2015 CO_2 Conference Week

Wednesday, December 9, 2015

Seminar on the Origins, Processes and Exploitation of Residual Oil Zones

Midland Center

Midland, Texas

Table of Contents for the ROZ Seminar

Section

Optional Field Trip to Seminole San Andres Unit *(Separate Ticket Required)*

5:30 -7:30 pm - Reception at the Midland Center

2015 CONFERENCE WEEK

Seminar Instructors

Hosting Organization: The Applied Petroleum Technology Academy

- Steve Melzer: Coordinator and Instructor - Melzer Consulting
- Dr. R. (Bob) Trentham – UTPB, APTA
- David Vance – Arcadis U.S.
- Vello Kuuskraa – Advance Resources International

With contributions from

- Dr. Peigui Yin and coworkers – Enhanced Oil Recovery Institute (WY)
- Charlie Gorecki and staff – The Energy & Environmental Research Center, UND

The Entire Seminar Manual is Available on

www.CO2Conference.net

The following are Selected Slides

Section 1

Introduction: The Evolving Understanding of Residual Oil Zones

An Overview

Steve Melzer

Transition Zone Thinking

- Our Industry has historically defined two categories of fluids
  1. Mobile – free from bonds to the rock and able to move readily within pressure or water driven flow fields.
  2. Immobile – Unable to move within normal pressure or water driven flow fields.
- There are regions where capillary and surface tension forces allow oil and water to intermix in the mobile phase. This is often referred to as the transition zone and is generally defined as that interval where co-production of oil and water occurs.
- The oil water contact (OWC) has been defined in a variety of ways based sometimes on oil cut, often on wireline log parameters but occasionally on other parameters

The industry most often defaulted to an explanation of zones below the oil water contact as transition zones where it was expected that oil saturations would linearly decay to zero below the OWC

Transition Zone Thinking (Cont'd)

The transition zones observed for homogeneous reservoirs are generally relatively thin, particularly in coarse-grained reservoirs. However, when thick transition zones are observed it is often dismissed as due to effects from reservoir heterogeneity. Interbedded lithologies with different capillary behaviors may result in a thick transition zone in which some lithologies produce hydrocarbons and others produce water. Rocks with complex pore networks complicate things also (such as combined fracture and matrix porosity) and may demonstrate apparent thick transition zones explained by different fluid types produced from different pore types. The cause of thick transition zones has occasionally been examined by core examination and capillary pressure tests.

Water- and Oil-Wet Systems (2)

- In the first century of our industry, we generally believed that all reservoirs were water wet.
- What were to become our oil reservoirs were originally deposited in water as, as burial occurred, much of that water was expelled as the formation lithified but water remained trapped in the pores
- As oil was generated due to heat and pressure at depth, some subsurface situations entrapped the generated oil in oil 'traps.' Let's call these paleo traps

Water- and Oil-Wet Systems (2)

- The bound water in the formation remained there and the mobile phase of oil displaced the mobile water in the reservoir system. This required the paleo traps to be water wet.
- The industry began to observe[1)] that, in some reservoirs, the oil saturations were quite high, even exceeding 80% suggesting some amount of oil that was bound in the reservoir system. Lab tests were developed to look at the wetting fluids.

[1)] My experience suggests that this enlightenment occurred during the 80's in many companies

Water- and Oil-Wet Systems (3)

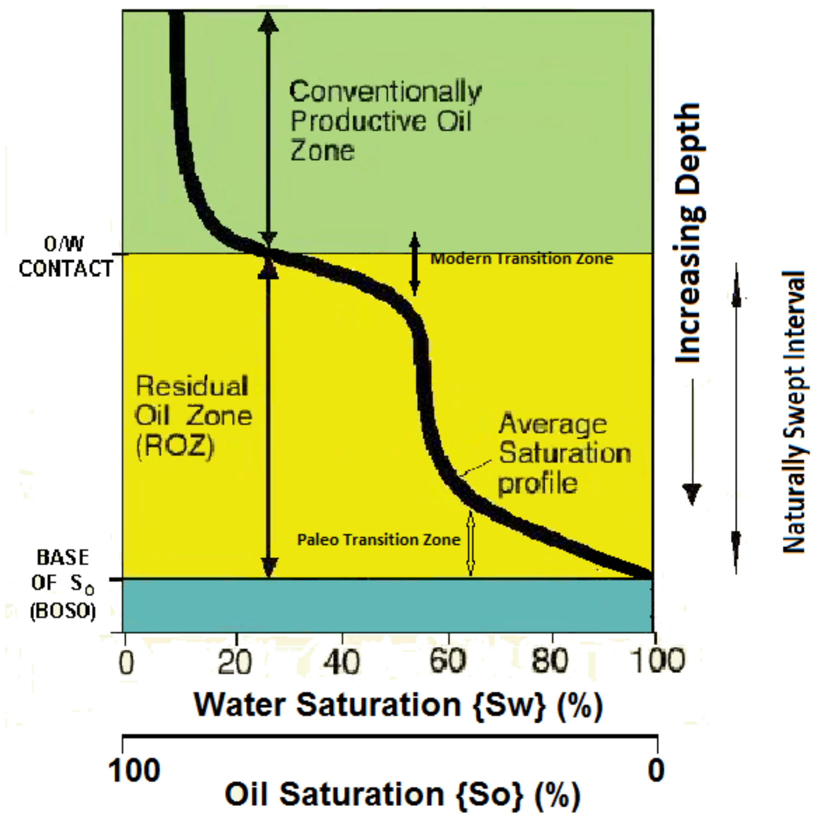
- The observations of immobile (wetted) oil were often explained away as oil that was mobile in geologic time frames but immobile in man's time frames
- New work is suggesting that, in some rocks, the oil has a preference as the wetting fluid and most of the water has been displaced[2)].
- We will come back to this wetting subject after the discussion in the next session (M) and attempt to put some science into why some zones appear so heavily oil wet.

2) It is fair to say that this preference to oil remains a controversial subject

Water- and Oil-Wet Systems (4)

- If we can extend this oil wet thinking to residual oil saturations after water flooding (S_{orw}), we can explain the 30-40% S_{orw} values that we commonly find in our water flooded flushed zones.

Figure 1 - Residual Oil Zones and Upper and Lower Transition



Overlaying a Concept of Natural Residual Oil Zones

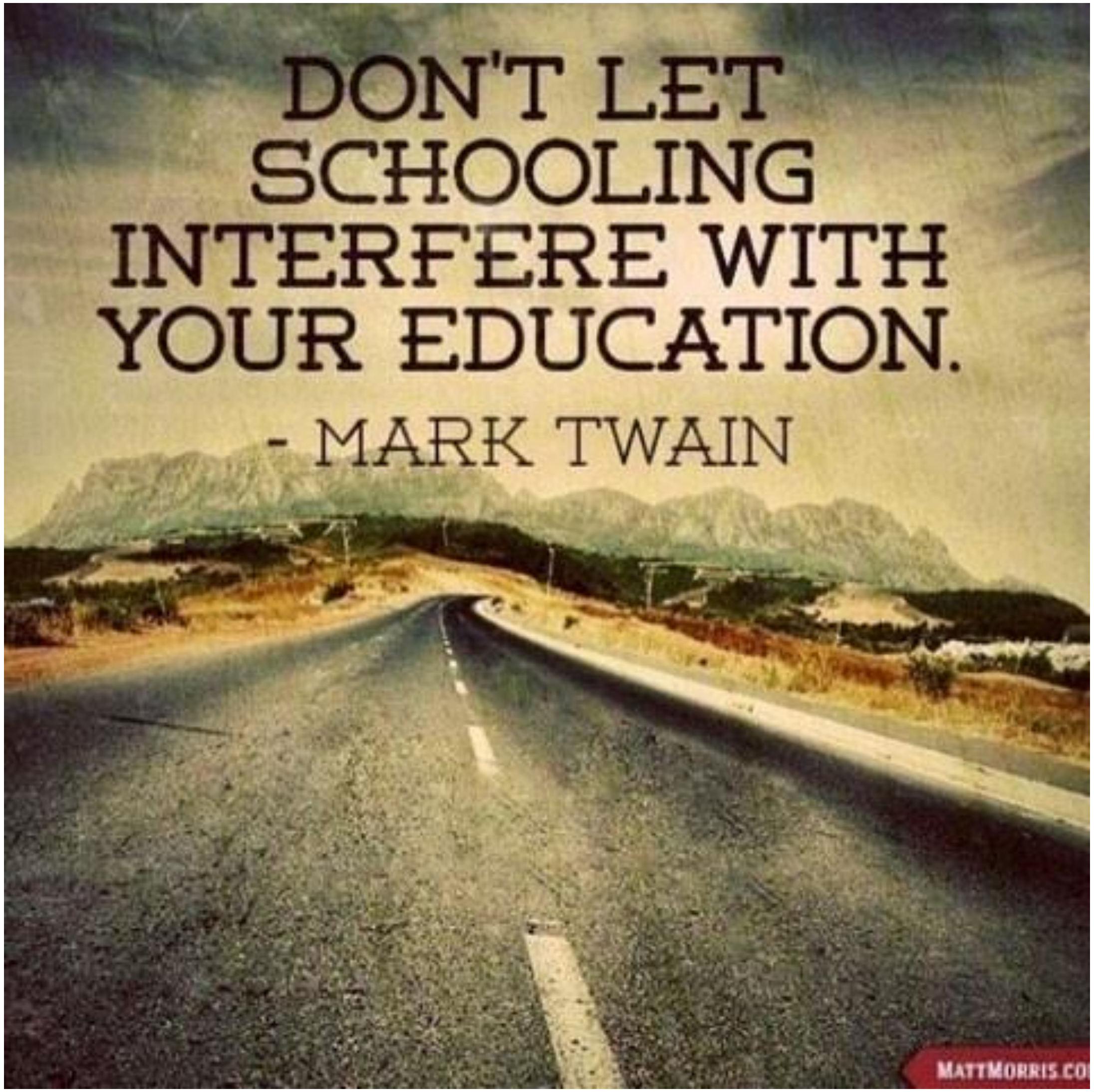
- The aforementioned-mentioned model of deposition, burial, oil generation and migration to a paleo trap is our classic understanding of oil entrapment
- What if something happens later to the reservoir after entrapment to move the oil and water around?
- In looking at the paleo trap, what this would entail is that the original mobile water in the reservoir was displaced by oil to make the paleo trap and then water reinvades the paleo trap. If the reservoir had become mixed wet, then the S_{orw} could be significant and, perhaps, a target for recovery say in EOR just like what we've done after our man-made water floods

This is the premise of our course today and, we believe, well supported by field data acquired over the last 30 years in our Permian Basin Industry

Going after S_{orw}

- The Classic approach for producing this S_{orw} is to inject a substance that causes the properties of the residual oil to change and become mobile in the resrvoir. We will show a number of case histories of this later (Section 5a) using CO_2 EOR
- Another Method has Emerged we call Depressuring EOR or Depressuring the Upper ROZ (DUROZ). We would argue that this is the same approach that is being used in the Dewatering plays (like in Oklahoma)

Caution: The Following May Test Your Creativity!



DEWATERING/DEPRESSURING

How Does the ROZ Concept Play into this Production Technique?

- Dewatering of Reservoirs as a Production Technique has been around for a While
  - In the Permian Basin – Bough “C” (Lea County)
  - In Oklahoma – Mississippian Lime/Hunton Dewatering Plays
  - Others
- Versus “Tight Oil” Play
- Can We Produce Immobile (Residual) Oil Via Techniques Other than Conventional EOR?

16

The "Camps"

1. Compartmentalized Pods of Mobile Oil (Main Payzones)
2. Tight Oil – A More Conventional Shale Play
3. Depressuring a Residual Oil Zone (Relative Permeability)

Which Camp are you in?

DEWATERING/DEPRESSURING

Does the ROZ Complete the Understanding?

- Production Coming from Mother Nature's Water Flooded Reservoirs
- Relative Permeability Approach to Understanding Production
- Scientific Approach (Gas Expansion)

We Prefer the Scientific Approach as it Helps Understand the Parameters that Control Production and Compare Reservoir Plays

Section 2

The Science of ROZs

Section 2

The Key Science Components Involved in Understanding the Residual Oil Zones

A. Depositional Facies of the ROZ Formation
B. An Oil Basin's Tectonic Stages
C. Types of Residual Oil Zones
D. Post Entrapment Changes to the Oil and Rocks (with a Heavy Bias to the Carbonate Formations and San Andres Formation in Particular)

Another View of ROZ Creation
Basin Tectonics

Let's Call the First Stage

Basin Subsidence…….plus

Oil Generation……plus

Migration to Traps

Is that All that Happens to the Basin?

