



Project Summary

Characterization of Two Core Holes from the Naval Oil Shale Reserve Number 1

R. D. Giauque, J. P. Fox, and J. W. Smith

This study was conducted by Lawrence Berkeley Laboratory for the Industrial Environmental Research Laboratory - Cincinnati, U.S. Environmental Protection Agency, and for the Laramie Energy Technology Center of the U.S. Department of Energy. Two hundred eighty (280) raw oil shale samples from two core holes on the Naval Oil Shale Reserve Number 1, located in the Piceance Basin of Western Colorado, were analyzed to determine the stratigraphic variability of major, minor, and trace elements and to determine their association with major minerals.

This Project Summary was developed by EPA's IERL, Cincinnati to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

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Introduction

Green River oil shale is a marlstone that contains about 20 percent organic material. It was deposited from an ancient lake that covered parts of Colorado, Utah and Wyoming. This lake was probably permanently stratified. The upper portion supported life, and the lower layer was probably a sodium

carbonate solution with a pH of 11 to 12. Oil shale was formed by lithification of sediments accumulated at the bottom of this lake. These materials entered the lake by overland runoff and atmospheric fallout of dust, pollen, and volcanic ash.

Vertical variability in major, minor, and trace elements and mineral phases in oil shale deposits have been previously noted. This variability is significant from an environmental, economic and processing standpoint. Vertical modified in-situ (VMIS) retorts will span 300 to 700 feet or more of a vertical section of oil shale. Large changes in elemental and mineral concentrations through these sections may produce oils, gases and waters of varying compositions. These variations may affect treatment of the waters and gases and upgrading of the oil. Significant changes in mineral forms and elemental composition across a VMIS retort will also affect the process energy balance and any catalytic effects due to specific elements. Similarly, in surface retorting, richer deposits are mined and retorted in surface retorts. If environmentally undesirable elements are concentrated in some horizons and not in others, it may be feasible to eliminate or minimize some environmental problems by preferentially mining the deposits.

Both environmentalists and geochemists are interested in the magnitude and significance of stratigraphic variations. To the geochemist, stratigraphic distribution is a variable answering questions about depositional trends. To the environmentalist, stratigraphic distribution

provides information on the size and significance of the overall consequences of developing that oil shale deposit and controls that might be used to prevent adverse environmental impacts. Environmental concerns center around potentially hazardous elements such as Hg, Cd, and Se.

This report provides some of this basic information. It discusses the stratigraphic distribution of elements, minerals and Fischer Assay oil and water content in two cores from the Colorado Naval Oil Shale Reserve No. 1, the site of much developmental testing and the source of most of the Green River Formation oil shale samples discussed in U.S. oil shale literature.

Method

The detailed measurements were made on 280 samples from core holes 15/16 and 25 and are presented in the report. A computerized data system was used to plot histograms.

For statistical purposes, the results determined for each core hole were broken down into individual groups. The groups corresponded to the different stratigraphic zones for which samples were composited at 5-foot (1.5 meter) intervals or less. The overlying oil shale, the upper Mahogany Zone, the Mahogany Bed, the lower Mahogany Zone and the rich oil shale were the five stratigraphic zones of core hole 15/16, for which the above criterion was met. The corresponding stratigraphic zones of core hole 25 were composited at intervals similar to those of core hole 15/16, except there was not a rich oil shale zone.

Relative minimum-maximum values were calculated for each variable on a group basis for each core hole. Pearson correlation coefficients and corresponding statistical significance values were determined for pairs of variables for each of the above groups.

The report lists the range of Fischer Assay and mineral results for both core holes, and summarizes concentration ranges for all the elements. In nearly all cases, the range of values for each variable is very similar for the two core holes. This illustrates, in a broad manner, the degree of horizontal uniformity across the Green River oil shale deposit.

The report summarizes relative minimum-maximum values determined for each variable by stratigraphic zone and presents them as bar graphs. The report presents histograms of results for indi-

vidual composite samples from the two core holes.

Pearson correlation coefficients and corresponding statistical significance values were calculated for each variable pair on a group basis.

Statistical significance values were determined for 48 individual elements paired with 29 of the same elements. Statistical significance values were also calculated for 48 individual elements paired with eight minerals and Fischer Assay products oil and water.

