UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

Relative importance of organic carbon and sulfide sulfur in a Wyoming roll-type uranium deposit

by

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Open File Report 81-580
1981

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Abstract

Organic carbon, sulfide sulfur and uranium content in samples from the Highland uranium mine, Powder River Basin, Wyoming are presented. These data show strong statistical correlation between organic C and S and U and S, but not between U and organic C. This is interpreted to mean that sulfide is the concentrating agent for the uranium in this roll-type deposit. However, organic carbon (possibly introduced) is the energy source for sulfate-reducing bacteria.

Introduction

Organic carbon and sulfide sulfur are common constituents in many roll-type uranium deposits but their exact roles in ore-forming processes is not completely understood. In the primary uranium deposits of the Ambrosia Lake district in New Mexico, the organic matter obviously plays a major role as a concentrator of uranium (by chelation and ion exchange). In the south Texas deposits, many of which contain little or no organic matter, sulfur is the reductant and concentrator of uranium. In the Wyoming roll-type deposits, both organic carbon and sulfide sulfur are present, usually in small amounts (<1 percent).

Harshman (1974, p. 177) suggested that since "there was no direct correlation between uranium and organic content".... there is "considerable doubt on the belief that organic carbon was directly involved" for five roll-type deposits he studied. King and Austin (1966) give results for a series of samples collected an oxidized, ore and reduced rock from the Gas Hills. Their plots show increased organic C, S, and U in the ore zone. The ore-zone U and S are several percent, whereas the organic carbon is about 0.5 percent.

In this paper we report the results of a statistical analysis involving uranium, organic carbon, and sulfide sulfur in samples collected from a roll-type deposit in Wyoming, and we discuss the relative importance of organic carbon and sulfur as concentrators of uranium. Our interpretation of the statistical data gives conclusions that are similar to the model proposed by Langen and Kidwell (1974) and Dahl and Hagmaier (1974) and provides data for the models proposed by Rackley (1972) and Granger and Warren (1974).

Acknowledgements

We thank the officials of Exxon, USA for permission to sample their property, particularly W. C. Duke who made us aware of the unique exposure of the roll geometry on the floor of the open pit which enabled us to obtain clear samples of both oxidized and reduced rock adjacent to the roll. We also wish to thank Van Shaw, and Paul Briggs and Hugh Millard, U.S. Geological Survey, for the analytical work. We also thank Charles Pierson (USGS) for helping us with the multiple regression analysis and use of partial correlation coefficients.

Samples and Analyses

The samples were collected in 1978 at the Highland open pit mine situated in the southern part of the Powder River Basin, Wyoming (fig. 1). Our samples are from the uppermost of three ore bodies in three successive sand units. Drill hole 47-45 (fig. 1). 77 m (250 ft) N.45°W. of sample OX-1-29 encounters 4.6 m (15 ft) of ore in the lower part of a 8.4-m (36-ft)-thick sand. We believe our samples are from a plane through the nose of the roll (as opposed to the limb). The samples were collected from the floor of the pit

