Analysis of 30 year CO_2-Brine Interaction with a West Texas Oil-Well Completion

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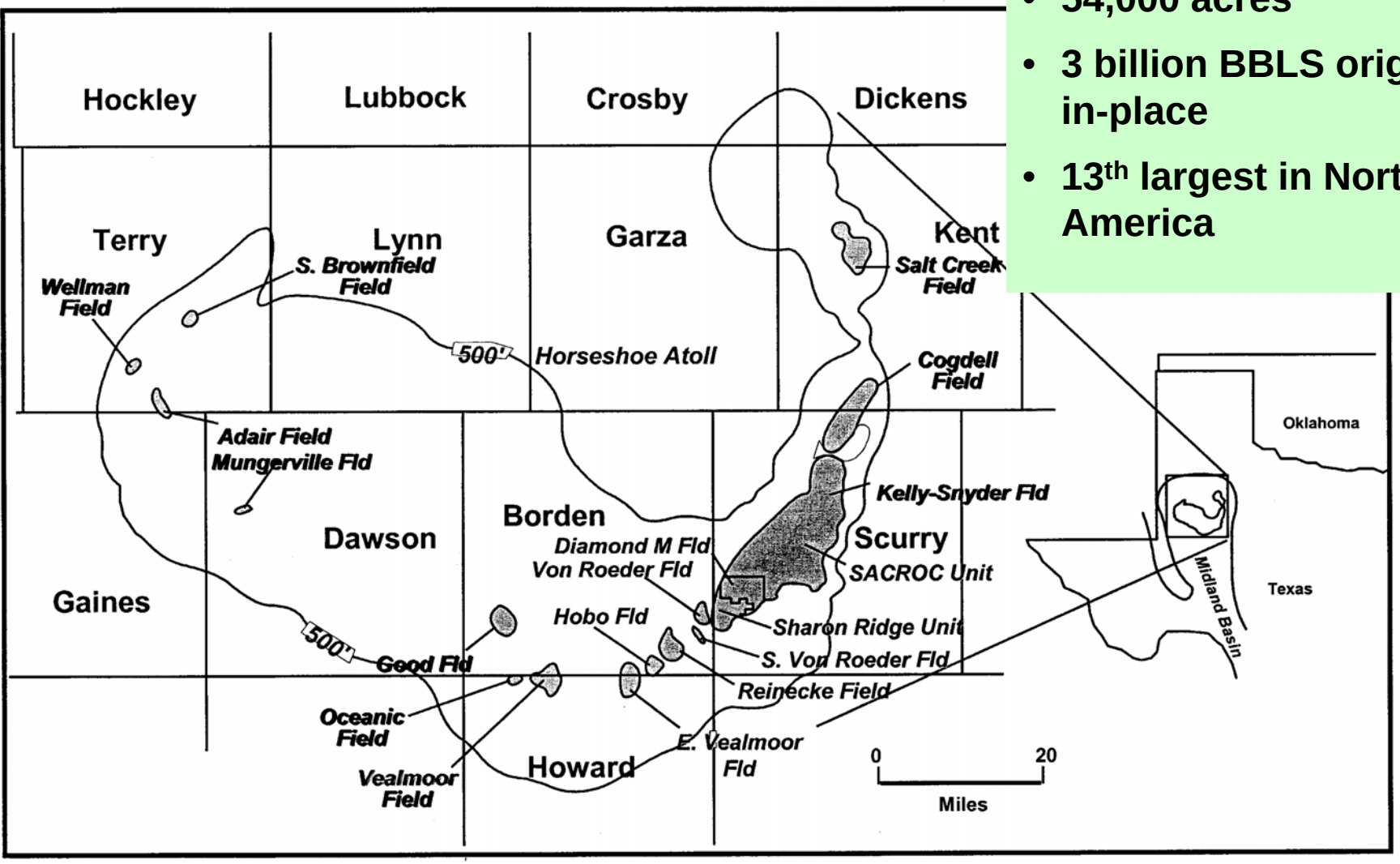
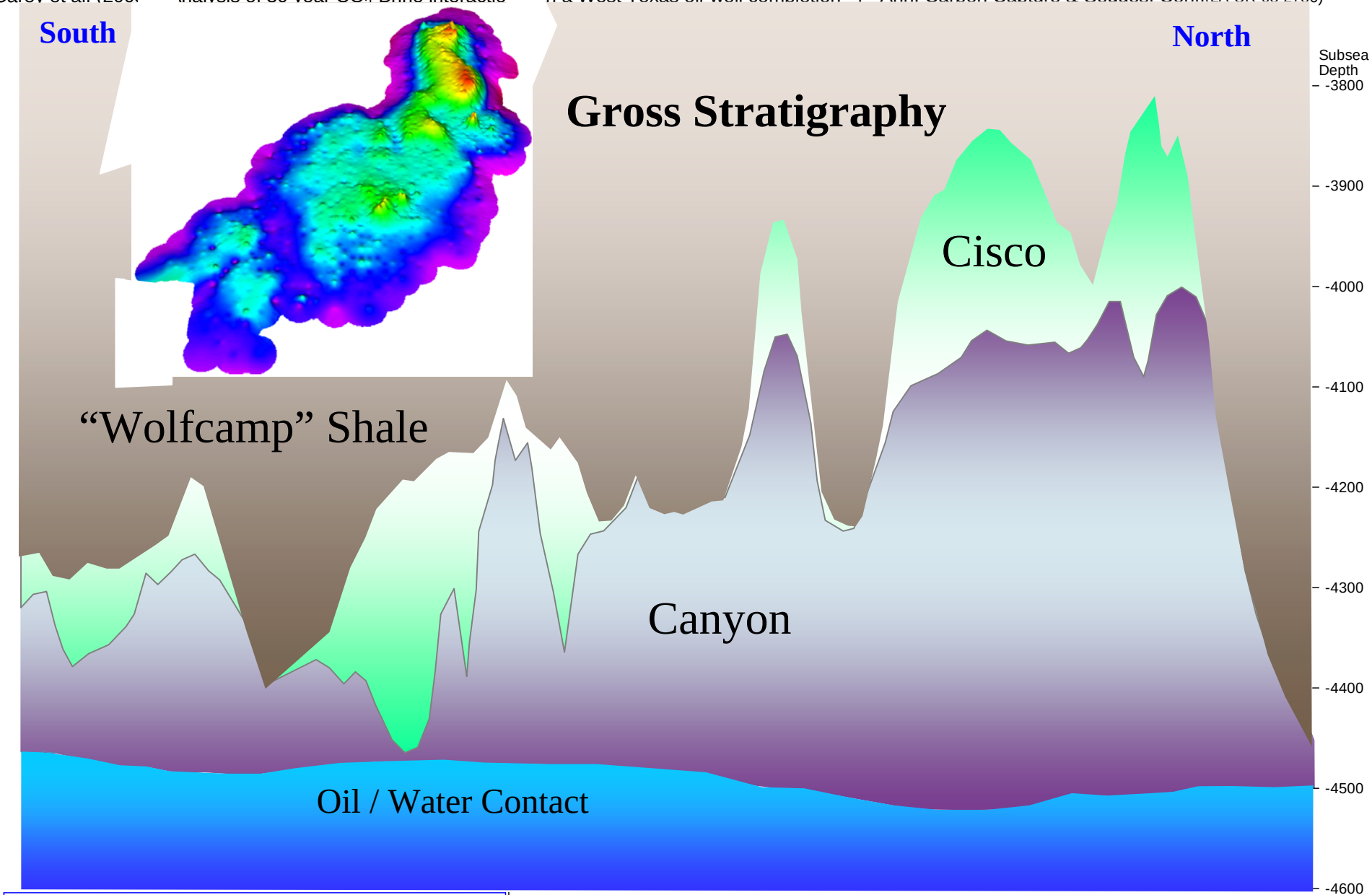
Field Studies: SACROC Overview

- Pennsylvanian age reef system
- Discovered 1948
- 54,000 acres
- 3 billion BBLS original oil in-place
- 13th largest in North America



Carey et al. (2005) "Analysis of 30 year CO_2-Brine interaction with a West Texas oil-well completion" 4th Ann. Carbon Capture & Seques. Conf. (LA-UR-05-2756)



SACROC Unit

Horizontal Scale = 9000.0 Ft.
Vertical Scale = 125.0
Vertical Exaggeration = 72.0x

