Modeling Reservoir Rock and Formation Fluid Geochemical Interactions: Implications for CO_2 Sequestration from Citronelle Oil Field, Alabama*

Amy Weislogel[1], Rona J. Donahoe[2], George Case[1], Keith Coffindaffer[1], and Theodore Donovan[2]

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Please refer to related article, entitled "Spaghetti with Marinara: Tertiary Oil Recovery in a Cretaceous Redbed Succession, Citronelle Field, Alabama," Search and Discovery Article #20207 (2013).
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Abstract

The Citronelle field in southwest Alabama is the site of a U.S. Department of Energy pilot project on long-term geologic storage of CO_2 and the efficacy of CO_2-EOR. The target for injection is the Donovan Sand, an assemblage of arkosic fluvial sandstones intercalated with mudstones within the Lower Cretaceous Rodessa Formation. Following injection in November, 2009, production from updip well Permit 706 increased 20% to 493 bbl/month in 3 months. However, after February, 2010, monthly production decreased by 50% to 250 bbl/month, and it has not been >300 bbl/month, as of March 2012, despite water-flooding beginning March, 2010. Reservoir rock samples from 6 cored wells were analyzed via thin-section petrography, bulk geochemistry, and SEM-EDS to model reservoir rock composition. Sand mineralogy is uniform, but authigenic mineralogy and porosity are heterogeneous. Porosity averages ~2-5%, but locally is up to ~13%. A total of 47 SP well logs were used to estimate bulk density, from which an estimated porosity curve and porosity distribution map were generated. Paragenesis indicates early calcite cementation and later calcite cement dissolution, combined with feldspar alteration, generated secondary porosity. In contrast, authigenic clay is rare, suggesting an open diagenetic system during feldspar alteration. A later generation of anhydrite and calcite concretions and pyrobitumen occludes both primary and secondary pores. Formation fluids collected during late CO_2 injection and the subsequent water-flood show increases in the concentrations of Br, Ca, and Fe, along with pH decreases for most wells. Saturation indices for minerals in the reservoir rock do not indicate that mineral-dissolution reactions could cause the observed element-concentration trends. Instead, ion exchange reactions between H^+, sourced from carbonic acid generated by injected CO_2, and cations on the surfaces of reservoir minerals is likely to be occurring. A simplified TOUGHREACT model of fluid flow was unable to simulate the observed breakthrough times for CO_2 in any of the observation wells, suggesting the primary fluid transport pathway may be fracture-controlled; thus, fluids may interact with minerals of non-porous lithologies or may generate redistributional porosity/mineral trapping in calcite-cemented zones. Iron fouling or possibly interactions between calcite and acidic formation fluid may have caused observed lowered injectivity during water-flooding.

References Cited

Esposito, R.A., J.C. Pashin, D.J. Hills, and P.M. Walsh, 2010, Geologic assessment and injection design for a pilot CO_2-enhanced oil recovery and sequestration demonstration in a heterogeneous oil reservoir: Citronelle Field, Alabama USA: Environmental Earth Sciences, v. 60/2, p. 431-444.

Janssen, A. A. Putnis, T. Geisler, and C.V. Putnis, 2010, The experimental replacement of ilmenite by rutile in HCl solutions: Mineralogical Magazine, v. 74, p. 633-644.

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AAPG 2013 Annual Convention & Exhibition

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Theme 7: Advances in Carbon Capture Storage

