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Isotopic and chemical data from carbonate cements in surface rocks over and near four Oklahoma oil fields

by

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ABSTRACT

Carbonate cements in outcropping sandstones overlying the Doyle, Fox-Graham, Velma, and part of Wheeler oil fields, Oklahoma, were analyzed for their C^{13}/C^{12}, O^{18}/O^{16}, iron, and manganese compositions. The peculiar areal distribution of the values obtained is interpreted to be the direct result of hydrocarbon microseepage.

INTRODUCTION

As part of a continuing program investigating techniques for the direct detection of buried hydrocarbons, the surface rocks overlying three oil fields, and part of a fourth, in southern Oklahoma, were studied (fig. 1). Previous studies (Donovan, 1974, Donovan and others, 1974) have shown that carbonate-cemented rocks overlying buried petroleum accumulations often display unusual ratios of stable carbon and oxygen isotopes.

This and other work (unpub. data) by us suggest that surficial petroleum-related geochemical anomalies in carbonate-cemented clastic rocks might also be manifested by variations in concentrations of iron and manganese within the cements. With these facts and hypotheses in mind, surface sandstones (Permian) overlying the Doyle, Fox-Graham, Velma, and part of the Wheeler oil fields were collected and analyzed.

We are indebted to R.L. Noble who carried out much of the field work in the Velma and Fox-Graham oil fields and also shared responsibility for the atomic absorption analyses.

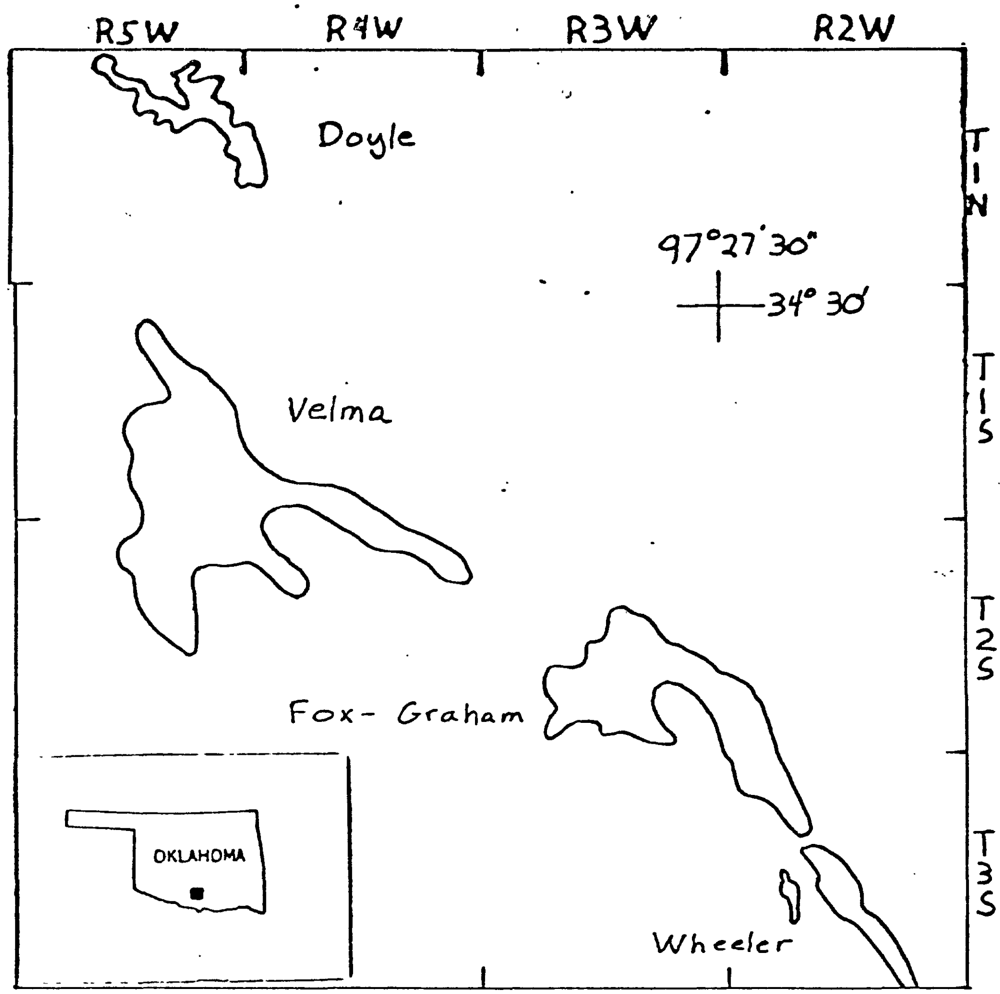

Figure 1.--Location and production limits (as of 1956) of the Doyle, Fox-Graham, Velma, and part of Wheeler oil fields, Stephens and Carter Counties, Oklahoma. From Billingsley, 1956.

METHODS

Carbon and oxygen isotope ratios of the carbonate cements were determined in the U.S.G.S. Denver laboratories by analytical methods reported elsewhere (McCrea, 1950, Craig, 1957; Epstein and others, 1964). These values are reported in standard δ terminology:

$$\delta = \left[\frac{R\ (\text{Sample}) - R\ (\text{Standard})}{R\ (\text{Standard})}\right] X\ 1000, \text{ where } R = C^{13}/C^{12} \text{ or } O^{18}/O^{16}.$$

The standards are the Pee Dee Belemnite Chicago standard (PDB) for carbon and Standard Mean Ocean Water (SMOW) for oxygen. No distinction was made for carbonate type (calcite or dolomite), therefore the oxygen isotope ratios for rocks containing appreciable dolomite are slightly in error. The maximum possible error would be +0.8 mil if the sample contained 100 percent dolomite. The effect of this dolomite error is considered small when compared to the anomalies of interest. It does not change the gross aspect of the data when disregarded. Results of the isotopic analyses are given in Tables 1, 2, and 3.

The concentrations of iron and manganese within the cements were determined in the field with a truck-mounted wet laboratory by atomic absorption spectrophotometry. The procedure used was a modification of that described by the Perkin-Elmer Corporation (1973). The concentrations determined are listed in Tables 1, 2, and 3.