<u>If it is, the Basin Must Become a Static Basin after the First Stage</u>

We are Still Looking for That Basin

- It is **N**ot the Permian Basin
- …**N**ot the Big Horn Basin
- …**N**ot the Williston Basin
- …**N**ot the Gulf of Mexico Basin
- …**N**ot the Arabian Basin
- …**N**ot the Baltic Region
- …**N**ot the Australian Cooper-Eromanga Basin

Post Depositional Tectonic Overprint Permian Basin

Quat	Holocene	-10 ka to present	Arid climate.
	Pleistocene	-2 Ma to –10 Ka	At ~600 Ka Capitan Aquifer hydrologically connects with Pecos River at Carlsbad. Possible draining of lower Carlsbad and Lechuguilla Caverns.
Cenozoic	Pliocene	-5 to -2 Ma	Base level downcutting of ancestral Pecos River. Regional Ground Water tables drop. Canyons downcut into Guadalupian Mtns. Cave entrances form.
	Late Miocene	-12 to -5 Ma	H2S ascends into Guadalupe Mtns from basin. Sulfuric acid caves develop from Se to NE, enlarge and cut across older thermal caves.
	Early Miocene	-25 to -12 Ma	Rio Grande Uplift accelerating. Maximum uplift of Guadalupe Mtns block begins (~20Ma). Delaware Basin geothermal gradient reaches 40-50ºC/km. "Second" maturation and migration of hydrocarbons. H2S produced where hydrocarbons react with evaporites. Thermal caves developing. Dewatering Calcite spar fills basin and range fault zones.
	Oligocene	-40 to -25 Ma	Trans-Pecos Magmatic Province: Tertiary intrusives and extrusives to SW, dikes in Delaware Basin.. Transition from volcanic to Basin and Range in Delaware Basin Delaware Basin tilts eastward and heats up. "Second" maturation and migration of hydrocarbons. H2S produced where hydrocarbons react with Castile anhydrite. Emplacement of Miss Valley type Pb-Zn. Begin Rio Grande Uplift in late Oligocene.
	Eocene	-58 to -40 Ma	Quiescent time. Laramide uplift stops.
	Paleocene	-65 to -58 Ma	Laramide uplift continues into Early Tertiary. Older caves get enlarged and connected.
Mesozoic	Cretaceous-Gulfian	-95 to -65 Ma	Late Cretaceous Laramide Orogeny begins. Guadalupe and Apache Mtns. Lifted 1000's of feet above sea level.
	Cretaceous - Comanchian	-135 to -95 Ma	Shallow sea advances across west Texas. Deltaic deposits in southwest-most Texas.
	Triassic-Jurassic	-250 to -135	Guadalupe Mts exposed? Deltaic, lacustrine and fluvial environments in west Texas.
Paleo	Ochoan	-251 to -250 Ma	Evaporite deposition in Sabkha (Salado) and Basin (Castile) followed by uplift to the west and deposition of red beds and limestones. First Guadalupe Mtns uplift.
	Guadalupian	-255 to -251 Ma	Seven Rives Yates and Tansill Backreef, Capitan Reef, Delaware Mountain Group Deposition. Early dolomitization in Apache and glass Mountains.

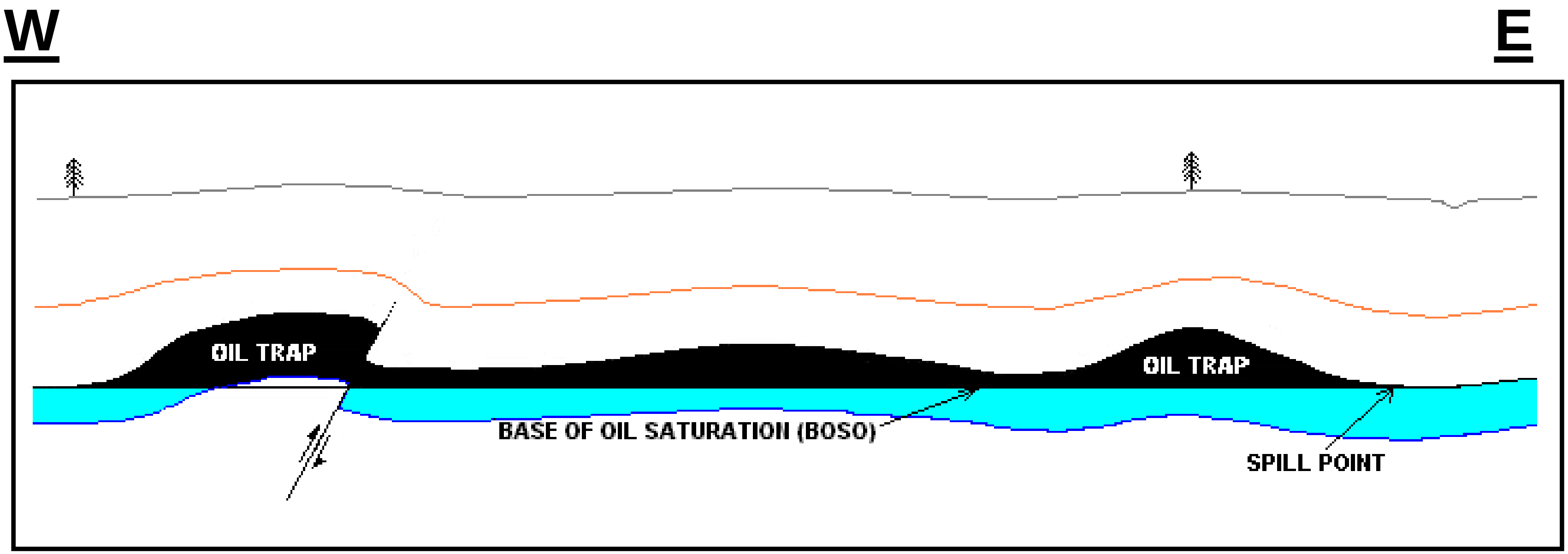
Oil Emplacement

Modified from Hill, 1996

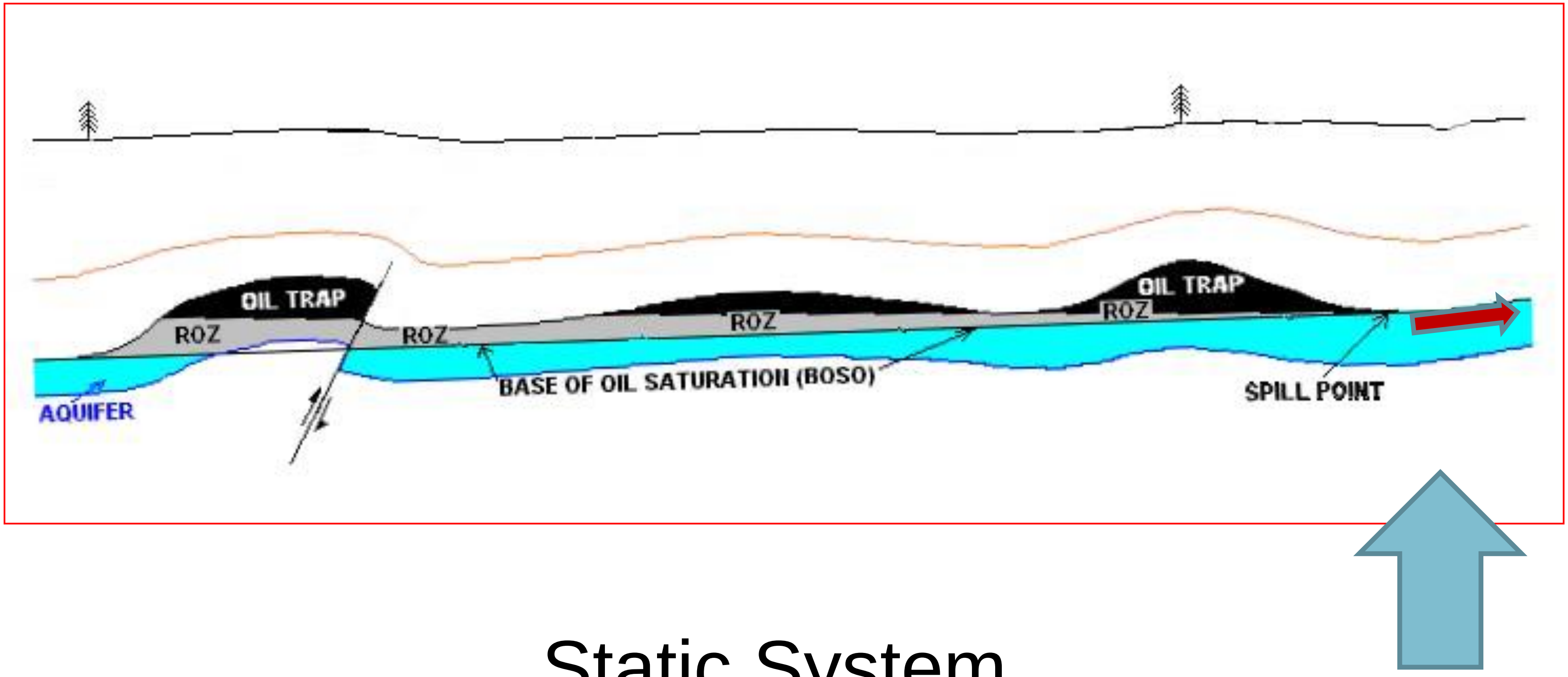
Types of Second Stage Adjustments

- Basin-wide Tilt
- Basement Readjustments and/or ‘Leaky Seals’
- Asymmetric Uplift and Lateral Sweep
  - Reservoir Outcrop and Meteoric Derived Water Sweep (aka Lateral Sweep)
  - Salt Diapirs

The Impact of Tectonism on the Reservoirs: Original Oil Accumulation Under Static Aquifer Conditions (A Hypothetical Example)

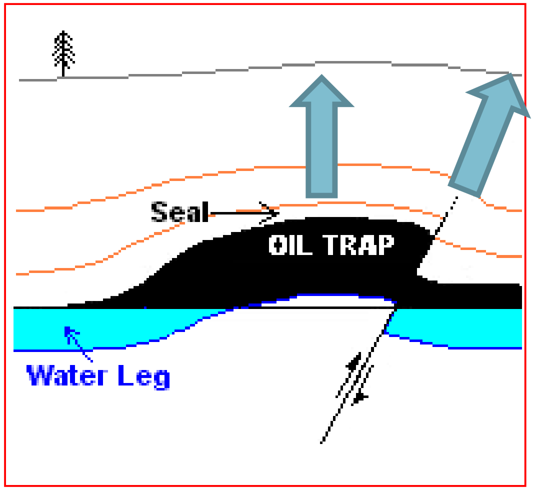


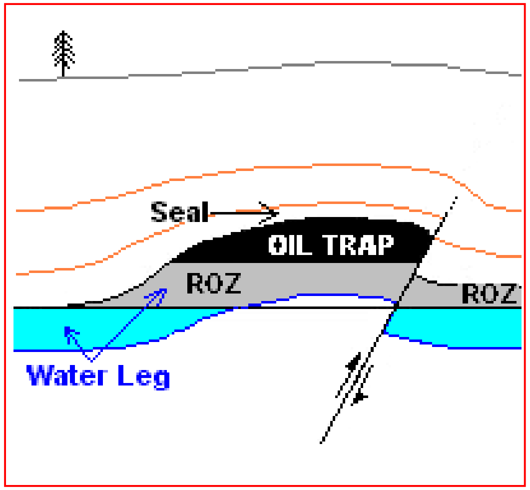
TYPE 1. Original Accumulation Subject to a Eastward Regional Tilt & Forming a ROZ.
The new O/W contact is horizontal
The base of the ROZ is tilted
Oil would have migrated out of the basin.



Static System

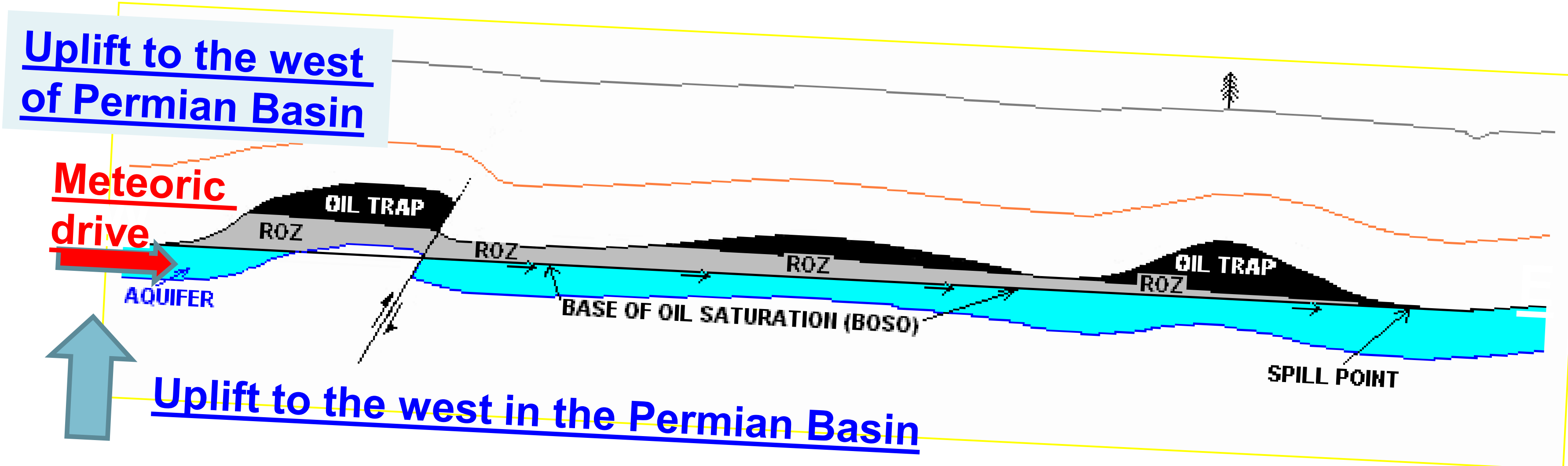
<u>TYPE 2.</u> Original Accumulation with a Breached, then Repaired, Seal, forming a ROZ/TZ.
A horizontal O/W contact on the main pay and the ROZ.
May also "de-gas" the reservoir.
Present in the Permian Basin.



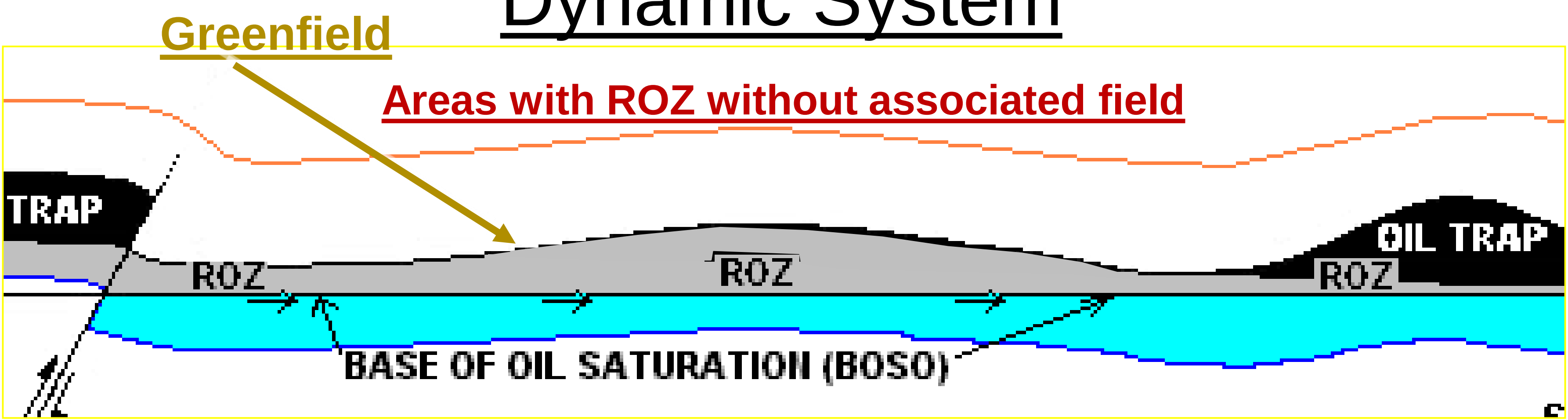


<u>Static System</u>

TYPE 3. Change in Hydrodynamic Conditions, Sweep of the lower part of the Oil Column and Development of a Residual Oil Zone. Oil/Water Contact is Tilted Base of the ROZ locally almost flat, regionally tilted.



