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MINERALOGICAL AND TEXTURAL VARIATIONS IN SHALE AND ITS SEAL INTEGRITY IN A CO_2-FLOODED ENVIRONMENT

Giday WoldeGabriel[1], Scott Wehner[2], Mike Raines[2], Steve Chipera[1], Melissa Fittipaldo[1], George Guthrie[1], and Rajesh Pawar[1]

1 - EES-6/MS D462, Earth Environmental Science Division
Los Alamos National Laboratory, Los Alamos, NM 87544
Tel. 505-667-8749, Fax 505-665-3285
2 – Kinder Morgan CO_2, Midland, TX 79701

ABSTRACT

Understanding interaction between CO_2 and shale and its implication on long-term CO_2 storage are critical for geologic sequestration. Experimental observations related to CO_2-shale interactions from core samples collected at the SACROC unit are highlighted. The physical, chemical, and mineralogical characteristics of the shale caprock from two SACROC unit wells were investigated to assess the decades-long effects of CO_2 flooding (Carey et al., 2005). Core samples from Wells 49-5 (CO_2 injector) and 49-6 (CO_2 injector/producer) were investigated using petrographic, X-ray diffraction (XRD), electron microprobe, and X-ray fluorescence (XRF) methods. Results indicate variations in textural, mineralogical, and chemical compositions of the shale caprock.

Samples from the injector well (49-5) exhibit ranges of mineralogy in quartz (19.3-34.6 wt%), illite (38.1-65.8 wt%), kaolinite/chlorite (1.1-3.5 wt%), pyrite (1.4-3.6 wt%), and calcite (0.2-3.3 wt%) contents. Variations in SiO_2 (55.1-56.9 wt%), CaO (1.7-2.5 wt %), and K_2O (3.6-4.2 wt%) chemistry are also apparent. Samples from the injector/producer well (49-6) also indicate variations in illite (34.8-60.9 wt%), quartz (18.9-24.1 wt%), kaolinite/chlorite (1.4-2.1 wt%), calcite (0.3-5.7 wt%), and pyrite (1.9-3.4 wt%) as well as in SiO_2 (55.5-58.5 wt%) and CaO (2.7-4.0 wt%) contents. With few exceptions, cavities and fractures are oriented parallel to bedding and contain calcite, minor halite, and calcite veinlets. The mineralogical, chemical, and textural variations appear to be primarily due to burial diagenetic processes. In addition, shale integrity does not appear to be compromised due to CO_2 flooding. However, signs of CO_2 diffusion into shale are being investigated by careful chemical analysis of calcite and other diagenetic mineral phases from veins, cavities, and fractures and analytical result show no evidence for effects of CO_2.

INTRODUCTION

SACROC (Scurry Area Capital Reef Operations Committee) unit is one of the oldest continuously CO_2-flooded oilfield operations in the United States

CO_2 flooding initiated in 1972 with most of the CO_2 gas primarily piped from McElmo Dome, Colorado

Study wells (49-5 and 49-6) located in the northern part of the SACROC unit in western Texas (Fig. 1)

Wells penetrated the Wolfcamp shale caprock and the underlying oil-producing Cisco and Canyon carbonate reef complex at a depth of 5600-7000 ft (Fig. 2)

Productive zone located at a depth of 7000 ft is as thick as 800 ft and is characterized by field temperature of 50ºC and initial pressure of 3200 psi (now at 2600 psi)

Over 30 years, 1300 Bscf CO_2 has been injected and according to mass balance calculations 62%

of all CO_2 appears to be successfully sequestered because drilling and production from zones above and below the Cisco/Canyon Reef complex have been free of CO_2

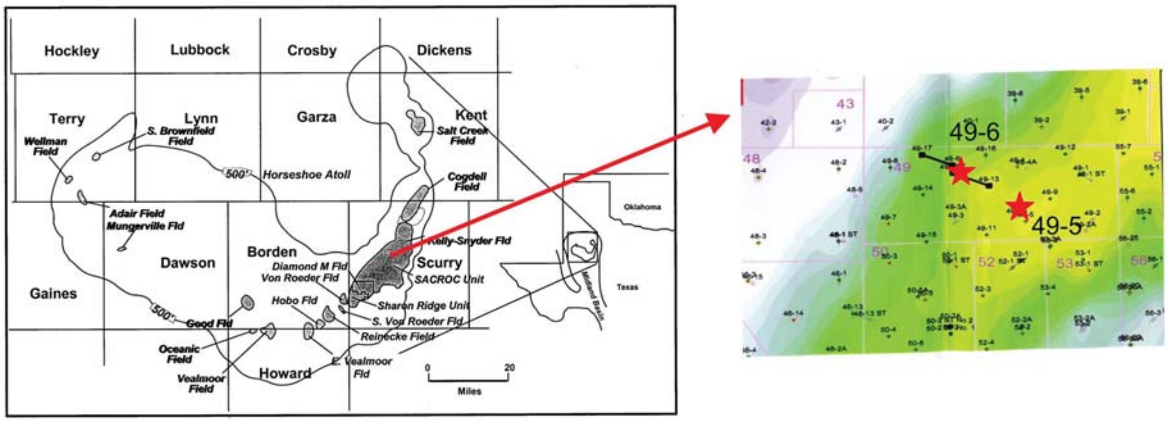


Figure 1 Location of the SACROC unit in western Texas. Wells 49-5 and 49-6 are indicated in the inset map.

