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Sulfur speciation and isotopic analyses of sediment samples from Walker Lake, Nevada

by

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Introduction

As part of an investigation of paleoclimates in the Basin and Range Province, sediment cores were obtained from Walker Lake, Nevada, in July, 1984. The purpose of the investigation was to obtain information from the sedimentary record of Walker Lake that would allow reconstruction of the paleoclimatic history of the area and the geochemical evolution of the lake. Prior to 5000 years before present (B.P.), the lake existed off and on as both an independent lake, as it is today, and as a part of a subbasin (Walker River basin) within Quaternary Lake Lahontan when water depths greater than 1308 m covered all divides separating the subbasins and united them as one large lake (Benson, 1978). Walker Lake was chosen as a coring site because its sediments provide a record of lake level fluctuations in Lake Lahontan and these fluctuations may be related to paleoclimatic changes. Walker Lake is also relatively steep-sided and narrow and its sedimentary record should be fairly sensitive to small climatic parameter changes, such as a net increase in lake water evaporation as the result of a dryer climate. These small changes cause correspondingly larger changes in lake levels and sedimentary deposits in a steep-sided, narrow lake than they would in a lake of a different geometry. Walker Lake cores were sampled by various investigators for a variety of purposes including geochronology, grain size analysis, pore fluid analysis, geochemistry, etc. Many of the findings and the data collected from the cores are summarized by Benson (1987). This report summarizes the results of sulfur speciation and isotopic analyses of sediment samples from cores 4 and 5 from Walker Lake. These data were obtained to determine paleoclimates from evidence provided by the sulfur geochemical record in the sediment.

Walker Lake is located in west-central Nevada (Fig. 1) and is the terminal lake for the Walker River. Walker River basin is a closed basin of approximately 11,000 km^2. The lake has an area of 150 km^2, a variable maximum depth of about 33 m and a length and width of 25 and 9 km, respectively (Rush, 1974). Walker Lake receives 80 percent of its water from the Walker River (Rush, 1974), whose two forks (East and West) originate in the Sierra Nevada Mountains and acquire 80 percent of their input from snowmelt during the months April through August (Vasey & Hastings, 1974). Annual precipitation on the lake is only 10 cm per year (Everett and Rush, 1967) whereas evaporation is about 120 cm/yr (Benson, 1981). The construction of reservoirs along Walker River for agricultural use, combined with withdrawal of water from the river for irrigation purposes, has decreased the flow into Walker Lake by 60 percent (Benson and Leach, 1979). As a result, Walker Lake is decreasing in size; its depth is 50 percent less and the volume is 67 percent less than in 1882 (Benson and Leach, 1979). Rush (1974) reports that recession of the lake is proceeding at a rate of about

0.61 m per year, interrupted only by small, short-term rises in lake level. Because Walker Lake is a closed terminus for water and because evaporation exceeds precipitation, the lake waters have become increasingly concentrated in total dissolved salts. In addition to the increasing total dissolved salts from natural concentration effects, there is also a net diffusion of soluble salts into the lake waters from sediments underlying the lake because of a salinity gradient (Benson and Leach, 1979). These salts most likely originate from sediment deposited during a prior desiccation of Walker Lake around 9,050 to 6,400 years B. P. (Benson, 1978).

The waters of Walker Lake currently have total dissolved solids (TDS) of about 10,400 mg/L comprised primarily of Na^+, HCO_3^-, Cl^-, and SO_4^{2-} ions. This TDS is considerably higher than the concentrations found in waters of the Walker River which contain about 400 mg/L (Benson and Leach, 1979). The lake is monomictic with an extended mixing of waters from November through April, during which time the hypolimnion becomes oxygenated and nutrients are dispersed throughout the water column (Koch and others, 1979). During the summer, the lake stratifies and the hypolimnion stagnates becoming anoxic.

Methods

Two sediment cores (Fig. 1) were taken in July, 1984 from Walker Lake utilizing a barge-mounted wire-line Mobil® drill rig outfitted with a split-spoon sampler. Core 4 penetrated 152 m of sediment, although not with complete recovery. Core 5 was taken at the same site to try to recover missing sections in core 4 and also penetrated 152 m of sediment. Subsamples of the cores were taken systematically at varying intervals, placed in clean, 125 ml polyethylene bottles, frozen, and transported to the laboratory. Samples that were analyzed in this study were chosen from both cores so that all intervals of the sedimentary record would be represented.

At the laboratory, the samples remained frozen until analyses were performed. Sulfur speciation analyses were performed on the samples using the method of Tuttle and others (1986). The sample bottle was removed from the freezer, placed in a glove bag under nitrogen and thawed. An aliquot of the wet sample was placed in a clean evaporating dish to air dry. After drying, 0.5 grams of dry sediment were weighed into a clean culture tube and treated with 6 N hydrochloric acid (HCl) until effervescence ceased. The sample was filtered and the residue weighed to determine the percentage of 6 N HCl-insoluble sediment residue. This percentage was used to convert the sulfur speciation data to a dry-sediment-weight basis.

