

THE EFFECTS OF BIOLEACHING ON GREEN RIVER OIL SHALE

W. C. Meyer and T. F. Yen
Departments of Geological Sciences
and Chemical Engineering
University of Southern California, University Park
Los Angeles, California 90007

INTRODUCTION

Bioleaching, utilizing a sulfuric acid medium generated by the sulfur oxidizing capabilities of Thiobacillus spp. has proved to be useful in releasing hydrocarbons from petroliferous rocks from the Mahogany Ledge of the Green River formation. As yet, however, these methods do not yield a high percentage of the kerogen trapped within the rock. The purpose of this paper is to investigate the texture and mineralogy of the Green River shale to ascertain the nature of kerogen entrapment and the physical effects of bioleaching. Such an understanding should ease the development of a method to increase the effectiveness of bioleaching in releasing kerogens for commercial extraction.

Shale Description

The Green River shale is a highly indurated, fine-grained, varved, calcareous sedimentary rock deposited in the Eocene fresh-water lake Gosuite. The rock varies in color from tan to black, depending on organic content. Rock of this type is technically a marl, but in this paper it will be called shale in convention with common usage.

Varves in the Green River shale consist of carbonate summer laminae, and fine grained winter laminae composed of clay and organic components. Thin sections of the shale show distinct banding of dark components enclosed in a light colored matrix composed of polymineralogic crystal aggregates, and small single crystals that, when large enough to identify, are predominantly dolomite. This crystalline matrix superimposes a granular texture over the entire rock.

Clays and associated (adsorbed) organics appear to be localized in small blob-like aggregates ($\approx 20\mu$) which string out to form the dark winter laminae. These organo-clay concentrations vary from diffuse dark brown bands to narrow opaque strings, but are always parallel to the varved textural grain. Light colored bands appear to be composed entirely of small matrix crystals and a few relatively coarse possibly detrital grains, with little evidence of clays or organics. The clays and visible organics are intimately associated, either because they were deposited simultaneously, or have become linked by processes of chem-adsorption. It would seem reasonable that the first step in liberating adsorbed or mechanically trapped kerogens would be the disaggregation of the crystalline matrix to release clays.

MINERAL COMPOSITION

X-ray Methods

All x-ray analyses were made using a Norelco diffractometer using $\text{CuK}\alpha$ radiation with a nickel filter, 0.006 inch slit at 40 kv and 20 MA. The optimum rate was found to be 1000 cps at $1^\circ 2\theta/\text{min}$.

Disordered powder mounts were used for whole-rock mineral analyses. Separate preparations were made for analysis of clay mineralogy, using the method devised by Jackson (5). The indurated nature of the shale made complete disaggregation impossible, but digestion of 50 gms of crushed shale in warm sodium-acetate solution (part of Jackson's method) released enough carbonate-free clay to analyze with no difficulty.

In order to separate different clay species, clay mounts were treated according to the method proposed by Carrol (3) to promote shifts in position of diagnostic x-ray peaks. This treatment includes dissication, glycolation, and heating to 350°C and 550°C respectively.

Whole Rock

Whole-rock mineral content can be divided into major and minor constituents based on relative peak intensities (Table I). The shale contains too many mineral species to be easily matched by addition of necessary comparative internal standard, therefore quantitative determination of mineral abundance were not made.

TABLE I

Whole Rock Mineralogy

<u>Major</u>	
Quartz	SiO ₂
Dolomite	CaMg(CO ₃) ₂
Calcite	CaCO ₃

Minor

Analcite	NaAlSi ₃ O ₈ · H ₂ O
Montmorillonite	Al ₄ (Si ₄ O ₁₀) ₂ (OH) ₄
Orthoclase	KAlSi ₃ O ₈
Plagioclase	Na(Ca)Al ₀₋₂ Si ₂₋₃ O ₈
Pyrite	FeS ₂

Clay Mineralogy

Montmorillonite	Al ₄ (Si ₄ O ₁₀) ₂ (OH) ₄
Illite	K ₀₋₂ Al ₄ (Si ₈₋₆ Al ₀₋₂)O ₂₀ (OH) ₄

Quartz and dolomite were found to be the predominant minerals in these samples. Calcite is also present, probably representing residual primary carbonate that has not undergone diagenesis. Dolomite and calcite appear to form the granular matrix observed in thin section. Feldspar, including albite rich plagioclase and orthoclase, occur primarily as detrital grains making up part of the primary sediment deposit. Pyrite probably formed in the sediment before or during lithification when organic-rich bottom sediments provided the reducing environment favorable to formation of this mineral.