DISCUSSION AND SUMMARY

Figures 1-7 present isopleths of chemical and isotopic data from surface rocks in the Doyle, Fox-Graham and part of Wheeler oil fields. Figure 10 shows only sample localities in the Velma oil field because the clustered nature of the sample sites precludes mapping. Seeping

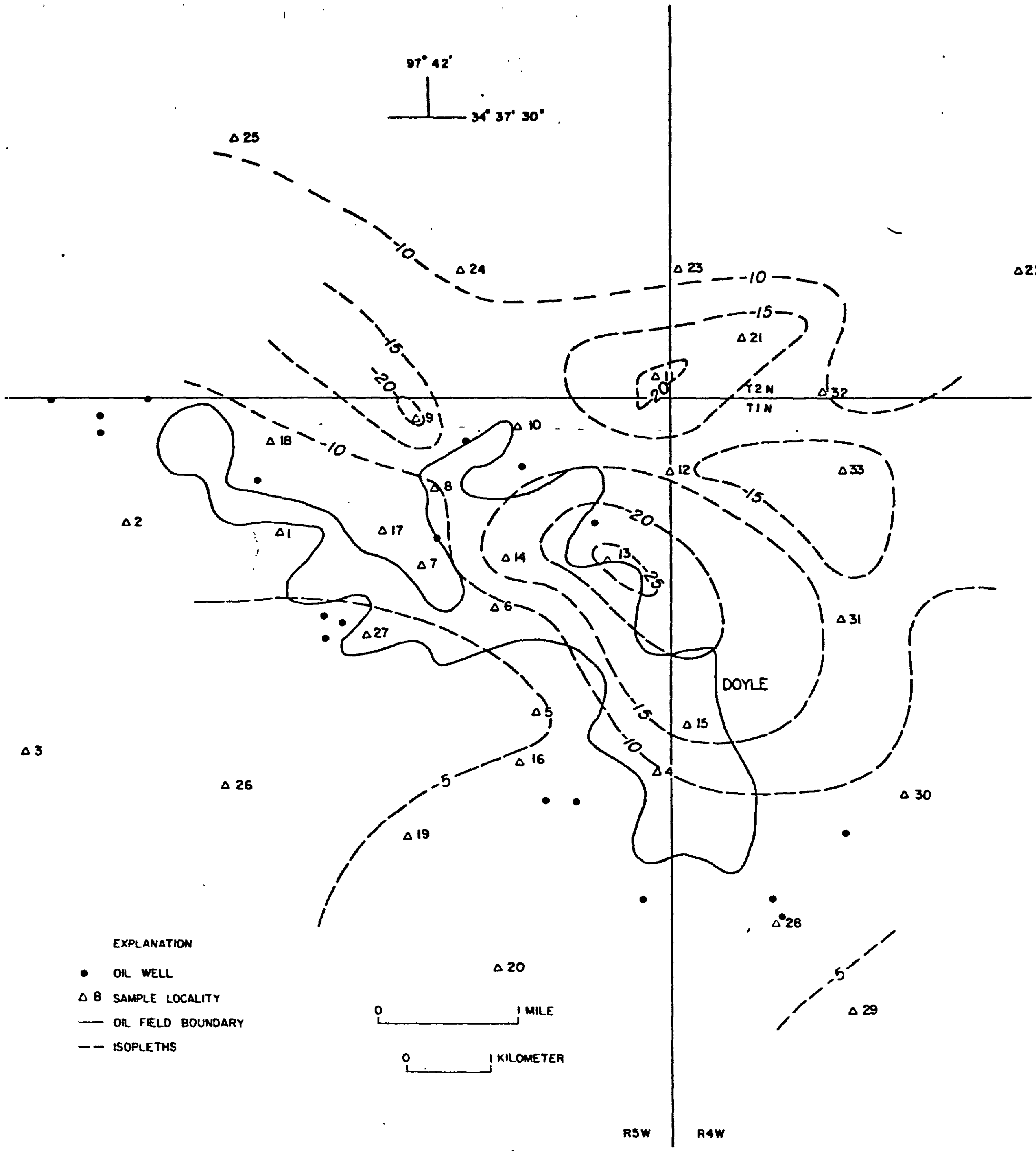

Figure 2.--Isopleth map of carbon isotope values for carbonate cements from surface rocks overlying the Doyle oil field, Oklahoma. Solid circles show producing oil wells near but outside indicated field boundary. Isopleth interval 5δC^{13}. Field limits from Billingsley, 1956.