A second aliquot of the wet sample was placed in a clean reaction vessel and the vessel was stoppered to prevent oxidation. The vessel was then removed from the glove bag, attached to a distillation apparatus, and 6 N HCl introduced. The HCl converted all acid-volatile sulfide species (monosulfides) to H_2S which was then collected as Ag_2S. The remaining sediment in the flask was filtered, rinsed, dried, weighed, and placed in another reaction vessel into which a solution containing Cr^{2+} and 6N HCl were added. The Cr^{2+} reduced the mineral disulfides in the sediment to H_2S which was then collected as Ag_2S. The sediment remaining from the Cr^{2+} reduction was filtered, rinsed, dried, weighed, and fused with Eschka's mixture according to ASTM procedure D3177 (ASTM, 1977). This procedure rendered the remaining sulfur (assumed to be organically bound) soluble by fusion with the Eschka flux, and this sulfur was then collected as a $BaSO_4$ precipitate. Inorganic sulfate concentrations in the sediment samples were determined by precipitating the sulfate contained in the 6N HCl acid-volatile filtrate. Inorganic sulfate analyses represent not only sulfate in the solid phases, but also the pore-water sulfate because the pore water was not removed prior to analysis. The coefficient of variation of the sulfur speciation method is less than 13 percent for all forms of sulfur except when the concentration of sulfur in the species approaches the limit of detection (0.01 percent S for a 5 g sample).

The amount of iron that is soluble in 6 N HCl and the amount of iron solubilized as a result of the Cr^{2+} treatment were determined on the solutions from the sulfur speciation analyses. Iron concentrations were determined using standard methods of analysis utilizing atomic absorption spectrophotometry. Values of iron reported are reproducible to within ± 10 percent.

Organic carbon and total carbon in the samples were determined from the aliquot dried in the evaporating dish. For organic carbon, approximately 50-75 mg of dry sample was weighed into a ceramic combustion crucible, placed into a 100 ml beaker, and 6 N HCl was added dropwise until effervescence ceased. Samples were allowed to digest and air dry for about 1 hour and were then thoroughly dried at 60-70°C in an oven. Organic carbon in this treated sample was determined using a LECO® induction furnace. Total carbon was determined for approximately 50 mg of dry, untreated sample in the induction furnace. Carbonate carbon was determined by difference. Carbon analyses have a coefficient of variation of less than 10 percent.

The isotopic compositions of the $BaSO_4$ and Ag_2S precipitates collected from the sulfur speciation analyses were also determined. Ag_2S precipitates were converted to SO_2 by slowly combusting a 20 mg charge of sulfide with 50 mg degassed CuO at 1025°C in an evacuated combustion-vacuum line. The SO_2 was collected, volumetrically measured, and its isotopic composition determined on a high resolution, six inch, 60-degree sector mass spectrometer. $BaSO_4$ precipitates were decomposed to SO_2 using a quartz reduction process that allows isotopic equilibration of the SO_2 with the quartz sand. The gas was then treated and analyzed the same as Ag_2S samples. All corrections for oxygen isotopic composition of the SO_2 and conversion to $\delta^{34}S$ (measured relative to Canyon Diablo troilite) were performed by a computer interfaced to the mass spectrometer. Reproducibility of replicate samples is within ± 2 per mil for samples taken through the sulfur speciation scheme.

Results

Results of analyses of sediment samples from cores 4 and 5 from Walker Lake are presented in Table 1 and Figures 2-5. Forms of sulfur that were speciated and analyzed were acid-volatile sulfides (monosulfides), disulfides, sulfate sulfur (principally pore-water sulfate), and organically-bound sulfur. The sulfur in acid-volatile mineral sulfides ranged from less than 0.01 to 1.7 wt. percent of the sample. The top 36 m of sediment show fairly constant values varying by about 0.5 wt. percent. The acid-volatile sulfur in the lower part of the cores (>36 m) show greater variability ranging from <0.01 to 1.7 wt. percent of the sample and the variations occur as broad cycles of higher and lower acid-volatile abundances (Fig. 2).

The variability in the percentages of sulfur in mineral disulfides below 36 m appear to be inversely cyclic to acid-volatile sulfide abundances in corresponding depths until about 112 m (Fig. 2) and range from 0.01 to 1.1 wt. percent. The upper sediments of Walker Lake have disulfide values from 0.01 to 0.28 wt. percent, a relatively narrow range similar to that of the acid-volatile monosulfides. The range of organically bound sulfur in these cores is from less than 0.01 to 0.13 wt. percent, relatively low abundances compared to those of the acid-volatile or disulfide sulfur. The percent of organically bound sulfur does not correlate with either disulfide or acid-volatile abundances, but, in general, does follow the pattern of lower variability and range in the upper sediments of the cores and greater range and variability at greater depths (Fig. 2).

