Subsurface Corrosion of Calcite and Dolomite by Fault-Sourced Hydrothermal Fluids*

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Abstract

Porosity in both limestone and dolomite reservoirs can be created and enhanced by fault-sourced hydrothermal fluids. Examples from the Pinda Formation of offshore Angola and the Cogollo Limestone of Venezuela will be used to show a subsurface origin for the dissolution. In the Pinda Formation of offshore Angola, both limestone and dolomite were dissolved in the subsurface. Dolomite (including some saddle dolomite) that formed at temperatures ranging from 65 to 160°C occurs as a cement in some grainstones where the grains are found as intact calcite, partially dissolved and completely dissolved. This dissolution of the calcite is therefore of a subsurface origin. Most of the porosity in some cores and thin sections is of a leached dolomite origin. The fact that the leaching occurred after this high temperature dolomitization confirms a subsurface origin. Hydrothermal fluids rich in H_2S are interpreted to have flowed up active faults and into the formation where they were oxidized to create sulfuric acid which did the dissolution. Pyrite and anhydrite precipitation closely follow the dolomite dissolution. This all occurred during early burial prior to oil migration.

In the Cogollo Limestone of Venezuela, there is burial corrosion of limestone reservoirs interpreted to have occurred along strike-slip faults known to have been active during early burial of the formation. The corrosion clearly postdates early near-surface diagnesis which is largely cementation and is followed but relatively high temperature dolomite, calcite, and kaolinite precipitation. There would not be a reservoir without this burial corrosion and as a result it is important to drill wells near the faults that were the source for the diagenetic fluids. At least three factors make fault-sourced hydrothermal fluids capable of corrosion of limestone: progressive cooling of the fluids, elevated salinity, and increased CO_2 in solution. Calcite and CO_2 both have retrograde solubility so as fluids cool they become progressively undersaturated and progressively more acidic. pH generally decreases as salinity increases so hypersaline brines coming up faults should be capable of leaching limestone.

Burial corrosion of limestone and dolomite also occur in many other carbonate reservoirs. It can commonly be linked to faults (typically strike slip or transtensional faults) and might therefore be predictable in cases where good seismic data is integrated with good core and petrographic data.

Selected References

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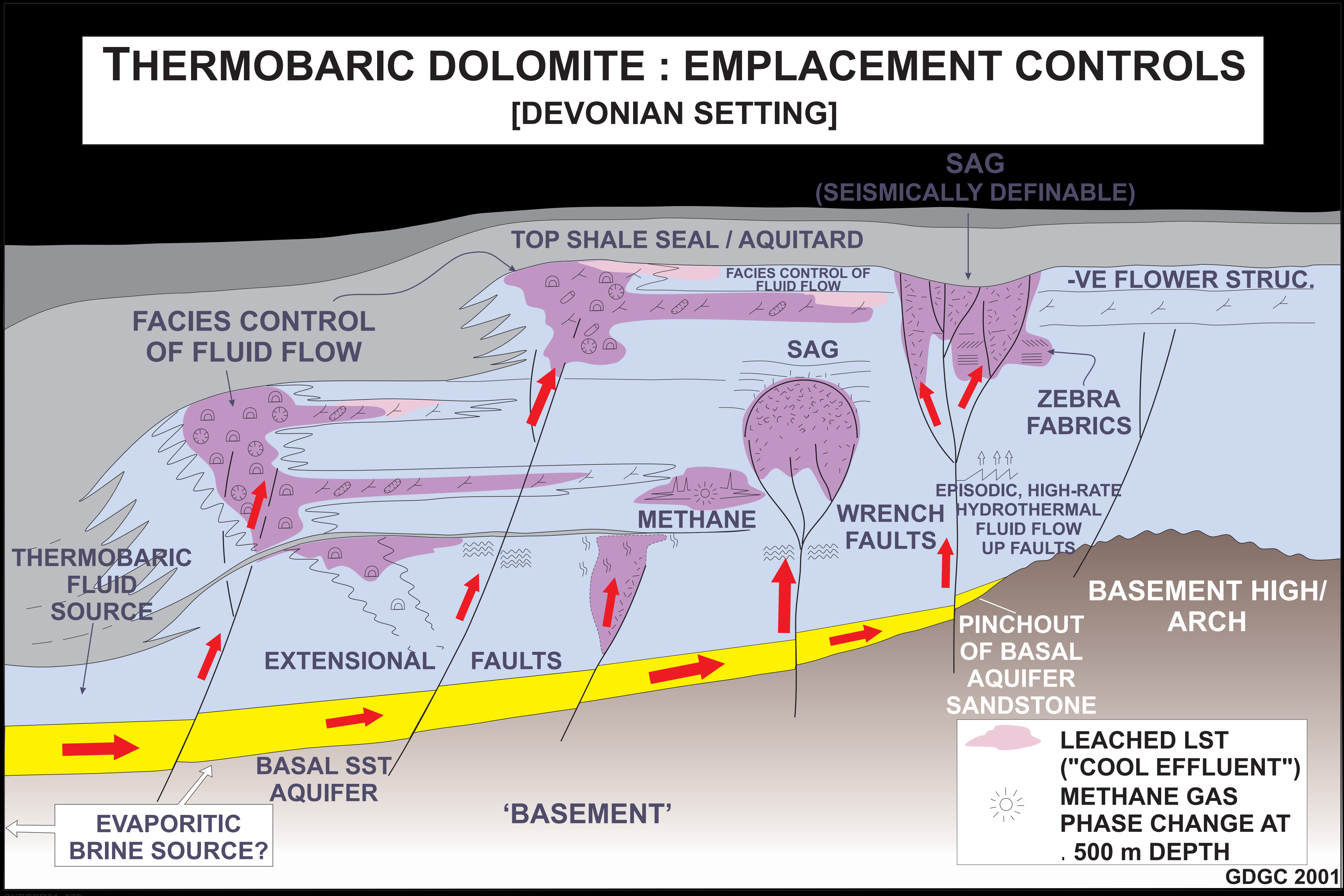
Smith Stratigraphic LLC

Introduction

- Dolomitization and leaching of carbonates take place in many different diagenetic environments
- One environment where these processes occur that has been historically underappreciated is in the fault-controlled hydrothermal realm
- This is an integrated structural-stratigraphic-diagenetic processes that require some understanding of each of these disciplines
- Some reservoirs are entirely formed by faulting and hydrothermal fluid flow while others are enhanced or degraded

The Basics of Hydrothermal Alteration Model

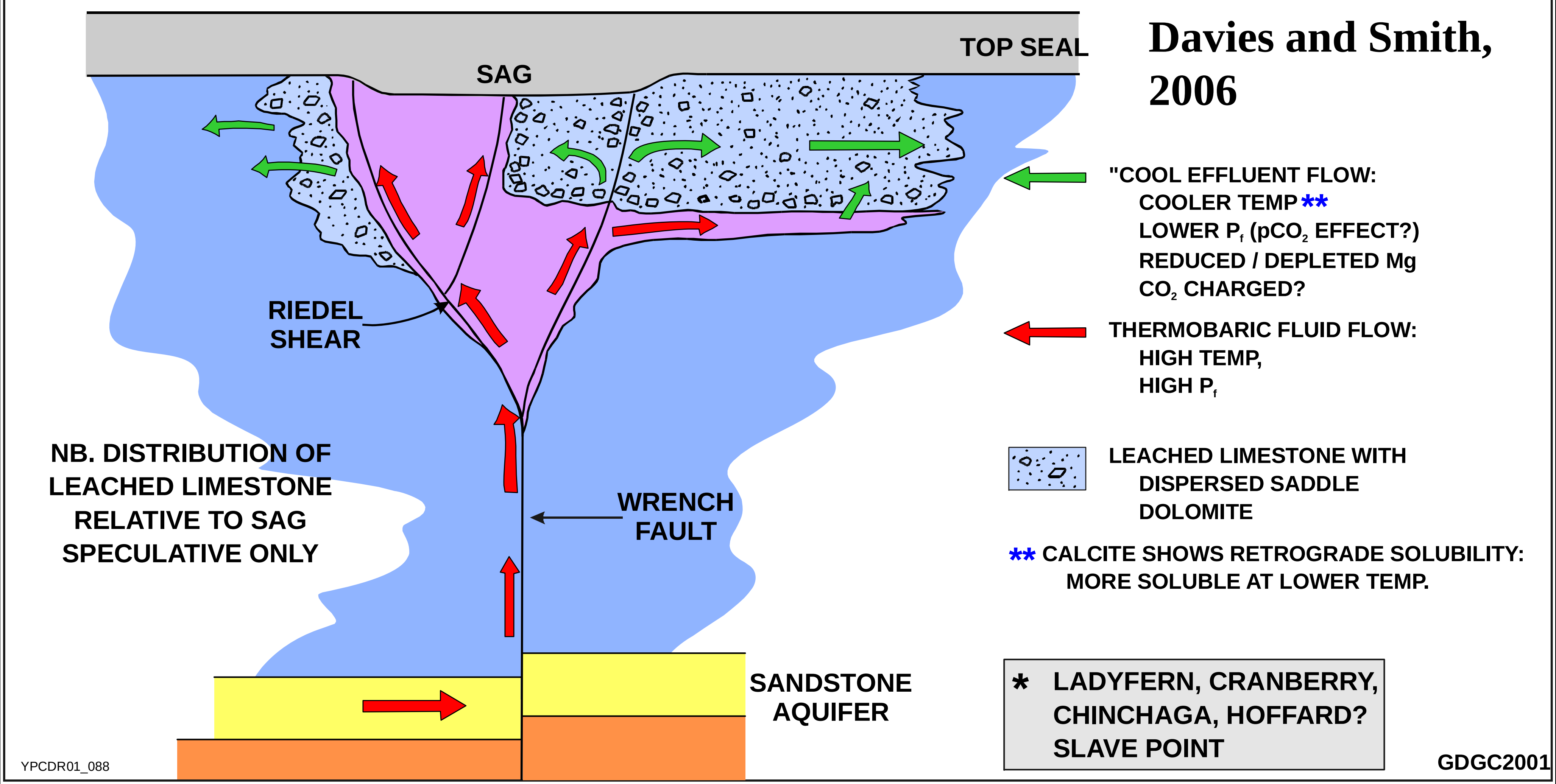
- Hydrothermal alteration occurs when fluids move up active faults and fractures and into formations
- Basement-rooted strike-slip, extensional and especially transtensional faults make best conduits
- If there is a seal or baffle (typically shale or evaporites), upward migrating fluids are forced laterally into uppermost permeable zone
- Alteration can and commonly does take place within a km of surface and probably more likely within 500m
- Fluids can change pressure, temperature, P_{CO2}, pH and salinity in formation on short time scales, all of which can trigger dissolution and precipitation of a range of minerals



Common sites of hydrothermal dolomitization and dissolution

THERMOBARIC "COOL EFFLUENT" LEACHED LIMESTONE

RESERVOIR MODEL*

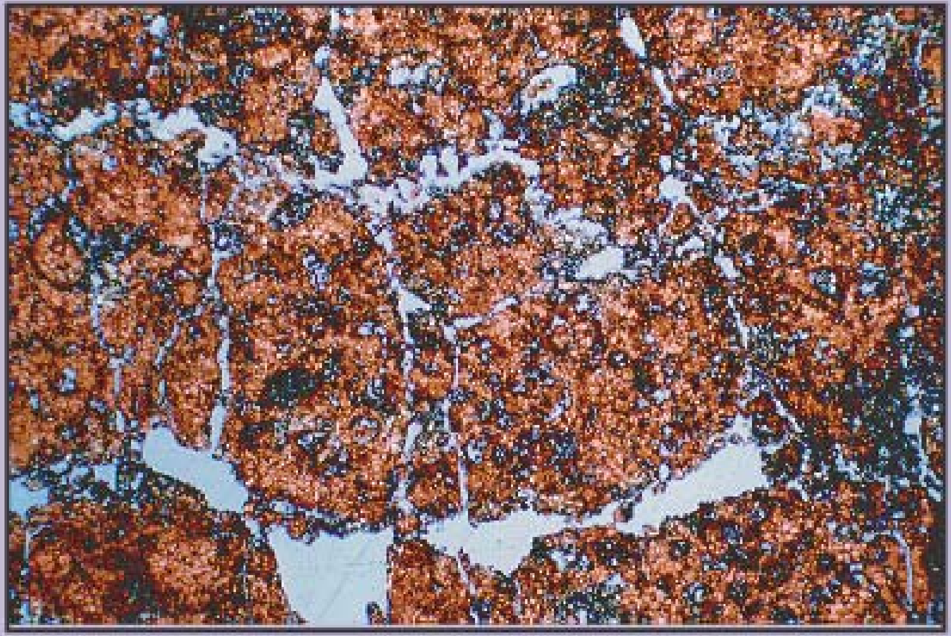


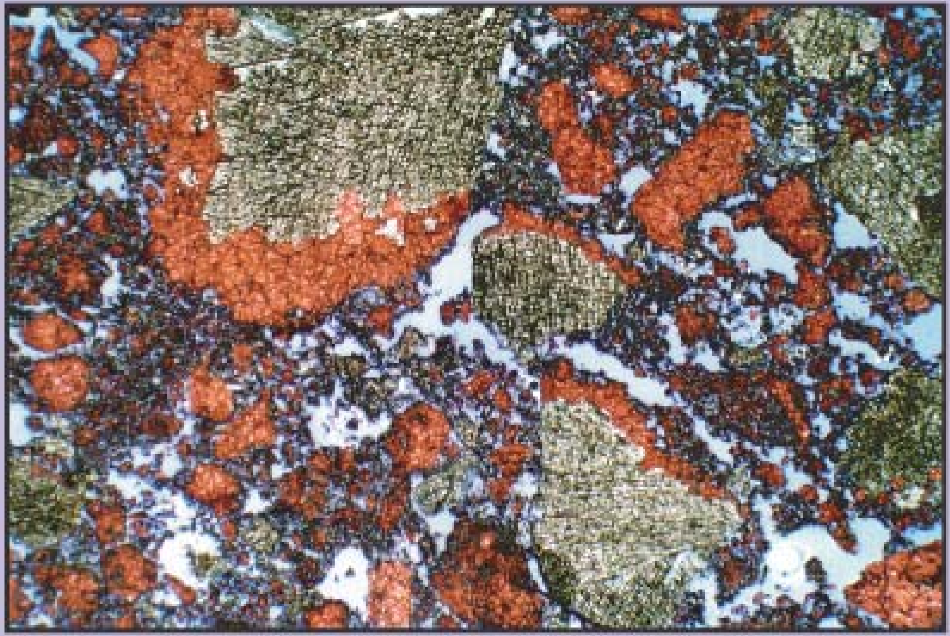
Hydrothermal mineralization and dissolution occur when high-pressure, high temperature fluids move up active faults (most commonly transtensional faults)

Examples of Slave Point Limestone alteration proximal to hydrothermal ßuid source at Ladyfern

A: Leached breccia from a heavily altered portion of the 4-26-94-13W6 core. This core represents the most complete stage of alteration of the Slave Point Limestones.
B: Photomicrograph of dissolution-enhanced fractures with biomoldic leaching of matrix from a-97-H/94-H-1.
C: Dissolution-enhanced intergranular porosity and saddle dolomite precipitation from a-97-H/94-H-1.

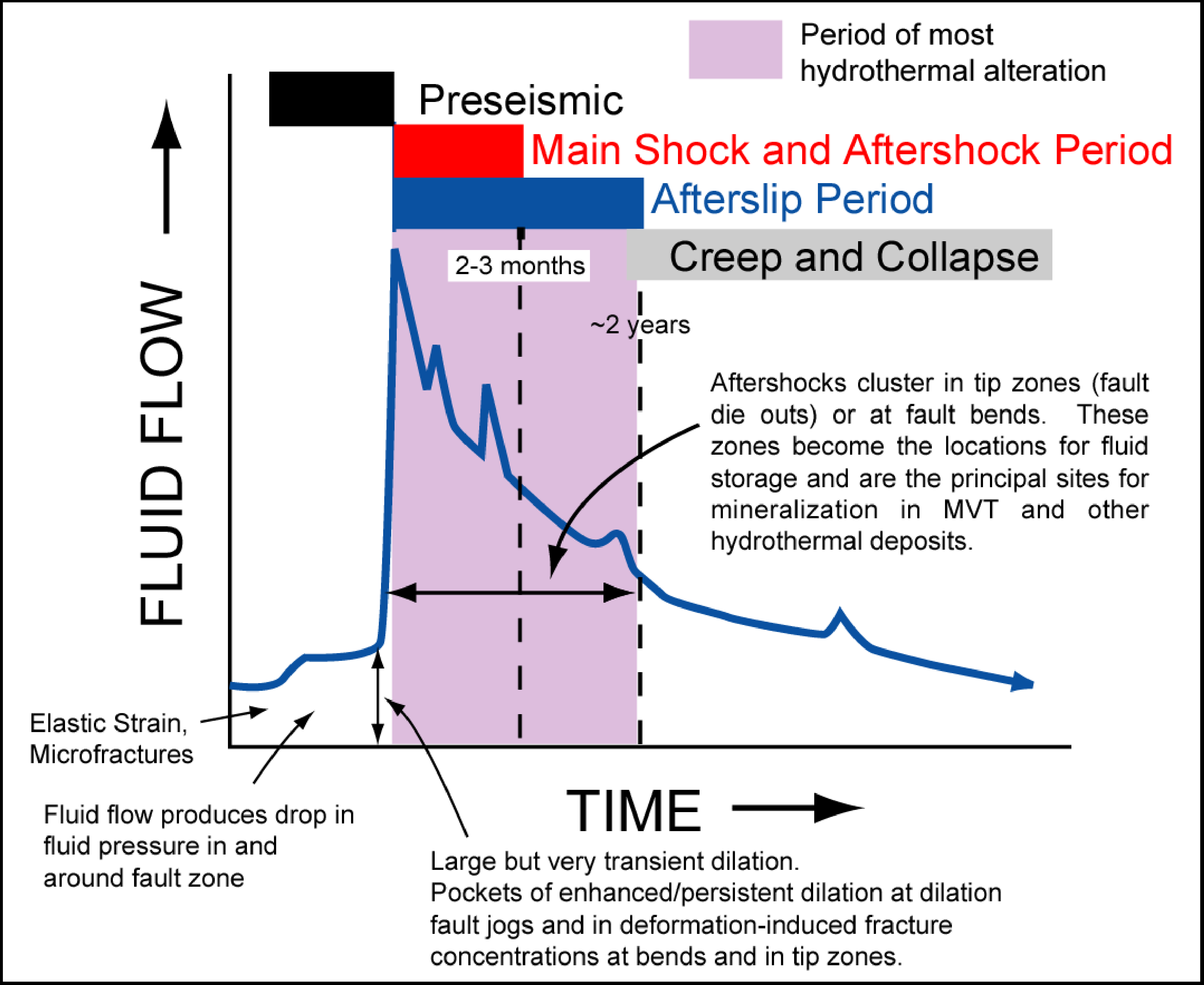
Photomicrograph magniÞcation approximately 10X. Photomicrographs courtesy of Tom Boreen.





