A STUDY OF HYDROCARBON MIGRATION EVENTS: DEVELOPMENT AND APPLICATION OF NEW METHODS FOR CONSTRAINING THE TIME OF MIGRATION AND AN ASSESSMENT OF ROCK-FLUID INTERACTIONS

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PROJECT SUMMARY

We are conducting the research to test and refine a paleomagnetic method for dating hydrocarbon migration, and to assess the chemical alteration of crude oils resulting from fluid-rock interactions. Samples were collected for paleomagnetic and organic geochemical investigations from several units. These include the Old Red Sandstone in Scotland, and the Schoolhouse Member of the Maroon Formation and the Belden Formation in Colorado. Studies of these units are completed or underway. In addition, simulation experiments, where we are attempting to form magnetite in the laboratory, are underway.

We currently have two M.S. students working on the project as well as two Ph.D. students. Four abstracts and three papers on the research have been published.

I. INTRODUCTION

Investigations of fluid migration in the subsurface are often hindered by a lack of temporal control and a fundamental appreciation of the potential for alteration of fluid composition via fluid-rock interactions. There is little doubt that the ability to constrain the time of oil migration and a better understanding of potential changes in oil composition during migration would be of significant benefit for oil exploration. For the past several years we have worked on the development of a paleomagnetic method for dating hydrocarbon migration. The refinement and field tests of this dating method are the primary objectives of this study. In addition, we are testing the paleomagnetic dating approach with another hydrocarbon dating method, Pb-Pb radiometric dating. A secondary objective of this study has been to document some of our previous observations concerning the effects of rock-fluid interactions on the composition of crude oils. One of the proposed study areas, an exposed reservoir in northwest Colorado (Schoolhouse Member, Maroon Formation), provides us with an opportunity to continue our assessment of the potential for chemical and stable isotopic alteration of crude oils resulting from fluid-rock interactions. Whereas we have conducted numerous studies of geochromatographic effects in the laboratory, it is important that we continue to compare the results of this work with natural systems.

The research supported under this grant involved both field and laboratory studies. Field tests include the Schoolhouse Member of the Maroon Formation (Pennsylvanian), an exposed reservoir in northwest Colorado, and the Belden Formation (Pennsylvanian), the presumed source for the hydrocarbons in the Schoolhouse Member. Another unit we are investigating is the Old Red Sandstone in Great Britain. Certain intervals contain uraniferous bitumen from which independent Pb-Pb dates for hydrocarbon migration can be determined. We have also begun laboratory simulation experiments in order to better understand the mechanism of magnetite precipitation.

II. SCHOOLHOUSE MEMBER, MAROON FORMATION, NW COLORADO

Samples for both paleomagnetic and geochemical investigations of the Schoolhouse Member of the Maroon Formation were collected and analyzed. Red samples of the Maroon Formation contain a stable magnetization that resides in hematite. Demagnetization to high temperatures suggests that this magnetization is detrital in origin and was acquired during deposition of the rock. Bleached and hydrocarbon-impregnated samples are magnetically distinct from the red samples (Elmore et al., 1993; Appendix I). On average, the magnetic intensities are lower, and rock magnetic studies suggest the magnetization resides in magnetite. At locations where the

hydrocarbon-impregnated sandstones are not well cemented, they contain a weak modern component or contain no stable remanence. At two locations (Miller Creek and Red Canyon), some of the sandstones are cemented by silica and carbonate, and some specimens contain stable directions. The magnetizations in some specimens have N-NW declinations and shallow to moderate inclinations. Other specimens, however, contain a complex magnetization, with apparently both normal and reversed components. These rocks are apparently remagnetized and contain a different magnetization than in the red beds. These studies of the Schoolhouse member of the Maroon Formation in Colorado are also consistent with a connection between hydrocarbons and magnetite authigenesis (Elmore et al., 1993).

A suite of samples was also collected for an organic geochemical study of the Schoolhouse Member. A vertical suite of samples was collected from six locations. We have also acquired some oil from the Rangely Anticline where the reservoir is in a unit laterally equivalent to the Schoolhouse Member. Samples of the Belden Formation have also been collected. We hope to see a positive oil/ reservoir/source rock correlation between the three sample sets. We are also examining the hydrocarbons in the Schoolhouse Member to see if there are lateral or vertical changes in biomarkers and molecular isotopes.

Twelve Schoolhouse samples have been extracted using a Soxhlet extractor and we currently have TOC and $\delta^{13}C$ values from all of the Belden samples. The rest of the samples will be extracted and fractionated in preparation for GC and isotopic analysis.