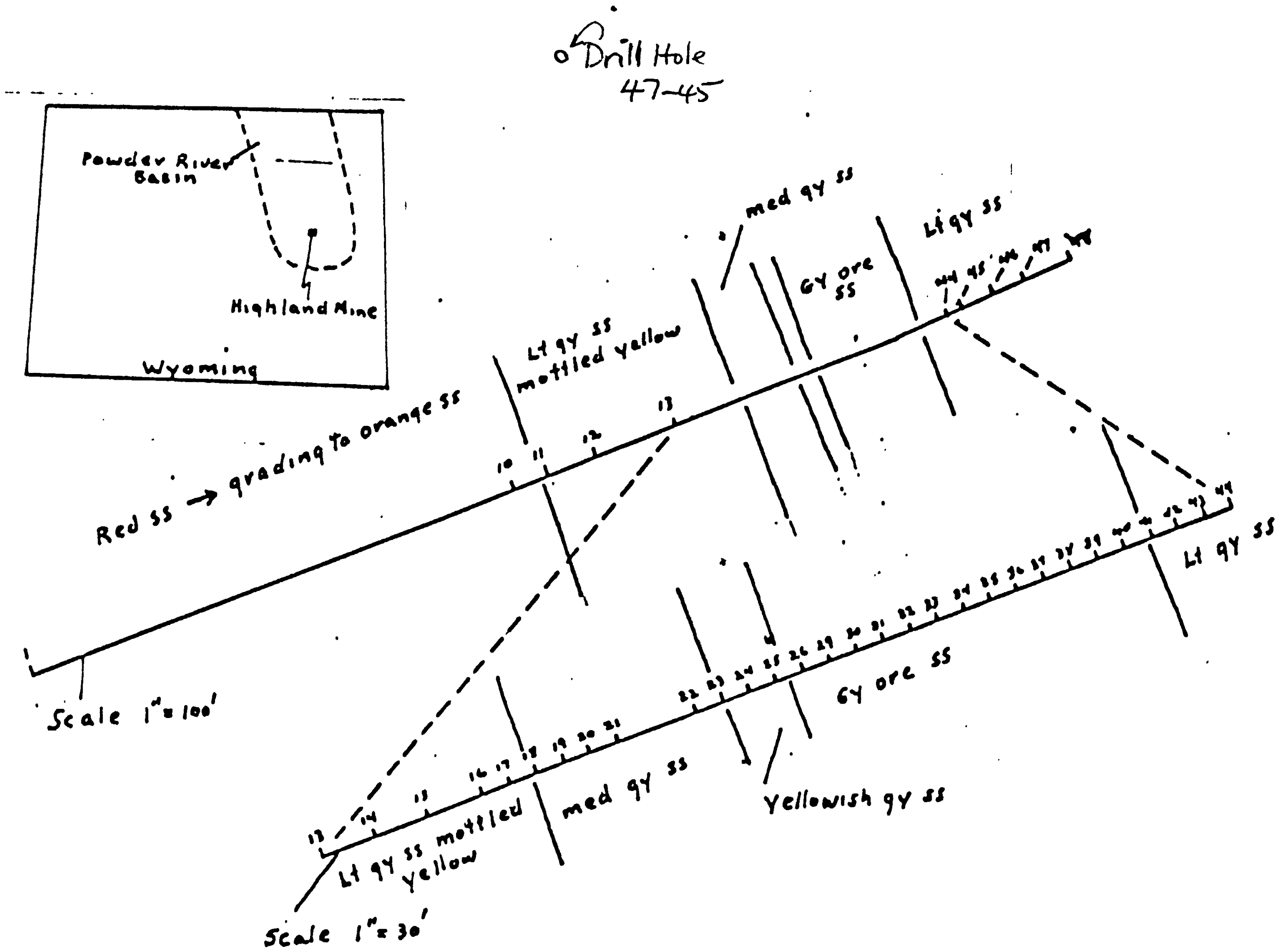

Figure 1. Plan view of pit floor, Highland mine showing sample localities..............................

immediately after a swath of fresh rock, oriented perpendicular to the ore zone boundaries, had been exposed by a bulldozer cut. Samples were collected at 6- to 15-m (20- to 50-ft) intervals in oxidized rock remote from the ore zone, and at 1.5-m (5-ft) intervals through the ore zone as well as near its boundaries. Figure 1 shows the locality and spacing of samples. Santos (1981) gives a complete description and chemical analyses of the samples.

The samples were analysed by the usual methods (Leventhal and others, 1978; Leventhal and Shaw, 1980) which include total carbon by LECO combustion, carbonate carbon by titration, and organic carbon by difference. Sulfide sulfur was measured by LECO combustion after removal of sulfate sulfur. Uranium was measured by the delayed neutron method (Millard, 1976). The results of analyses are shown in table 1. Samples 1-15 are on the oxidized side of the roll, samples 16-22 and 25-41 are in ore, samples 23 and 24 are in a slightly oxidized bleached zone, and samples 42-48 are on the reduced side of the ore zone.