Analcite, abundant here and in some other members of the Green River formation, is thought to have formed authigenically shortly after deposition of the primary sediment (1). It is possible that some of the plagioclase content of the shale may have been formed by reaction of analcite and quartz (2). The temperature required for this conversion is about 190°C, somewhat higher than would be expected in these deposits, but in the presence of concentrated brine, conversion temperature would be lowered (1).

To see what effect bioleaching has on mineralogy, the x-ray pattern of raw shale was compared to that of a sample that had undergone a 38.4% weight loss during bioleaching. The mineral composition of both samples

are identical, however, peak intensities of carbonate minerals are strongly reduced suggesting they have been dissolved and partially removed. Peak size is not linearly related to the amount of mineral present, so quantitative induration of carbonate removal is not indicated by comparing peak heights.

To quantify the amount of carbonate removed by bioleaching, whole-rock weight percentages of organic carbon, carbonate ion, and mineral carbonate were determined on duplicate one-half gram samples (270 mesh) using the Leco gasometric analyser (6). Calculation of mineral carbonate uses a constant (8.33) derived from the relative weight of calcium at carbonate ion in calcite. Since it was not possible to quantitatively evaluate the ratio of calcite to dolomite in the mineral carbonate fraction, the calcite constant was used for calculations. This causes the calculated weight percentages of mineral carbonate to be slightly lighter than actual values. Organic carbon was sufficiently abundant to necessitate halving the normal sample weight (0.25 g) for analysis.

Carbon and carbonate data are expressed as weight percent. Raw shale proved to be about 33% mineral carbonate by weight, and 10% carbon contained in organic compounds. Assuming an average hydrocarbon chain is C_{16} in the Green River material, the added hydrogen would bring the total weight of organic constituents to approximately 11%.

To ascertain if bioleaching is removing the available carbonate, samples of crushed (16 mesh) bioleached material were analysed for residual carbonate. The sample used for this experiment had lost 36.5% of its weight during leaching, and it was found to have approximately 2.3% residual mineral carbonate indicating that bioleaching is quite effective.

Clay

A peak at 18.8 Å in the clay and whole-rock mounts suggest montmorillonite, reported from Green River samples by previous investigators (1), is the dominant clay group in the studied samples. This peak occurs at somewhat higher angstrom values than is normal for montmorillonite, but the presence of abundant organics often causes aberration in x-ray patterns, explaining the observed shift (7).

Montmorillonite is a poorly crystallized mineral and is often not detectable by x-ray unless present in excess of 15% of the sample (3). The presence of a montmorillonite peak in the whole-rock pattern suggests, therefore, this mineral may be present in significant quantities. Water is readily absorbed into the montmorillonite structure causing swelling. If the quartz and dolomite are removed from the shale, the expansive forces of swelling montmorillonite may be useful in disaggregation of the residual fraction.

Illite is the second abundant clay mineral, and may represent primary clays, degraded mica, or potassium enriched primary clays of other species. Garrels and Mackenzie (4) show that, through time, most clay species will alter to montmorillonite, illite, or chlorite. The age of the Green River formation (Eocene) would be more than sufficient for alteration of primary clays.

It is not possible to accurately determine what percent of the shale is clay without data on the whole-rock distribution of elemental oxides. A process of elimination by comparison with mineralogy would reveal how much of these elements are contained in clays, but as yet the appropriate

analyses have not been performed.

VISIBLE EFFECTS OF BIOLEACHING

Scanning electron micrographs were taken of shale samples treated for various periods of time to see the effects of bioleaching. Samples were cut to convenient size and polished to a flat surface with #600 grit prior to treatment. Control samples of polished unleached shale (Fig. 1), and unleached fractured rock surface (Fig. 2) were photographed to ascertain if any material was being removed by crystal plucking during polishing. Neither control showed evidence of pitting due to mechanical processes, so it seems safe to conclude that pitting observed in treated samples is due to chemical action.