OBJECTIVE

Shale core samples were studied to determine the long-term CO_2-shale caprock interactions in a CO_2-rich brine at the SACROC unit to evaluate the validity of CO_2 geological sequestration.

Petrographic properties and chemical and mineralogical compositions of shale core samples collected at different stratigraphic levels (Fig. 2) above the injection zone were determined using various analytical methods that included optical and scanning electron microscope, electron microprobe, X-ray fluorescence, and X-ray diffraction to document the effects of CO_2 on shale caprock.

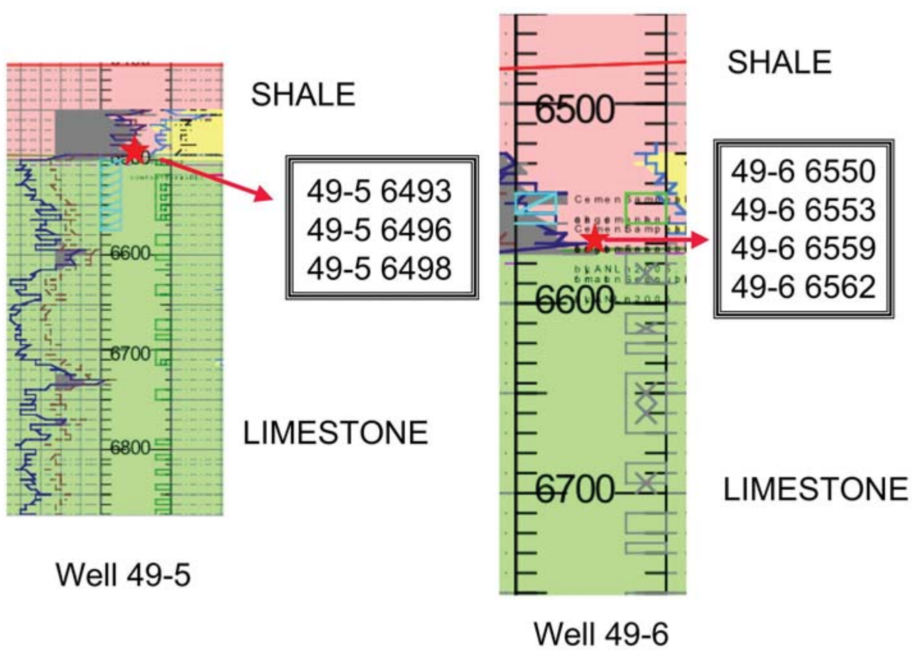


Figure 2 Sample locations within the lowermost parts of Wells 49-5 and 49-6.

CHARACTERIZATION OF SHALE SAMPLES

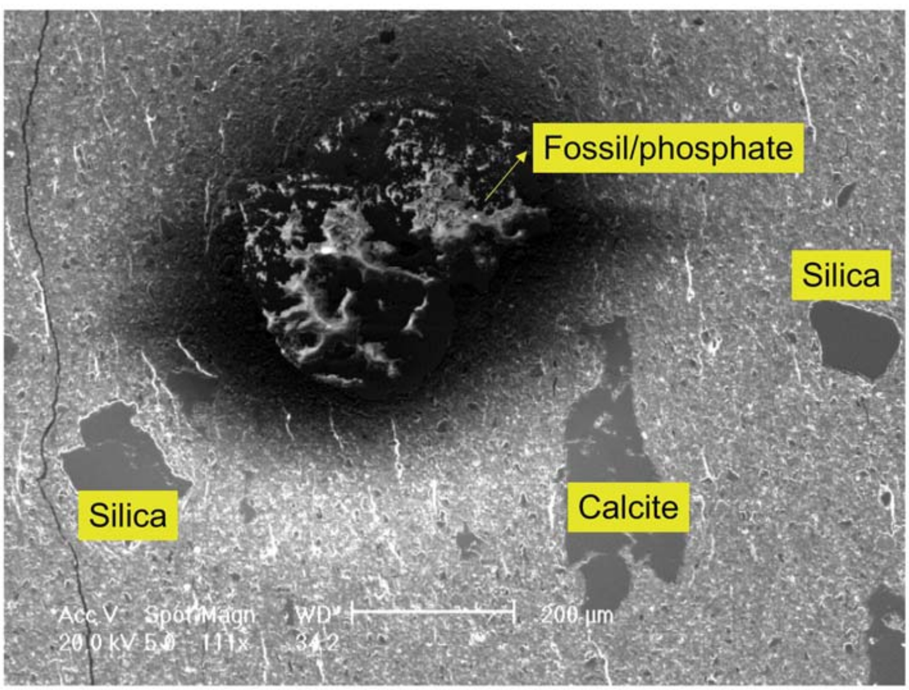
WELL 49-5

- Three samples (49-5 6493, 49-5 6496, and 49-5 6498) collected from different stratigraphic levels in lowermost part of well (Fig. 2a)
- Sparse fossil casts replaced by carbonate, phosphate, or pyrite; abundance increases with depth
- Core samples are fine grained, bedded, and fossiliferous
- Samples are least fractured and most secondary minerals are deposited along bedding planes
- Abundant slickenside fractures present close to the contact with underlying carbonate unit