Statistical

Results from samples 16-41 were treated statistically for linear-least-squares fit to the equation $y=mx + b$, where y is the dependent variable, x is the independent variable, m is the slope, and b is the intercept. This was done in three ways: with uranium as y and sulfur as x; with uranium as y and organic carbon as x; and with sulfur as y and organic carbon as x. In each case, that removing one to four samples changed the correlation coefficient (r). The significance of the fit to the linear equation was judged by the r value and number of pairs of data values based on standard statistical

Table 1.--Analyses of 38 samples from the Highland mine

Sample No.	U (ppm)		Organic Carbon (percent)	Sulfide Sulfur (percent)
OX-1-1	5.5		0.04	<.01
10	12.0		.03	<.01
11	4.18	oxidized	.05	<.01
12	17.3	zone	.02	<.01
13	11.0		.03	<.01
14	392		.08	<.01
15	23.2		.04	<.01
16	625		.05	.01
17	603		.13	.01
18	5370		.14	.13
19	3450		.08	.01
20	1260		.09	.04
21	2380		.12	.03
22	832		.15	.01
23	28		.04	<.01
24	2000		.07	.02
25	1070		.18	.02
26	5620	ore	1.22	.51
29	2230	zone	.16	.07
30	5950		.28	.11
31	9600		.26	.17
32	2340		.59	.04
33	5580		.09	.07
34	1590		.03	.02
35	698		.13	.04
36	996		<.01	.02
37	1080		.21	.02
38	1130		.01	.01
39	659		.38	.04
40	621		.18	.01
41	1130		.10	<.01
42	135		.63	.09
43	120		.19	.01
44	271	reduced-	.26	.03
45	96.3	barren	.25	.06
46	83.9	zone	.18	.01
47	150		1.97	.09
48	24.7		.07	.04

tables. Multiple regression analysis was also run for the equation $U=i + jC + kS$, where i is a constant, j and k are slopes, C and S are carbon and sulfur, the independent variable, and U is uranium, the dependent variable. Partial correlation coefficients were also calculated for

$$r_{ij \cdot k} = \frac{r_{ij} - r_{ij} r_{ik}}{\sqrt{(1 - r_{ik}^2)(1 - r_{jk}^2)}}$$

(Krumbein and Graybill, 1965).

Discussion

Table 1 shows that, in many samples, the weight-percent of uranium exceeds that of sulfide-sulfur and organic carbon, but this low concentration of S and C relative to U does not violate the ideas presented here. As uranium was reduced, sulfide and organic C (if organic C was a reductant) were oxidized. Some organic carbon may also have been consumed by bacteria that reduced sulfate to sulfide. The reducing power of sulfide, when it is oxidized to sulfate, is such that about 25 times its weight of uranium can be converted from U^{+6} to U^{+4}. In the oxidation of sulfide to sulfate, 7 electrons per atom of sulfur (atomic wt. = 32) become available for the reduction of 3.5 atoms of uranium (atomic wt. = 238). Thus, 0.02 percent sulfide will reduce about 0.5 percent uranium. If the oxidation of sulfide is incomplete and stops at an intermediate stage, as when sulfide oxidizes to thiosulfate, about 10 times its weight of uranium could be reduced. Although greatly simplified here, the calculations involving the reduction of U that can be attributed to the complete or partial oxidation of sulfide are given by Warren and Granger (1973).

Figures 2, 3, and 4 show plots of the data for organic carbon versus sulfur, organic carbon versus uranium, and sulfur versus uranium. A rough increase of sulfur with increase of organic carbon (fig. 2), was observed in these samples. This increase may be similar to the covariance of C and S which has been observed in many recent and ancient sediments (Goldhaber and Kaplan, 1974, for review; Leventhal and Goldhaber, 1978; Leventhal, 1979) which is due to micro-organisms that utilize organic matter and sulfate to produce CO_2 and sulfide. This reaction does not go to completion, so the sediments contain the residual organic material and sulfide in a relatively constant proportion; hence the covariance of carbon and sulfur. This relation holds for _in-situ_ (syngenetic or epigenetic) reactions but does not apply to migrated sulfides such as H_2S moving up faults (Goldhaber and others, 1979).