Dynamic System



Key Concepts/Definitions for Residual Oil Zones

ROZ Definition: That Portion of a Reservoir Below the Oil/Water Contact Where Residual Oil Resides but the Mobile Phase is Water

Brownfield: Defined as a ROZ that Exists Under a Developed Oil Field (Main Payzone (MPZ)) – Example: SSAU

Greenfield: A ROZ that has no Overlying MPZ

Fairway: A Large Region Where Greenfield ROZs Exist and Align Geographically

ROZ Microbes: Those Naturally Occurring Anaerobic Bacteria that Must Live in Water that Use Hydrocarbons for their Life Processes (Their effects are inhibited in the MPZs)

Which ROZ Types Tend to Predominate in a Given Region?

The Understandings of WW Basin ROZs are Very Immature….

It is Still Early to Say Which Types Predominate Except…

In the Permian Basin, it Clearly is Type 3*

__We do see Type 2's and some Evidence of Type 1's but, volumetrically, they have much less oil in place and apparently occur only in Brownfields__

Type 3 Predominates
(in the Permian Basin)*

Post Entrapment Western Uplift and San Andres Outcrops

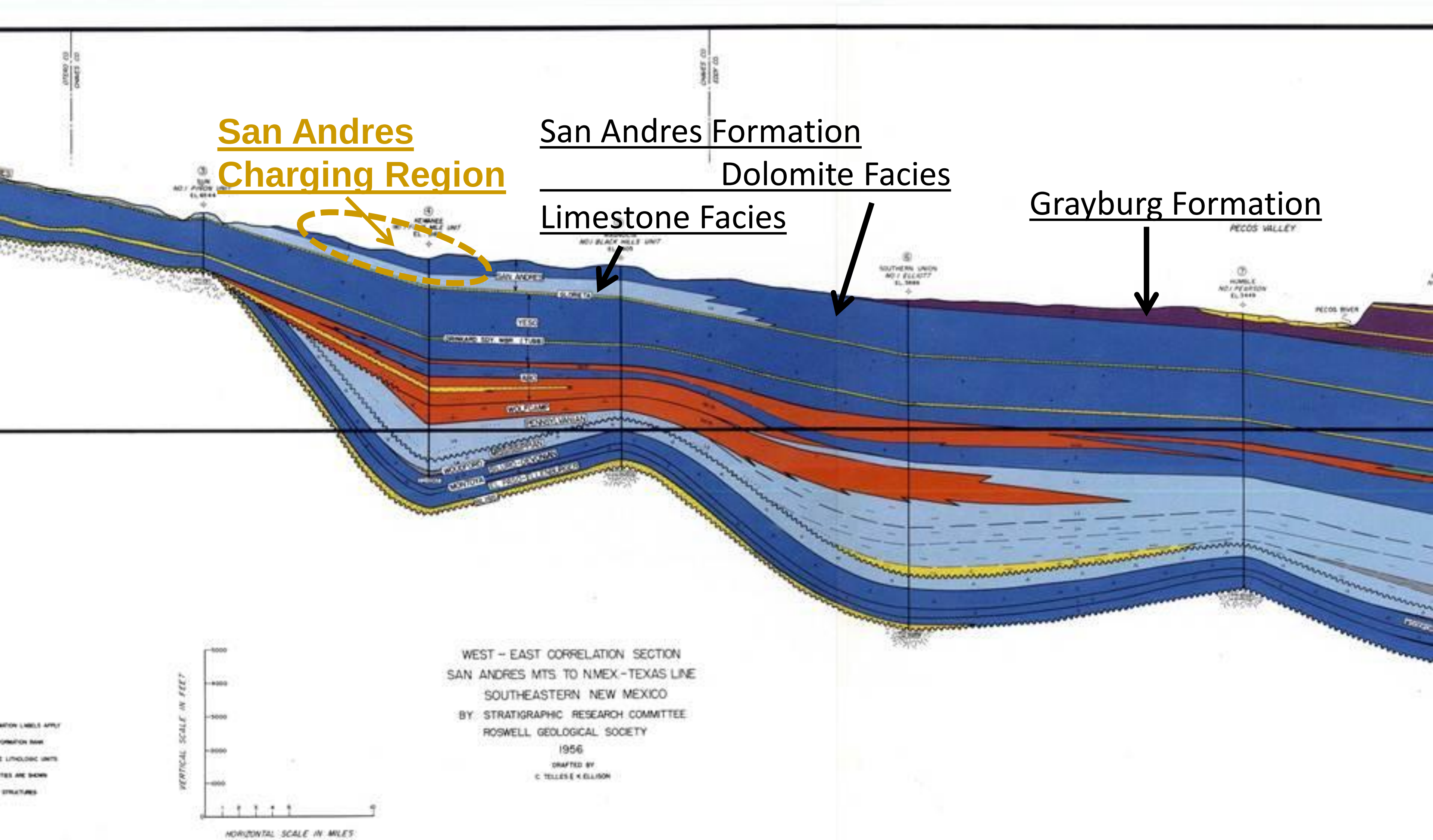
Tilted Oil Water Contacts

Ubiquitous shows Suggesting that a (Very) Large Paleo Trap in the Cretaceous Period was Swept by a Natural Waterflood in the early to mid-Tertiary Era

**** This Hydrodynamic Sweep also Predominates in the Big Horn and Williston Basin ROZs as Well***

San Andres Modern Charging Area

Re: Roswell Geological Survey Cross Section



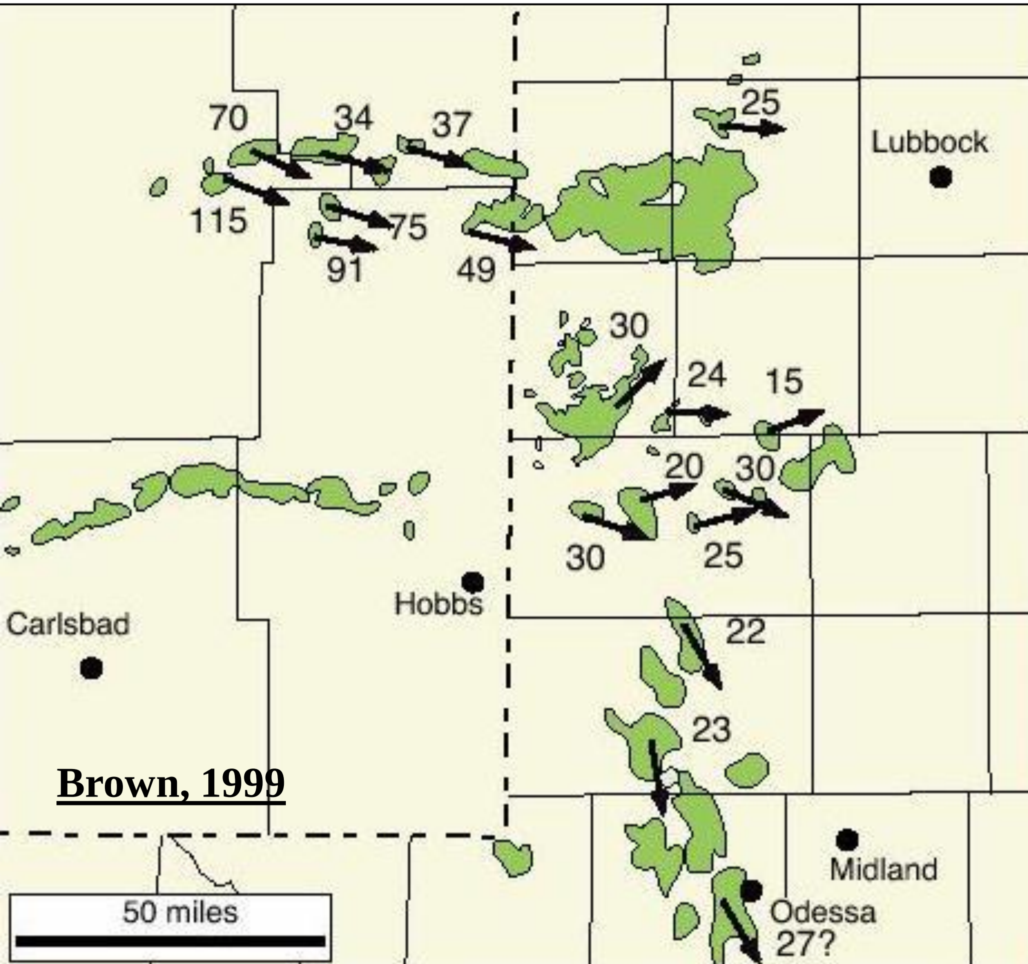
ROZ Types and Attributes

RESIDUAL OIL ZONE TYPES AND ATTRIBUTES

ROZ TYPE	Oil-Water Contact	Base of Oil Saturation	Other Characteristics
Regional Tilt (1)	Horizontal	Tilted	Wedge with thin side Updip
Breached Seal and Reaccumulation (2)	Horizontal	Horizontal	Stratified Tar Mats, Anomolously Low GOR
Hydrodynamic Tilt (3)	Tilted	Horizontal	Wedge with thin side in Direction of Flow (to Spill Point)

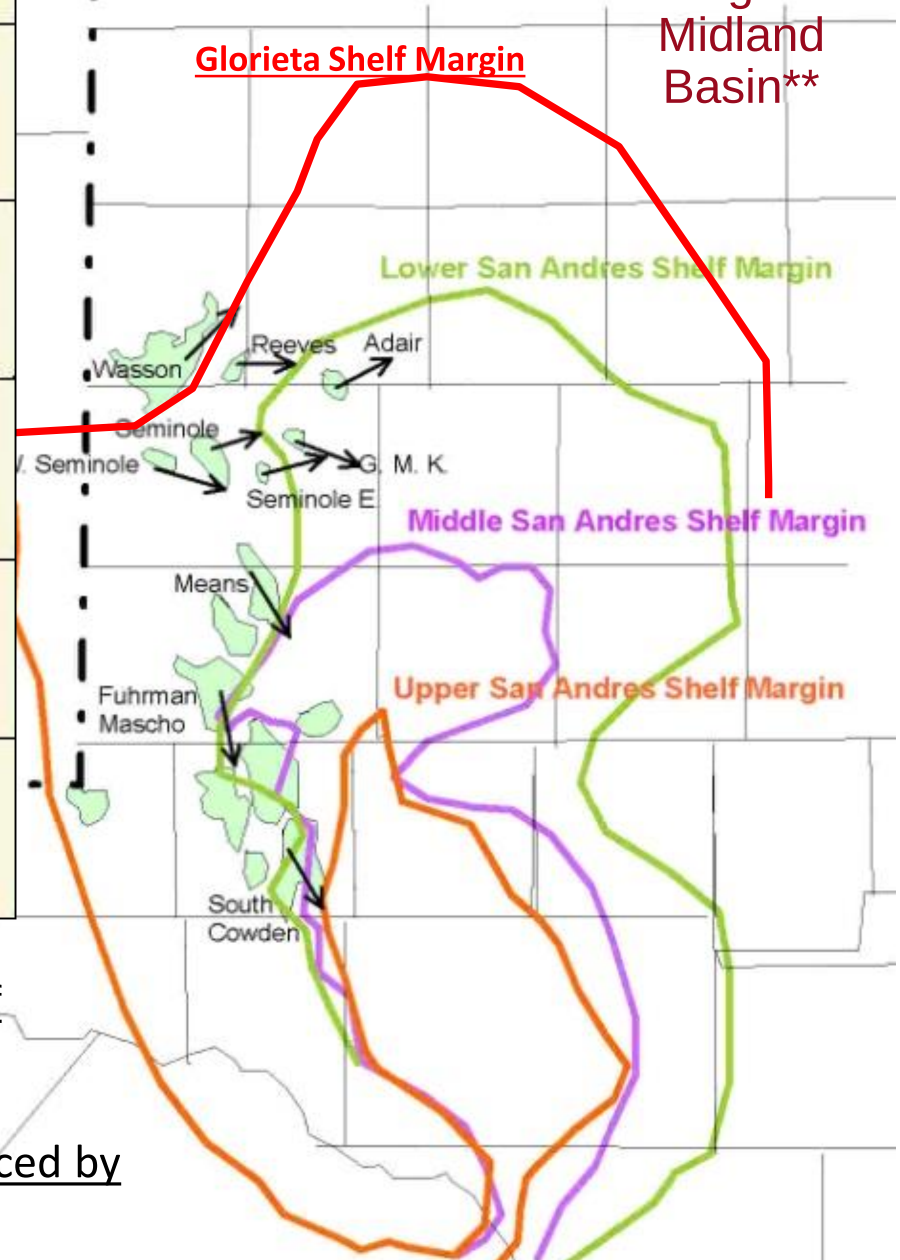
So Let's Examine the Evidence for Type 3 in the Permian Basin

All ROZ Types can lead to a Greenfield but in Type 3 fairways, they can be ubiquitous (more on this later)



Distribution of Tilted Oil-Water Contacts in the Northern Shelf and Central Basin Platform Areas of the Permian Basin*