Total Length of Cross-Section is 16.25 miles

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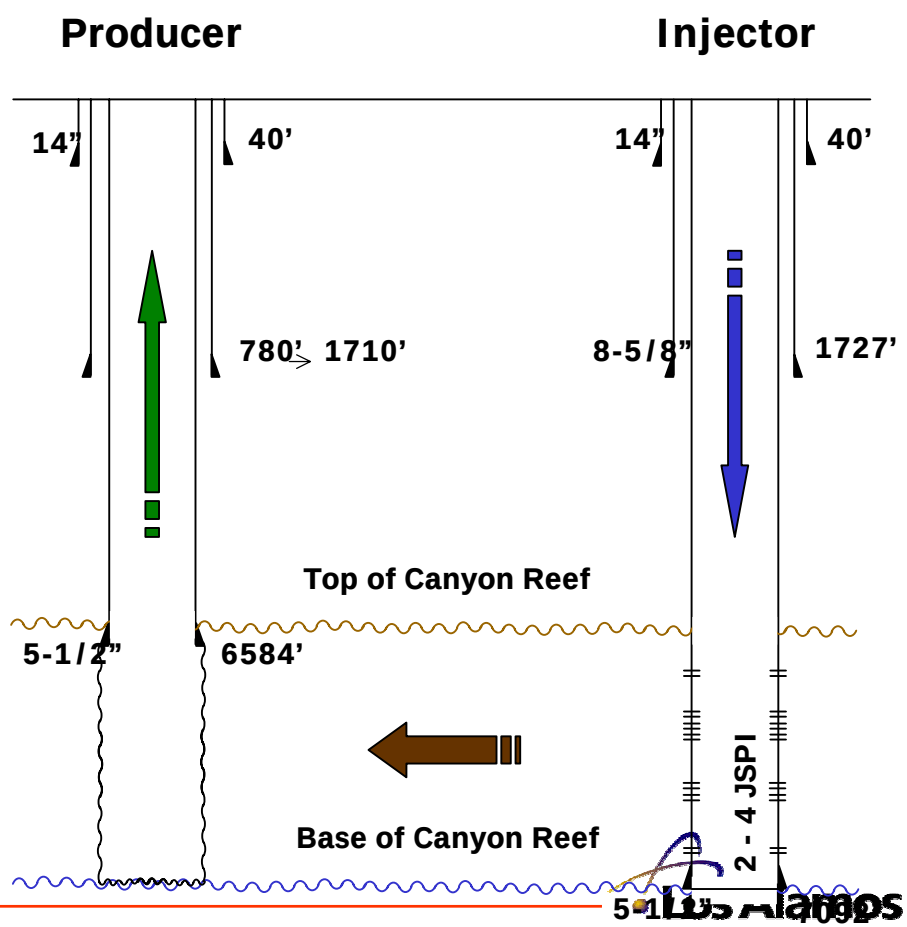
SACROC
(Scurry Area Capital Reef Operations Committee)

- 81 mi^2, 1800 wells, 600 operational
- Productive zone at 7000' and is as thick as 800'
- Field temperature 50 ºC; Initial pressure 3200 psi (now 2600 psi)
- CO_2 flooding initiated 1972 (only one field in the world is older)
- CO_2 now obtained primarily from McElmo Dome, CO
- 62% of all CO_2 injected is not recovered (effectively sequestered)
- Drilling and production from zones above and below the Cisco/Canyon Reef complex have been free of CO_2

SACROC Study Goals

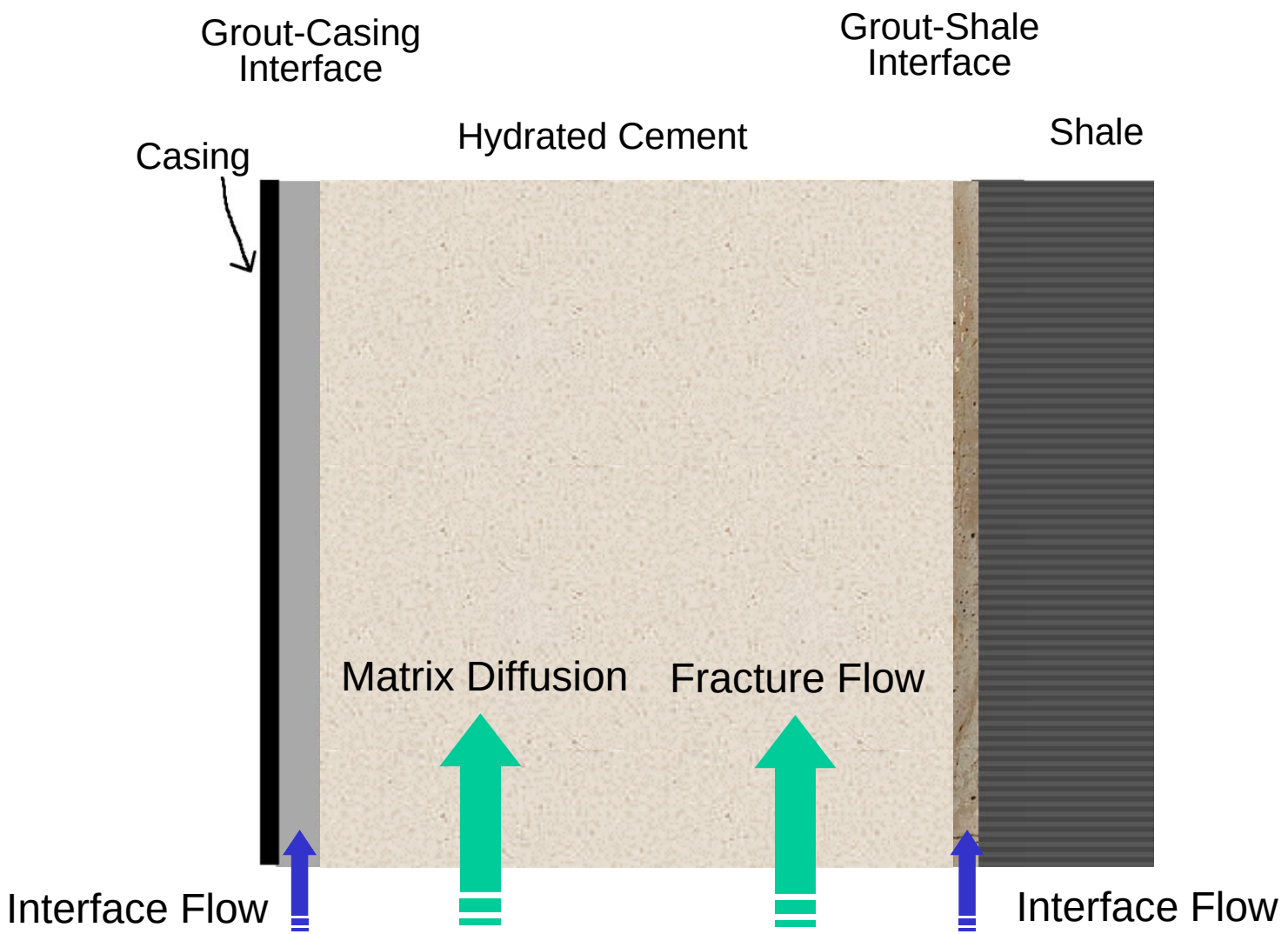
- Determine long-term effects of CO_2 on casing, cement, and shale
- Conduct detailed studies of critical interfaces: casing/cement, cement/shale, and shale/limestone
- Focus on changes in mineralogy, hydrologic properties, and mechanical properties
- Obtain sidetrack cores from existing injection wells (have experienced slugs of high-pressure CO_2) and producer wells (have experienced CO_2-saturated brine and oil).
- Obtain core from new drilling operations



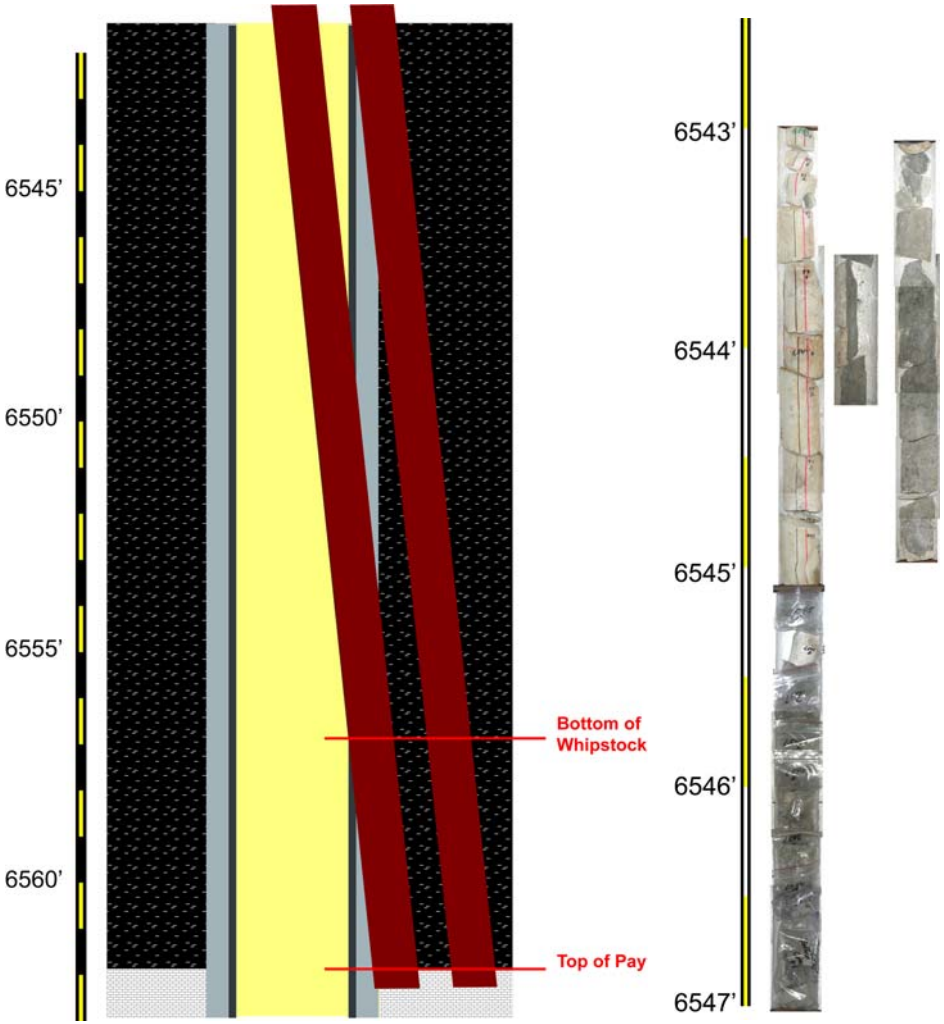
Potential Effects of Carbonation

- Decrease in porosity
- Decrease in permeability
- Increase in strength
- Reduction of pH of pore fluid
  - May allow corrosion to occur at casing interface
- Carbonation-induced shrinkage
  - Formation of cracks (potentially filled with carbonate)
- Reduction of casing/cement and/or cement/caprock interface integrity
- Loss of structural integrity at ultimate carbonation state
  - $CaCO_3$ + amorphous silica, alumina, and ferric hydroxides
- Important factors controlling rates of carbonation
  - Saturation and relative humidity
  - Water/Cement ratio
  - Age of cement

Potential Pathways for Well-Bore CO_2 Migration



Sacroc Core: 49-6 Producer/Injector



Drilled 1950
First CO_2 exposure 1975
Years of CO_2 operation: 17
Amount of CO_2 produced/injected: 2.2 Bscf

SACROC Core: 49-5, Producer

Drilled ~1950
First CO_2 exposure 1974
Years of CO_2 operation: 21
Amount of CO_2 produced: 0.33 Bscf

Limestone-Shale Contact in 49-5

Phase	Limestone
Calcite	Predominant
Ankerite	Minor
Quartz	Minor

Phase	Dark lenses
Illite	n.a.
Calcite	n.a.
Ankerite	n.a.
Quartz	n.a.
Chlorite	n.a.