Canadian Discovery Digest, 2002

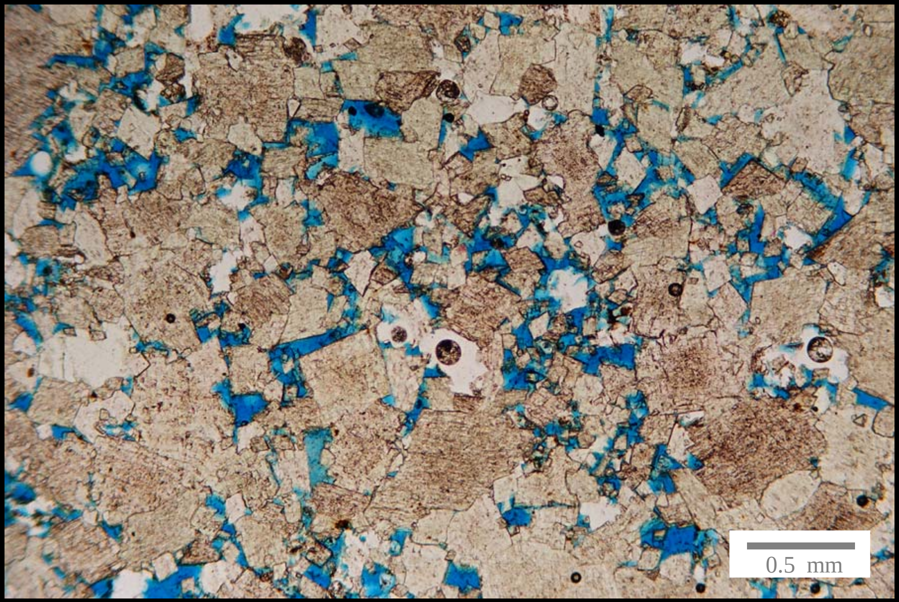
Hydrothermal leached limestone from Western Canada-Ladyfern



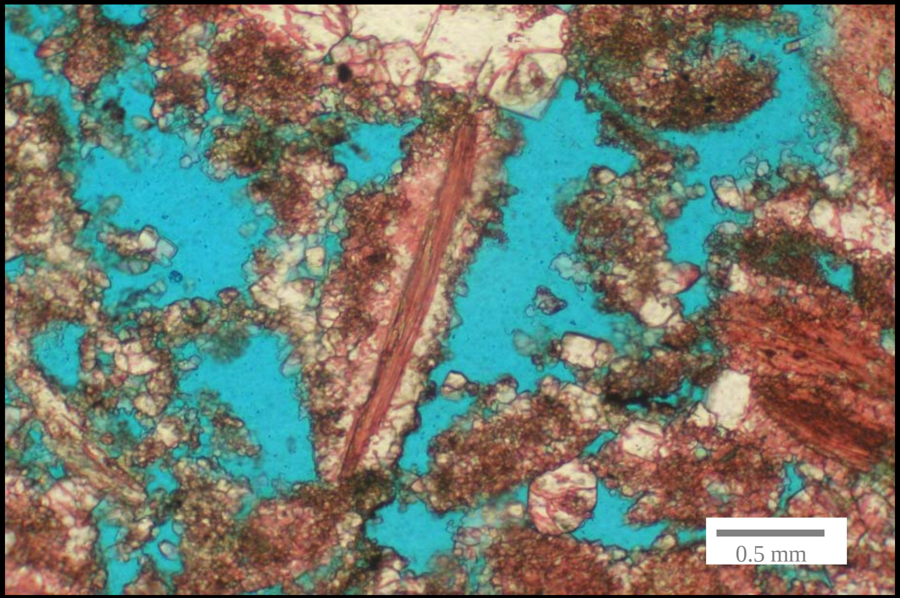
Idealized Permeability Evolution of a Fault Zone Modified from Knipe, 1993 and Davies, 2001

Some Reservoir and Pore Types Produced by Hydrothermal Alteration

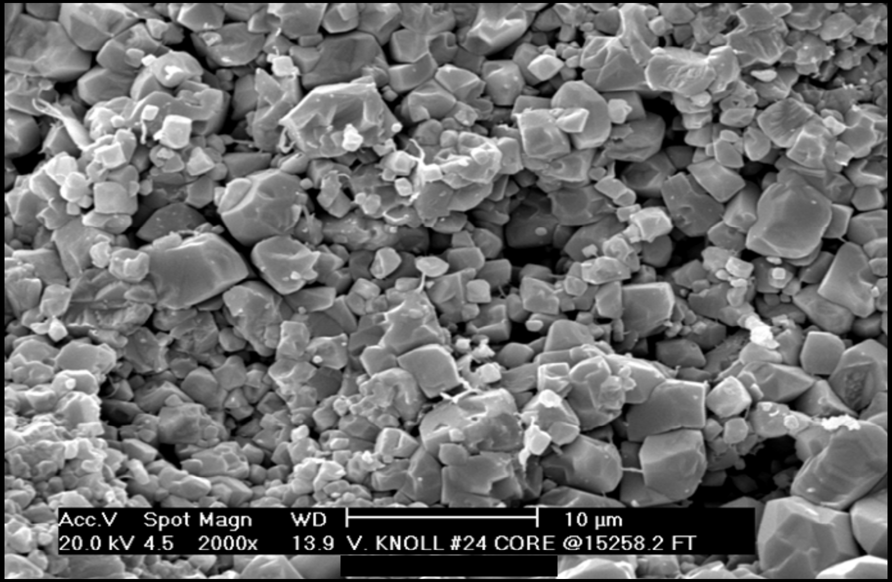
Vugs, Breccias, Fractures



Matrix dolomite



Leached limestone

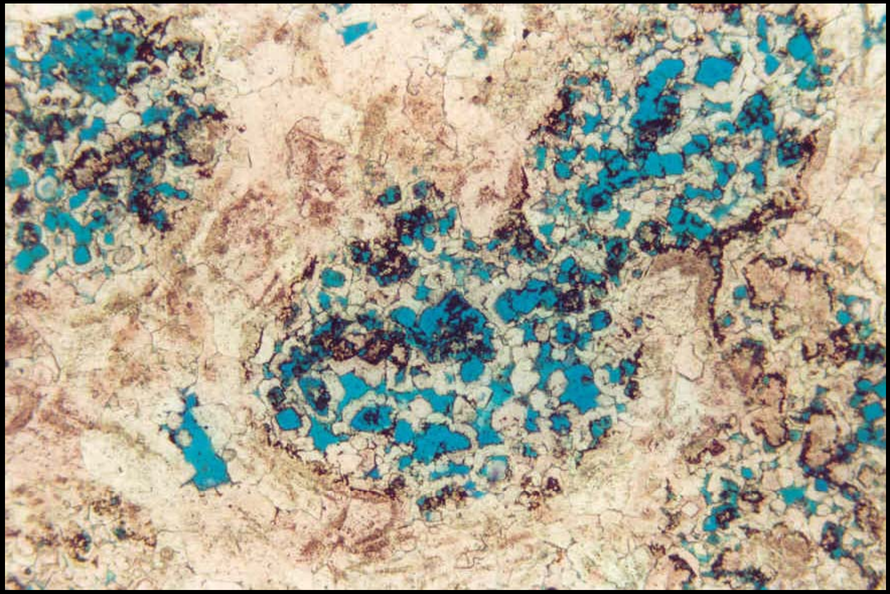


Microporosity

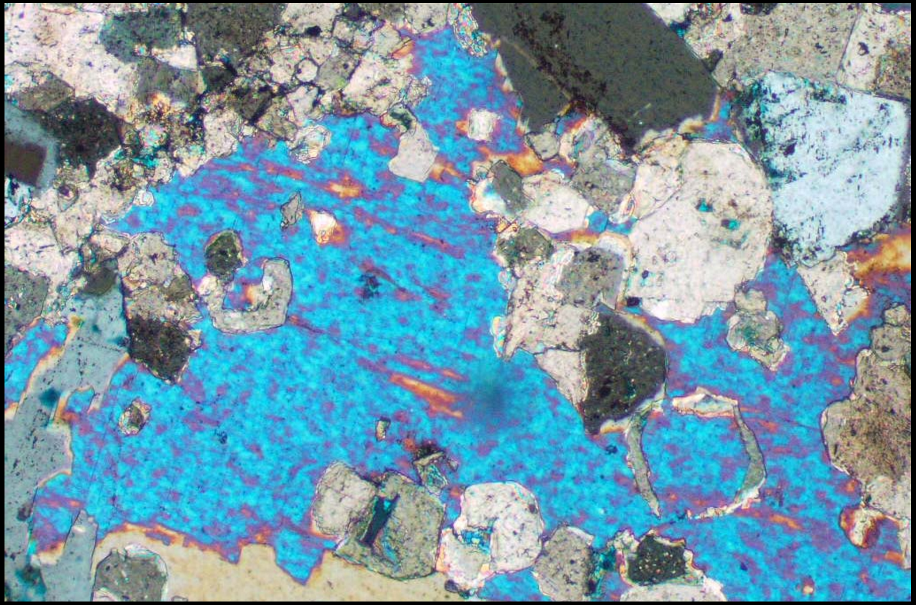
Some Indicators of Hydrothermal Alteration

Saddle dolomite cemented breccias

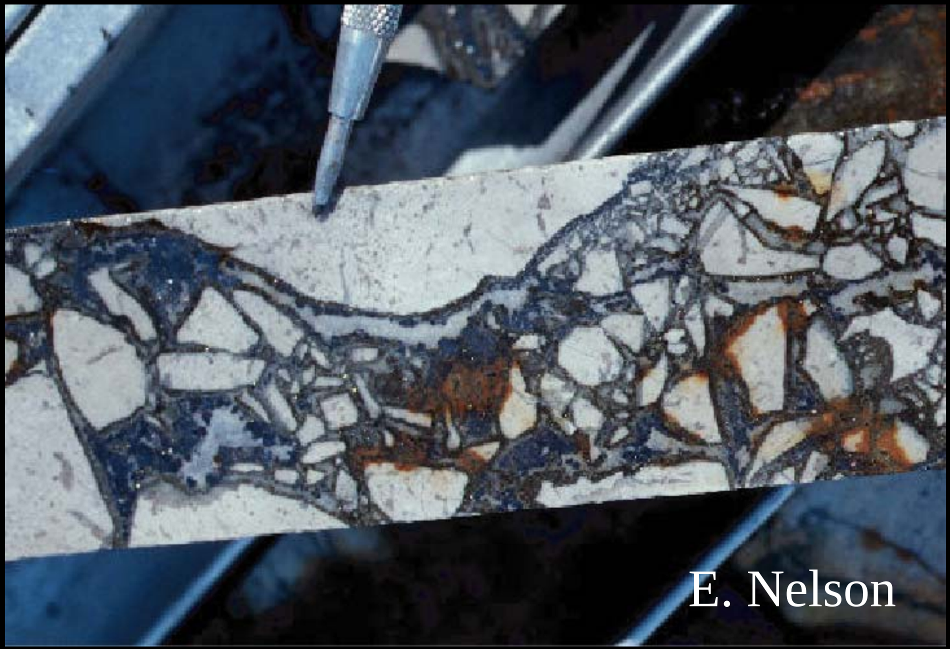
Zebra and boxwork fabrics



Leached dolomite



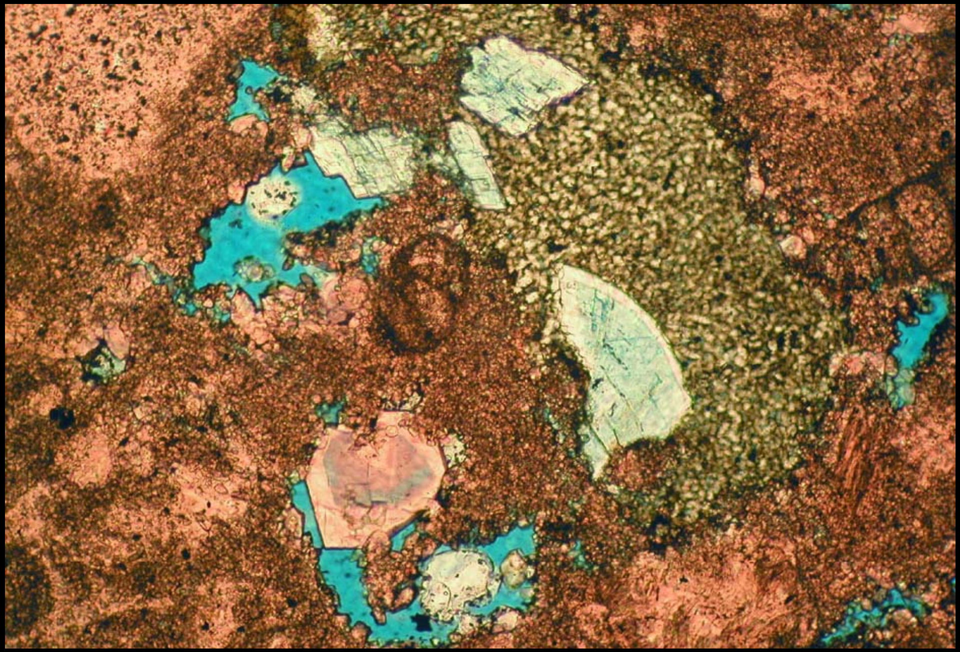
Anhydrite and other sulfates



Sulfides

Calcite and Bitumen

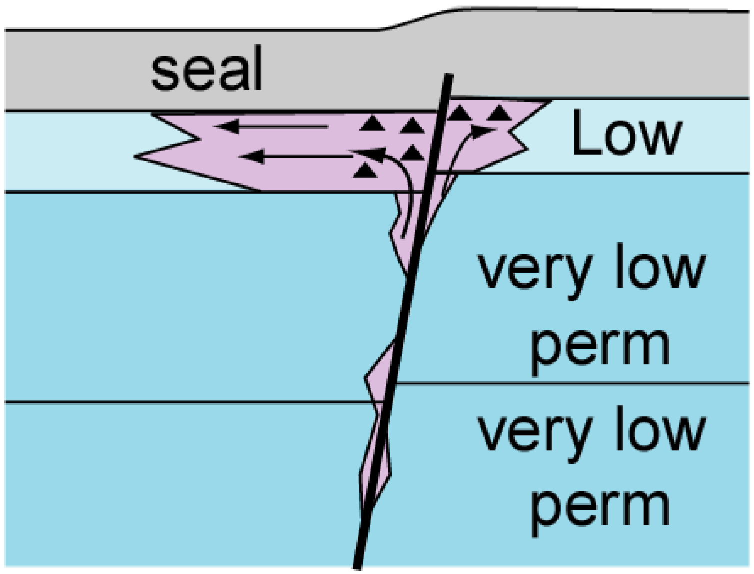
Chert and chalcedony



Kaolinite and other authigenic clays

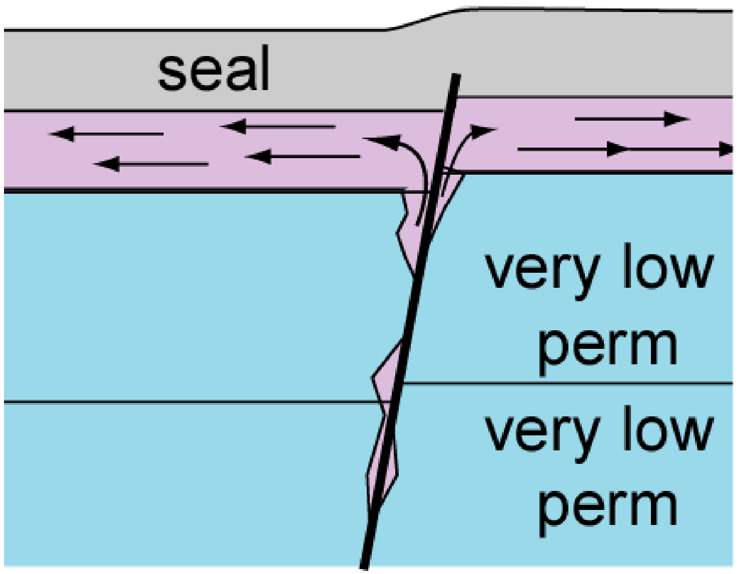
Facies Control on Extent of Alteration

Low to Moderate Original Perm



Only dolomitized around faults
Breccias and fractures common.
More alteration on down-thrown side.