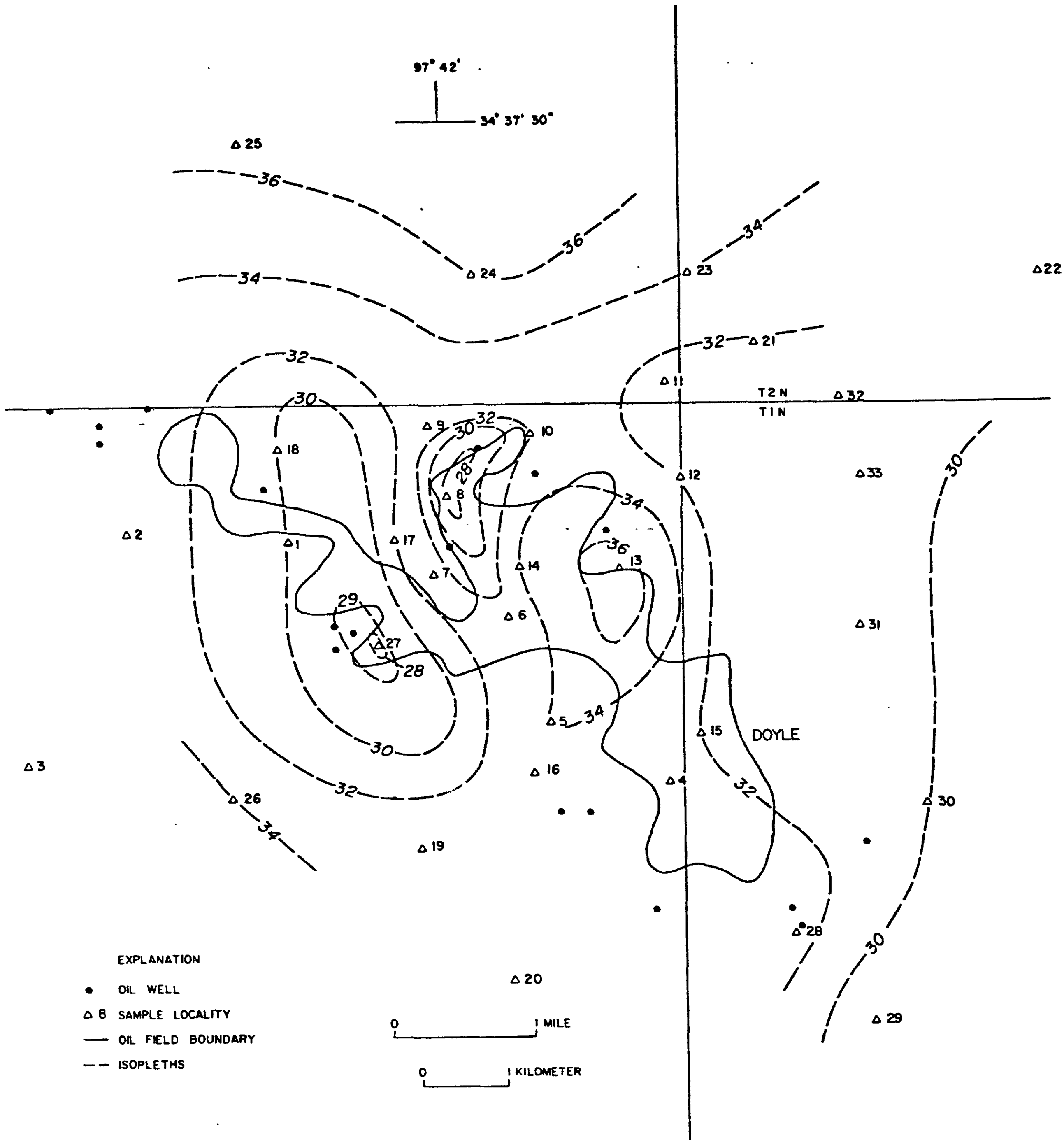

Figure 3.--Isopleth map of the oxygen isotope values for carbonate cements from surface rocks overlying the Doyle oil field, Oklahoma. Solid circles show producing oil wells near but outside indicated field boundary. Isopleth interval 2δO^{18}. Field limits from Billingsley, 1956.

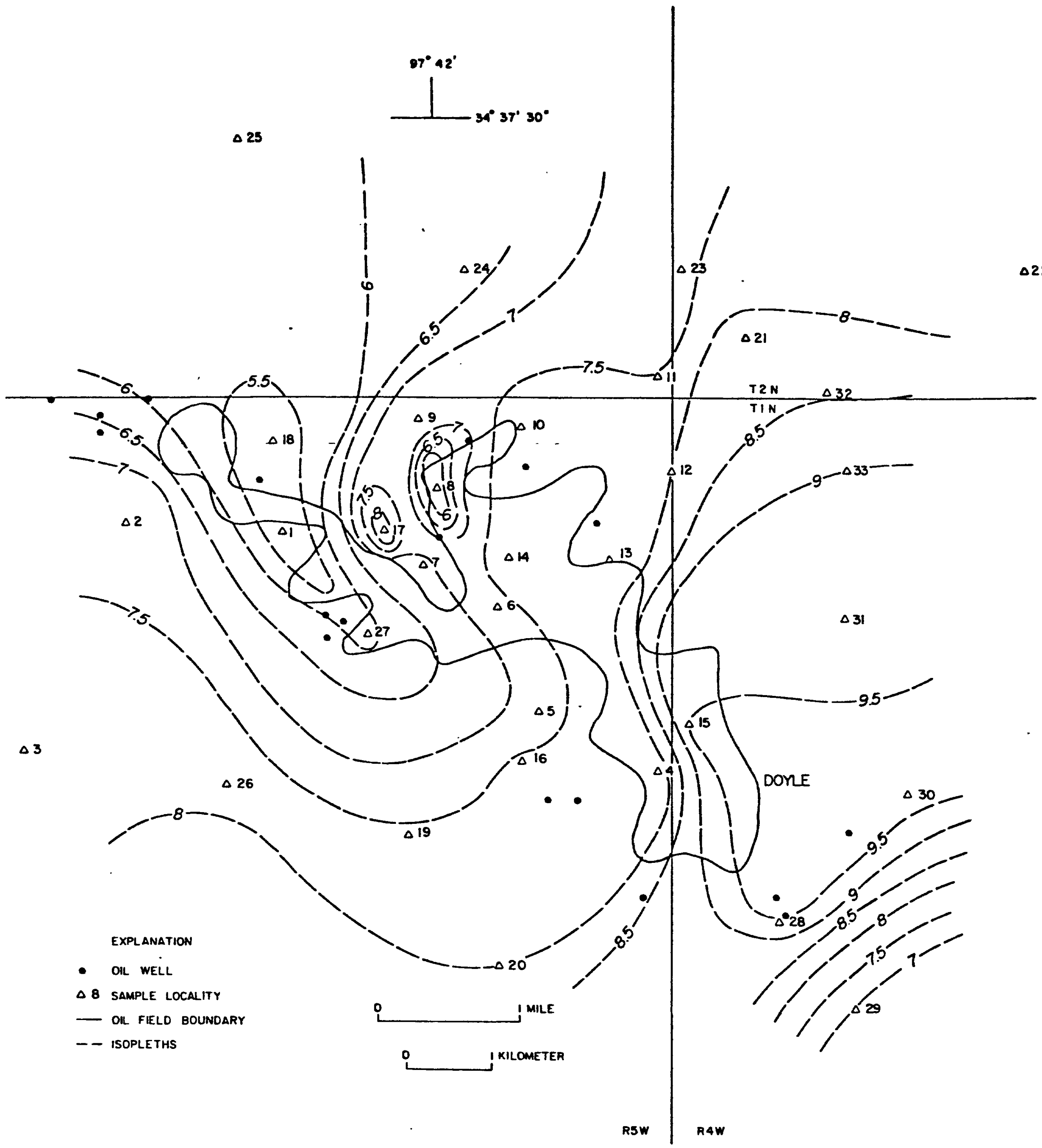

Figure 4.--Isopleth map of the iron concentrations within carbonate cements from surface rocks overlying the Doyle oil field, Oklahoma. Solid circles show producing oil wells near but outside indicated field boundary. Owing to the wide range of concentrations, natural logarithms of the values given in parts per million (ppm) were mapped rather than actual values. Isopleth interval 0.5 $\log_e$ unit. Field limits from Billingsley, 1956.