III. BELDEN FORMATION, NW COLORADO

We are also conducting a geochemical and paleomagnetic study of the Belden Formation, the presumed source rock for the hydrocarbons in the Schoolhouse Member. Organic-rich limestones in the Belden Formation on an asymmetric anticline near Sweetwater, Colorado contain a Cretaceous, apparently synfolding remagnetization that resides in magnetite (Fruit and Elmore, 1992; Appendix I). The Belden locally consists of a number of repetitive shoaling upward parasequences some of which are capped by arkosic sandstone. Magnetic intensities of the remagnetization, which vary by nearly three orders of magnitude, are controlled by lithology rather than structural position. This disproves an initial working hypothesis that high strain in the hinge area of the fold caused increased magnetic intensities directly, or indirectly by allowing increased access to remagnetizing fluids. Some samples with high intensities have abundant organic-rich fecal pellets containing pyrite with alteration rims, possibly magnetite. We have begun to characterize the carriers of the magnetization in the samples using the SEM and to determine their composition using a Scanning TEM. Selective demagnetization suggests that the pellets contain much of the magnetization in these samples. These results suggest that intensity is at least partly controlled by original composition and that the remagnetization may involve the alteration of pyrite to magnetite. Two hypotheses for the origin of the chemical remagnetization are currently being tested: alteration by external (basinal?) fluids or alteration without the addition of external fluids. Preliminary $^{87}Sr/^{86}Sr$ isotopic data indicate that the Belden was altered by a radiogenic fluid. It is not yet clear if the alteration caused by this fluid is related to the Cretaceous remagnetization. We are also attempting to test whether there is a relationship between the abundance of hydrocarbons and the remagnetization.

IV. SIMULATION STUDIES

We are currently conducting laboratory simulation studies in an attempt to understand the process of magnetite precipitation. During the past two years we have focused on two models for magnetite precipitation; one involves in situ organic mediated conversion of pyrite to magnetite and

the other involves secondary magnetite precipitation triggered by migrating fluids. We have conducted simulation experiments to investigate the replacement of pyrite by magnetite in the presence of organic matter which we believe is the major process of magnetite authigenesis in the Belden (Brothers et al., 1993). We have successfully produced magnetite by a dissolution-reprecipitation process which may simulate diagenesis at temperatures below 100°C and is one possible pathway for magnetite authigenesis.

IV. OLD RED SANDSTONE, SCOTLAND

We have collected and analyzed a suite of samples from red as well as hydrocarbon-impregnated sandstones from the Old Red Sandstone (Devonian) in Scotland. Preliminary results indicate that the impregnated rocks contain a magnetization residing in magnetite in contrast to the red samples where the magnetization resides in hematite. We have not been able to isolate a stable direction from the impregnated samples. We have, however, found a stable late Paleozoic magnetization (in magnetite) in lacustrine organic-rich silts in the unit (Plaster-Kirk et al., 1993). The results we have obtained are encouraging and we plan to conduct an additional sampling trip.

One of the key objectives of the research is to compare the paleomagnetic dating method with a Pb-Pb radiometric dating approach used by our colleague, John Parnell. He has had problems with his laboratory and we have no radiometric dates to report as yet. As soon as the lab is functional, we plan to acquire dates from the same rocks we sampled in Scotland.

VI. STUDENT PARTICIPATION

A significant proportion of the funds in the grant is being used to support the research of four graduate students. Mr. David Fruit, a Ph.D. candidate under the supervision of Dr. Elmore, is working on the paleomagnetism and geochemistry of the Schoolhouse and Belden formations. Ms. Lisa Plaster-Kirk, a M.S. student working with Dr. Elmore, is working on the paleomagnetism of samples from Scotland and helping with the analysis of the rocks from Colorado. Ms. Kendra Brisman, a M.S. student under the supervision of Dr. Engel, is working on the organic geochemistry of the Schoolhouse and Belden formations. Ms. Cindy Brothers, a Ph.D. candidate under the supervision of Dr. Engel, is working on the laboratory simulation experiments.

VII. PRESENTATIONS AND PUBLICATIONS

The presentations and papers that were partially or completely supported by this grant are listed below. Papers are included in the Appendix.

Brothers, L., Engel, M.H., Elmore, R.D., and Fruit, D., 1993, Formation of magnetic minerals via diagenetic reactions of iron and organic matter: Implications for paleomagnetic dating: Amer. Chem. Soc. National Meeting, GEOC 74.

Elmore, R.D., 1992, Remagnetization and fluids: EOS, v. 73, p. 35.

Elmore, R.D., Imbus, S., Engel, M., and Fruit, D., 1993, Hydrocarbons and magnetizations in magnetite: SEPM Special Publication #49, 181-191.

Elmore, R.D., and Engel, M.H., A study of hydrocarbon migration events: Development and application of new methods for constraining the time of migration and an assessment of

rock-fluid interactions: DOE Workshop, Sedimentary Basin Geochemistry and Fluid-Rock Interactions, Norman, OK, 1991.

Fruit, D.J. and Elmore, R.D., 1992, Lithologic control on a secondary magnetization, Pennsylvanian Belden Formation, NW Colorado (abs.): AGU Trans., v. 73, p. 97.

Imbus, S., Macko, S., Elmore, R.D., and Engel, M.H., 1992, Stable isotope (C, S, N) and molecular studies on the Precambrian Nonesuch shale: Evidence for differential preservation rates, depositional environment, and hydrothermal influences: Isotope Geoscience, v. 101, 255-281. Supported by previous DOE grant to Engel and Elmore (DE-FG05-89ER14075) which ended 8/30/91.

Plaster-Kirk, L. and Elmore, R.D., 1993, Paleomagnetism of organic-rich lacustrine deposits and hydrocarbon saturated sandstones, Old Red Sandstone, Scotland: EOS Trans., v. 74, 114-115.

VIII. APPENDIX I

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