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GEOLOGICAL SURVEY CIRCULAR 837

Biogeochemical Evidence for Subsurface Hydrocarbon Occurrence, Recluse Oil Field, Wyoming: Preliminary Results

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By Mary C. Dalziel and Terrence J. Donovan

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ABSTRACT

Anomalously high manganese-to-iron ratios occurring in pine needles and sage leaves over the Recluse oil field, Wyoming, suggest effects of petroleum microseepage on the plants. This conclusion is supported by iron and manganese concentrations in soils and carbon and oxygen isotope ratios in rock samples. Seeping hydrocarbons provided reducing conditions sufficient to enable divalent iron and manganese to be organically complexed or adsorbed on solids in the soils. These bound or adsorped elements in the divalent state are essential to plants, and the plants readily assimilate them. The magnitude of the plant anomalies, combined with the supportive isotopic and chemical evidence confirming petroleum leakage, makes a strong case for the use of plants as a biogeochemical prospecting tool.

INTRODUCTION

Classical surface geochemical and biogeochemical exploration methods have been used extensively in the worldwide search for metals and in the search for petroleum in the USSR, but in general they have not received widespread attention from North American petroleum explorationists (Hawkes, 1957; Kartsev and others, 1959; Boyle and Garrett, 1970; and Brooks, 1972). Geochemical and biogeochemical petroleum exploration techniques have been directed primarily toward the detection of trace amounts of hydrocarbons in soils or soil gases and the metabolic byproducts of microbial attack on hydrocarbons at or near the surface (Laubmeyer, 1933; Horvitz, 1939; Pirson, 1940; Rosaire, 1940; Kartsev and others, 1959; Davis, 1967; and Debnam, 1969). More recently, diagenetic or epigenetic indicators of subsurface petroleum deposits have received attention (McCulloh, 1969; Donovan, 1974; Donovan and others, 1974; Donovan and Dalziel, 1977). This report presents preliminary data on pronounced systematic elemental variations in pine needles and sage leaves that closely correspond with several kinds of epigenetic anomalies in rocks and soils overlying the Recluse oil field, a large stratigraphic trap in Wyoming.

The Recluse oil field is in T. 56 and 57 N., R. 74 and 75 W., Campbell County, Wyo., along the northeastern flank of the Powder River Basin (fig. 1). The field was discovered in 1967 and has been interpreted to be a Cretaceous Muddy Sandstone barrier island (Woncik, 1969). The productive part of the northwest-trending bar is about 13 km long and ranges from 1 to 5 km wide. Maximum drilled thickness of the reservoir is 14 m. The regional dip is southwest, and oil and some gas are trapped along the updip edge of the sandstone body. The average drilled depth is about 2,330 m (fig. 2). Produced oil has an API gravity of 32 degrees.

The Fort Union Formation of Tertiary age crops out over the Recluse oil field and includes sandstone, shale, and coal of the Tongue River Member, a 400- to 500-m-thick nonmarine sequence. Sandstone is normally fine to medium grained, friable, and yellowish gray. Shale is medium gray and waxy. Coal lenses and widespread coal seams as much as 5 m thick occur in the area; clinker is also common (Olive, 1957).

MANGANESE AND IRON ANOMALIES IN PINE NEEDLES AND SAGE LEAVES

Methods

Samples of pine needles (*Pinus ponderosa*) and sage leaves (*Artemisia tridentata*) were collected over the Recluse oil field and surrounding area. The samples were washed in an ultrasonic bath using an aqueous, phosphate-free detergent solution followed by two successive

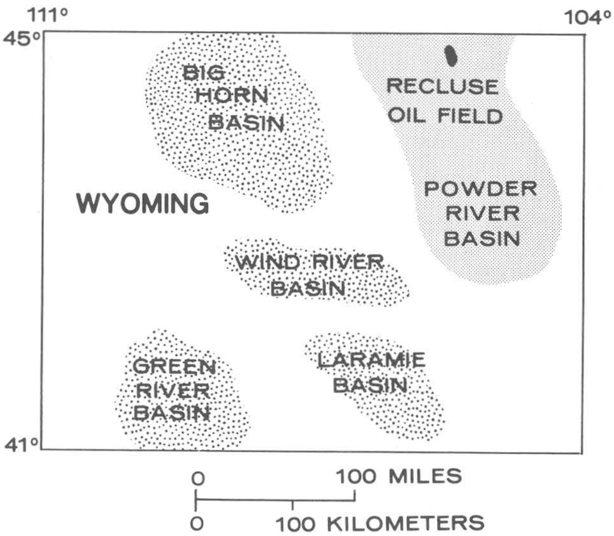

Figure 1.--Map of Wyoming showing the outline of the Recluse oil field, Campbell County, Wyoming (black area), as well as the Powder River Basin (shaded area).