ANALYTICAL RESULTS

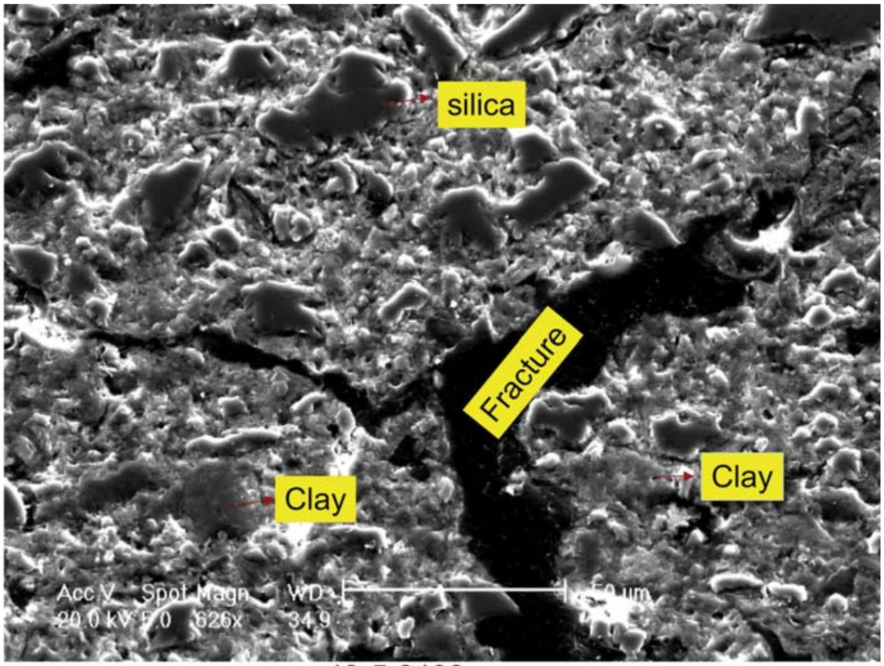
I. PETROGRAPHY

- Optical and SEM examinations of samples provided information on texture, microfractures, and primary and secondary minerals
- Sample 49-5 6493 is fine grained and massive (Fig. 3a)
- Contains comparable amounts of dark brown matrix and microcrystalline mineral phases
- Samples 49-5 6496 and 49-5 6498 are also fine-grained, bedded, and banded (Fig. 3b)
- Bands defined by dark and medium brown clay matrix
- More cavities and fossils noted in these samples
- Cavities mostly aligned to bedding plane
- Calcite is the dominant diagenetic phase in cavities and matrix
- Fractures with secondary minerals are rare



49-5 6498

Figure 3a SEM photograph, showing fine-grained clay and silica minerals and open fracture



49-5 6493

Figure 3b SEM photograph, showing fossil remains and calcite and silica in fine-grained clay matrix

II. MINERALOGICAL RESULTS

- Shale samples from lowermost section of Well 49-5 contain variable amounts minerals (Fig. 4)
- Illite and quartz are dominant minerals phases followed by mica, smectite, plagioclase, and pyrite
- Other minerals include kaolinite, K-feldspar, calcite, chlorite, and dolomite
- Illite and pyrite increase with depth, whereas other minerals randomly vary with depth
- Abundance of illite and silica may be attributed burial diagentic process