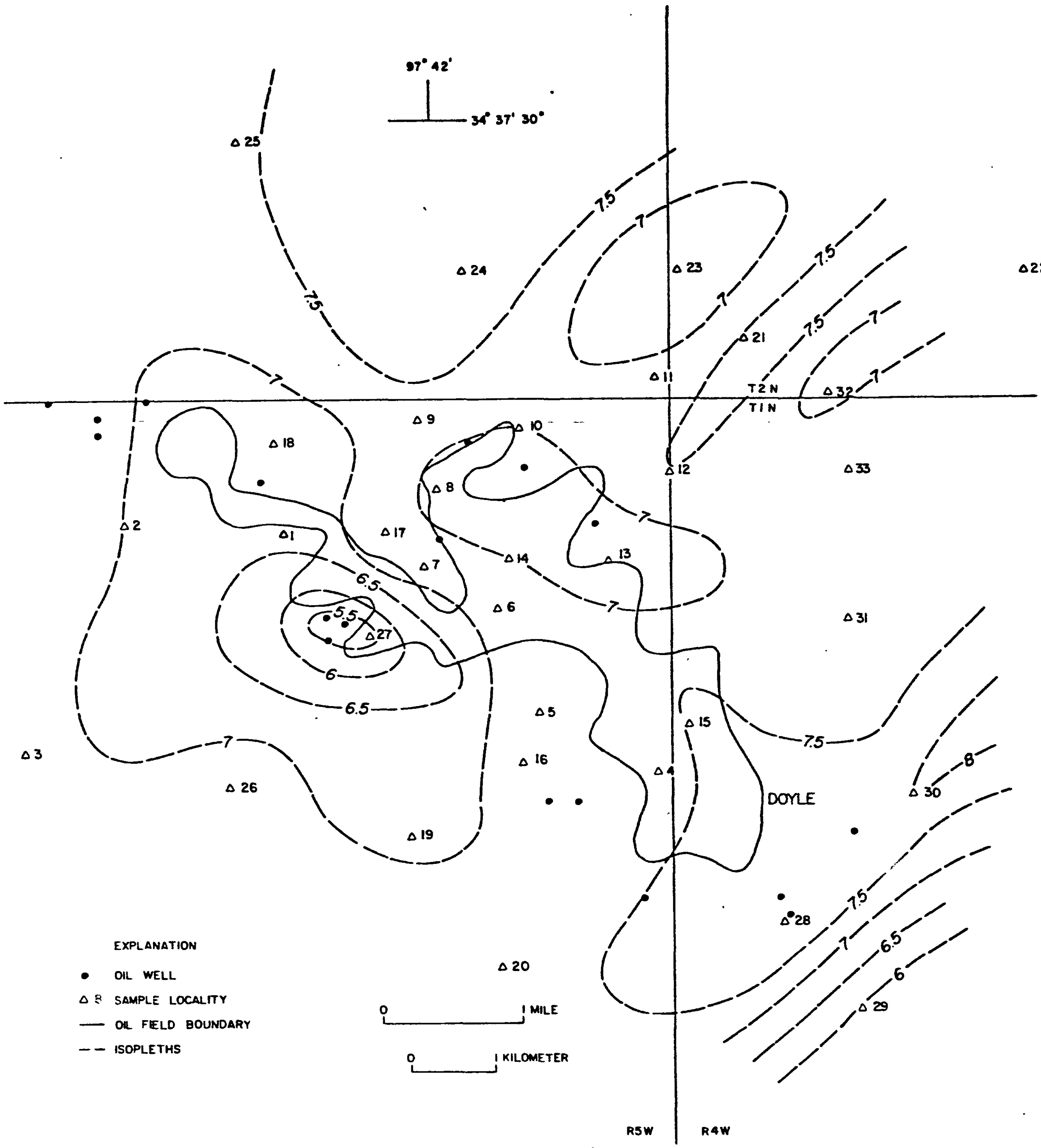

Figure 5.--Isopleth map of the manganese concentrations within carbonate cements from surface rocks overlying the Doyle oil field, Oklahoma. Solid circles show producing oil wells near but outside indicated field boundary. Owing to the wide range of concentrations, natural logarithms of the values given in parts per million (ppm) were mapped rather than actual values. Isopleth interval 0.5 $\log_e$ unit. Field limits from Billingsley, 1956.