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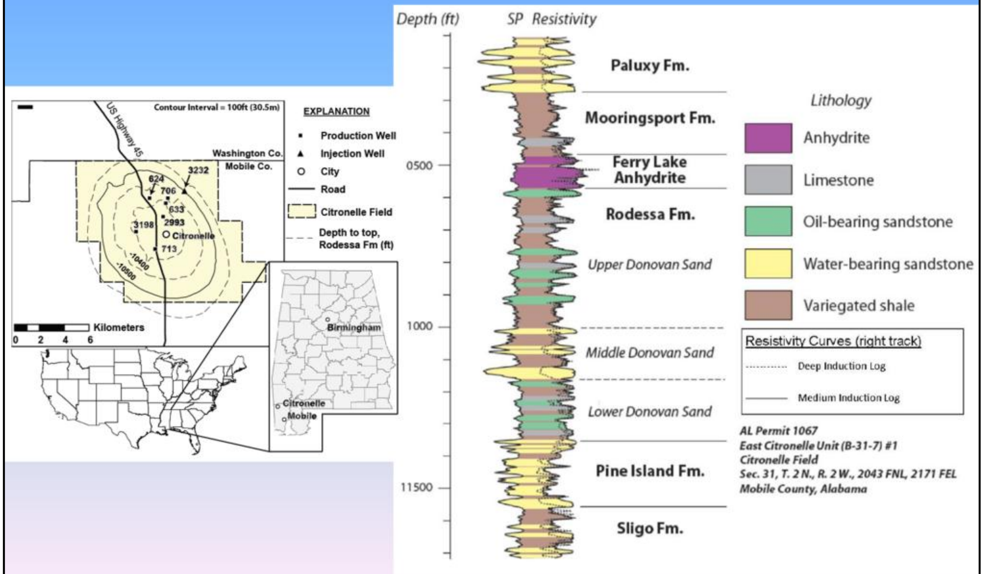
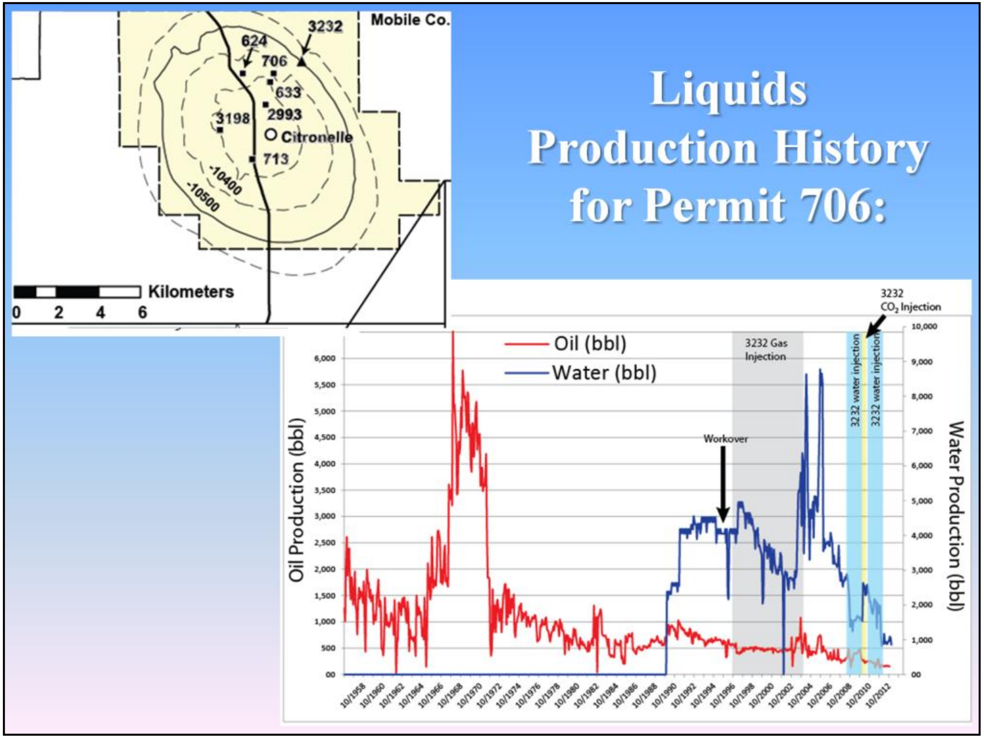
Donovan Sand of the Cretaceous Rodessa Fm.:

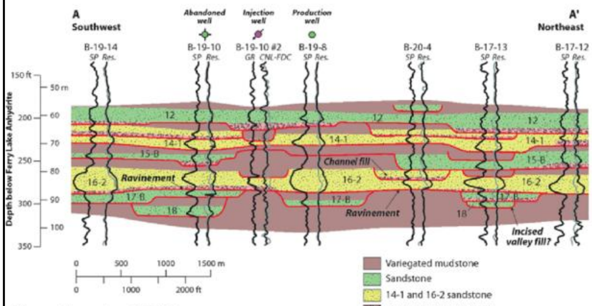


Presenter's notes: Our study is focused on the Donovan sand of the Rodessa Formation shown here. It is a subsurface unit of the AL coastal plain succession that formed in a Cretaceous marginal marine environment. The Rodessa Formation is the major reservoir unit of the Citronelle field located on the crest of the Citronelle dome, a giant salt-cored anticline with 4-way closure. There the Rodessa Formation has produced nearly 170 million barrels from ~524 wells and recovered about one-third of the oil in place The reservoir is sealed by the regionally extensive and thick Ferry Lake Anhydrite. Donovan pay interval, ~200 feet thick, contains 10's of productive sand bodies.

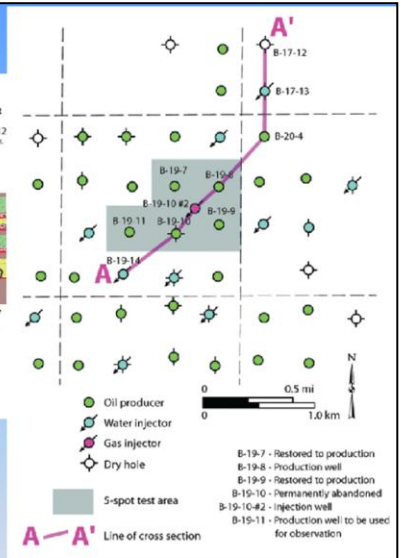


Presenter's notes: Citronelle Field has been in water flood since 1961. 63% of oil production was produced prior to 1973.

CO_2-EOR Project:

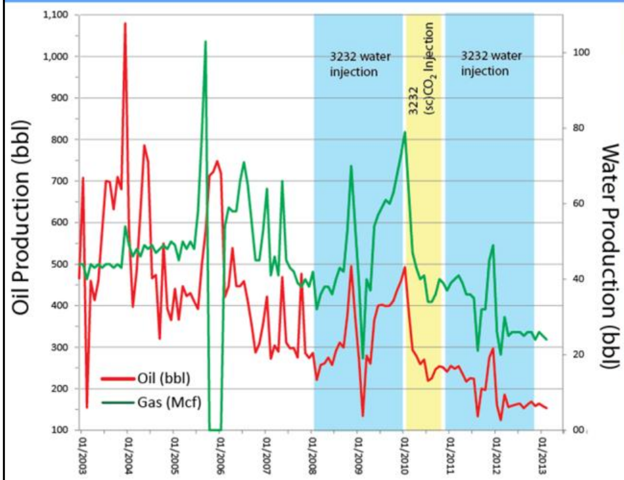


From Esposito (2010)