High Original Perm

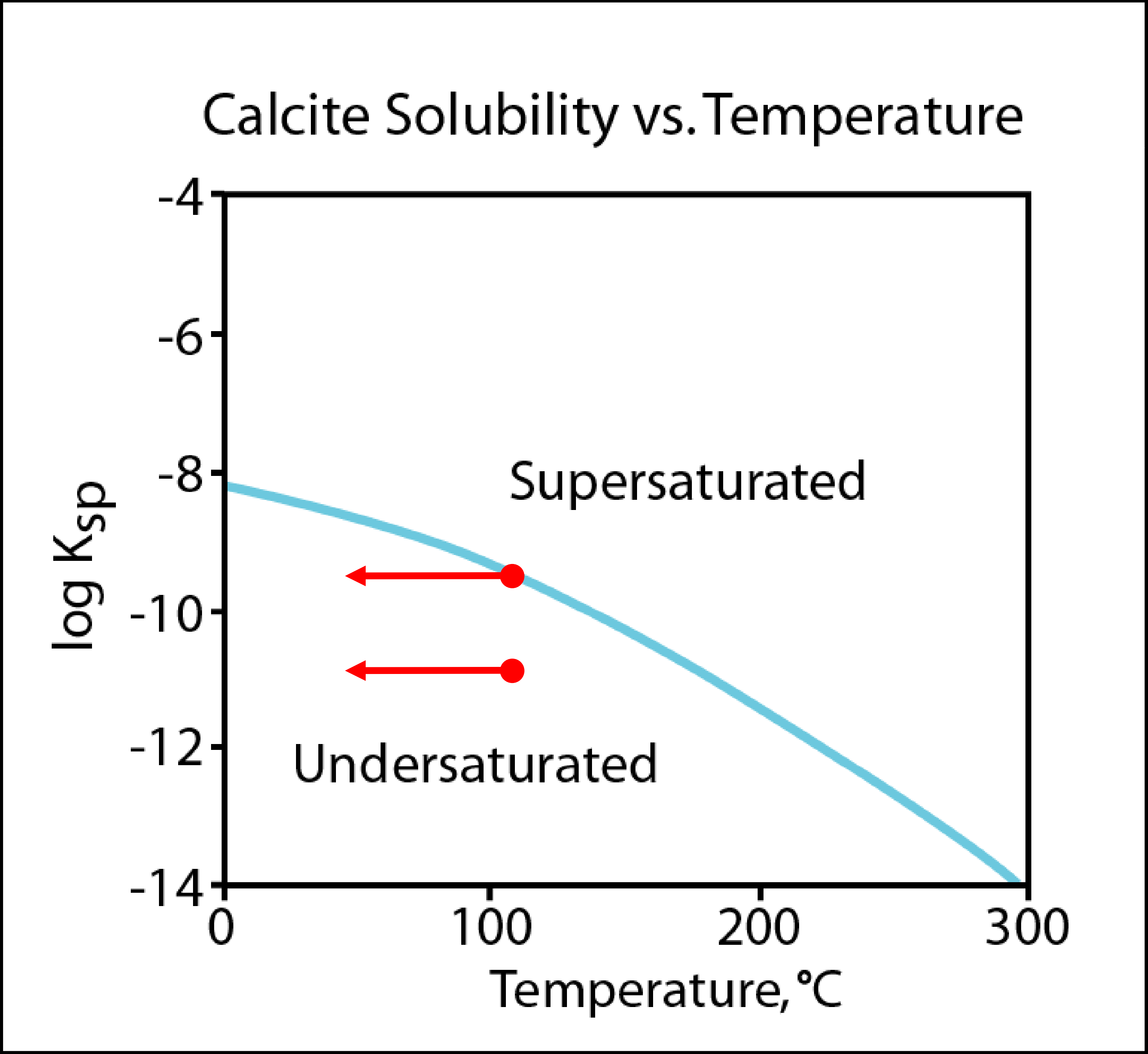


Strata are pervasively altered far from faults and leached limestone is more likely

Formations that are high-perm throughout may show few obvious signs of hydrothermal alteration

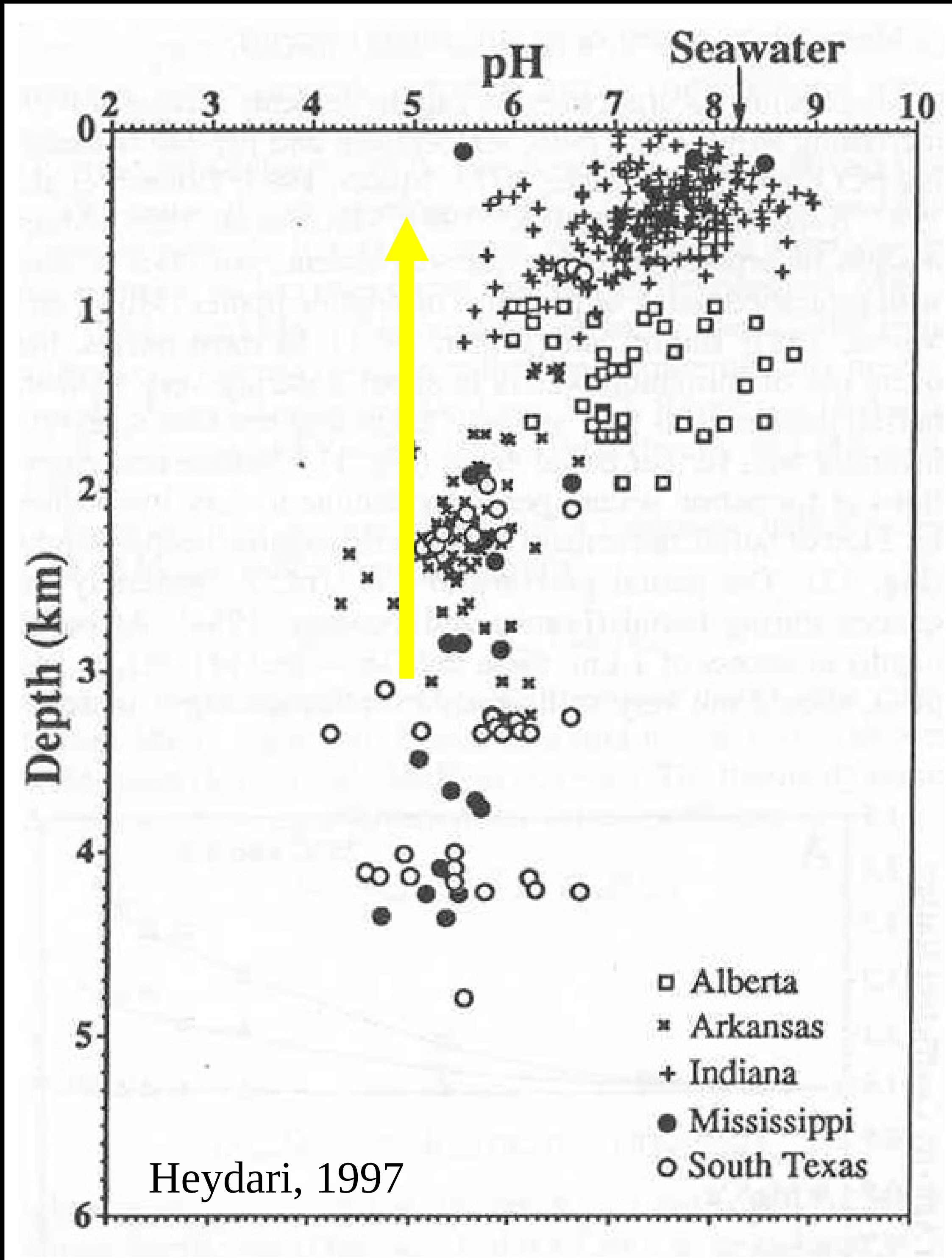
Fault-Related Hydrothermal Leaching Mechanisms

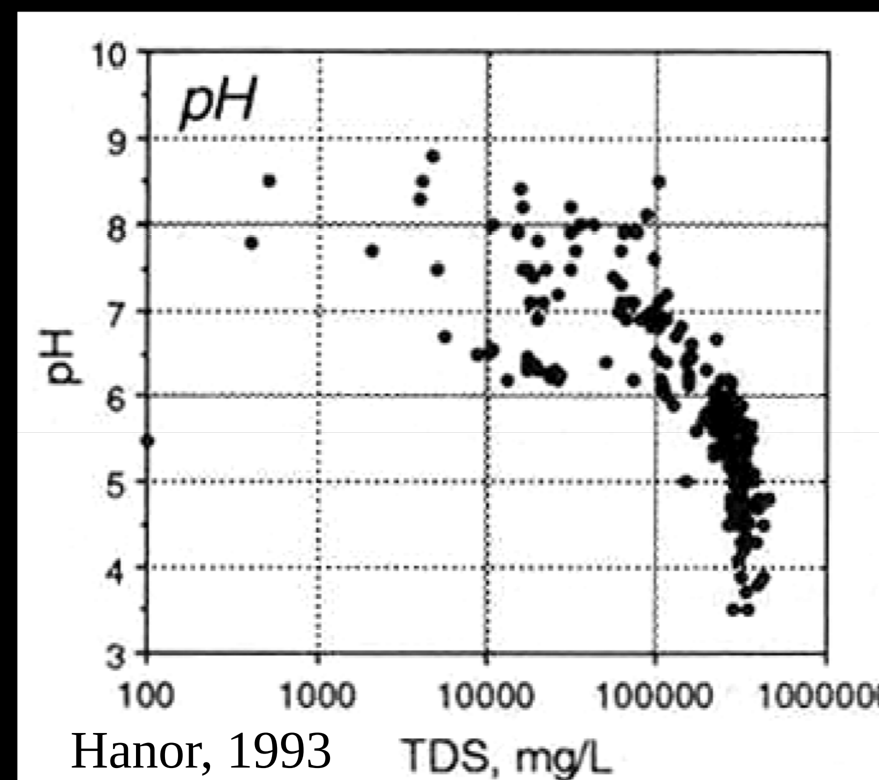
- Cooling hydrothermal fluids – both calcite and CO_2 have retrograde solubility
  - As fluids cool, they can hold progressively more calcite in solution
  - As fluids cool, any CO_2 in vapor form will go into solution, dropping the pH and making fluids more aggressive
- Salinity increases and pH commonly decreases with depth – if more acidic brines flow up faults, will be lower pH than *in situ* fluids and capable of leaching
- H2S moves up faults and gets oxidized creating sulfuric acid which has potential to leach limestone and dolomite



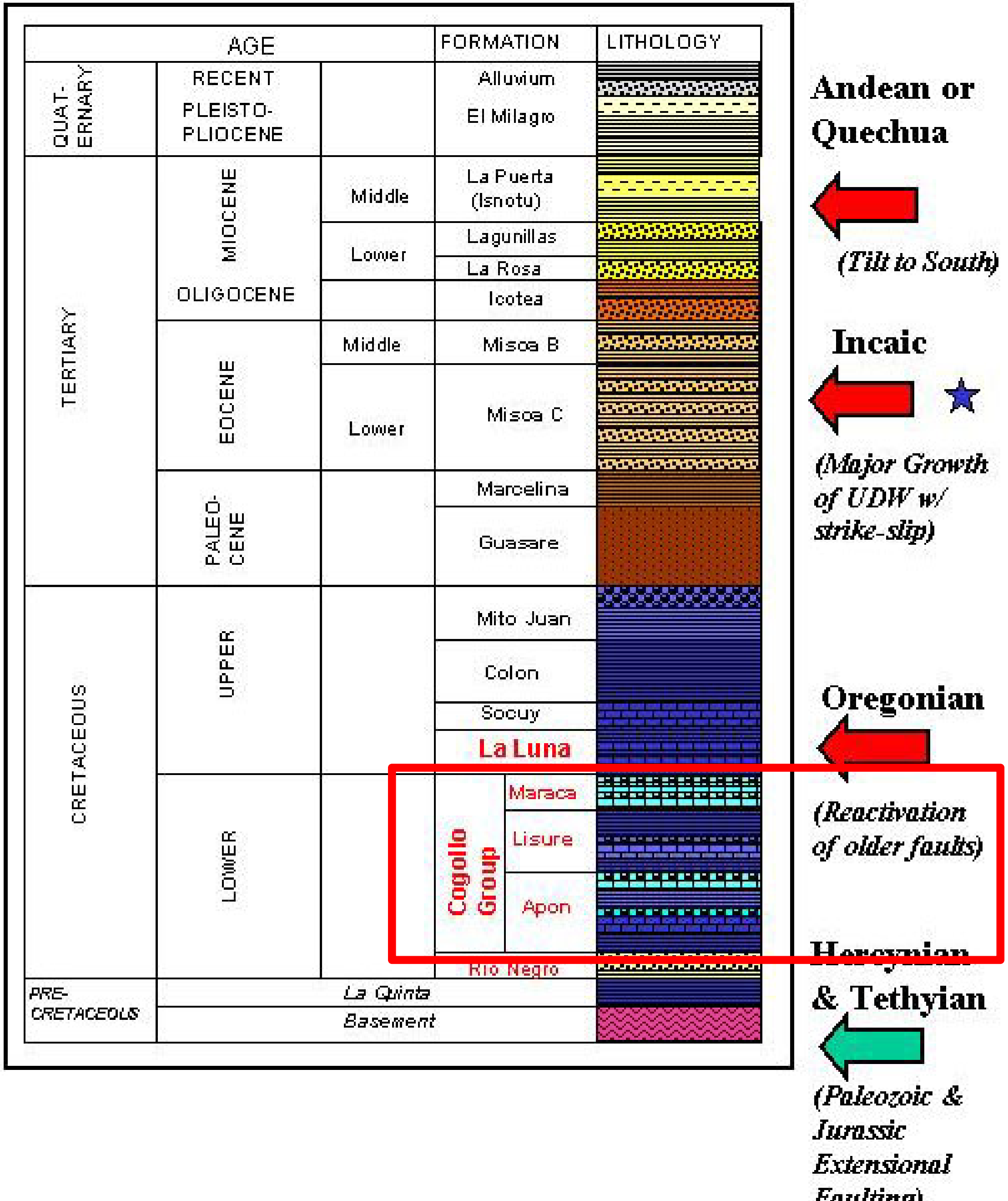
Leaching of $CaCO_3$ can occur simply due to cooling fault-derived fluid (modified from Rimstidt, 1997)

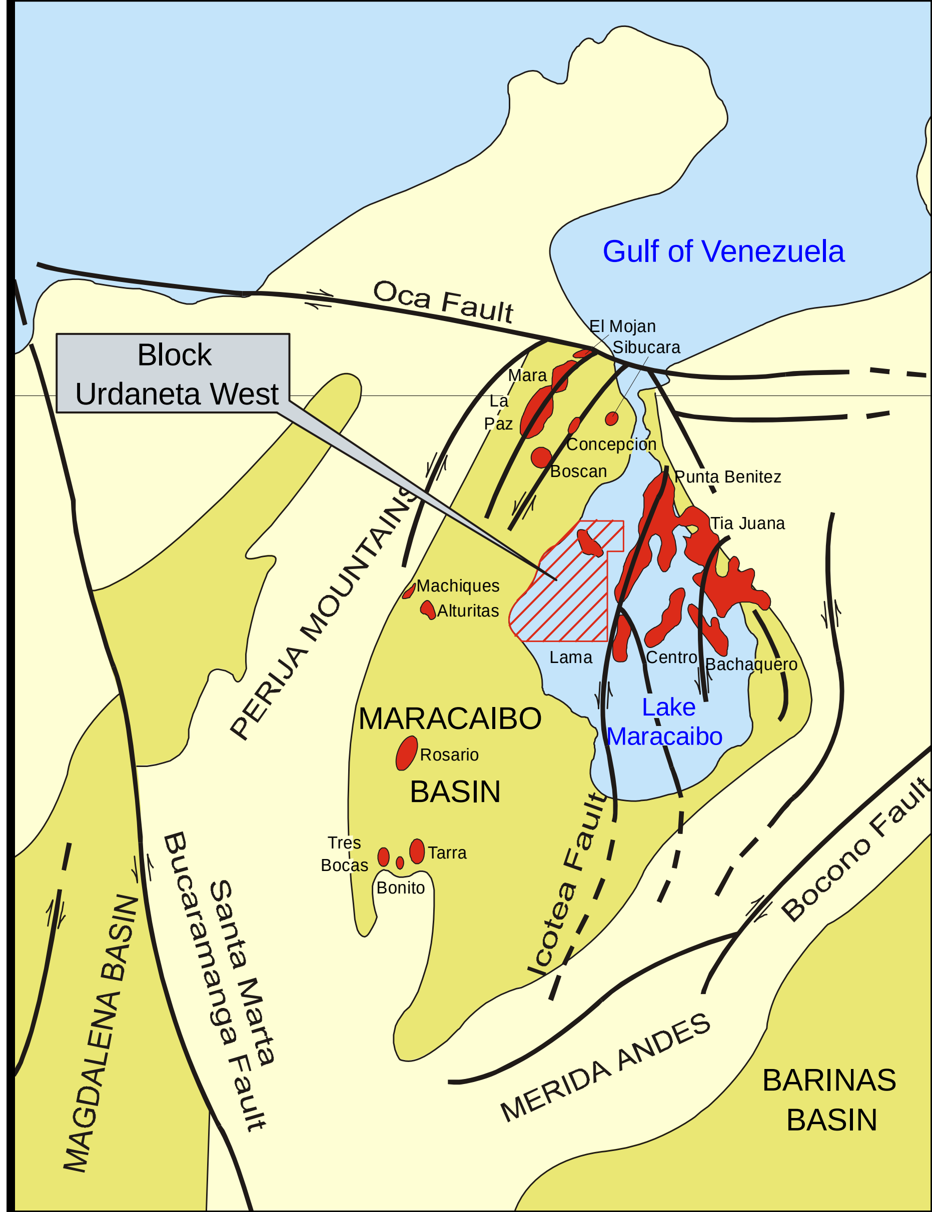
Fluids flowing up faults should have higher salinity and lower pH than fluids higher in the section – this could promote leaching