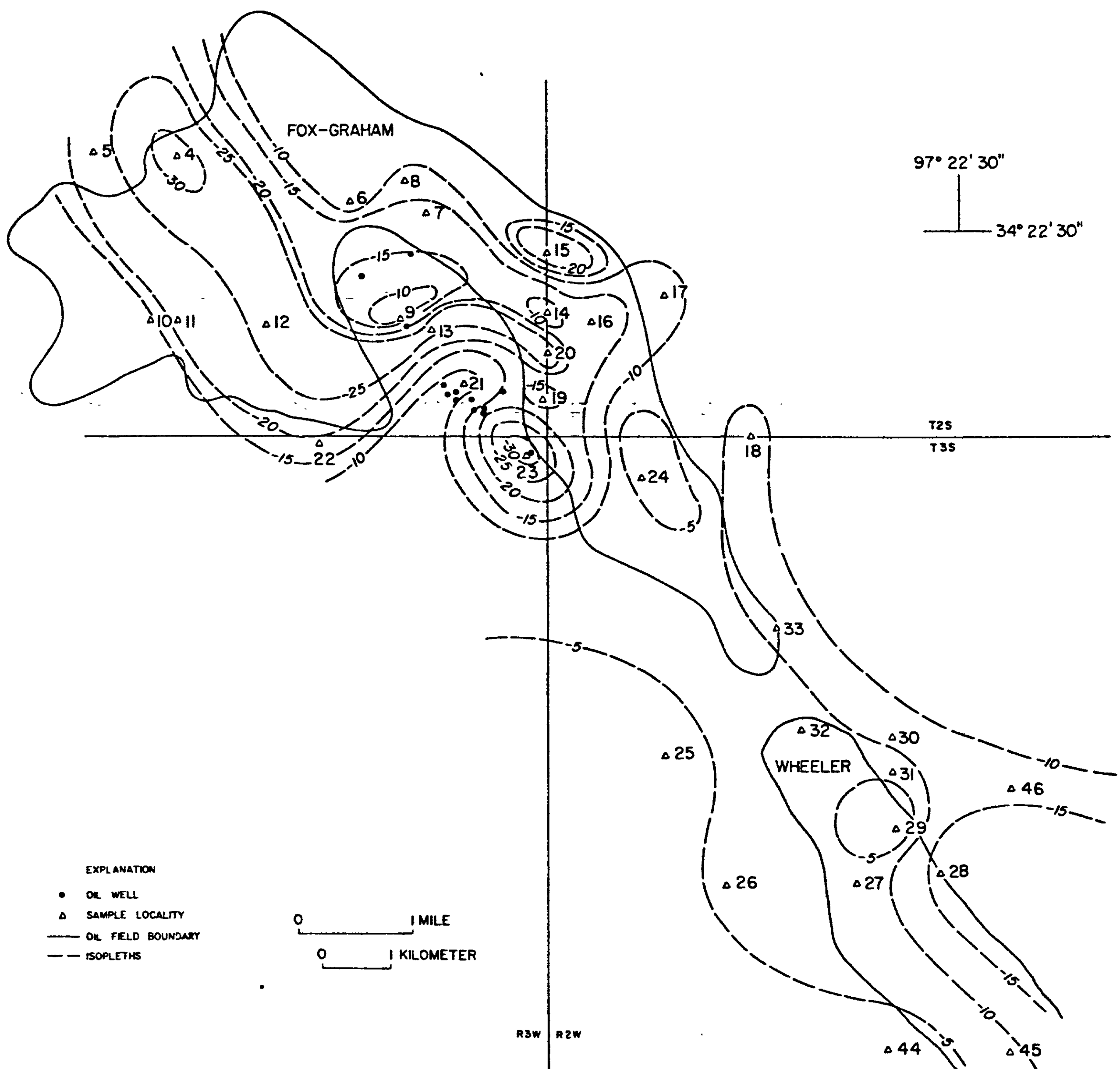

Figure 6.--Isopleth map of the carbon isotope values for carbonate cements from surface rocks overlying the Fox-Graham and part of the Wheeler oil fields, Oklahoma. Solid circles show producing oil wells near but outside indicated field boundary. Isopleth interval 5δC^{13}. Field limits from Billingsley, 1956.

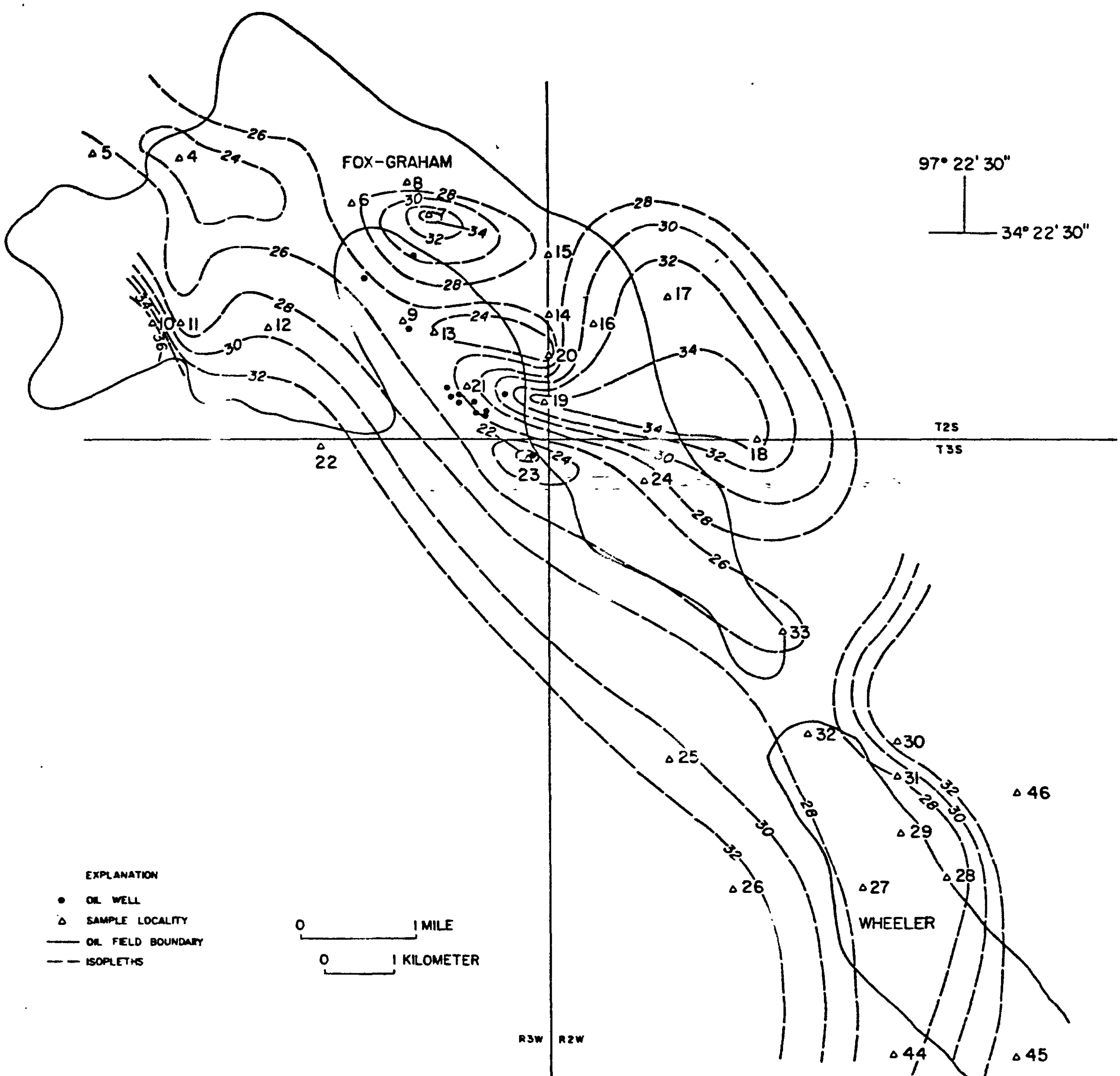

Figure 7.--Isopleth maps of the oxygen isotope values for carbonate cements from surface rocks overlying the Fox-Graham and part of the Wheeler oil fields, Oklahoma. Solid circles show producing oil wells near but outside indicated field boundary. Isopleth interval $2\delta O^{18}$. Field limits from Billingsley, 1956.