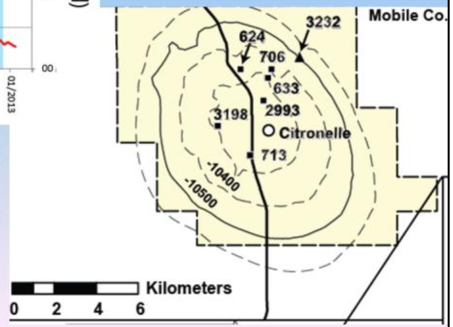


- 7500 tons of CO_2 injected into well Permit 3232/B-10-10 beginning late November 2009
  - Continuous injection achieved from 1/27-9/25/10
  - Average injection rate = 31 tons/day (35 tons/day anticipated by reservoir simulations)

Presenter's notes: DOE-sponsored project has been testing CO_2-EOR and potential storage in the Citronelle field.

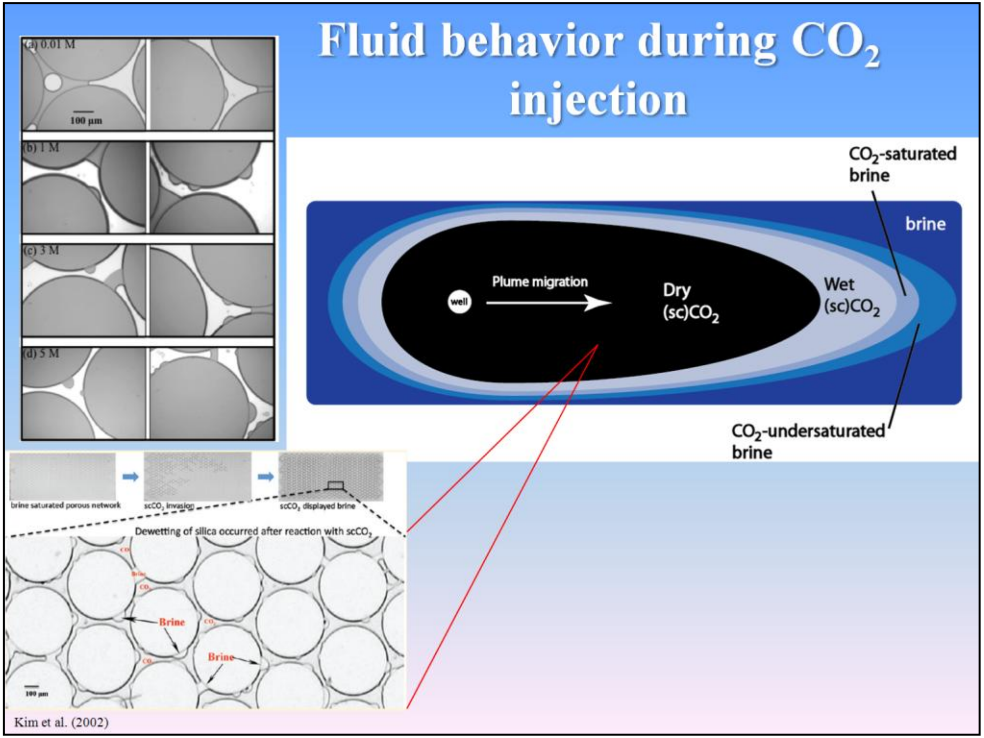


Impact of CO_2-EOR: Permit 706 production



- **Loss in production from Permit 1209/B-19-11**
- **Loss of injectivity to Permit 3232/B-19-10**
  - Injectivity to water decreased from ~140 to 20 bbl/day in the upper sand but remained approximately the same at 31-39 bbl water/day in the lower sand

Presenter's notes: Less-than-hoped-for, but still considered moderately successful as production decline appears to be flattening and holding steady after post-CO_2 waterflood.

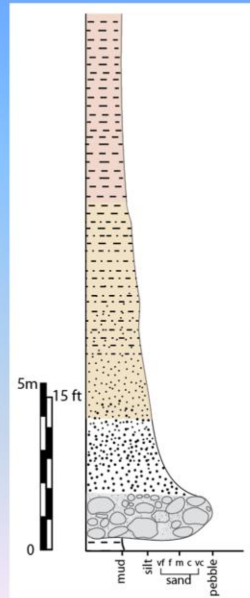


Presenter's notes: The goal of our project is to identify potential for interaction between pore fluids and reservoir rock. Injection of supercritical (sc) CO_2 forms a plume and CO_2 of that plume will not directly interact with rock-matrix minerals. However, lab studies of CO_2 injection show that connate fluids will be largely flushed from the pore network, but thin films and droplets of water can remain, and CO_2 could dissolve in that water and drive down pH of pore fluids.