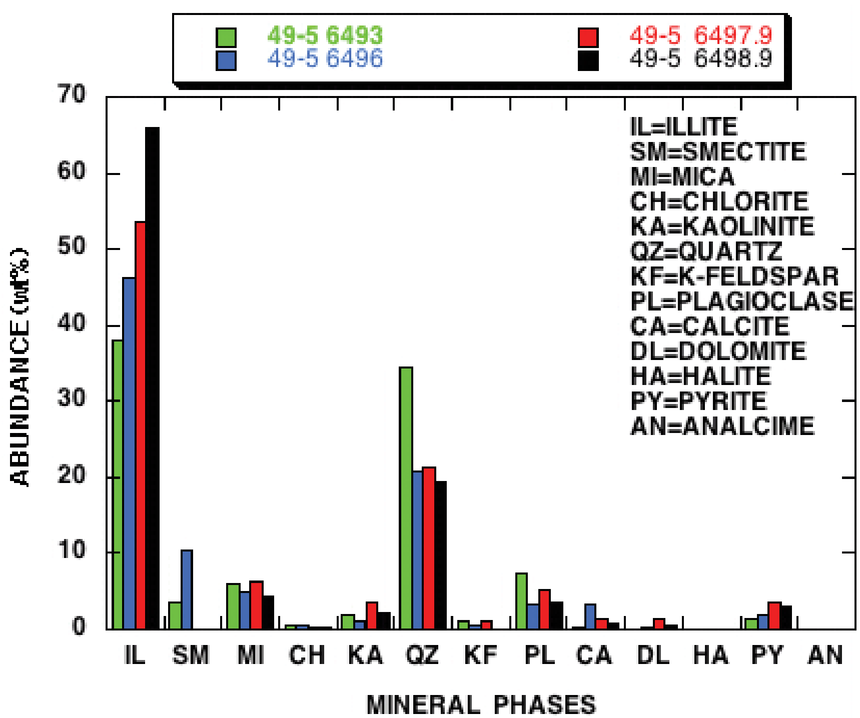


Figure 4 Mineralogical compositions of shale samples from 49-5 well

III CHEMICAL RESULTS

- Major and trace element compositions determined on three shale samples
- Variations in Fe, Mg, Ca, and Sr contents in sedimentary rocks commonly used to assess depositional environments and diagenesis (Vincent et al., 2006)
- Plots of CaO, Fe_2O_3, K_2O, MgO, Na_2O, and Sr against depth exhibit significant variations except for Na_2O (Fig. 5)
- Elemental concentrations increase with depth

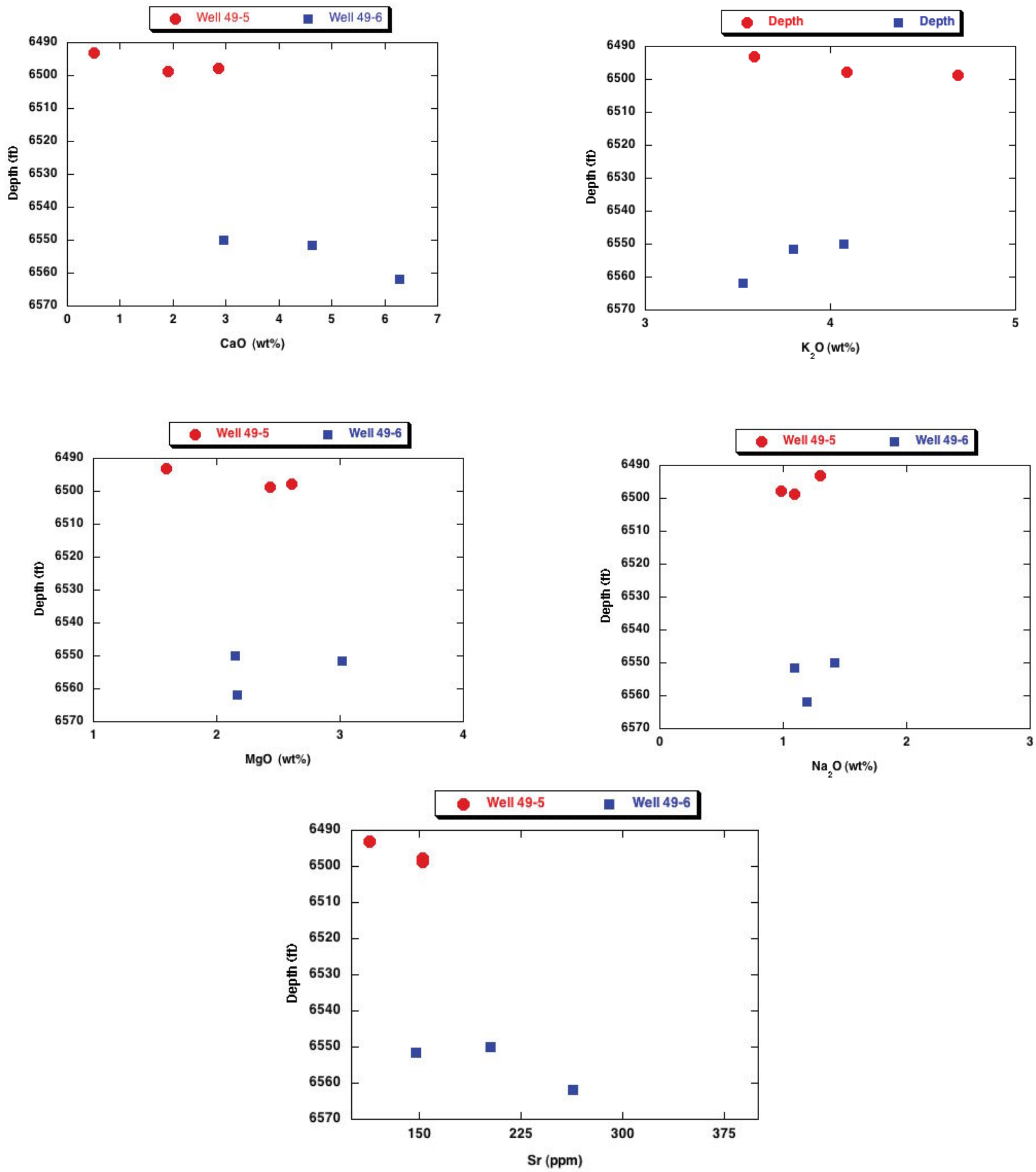


Figure 5 Variation diagrams of depth versus CaO, Fe_2O_3, K_2O, MgO, Na_2O, and Sr for shale samples from Wells 49-5 and 49-6.