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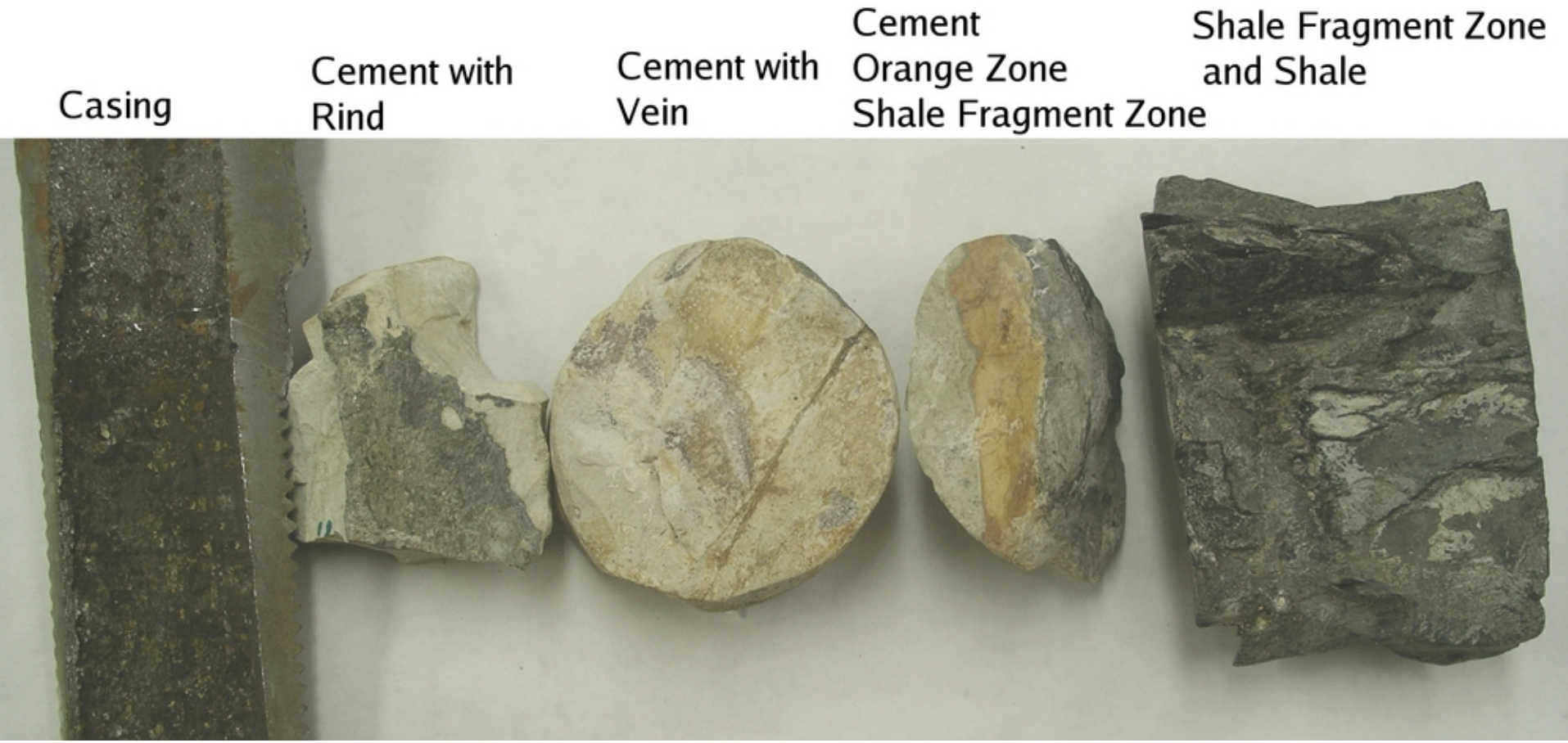
Cross-Section Through Well-Bore: 49-6

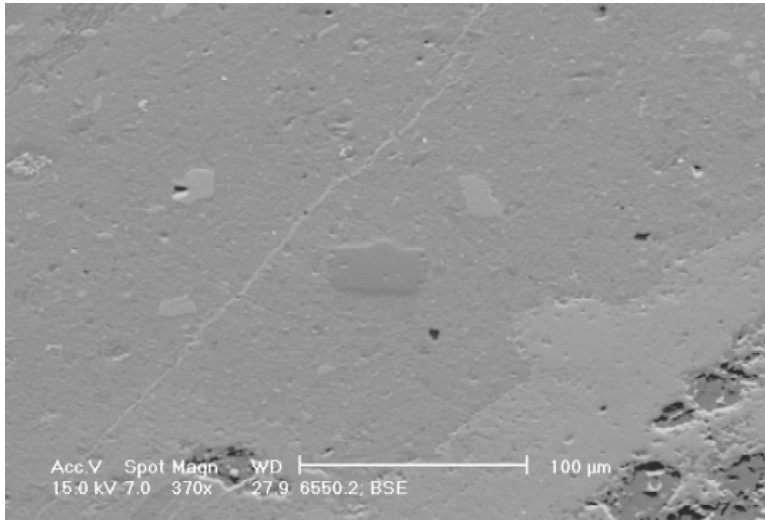


Casing and Casing Rind

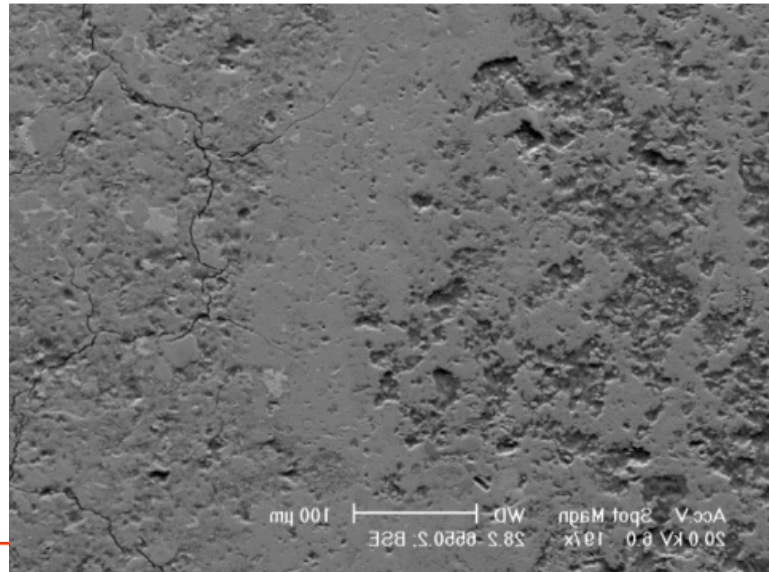
Phase	Casing Rind
Aragonite	60.3%
Calcite	24.0%
Halite	14.3%
Quartz	1.4%

Gray Cement – Orange Zone – Shale Fragment Zone

Phase	Gray Zone
Amorphous	Major
Portlandite	15-58%
Calcite	0-28%
Katoite	22-26%
Brucite	3-9%
Ettringite	3-4%
Friedel's Salt	2-4%
Halite	9-32%