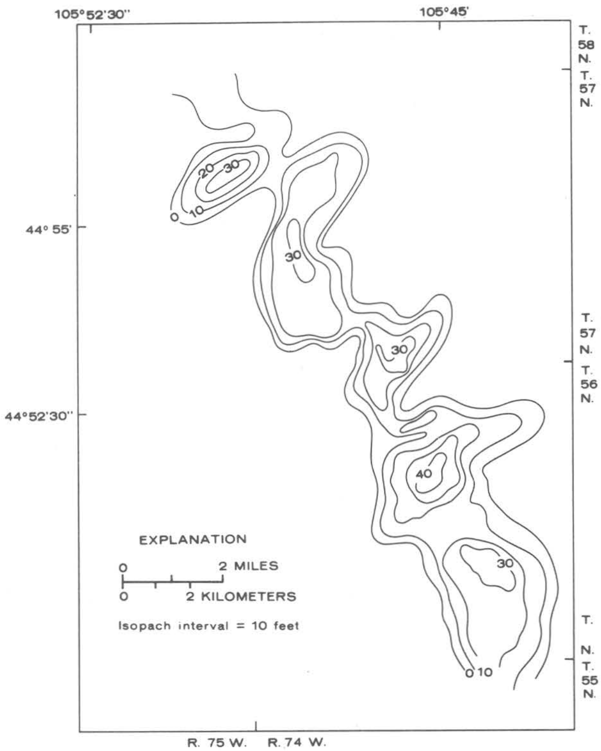

Figure 2.--Isopach map of the producing Muddy Sandstone, Recluse oil field, Wyoming, Modified from Woncik, 1969.

rinses with distilled water (Mitchell, 1960; Mason, 1953). After air drying, the samples were ground in a coffee grinder and 4 g were ashed at 450°C for 6 hours.

Samples of 100 mg of ash were digested in 4 mL of 3 N hydrochloric acid and gently heated without stirring for 15 minutes. The supernatant was diluted to 100 mL with distilled water and analyzed for iron and manganese by atomic absorption spectrophotometry (Ward, and others, 1969). The data from these analyses are tabulated in a U.S. Geological Survey open-file report (Dalziel and Donovan, 1980).

Mn/Fe Ratios in Plants

Figure 3 shows the distribution of Mn/Fe ratios in pine needles collected over the Recluse oil field. Because of the large range (about three orders of magnitude; Dalziel and Donovan, 1980) of the ratio, log values were used to construct the isopleth map. Distinctly high ratio values occur along the trend of the productive part of the field. A complex double-lobed area of high values occurs over the northwestern end of the field.

A similar double-lobed area of high values in the sage data also occurs over the northwestern part of the field (fig. 4). The mapped pattern of the Mn/Fe ratios in sage leaves appears more convoluted and complex than that of pine; this may be partly attributed to the sampling density being greater for sage than for pine. Another factor contributing to the differences in the ratio patterns is the overall higher concentration of manganese in the pine needles (Dalziel and Donovan, 1980). This is reflected in a broader and areally larger anomaly pattern for pine.

Both figures 3 and 4 clearly suggest a correlation between anomalously high Mn/Fe values in plants and the distribution of subsurface petroleum. This apparent correlation can be made for the Recluse field and for smaller producing oil fields in the immediate region as well (Petroleum Information Corporation, 1979).

PETROLEUM MICROSEEPAGE AT THE RECLUSE OIL FIELD, WYOMING

Hydrocarbons can escape their subsurface reservoirs by one or any combination of the following three mechanisms: (1) effusion of gases and liquids, (2) dissolution and subsequent migration of low-molecular-weight hydrocarbons in water, and (3) diffusion of gases through an aqueous phase (Donovan and Dalziel, 1977).

Seeping hydrocarbons are microbially attacked in porous rock in the near-surface oxidizing zone. Increasing amounts of the resulting carbon dioxide go into solution and precipitate as isotopically distinctive, pore-filling carbonate cements that are characteristically depleted in C^{13} and either

