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SHALE MINERALOGY AND BURIAL DIAGENESIS OF FRIO AND VICKSBURG
FORMATIONS IN TWO GEOPRESSURED WELLS, MCALLEN RANCH AREA,
HIDALGO COUNTY, TEXAS

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ABSTRACT

Thirty-six shale samples ranging in depth from 1,454 ft to 13,430 ft from Shell Oil Company No. 1 Dixie Mortgage Loan well and 33 shale samples ranging in depth from 2,183 ft to 13,632 ft from Shell Oil/Delhi-Taylor Oil Corporation No. 3 A.A. McAllen well were examined by x-ray techniques to determine the mineralogical parameters of the geopressured zone in the Vicksburg Fairway. Both wells have the same weight-percent trends with depth for the mineralogy: quartz, calcite, total clay, and potassium feldspar are constant; plagioclase feldspar gradually increases; kaolinite increases; discrete illite decreases; total mixed-layer illite-smectite (I/S) decreases; illite in mixed-layer I/S increases; and smectite in mixed-layer I/S decreases. Chlorite is found only in the geopressured zone of each well.

Significant diagenetic changes begin at calculated equilibrium temperatures of 58° - 69° C. The most important change is the transformation of smectite to illite within the mixed-layer I/S phase which occurs according to the reaction suggested by Boles and Franks (1979) with Al^{3+} acting as an immobile component. The source of K^{+} for this reaction is discrete illite. The breakdown of discrete illite results in two other changes with depth:

the formation of kaolinite; and the increase of plagioclase feldspar which is due to reaction with Na^+ and Ca^{2+} provided by the smectite to illite transformation.

The Boles and Franks model is compatible with a steady supply of original mixed-layer I/S during the depositional history of the McAllen Ranch area. The constant content with depth of calcite, quartz, and potassium feldspar indicates that limited material, if any, is supplied by the shales to surrounding sands. The ions generated by changes within the clay minerals are involved in further clay mineral reactions as outlined above. In addition, magnesium and iron are involved in forming chlorite within the shales.

INTRODUCTION

This report is part of a major study of the reservoir parameters for geopressured geothermal energy in the Gulf Coast region, funded by the Division of Geothermal Energy, U.S. Department of Energy, and administered by the Bureau of Economic Geology, The University of Texas at Austin. In particular, this report concentrates on shale mineralogy, using x-ray analysis to both identify and quantify individual minerals in the shales.

Shale samples from two wells in the McAllen Ranch Area, Hidalgo County, Texas were examined: 1) 36 samples ranging in depth from 1,454 ft to 13,430 ft from Shell Oil Company #1 Dixie Mortgage Loan Company well; and 2) 33 samples ranging in depth from 2,183 ft to 13,632 ft from Shell Oil Company/Delhi-Taylor Oil Corporation #3 A.A. McAllen well. A location map for these wells is given in Loucks and others (1980).

The purpose of this study is to determine the mineralogical parameters of the shales in the Frio and Vicksburg Formations, and to determine the extent of interaction between shales and adjacent sandstones during diagenesis.

GEOLOGIC SETTING

The Oligocene Vicksburg Formation is a shallow water, high-constructive lobate delta deposit (Han, 1980). Sediments were deposited on the downthrown side of a major growth fault (Berg and others, 1979; Loucks, 1978). The displacement along the fault is more than 4,000 ft (Loucks, 1978; Loucks and others, 1980).

The basal Frio Formation (Oligocene) overlies the Vicksburg Formation, and is also a delta deposit. The boundary between the Frio and Vicksburg Formations has been estimated from electric logs to occur at approximately 7,300 ft in the #1 Dixie Mortgage Loan Company well, and at approximately 8,650 ft in the #3 A.A. McAllen well.

The top of the "hard" geopressed zone (0.7 psi/ft) is encountered in the basal Frio Formation of both wells: approximately 6,900 ft in the #1 Dixie Mortgage Loan Company well; and approximately 7,800 ft in the #3 A.A. McAllen well (R.G. Loucks, personal communication).

ANALYTICAL METHODS

Both selection of sample intervals and sample preparation were performed by the Bureau of Economic Geology. Each sample was sieved and hand-picked under a microscope to remove sand and silt. Samples were then crushed with mortar and pestle and separated into less-than-62-micron and less-than-2-micron fractions.

The less-than-62-micron fraction was used for x-ray determination of bulk mineralogy. Diffractometer tracings were obtained with a Philips diffractometer utilizing a scintillation detector and pulse height analyzer. $\text{CuK}\alpha$ radiation was generated at 35 kilowatts and 15 milliamperes. Each sample was scanned from $4^{\circ} 2\theta$ to $70^{\circ} 2\theta$ at a rate of 1° per minute with 1° divergence and scatter slits and a 0.1 mm receiving slit.