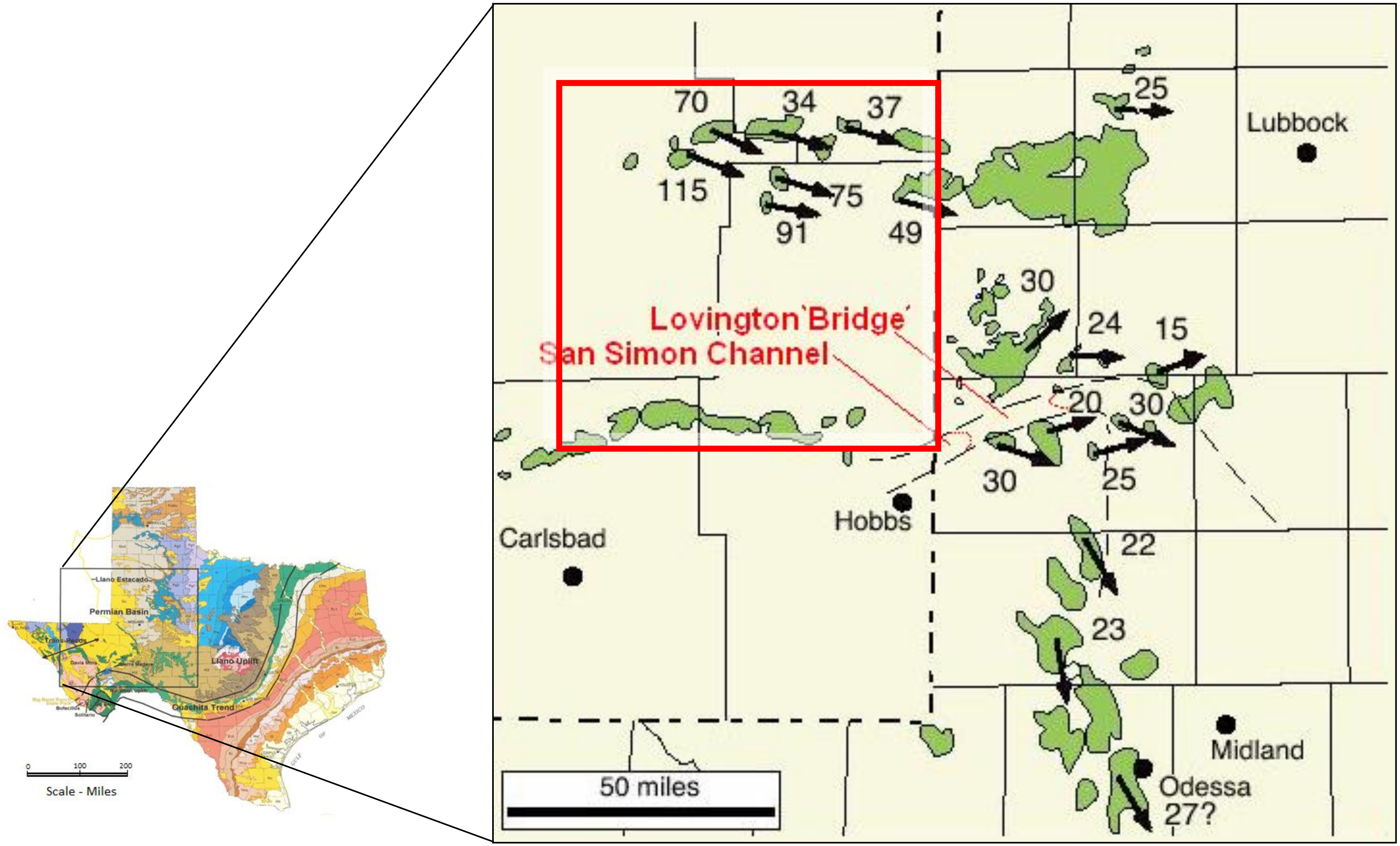
Closing of the Midland Basin**



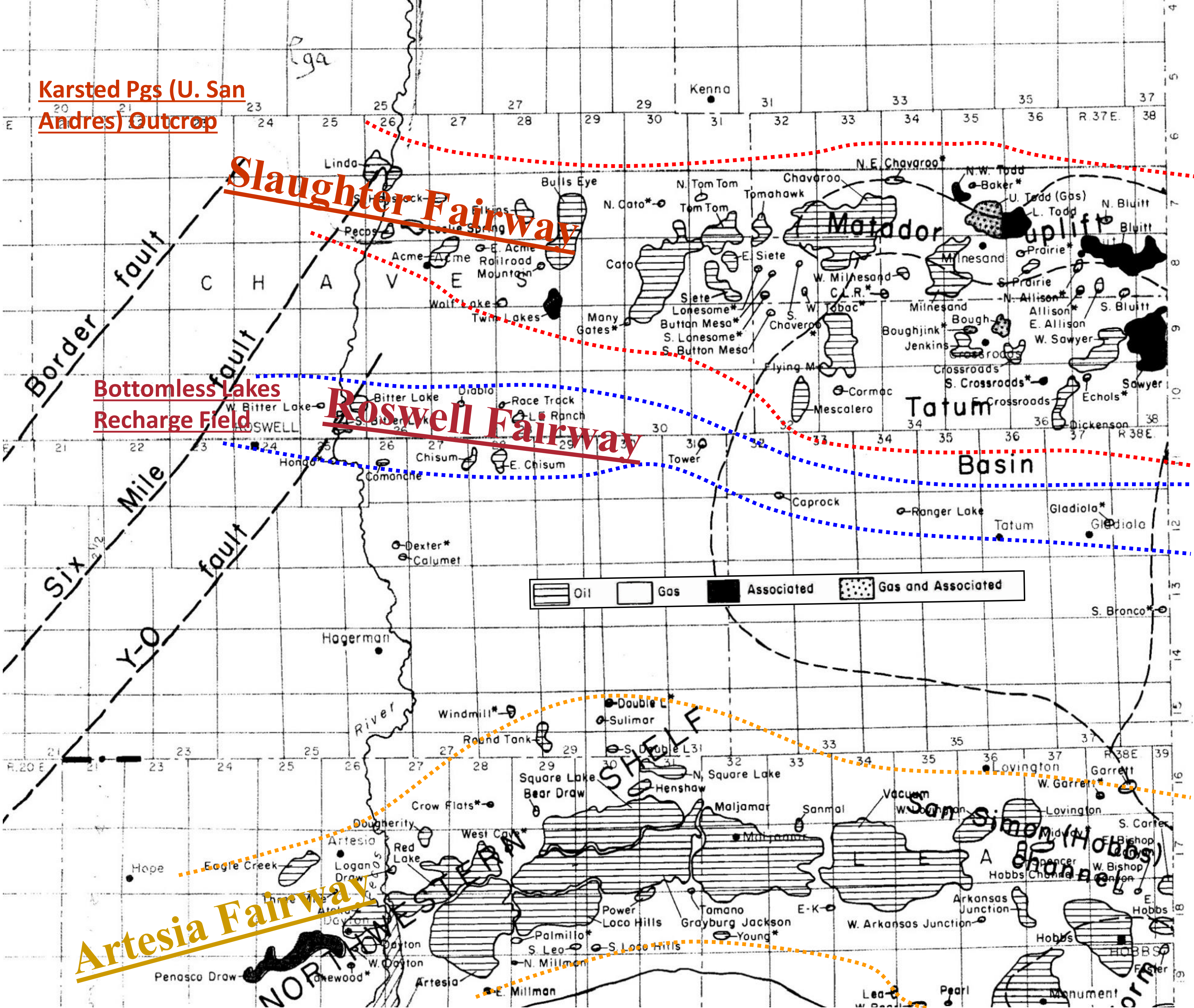
The direction of OWC tilt may be influenced by the age of the producing interval and it's relationship to the shelf margin

* Brown, 1999,
** Ward et al, 1986

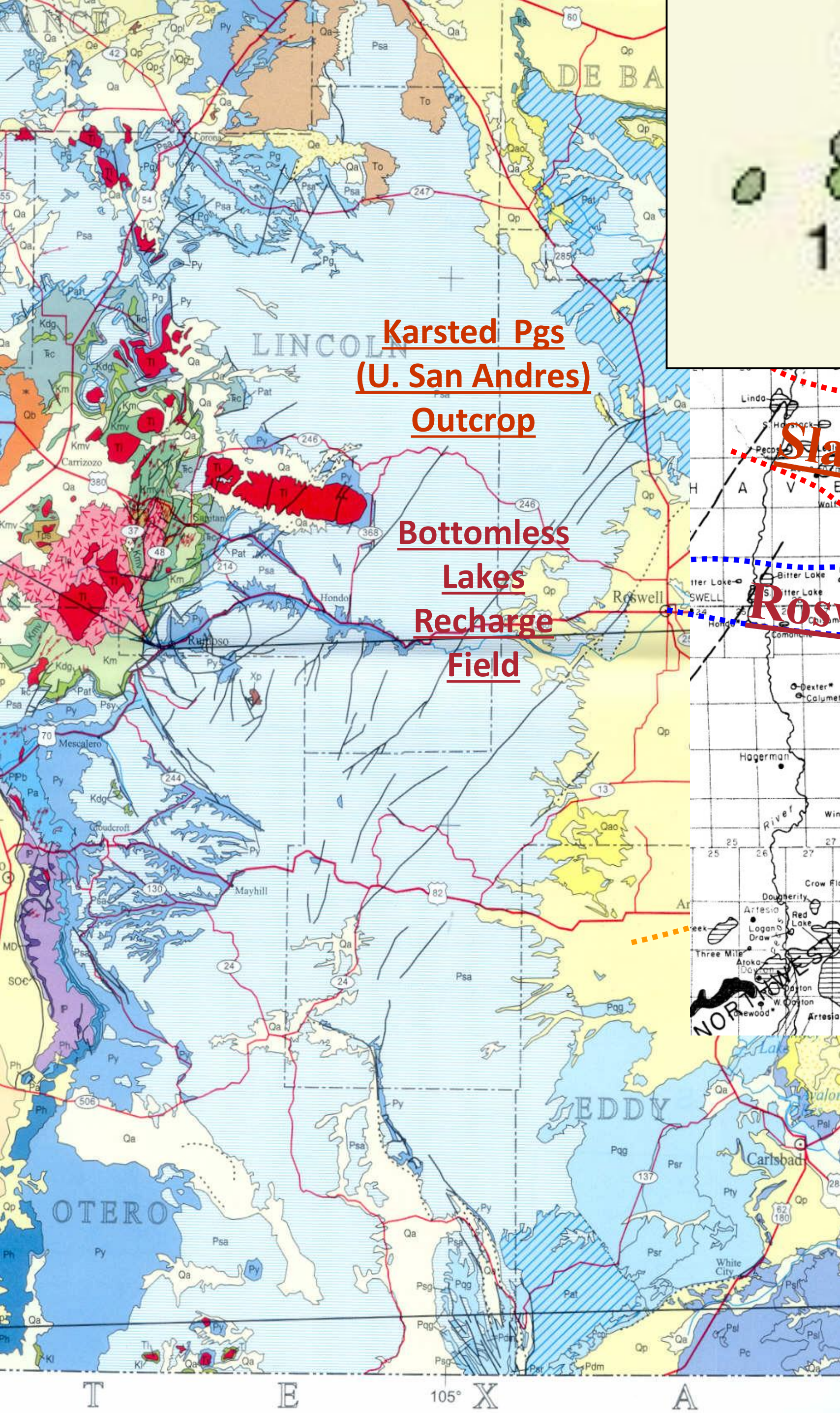
Distribution of Tilted Oil-Water Contacts in the Northern Shelf & Central Basin Platform Areas of the Permian Basin*

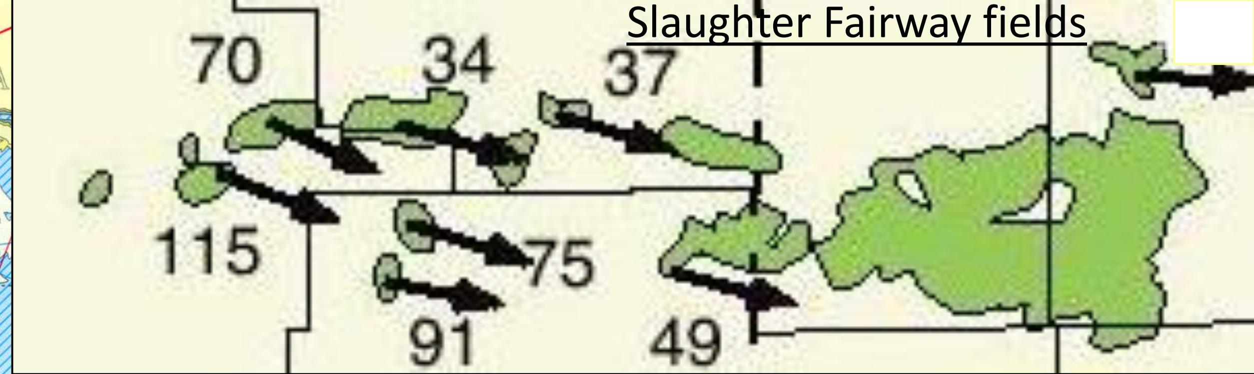


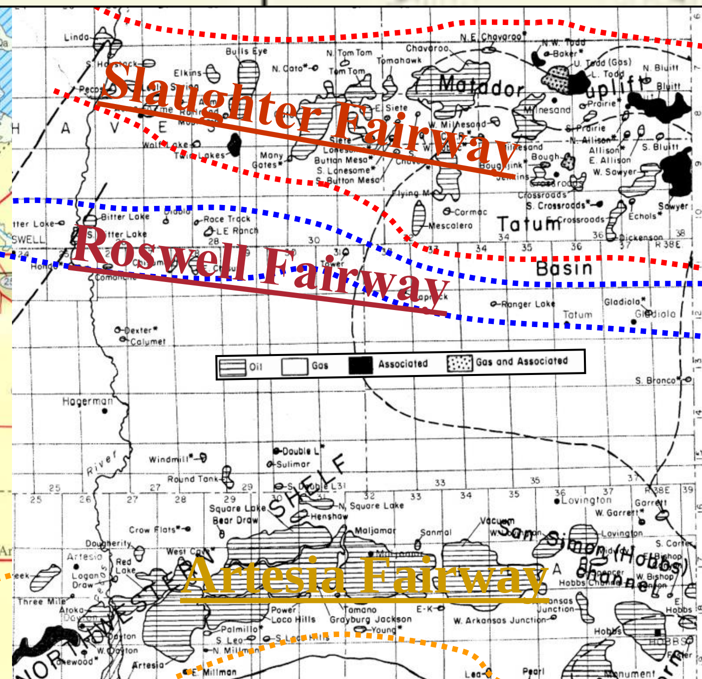
<u>* Adapted from Alton Brown, WTGS Fall Symposium (2001)</u>