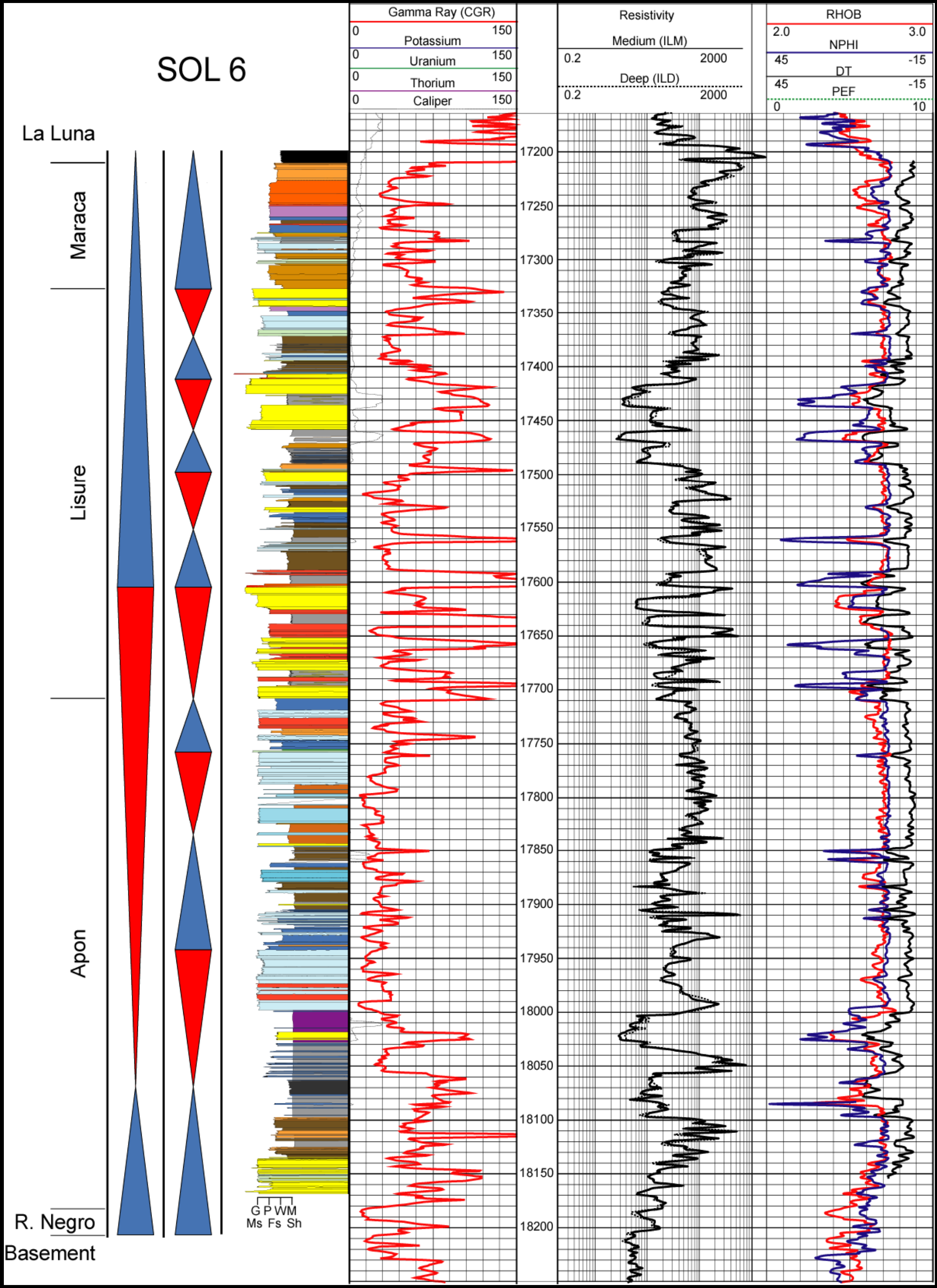
Stratigraphic Column with Tectonic Events at Urdaneta West

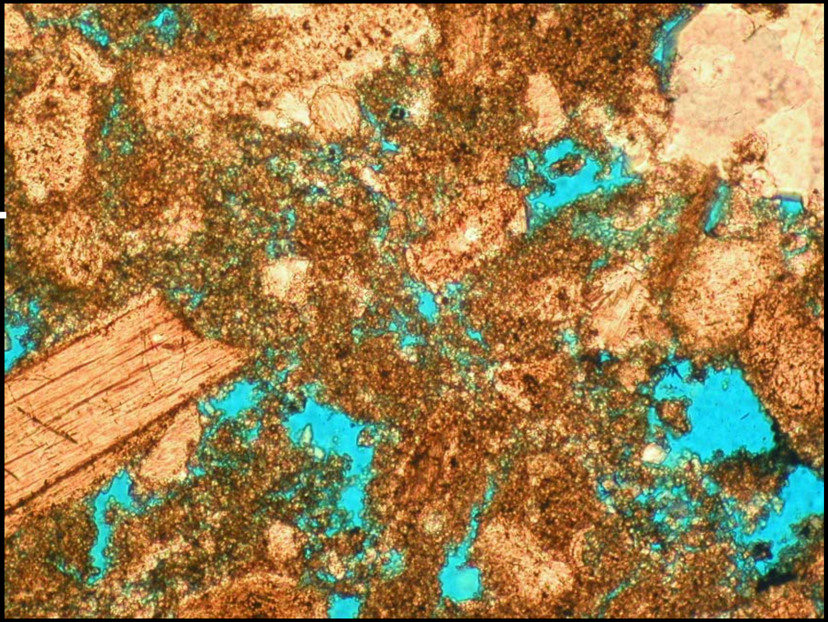




Cogollo Group, Venezuela
>1billion barrels in place in Urdaneta West

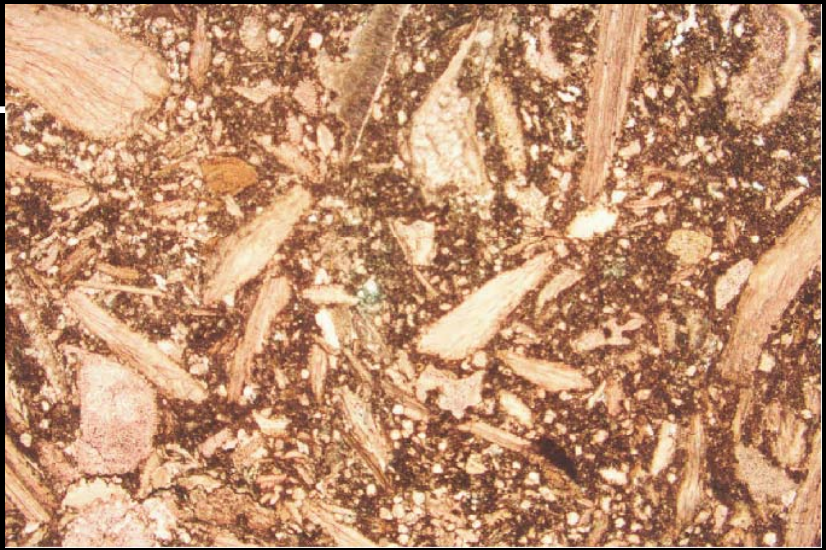
Thanks to Shell Venezuela





Leached limestone with microporosity

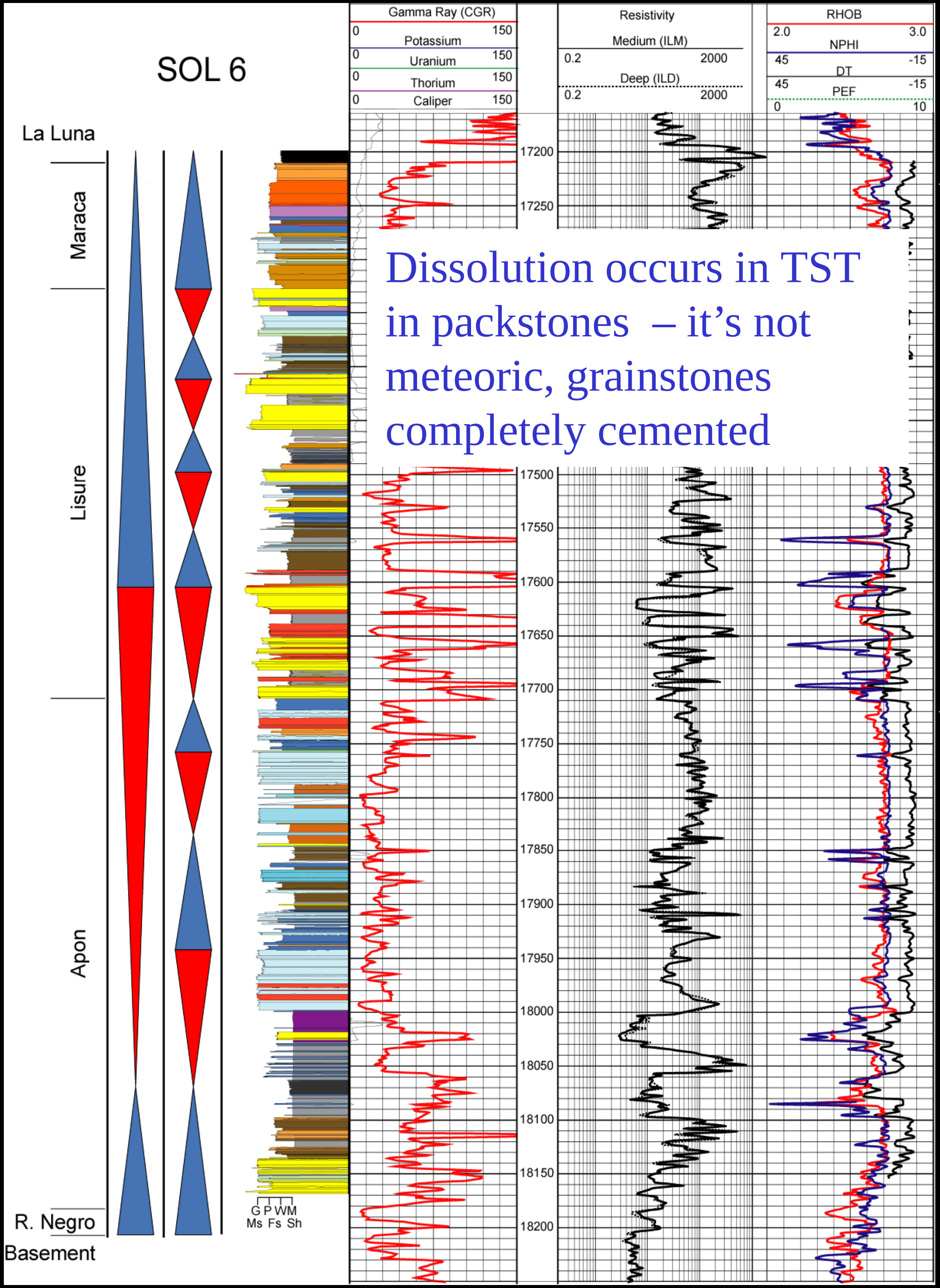
0.5 mm



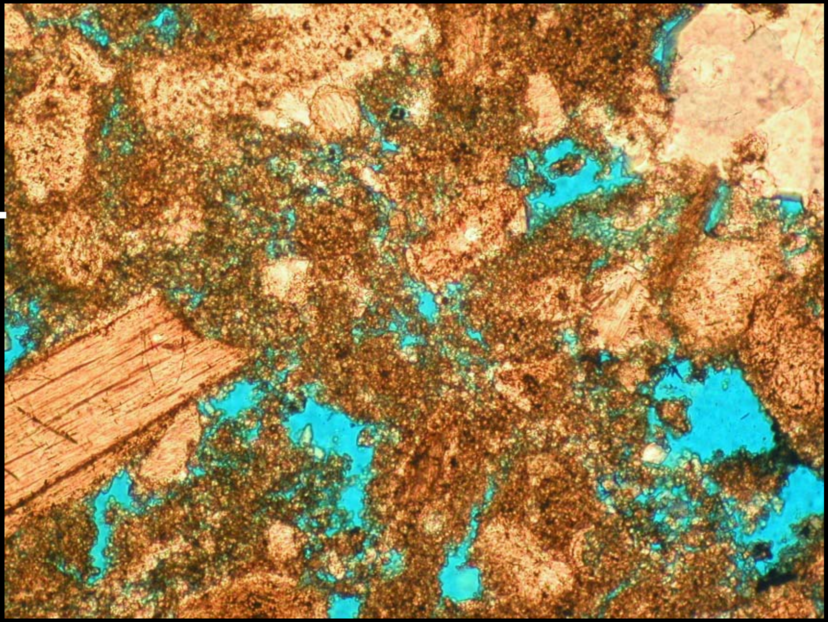
Unleached limestone with no microporosity

1 mm

Most leached limestone reservoirs are only microporous in and around where they are leached



Dissolution occurs in TST in packstones – it's not meteoric, grainstones completely cemented



Leached limestone with microporosity

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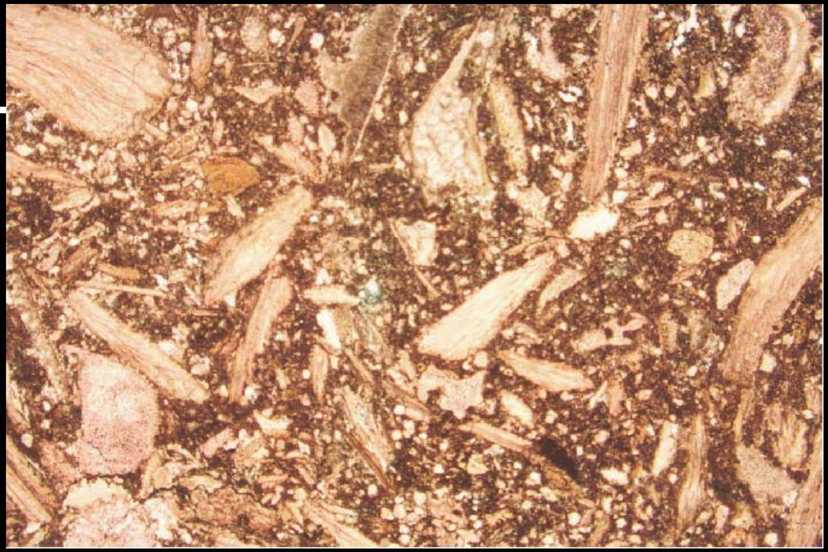

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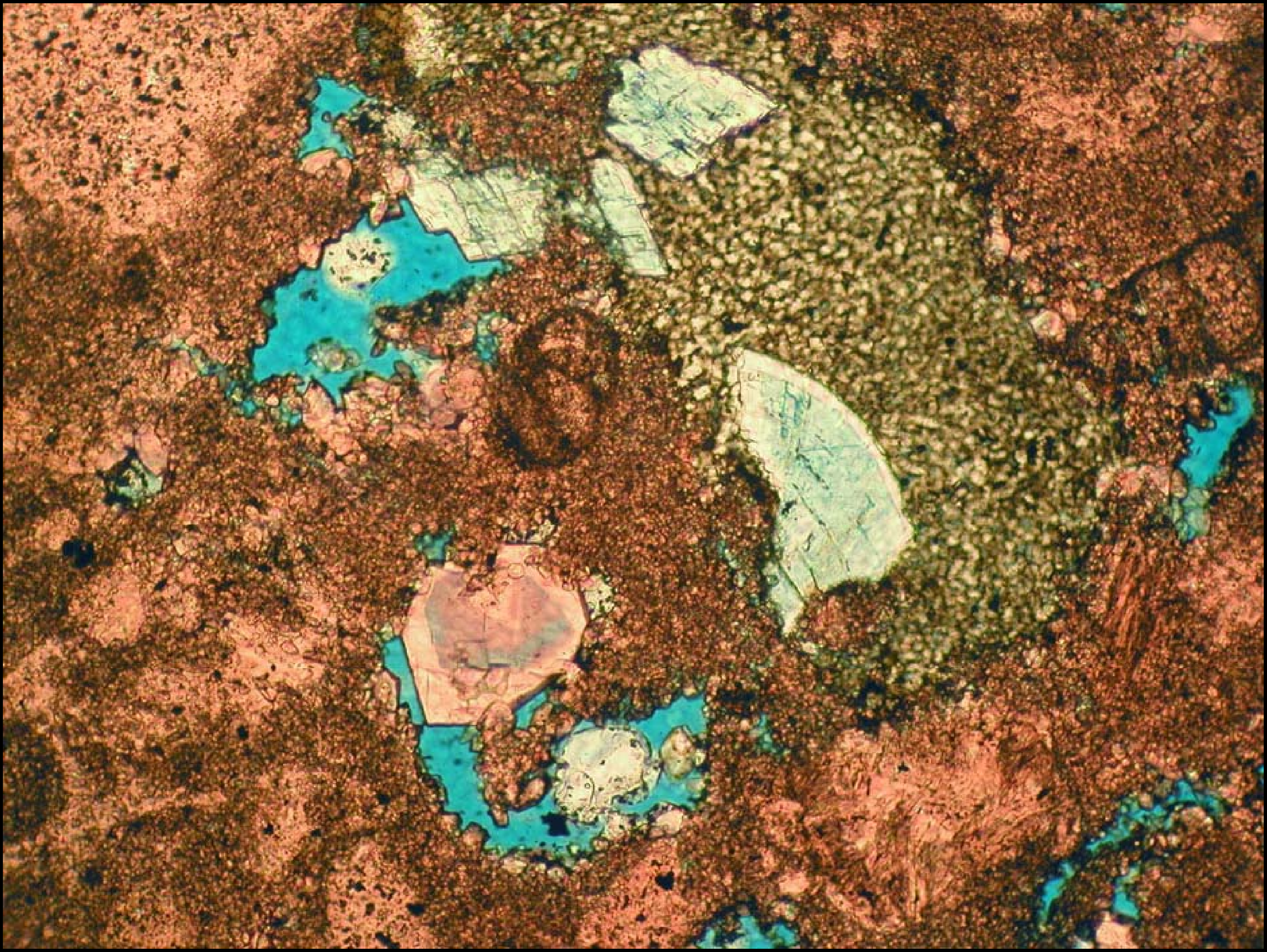
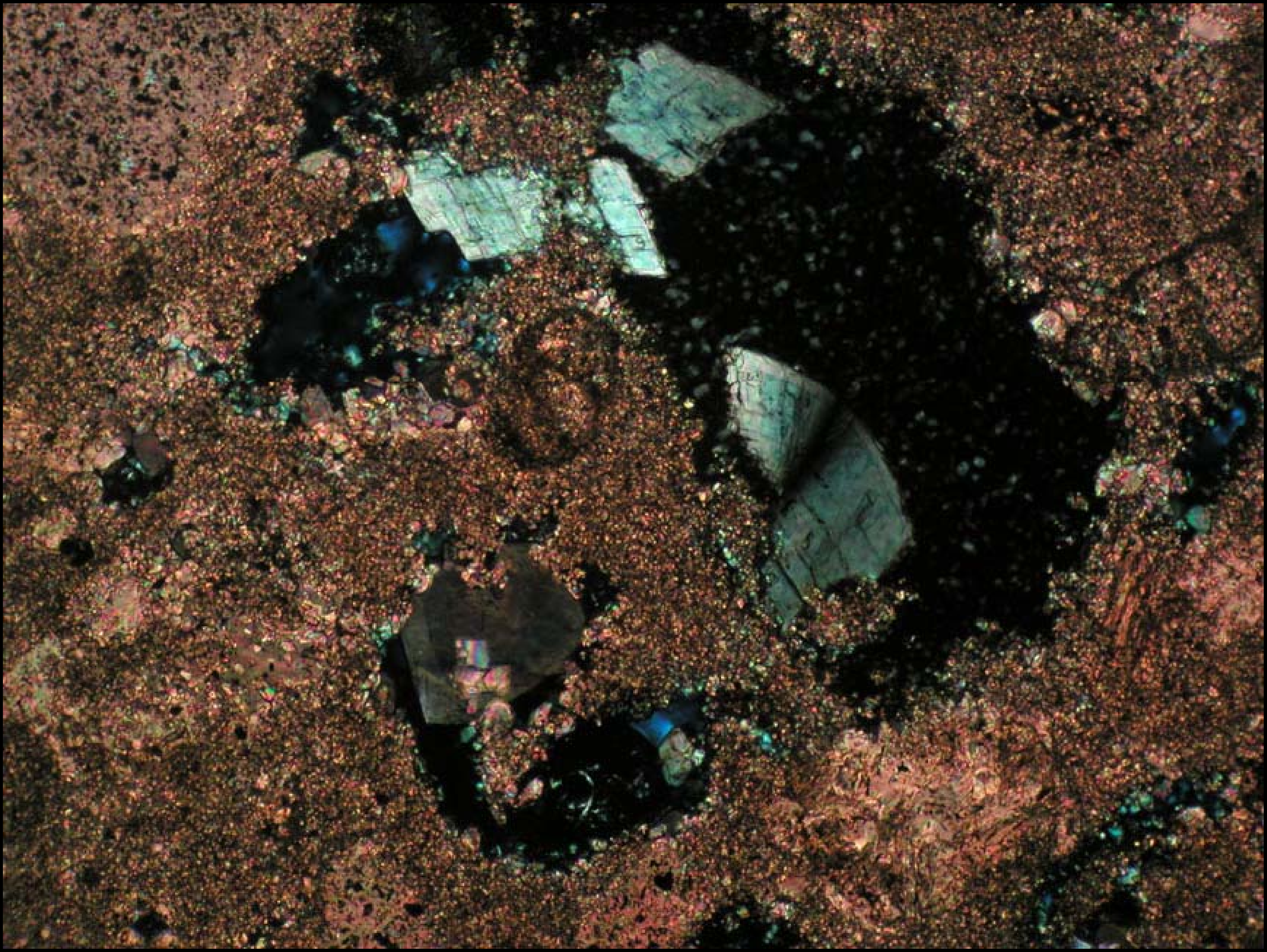


