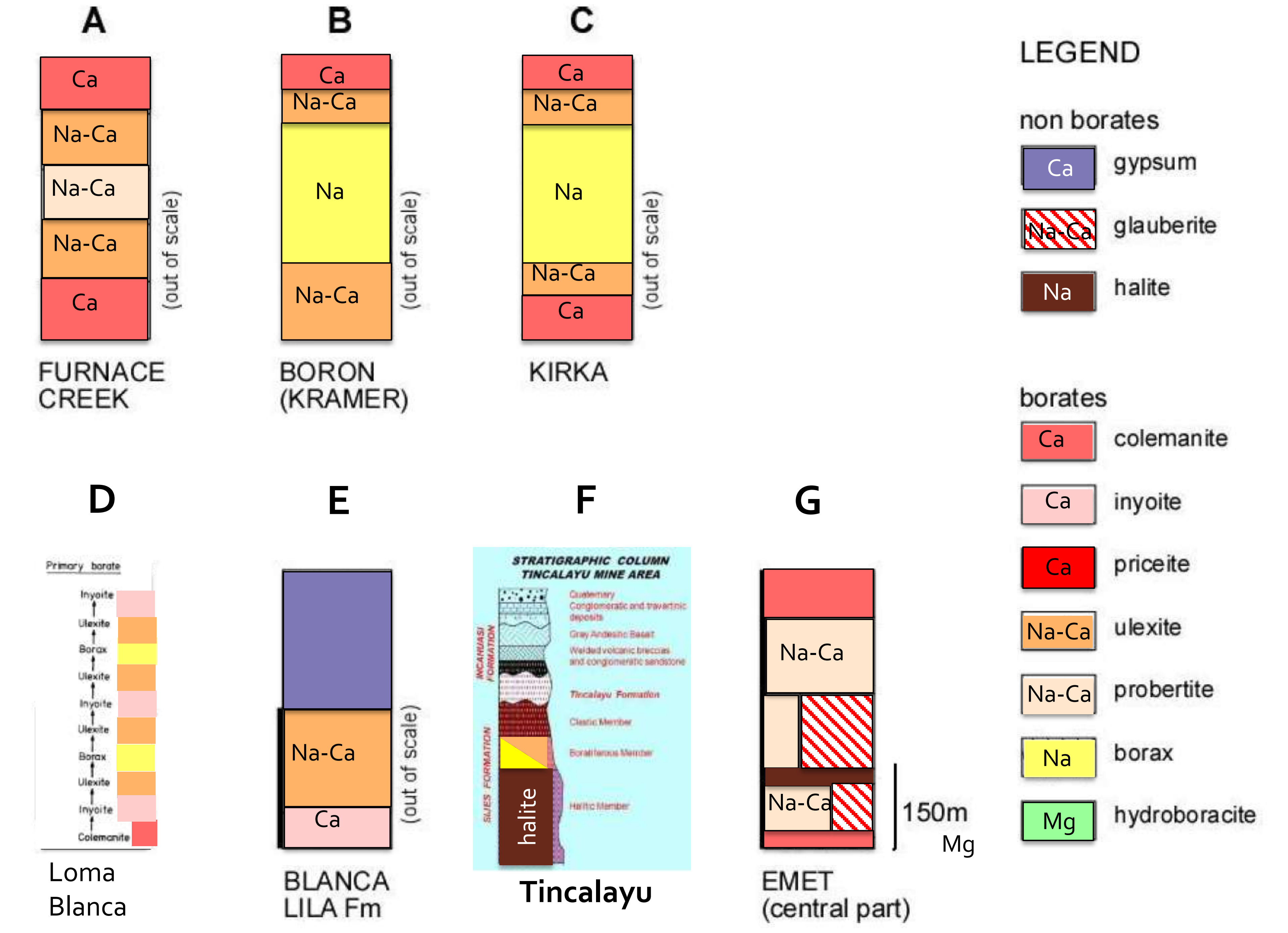


Boron vs Chlorine in thermal spring waters

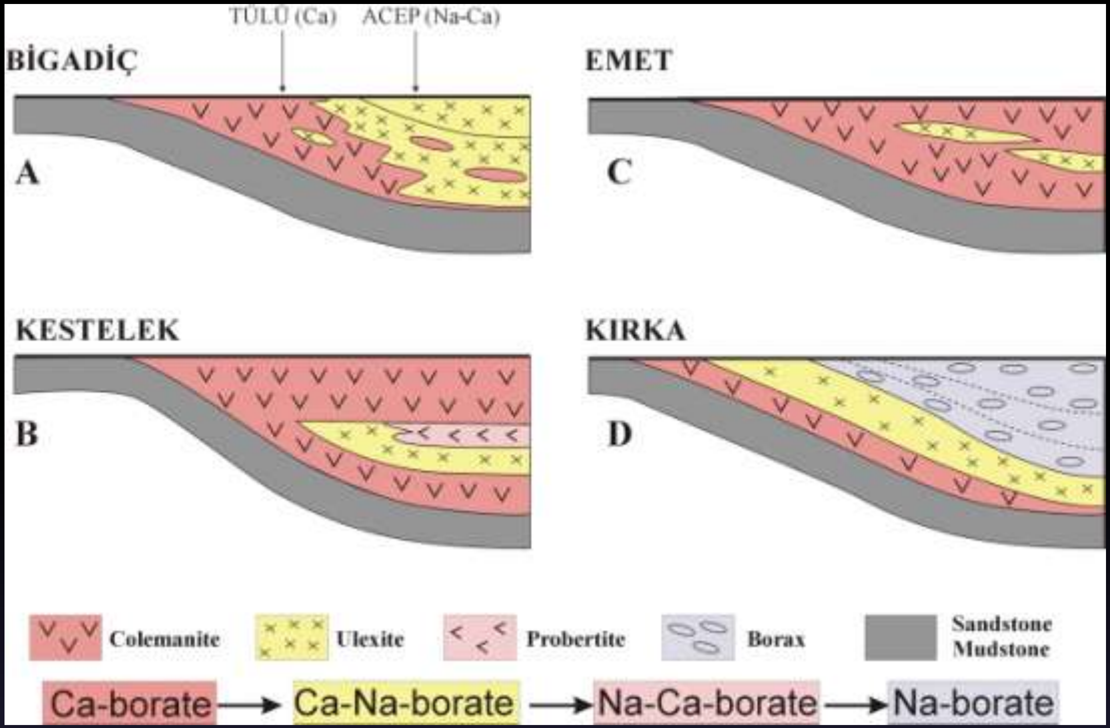


Other Borate Deposits

- Historic (Borax Lake, Death Valley, Searles Lake, ….)
- Active:
  - Turkey
    - Kirka
    - Emet
    - Bigadic
  - South America
    - Tincalayu
    - Loma Blanca


A
B
C
LEGEND
Ca
Na-Ca
Na-Ca
Na-Ca
Ca
(out of scale)
FURNACE CREEK
Ca
Na-Ca
Na
Na-Ca
(out of scale)
BORON (KRAMER)
Ca
Na-Ca
Na
Na-Ca
Ca
(out of scale)
KIRKA
non borates
Ca gypsum
Na-Ca glauberite
Na halite
borates
Ca colemanite
Ca inyoite
Ca priceite
Na-Ca ulexite
Na-Ca probertite
Na borax
Mg hydroboracite
D
E
F
G
Primary borate
Inyoite
Ulexite
Borax
Ulexite
Inyoite
Ulexite
Borax
Ulexite
Inyoite
Colemanite
Loma Blanca
Na-Ca
Ca
(out of scale)
BLANCA LILA Fm
STRATIGRAPHIC COLUMN
TINCALAYU MINE AREA
Tincalayu Formation
halite
Tincalayu
Na-Ca
Na-Ca
150m
Mg
EMET (central part)

Turkish Deposits



Courtesy Calvit Helvaci (2015)