Karsted Pgs (U. San Andres) Outcrop
Slaughter Fairway
Bottomless Lakes Recharge Field
Roswell Fairway
Artesia Fairway
Border fault
Six Mile fault
Y-O fault
CHAVES
Matador uplift
Tatum Basin
NORTHWESTERN SHELF
San Simon (Hobbs) Channel
LEA
Kenna
Roswell
Hagerman
Artesia
Hope
Tatum
Lovington
Hobbs
Pecos River
Oil
Gas
Associated
Gas and Associated

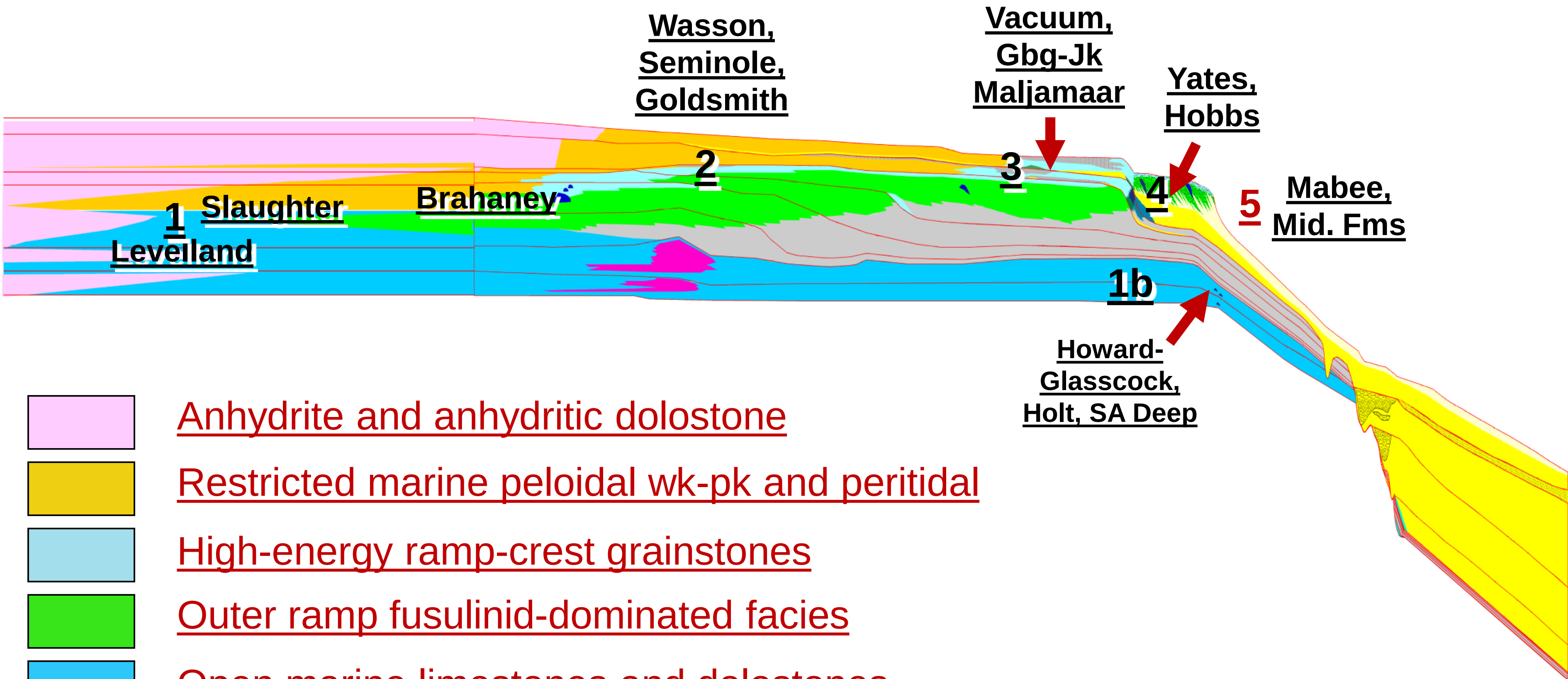






Relationship of San Andres outcrops and San Andres Fairways in New Mexico.

San Andres Reservoir Main Pays can be found in Restricted Marine, High Energy Ramp Crest, Outer Ramps, or Open Marine

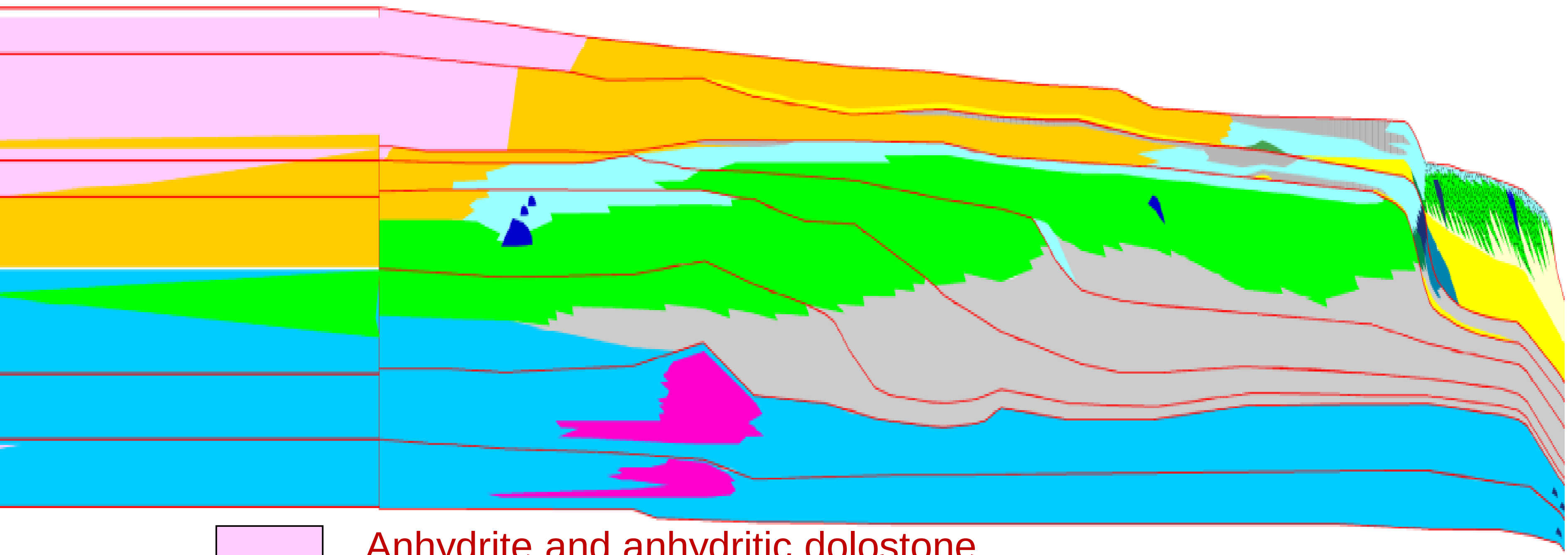


- Anhydrite and anhydritic dolostone
- Restricted marine peloidal wk-pk and peritidal
- High-energy ramp-crest grainstones
- Outer ramp fusulinid-dominated facies
- Open marine limestones and dolostones,
- Deeper-water mudstones (Cutoff)

and most of these major fields have associated ROZ's

. Kerans,2006,

Whereas, most of the ROZ's are found in The Outer Ramp to Open Marine



Anhydrite and anhydritic dolostone

Restricted marine peloidal wk-pk and peritidal

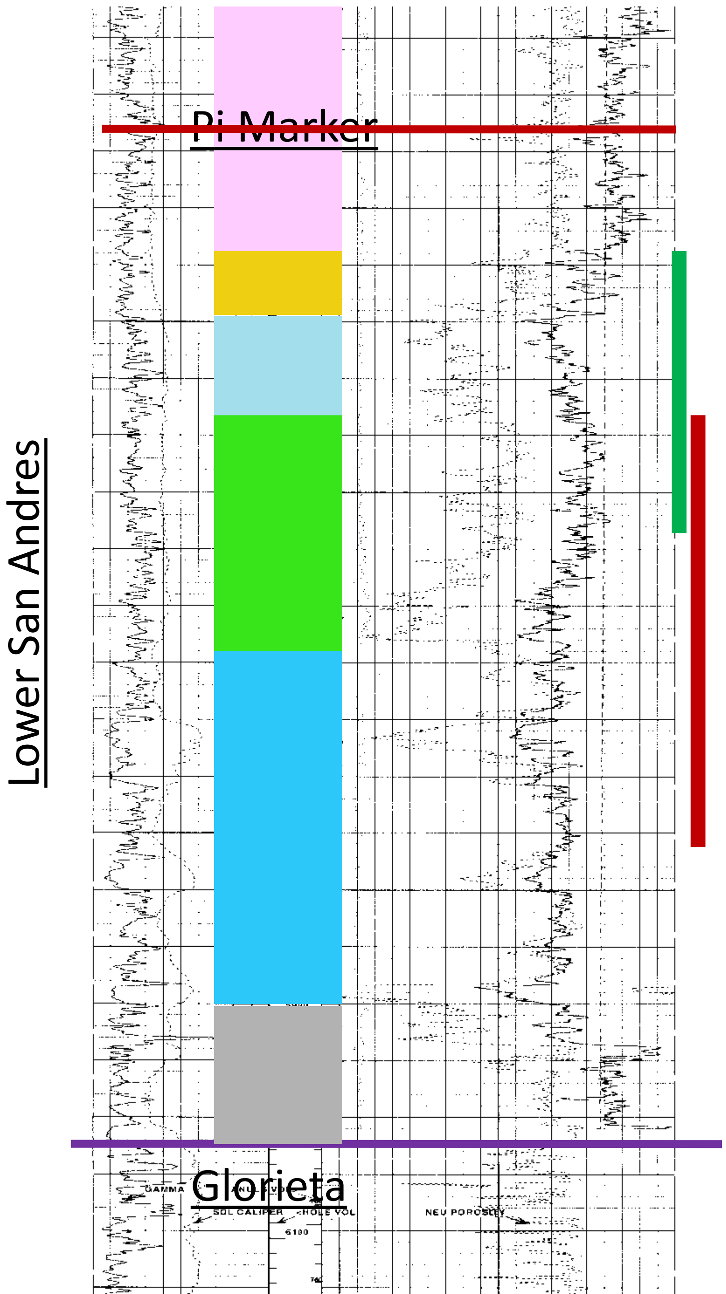
High-energy ramp-crest grainstones

Outer ramp fusulinid-dominated facies

Open marine limestones and dolostones,

C. Kerans, Bureau of Economic Geology, PBGSP Annual Meeting, 2/27-8/06, Austin, TX

Huntington 2 Walden
501 34599



MAIN PAY

ROZ

Anhydrite and anhydritic dolostone

Restricted marine peloidal wk-pk & peritidal

High-energy ramp-crest grainstones

Outer ramp fusulinid-dominated facies

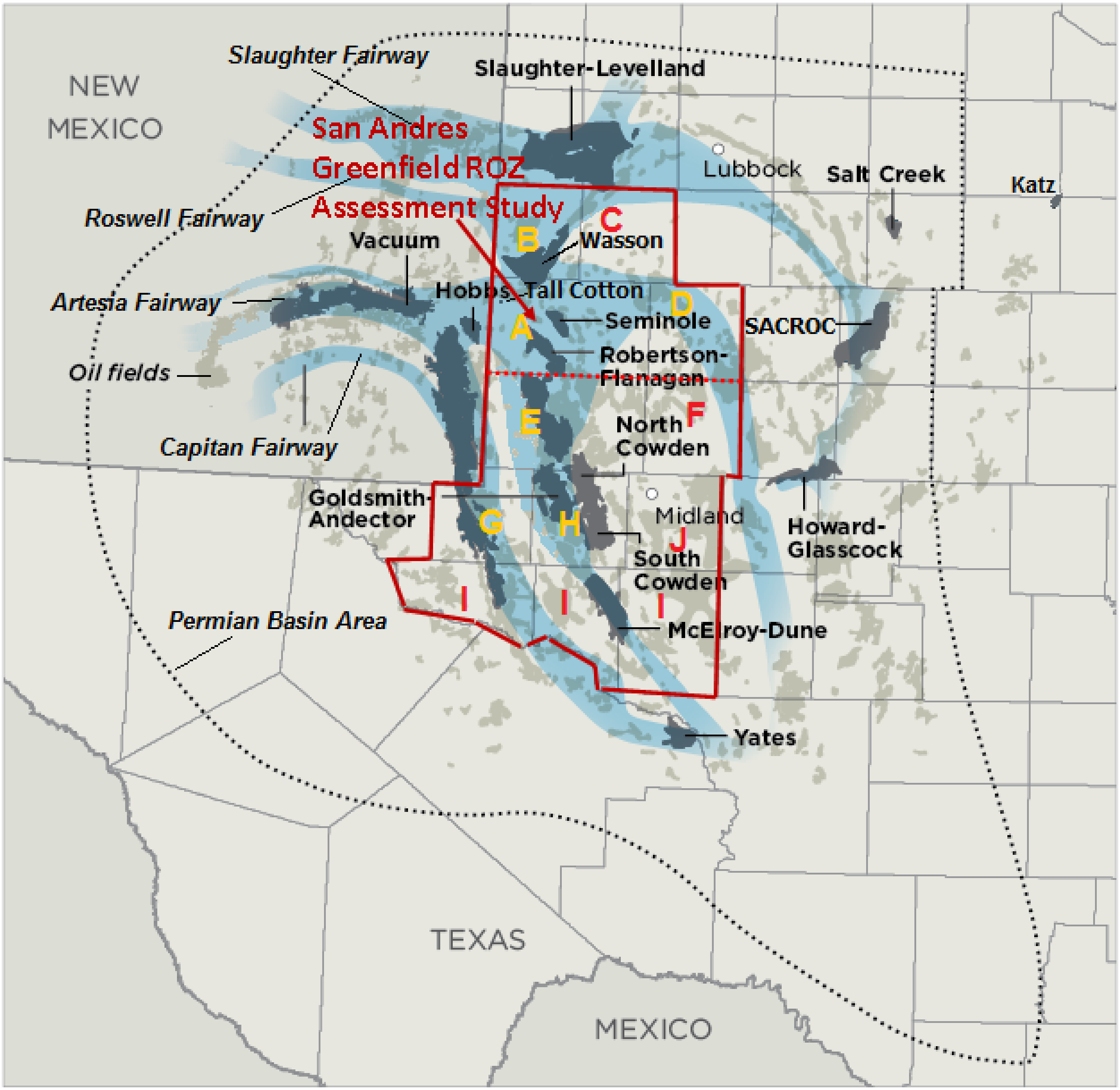
Open marine limestones & dolostones,

Deeper-water mudstones (Cutoff)