A statistical treatment involving carbon and sulfur was performed on samples 16 through 41, samples mostly in the ore zone (sample 23, not mineralized, was excluded in this and subsequent operations). Table 1 and figure 2 show that sample 26 is anomalous in that it contains much more of both carbon and sulfur than do the other samples in the group. When sample 26 is included, the statistical treatment yields an r value of 0.85, which is significant at the 99.9-percent level. When sample 26 is omitted, an r value of 0.32 is obtained, which is not statistically significant. Thus, one unusual (outlier) sample can change the statistical conclusions. For this reason we have done our statistics in several ways to see this effect. Inspection of the data reveals that samples 32 and 39 are also somewhat anomalous in that they have a higher carbon content than do the other samples in the group, coupled with a low sulfur content. Omission of samples 26, 32, and 39 yields an r value of 0.59, which is significant at the

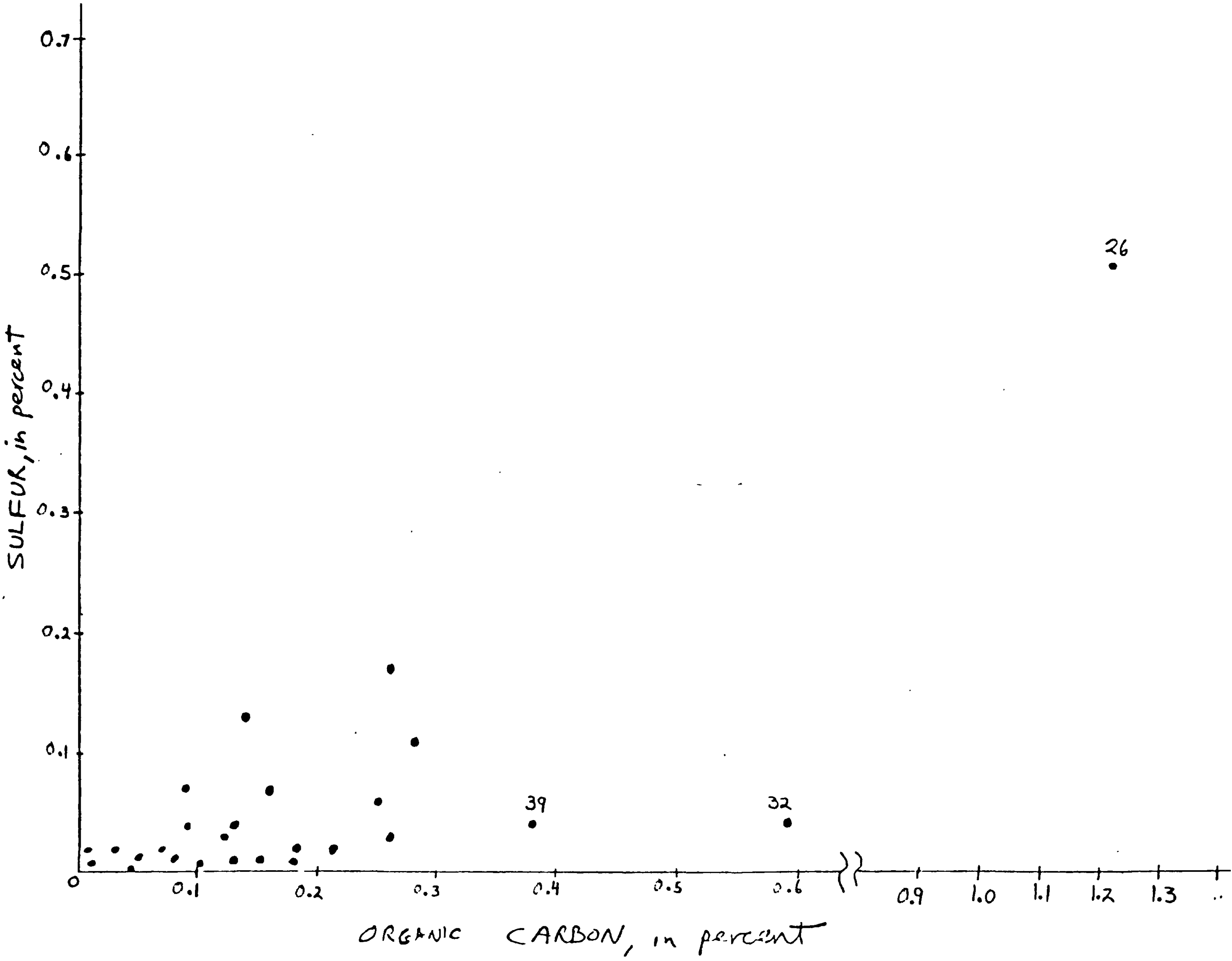

Figure 2. Plot of organic carbon versus sulfur
Numbers refer to sample number on table 1.

