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A Possible Petroleum-Related Geochemical  
Anomaly In Surface Rocks,  
Boulder and Weld Counties, Colorado

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Abstract

Chemical variations in outcropping Cretaceous sandstones showing anomalous chemical variations and isotopic peculiarities in their calcareous pore-cements crop out in an area of about 30 km<sup>2</sup> centered near Panama Reservoir No. 1, about 12 km northeast of Boulder, Colorado. This anomaly is similar to those described over known oil fields and may reflect the effects of petroleum microseepage.

Carbon isotopic values systematically become lighter ( $\delta C^{13}$  range: -2.5/mil to -18.0/mil relative to PDB) toward the interior of the aureole-patterned anomaly as do the oxygen values ( $\delta O^{18}$  range: 24.1/mil to 11.2/mil relative to SMOW). Variations in iron and manganese content closely correlate with the isotopic patterns. The principal developments of the geochemical anomaly are also expressed geomorphically because the areally restricted pore-mineralization produces an irregular topography due to differential erosion.

The interpreted petroleum microseepage may have been initiated in part by washing of a hydrocarbon deposit at depth by meteoric water moving downdip from recharge in outcrops along the Front Range about 15 km to the west. Analysis of the available regional subsurface control supports the possibility of a buried petroleum accumulation in Cretaceous sandstone reservoirs.

## Introduction

Gun Barrel Hill (fig. 1), a topographically high area northeast of Boulder, Colorado, appears similar to anomalous high areas over known oil accumulations (Donovan, 1974a; Donovan, Friedman, and Gleason, 1974). Such features can result indirectly from the effects of petroleum microseepage. Detailed geomorphic analysis, sampling and geochemical analysis, mapping, and reconnaissance gravimetry in the Gun Barrel Hill-Panama Reservoir No. 1 region has documented a geochemical anomaly which may reflect an undiscovered petroleum deposit.

### General geology of the Panama Reservoir No. 1 region

In the Panama Reservoir No. 1 area (fig. 1) conformable Upper Cretaceous rocks crop out; from west to east, they comprise the Pierre Shale, the Fox Hills Formation, and the Laramie Formation in order of decreasing age (fig. 2) (Spencer, 1961; Trimble, 1974). Remnants of Pleistocene alluvial terraces occur locally throughout the area masking much of the geology. The gently eastward dipping rocks are mildly disrupted by numerous high-angle reverse and normal faults having throws which range from about 30 to 90 m. The principal structural feature is the east-dipping limb of the west side of the Denver basin (Emmons, Cross, and Eldridge, 1896, Plate IV; Davis, 1974; and Spencer, 1961). The presence of locally cemented rocks, being more resistant, results in irregularities which are subtly superimposed upon the rolling topography.

### Petroleum occurrence

In the region adjacent to the Panama Reservoir anomaly, oil is produced from fractured Pierre Shale in the Boulder field (Cary, 1961) about 12 km west of Panama Reservoir No. 1 and from the Hygiene sands of the Pierre in the Spindle field (Matuszczak, 1973) about 3 km to the east. Conceivably, our anomaly overlies an extension to the Spindle field. Gas is the major produced fluid of the large Wattenberg field, a large stratigraphic accumulation in lower Cretaceous rocks, which sits athwart the axis of the Denver basin just east of the Panama Reservoir area (Matuszczak, 1973). Initial attempts to drill for oil in the late 1800's in the Boulder region were predicated on hydrocarbon seepages from the Hygiene and petroliferous odors emanating from the Benton and Niobrara Formations (Daniels and Meader, written commun., 1951).