Results

The most notable result of this study was the demonstration of a remarkable stratigraphic uniformity in mineral and element composition of oil shale from both cores. This uniformity is apparent in the histograms and in the average elemental concentrations summarized by stratigraphic zone. The resulting averages and their associated standard deviations demonstrate the uniformity under discussion. However, some elemental averages do not show uniformity. Fluorine and boron do not because of their analytical uncertainties. As, Hg, K, Sb, and Se are other elements with 99 percent error limits larger than two times their means. They appear to fall into two groups. As, Hg, and Se appear to have been collected by organic matter. K and Sb are part of a group associated with incursion of airborne clastic influx.

Many of the elements occur in the oil shale at levels at or below crustal abundance. Using Mason's 1960 crustal abundance table, only the carbonate elements Ca, Mg, Ba, and Sr plus U, Mo, As, Se, and perhaps Pb and W appear enriched. The enrichment mechanisms for the carbonate minerals depend on

their ease of precipitation. Barium may be present as barite as well, but about half the Ba is soluble in dilute HCl. The elements U and Mo appear to be associated with organic matter. The As, Se and perhaps Pb and W were probably initially collected by the organic matter and then released to form sulfides. Two more of the elements appear enriched, F and B. Enrichment of these in a saline lake is to be expected, but the certainty of their analytical results is limited.

Conclusions

The principal phases with which the various major, minor, and trace elements are associated (based on statistical analyses) are summarized in Table 1. Specific conclusions follow.

1. Oil shale from both core holes was comprised principally of dolomite, quartz, analcime, calcite, Na-feldspar, K-feldspar, and organic matter. Mg-siderite, illite, pyrite, and aragonite were also detected in many of the samples. Illite was detected more frequently in core hole 25 (from the edge of the depositional basin) while pyrite and aragonite were detected more frequently in core hole 15/16 (center of the basin). Dawsonite and fluorite were detected in a few samples. The concentrations of dolomite and quartz were relatively constant. These two minerals typically accounted for forty weight percent of the matrix.
2. Over one-half of the elements determined correlated well with two minerals, Na-feldspar and K-feldspar (Table 1). Most of these elements did not vary in concen-

Table 1. *The Principal Phases with which the Various Major, Minor, and Trace Elements are Associated*

	<i>K-feldspar, Mg-siderite, Na-feldspar</i>
<i>Al, B, Ce, Co, Cr, Cu, Dy, Eu, Fe, Ga, Hf, La, Mn, Nd, Ni, Pb, Sb, Sc, Sm, Ta, Tb, Th, Ti, V, Y, Yb, Zn, Zr</i>	
<i>K, Rb</i>	<i>K-feldspar, Mg-siderite</i>
<i>Na</i>	<i>Na-feldspar, Analcime, Water</i>
<i>Cs</i>	<i>Analcime, Water</i>
<i>Ba, C_{min}, Ca, Sr</i>	<i>Calcite</i>
<i>Mg</i>	<i>Dolomite</i>
<i>As, H, Hg, Mo, N, Se, U</i>	<i>Org, Oil</i>
<i>Cd, F</i>	<i>Unknown</i>

- tration by more than a factor of three or four.
3. High Fischer Assay oil yields and elevated Na- and K-feldspar concentrations were concurrent in the oil-rich Mahogany Bed for both core holes.
 4. The composition of the two core holes was very similar for corresponding stratigraphic zones even though core holes 15/16 and 25 were from the center and the edge of the depositional basin, respectively, and ten kilometers apart. These studies agree with previous investigations that revealed that oil shale is remarkably uniform laterally.
 5. Concentrations of major organic elements—organic carbon, hydrogen, and nitrogen—varied by an order of magnitude. Similar concentration variations were observed for As, Cd, Hg, Mo, Se, B, and F, which are trace elements of potential environmental significance. The first five of these elements may be partly associated with the organic fraction of the oil shale matrix. Boron is associated with the mineral phase. No definitive conclusions could be made for F associations based on this work.
 6. The trace elements Co, Cu, Ni, Pb, Sb, and Zn showed consistent associations. These elements are probably present in oil shale as sulfides.
 7. Fischer Assay water yield was strongly associated with analcime content in both cores. However, the water in analcime typically accounted for only about one-third of the water content determined by Fischer Assay.

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Edward R. Bates is the EPA Project Officer (see below).

The complete report, entitled "Characterization of Two Core Holes from the Naval Oil Shale Reserve Number 1," (Order No. PB 81-167 736; Cost: \$15.50, subject to change) will be available only from:

National Technical Information Service

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