The $\delta^{34}S$ values for the sediments, excluding sulfate values, range from -42 to +24 per mil, the mineral disulfides having the greatest range. The acid-volatile mineral sulfides have a slightly smaller range of $\delta^{34}S$ values, -41 to +18 per mil, and the $\delta^{34}S$ values of the organically-bound S in the sediments vary from -26 to +8 per mil. Distinct patterns are apparent from depth plots of $\delta\ ^{34}S$ for all of the sulfur species (Fig. 5), excluding sulfate. Samples from the top portion of the cores have values starting slightly below mid-range and decreasing with depth to the minimum value for each species at about 21 meters. Isotopic values then gradually increase to the maximum for each species at approximately 96 m. Isotopic values for acid-volatile and disulfide mineral sulfides gradually decrease from their maximums to another relative minimum at 130 meters. Organically bound sulfur isotope values below 112 m were not obtained so the correlation of this pattern with the acid-volatile and disulfide isotopic values below this depth could not be made.

Total carbon in cores 4 and 5 varies from 0.4 to 4.2 wt. percent with considerable variation throughout the length of the cores (Fig. 3). Carbon contents are greatest in the upper 14 m of the core and average 4 wt. percent. Below 14 m they decrease and become increasingly variable with depth, ranging from 0.4 to 3.4 wt. percent total C. The organic carbon fraction ranges from 0.3 to 3.1 wt. percent; again, highest values (1.8 to 3.1 wt. percent) occur in the upper portions of the cores. The values decrease and become more variable with depth. The inorganic carbon values (obtained by difference between the measured total and organic carbon fractions) are variable and range from 0.1 to 2.3 wt. percent.

Concentrations of acid-soluble iron leached from the sediments and pore water during the first step of the sulfur speciation analysis are also presented in Table 1 and Figure 4. These values range from 1.3 to 7.1 wt. percent and represent mostly iron contained in oxides and carbonates. The percentage of iron released in the second part of the sulfur speciation scheme from reduction of the iron sulfides ranges from less than 0.1 to 1.0 wt. percent. The patterns with depth for both the acid-soluble and disulfide iron are the same as those for the respective abundances of sulfur for these species.

Summary

Sulfur concentrations and isotopic values and iron concentrations in the sediments have broad cyclic trends with depth and the variations are greater than can be attributed to analytical variability of the methods. Acid-volatile mineral sulfide abundances are inversely correlated with disulfide abundances between 36 and 112 m in the cores. The $\delta^{34}S$ values in the samples ranges from -42 to +24 per mil and the cycles of the values with depth are the same for all species of sulfur measured, excluding the sulfur attributed to sulfate which was contaminated. These data, when combined with other data such as pore fluid chemistry and stable isotope values, provide important evidence for determining the diagenetic history of Walker Lake and the paleoclimatic history of the Walker Lake area.

References

American Society for Testing Materials (ASTM) Annual Book of Standards, 1977, Total sulfur in the analysis sample of coal and coke: Philadelphia, Pennsylvania, part 26, p. 322-326.

Benson, L. V., 1978, Fluctuation in the level of pluvial Lake Lahontan during the last 40,000 years: Quaternary Research, vol. 9, p. 300-318.

Benson, L. V., 1981, Paleoclimatic significance of lake-level fluctuations in the Lahontan Basin: Quaternary Research, vol. 16, p. 390-403.

Benson, L. V., 1987, Preliminary paleolimnologic data for the Walker Lake subbasin, California and Nevada: U.S.G.S. Water-Resources Investigations Report 87-4258, 50 p.

Benson, L. V. and Leach, D., 1979, Uranium transport in the Walker River basin, California and Nevada: Journal of Geochemical Exploration, vol. 11, p. 227-248.

Benson, L. V. and Spencer, R. J., 1983, A hydrochemical reconnaissance study of the Walker River basin, California and Nevada: U.S. Geological Survey Open-File Report 83-740, 53 p.

Everett, D. E. and Rush, F. E., 1967, A brief appraisal of the water resources of the Walker Lake area, Mineral, Lyon, and Churchill Counties, Nevada: Nevada Dept. Conservation and Natural Resources, Water Resources--Reconn. Ser. Rept. 40, 44 p.

Koch, D. L., Cooper, J.J., Lider, E.L., Jacobsen, R.L. and Spencer, R.J., 1979, Investigations of Walker Lake, Nevada: dynamic ecological relationships: Desert Research Institute, Publication No. 50010, Univ. of Nevada, Reno, 191 p.

Rush, F. E., 1974, Hydrologic regimen of Walker Lake, Mineral County, Nevada: Dept. of Conservation and Natural Resources, Division of Water Resources, Water Resources Information Series Report 21, 1 p..

Tuttle, M. L., Goldhaber, M. G., and Williamson, D. L., 1986, An analytical scheme for determining forms of sulphur in oil shales and associated rocks: Talanta, v. 33, no. 12, p. 953-961.