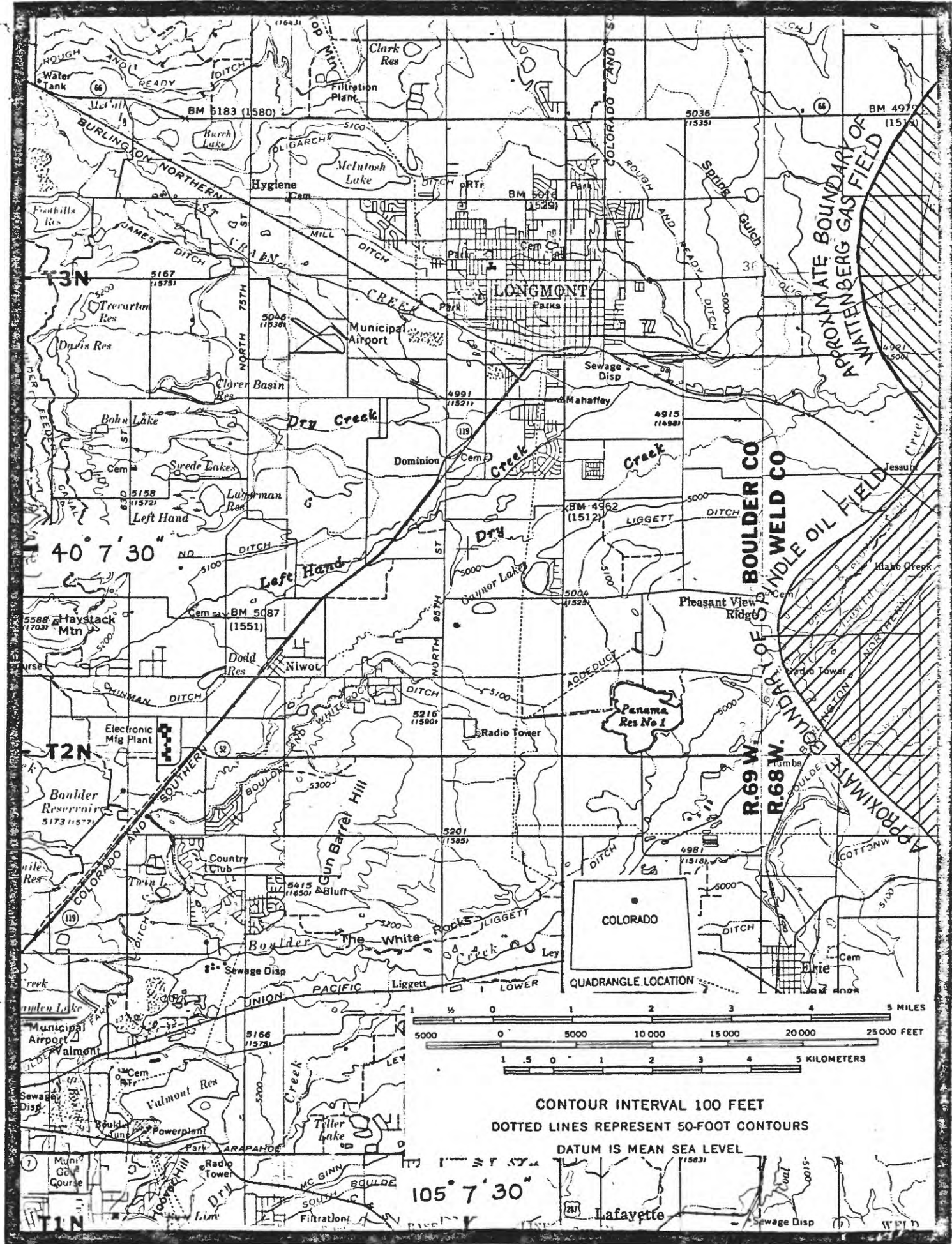


Figure 1. Index map of the Panama Reservoir No. 1 region.

Series	Formation	Description
UPPER CRETACEOUS	Laramie Formation	Interbedded claystone, siltstone, medium-grained sandstone, and lignite beds. Siltstones and sandstones are light yellow to pinkish gray, weathering to yellowish orange to reddish orange. Hard calcareous concretions occur locally within the formation. About 200 m thick.
	Fox Hills Formation	Light-gray to light-yellow fine- to medium-grained crossbedded sandstone in upper part and greenish-buff fine- to coarse-grained quartzose sandstone containing dark-brown calcareous concretions in lower part. At the southern end of Gun Barrel Hill along Boulder Creek the upper part is unusually light colored (White Rocks). Upper and lower parts are separated by a thin (about 20 cm) coal bed overlying a mudstone-claystone lens. The upper part characteristically displays polygonal joints. About 200 m thick.
	Pierre Shale	Lead-gray to brown and black marine shale, which weathers to olive gray brown. Generally homogeneous; is increasingly sandy upward and contains beds of siltstone, silty sandstone, and limestone as well as calcareous concretions. About 2,500 m thick.

Figure 2.--Stratigraphic nomenclature and descriptions. Modified from Weimer (1973).

### Sampling and analytical procedures

Samples of calcareous sandstones were collected from outcrops of sandstone in the Fox Hills and Laramie Formations. The limited distribution of outcrops governed the sampling locations. In the laboratory, samples were split, crushed to powder, and X-rayed to determine the proportions of calcite versus dolomite in the pore-filling cements. Only trace amounts of dolomite were observed. Powdered samples were placed in reaction flasks with 100 percent  $\text{H}_3\text{PO}_4$  at  $25^\circ\text{C}$  for at least four hours and isotopic measurements were made on the  $\text{CO}_2$  evolved. The isotopic analyses are reported here in the  $\delta$  terminology:

$$\delta = \frac{R_{\text{(sample)}} - R_{\text{(standard)}}}{R_{\text{(standard)}}} \times 1,000$$

where  $R = \text{Ratio} = \text{C}^{13}/\text{C}^{12}$  or  $\text{O}^{18}/\text{O}^{16}$ . Our standards are the Chicago PDB standard for carbon and Standard Mean Ocean Water (SMOW) for oxygen. The analytical procedures are those of McCrea (1950), Craig (1957), and Epstein, Graf, and Degens (1964). The  $\delta$  values are reported to  $\pm 0.1/\text{mil}$  (2  $\sigma$ ).