Phase	Orange Zone
Calcite	44%
Aragonite	8%
Vaterite	33%
Halite	13%



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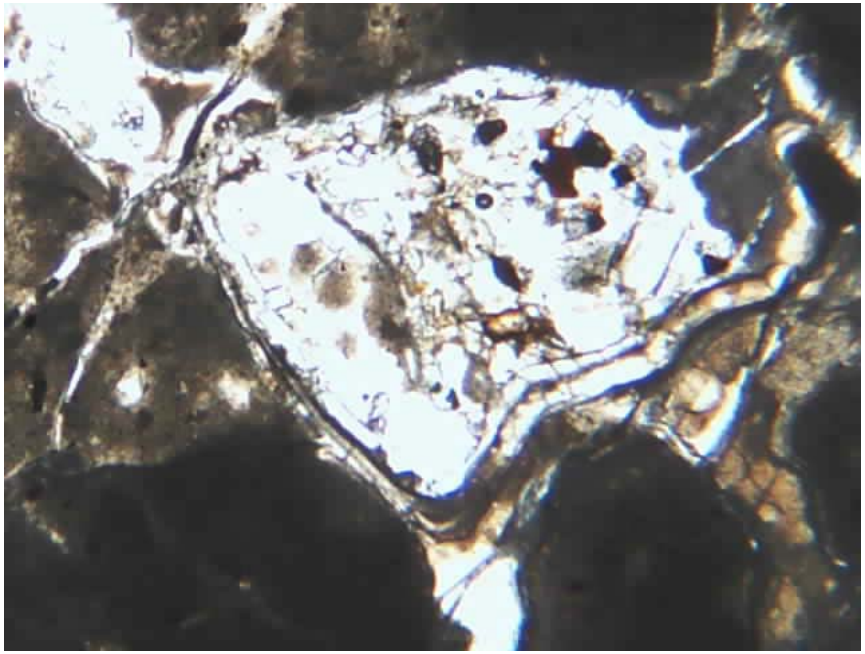
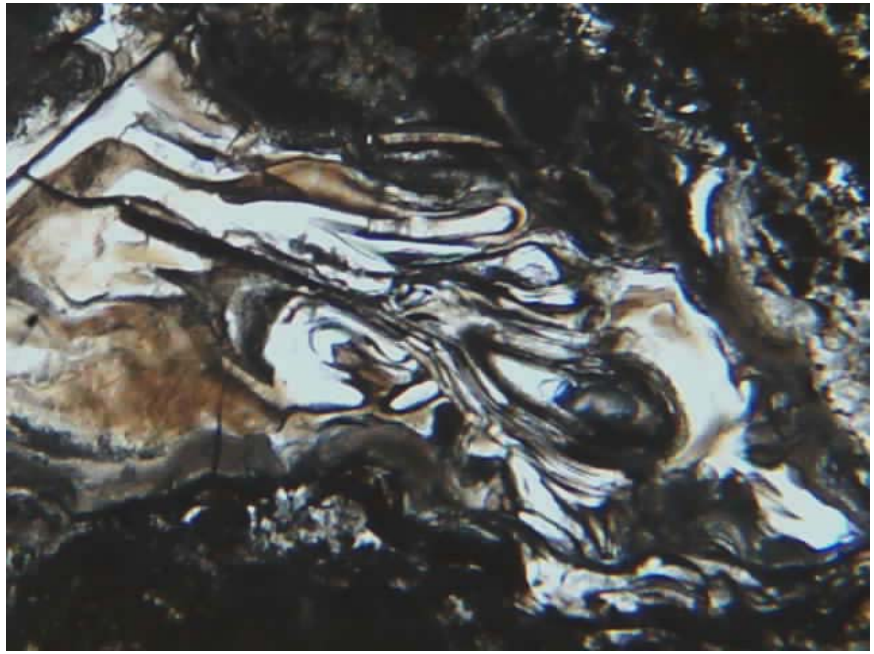
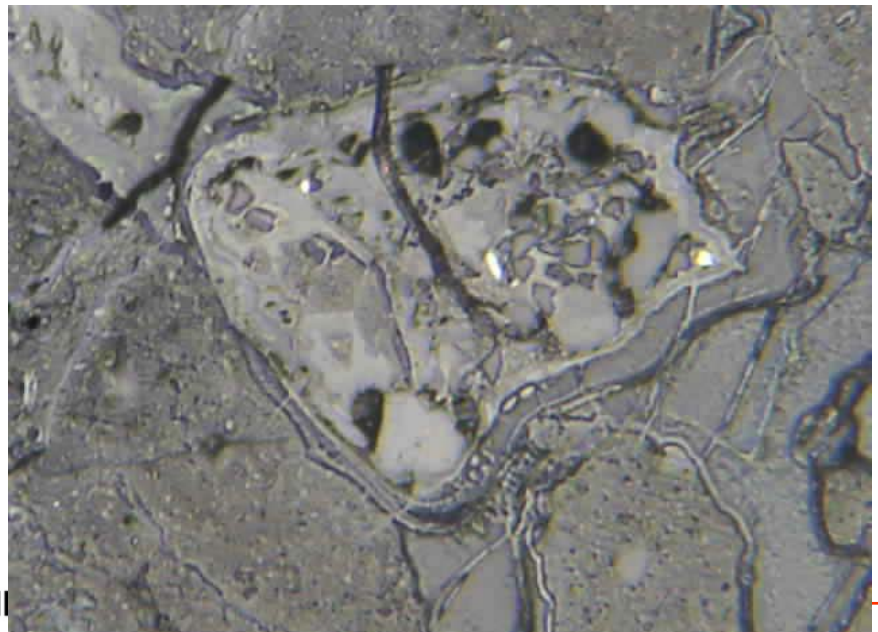
Transmitted (above) & reflected (below) optical images of shale fragment zone: 1mm width

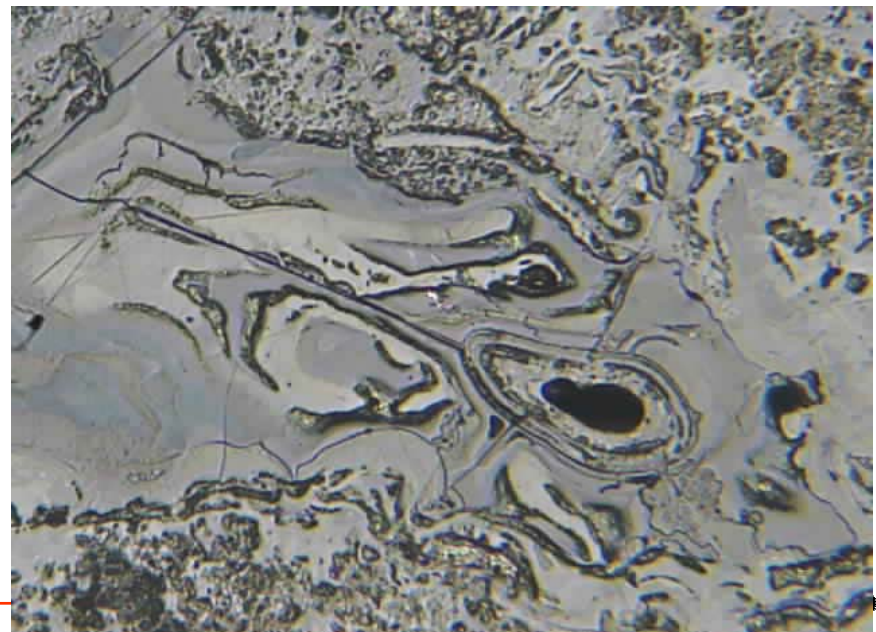




Nodule with carbonate rim

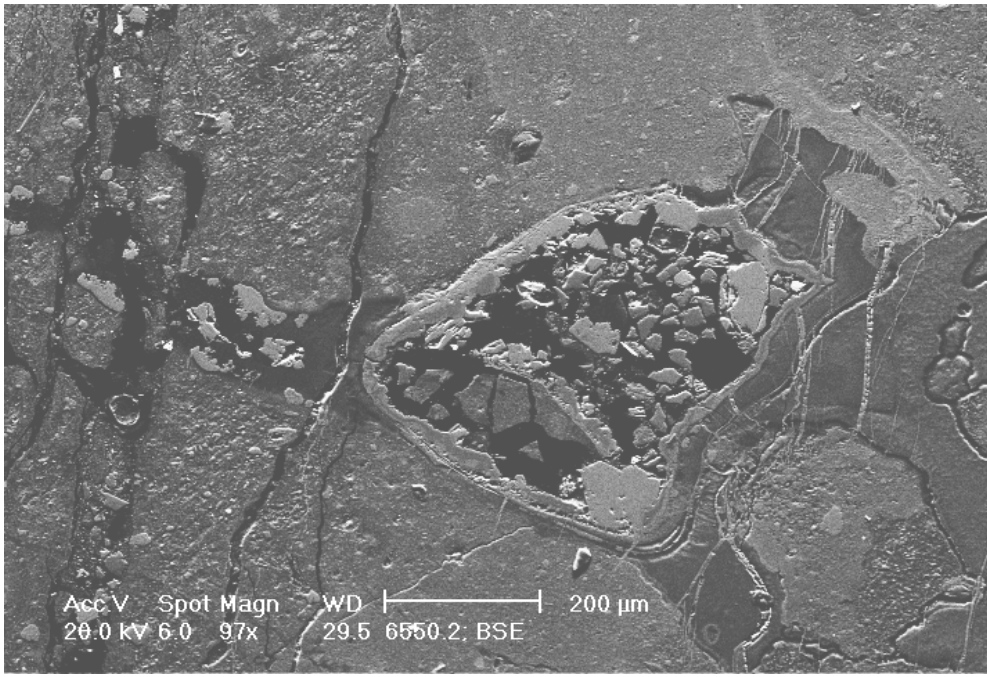
Agate-textures in intrusion-like feature