CHARACTERIZATION OF SHALE SAMPLES

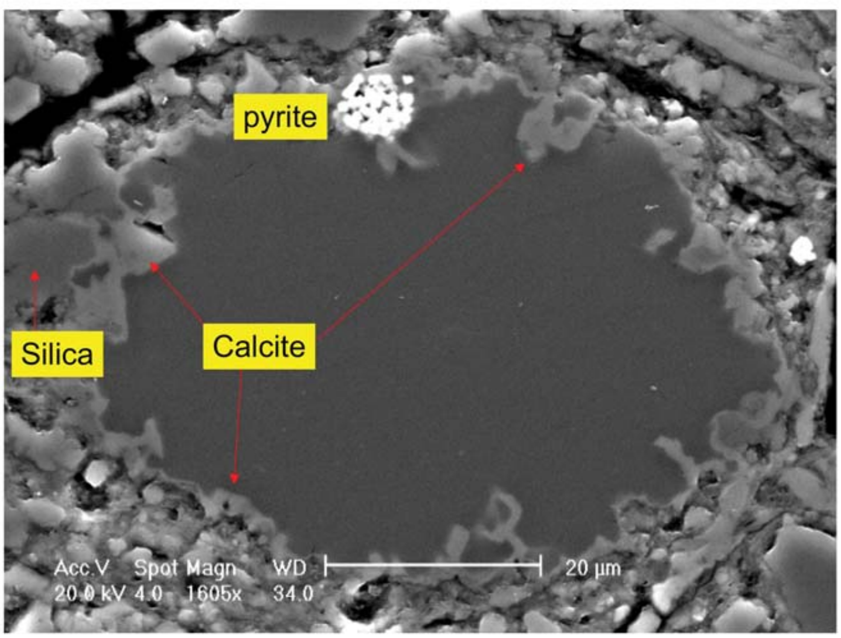
WELL 49-6

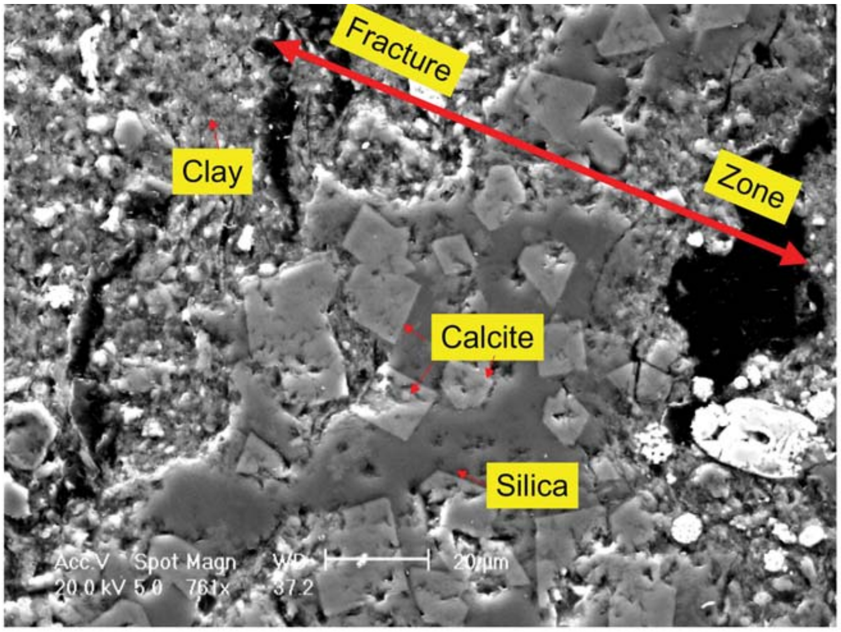
- At least four shale samples (49-6 6550, 49-6 6553, 49-6 6559, and 49-6 6562) selected from lowermost caprock (Fig. 2b)
- Shale fragments are dense, dark gray, fine-grained, bedded, and contain calcite in cavities and along bedding planes
- Fossil casts partially replaced with calcite and/or pyrite were noted and are common in lower samples
- Fractures are rarely seen in hand specimen