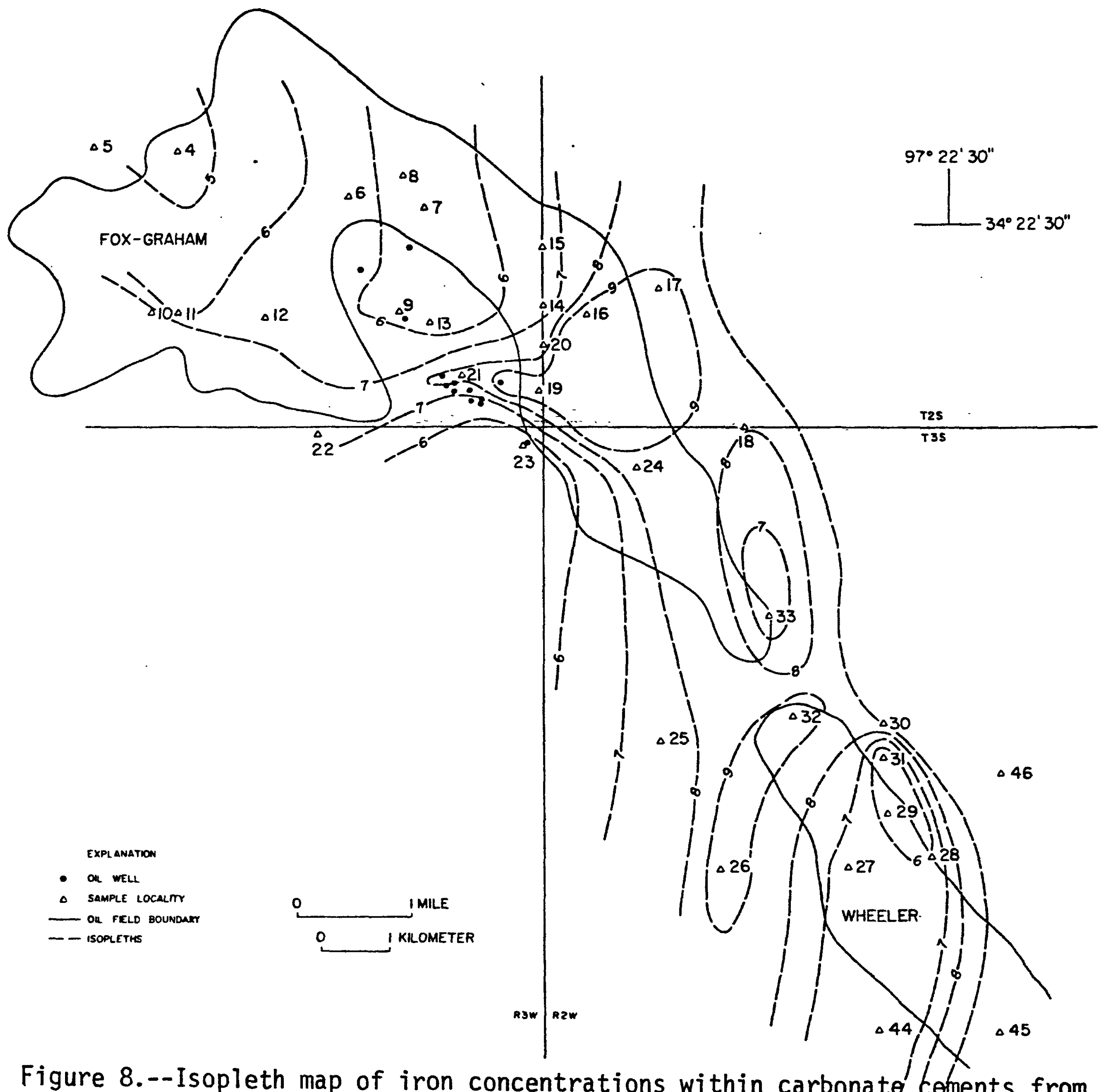

Figure 8.--Isopleth map of iron concentrations within carbonate cements from surface rocks overlying the Fox-Graham and part of the Wheeler oil fields, Oklahoma. Solid circles show producing oil wells near but outside the indicated field boundary. Owing to the wide range of concentrations, natural logarithms of the values given in parts per million (ppm) were mapped rather than actual values. Isopleth interval 1.0 $\log_e$ unit. Field limits from Billingsley, 1956.