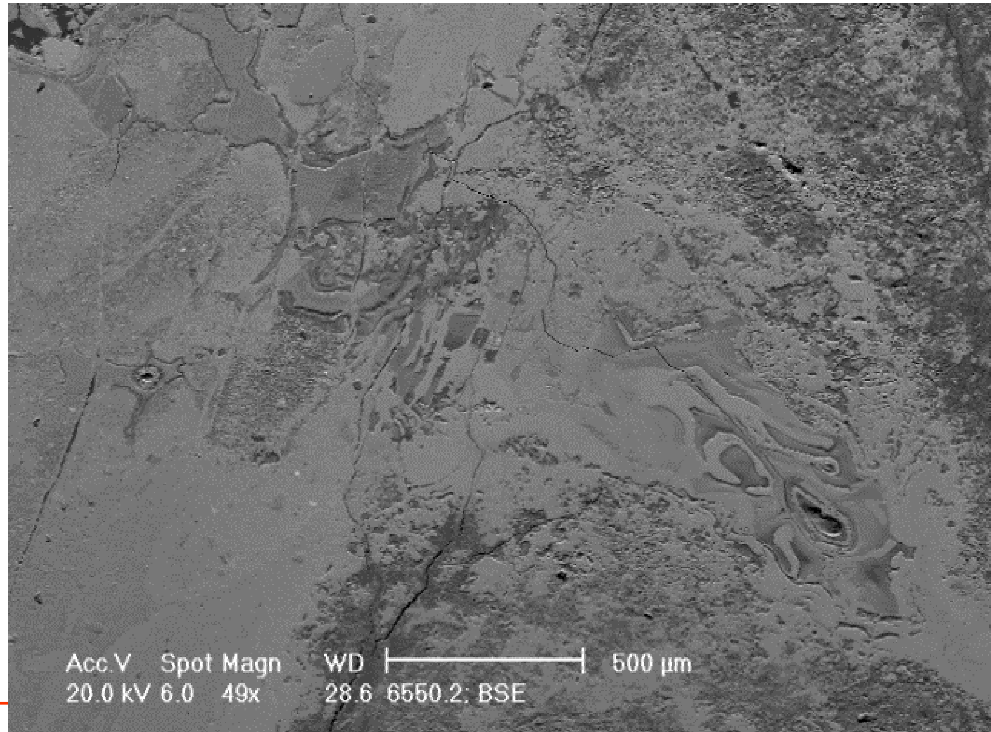




Shale Fragment Zone

Mineralogically a mixture of shale and orange-zone





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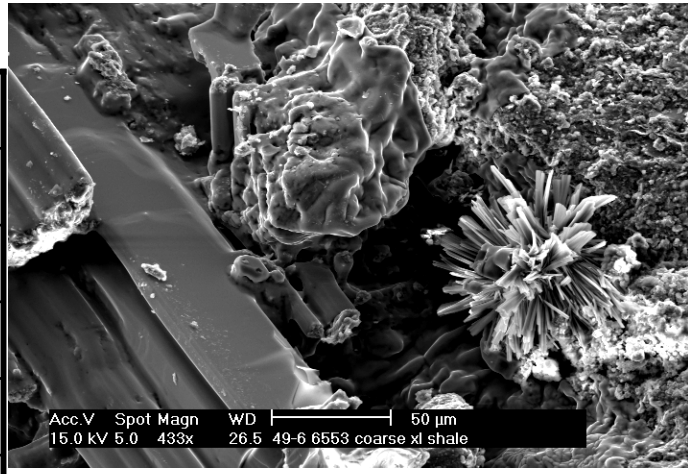
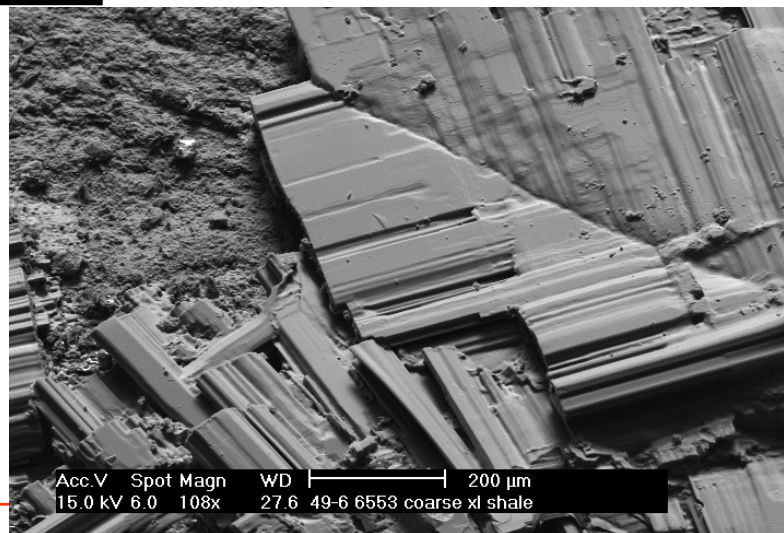
Shale

Mineral	
Illite	57.5%
Quartz	26.0%
Mica	7.7%
Plagioclase	5.0%
Pyrite	1.8%
Chlorite	0.9%
K-Feldspar	0.8%

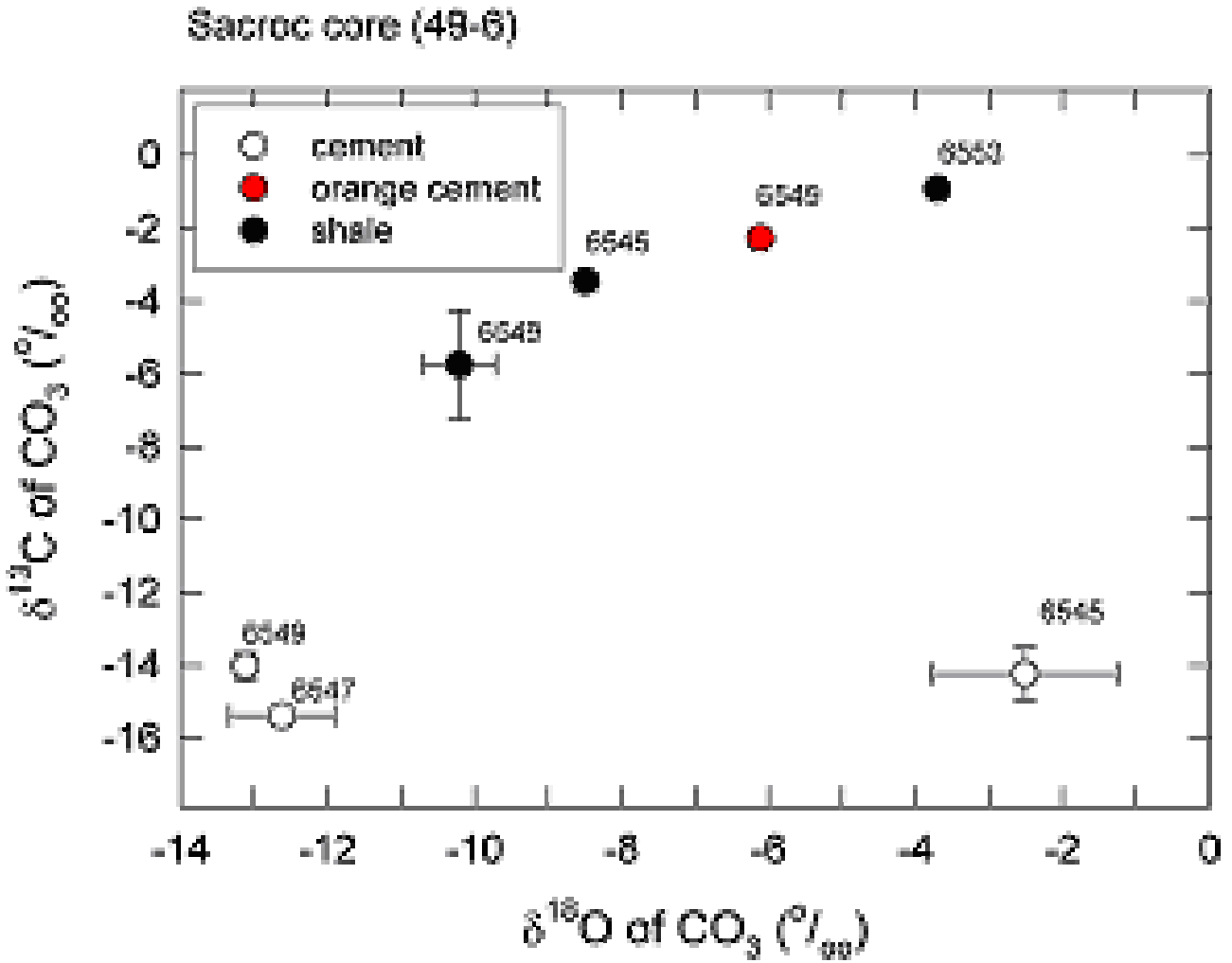




Cement-Limestone Contact 1000' Above Pay

Phase	Cement
Amorphous	Major
Quartz	13%
Calcite	17%
Portlandite	5%
Katoite	7%
Brownmillerite	22%
Friedel's Salt	2%
Ettringite	7%
Larnite	22%
$Ca_2SiO_4.H_2O$	5%