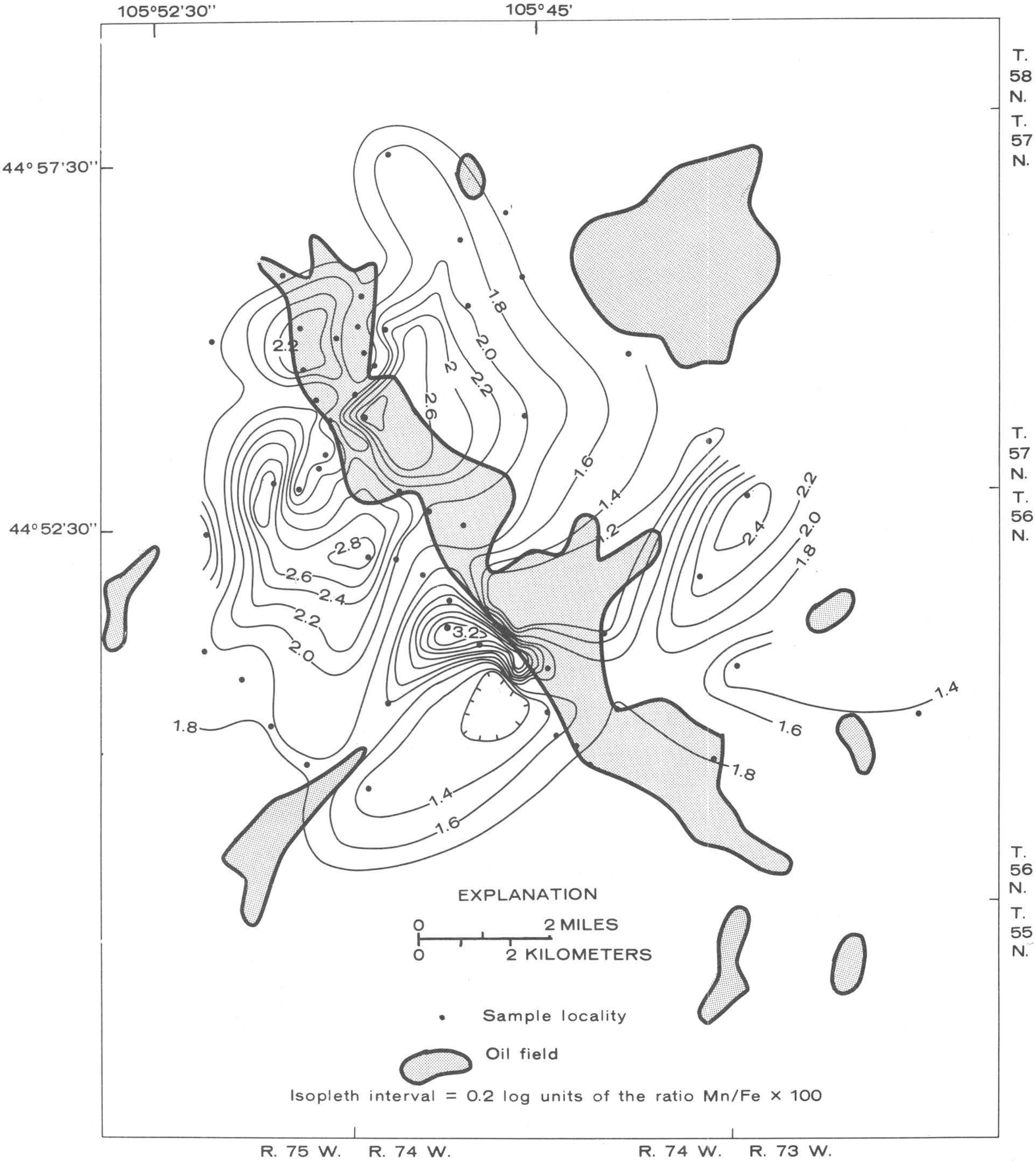

Figure 3.--Isopleth map of the ratio of manganese to iron in pine needles (*Pinus ponderosa*) collected over the Recluse oil field, Wyoming.

enriched or impoverished in O^{18}; the direction of oxygen isotopic fractionation provides important clues as to which of the three microseepage mechanisms has dominated (Donovan and Dalziel, 1977).

Data demonstrating the anomalous character of the overlying rock and soil at Recluse have been presented previously (Donovan, in press; Dalziel and Donovan, 1980). Figure 5 is a map of δC^{13} values in carbonate cements in sandstone