Vasey, B. J. and Hastings, G. C., 1974, Alternative plans for water resource use, Walker River Basin Area: Report of the Nevada Division of Water Resources, State Eng. Office, 75 p.

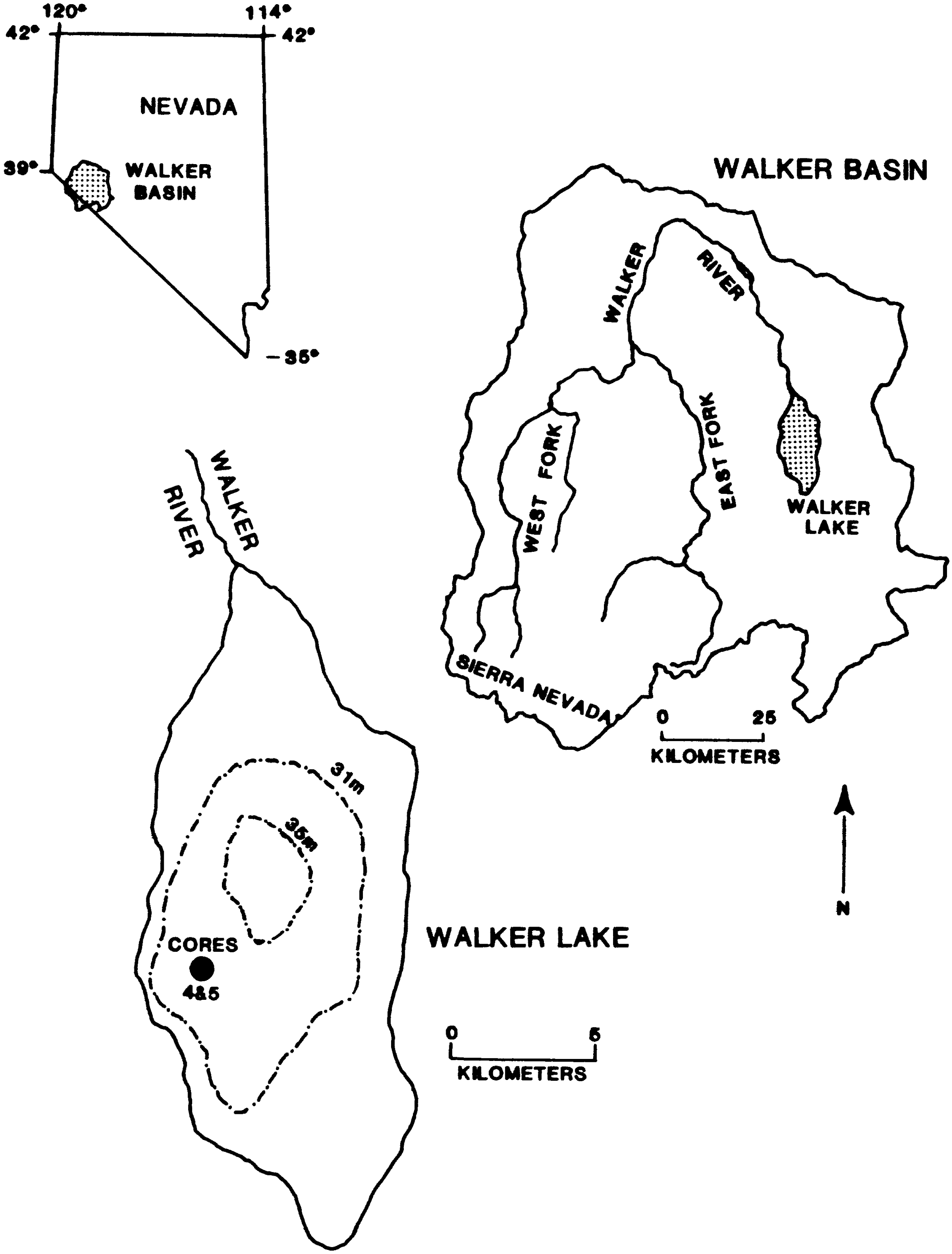

Figure 1. Location of Walker Lake and Walker basin, Nevada and approximate location of cores 4 and 5 in Walker Lake. Contours are in meters. (from Benson and Spencer, 1983)

Table 1. Sulfur speciation, isotopic data and associated analyses of samples from Walker Lake. Concentrations of sulfur, iron, and carbon are reported in weight percent of dry sediment. Sulfur isotopes values are per mil relative to Canyon Diablo Troilite. AV, acid-volatile.