Iron and manganese contents of the samples were measured by X-ray fluorescence using the analytical technique described by Adler (1966). The relative uncertainty of the values is about  $\pm 10$  percent.

### Geochemical results

The results of our analyses are reported in table 1. Although the  $\delta\text{C}^{13}$  and  $\delta\text{O}^{18}$  values fall within the "fresh-water limestone" field of Murata, Friedman, and Madsen (1969), their pattern of areal distribution is striking; it is the pattern of the isotopic variation that is significant, not the absolute values themselves (see, for example, Donovan and others, 1974).

Systematic variation of iron content in rocks over oil fields has been documented (Donovan, 1974a). In addition, manganese is commonly concentrated in surface-rock cements; these and other data suggest that manganese may be useful as a petroleum pathfinder element.

### Interpretation of results and construction of maps

The data documenting the geochemical anomaly surrounding Panama Reservoir are presented in a series of maps (plates 1-4). Plates 1 and 2 show the variation in carbon and oxygen isotopic composition of interstitial calcite



Table 1.--Isotopic and elemental composition of sandstones of the Fox Hills and Laramie Formations and their calcareous cements, Panama Reservoir No. 1 area, Boulder and Weld Counties, Colorado

Sample	CaCO <sub>3</sub> Weight percent	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Mn (ppm)	Fe (percent)
1	27	- 7.54	12.19	1420	1.35
2	26	- 3.69	21.69	220	1.35
4b	38	- 9.22	15.20	1300	2.62
5	34	- 8.27	14.27	1050	1.62
6	33	- 4.56	14.80	1050	2.20
7	33	-10.10	13.52	3050	2.05
8	36	-11.59	14.89	640	1.40
9	38	-11.36	16.94	500	1.62
10	9	- 2.52	24.10	120	1.78
12	40	- 7.47	16.15	1800	1.56
13	38	- 8.21	16.69	1620	1.98
14	51	-10.38	19.35	4675	1.94
15	27	- 3.25	14.21	2180	1.83
16	43	- 6.98	17.25	3200	1.35
17	36	-10.99	13.93	1310	1.30
18	41	-10.25	14.43	625	1.40
19	37	-14.58	14.45	860	1.03
20	26	- 6.66	19.33	895	2.41
22	39	- 6.17	15.64	940	1.25
23	41	- 6.70	15.89	655	1.18
24	36	- 4.10	14.00	1140	1.13
25	32	- 9.20	14.60	815	1.08
26	38	- 9.70	14.90	1080	1.51
27	38	- 7.63	15.00	2080	1.83
28	38	-13.21	14.69	3350	1.13
29a	60	- 5.51	22.05	720	1.13
30	36	- 9.94	15.05	1080	1.35
31	31	- 3.51	17.40	3650	2.10
32	18	- 8.25	11.21	--	--
33	34	-18.00	13.74	--	--
35	21	- 8.33	18.40	--	--
36	27	- 6.35	14.00	550	2.16
37	27	- 7.37	14.47	260	1.90
38	30	-12.50	12.96	3350	--
39	30	- 8.48	17.37	460	1.27
40	29	-14.07	11.54	935	1.00
41	24	-18.21	12.93	125	1.55
42	35	- 5.80	17.46	2800	1.80
43	26	- 6.28	12.54	4500	2.38
44	39	- 8.71	16.62	2650	1.63
45	64	- 3.01	21.26	5400	1.58
46	41	- 6.21	15.33	550	--
47b	25	- 3.77	17.78	930	1.20

cements in outcropping Fox Hills and Laramie sandstones. The outer boundaries of the halo are practically defined by the -4/mil carbon isotope contour; very little carbonate cement is found beyond this boundary line. The carbonate cements (largely calcite but with small amounts of admixed dolomite) become lighter with respect to both isotopes toward the interior of the halo; carbon values range from -2.5 to -18.0/mil relative to PDB and oxygen values range from 11.2 to 24.1/mil relative to SMOW.

Total iron content of carbonate cemented surface samples likewise diminishes toward the interior of the halo, ranging from about 2.9 percent to 1.0 percent (plate 3; table 1). Manganese content of the carbonate cements, however, increases dramatically toward the interior of the halo ranging from 120 ppm to 5,400 ppm (plate 4; table 1).

The geochemical patterns cross stratigraphic boundaries without apparent offset or departure of trend. This implies that secondary processes operating independently of stratigraphic constraints are the cause of the geochemical anomaly.