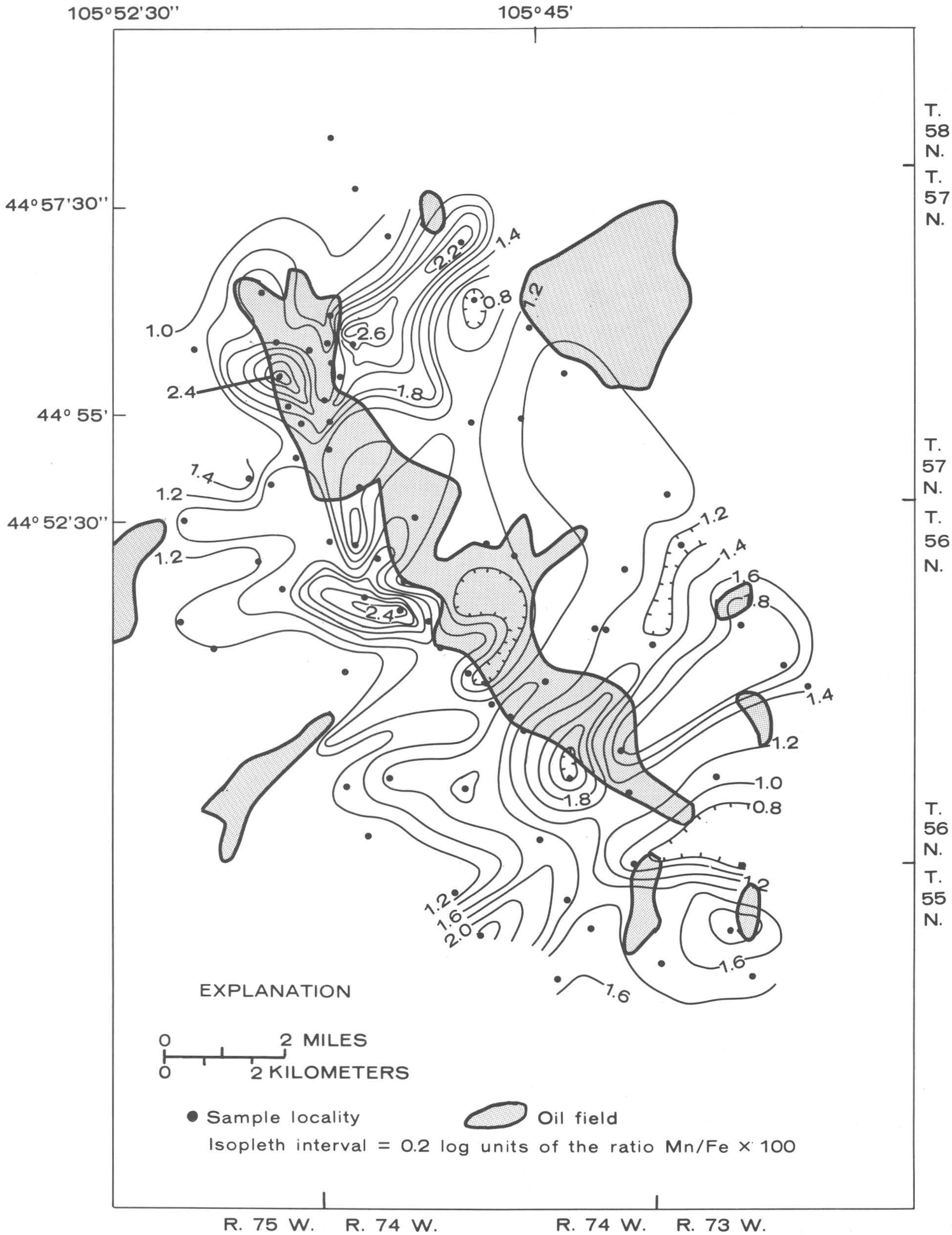

Figure 4.--Isopleth map of the ratio of manganese to iron in sage leaves (*Artemisia tridentata*) collected over the Recluse oil field, Wyoming.