CORE	DEPTH	AV	Disulfide	Organic	Sulfate	Total	Organic	Inorganic	AV	Disulfide	$\delta^{34}S$	$\delta^{34}S$	$\delta^{34}S$	$\delta^{34}S$
	m	S	S	S	S	C	C	C	Fe	Fe	AV	Disulfide	Organic	Sulfate
		Wt.%	Wt.%	Wt.%	Wt.%	Wt%	Wt.%	Wt.%	Wt.%	Wt.%	‰	‰	‰	‰
4	4	0.29	0.08	0.05	0.17	3.9	3.1	0.77	2.6	0.23	-2.7	-4.6	4.0	30.9
4	8	0.01	0.17	0.06	0.29	4.0	2.8	1.7	2.8	0.24	-6.1	-5.2	-21.4	
4	10	0.28	0.14	0.05	0.15	4.2	3.0	1.3	2.4	0.18	-2.5	-31.0		
4	12	0.09	0.20	0.04	0.56	3.7	2.1	1.6	2.2	0.18	-9.9	-10.8		
4	13	0.50	0.21	0.05	0.91	3.7	1.8	1.9	4.5	0.18	-1.2	-17.3	2.9	26.6
4	16	0.10	0.08	0.00	0.34	2.0	0.82	1.2	1.3	0.50	-33.3			
4	17	0.33	0.18	0.02	0.39	0.47	0.29	0.18	3.6	0.09	-37.5			
4	19	0.12	0.15	0.01	0.35	0.43	0.32	0.11	3.8	0.08	-40.5	-28.9	-26.5	26.8
4	21	0.26	0.13	0.01	0.39	0.43	0.29	0.14	3.5	0.14	-39.8	-38.9		
4	26	0.26	0.16	0.02	0.21	1.8	0.56	1.3		0.10	-37.2	-41.5	-21.4	28.5
4	27	0.16	0.28	0.04	0.34	2.1	0.86	1.2	3.2	0.04	-38.0	-36.0		
4	29	0.28	0.09	0.02	0.25	1.8	0.72	1.0	3.3	0.05	-34.8	-31.0		
4	31	0.49	0.01	0.02	0.25	1.8	0.55	1.3	3.2	0.05	-35.3			
4	32	0.43	0.01	0.02	0.22	1.9	0.49	1.5	3.1	0.12	-27.6	-28.2		
4	35	0.23	0.11	0.03	0.14	1.7	0.60	1.1	3.9	0.05	-34.3	-36.2		
5	36	0.27	0.27	0.04	0.23	3.1	0.89	2.2	2.7	0.24	-23.3	-24.9		
4	38	0.03	0.66	0.04	0.16	2.8	0.99	1.8		0.62		-25.8		
5	39	0.01	0.19	0.02	0.06	1.2	0.57	0.60	1.7	0.26				
5	50	0.06	1.1	0.01	0.10	0.67	0.40	0.27	3.0	0.90	-11.6	-12.7		
5	52	0.05	0.80	<0.01	0.18	0.72	0.38	0.34	3.0	0.83				
5	56	0.05	1.1	0.05	0.06	0.85	0.37	0.48	2.8	0.95		-5.2	-3.3	
5	62	0.77	0.34	0.13	0.05	3.2	2.3	0.85	3.4	0.28	-4.3	2.7	-2.5	4.5
5	75	0.46	0.36	0.06	0.04	1.8	1.2	0.60	3.9	0.08	3.1	4.8	-0.1	4.9
5	79	0.68	0.35	0.04	0.52	2.3	1.1	1.2	3.2	0.33	-2.7	-7.4		
5	85	0.27	0.92	0.09	0.36	2.3	1.3	1.0	3.0	0.68	14.1	2.4	1.6	8.6
5	94	0.05	1.0	0.07	0.12	2.4	0.89	1.5	2.2	0.99		24.4		
5	98	0.61	0.28	0.07	0.37	3.1	1.2	1.9	2.7	0.36	17.4	11.3	8.1	13.6
5	99	1.7	0.35	0.08	0.64	2.9	1.2	1.8	3.1	0.27	18.4	4.3	7.2	14.7
5	100	0.10	0.34	0.12	0.52	3.4	1.3	2.0	2.8	0.27		4.9		
5	106	0.05	0.84	0.05	0.16	2.4	0.87	1.5	2.4	0.84				
5	108	0.02	0.92	0.04	0.08	3.0	0.68	2.3	2.4	0.90		-4.6		
5	112	0.44	0.26	0.03	0.05	1.2	0.38	0.80	3.7	0.16	-18.5	-17.1	-1.0	5.1
5	114	<0.01	0.09	0.03	0.03	1.5	0.34	1.2	3.4	0.13		-12.5		
5	120	<0.01	0.46	0.02	0.09	2.2	0.89	1.3	4.2	0.39		-24.5		
5	130	0.94	--	0.05	0.05	1.1	0.42	0.71	7.1		-29.0	-28.1		
5	137	0.30	0.13	0.01	0.02	1.1	0.29	0.81	4.1	0.03	-22.4	-19.9		