Donovan Sandstone Lithofacies:

Upward-fining facies succession:

1. **Rudstone conglomerate**
2. **Cross-bedded fine sandstone**
3. **Massive to horizontally laminated fine sandstone**
4. **Ripple-laminated siltstone**
5. **Massive to horizontally laminated siltstone**
6. **Gray-green-red bioturbated siltstone**
7. **Horizontally laminated dark shale**
8. **Calcareous mudstone**



Donovan Sandstone Lithofacies

***red indicates hydrocarbon stain observed**

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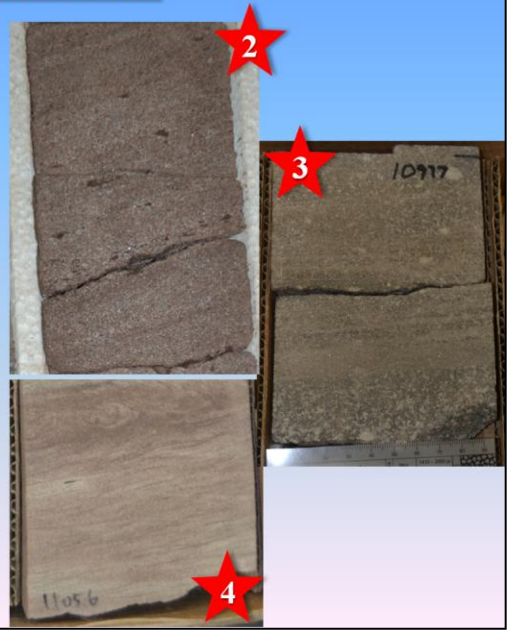
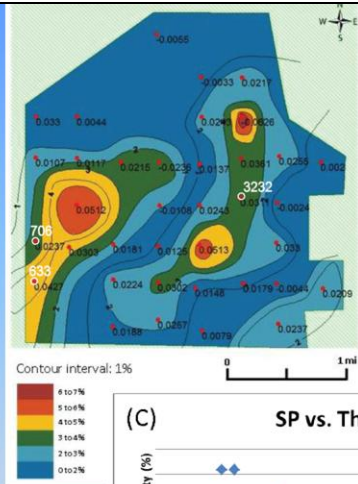
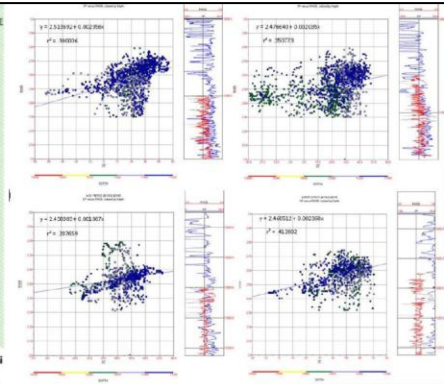
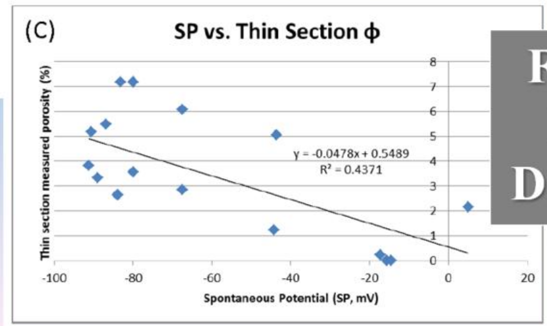


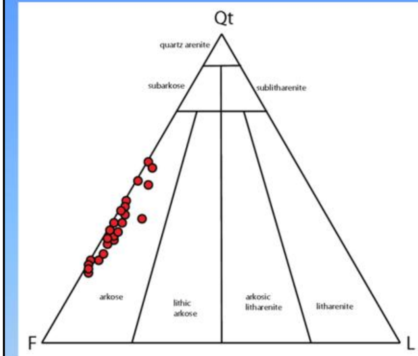
Field-scale Porosity Distribution

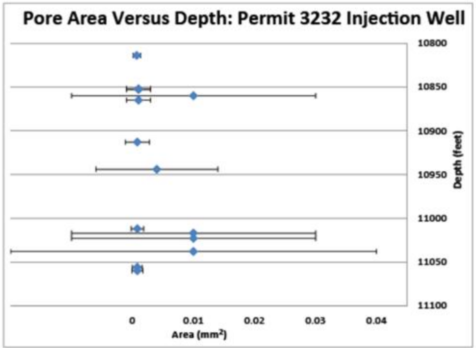


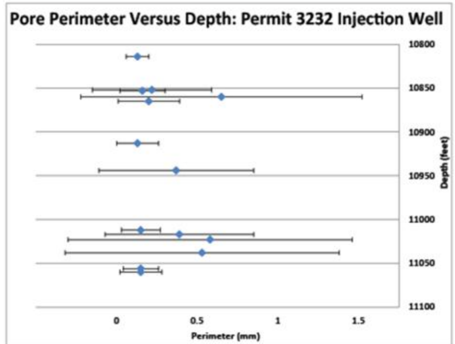




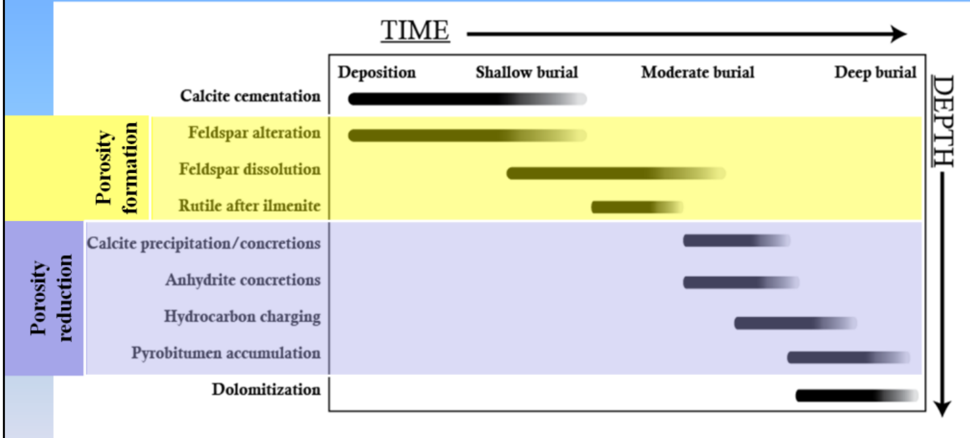
Homogeneous sandstone composition; Heterogeneous porosity development