ANALYTICAL RESULTS

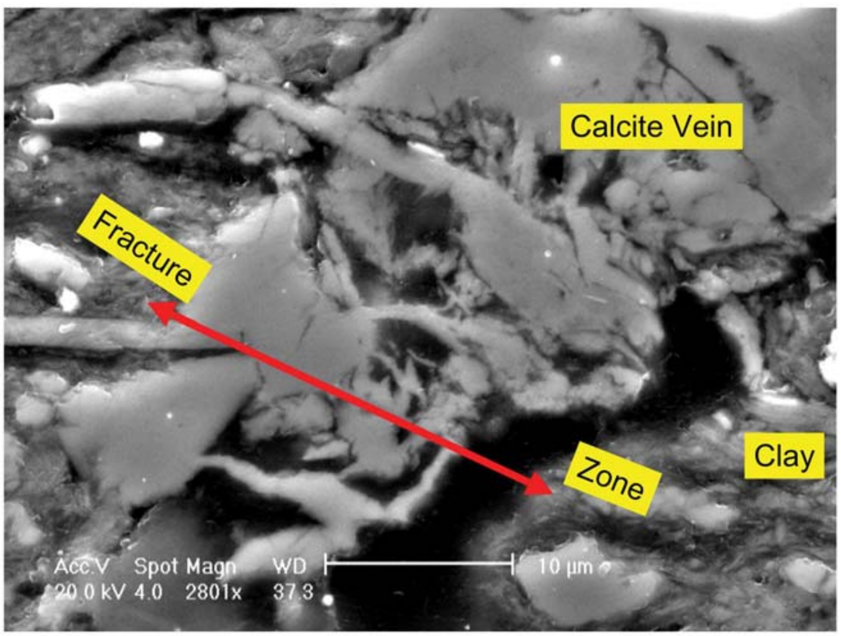
I. PETROGRAPHY

- Optical and SEM examinations indicate similar textural features and mineral assemblages (Figs. 6ae)
- Shale samples are bedded and banded defined by medium and dark brown fine-grained matrix
- Uppermost three samples contain abundant microcrystalline minerals in cavities stretched parallel to bedding
- Coarse detrital quartz and feldspar grains occur as lenses in lowermost sample (49-6 6562)
- Rare microfractures filled with calcite veinlets cut bedding planes
- Calcite minerals are partially altered