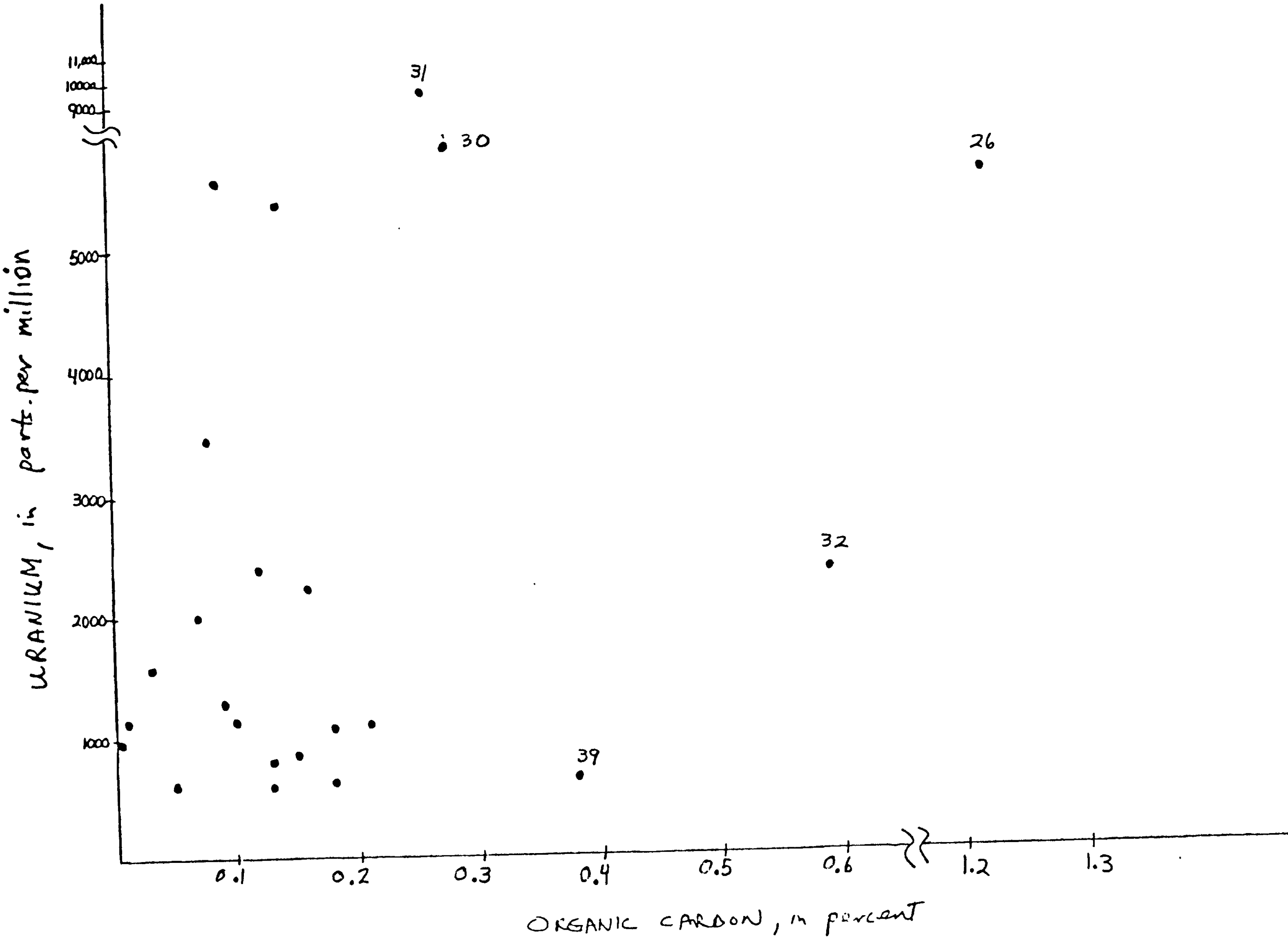

Figure 3. Plot of organic carbon versus uranium
Numbers refer to sample number on table 1.