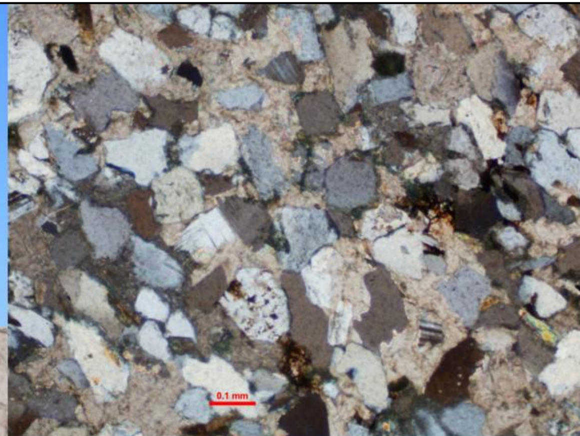


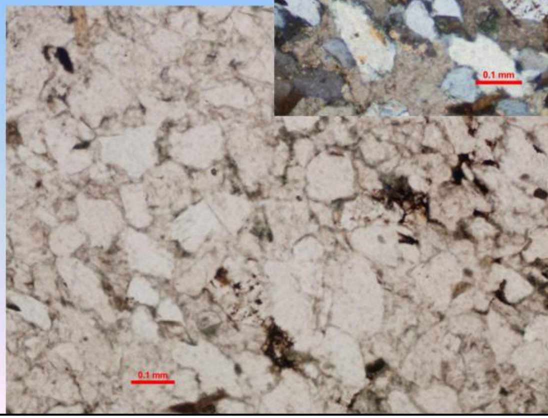


Diagenetic Evolution:



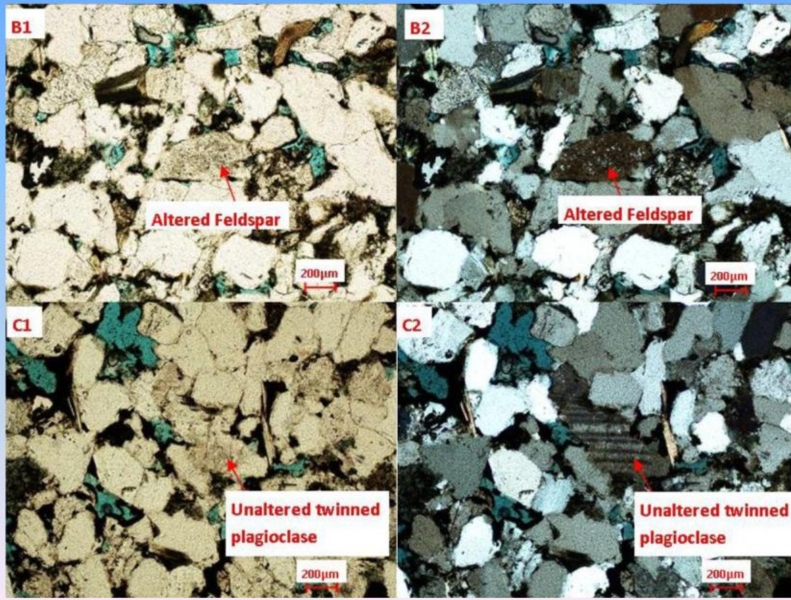
Early calcite cement:





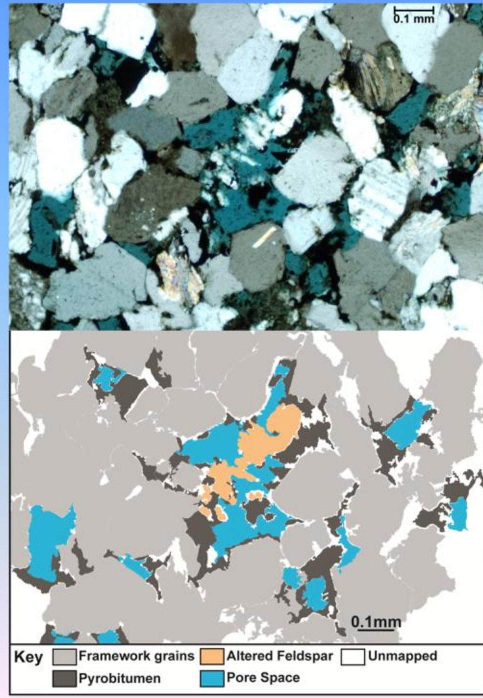
- Open grain packing preserved

Feldspar stability in compacted sandstone:



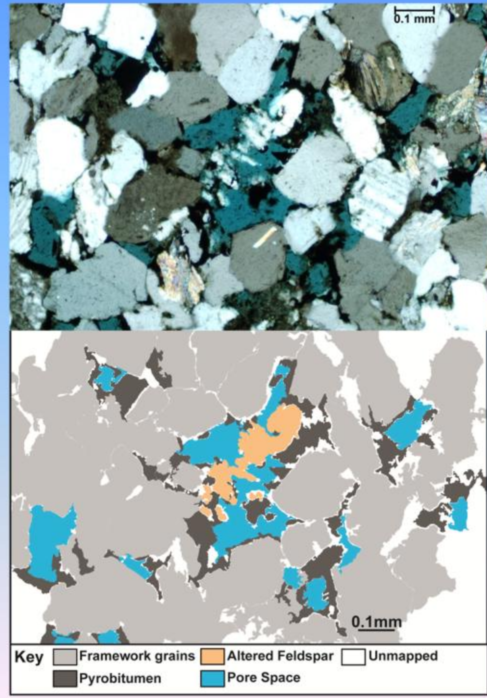
Feldspar dissolution

- *In situ* grain dissolution in moderately compacted sandstone
  - No early calcite cementation
- Creates secondary porosity
  - Meso-, micro-, & nano-scale

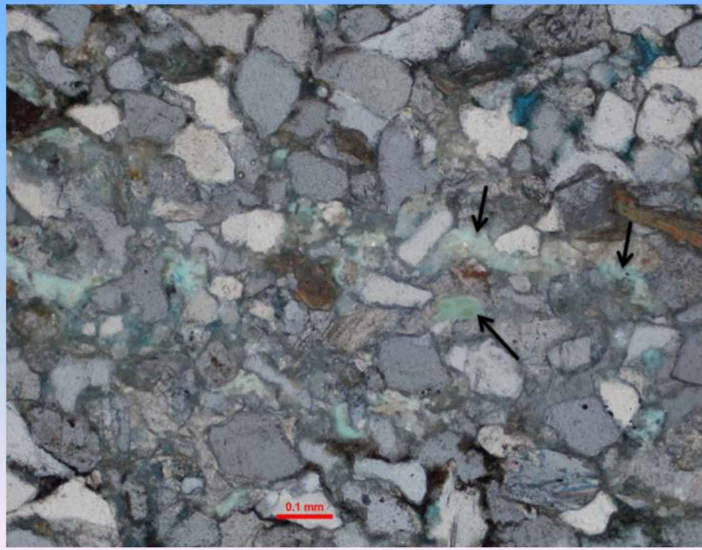


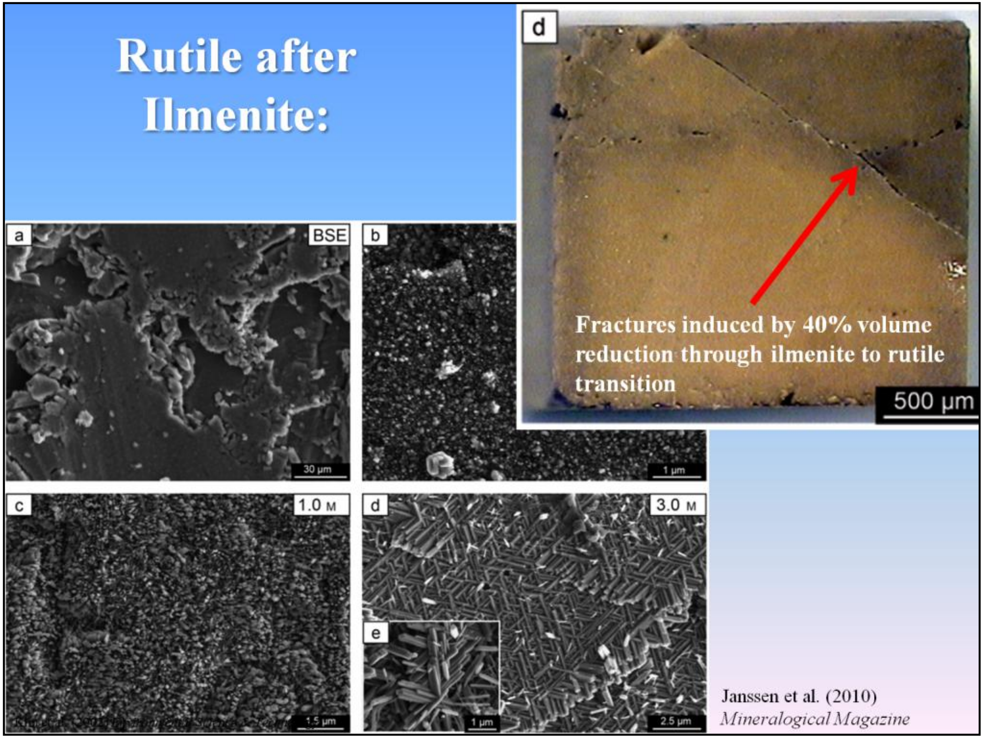
Feldspar dissolution

- Lack of clay precipitation:
  - Organic complexing of Al^{3+} ions
  - Acidic formation fluids
  - High fluid flux
  - Fluid pressure driven by hydrocarbon charge