0.25 mm

SOL 6 17240 Dissolution followed by saddle dolomite and kaolinite (dickite?) in oyster packstone of Maraca



0.25 mm

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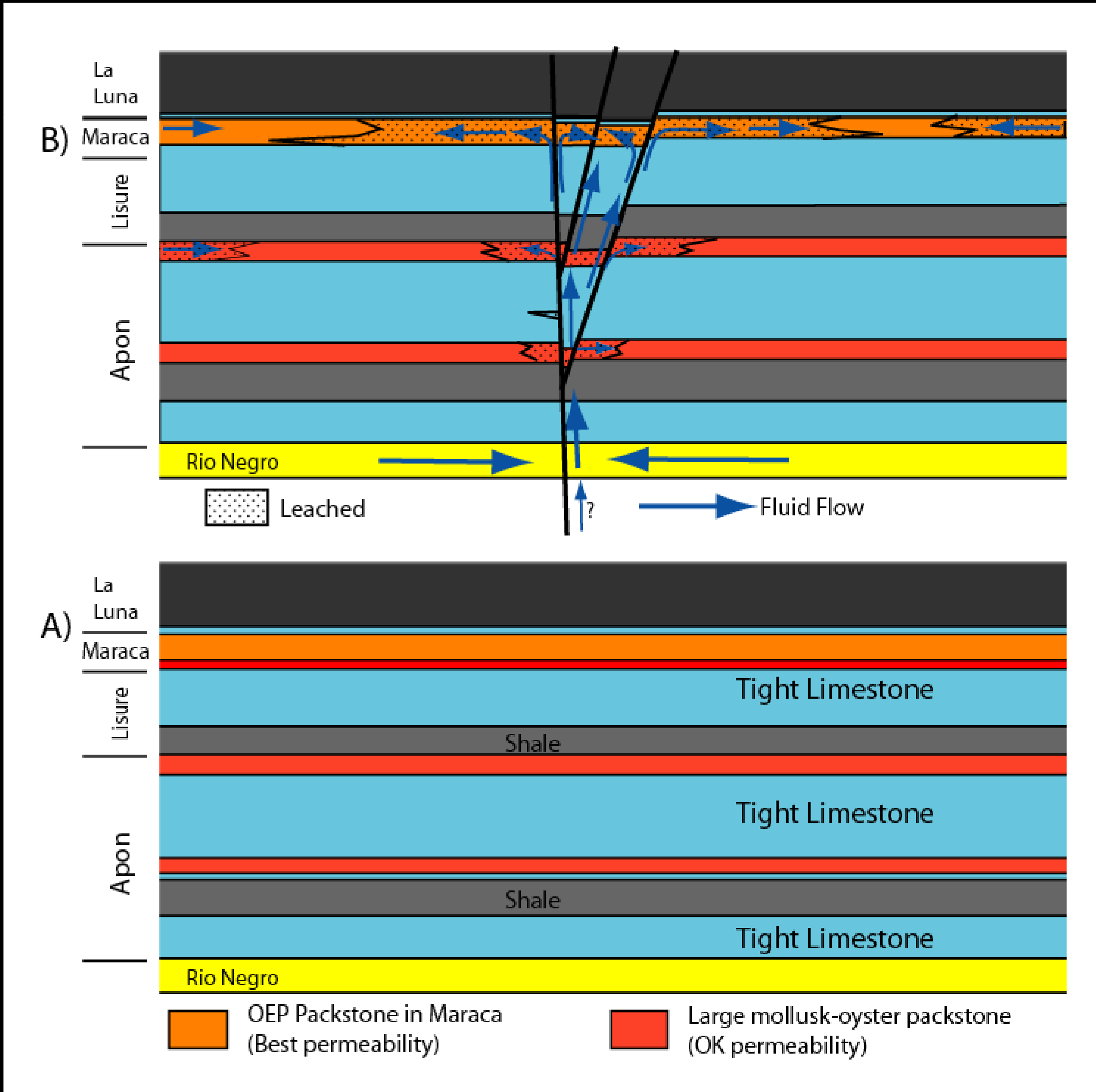
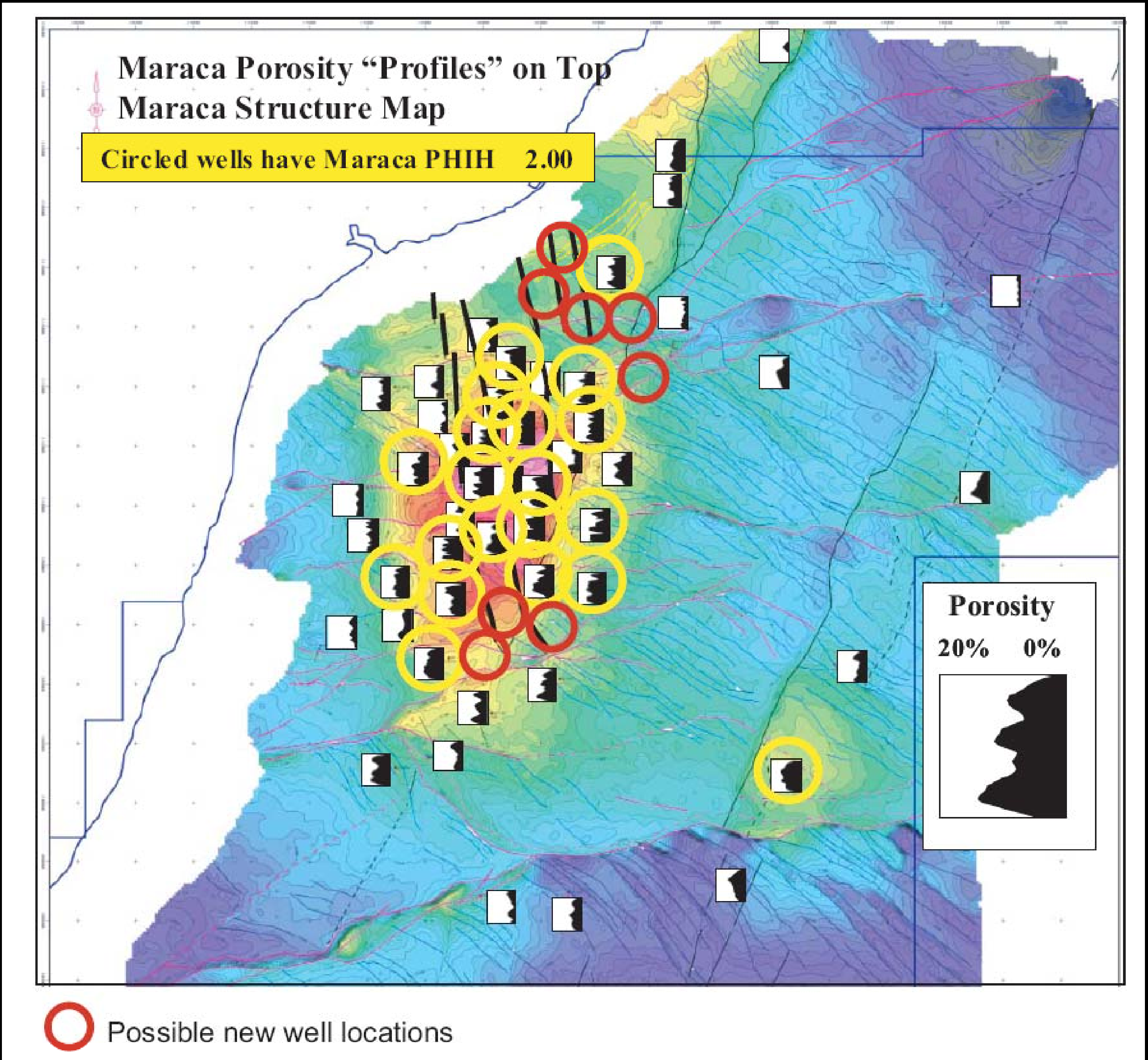
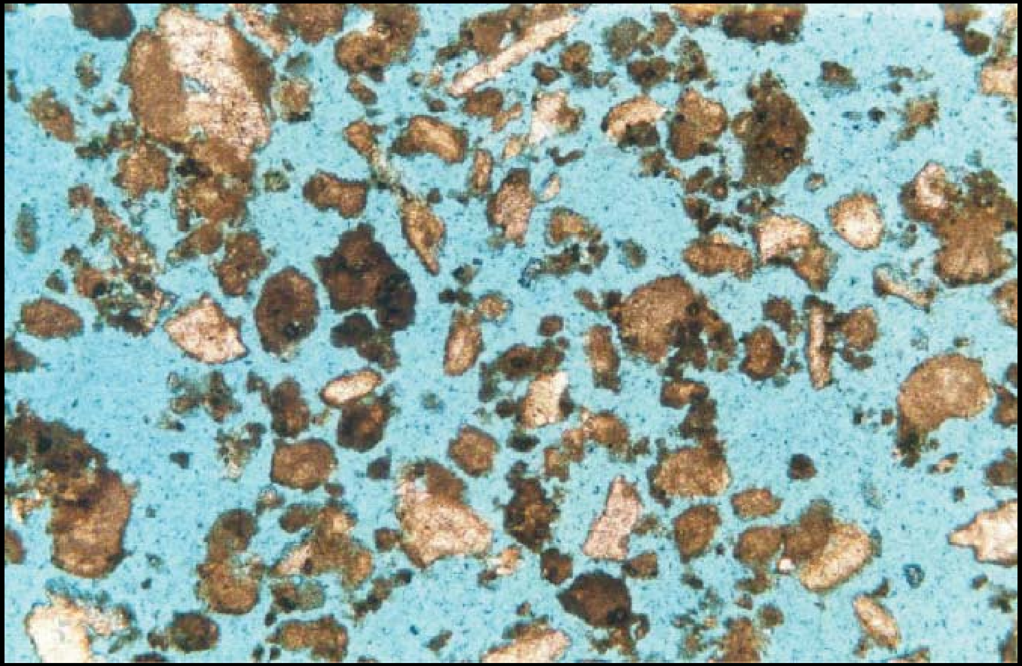


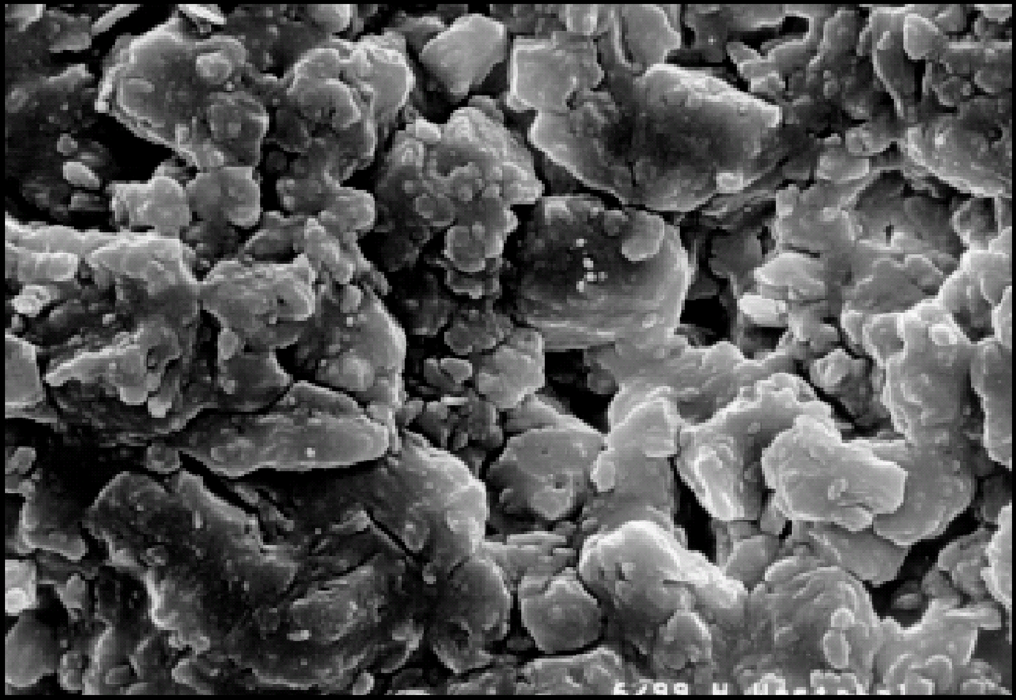
Leaching occurred in facies with best remaining perm at time of alteration

Leaching by cooling hydrothermal fluids that may have been CO_2 charged



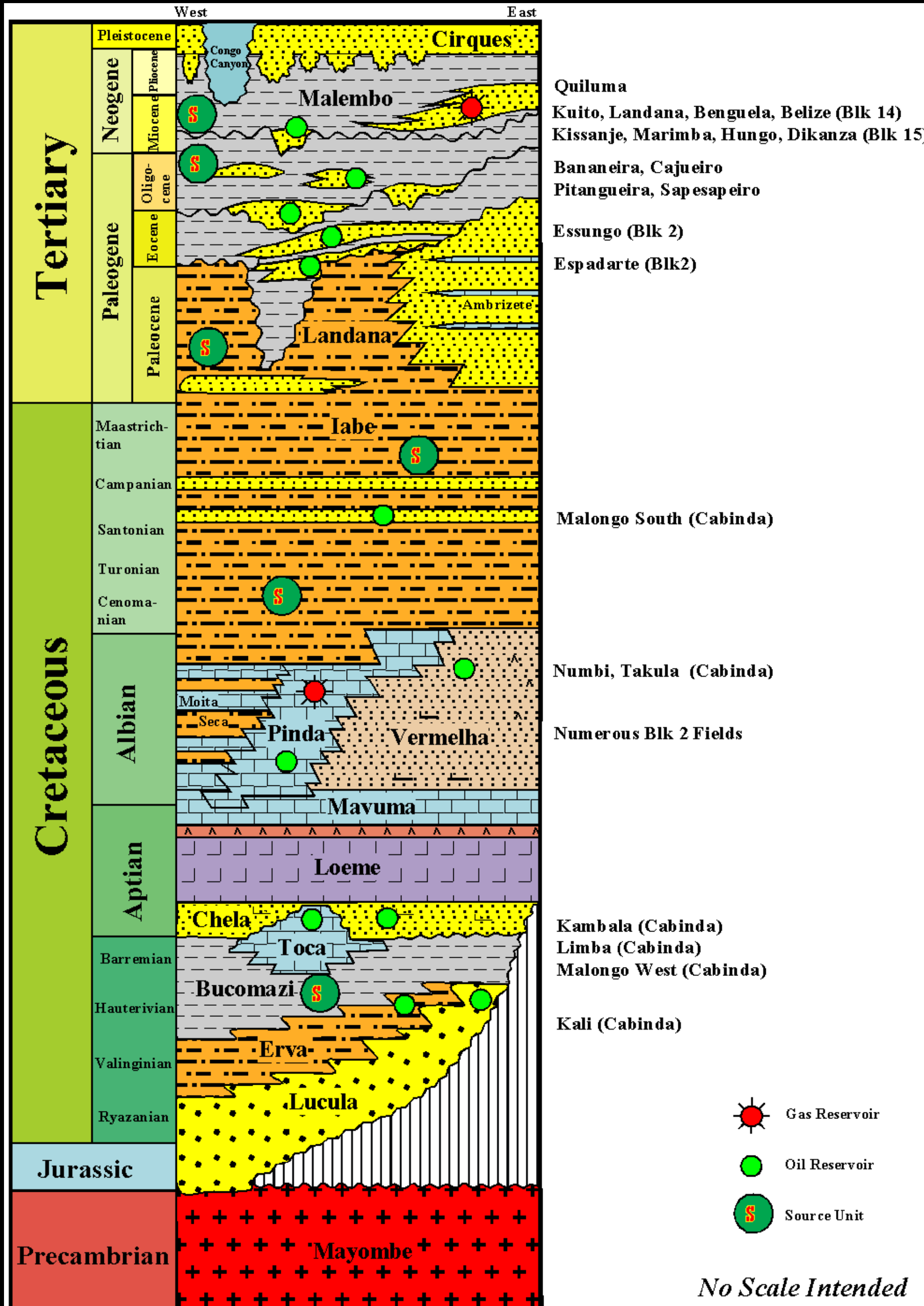
Well locations proposed based on proximity to faults thought to be conduits for leaching fluids