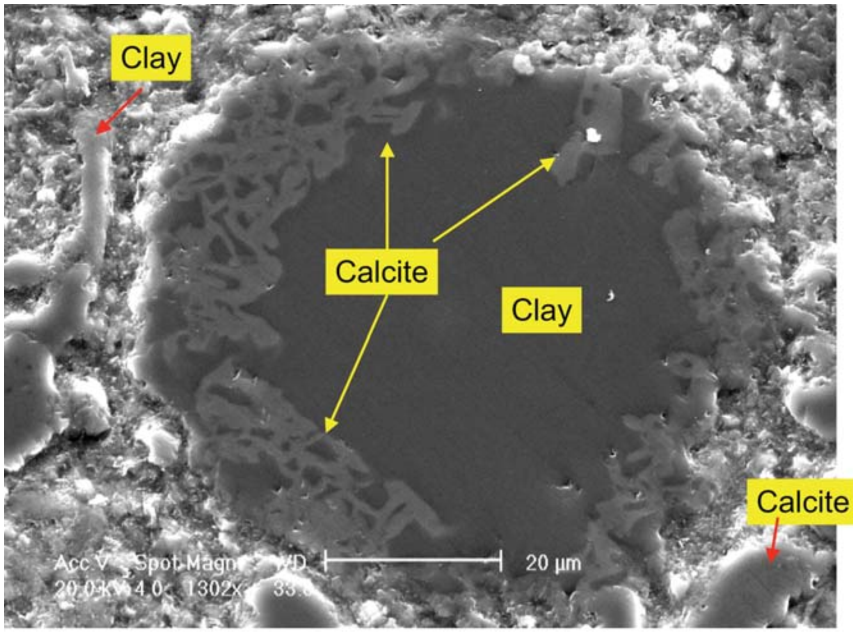




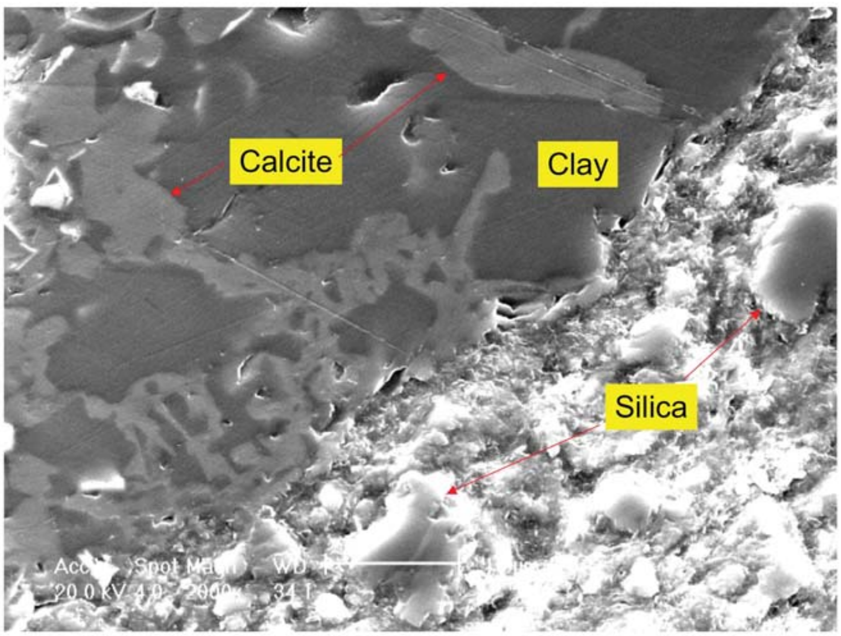
49-6 6553



49-6 6550



49-6 6559



49-6 6562

Figure 6a-e SEM photographs, showing fine-grained clay, discrete and disseminated calcite, silica, and pyrite minerals and open fractures are filled with calcite and silica

II. MINERALOGICAL RESULTS

- Five shale samples contain similar mineral assemblage (Fig. 7ab)
- Illite and quartz are dominant minerals
- Mica, smectite, plagioclase feldspar, and pyrite are the next abundant minerals
- Calcite, dolomite, K-feldspar, kaolinite, chlorite, analcime, and trace amounts of halite represent least abundant assemblage
- Illite and smectite contents decrease with depth, whereas quartz increased slightly

- Calcite contents are higher in the lowermost two samples
- Increase in illite and quartz and decrease in smectite may be attributed to burial diagenesis

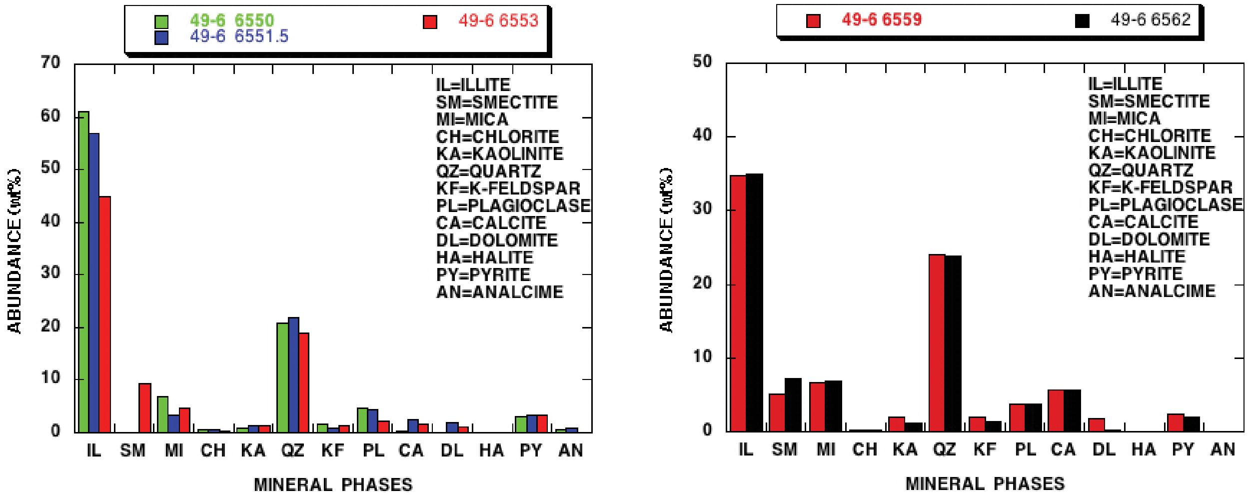


Figure 7ab Mineralogical composition of shale samples from 49-6 well

III. CHEMICAL RESULTS

- Major and trace element compositions of three shale samples from lowermost section of Well 49-6 determined (Table 2).
- Major element compositions of discrete and disseminated carbonate minerals in four shale samples were analyzed using electron microprobe (Table 3).
- Plots of CaO, Fe_2O_3, K_2O, MgO, Na_2O, and Sr against depth exhibit significant variations except for Na_2O (Fig. 5).
- CaO, Fe_2O_3, and Sr increase with depth.
- Carbonate minerals are mostly composed of $CaCO_3$ (94-99 wt%) with trace amounts $FeCO_3$, $SrCO_3$, and $MgCO_3$ (Fig. 8).
- $CaCO_3$ and $MgCO_3$ contents generally increase with depth, whereas $FeCO_3$ and $SrCO_3$ concentrations show the opposite trend.