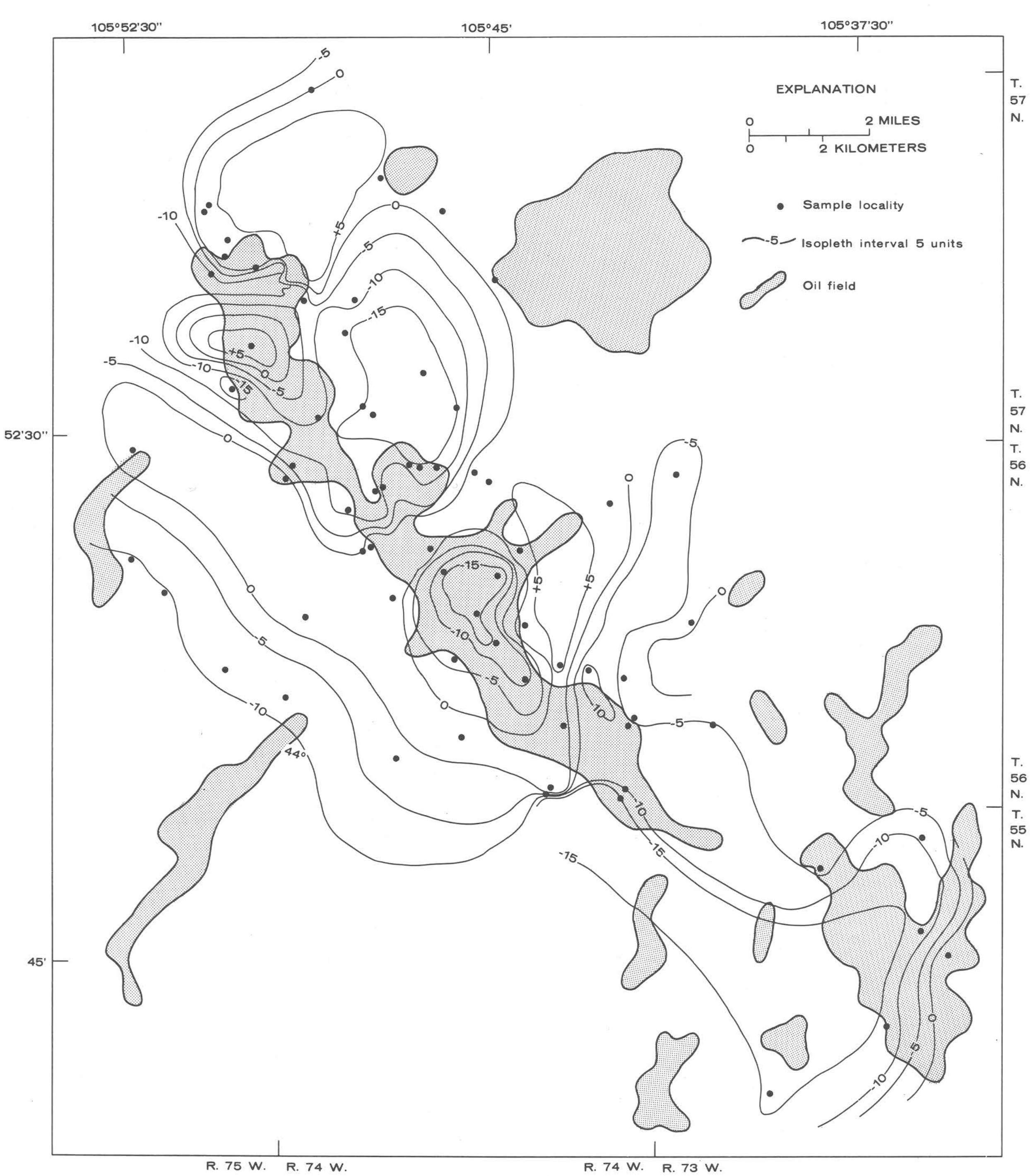

Figure 5.--Isopleth map of δC^{13} values in carbonate cements from sandstone outcrops, Recluse oil field, Wyoming.

cropping out over the Recluse oil field. Thin-section examination of samples reveals that the primary cement is calcite, with secondary ferroan dolomite and minor hematite. The systematic pattern of the δC^{13} isopleths corresponds strikingly with the mapped occurrence of petroleum and gas in the Muddy reservoir. The δO^{18} pattern of variation (fig. 6) appears slightly more variable, probably owing to some admixing in the ground waters between seeping waters and homogenizing meteoric waters; however, the general distribution of O^{18}-depleted carbonate cements immediately overlying and along the trend of the subsurface