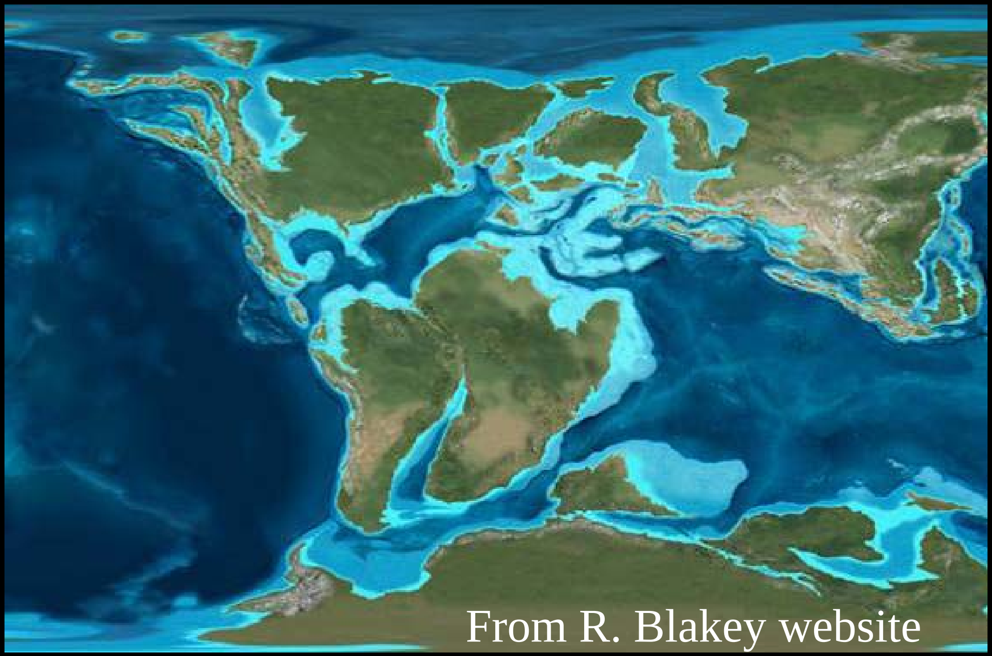




Leached Limestone from the Natih E reservoir at Al Ghubar Field, Oman

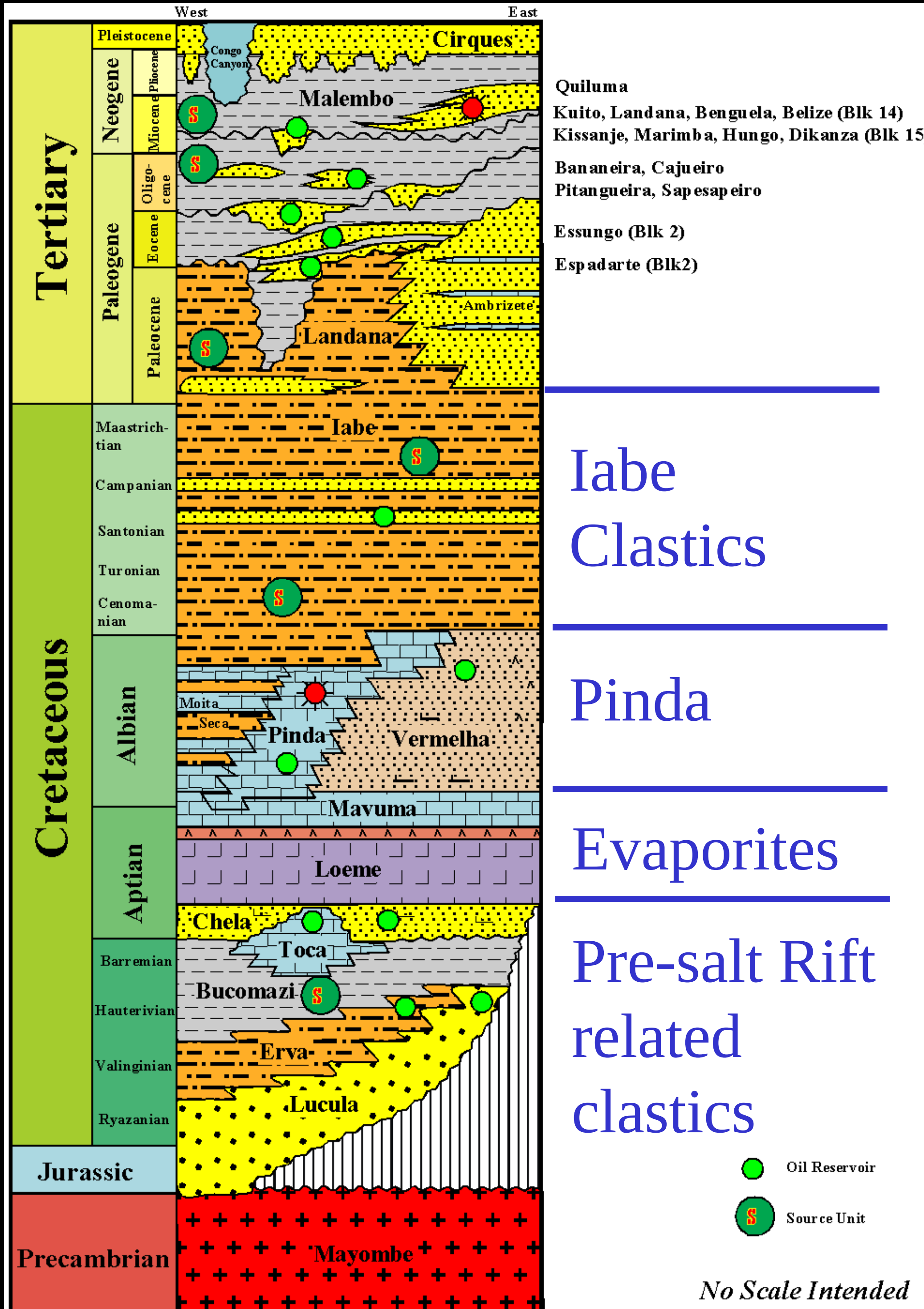
Porosity over 40% in some intervals

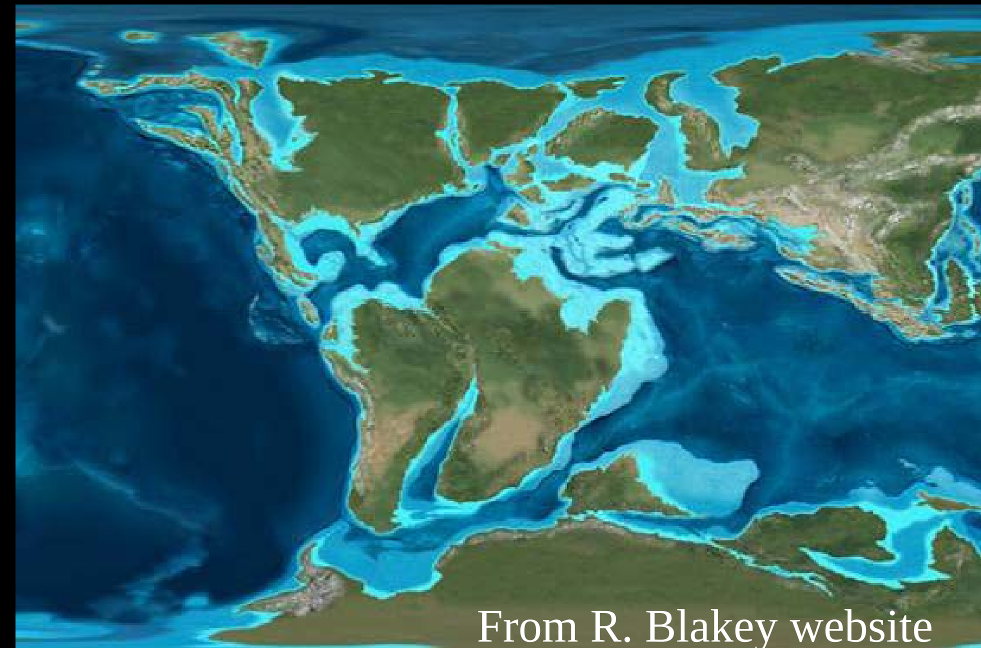




Studied Albian Pinda Carbonates

Thanks to Angola LNG





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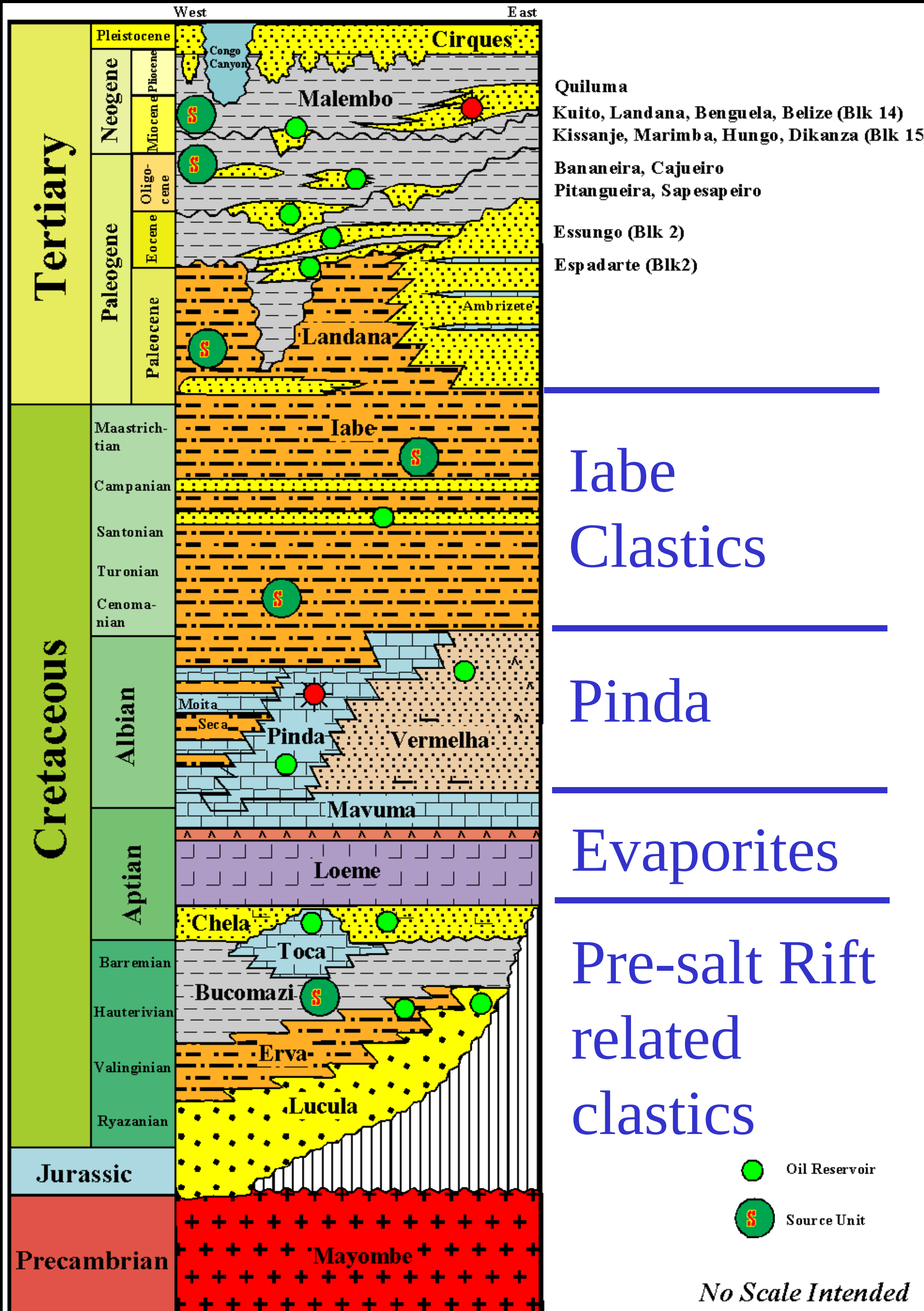
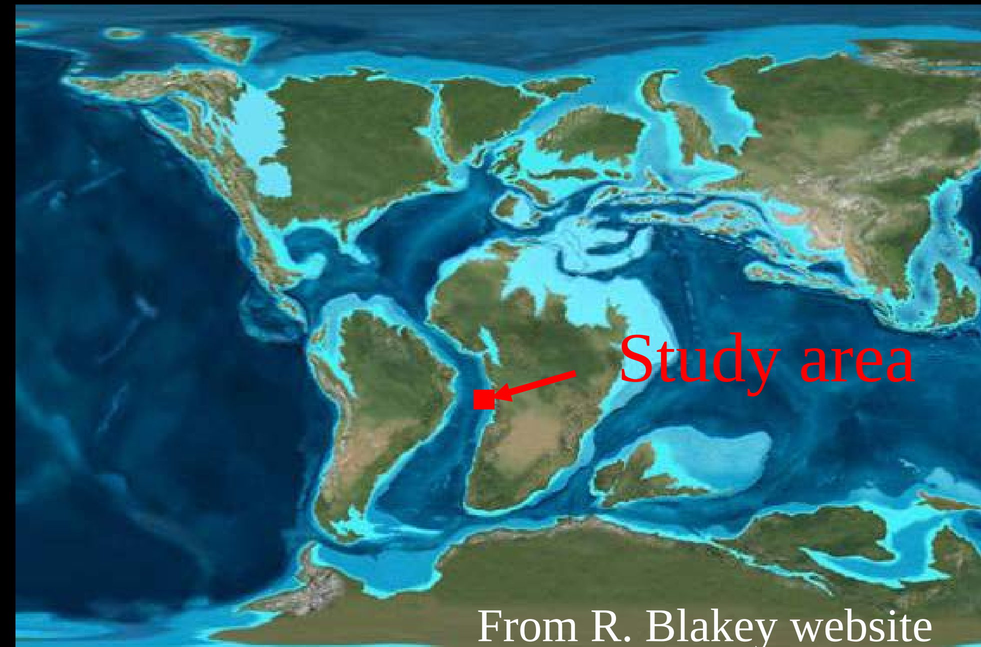




Studied Albian Pinda Carbonates

Thanks to Angola LNG

Study Conducted in Block 2, offshore Angola

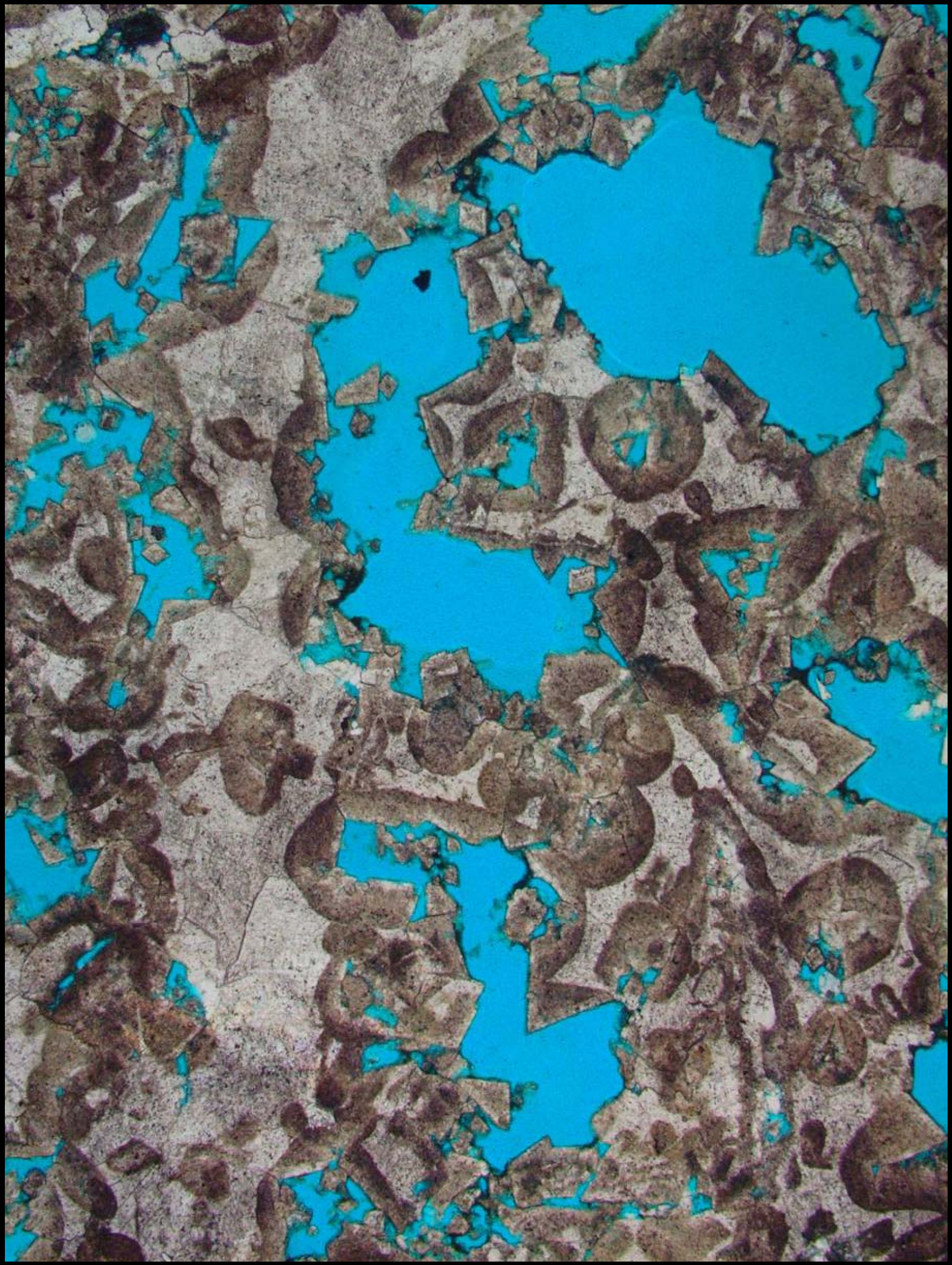
Study included 18 cores and cuttings thin sections from ten wells