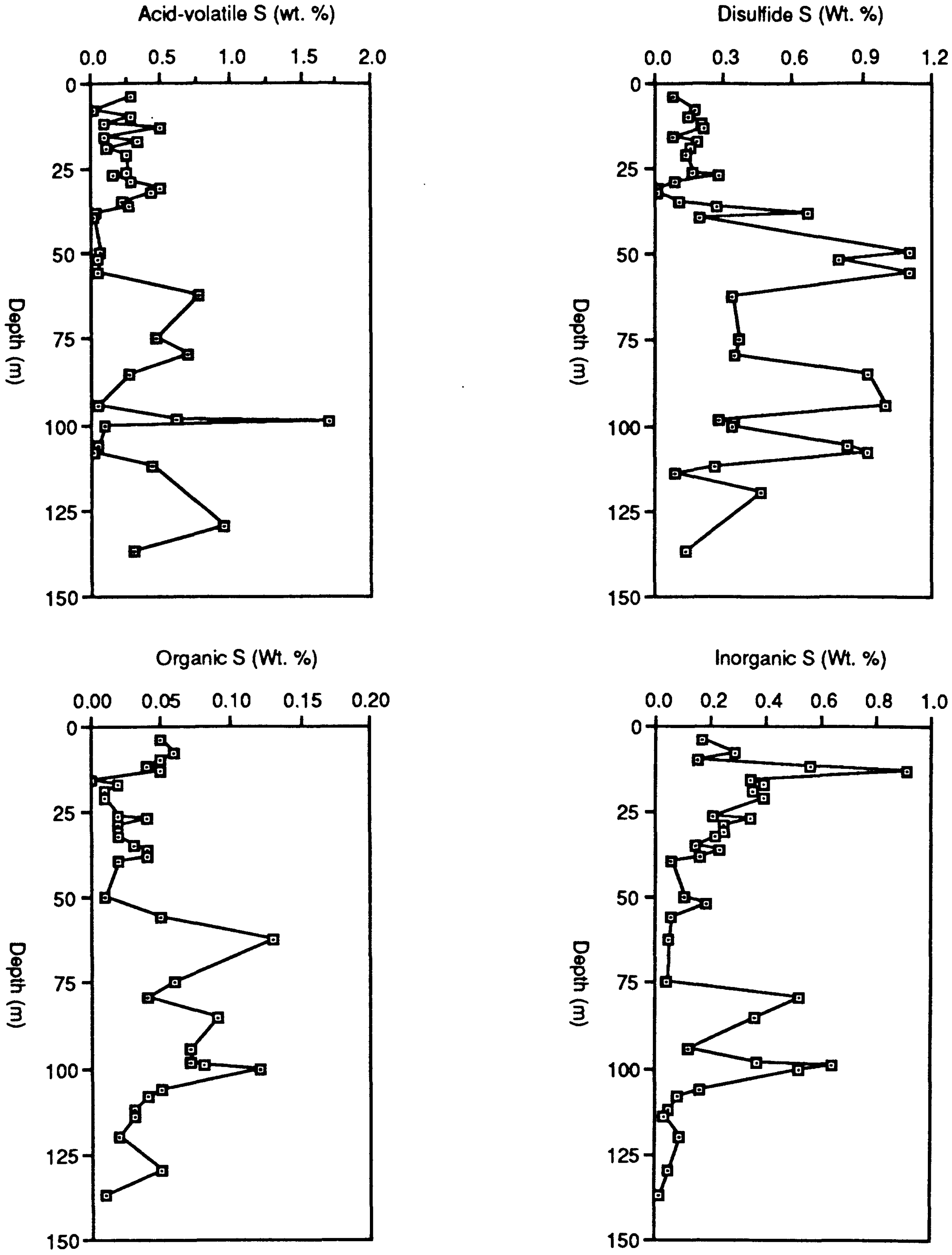

Figure 2. Weight percent sulfur versus depth in Walker Lake sediment samples. Percentages are on a dry sediment weight basis.