Lower San Andres facies tracts on Northwest Shelf (Yoakum), in overall shallowing upward sequence

Residual Oil Zone Fairway Mapping with Superimposed Major Permian and Pennsylvanian Oilfields

and Showing the First Pure ROZ Greenfield ROZ CO_2 Project



Post Entrapment Changes to the Oil and Rocks

Section 2 (Cont'd)

Biogeochemistry In Residual Oil Zones

Midland, Texas

David Vance

ARCADIS

2015 CONFERENCE WEEK

Biogeochemistry In ROZs
Key Processes

- Introduction
- Microbial Self Limitation
- Diagenesis
- Wettability

Introduction

Anaerobic Microbial Processes
and the Biogeochemistry of Sulfur in San Andres ROZs

ROZ Oil BioGeoChemistry

Biodegradation Microbial Processes

Biodegradation Process Controls

Active Microbes ↔ In Situ ROZ Properties

Microbial Processing of Petroleum with Positive and Negative Feedback Loops

- Specific degradation pathways can be associated with single or multiple organisms with gene coding that can be turned on/off in response to conditions
- Often degradation sequences require consortia of multiple microbes in cooperating communities
- Hydrocarbon structure has an effect
- Biosurfactant production effects interfacial properties
- Degradation by-products like H_2S can be inhibitory to microbes

- Availability of electron acceptors in order of importance: Sulfate; Iron; Bicarbonate; Nitrate; Oxygen
- Salinity/Temperature/Pressure
- Porosity/Permeability/Surface Area and modification by microbial activity
- Hydraulic heads and flow rates
- Chemistry of the mineral matrix
- Water/Petroleum/Gas interfacial forces
- Chemical, physical properties and structure of the petroleum

Anaerobic Bacteria

1) Requirements of Life
    1) Have to Live in Water
    2) Use Components out of the Oil for carbon and energy
    3) The sulfur in sulfate acts as a powerful oxidizing agent **(accepting 8 electrons donated by the hydrocarbon)** to support energy generation (the Microbes are the Agents or ‘Brokers’)
2) All Requirements Met in the ROZ (not met in the MPZs)
3) Evidence of their “Work”
    1) Soured Oil and Gas
    2) Occasional Free Sulfur
    3) Altered Rock Properties

Fundamental Anaerobic Redox Chemistry Electron Transfer Capacity

Sulfate has 8 reacting electrons between sulfate (S^{+6}) and sulfide (S^{-2})

Iron only has 1 reacting electron between ferric iron (Fe^{+3}) and ferrous iron (Fe^{+2})

Carbon has 8 reacting electrons between carbon dioxide (C^{+4}) and methane (C^{-4})

Redox Based Biogenic Reactions

$$_{(aq)}CaSO_4 + CH_4 \rightarrow CaCO_3 + H_2O + H_2S$$

S is +6 C is -4 C is +4 S is -2

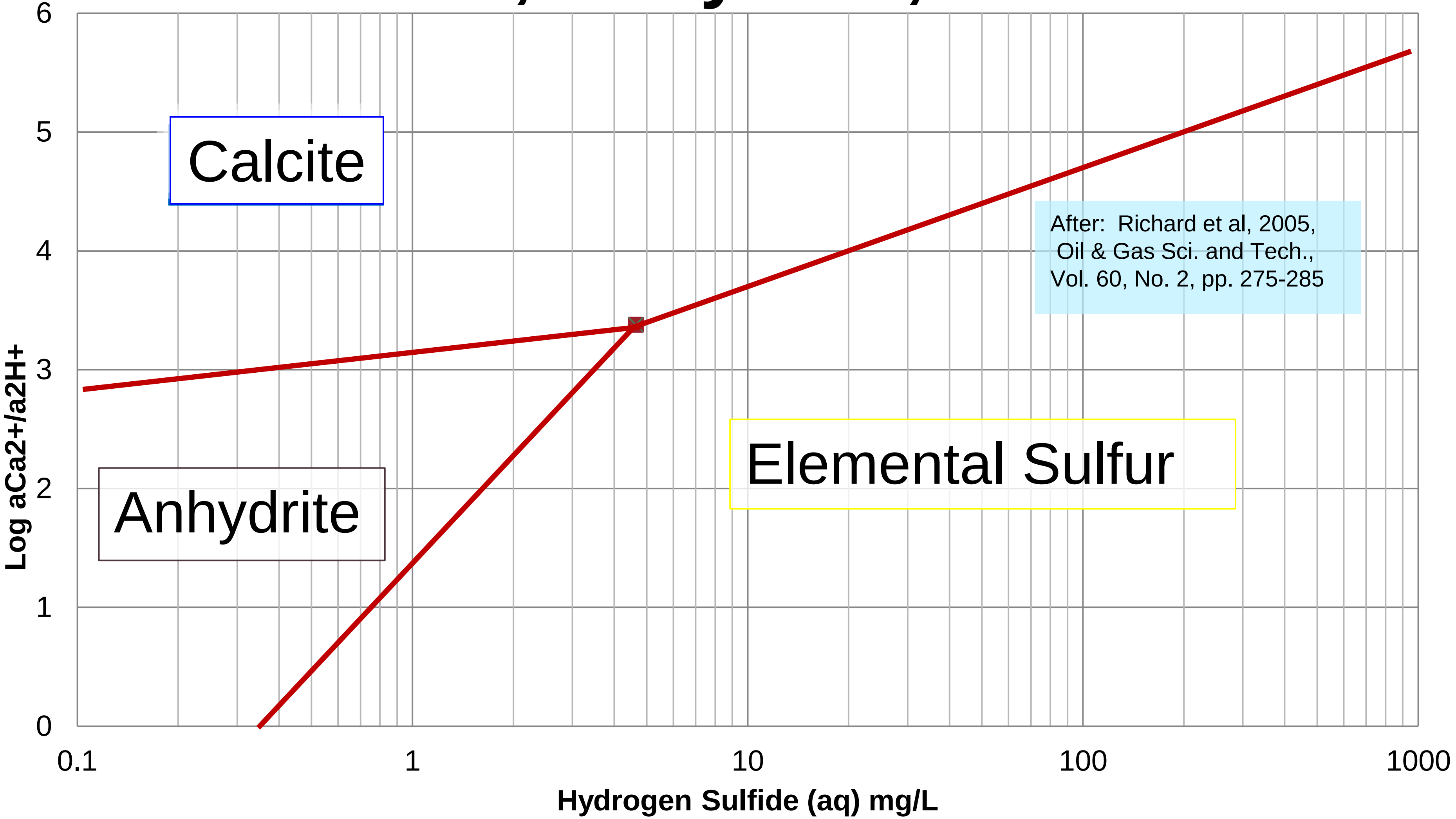
Microbes remove 8 Electrons from the Carbon and transfer them to the Sulfur

H_2S is Often Oxidized Back to Elemental Sulfur S^0

Dolomitization Typically Follows as Well

$$CaCO_3 + Mg \rightarrow MgCa(CO_3)_2$$

Modified Activity Diagram – Calcium, Anhydrite, Sulfur



Biogeochemistry
Microbial Self Limitation
(MSL)

Why Producible Oil Saturations are in ROZs In Spite of Biodegradation and Water Sweeping Over Geologic Time Frames

There are two dynamic processes that preserve oil in an ROZ

One is Microbial Self Limitation

- Daughter Products of Microbial Biodegradation stop the Degradation Process

The Second is the Creation of an Oil Wet System

- Oil is physically retained on mineral surfaces making it resistant to physical hydraulic flushing

Microbial Self Limitation (MSL)

The Effect of Hydrogen Sulfide from Sulfate Reduction is Dominant in Sulfate Rich Systems (Generating Sour Oil)

In Sweet Oil Systems with No or Limited Sulfur Inhibition of Methanogenesis is More Important

The Presence of Iron (Particularly in Clastic Systems) may Limit MSL Effects

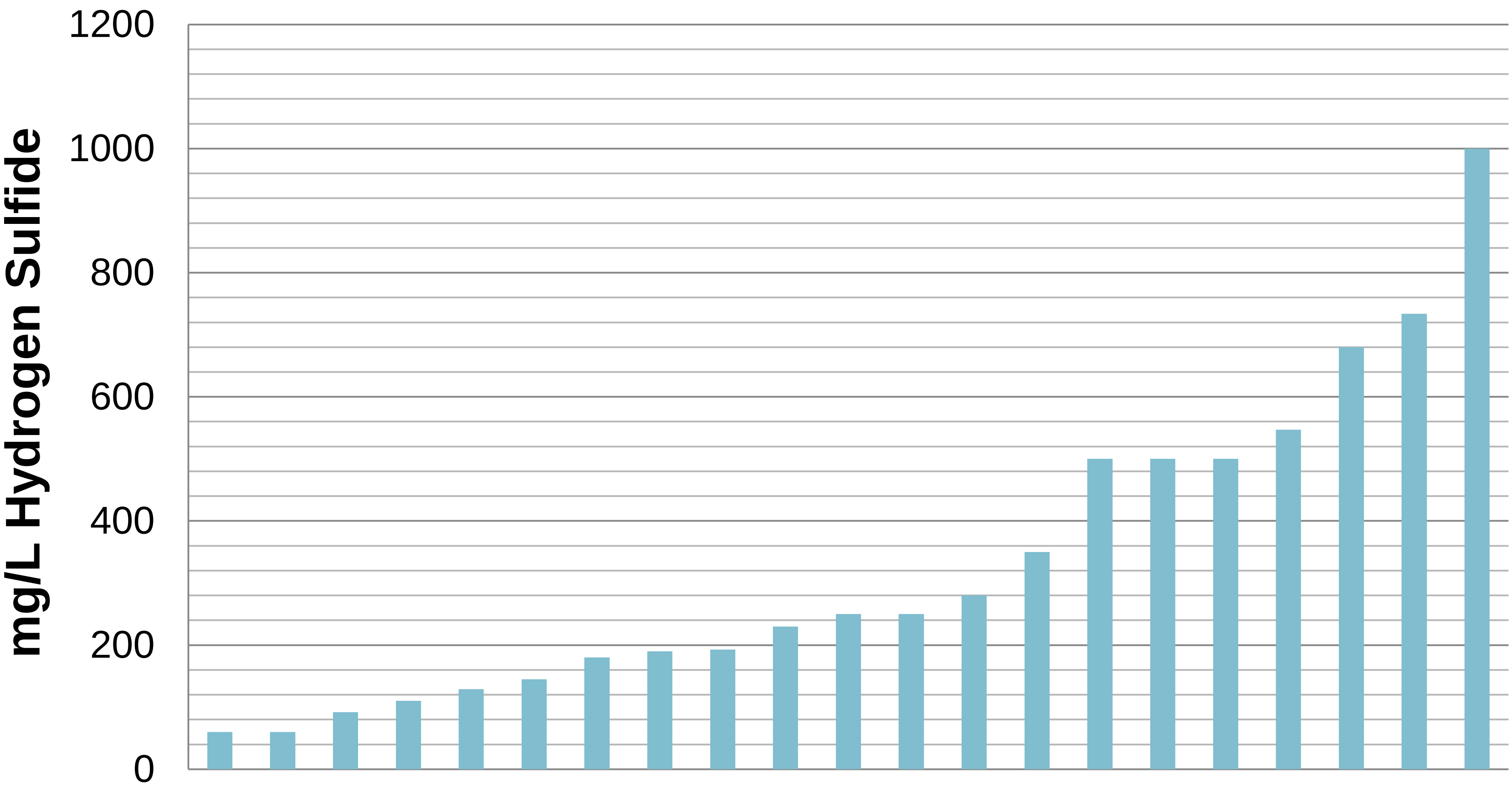
Irrespective, MSL Governs Residual Oil Concentrations and the Geometry of ROZs and Transition Zones

That knowledge may be used as an Assessment and Exploration tool

2015 CONFERENCE WEEK

ARCADIS

Published Concentrations of H_2S that Causes Microbial Inhibition



H_2S – Phase Distribution
Initial Rules of Thumb

- The mass loading of H_2S in the petroleum phase will be **3 to 10 times** higher than the concentration of H_2S in water in contact with that petroleum
- The mass loading of H_2S in any confined free gas phase can be **100 times** the concentration of H_2S in the petroleum

Microbial Self Limitation (MSL) *Consequences*

MSL Governs Residual Oil Concentrations and the Geometry of ROZs and Transition Zones

MSL Effects Apply to Sour and Sweet Oil Systems, Carbonate and Clastic Geologic Systems

Applicable to Petroleum Systems Shallow Enough to Allow for Temperatures Suitable for Microbial Activity