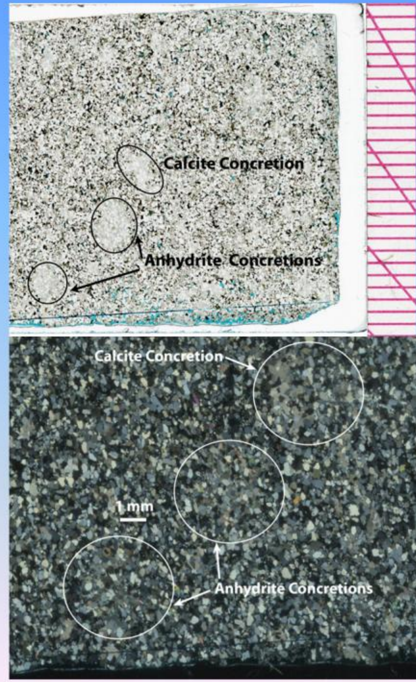


Rutile after Ilmenite: evidence for acidic pore water



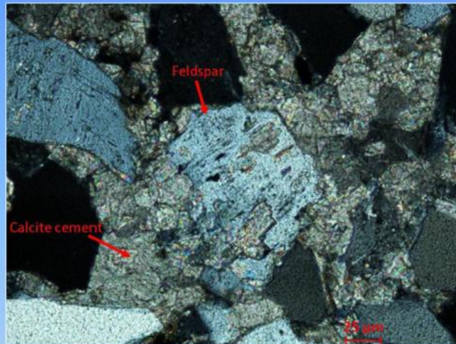

Rutile after Ilmenite:
a
BSE
30 µm
b
1 µm
c
1.0 M
1.5 µm
d
3.0 M
e
1 µm
2.5 µm
d
Fractures induced by 40% volume reduction through ilmenite to rutile transition
500 µm
Janssen et al. (2010)
Mineralogical Magazine

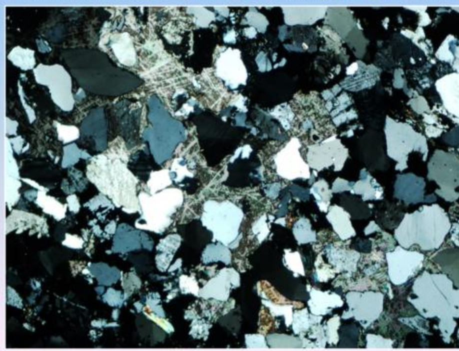
Late-stage concretions



Anhydrite <u>and</u> calcite:

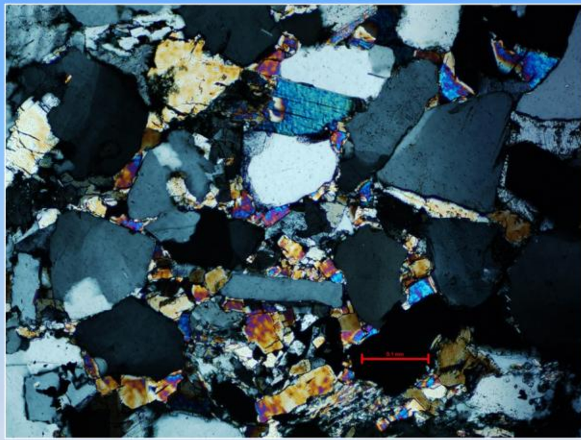
Late-stage Concretions: Calcite

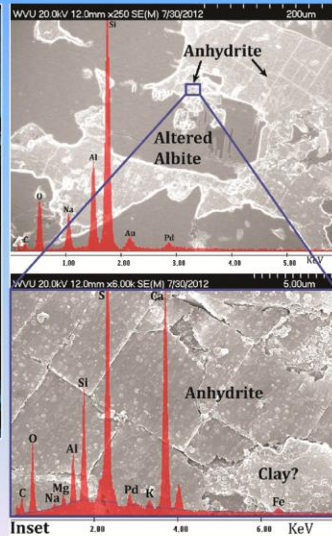




- Dissolution of feldspar arrested
- Concretions locally fill secondary and primary pores

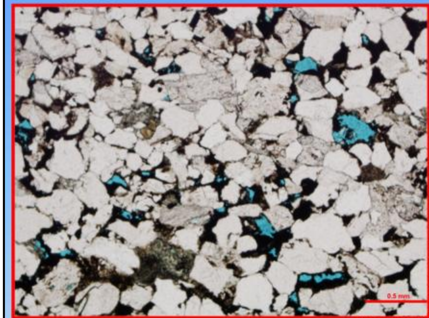
Late-stage Concretions: Anhydrite

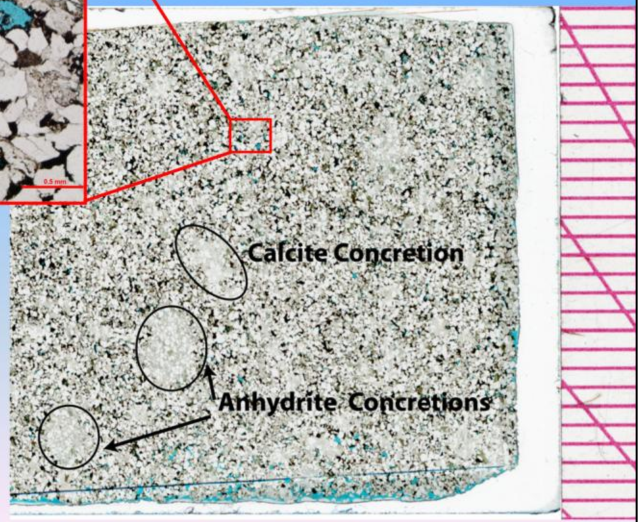




- Sulfur sourced from early-charge fluids induces switch to anhydrite precipitation.