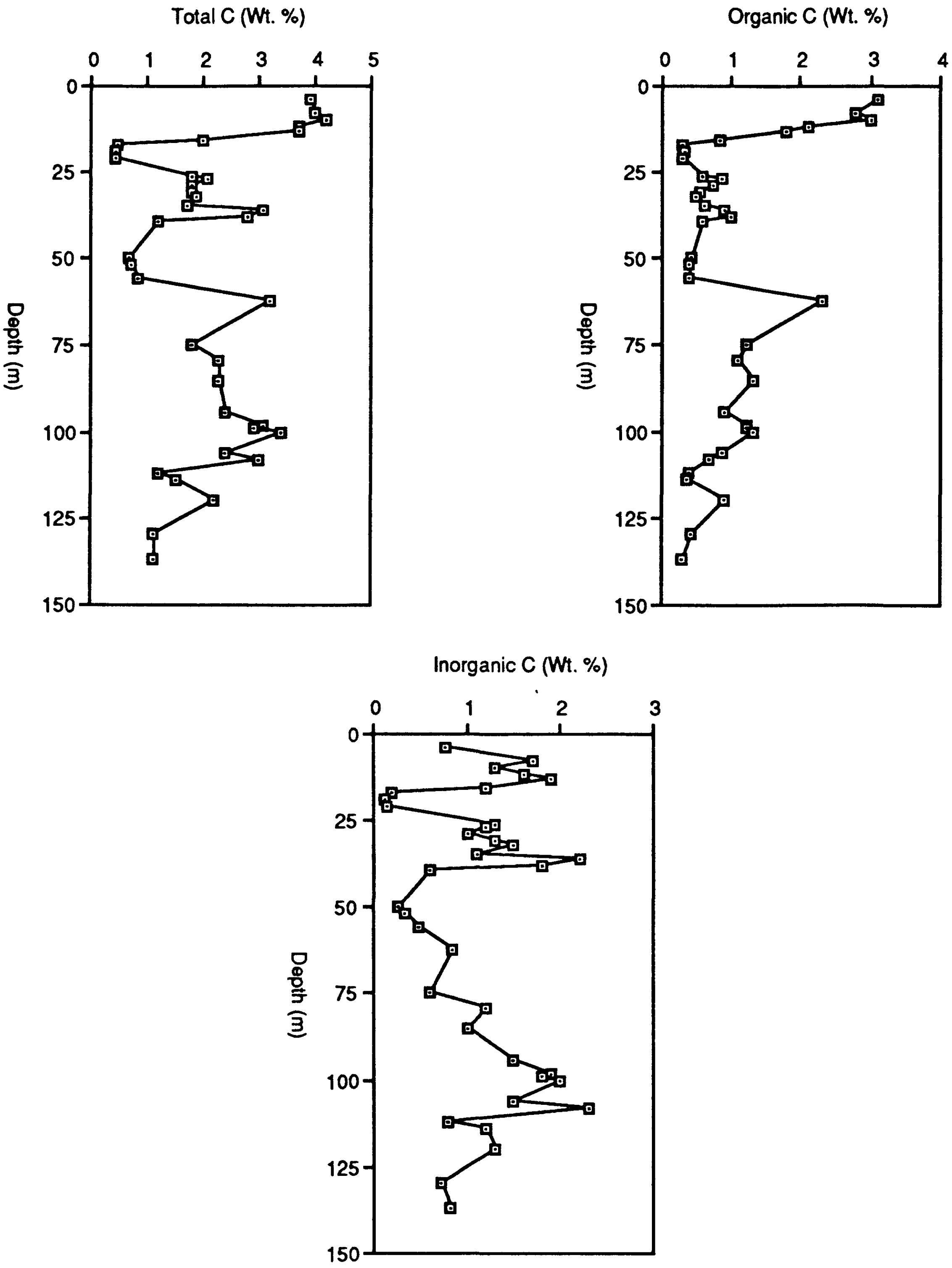

Figure 3. Weight percent carbon versus depth in Walker Lake sediment samples. Percentages are on a dry sediment weight basis.