CHEMICALLY ZONED - GENERALIZED

Calcium Borates

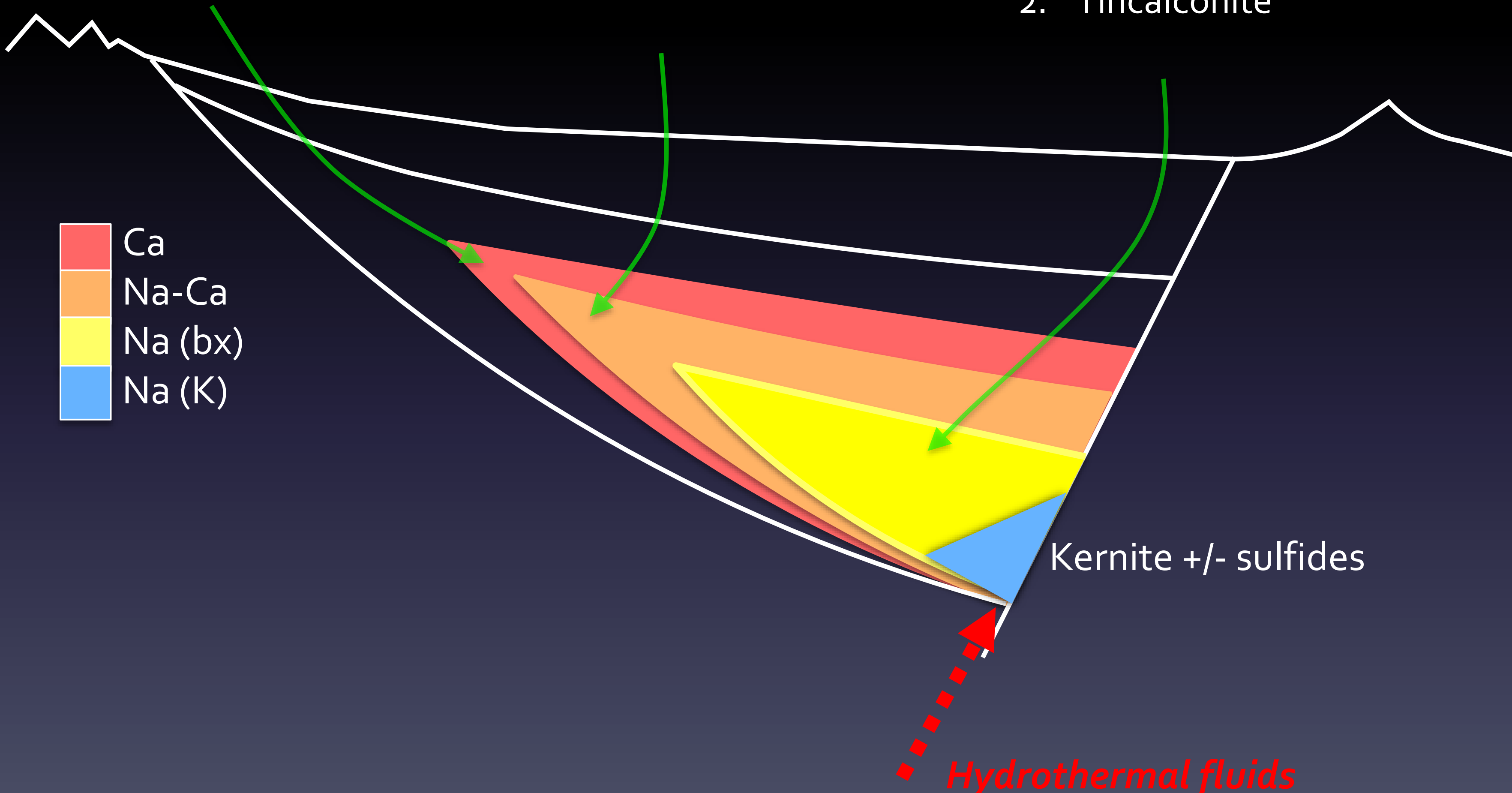
1. Meyerhofferite
2. Inyoite
3. Colemanite

Sodium-Calcium Borates

1. Ulexite
2. Probertite

Sodium-Borates

1. Borax
2. Tincalconite



Isotopic systematics

$$\delta^{11}B=[(^{11/10}B_{sample})/(^{11/10}B_{standard})-1]*1000$$

Isotopic concentration factors

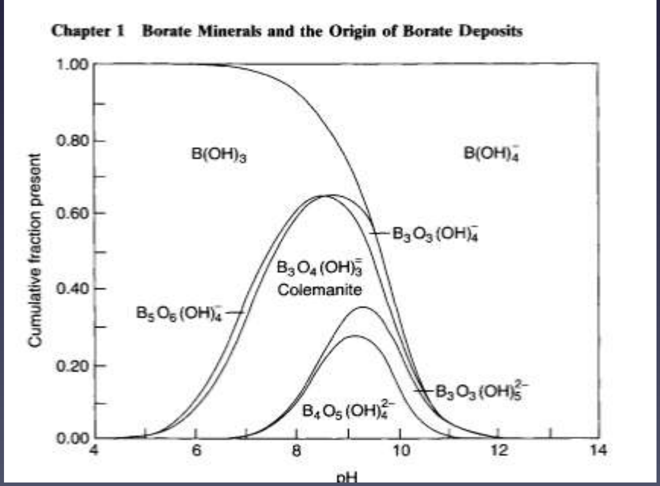
1- Water-rock interaction (inherent fluid composition)