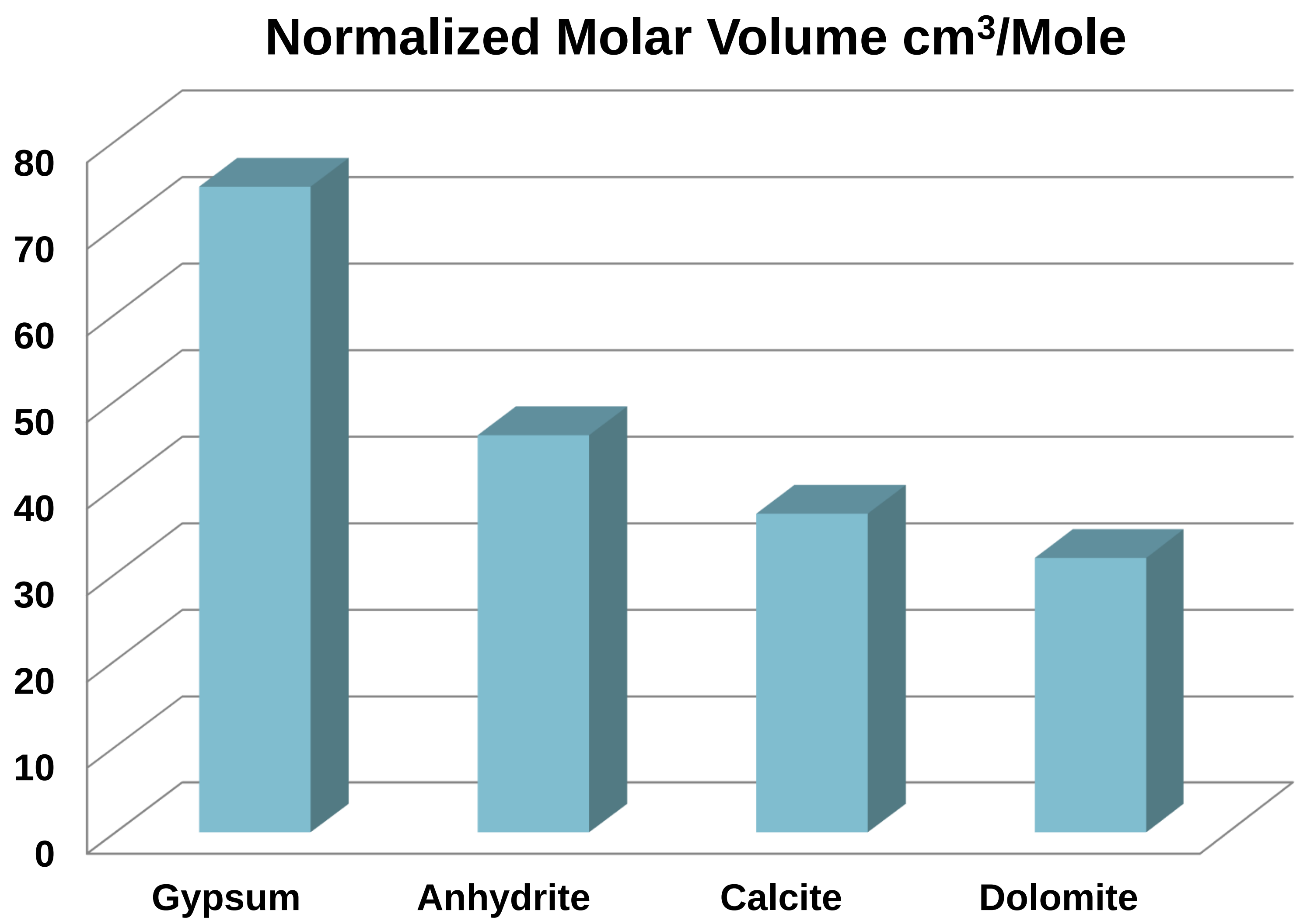
Knowing that MSL is Taking Place can be used as an Assessment and Exploration tool Allowing for Fact Based Economic Decision Making Regarding Targeted ROZs

Biogeochemical Diagenetic Processes

Biogeochemical Diagenesis

- Sulfate Reduction of Anhydrite or Gypsum in the Mineral Matrix Increases Porosity
- Dolomitization also Increases Porosity
- Biogeochemical Components to Dolomitization
  - Biofilms Associated with Microbial Activity have Negative Charges and Scavenge Magnesium
  - Partially Biodegraded Petroleum has Negatively Charge Carboxyl Groups that Scavenge Magnesium
  - All of These Processes Preferentially take Place on Mineral Surfaces as Coatings – Exceeding Diffusion Effects and Enhancing Dolomitization Processes
- All of These in Turn Also Induce Oil Wet Conditions

Changes in Molar Volume



Biogeochemical Controls on Oil Wettability

An Oil Wet System Is Resistant To Physical Hydraulic Sweeping Over Geologic Time

Complex Interfacial Forces are at Work

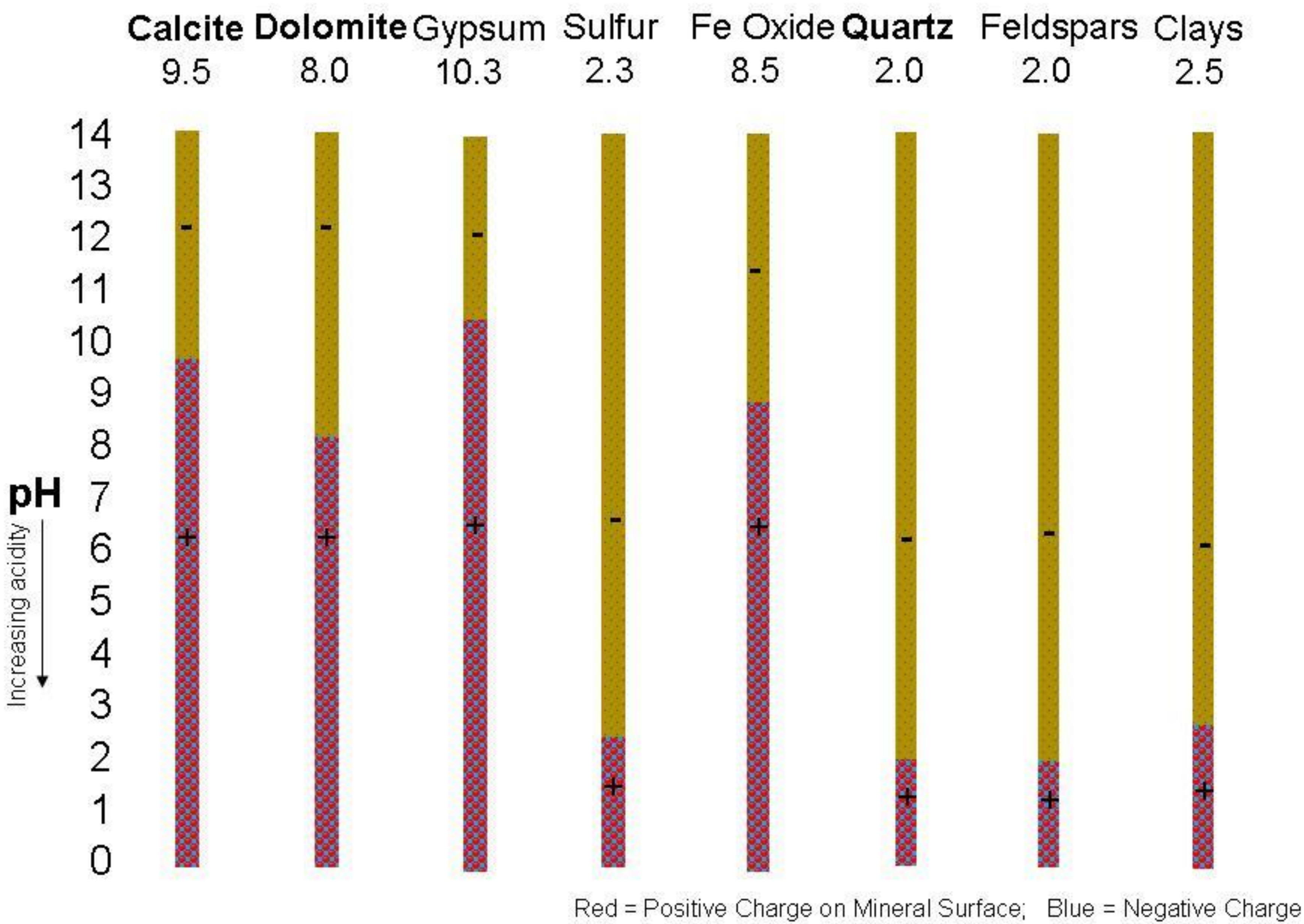
Mineral surfaces have a positive charge at normal pH and those surfaces may have biofilms with positively charged sites

Initial Biodegradation Produces Smaller and lighter molecules that have a higher velocity than larger molecules or agglomeration of molecules

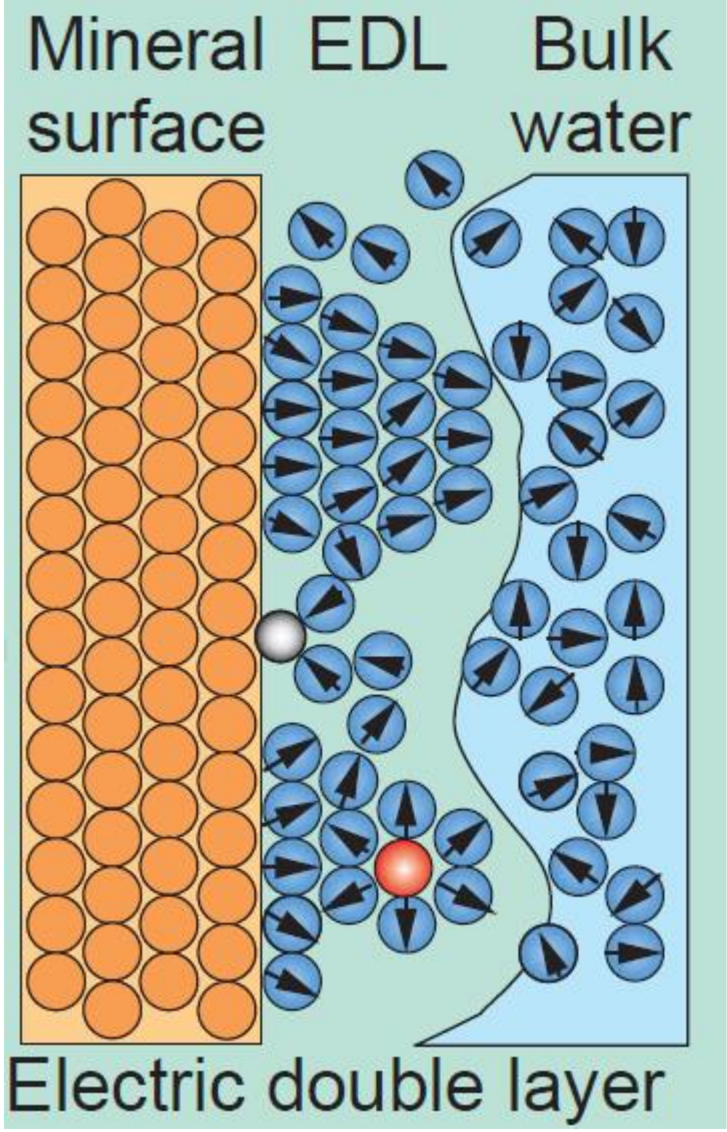
Petroleum biodegradation also generates small soluble charged and polar molecules

Higher physical kinetic velocities of smaller molecules contribute to migration to a mineral surface