The method of Schultz (1964) was used to make semiquantitative estimates of the weight percent for total clay, barite, analcime, quartz, potassium feldspar, plagioclase feldspar, calcite, pyrite, and hematite. The number of mineral constituents in any one sample ranged from four to six. The variation in the weight percent sums of each sample's constituents differed in each well: 89% to 109% in the #1 Dixie Mortgage Loan well; and 91% to 110% in the #3 A.A. McAllen well. These sums have been normalized to 100% in determining values for individual samples. Although the precision is at best $\pm 10\%$ of the amount present and the accuracy is even less reliable (Hower and others, 1976), major changes in individual mineral contents are readily observed and this method is considered useful for noting mineralogical trends with depth.

After removing calcite and organic matter, the less-than-2-micron fraction was used to prepare oriented clay samples for x-ray analysis. Each of these samples was scanned from $2^{\circ} 2\theta$ to $36^{\circ} 2\theta$ three separate times: 1) oriented clay sample with no further treatment; 2) after solvation with ethylene glycol for a minimum of 12 hours in a vacuum desiccator; and 3) after heating to 550°C for one hour. Machine settings were the same as those used for the bulk mineralogy samples, with the exception that some samples required different kilovolt and milliampere settings to keep the diffractometer tracings within the range of the chart recorder. In these situations the three clay scans for any one sample were produced at identical settings.

The methods of Johns and others (1954) and Perry and Hower (1980) were used to make semiquantitative estimates of the weight percent of discrete illite, kaolinite, chlorite, and mixed-layer illite-smectite (I/S). The term "discrete illite" is used in this report to mean illite that is not

involved in the mixed-layering of illite and the swelling clay, smectite. The proportions of illite and smectite in the mixed-layer I/S were determined by scanning the solvated sample from $15^{\circ} 2\theta$ to $18^{\circ} 2\theta$ at $\frac{1}{4}^{\circ}$ per minute (Reynolds and Hower, 1970).

RESULTS

Both wells have the same weight-percent trends with depth for the bulk mineralogy. Quartz, calcite, total clay, and potassium feldspar are constant. Plagioclase feldspar content gradually increases, although this trend is not as pronounced in the #3 A.A. McAllen well. Pyrite is found at depths deeper than 6,000 ft in both wells; hematite is present at shallower depths. Barite is found in a few samples and it is considered to be a contaminant from the drilling fluids. Analcime was found in only one sample from the #3 A.A. McAllen well; it is probably authigenic in origin.

Although individual clay mineral contents vary widely from sample to sample, similar depth trends can be observed in both wells (fig. 1 and 2): kaolinite increases; discrete illite decreases; and mixed-layer I/S decreases. No discrete smectite was observed in any samples.

The proportions of illite and smectite in mixed-layer I/S (fig. 3 and 4) show three distinct zones which characterize the physical arrangement of illite and smectite within the mixed-layer phase:

- 1) At proportions of illite layers approximately 50% and less, the illite and smectite are arranged in a random interstratification.
- 2) At proportions of illite layers approximately 50-70%, the illite and smectite are arranged in a weak order interstratification. This ordering is noted by the presence of a weak superlattice reflection between the illite and smectite maxima on the diffractogram of the solvated, oriented clay sample.

- 3) At proportions of illite layers approximately 70% and more, illite and smectite are arranged in a strong order interstratification. This ordering is noted by a distinct superlattice reflection between the illite and smectite maxima on the diffractogram of the solvated, oriented sample.

The boundary markers between random, weak, and strong order also are valuable in outlining general relationships between discrete illite and kaolinite (figs. 1 and 2): within the random order zone, more discrete illite than kaolinite is present; within the weak order zone, the discrete illite and kaolinite are subequal in amount; within the strong order zone, kaolinite dominates over discrete illite. In addition, chlorite is found only in the strong order zone of each well.

In the #1 Dixie Mortgage Loan well, diagenetic changes are first observed at a depth of approximately 4,700 ft. These changes include a decrease in discrete illite (fig. 1) and a change in illite and smectite proportions in the mixed-layer phase (fig. 3). The calculated equilibrium temperature at 4,700 ft is 69°C.

In the #3 A.A. McAllen well, diagenetic changes are marked by a decrease of discrete illite (fig. 2) at a depth of approximately 6,300 ft. The calculated equilibrium temperature for this depth is 58° C.

DISCUSSION AND CONCLUSIONS

The most important change in both wells is the transformation of smectite to illite within the mixed-layer I/S phase. Two different reaction mechanisms for this transformation have been suggested. The first (Hower and others, 1976) adds both K^+ and Al^{+3} to produce illite. In the second (Boles and Franks, 1979) Al^{+3} acts as an immobile component in the system and only

K^+ is added to smectite. As noted by Boles and Franks (1979), the ions released by either reaction are essentially the same, but the quantities given up when Al^{+3} is considered to be immobile are much greater than from the reaction with Al^{+3} as a mobile component.