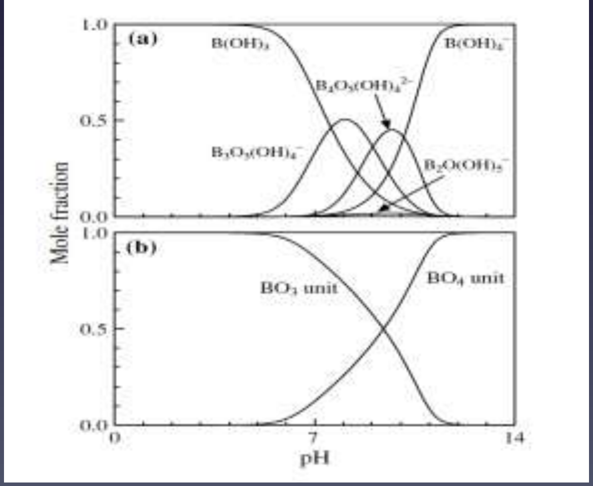
2- Mineral precipitation from saline water

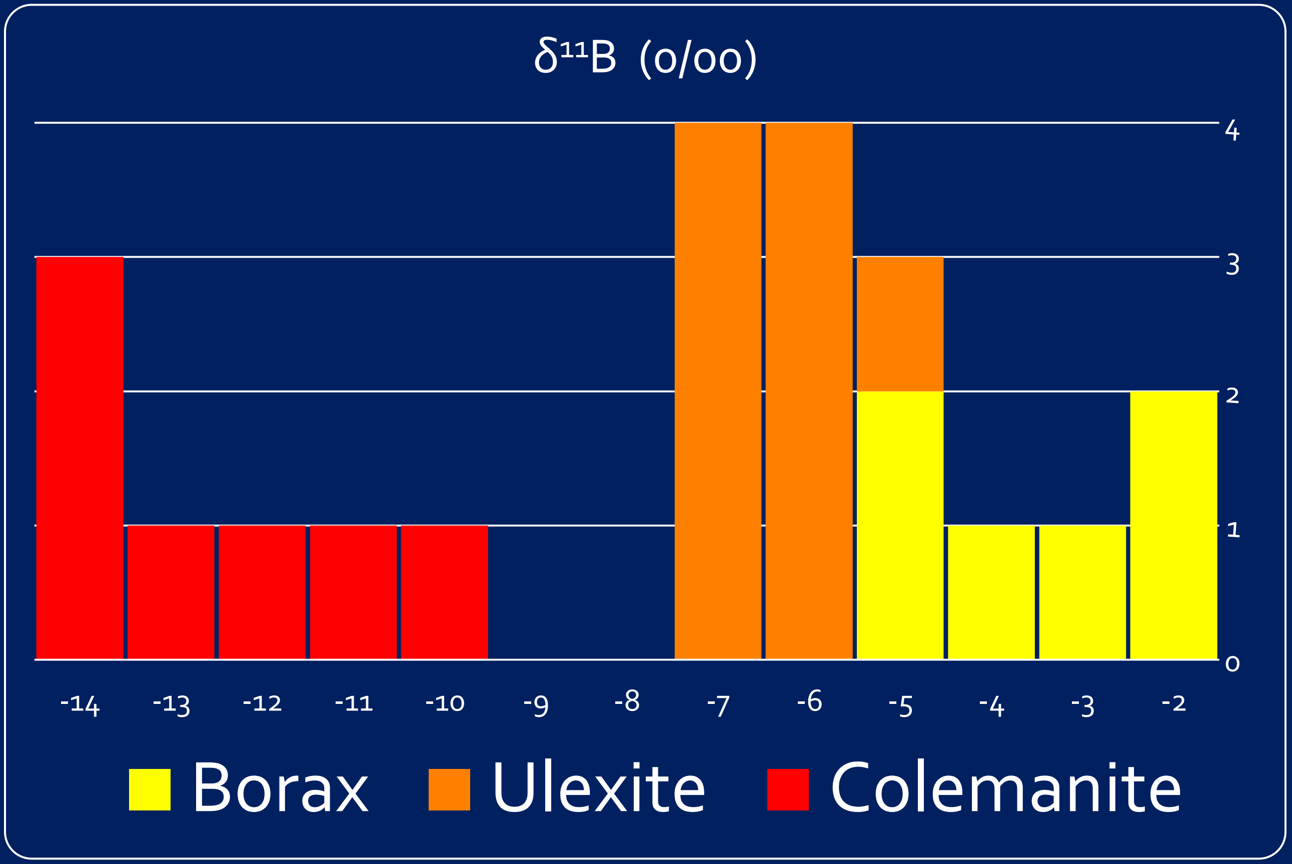
a-Releigh fractination-

b- pH dependency ($B(OH)_4$ vs $B(OH)_3$

c- boron coordination effects (tetrahedral >? Trigonal coord)






δ11B (o/oo)
4
3
2
1
0
-14
-13
-12
-11
-10
-9
-8
-7
-6
-5
-4
-3
-2
Borax
Ulexite
Colemanite

Summary of Isotopic Conclusions (Kramer)

1. Borax maintained near same isotope composition for life of the deposit (est. 5-7*10^4 years)
2. Within layer changes may reflect Raleigh fractionation (supports a shallow lake hypothesis)
3. Relative isotope ratios of borax, ulexite, and colemenite fits xl-structural model, but …
4. Colemanite is isotopically lighter than expected for brine equilibration and probably formed in lower pH interstitial waters (later or in more dilute, lake margin waters)
5. Ulexite formed in lake margins (contemporaneous)
6. Data consistent with thermal spring origin for boron
7. Palmer and Helvaci (1959, 1961) draw same conclusions for Kirka deposit in Turkey
8. After 50+ years …

Swihart, et.al. (1996)

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VINDICATION!

Swihart, et.al. (1996)

Unexplored use of oxygen and hydrogen isotopes

Two boron sites
Three oxygen sites
Two hydrogen sites

$Na_2B_4O_5(OH)_4 \bullet 8(H_2O)$

$\delta^{18}O$ and $\delta^{2}H$

$\delta^{18}O$ and $\delta^{2}H$

$\delta^{11}B_{trigonal\ coord}$ and $\delta^{11}B_{tetrahedral\ coord}$

MODERN ANALOGUES?

Borax Lake, CA

South American Springs

Borax Lake and Sulfur Bank hydrothermal area

Borax Lake

Figure 2. Rio Alumbrio spring deposit, Argentina. The light-colored material is ulexite.

Figure 3. Largest of the Alumbrio spring deposits. In left center of picture is a well-developed cone, now extinct, formed of ulexite and calcareous tufa. Cerro Supisaimo is in the upper center.