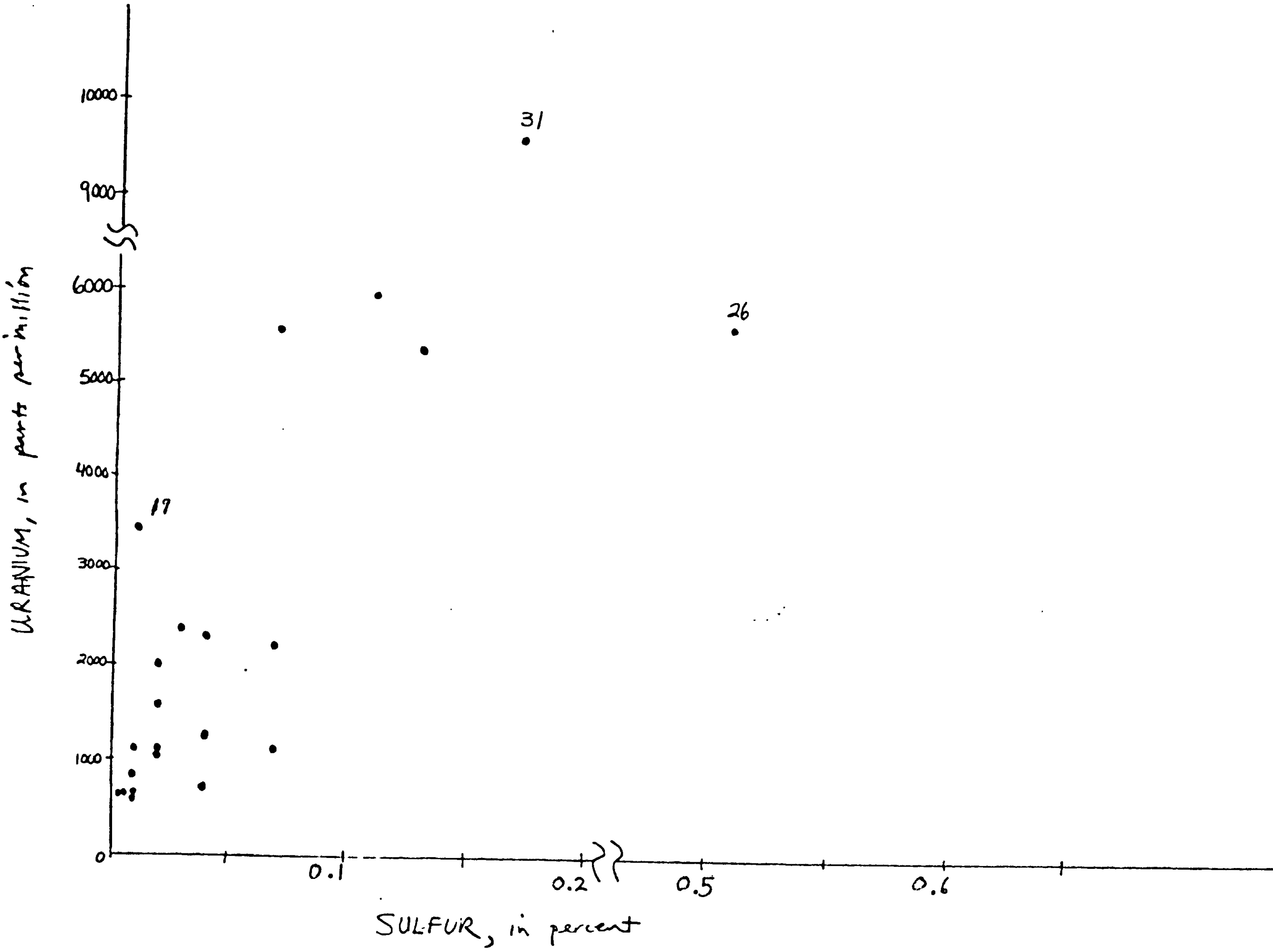

Figure 4. Plot of sulfur versus uranium.
Numbers refer to sample number on table 1.

99 percent level. The correlation of carbon and sulfur, when the three samples mentioned are disregarded, suggests that in situ sulfate reduction may be the origin of the sulfide in the ore zone.

Linear-least-squares computation involving uranium and organic carbon yields an r value of 0.36 for all samples 16 through 41. In an analogous fashion to C and S data treatment, above, we find r values of 0.25, 0.32, 0.15, and 0.33 when various samples that might be considered anomalous (samples 26, 26 + 32, 26 + 32 + 31, and 26 + 32 + 31 + 39, respectively) are omitted singly or collectively (fig. 3). All these r values are less than 0.39, which is the value required for statistical significance (even) at the 90-percent level.

Linear-least-squares computation involving sulfur and uranium (fig. 4) yields an r value of 0.61 for all samples 16 through 41, which is significant at the 99-percent level. Omission of samples that might be considered anomalous (samples 26, 31, and 19), either singly or collectively, yields r values of 0.89, 0.81, and 0.87, which are all significant at the 99.9-percent level. The linear regression of U versus C, C versus S or U versus S on this small number of samples yields results that depend somewhat on choice of samples. However, the statistical significance seems to have only one interpretation (see Conclusions).

The complex geologic samples can be examined another way. Multiple regression analysis and partial correlation coefficients were calculated by C. T. Pierson (U.S. Geological Survey). The results show the following: For all 3 variables (C and S as independent), the equation is $U = 4.28 - 0.062\ C + 0.766S$. The correlation coefficients are $r_{UC} = .352$, $r_{US} = .688$, $r_{CS} = .569$. The partial correlation coefficient is $r_{UC.S} = - .067$, which is not significant (0.35 is needed for even 90-percent significance), where $r_{UC.S}$, is the correlation coefficent for U and C with variable S is held fixed. Conversely, the $r_{US.C} = 0.634$, which is significant at the 99-percent level.

Conclusions

The results of these statistical analyses indicate that sulfur is much more closely related to uranium than is organic carbon for this roll-type deposit. Two related explanations are given: (1) The organic matter is not of primary importance as an agent to localize uranium in this particular roll-type deposit, but the sulfide is. (2) The fact that the organic matter and sulfide are genetically related is not violated: the sulfide migrates after formation and the residual organic matter is immobile; or perhaps mobile organic matter of external source was the energy source for sulfate reduction. Thus, carbon and sulfur both play essential, but distinct, roles in formation of this type of deposit.

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