In constructing these maps we made the conservative assumption that dry boreholes drilled to depths greater than 1,200 m (4,000 ft) were an adequate test for the presence of oil in the immediate surrounding area (say, one section). Where surface sample control is good and where there are dry boreholes nearby, for example, near the western edges of the mapped area, it is possible to roughly relate the contoured geochemical parameters with the distribution of dry holes and to extrapolate a similar relationship where the geochemical data are sparse or lacking due to inadequate exposures. In other words, we assumed that dry holes were peripherally located with respect to what might be considered the petroleum prospective area and lie either within or completely without the outer perimeter of the halo. We used this assumption as an aide in contouring where data points are far apart or absent.

An east-west gravity profile (not shown), corrected for topographic and regional effects, indicates that the mineralization (cementation) is a near-surface phenomenon, and is best developed in the western part of the area. The gravity data are similar to those reflecting near-surface cementation over petroleum deposits (McCulloh, 1969; and unpublished data). The near-surface

gravity manifestations are weakly developed on the east edge of the halo, just as are the chemical data. The better developed cementation on the western periphery resulted in the development of a coarser topography there than to the east, owing to more marked differential erosion and weathering.

#### Possible mechanism of cementation

The similarity between the isotopic and elemental distribution patterns within the halo suggests that areally limited interrelated cementation processes have been operative. On the basis of our prior study of petroleum-related surface geochemical anomalies we offer the following interpretations of these data.

1. The range, distribution pattern, and lightness of the carbon isotopic composition of calcite cements in the surface rocks is consistent with oxidation (biochemical?) of hydrocarbons and subsequent conversion of the resulting  $\text{CO}_2$  to carbonate (after possible admixture with isotopically heavier primary carbonates). (Donovan, 1974a; Donovan and others, 1974).

2. The oxygen isotopic composition of the cements reflects the composition of the mother waters with which they have equilibrated and from which they precipitated and which were also isotopically light with respect to oxygen. The light values are consistent with a meteoric source. We tentatively postulate that the distribution pattern and lightness of the oxygen isotopic composition of the calcite cements in the surface rocks may reflect the possibility of ultrafiltration fractionation by shales of vertically moving water (Coplen and Hanshaw, 1974).

3. The distribution of iron versus manganese substitution in the carbonate cements probably reflects the combined effects of differences in solubility and redox stability. Iron carbonate is more insoluble than manganese carbonate and should be enriched in cement precipitating under more reducing conditions (compared to the iron/manganese ratio in the solution from which it is precipitating). However, divalent iron is unstable under even slightly oxidizing conditions, while  $\text{Mn}^{++}$  has a much wider range of redox stability. Thus, the relatively high manganese/low iron cement may represent that which precipitated under the more oxidizing conditions.

4. Low salinities are generally reported for Denver basin waters associated with petroleum (Parker, 1961). This suggests dilution of oil field brines by meteoric water. Outcrops of the basin rocks along the Front Range provide ample area and opportunity for charging of the subsurface section with fresh water. Artesian circulation of fresh water through or past a petroleum deposit can introduce molecular oxygen resulting in biodegradation (Winters and Williams, 1969; Bailey, Jobson, and Rogers, 1973) and (or) promote water-washing of the more soluble hydrocarbons (Bailey, Krouse, Evans, and Rogers, 1973; Rogers, McAlary, and Bailey, 1974; Deroo, Tissot, McGrossan, and Der, 1974). Water-washing provides a ready mechanism for bringing hydrocarbons to the surface and near-surface environment in sufficient quantity to permit detection of their oxidation products although strong empirical evidence indicates diffusion of low-molecular-weight hydrocarbons through anticlinal roofs also occurs (Donovan, 1974a; Donovan and others, 1974). Surface halos are believed to develop above and peripheral to buried hydrocarbon deposits as a result of vertical bypass leakage at the edge-water/oil contact. The halo illustrated in plates 1-4 may be a reflection of chemical activity at the edge-water/oil contact of a buried hydrocarbon deposit. Alternatively, the surface anomaly may not be directly related to fresh-water circulation, but may instead reflect vertical bypass leakage and diffusion of low-molecular-weight hydrocarbons around the reservoir seal, with subsequent surface oxidation.

#### Conclusions and recommendations

We conclude that the data presented in plates 1-4 and the interpretations of their significance outlined above, suggest a potential petroleum prospect centered near Panama Reservoir No. 1. We cannot estimate the potential volume of producible reserves nor can we predict the exact depth at which they might occur. Regional considerations and comparisons with nearby oil fields indicate Cretaceous sandstone bodies could occur at depth less than 1,500 m (5,000 ft). Our maps suggest an area of about 20 km<sup>2</sup>.

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