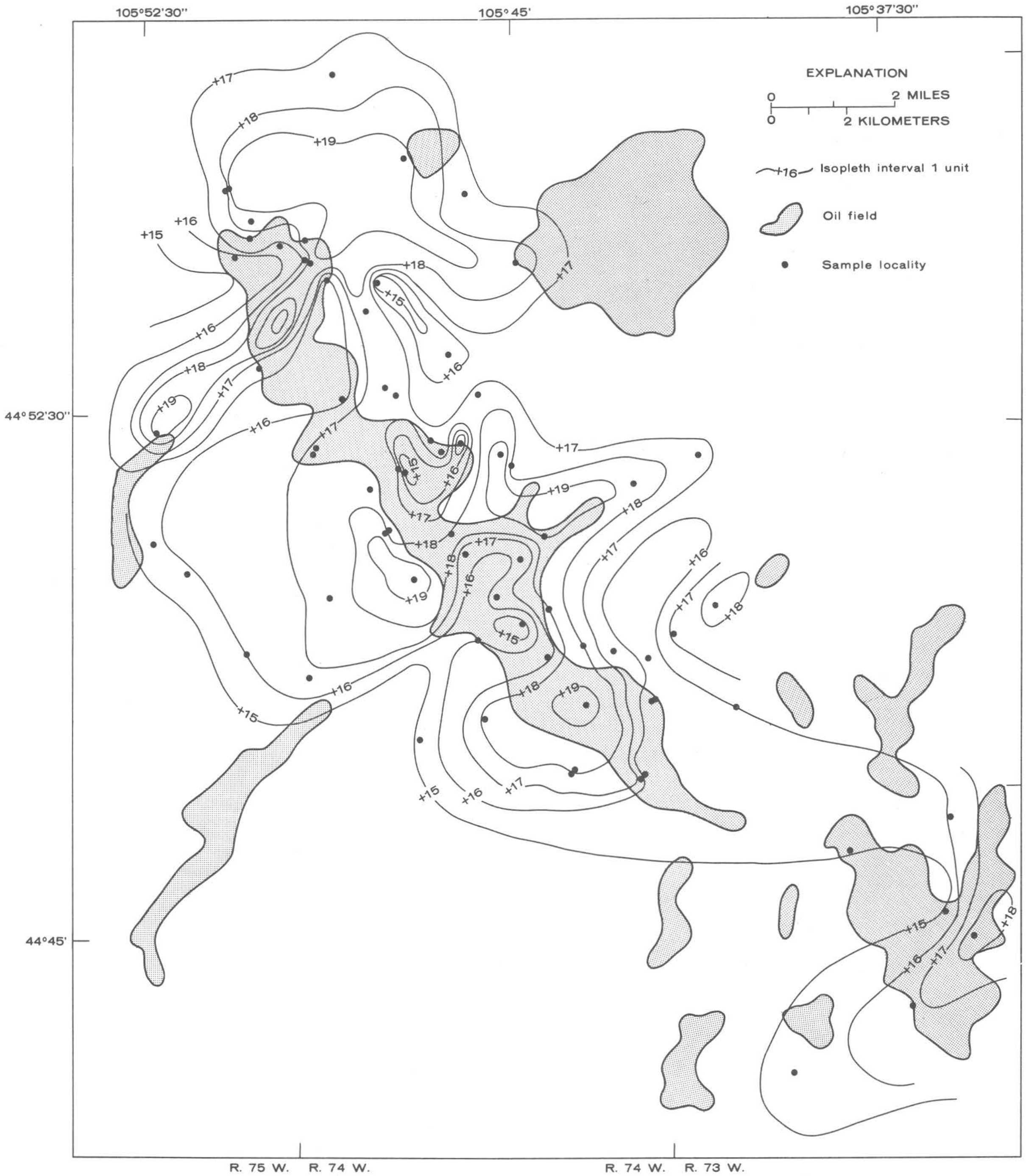

Figure 6.--Isopleth map of δO^{18} values in carbonate cements from sandstone outcrops, Recluse oil field, Wyoming.

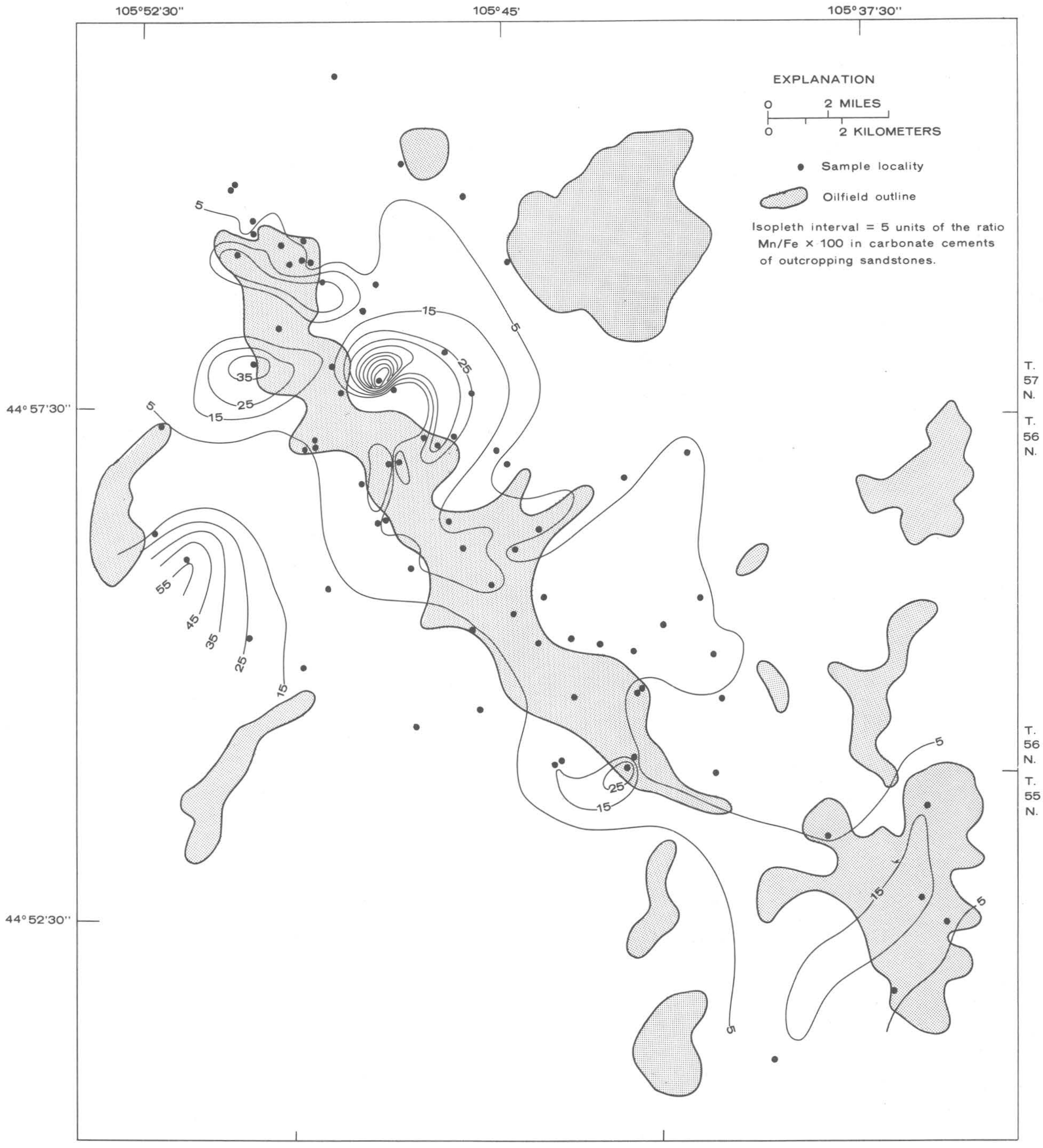

Figure 7.--Isopleth map of the ratio of manganese to iron in carbonate cements of sandstone outcrops, Recluse oil field, Wyoming.

reservoir suggests micropore filtration of upward-moving waters carrying dissolved hydrocarbons (Donovan and Dalziel, 1977).