Made and described hundreds of thin sections

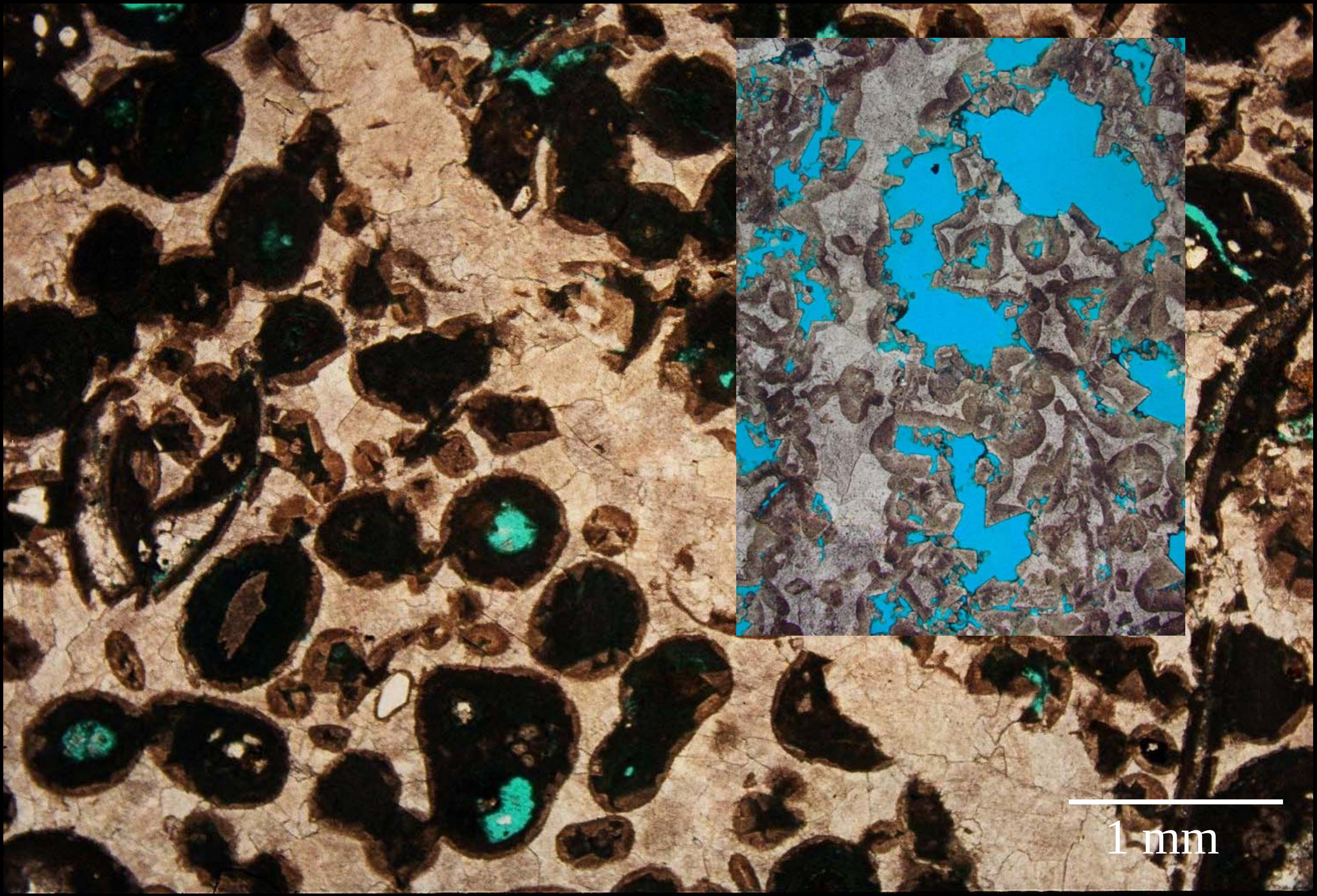
Covered Northern, Central and Southern Fields Areas

Core studies

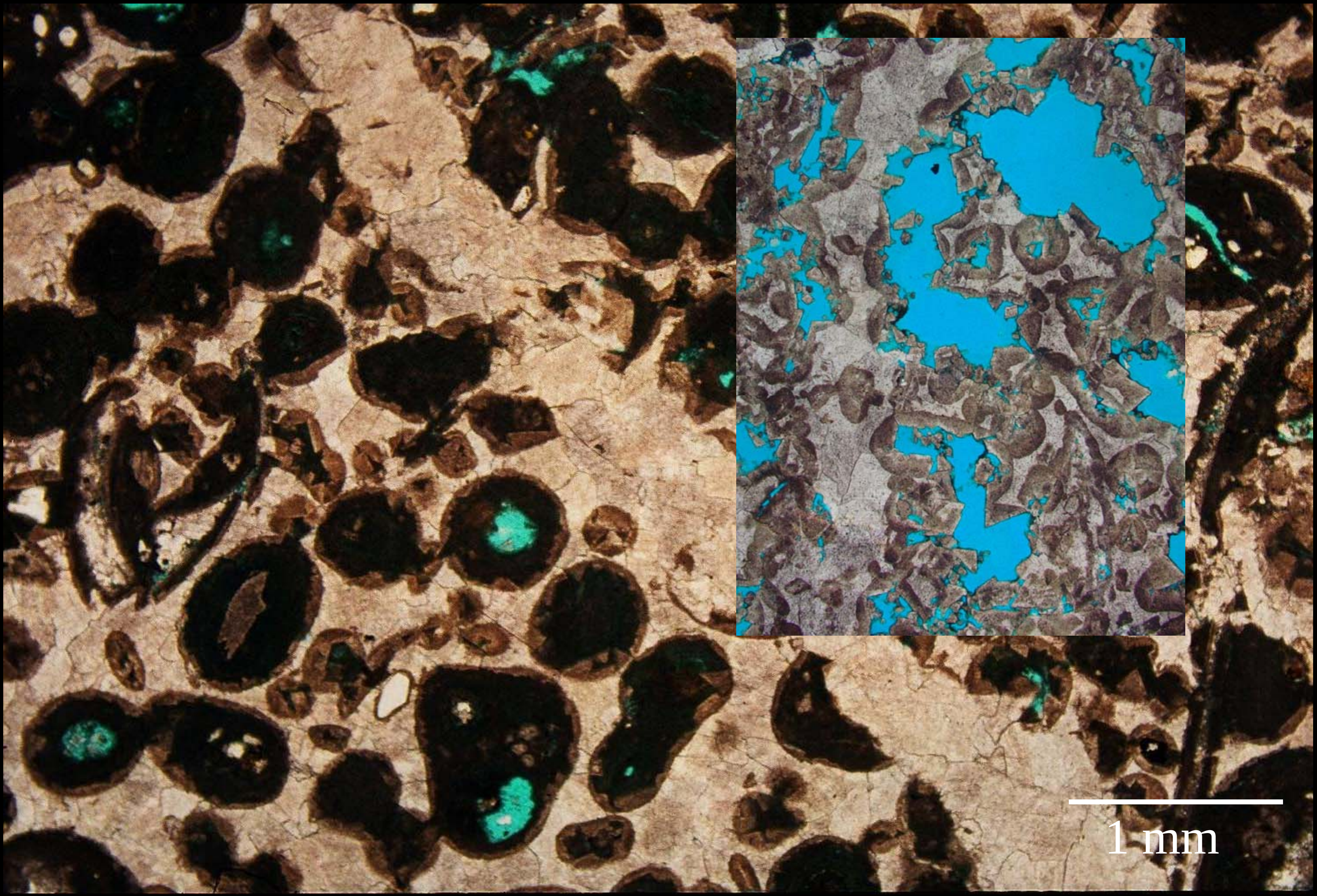
Cuttings Thin Section Studies (some more than 3000 feet of section)



Reservoirs in sandstones and coated grain-oncoid grainstones and rudstones – best carbonate reservoirs are dolomitized and subsequently leached



Dolomite starts out as cement (saddle where large xtals), not as replacement of grains – this dolomite precipitated directly out of supersaturated fluid sourced from fractures– only minor compaction prior to dolomitization suggests shallow burial



Dolomite starts out as cement (saddle where large xtals), not as replacement of grains – this dolomite precipitated directly out of supersaturated fluid sourced from fractures– only minor compaction prior to dolomitization suggests shallow burial

Evidence for Hydrothermal Dolomitization

- Dolomitization only occurs where basement-rooted faults visible on seismic offset Loeme and cut into Pinda
- Primary fluid inclusions almost all two-phase inclusions with T_H between 65 and 160°C and salinities of 20 wt% - hotter than ambient burial temps at time of dolomitization
- Stable isotopes, strontium isotopes and trace elements all support
- Only minor compaction prior to dolomitization which suggests shallow but hot
- Saddle dolomite in fractures and matrix

Dolomite leaching

- Dolomite leaching is extensive in the Pinda
- It is not reported much in the literature
- The leaching fluids enlarge fractures and are here interpreted to have been sourced from the fractures
- Without dolomite leaching, there might not be fields in some areas

Dolomite Leaching

Enlarged fractures

Vugs

Matrix dissolution

Dolomite leaching occurred in fractures vugs and matrix – presence of leaching in fractures suggests fluids flowed up faults and fractures and into matrix

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Matrix dissolution

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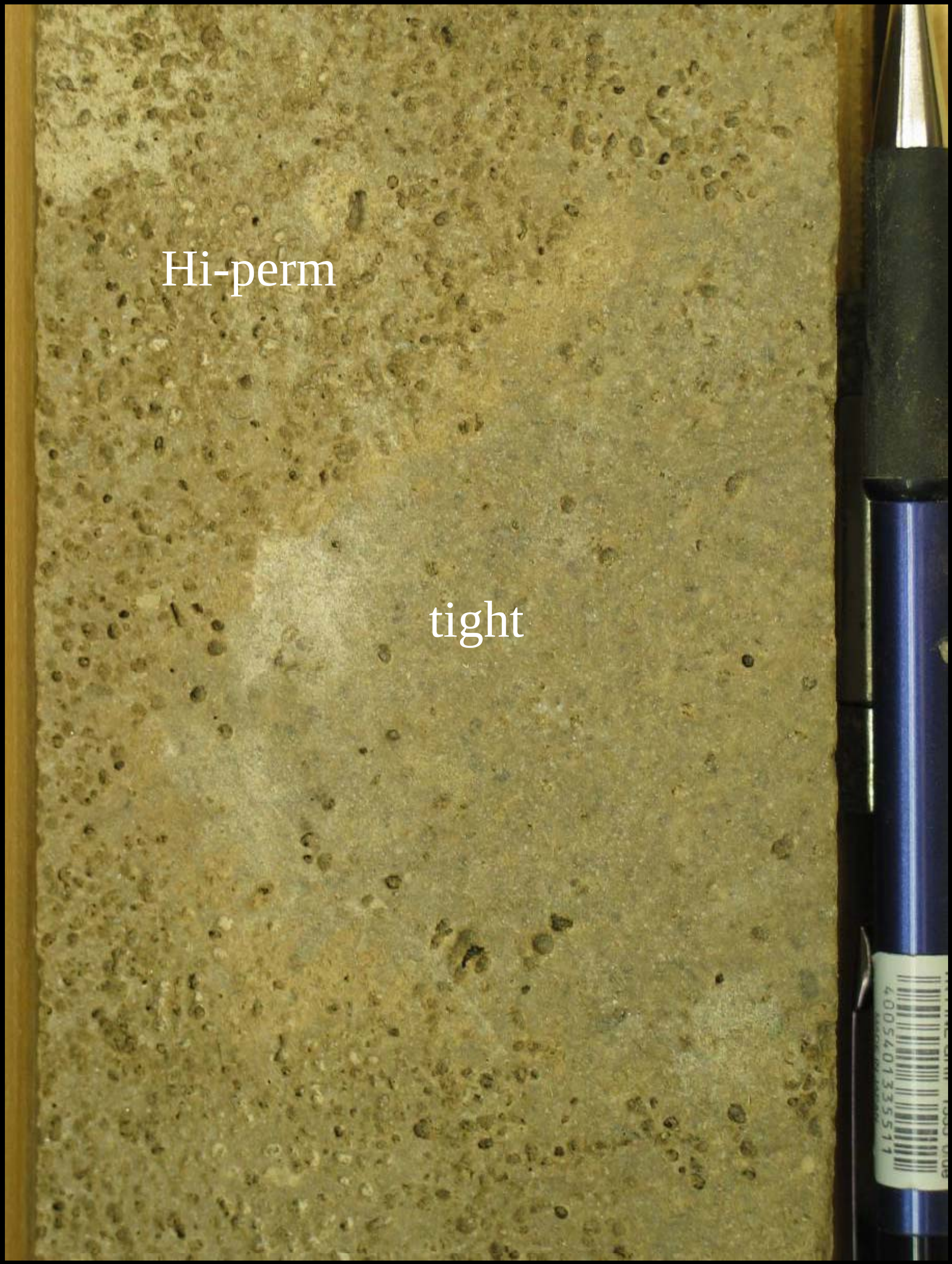
Chopa 2 8110