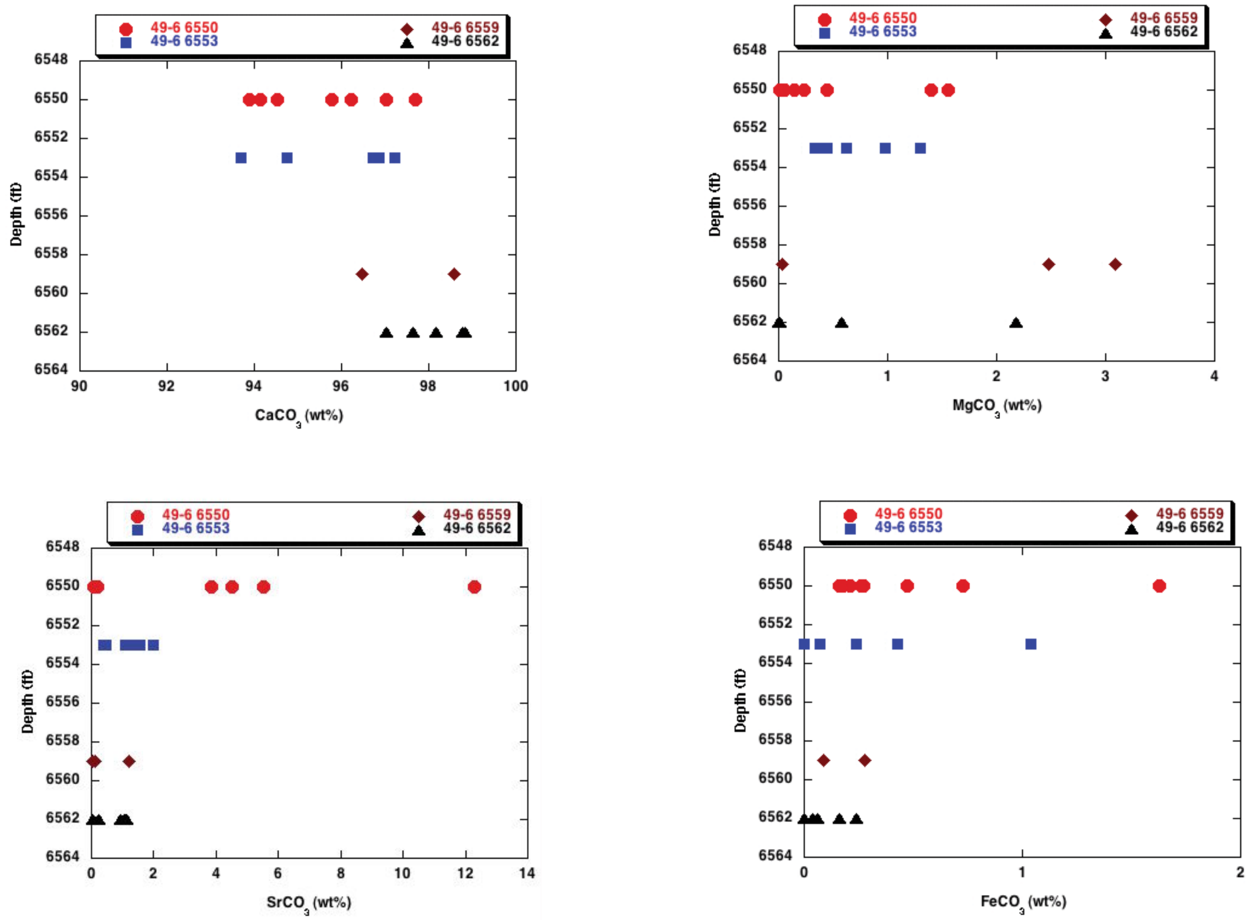


Figure 8 Variation diagrams of depth versus $CaCO_3$, FeCO3, $SrCO_3$, and $MgCO_3$ for shale samples from 49-6 well.

DISCUSSION AND CONCLUSION

- Shale samples from Wells 49-5 and 49-6 are characterized by different textural features. No discrete and disseminated carbonates were recognized in 49-5 samples (Figs. 3ab). Shale samples show very few microfractures that are partially filled with secondary calcite and silica in Well 49-6 samples. Discrete calcite minerals are partially altered (Figs. 6a-e).
- Despite variations in abundances, all samples contain similar mineral assemblage. Samples from Well 49-5 contain more illite and quartz than those from Well 49-6 (Figs. 4 and 7ab). In Well 49-5 samples, illite concentration increases with depth, whereas quartz and calcite exhibit the opposite trend. In Well 49-6, illite decreases with depth, calcite concentration increases, and other mineral phases show minor variations.
- Increase in calcite minerals in shale caprock along the contact with underlying carbonate may be caused by upward diffusion of carbonate-rich fluids into the shale unit.
- Minor increase of calcite content in Well 49-6 suggests absence of CO_2 diffusion into overlying shale that would have led to decreased pH and alteration of carbonate minerals.
- Partial alteration in discrete carbonate crystals deposited along microfractures may be caused by oxidation of pyrite that leads to formation of sulphuric acid.
- Despite slight decrease in calcite contents in shale samples from Well 49-5, results from petrographic, mineralogical, and chemical analyses suggest that no evidence of CO_2 diffusion was noted in the shale caprock, proving its sealing quality in a CO_2-flooded environment.

ACKNOWLEDGEMENT

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