THE CHEMISTRY OF MANGANESE AND IRON IN MICROSEEPAGE ENVIRONMENTS

The near-surface chemically reducing environment created by the presence of seeping hydrocarbons contributes to reduction, dissolution, and mobilization of iron and manganese from their solid mineral phases. In shallow superincumbent rocks, manganese is precipitated in the presence of dissolved carbonate to take up residence in pore-filling carbonate-cement lattices. Depending upon the pH and redox potential of the environment and the rapidity with which they are subject to change, mobilized manganese and iron may either be transported together or be effectively separated (Krauskopf, 1957). Although systematic variations in manganese and iron concentrations occur in both rocks and soils in the Recluse oil field, manganese appears to display a greater variability. Mn/Fe ratio maps were constructed to illustrate the anomalous nature of their distribution pattern, because it has been shown that the manganese-to-iron ratio in carbonate cements is a striking indicator of microseepage (Donovan and Dalziel, 1977; Donovan and others, 1975). A particularly strong correlation is suggested between the Mn/Fe ratio in the carbonate cements and the subsurface accumulation of oil in the Recluse oil field (fig. 7). Of special interest also are the Mn/Fe ratios in soils overlying the Recluse field area (Dalziel and Donovan, 1980; fig. 8); the soil data suggest relatively depleted Mn/Fe ratios over and along the producing trend in the Recluse oil field.

Manganese and Iron Behavior in Soils

The most likely forms that manganese takes in soils are (1) absorbed Mn^{2+} in strongly reduced soil; (2) manganese in aqueous solutions, most likely present as complexes rather than as a simple ion; and (3) absorbed Mn^{2+}, which may persist in considerable amounts in oxidizing soils, but much of which should occur as highly insoluble oxide minerals (Krauskopf, 1972). Further, the low solubility of $Fe(OH)_3$ and the observation that iron-rich soils commonly develop over iron-rich rocks indicate that soils largely reflect the iron composition of their parent rock (Krauskopf, 1972). Under reducing conditions, both Fe^{2+} and Mn^{2+} increase in solubility sufficiently to become adsorbed or exchangeable ions (Mandal, 1961), and as much as 90 percent of the manganese in soil solution may actually be organically bound (Geering and others, 1969). Adsorption reactions involving Fe^{2+} and Mn^{2+} may represent intermediate phases between the true solution and precipitation of insoluble oxides and hydroxide (Ellis and Knezek, 1972), but such intermediate phases could be expected to persist indefinitely if the amount of organic material in the soil and the chemical environment there remain relatively fixed. Viets (1962) stressed that divalent iron and manganese would also be subject to strong adsorption on negatively charged clay particles as well as on humus. Additionally, these metals may enter into other adsorption reactions, such as bonding to specific functional groups on the clay surfaces. Chelation also appears to be an important bonding mechanism (Ellis and Knezek, 1972).

Uptake of Elements by Plants

The total uptake of nutrient elements by plants has been resolved into two components: metabolic and nonmetabolic (Jacobson and others, 1958). The metabolic component involves root-absorption phenomena, whereas the nonmetabolic component refers to diffusion and mass flow of ions in external solution in free water and Donnan microregions surrounding the root. Upon chelation (or ion-pair formation), both the concentration and the concentration gradient of the chelated ion in solution can be significantly greater than that of the unchelated ion, thus markedly increasing transfer by diffusion (Wilkinson, 1972). The contact-exchange mechanism defined by Jenny and Overstreet (1939) includes the hypothesis that an ion passes directly from the adsorbed state on solids to the root through the exchange of adsorbed H^+ or other ions, bypassing direct solution. When chelated ions contact the root surface, the plant can similarly liberate the ion from the chelating agent and absorb it (Hodgson, 1968; Chaney and others, 1972). Thus, plants may assimilate elements from soils even though no measurable water-soluble pool of ions is available in true solution.

We speculate that the reducing conditions provided by seeping hydrocarbons from the subsurface in the Recluse oil field have facilitated the release of Mn^{2+} and Fe^{2+} from their solid mineral phases and resulted in immediate complexation, chelation, and adsorption by the soils. In these organically bound and adsorbed states, their uptake by pine and sage roots has been accelerated, resulting in anomalous concentrations in needle and leaf tissue. This accelerated direct uptake by the plants has further resulted in these elements bypassing the soil-formation process wherein they would have ultimately precipitated as insoluble oxides or hydroxides. This phenomenon is interpreted to be the cause of the Mn/Fe ratio in the plants more closely resembling the ratio in the parent rocks rather than that in their overlying soils. This in turn suggests that plants can assimilate these micronutrient elements in direct proportion to their availability, which may be enhanced in a microseepage environment.