Shale bioleached for two days shows a pitted, spongy-appearing surface texture caused by solution of mineral material (Fig. 3). Bioleaching for one week caused no apparent increase in the number of pits per unit area, but an increase in pit size was noted. Two weeks exposure to bioleaching medium seemed to further increase pit size but did not result in formation of additional pits (Fig. 4).

In order to quantify the effects of bioleaching, photomicrographs of shale samples bioleached for varying time (Figs. 1-4) were used to count and measure the cross sectional dimensions of solution pits as an indication of the amount of material removed by solution. This data shows that solution pits form rapidly after exposure to the leaching medium. The number of pits on each sample ranged from 29 to 33 independent of time. Average pit size (calculated as surface area using the two maximum diameters for each pit) did vary directly with time, increasing from a minimum of $24.8 \mu^2$ after two days, to a maximum of $54.3 \mu^2$ after two weeks, indicating that the volume of carbonate removed is a fraction of time exposed to the bioleaching medium.

Paired microphotographs of the same area can be used as a stereopair if they are taken at slightly different tilt angles. Using an equation modified from that devised for interpretation of aerial photographs, these photographs can be used to determine pit depth. On an average the pit depth is in the order of 2.2μ (Fig. 5).

The irregular bottom of this pit is a typical effect of solution. The shelf-like false bottom, and the small penetration of the true bottom indicate that continued solution would result in farther deepening. This fact, coupled with the absent lateral enlargement with time should result in neutral and lateral interconnection of soluble sites causing an increase in porosity and permeability. This will prove to be an important mechanism to facilitate exposure of fresh surface to the leaching medium and form conduits for the migration of liberated hydrocarbons.

CONCLUSIONS

Kerogens in the Green River shale are trapped in an inorganic mineral matrix composed primarily of quartz and dolomite (calcite). Liberation of hydrocarbons will depend upon the degree to which this matrix can be disaggregated, exposing kerogen for extraction. Thin sections show organic components within this rock are associated with the clay fraction, possibly through a process of chemical adsorption. Expansive properties of montmorillonite, the dominant clay component, may be useful in final disaggregation of the shale after removal of mineral matrix.

Biobleaching effectively removes carbonate minerals from the shale eliminating matrix material, and thereby developing porosity and permeability which are effectively nil for untreated shale. This brings more rock surface in contact with the leaching medium, increasing solution of matrix and enlarging pathways for migration of liberated hydrocarbons. Carbonate removal during biobleaching proceeds rapidly upon exposure to the leaching medium, and continues as a function of time.

ACKNOWLEDGEMENT

This work is supported by NSF Grant No. GI-35683.

REFERENCES

1. Bradley, W. H. and H. P. Eugster, U. S. G. S., Prof. Paper, 49b-B, p. 1-71, 1969.
2. Campbell, A. S. and W. S. Fyfe, Am. J. Sci., 263, 807 (1965).
3. Carroll, D., Geol. Soc. Amer., Spec. Pub., No. 126, p. 1-80, 1970.
4. Garrels, R. M. and F. T. Mackenzie, Evolution of Sedimentary Rocks, W. W. Norton, Inc., N. Y., 1971, p. 235.
5. Jackson, M. L., "Soil Chemical Analyses---Advanced Course," Madison, M. L. Jackson, 1956, p. 31-59.
6. Kolpack, R. L. and A. S. Bell, J. Sed. Pet., 38, 617 (1968).
7. Seyfreid, Personal Communications, 1973.