One important consequence of the reaction with Al^{+3} as an immobile component is a significant weight loss of mixed-layer I/S as the proportion of illite within the mixed-layer phase increases (Boles and Franks, 1979). If the amount of mixed-layer I/S had been initially the same for each clay sample, then this weight loss during the reaction would be approximately 20% as the illite proportion increases from 30% to 80%. This 20% weight loss in mixed-layer I/S is observed in both wells (figs. 1 and 2). If the reaction suggested by Boles and Franks (1979) is adopted as a model for this study, then the supply of mixed-layer I/S was fairly constant during the depositional history of each well.

The smectite to illite reaction within the mixed-layer phase requires K^+ from an external source. The source in both wells appears to be the breakdown of discrete illite. Potassium feldspar is unchanged with depth, and a correlation is suggested by the decrease in discrete illite weight percent (figs. 1 and 2) and a corresponding change in mixed-layer illite and smectite proportions (figs. 3 and 4).

The breakdown of discrete illite is compensated by an increase in kaolinite content (figs. 1 and 2). This suggests that kaolinite forms as a result of the discrete illite breakdown.

Chlorite appears only in the zone of strong order, with temperatures in excess of $97^{\circ}C$. This chlorite is considered authigenic and is thought to form due to the interaction of magnesium and iron, supplied by the mixed-layer I/S reaction (Boles and Franks, 1979; Hower and others, 1970), with

discrete illite. Chlorite formed in this manner would have a high aluminum content.

The increase of plagioclase feldspar, observed in both wells, is probably related to the reactions discussed above, with Na^+ and Ca^{+2} supplied by the smectite to illite transformation within the mixed-layer phase.

The Frio and Vicksburg sandstones in South Texas (Loucks, 1978 ; Loucks and others, 1979; Loucks and others, 1980; Richmann and others, 1980) are chemically unstable and include feldspar, carbonate rock fragments, and volcanic rock fragments. Richmann and others (1980) point out that authigenic calcite is a major factor in the destruction of both primary and secondary porosity, and that other authigenic minerals are minor in comparison. It is difficult to assess the extent of interaction between the shales and adjacent sandstones without a more detailed knowledge of the chemistry of both. However, the mineralogical evidence suggests the following:

- 1) Mixed-layer smectite changes to mixed-layer illite according to the reaction suggested by Boles and Franks (1979); Al^{+3} is therefore an immobile component within the mixed-layer phase.
- 2) The source of K^+ for the smectite to illite reaction is discrete illite within the shales.
- 3) The increase in plagioclase feldspar can be explained by the breakdown of discrete illite and the smectite to illite reaction.
- 4) Potassium feldspar and calcite are unchanged with depth; this suggests that they are not involved in any major diagenetic changes within the shales.

- 5) Magnesium and iron are involved in forming aluminous chlorite within the shales.
- 6) The constant quartz content in the shales, together with the large volume of silica generated by the reaction suggested by Boles and Franks (1979), indicates that silica may be provided by the shales to the sandstones. However, Loucks and others (1980) and Richmann and others (1980) point out that quartz is a volumetrically minor cement in the Vicksburg sandstones in the McAllen Ranch area.
- 7) Kaolinite probably forms in the shales from the breakdown of discrete illite; no kaolinite is found in the Vicksburg sandstones (Loucks and others, 1980; Richmann and others, 1980).

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Figure Captions

Figure 1. Shell Oil Company #1 Dixie Mortgage Loan Company, Hidalgo County, Texas: Semiquantitative weight percent estimates for kaolinite, discrete illite, and mixed-layer illite/smectite. Dashed lines indicate a missing less-than-2-micron sample.

Figure 2. Shell Oil Company/Delhi-Taylor Oil Corporation #3 A.A. McAllen, Hidalgo County, Texas: Semiquantitative weight percent estimates for kaolinite, discrete illite, and mixed-layer illite/smectite. Dashed lines indicate a missing less-than-2-micron sample or no total clay value available.

Figure 3. Shell Oil Company #1 Dixie Mortgage Loan Company, Hidalgo County, Texas: Estimated illite and smectite proportions in mixed-layer illite/smectite. Dashed line indicates no information available. Lines on either side of individual data points indicate the range of uncertainty in determining the proportions of illite and smectite from the diffractograms. Equilibrium temperatures have been calculated using the relation developed by Kehle (Bebout and others, 1978, p. 74). See text for discussion of order relationships.

Figure 4. Shell Oil Company/Delhi-Taylor Oil Corporation #3 A.A. McAllen, Hidalgo County, Texas: Estimated illite and smectite proportions in mixed-layer illite/smectite. Dashed line indicates no information available. Lines on either side of individual data points indicate the range of uncertainty in determining the proportions of illite and smectite from the diffractograms. Equilibrium temperatures have been calculated using the relation developed by Kehle (Bebout and others, 1978, p. 74). See text for discussion of order relationships.

Fig 1

FIG 2

FIG 4