Late-stage concretions

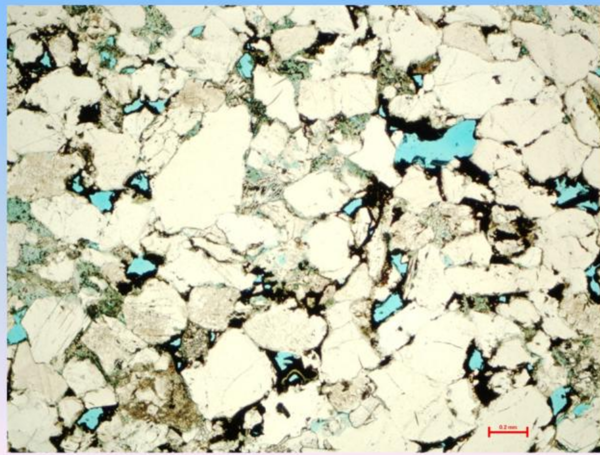


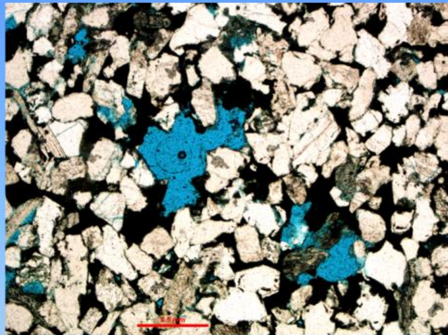


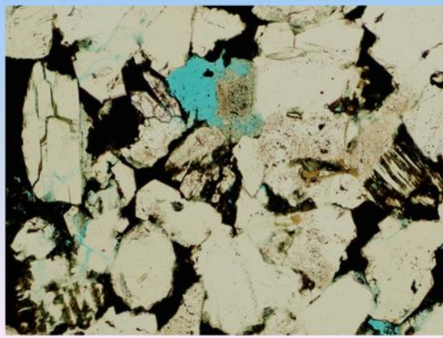
- **Localized concretion development**: Pore space preserved away from concretions

Hydrocarbon Charge:

- Early-charge fluids may have facilitated dissolution of grains and early cement
- Later hydrocarbons infilled secondary and primary pores







Hydrocarbon charging:

- Degraded oil/ pyrobitumen now occludes some of the original-charged porosity & isolates reactive mineral surfaces
  - Prevented further cementation

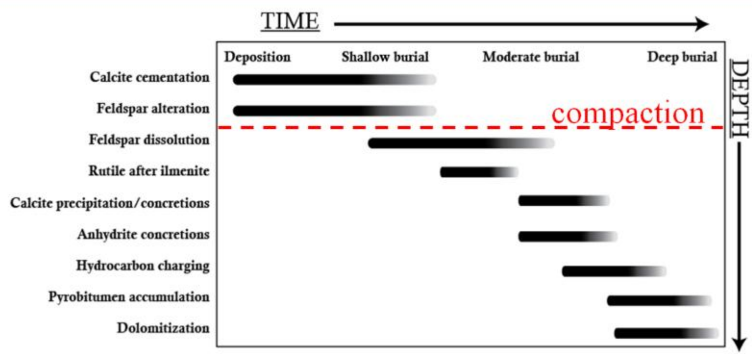
SUMMARY: Heterogeneity

- Rodessa Fm. consists of upward-fining sandstone units of mixed reservoir and non-reservoir facies
  - Laterally discontinuous = variable horizontal porosity

- Heterogeneous vertical porosity distribution controlled by interbedded porous and non-porous lithologies

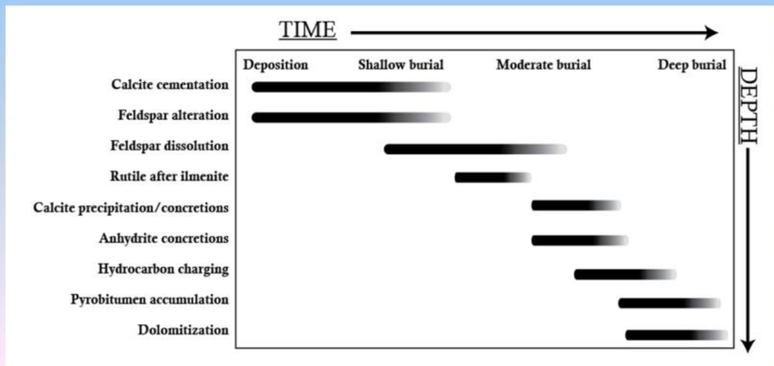
SUMMARY: Pore system

- Keys to porosity development:
  - Fairly uniform arkosic sandstone composition
  - Early calcite cement created non-porous facies
  - Lack of early calcite cement allowed interaction with acidic pore water



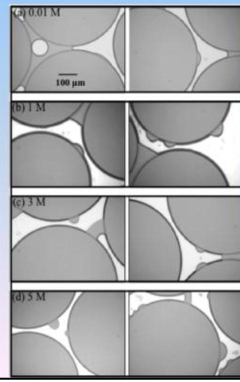
SUMMARY: paleo-fluid composition

- Later development of secondary porosity likely due to high flux of acidic pore water driven by early-charge-generated fluids
  - Feldspar dissolution
  - Lack of clay cement
  - Conversion of ilmenite to rutile



SUMMARY: implications

- Acidification of thin water films and "bubbles" left on grains could replay diagenetic processes in reverse during (sc)CO_2 –EOR or carbon sequestration
  - Pore throats and micro/nano-pores susceptible to precipitation of carbonate dissolved by acidic water films and bubbles
  - Pyrobitumen coats could impede this



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