Stable Isotope Studies of Core Samples



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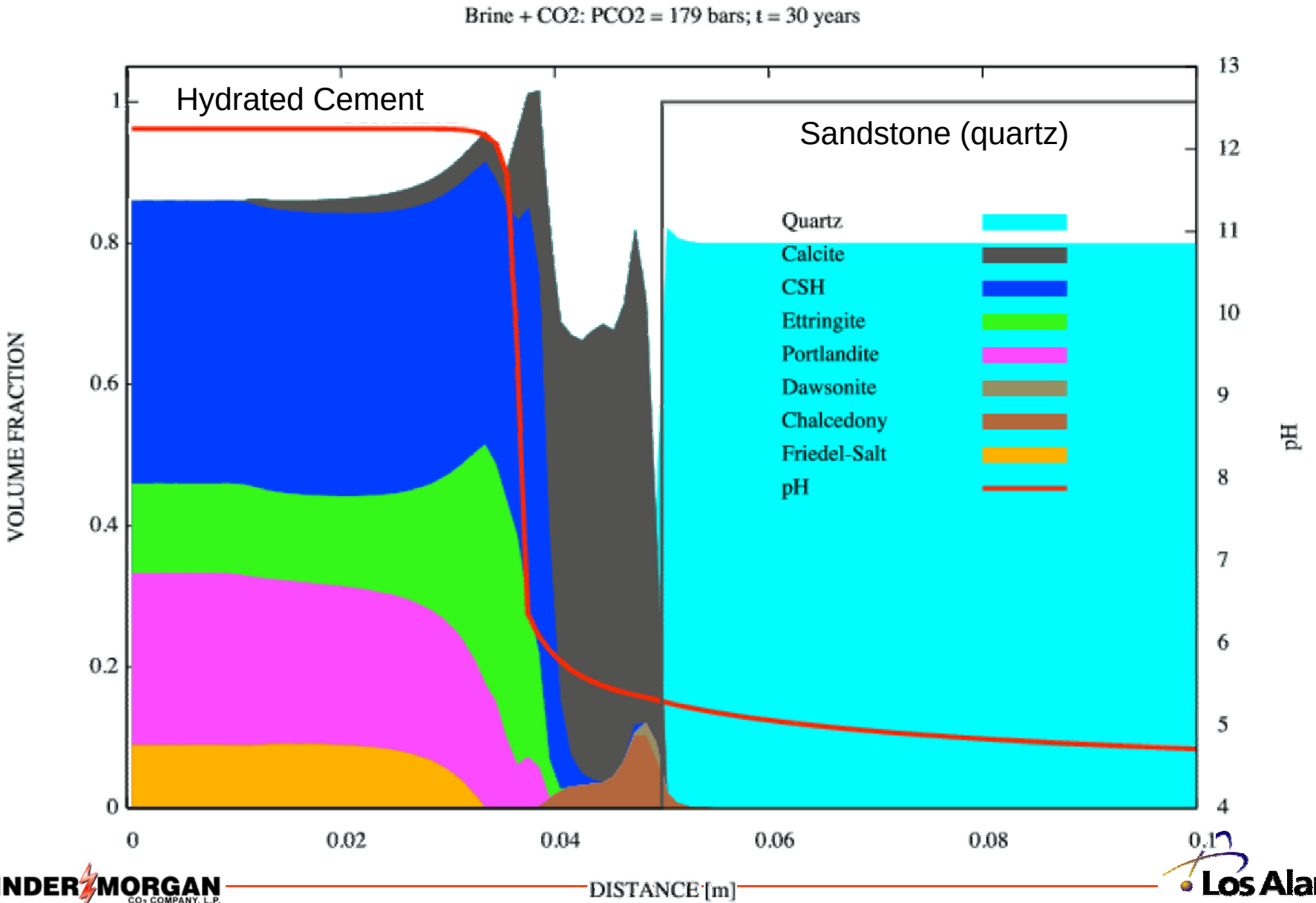
Reactive Transport Modeling: Carbonation Front

1-D Diffusion of CO_2-saturated brine into fully hydrated cement



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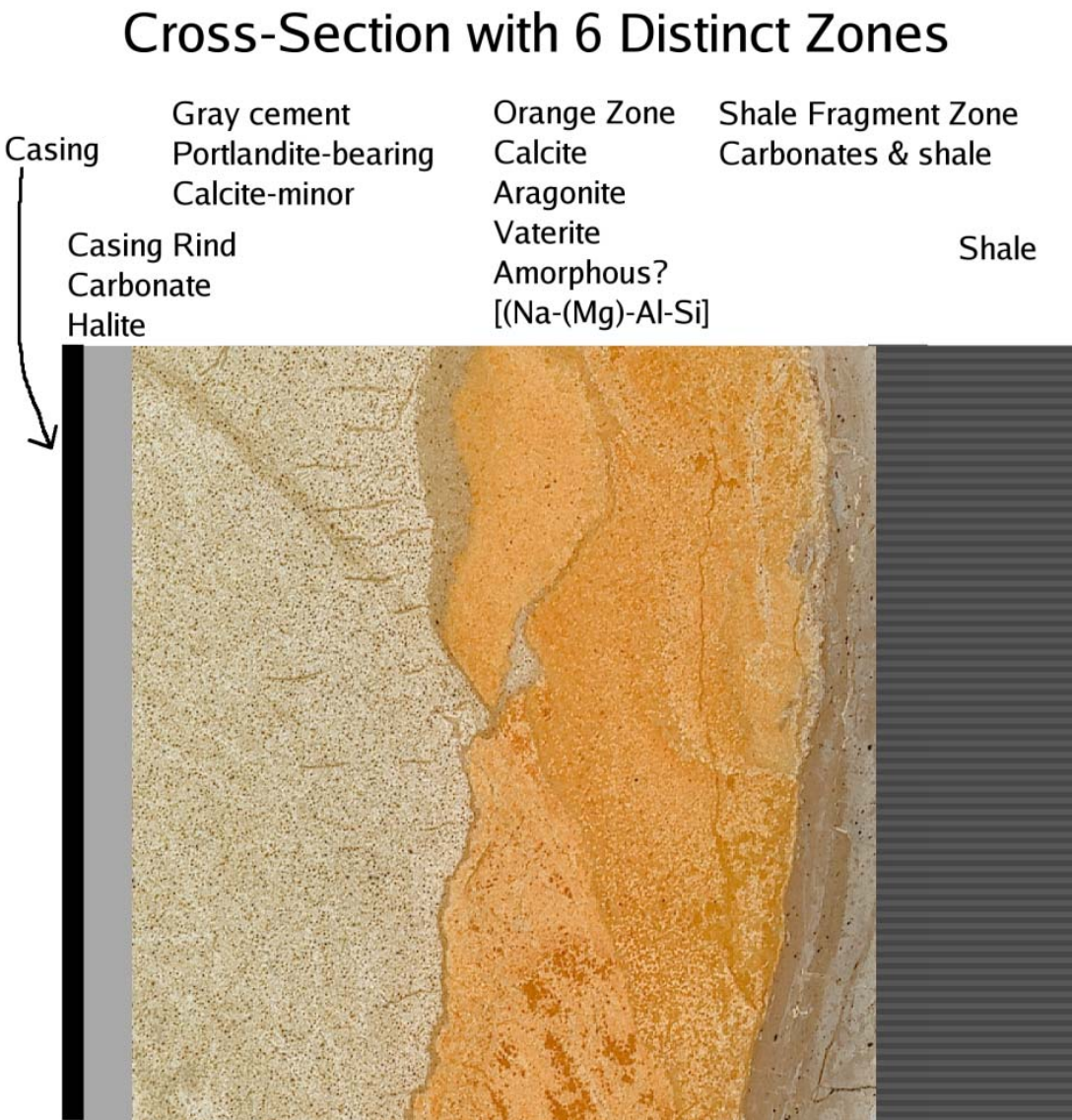
Composite "Section" Observation Summary

- Cement recovered: retains structural integrity
- Shale-cement interface not preserved: low bond quality?
- Limestone-cement interface preserved: high bond quality
- A thick carbonated zone occurs between cement and shale
- Shale fragment zone contains carbonate and "mobile" silica
- Gray cement contains portlandite [$Ca(OH)_2$]
- Gray cement contains calcite veinlets
- A carbonated rind exists between the cement and casing

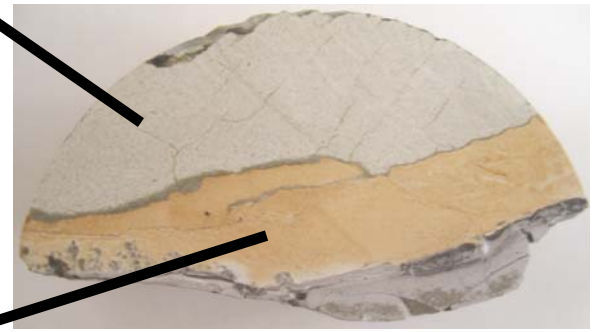


Origin of Orange Zone

- **Altered (carbonated) cement**
- **Abundant calcite, vaterite, and aragonite**
- **Amorphous component: Al-Si silicates with Na derived from brine**
- **Difference in presence or absence of portlandite indicates effective chemical separation of the orange zone and the cement**
- **Isotopic studies show that the carbonate in the orange zone and cement are distinct**
- **Orange zone may reflect diffusion of CO_2 and formation of a reaction front with the remaining cement**
- **Orange color may not reflect oxidation/reduction so much as decomposition of AFm phases and precipitation of ferric hydroxides**

Air-Permeability Measurements of Cement and Shale in milliDarcy

Zone	Air Dried (mD)	Oven Dried (mD)
Upper Cement	0.09	74.00
Gray Zone C		0.10
Gray Zone A1	0.09	38.54
Gray Zone A2	0.07	48.22
Gray Zone A3	0.11	18.94
Gray Zone B1		5.75
Gray Zone B2		3.33
Gray Zone B3		8.40
Orange Zone A1	0.38	0.43
Orange Zone A2	0.19	0.19
Orange Zone A3	0.11	0.05
Orange Zone B1		0.17
Orange Zone B2		0.14
Orange Zone B3		0.22
Orange Zone B4		1.22
Shale along layers		8.57



Observations

- **Presence of structurally competent cement (and orange zone) precludes inundation of well-bore contact zone with circulating, CO_2-rich fluids**
- **Air permeameter data show cement with increased permeability but still resistant to flow**
- **Presence of calcium carbonate indicates some CO_2 mobility**
- **Presence of portlandite in cement indicates incomplete carbonation**
- **CO_2 pathways appear along the casing-cement interface and the cement-shale interface**
- **Amount of CO_2 moving along these interfaces unknown**
- **Point of origin of CO_2 moving along these interfaces unknown**

Bulk Composition of Cement and Shale Core (X-ray Fluorescence)