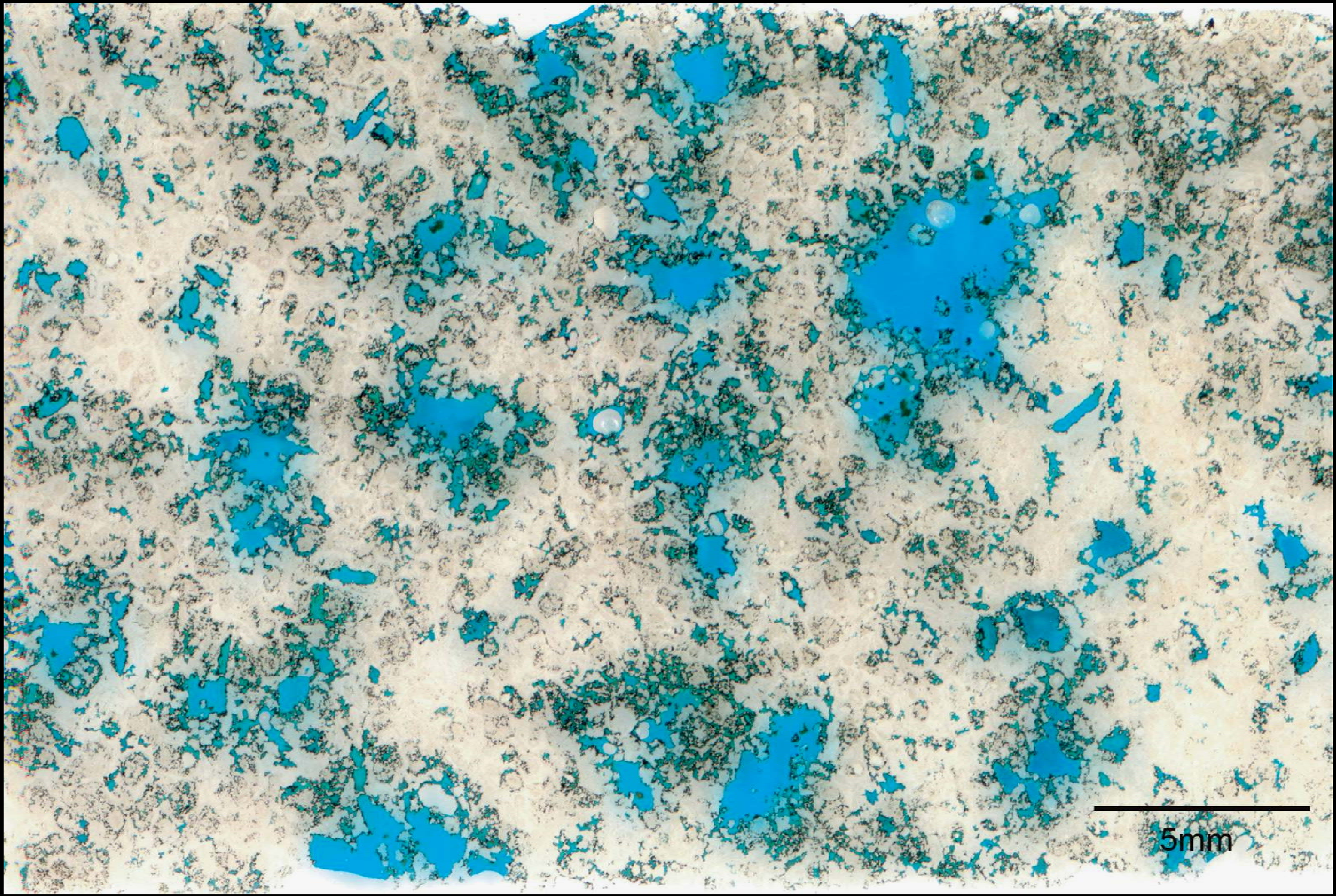
Chopa 2 8092.5

Chopa 2 and most other cores showed evidence for strong dolomite leaching

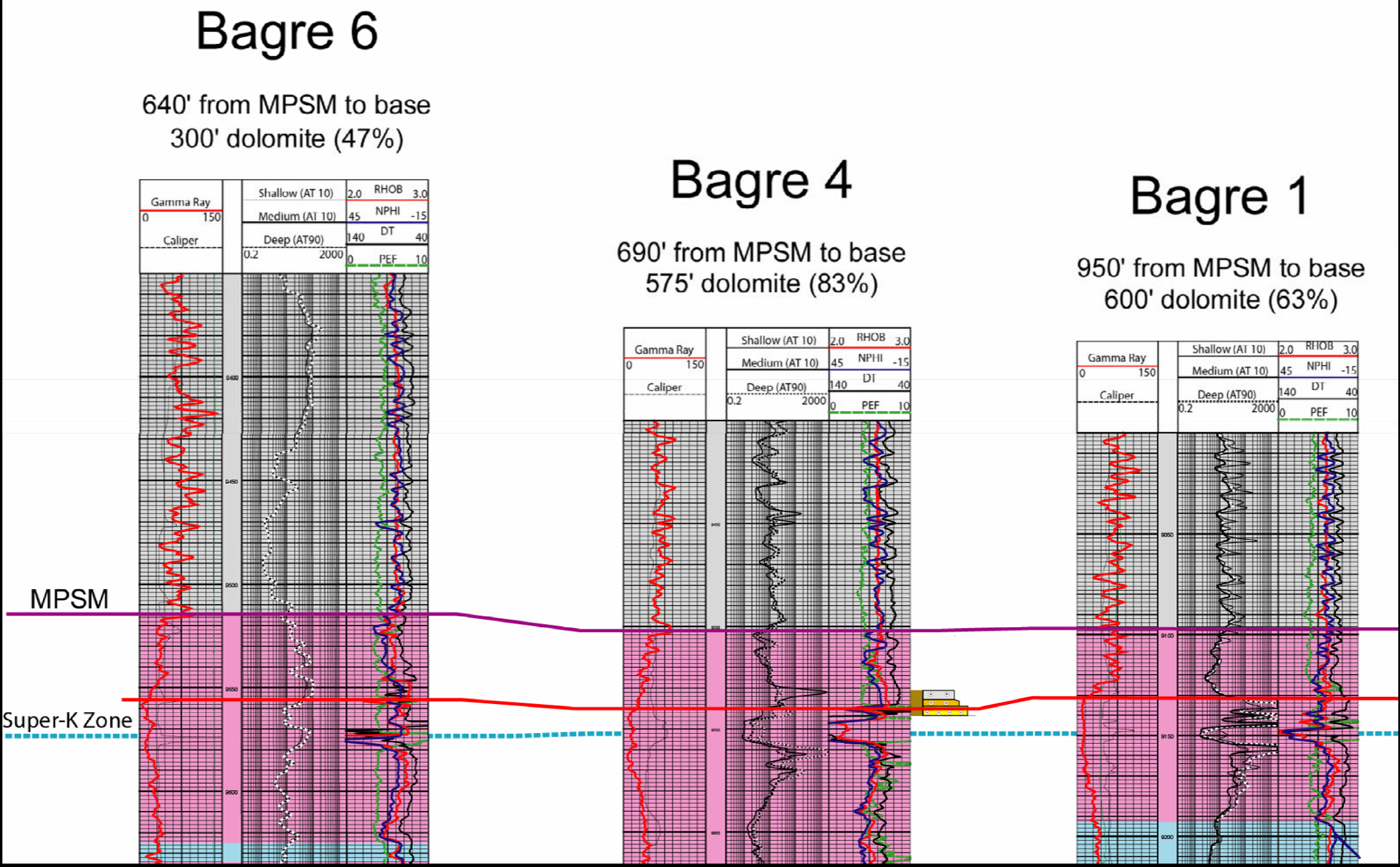


Chopa 1 6982.5

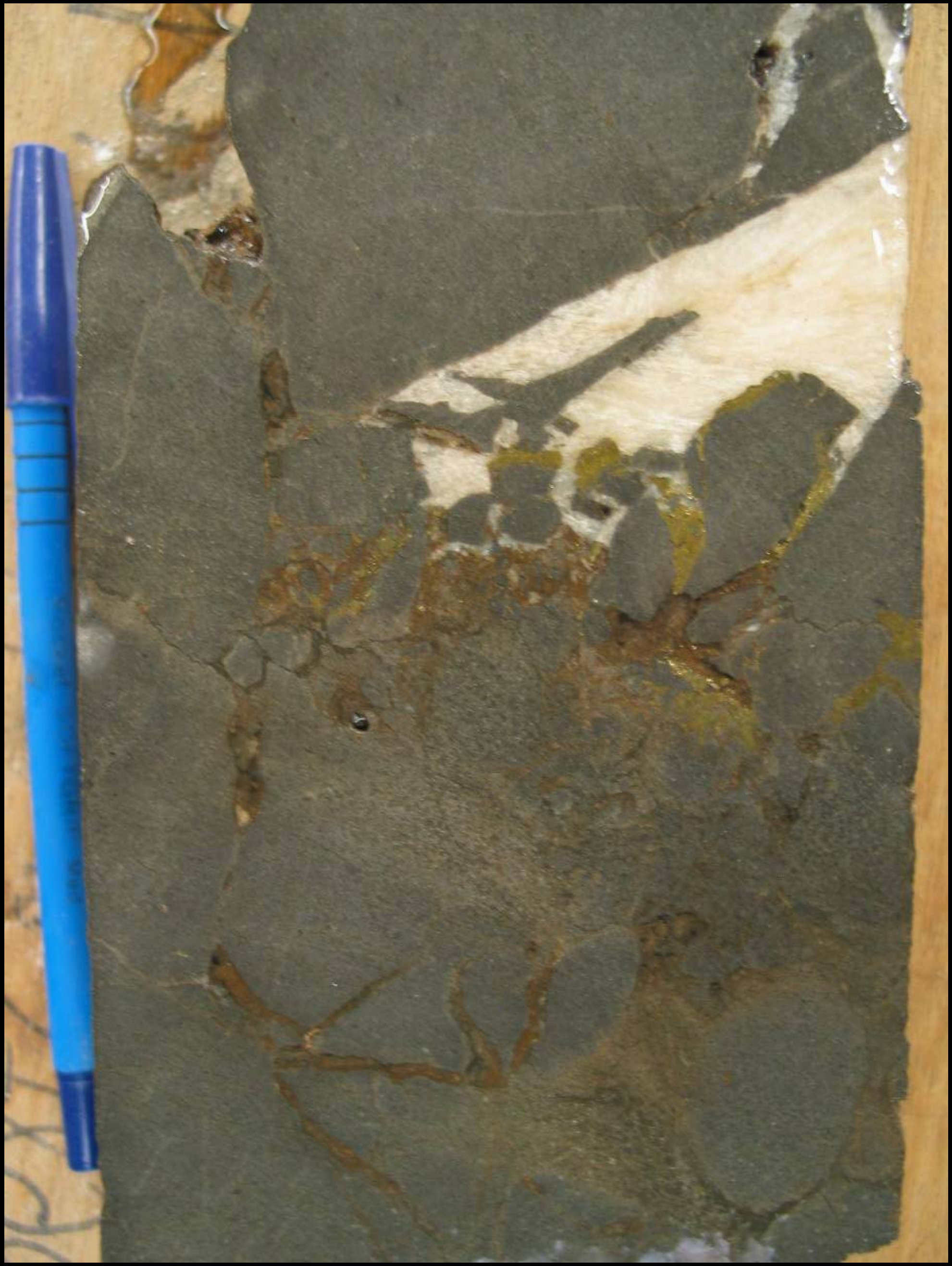
Grainstones variably leached –without leaching, no perm



In some fields, >75% of the porosity appears of be of a leached dolomite origin as it is in this thin section scan

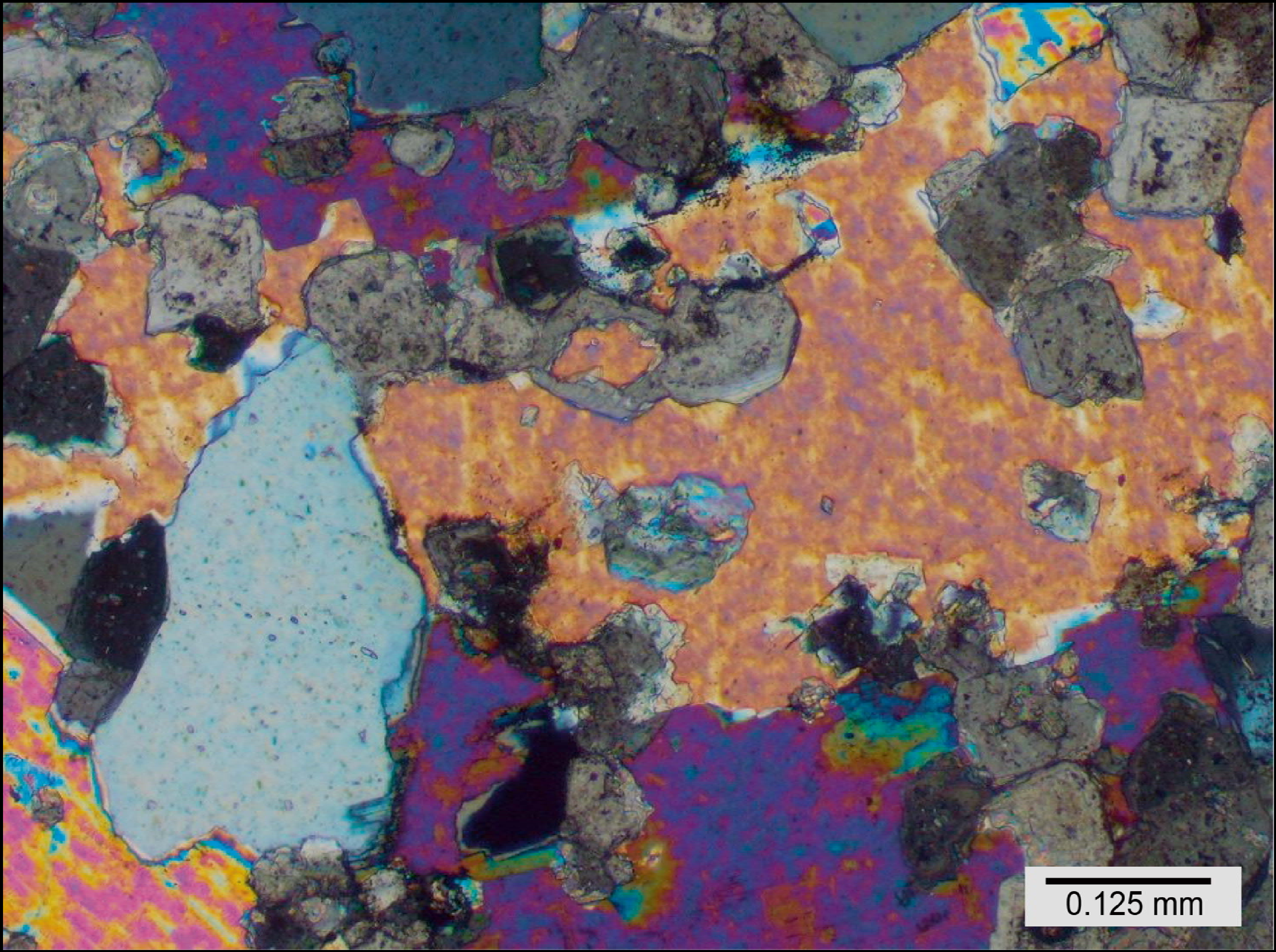


Dissolution proceeds near the tops of some intervals to the point where super-k zones form

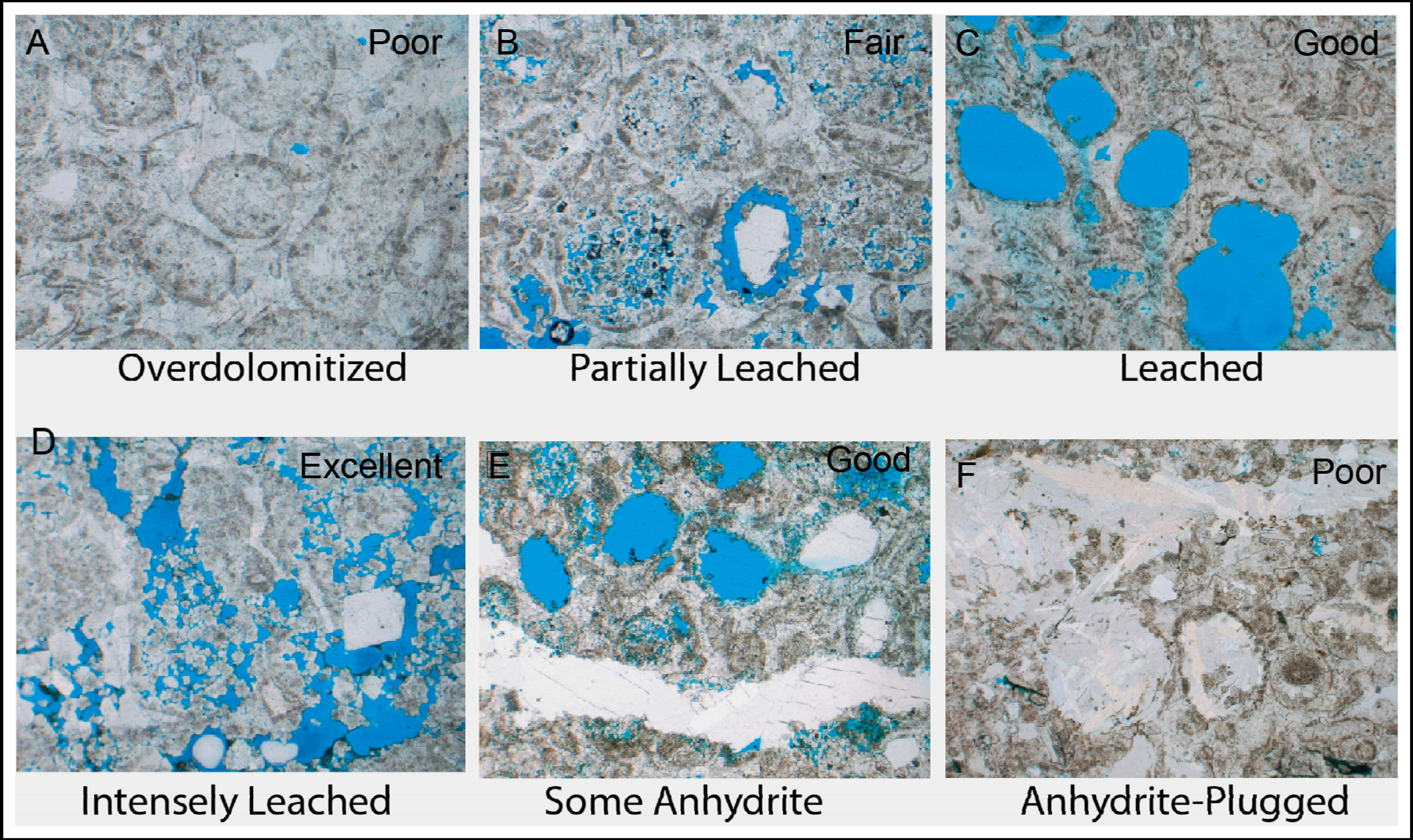


Lombo North 3 10187

Pyrite followed by anhydrite is very common in fractures and breccias in the Pinda cores from many fields



Post-leaching anhydrite



Impact of Diagenesis in Pinda – all same rock type – Dolomite is good, too much dolomite (overdolomitization) is bad, leaching is good to really good, anhydrite plugging ranges from OK to really bad

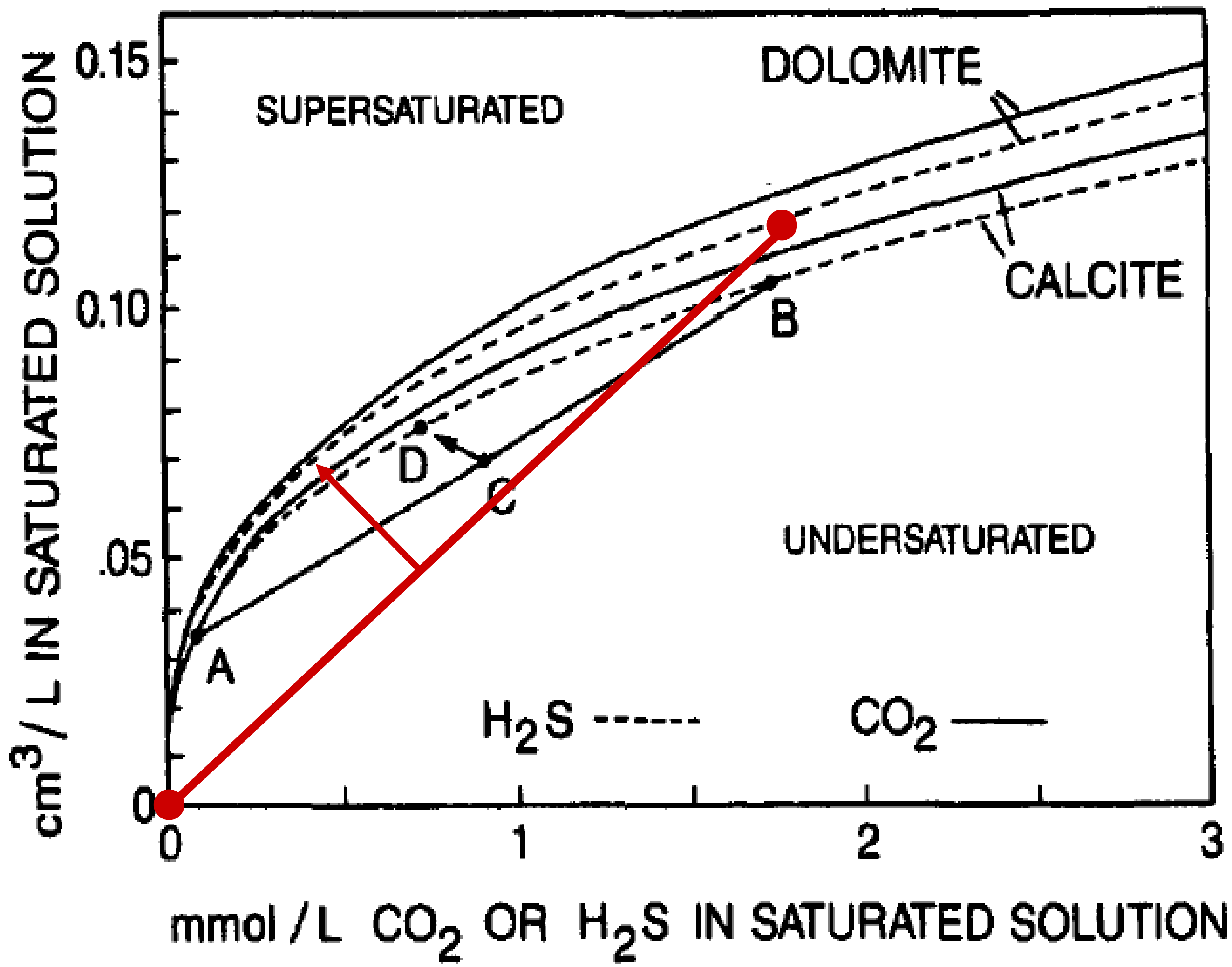


Figure 1. Saturation concentration of calcite and dolomite as a function of CO_2 or H_2S concentration in volume of dissolved solid per liter. Mixing of two saturated solutions (e.g., A and B) produces an undersaturated solution (C) and renewed aggressiveness. Subsequent dissolution follows line C–D. After Palmer (1991).

Leaching interpreted to have been caused by H_2S coming up faults

Either oxidation of H_2S to make sulfuric acid or mixing of two different fluids with varying H_2S composition could make fluids capable of leaching dolomite

Common byproducts of sulfuric acid leaching are $CaSO_4$ (gypsum or anhydrite) and FeS (pyrite) (Hill, 1995)

Conclusions

- Carbonate dissolution, or burial corrosion, is a common process in the subsurface
- It commonly occurs around transtensional faults which when active are conduits for hydrothermal fluids which evolve over time and can produce a range of mineralization and dissolution