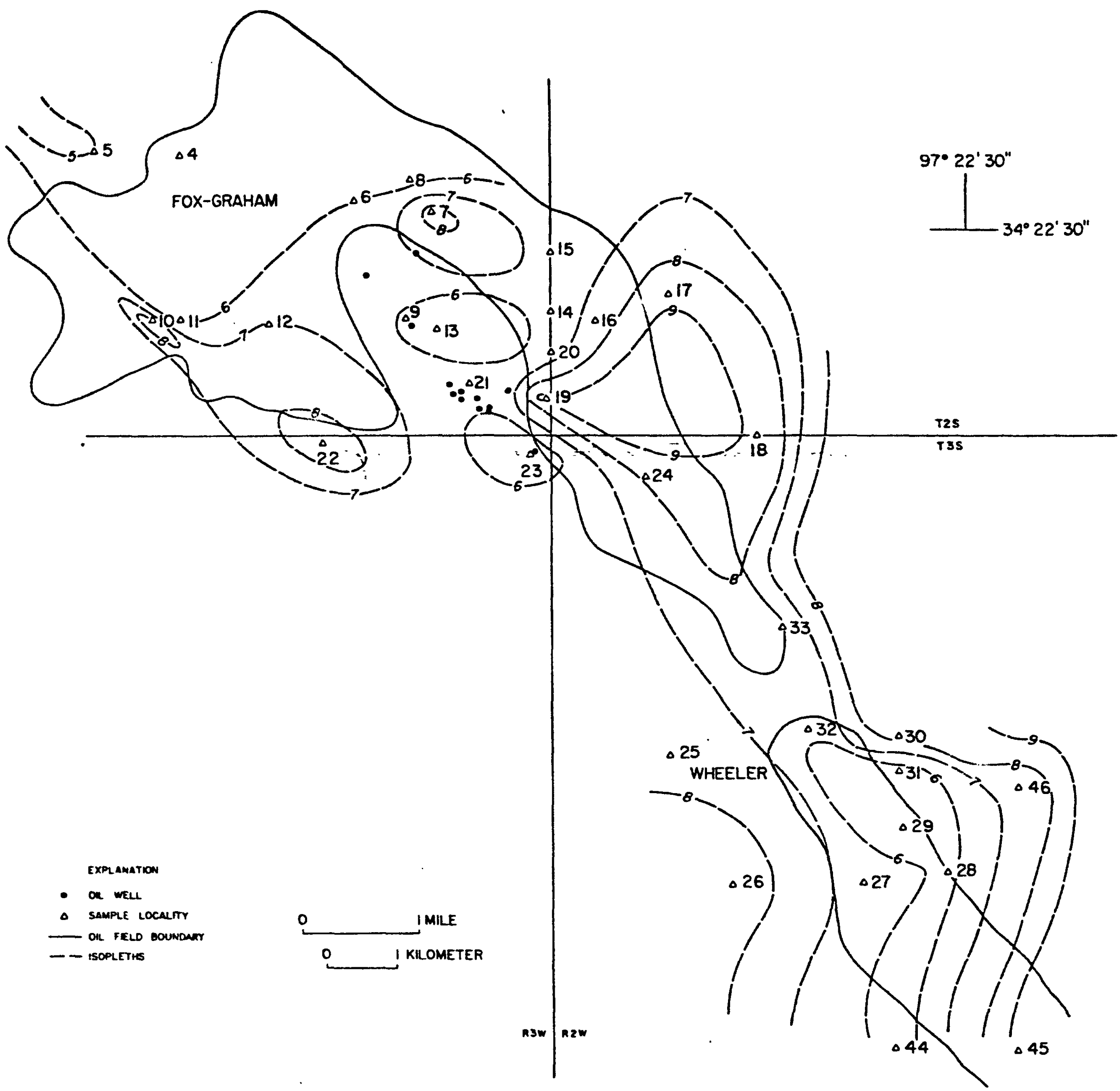

Figure 9.--Isopleth map of manganese concent tions within carbonate cements from surface rocks overlying the Fox-Granam and part of the Wheeler oil fields, Oklahoma. Solid circles show producing oil wells near but outside the indicated field boundary. Owing to the wide range of concentrations, natural logarithms of the values given in parts per million (ppm) were mapped rather than actual values. Isopleth interval 1.0 $\log_e$ unit. Field limits from Billingsley, 1956.

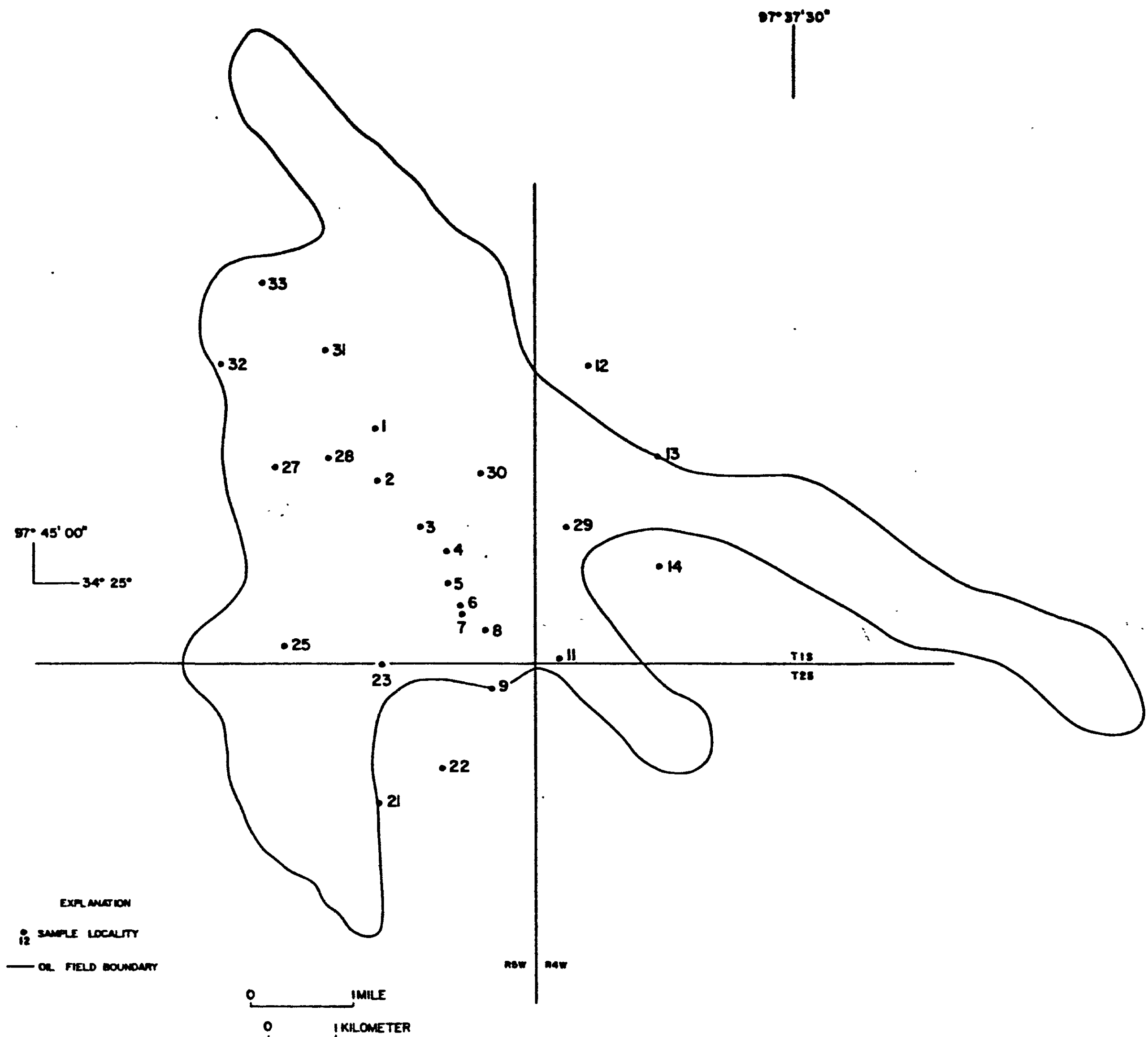

Figure 10.--Boundary (as of 1956) and sample localities in the Velma oil field, Oklahoma. Modified from Billingsley, 1956.

hydrocarbons are oxidized near the earth's surface and the resulting carbon dioxide combines with dissolved salts in ground waters which subsequently precipitate as diagenetic carbonate cements that have distinctive compositions. Seeping hydrocarbons and associated compounds, such as hydrogen sulfide, produce a locally reducing environment which induces reduction, mobilization, and redistribution of iron and manganese. Both of these metals are anomalously distributed as substitution elements in carbonate cements. Our maps show the close correlation between anomalies in surface rocks and the oil and gas production limits of the fields studied. A more detailed interpretation of the significance of these kinds of anomalies occurring over oil fields has been presented by Donovan and Dalziel (1977).

Table 1.--δC^{13}, δO^{18}, iron, and manganese values of carbonate cements from outcrops over and near the Doyle oil field, Oklahoma. [N.D. indicates not determined.]