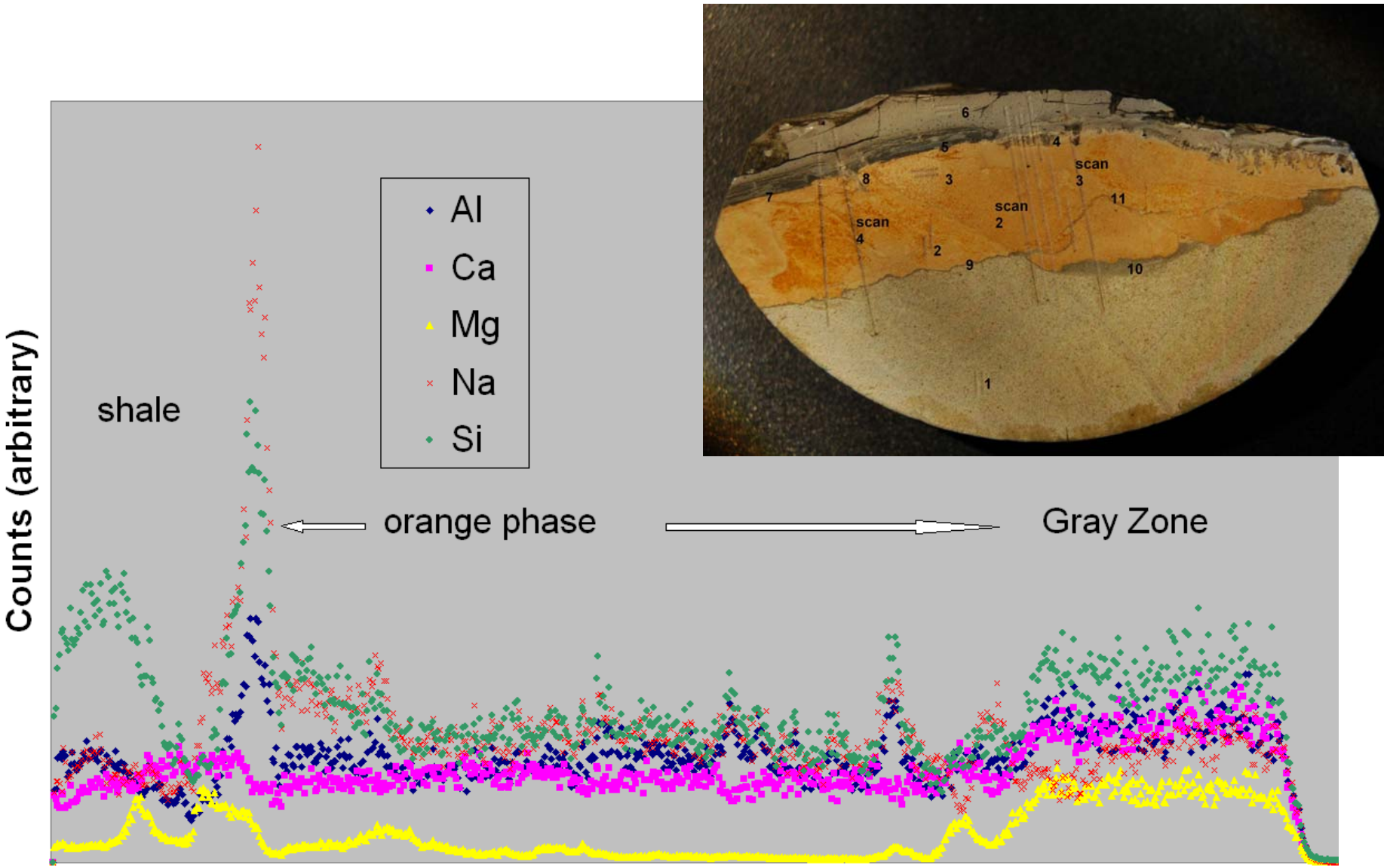
Normalized to non-volatile mass

Depth	6545	6549	6549	6549.2		6550	6551.5
Oxide	**Gray Cem.**	**Oran. Cem.**	**Gray Cem.**	**Gray Cem.**	**Delta Orange-Gray**	**Shale Frag Zone**	**Shale**
CaO	63.61	59.16	63.07	62.45	-3.88	2.92	4.56
MgO	3.66	1.38	3.68	3.66	-2.29	2.17	2.97
MnO	0.10	0.10	0.11	0.11	-0.01	0.03	0.03
P_2O_5	0.09	0.10	0.10	0.10	0.00	1.11	0.11
TiO_2	0.24	0.27	0.24	0.25	0.02	0.69	0.73
Fe_2O_3	2.52	2.69	2.59	2.76	0.06	5.86	6.46
K_2O	0.04	0.19	0.04	0.05	0.15	4.02	3.82
Al_2O_3	4.65	5.16	4.83	4.83	0.39	16.81	16.30
Na_2O	2.36	4.38	2.04	1.93	2.27	1.44	1.15
SiO_2	22.65	26.51	23.24	23.81	3.27	64.76	63.68
LOI	18.67	35.26	19.16	25.23	14.24	9.26	11.24

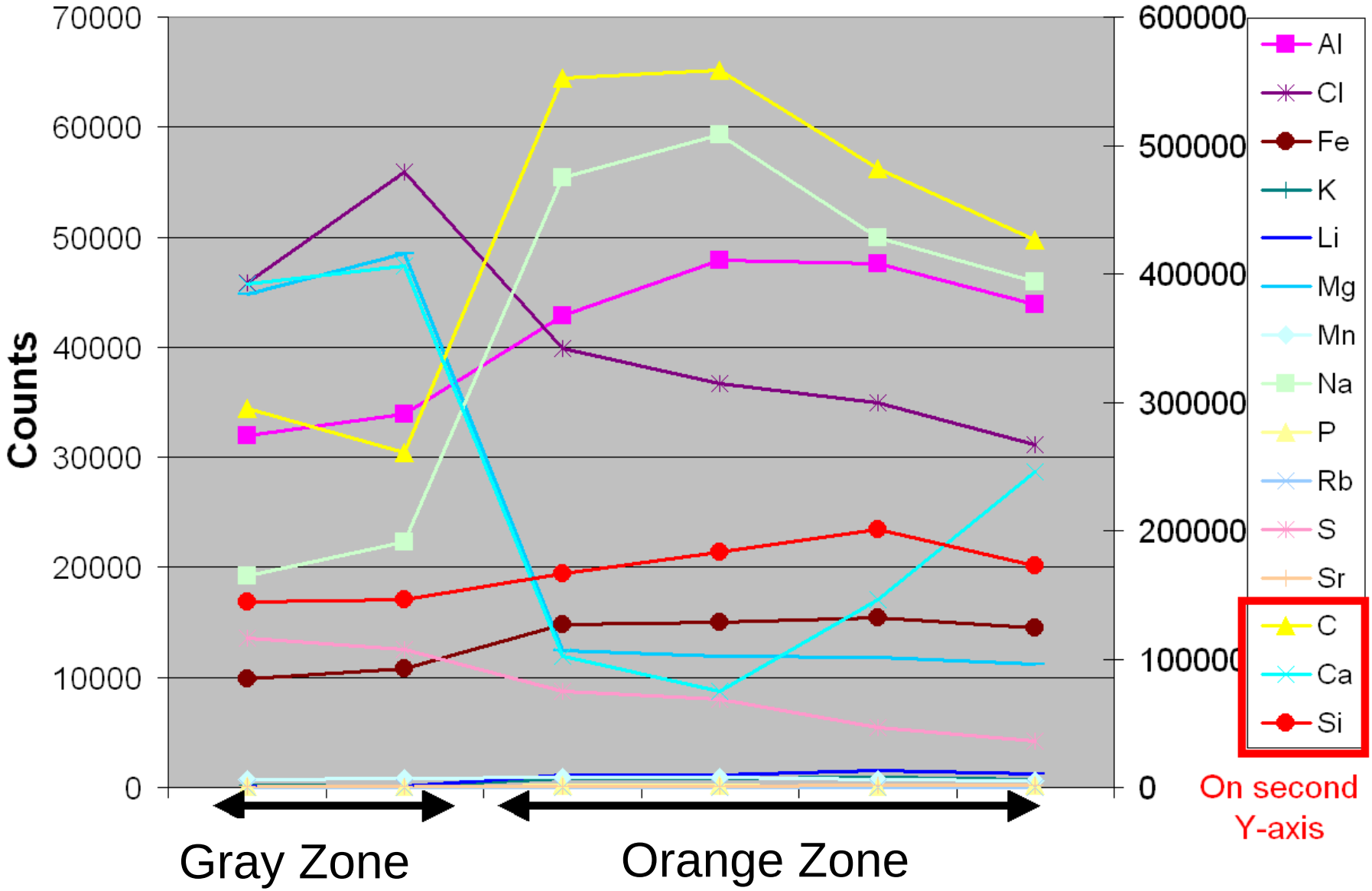
LOI: Loss-on-ignition (H_2O, CO_2, organics) values are not normalized.