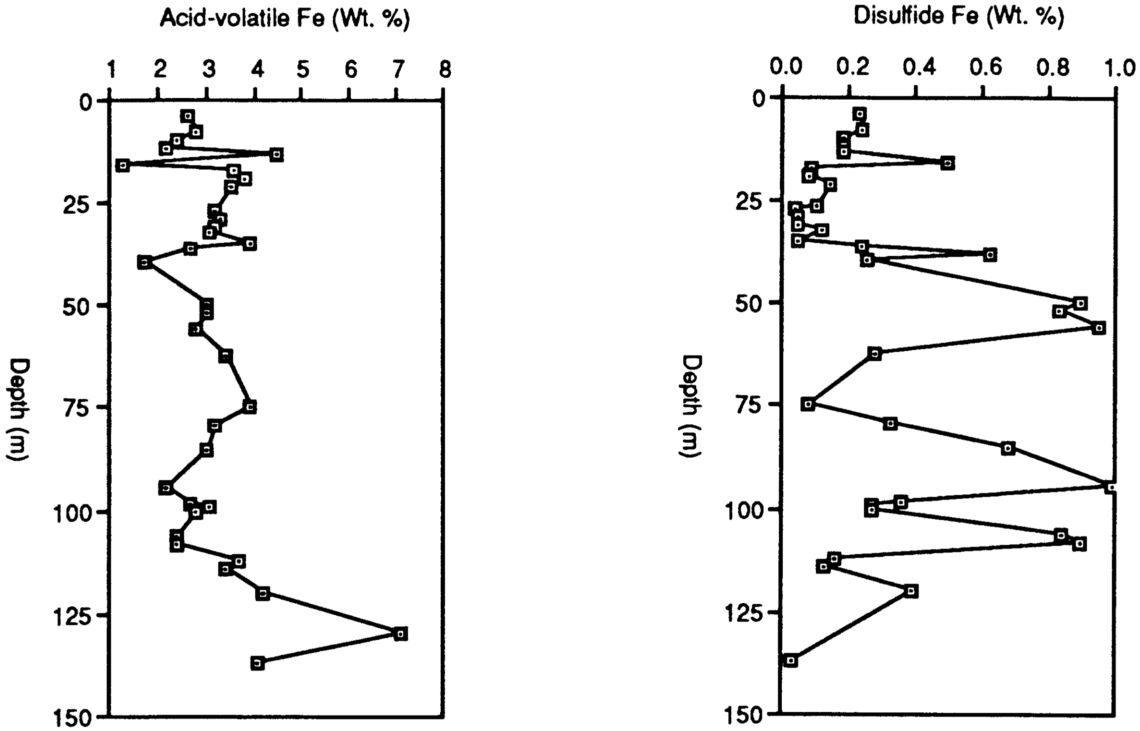

Figure 4. Weight percent iron versus depth for Walker Lake sediment samples. Percentages are on a dry sediment weight basis.

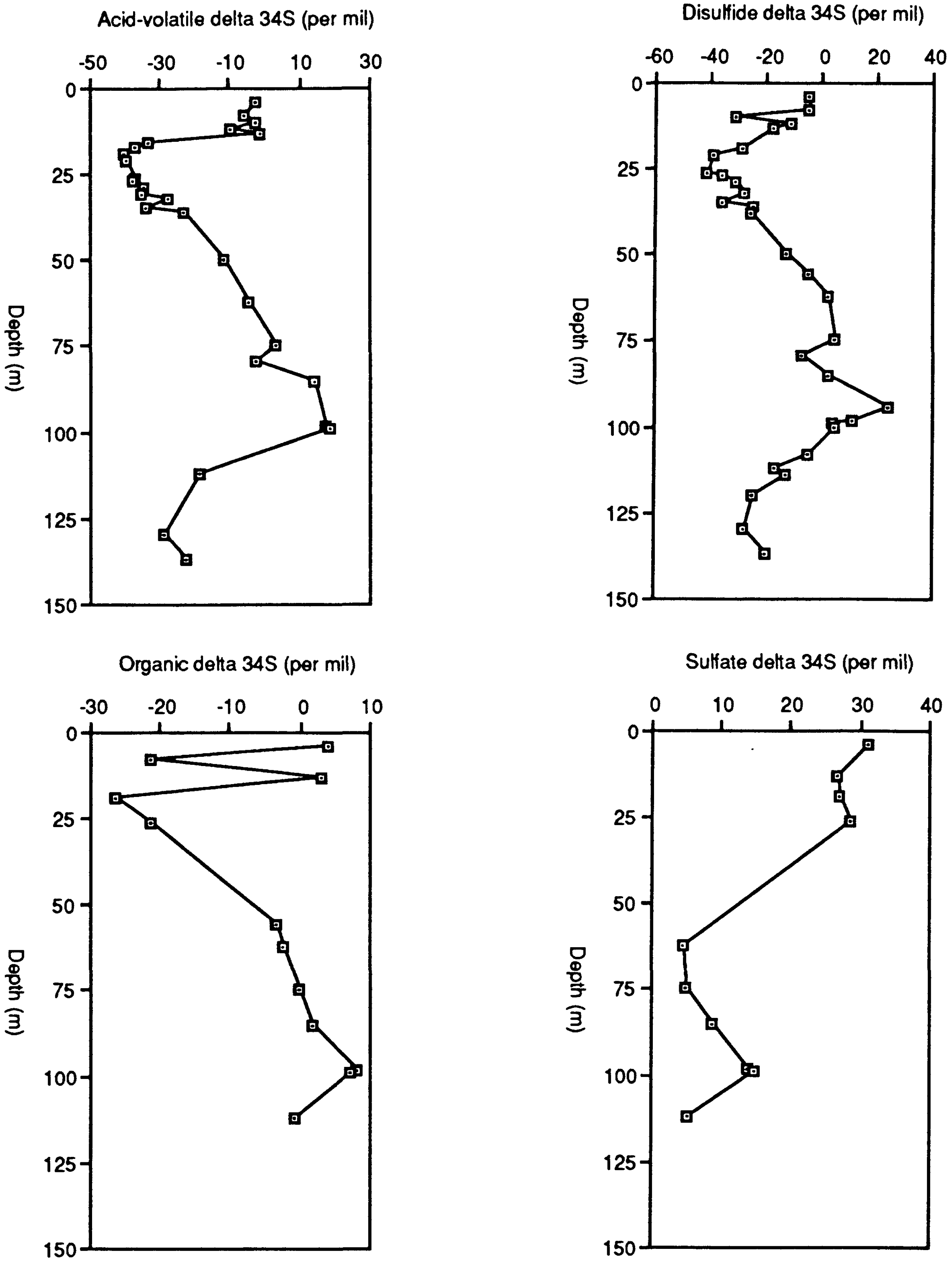

Figure 5. $\delta^{34}S$ versus depth for sediment samples from Walker Lake. Isotopic values are in parts per mil relative to Canyon Diablo troilite.