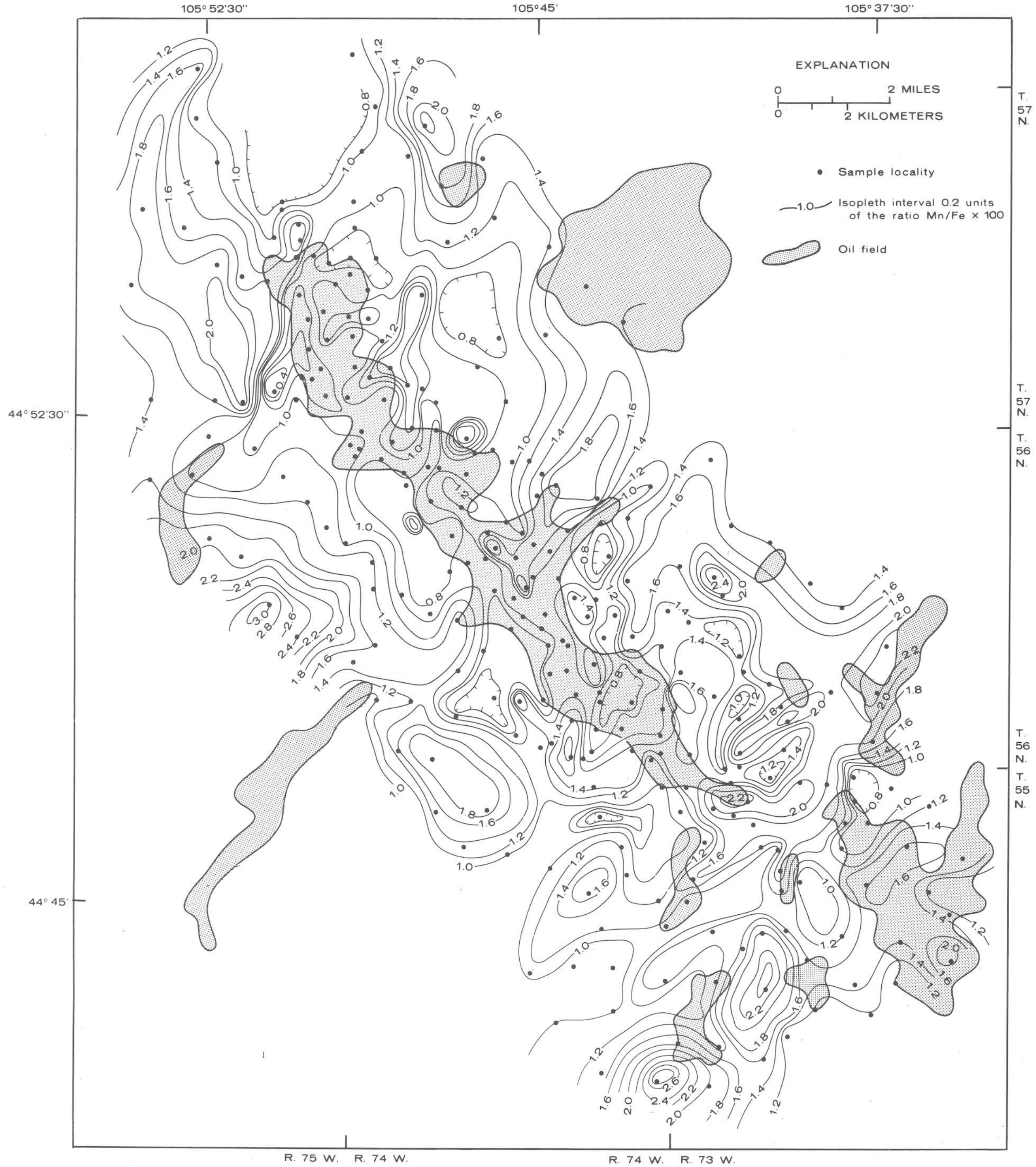

Figure 8.--Isopleth map of the ratio of manganese to iron in soils, Recluse oil field, Wyoming.

SUMMARY

Systematic anomalously high Mn/Fe ratio values in pore-filling carbonate cements in bedrock over the Recluse oil field are the direct consequence of petroleum microseepage, an interpretation confirmed by diagnostic δC^{13} and δO^{18} distribution patterns. Continued seepage of hydrocarbons produced a near-surface reducing environment over the field sufficient to release Mn^{2+} and Fe^{2+} from their solid mineral phases, enabling them to be organically bound or adsorbed on solids in soils. In these forms, manganese and iron are readily assimilated by pine and sage, resulting in high Mn/Fe ratios in the needles and leaves and lower ratios in the soil. The data suggest that biogeochemical analysis may be a promising petroleum prospecting tool.

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