Typical Cement: CaO (61-65%), MgO (0.9-5.0%), Fe_2O_3 (1.5-4%), Al_2O_3 (4-6%), SiO_2 (19-22%)

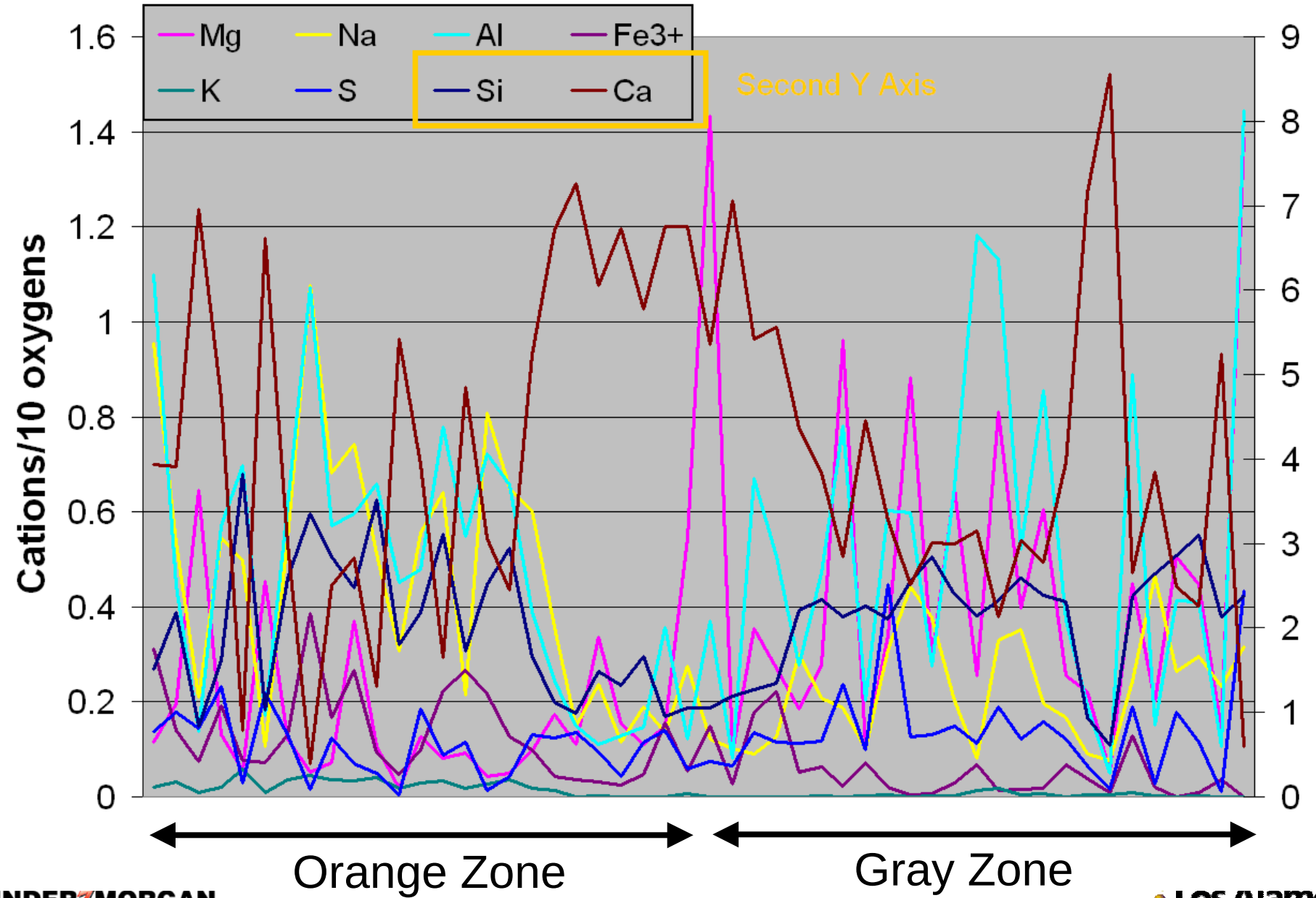
Laser Ablation: Continuous Scan, position #2



Laser Ablation Results: Average Values



Electron Microprobe Data: 10 um spot

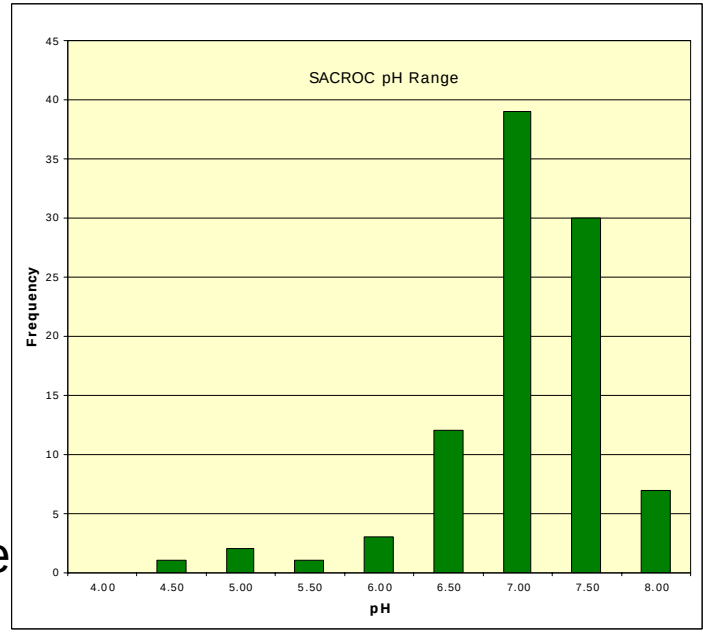


Summary of Chemical Analyses

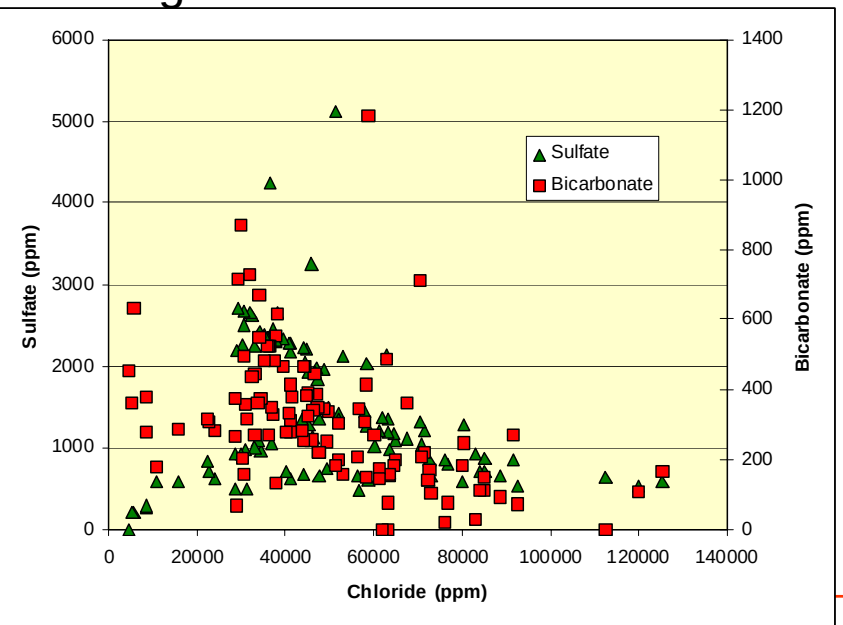
- **Gray and orange zones have chemistry characteristic of Portland cements**
- **Orange zone contains substantial volatile component (carbonated relative to gray zone)**
- **Orange zone characterized by substantially greater Na and Si and significantly less Ca and Mg than gray zone**
- **Electron microscopy reveals veins of carbonate and a zone of mobilized silica and carbonate at the shale-orange zone interface**
- **The interface between the orange and gray zones is not chemically distinctive—The region is perhaps more consistently richer in Ca and poorer in Al, Na, and Cl.**
- **The shale is chemically distinct with much greater concentration of Si and much lower Ca.**

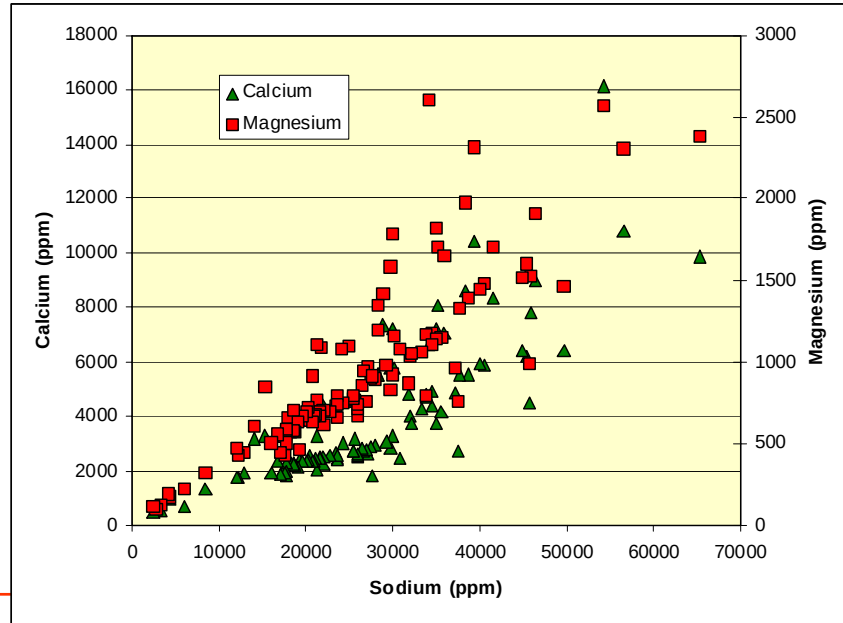
Average SACROC Brine from Depth 6745-6860 ft

pH	7.12
$HCO3^-$	1181 ppm
Cl^-	58903 ppm
$SO4^{2-}$	599 ppm
Na^+	30092 ppm
Ca^{2+}	5786 ppm
Mg^{2+}	1158 ppm



data from ~100 analyses in the NETL Brine database filtered to include only those analysis where charge balance is within 2%.





Conclusions

- **EOR sites have tremendous potential for evaluating feasibility of CO_2 sequestration**
- **Need to pay just as much attention to the cement/casing that is absent as the core that can be recovered**
- **Recovery of core at SACROC and from the Tensleep Formation demonstrate that cement can retain integrity for decades**
- **CO_2 does attack cement but there are stages of carbonation that precede and help prevent mechanical failure**
- **Experimental studies of the carbonation process are necessary to interpret the observed textures**
- **Numerical modeling is helpful in understanding processes and time-scales of implied by the observed mineralogy and texture**