pH Point of Mineral Surface Zero Charge

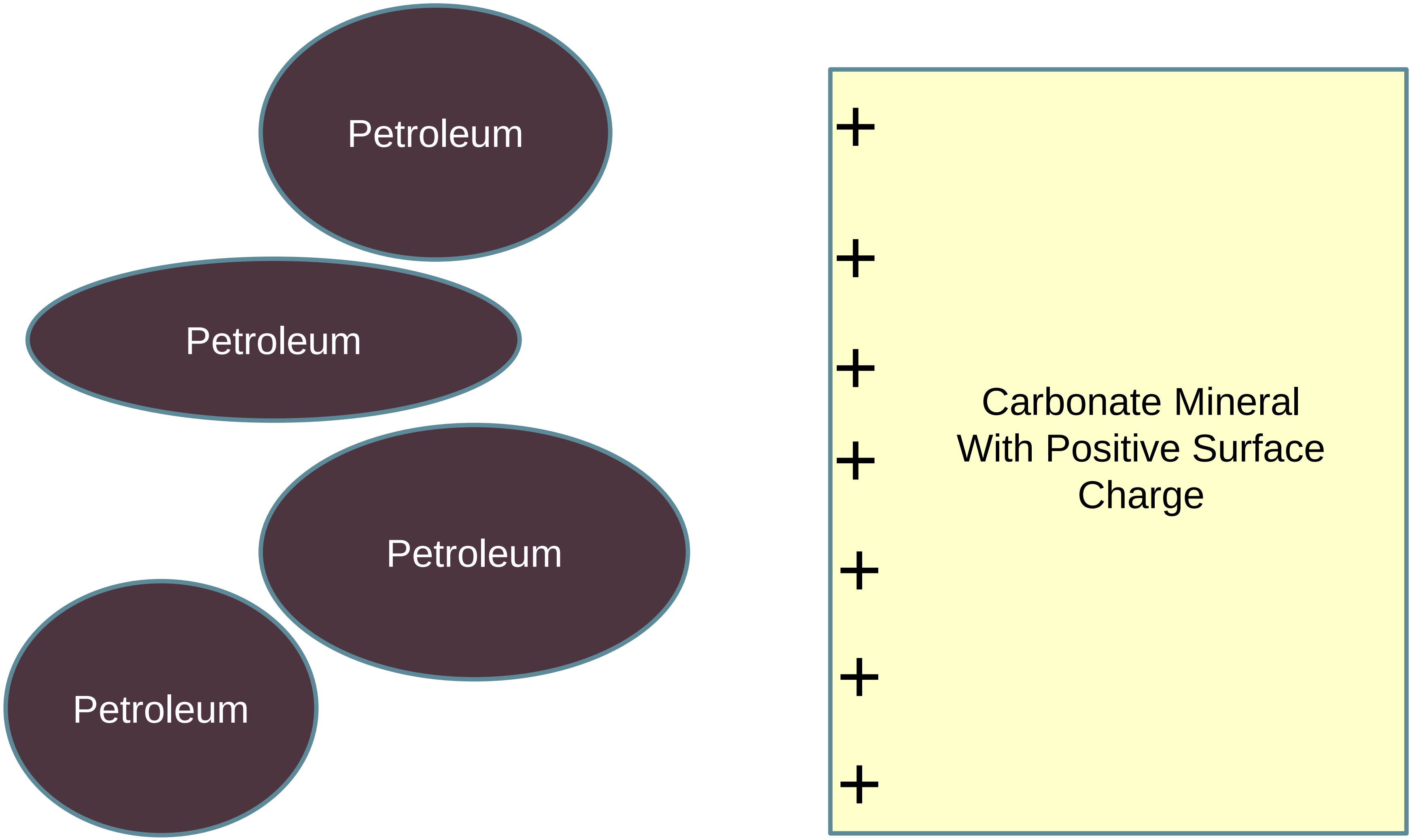


Water Wet Mineral Surface

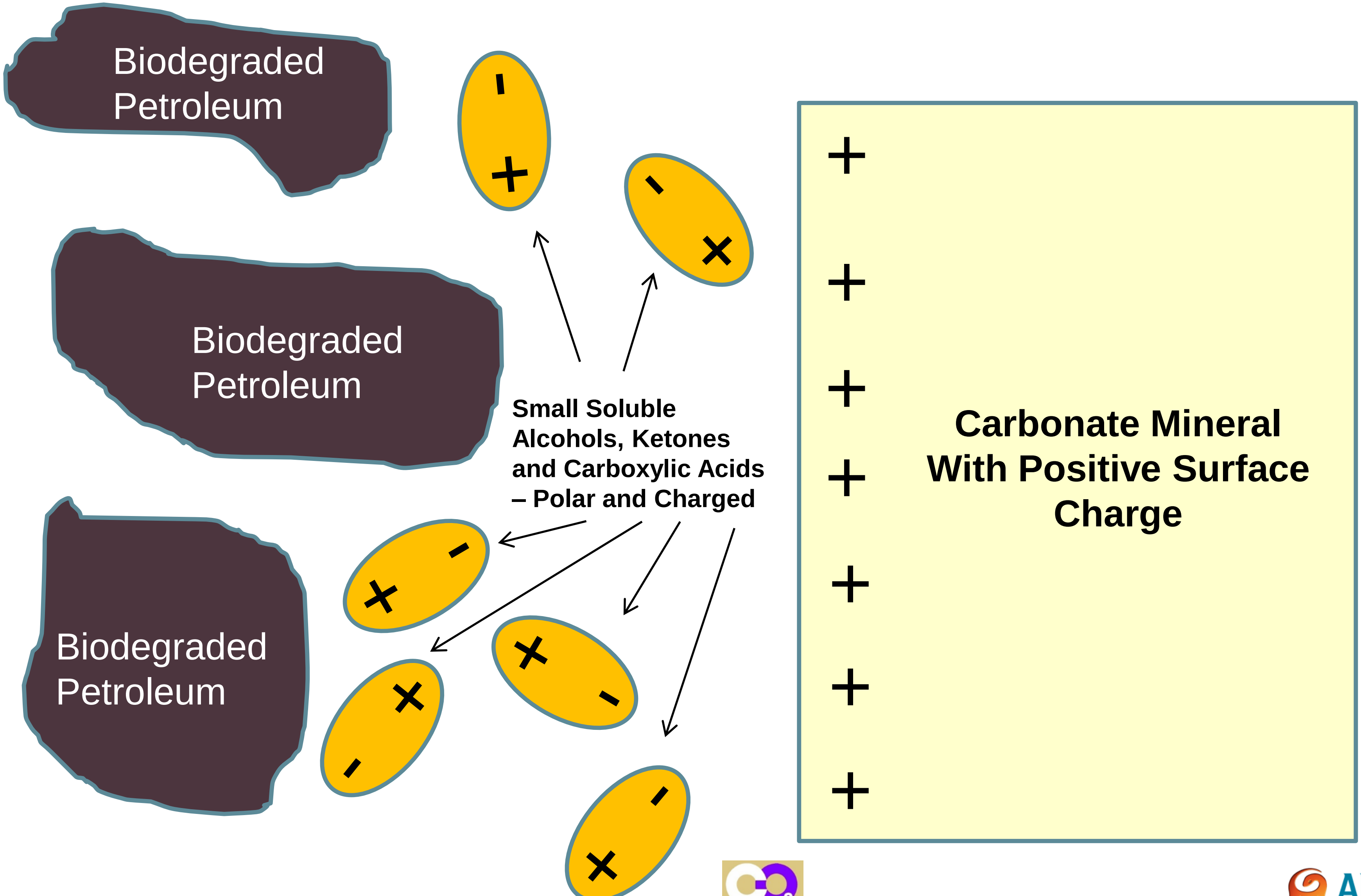


After Brown 2001
Science Vol. 294
pp. 67-70

Becoming Oil Wet

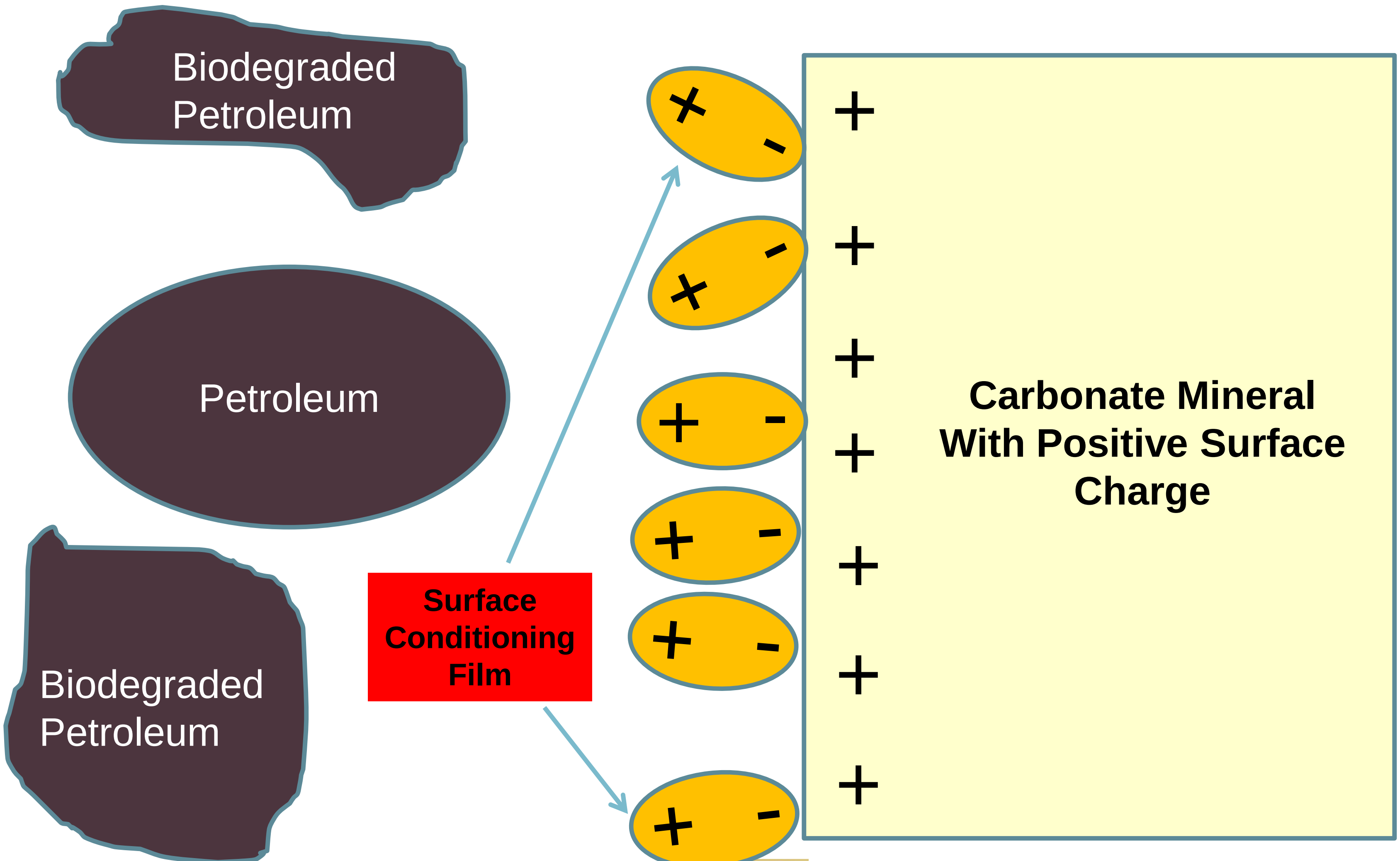


Becoming Oil Wet
Biodegradation & Biogenic Products



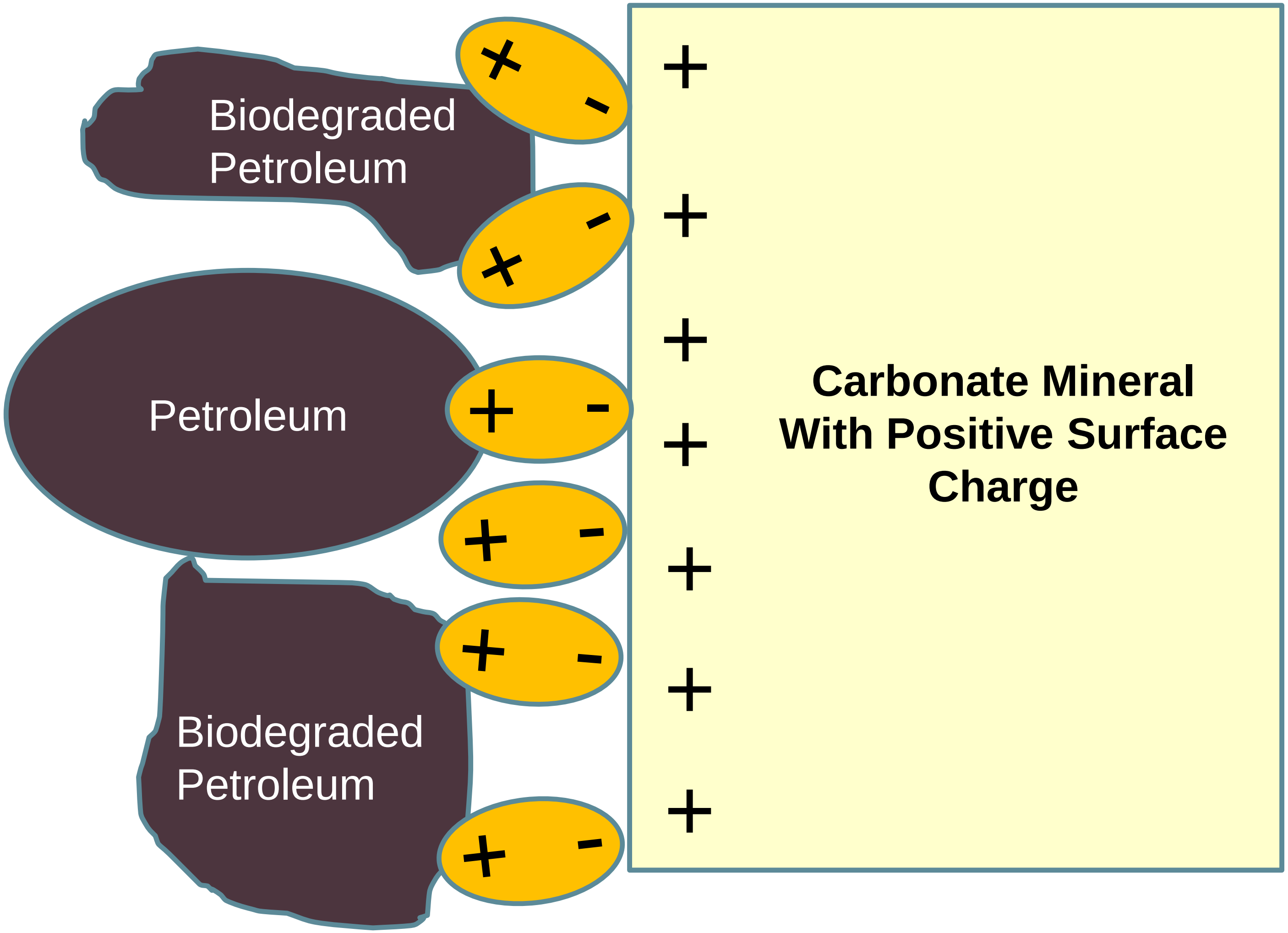
Becoming Oil Wet

Attachment of Small Soluble Charged and Polar Species – Degradation and Biogenic



Becoming Oil Wet

Co-Adsorption and Agglomeration on Non-Polar Liquid Hydrocarbon



Oil Wetting Summary

Sulfate reduction generates new dolomitic mineral surfaces with positive charges under normal pH conditions that may also be coated with biofilms that contain positively charged sites

Sulfate reducing microbes biodegrade constituents in petroleum producing negatively charged carboxylic acid groups in the petroleum and small polar alcohols and ketones that go into the dissolved phase

Light negatively charged and polar constituents adsorb to the mineral surface first, followed by heavier hydrocarbons, creating an oil wet mineral surface

The Role of Microbial Biogeochemistry in ROZs (1)

- Biogenic processes working on the sulfate and carbonate mineral suites alter the mineral suites which are porosity (and permeability) enhancement processes

- Chemical composition of the petroleum
  - Hydrocarbons are initially consumed and degraded by sulfate reducing microbes (in the San Andres) – the evidence is that this is not anywhere near a complete consumption or degradation in the San Andres ROZs
  - **That process generates hydrogen sulfide that, if allowed to accumulate, inhibits further microbial activity at concentrations over 100 to 200 mg/L – Preventing total hydrocarbon consumption**

The Role of Microbial Biogeochemistry in ROZs (2)

The production of small soluble charged and polar organic species by biodegradation in combination with the new dolomitic surfaces initiates the oil wetting process

- Charged/Polar species attach to mineral surfaces
- Non-polar and liquid petroleum then adsorb to the film and agglomerate
- Biogenic diagenesis also assists with the modification of mineral composition and subsequent changes in system porosity

Thank you

dvance@arcadis-us.com