Sample	δC^{13}	δO^{18}	Fe(ppm)	$\log_e Fe$	Mn(ppm)	$\log_e Mn$
1	- 7.85	26.90	200	5.29	750	6.62
2	- 6.33	32.84	2,550	7.83	1,050	6.95
3	- 4.38	36.22	1,000	6.91	1,150	7.04
4	- 9.34	33.22	2,575	7.85	1,075	6.98
5	- 3.57	33.90	1,175	7.07	1,425	7.26
6	- 7.95	32.85	1,675	7.42	1,450	7.28
7	- 5.05	33.65	950	6.86	1,300	7.17
8	- 9.27	26.92	375	5.93	800	6.68
9	-21.18	33.15	1,700	7.44	1,650	7.41
10	-12.73	32.33	2,275	7.73	1,125	7.03
11	-20.67	31.34	1,800	7.49	1,250	7.13
12	-14.92	32.04	2,850	7.96	1,875	7.54
13	-26.60	36.58	2,050	7.63	825	6.72
14	-18.19	34.10	2,350	7.76	1,350	7.21
15	-16.82	32.31	12,750	9.45	2,050	7.63
16	- 5.46	33.53	1,950	7.58	1,250	7.13
17	- 6.33	31.86	3,375	8.12	1,700	7.44
18	- 8.29	29.92	175	5.16	675	6.51
19	- 5.35	33.64	2,000	7.60	975	6.88
20	- 6.19	34.63	2,875	7.96	1,425	7.26
21	-18.31	32.11	4,100	8.32	1,875	7.54
22	- 7.86	33.24	475	6.16	N.D.	N.D.
23	- 8.14	34.32	1,600	7.37	925	6.83
24	- 6.89	36.42	500	6.21	2,310	7.75
25	- 7.34	36.91	325	5.78	1,675	7.42
26	- 4.07	33.65	2,750	7.92	1,215	7.10
27	- 3.13	27.73	350	5.86	300	5.70
28	- 9.11	32.87	13,250	9.49	2,650	7.88
29	- 2.52	27.70	1,200	7.09	400	5.99
30	- 8.36	30.13	18,750	9.84	2,800	7.94
31	-14.09	31.15	10,500	9.26	1,400	7.24
32	-10.38	31.24	4,250	8.35	975	6.88
33	-17.26	31.39	8,000	8.99	1,500	7.31

Table 2.--δC^{13}, δO^{18}, iron, and manganese values of carbonate cements from outcrops over and near the Fox-Graham (samples 4-24) and part of the Wheeler fields (samples 25-46), Oklahoma. [N.D. indicates not determined.]

Sample	δC^{13}	δO^{18}	Fe(ppm)	$\log_e$Fe	Mn(ppm)	$\log_e$Mn
4	-31.07	22.21	100	4.61	375	5.93
5	-23.44	27.10	125	4.83	150	5.01
6	- 4.04	27.03	1,000	6.91	400	5.99
7	-19.66	34.38	11,500	9.35	5,000	8.52
8	-11.12	26.37	125	4.83	250	5.52
9	- 9.44	25.88	300	5.70	350	5.86
10	-13.41	36.13	2,175	7.68	4,200	8.34
11	-22.03	26.59	300	5.70	300	5.70
12	-26.86	29.42	925	6.83	1,100	7.00
13	-25.92	24.02	175	5.16	175	5.16
14	- 7.52	26.74	750	6.62	500	6.21
15	-21.99	27.16	675	6.51	1,000	6.91
16	-18.83	31.36	8,750	9.08	2,175	7.68
17	-10.79	33.53	18,750	9.84	8,750	9.08
18	-10.14	34.94	3,350	8.12	8,750	9.08
19	-12.16	35.10	25,000	10.13	9,000	9.10
20	-29.19	22.61	1,625	7.39	500	6.21
21	- 7.79	26.57	3,350	8.12	625	6.44
22	-19.50	33.09	2,000	7.60	4,350	8.38
23	-34.15	21.59	150	5.01	175	5.16
24	- 3.44	26.96	7,000	8.85	3,150	8.06
25	- 2.04	30.30	1,800	7.50	2,300	7.74
26	- 8.83	32.35	17,500	9.77	6,250	8.74
27	- 7.44	26.99	750	6.62	650	6.48
28	-17.58	26.66	350	5.86	325	5.78
29	- 3.05	26.36	325	5.78	250	5.52
30	-12.14	33.66	14,250	9.56	5,750	8.66
31	- 7.23	26.98	100	4.61	250	5.52
32	N.D.	N.D.	17,000	9.74	750	6.62
33	-10.88	25.89	500	6.21	400	5.99
44	- 3.93	26.46	275	5.62	225	5.42
45	- 9.58	33.60	27,000	10.20	10,000	9.21
46	-12.60	36.21	1,050	6.96	6,500	8.78

Table 3.--δC^{13}, δO^{18}, iron, and manganese values of carbonate cements from outcrops over and near the Velma oil field, Oklahoma. [N.D. indicates not determined.]

Sample	δC^{13}	δO^{18}	Fe(ppm)	$\log_e$Fe	Mn(ppm)	$\log_e$Mn
1	-10.04	26.58	700	6.55	375	5.93
2	-35.45	22.67	29,000	10.27	2,500	7.82
3	-27.93	24.54	450	6.10	300	5.70
4	-28.61	28.16	1,000	6.90	325	5.78
5	-35.30	25.86	150	5.01	125	4.83
6	-35.79	21.56	275	5.61	125	4.83
7	-15.92	25.95	150	5.01	150	5.01
8	-29.39	29.30	450	6.10	400	5.99
9	-36.72	29.77	200	5.29	200	5.29
11	-35.84	22.98	450	6.10	N.D.	N.D.
12	-33.38	30.42	N.D.	N.D.	975	6.88
13	- 9.82	32.09	N.D.	N.D.	1,700	7.44
14	-17.90	25.99	N.D.	N.D.	350	5.86
21	-13.11	27.13	N.D.	N.D.	1,250	7.13
22	-23.11	37.90	N.D.	N.D.	3,500	8.16
23	-34.80	24.45	N.D.	N.D.	150	5.01
25	- 7.75	27.20	N.D.	N.D.	625	6.43
27	-24.15	29.95	N.D.	N.D.	2,050	7.62
28	-37.55	22.93	N.D.	N.D.	400	5.99
29	- 8.11	27.33	N.D.	N.D.	450	6.10
30	-33.15	29.31	N.D.	N.D.	312	5.74
31	-11.00	32.93	N.D.	N.D.	1,825	7.51
32	-25.89	30.40	N.D.	N.D.	2,000	7.6
33	-35.70	30.24	N.D.	N.D.	N.D.	N.D.

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