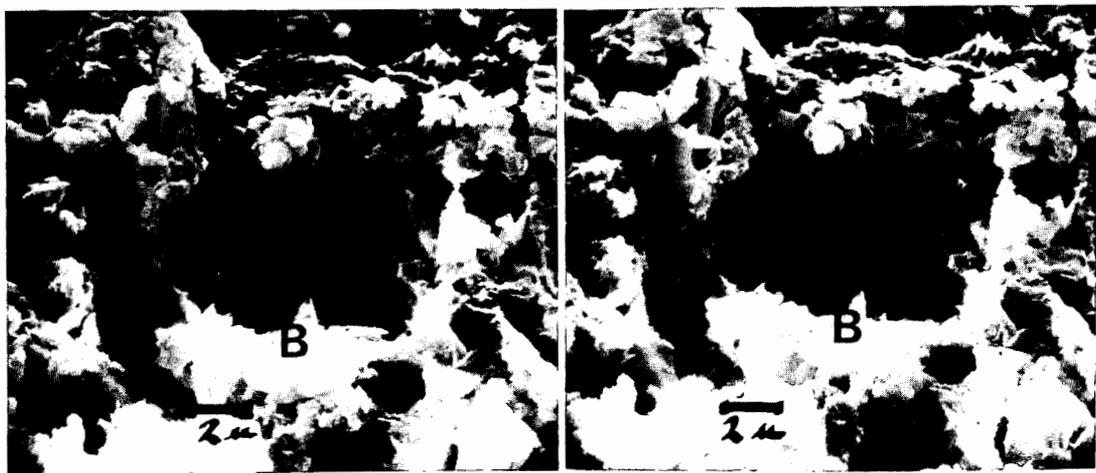


Fig. 5 Polished, leached two weeks, 0° tilt (Left)
 Polished, leached two weeks, 7° tilt (Right)

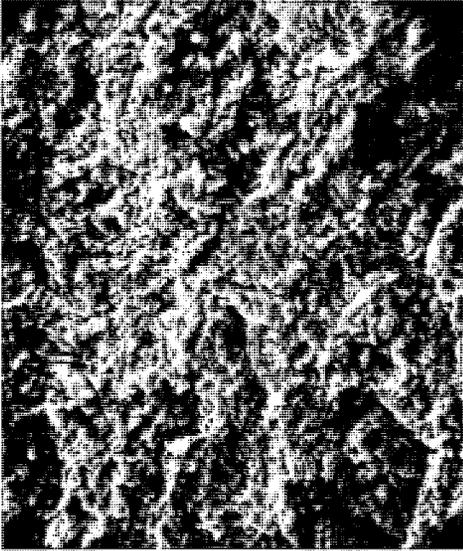


Fig. 1 Polished, unleached

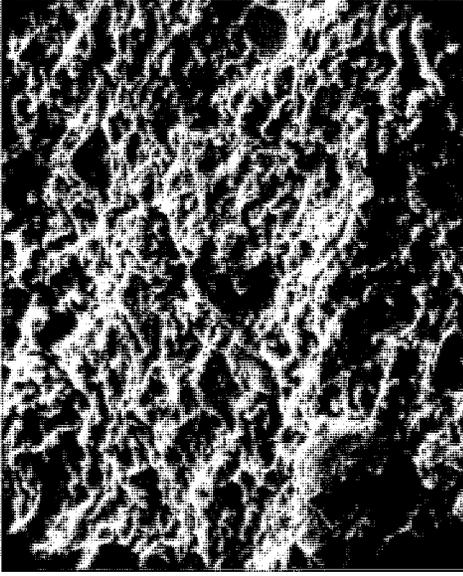


Fig. 2 Fractured, unleached

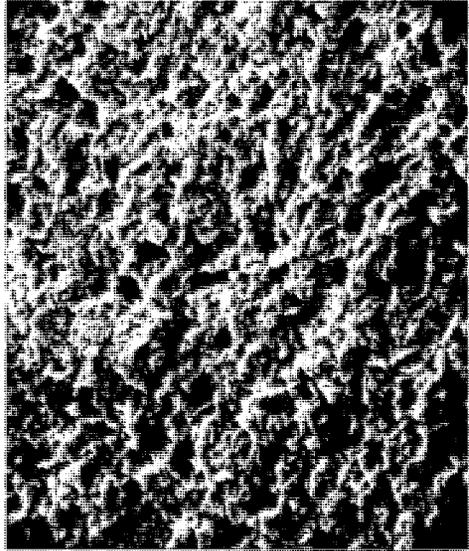


Fig. 3 Polished, leached two days



Fig. 4 Polished, leached two weeks