Figure 4. Deposit shown in Figure 3. Note the small cone on left skyline. The larger deposit is predominantly ulexite and has a vigorously bubbling spring in its flat top.

Figure 5. Volcancito spring deposit, Argentina. Middle cone is shown in lower center of picture. Prominent cliff is formed of extensive quartz-biotite flow. Minor perennial stream is on left edge of ulexite, which is white.

From: Muessig, 1966

Summary

1. Shallow, merimictic lake, probably on order of 10-20 ft
2. Borax largely deposited on lake bottom sediments with overlying brine.
3. Synsedimentary current transport of fine grain crystals, reworking and crystal overgrowth
4. mm scale zonation in borax reflects diurnal growth rate variations.
5. No other evaporite minerals deposited with borax (except lateral ulexite and perhaps colemanite)
6. Alternating periods of lake saturation (months) and undersaturation (years), even playa conditions
7. Nodular (cottonball) forms of ulexite and perhaps ‘in mud’ borax crystals formed under playa (dry lake) conditions.

Summary (cont.)

8. Lake composition essentially pure Na borate
9. 300 ft of total lake seds, est. 75% borax means that the total boron deposited must come from a source active at the time of the lake.
10. Zonal distribution of Ca-NaCa-Na borates and low solubilities of Ca and NaCa borates provides an effective geochemical shield protecting the lake from silicate weathering derived groundwater solutions.
11. Co-deposited sulfide minerals and kernite crystallization indicate spring was within or marginal to the lake.
12. High pH of brines and diagenetic fluids mobilized Si and Al leading to extensive zeolitization and borate remobilization (akin to sodic alteration seen in ore deposits.


C’est fini