ANALYSES OF THE SULFUR SYSTEM IN WATERS FROM THE GALAPAGOS RIDGE HYDROTHERMAL VENTS

by

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Thesis Supervisor

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Submitted to the Department of
Earth and Planetary Sciences
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for the Degree of Master of Science

ABSTRACT

Samples collected from the Galapagos hydrothermal vents show a decrease in sulfate with temperature resulting in a flux of 5.3 x 10^{12} mol/year from the ocean assuming that these vents are representative of a global process. Sulfide concentrations increased with temperature (flux of 2.6 x 10^{11}-2.6 x 10^{12} mol/year to the ocean). Reduced species of sulfur including sulfite, thiosulfate, trithionate and tetrathionate were found in minimal amounts, if at all. A substantial portion of the iodine reactive species (otherwise unaccounted for) was hypothesized to be elemental sulfur.

Reduced sulfur species were not found in the overlying water column.

Name of Supervisor: Professor John M. Edmond, M.I.T.

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TABLE OF CONTENTS

Page Number

List of Figures

List of Tables

CHAPTER 1

INTRODUCTION

Over geologic time, sulfur chemistry in the oceans is controlled by reactions occurring between water, rock and sediment phases (Goldhaber and Kaplan, 1974). Under surface temperatures and pressures, for instance, it is thermodynamically favorable for sulfate to be reduced by organic matter to sulfide in the absence of oxygen. However, this reaction is not observed, unless there is biological intervention.

Biologically mediated reduction of sulfate might occur in the water column in areas of the ocean where the oxygen concentration approaches zero (e.g., the eastern tropical Pacific). This phenomena has not been observed, however, probably because bacteria preferentially reduce nitrate and nitrite before sulfate (Brewer, 1975, Cline and Richards, 1972).

Chemical reduction of sulfate can occur in processes such as reaction (1) when seawater and basalt react at high

$$\underset{\text{fayalite}}{11\ Fe_2SiO_4} + SO_4^{-2} + 4H^+ = \underset{\text{magnetite}}{7\ Fe_3O_4} + \underset{\text{pyrite}}{FeS_2} + 11\ SiO_2 + 2H_2O \quad (1)$$

temperature, as in the case of ridge crest hydrothermal systems (Bonatti, 1975), (Figure 1.1). In experiments in which basalt and seawater were reacted at 300 ^{o}C, much of the sulfate present was incorporated in anhydrite, $CaSO_4$, and some pyrite with perhaps 10% being reduced to aqueous sulfide. In many of these experiments, the total reduced sulfur measured exceeded the amount of total sulfur available from seawater, indicating that sulfur was also being leached from the rock (Mottl, et al., 1979). Pyrite was not found in hydrothermally altered pillow basalts from the Mid-Atlantic Ridge which led to the conclusion that the reduction of sulfate must be a minor process relative to the total water flux through the crust (Humphris, et al., 1978). Another possible source for reduced sulfur in the hydrothermal waters are volcanic gases liberated beneath spreading centers that might be dissolved in the ascending seawater (Bonatti, 1975). With these discrepancies in the literature between laboratory experiments, field observations, and theory, a more detailed look into the sulfur chemistry of hydrothermal waters is needed.

Seawater, when it reacts with basalt at the ridge crest, is heated to about 300 ^{o}C, decreases in pH, the result of magnesium fixation, and potential electron acceptors (oxygen, nitrate, sulfate, etc.) are consumed resulting in a reducing solution containing hydrogen sulfide (Edmond, et al., 1979a). Ambient water entrained along faults and cracks in the crust would lead to oxygenated water mixing with these reduced fluids as they rise or to oxidation of some of the pyrite (FeS_2). Large amounts of sulfur-oxidizing bacteria living in and around the vents would also contribute to the oxidation of the hydrothermal solution (Corliss, et al., 1979), (Figure 1.1). With the many redox reactions possible for sulfur under the above conditions, it is possible that some of the intermediate species might be measured in the hydrothermal fluids (Figure 1.2). Thermodynamic calculations indicate that sulfate, sulfide, and/or elemental sulfur would be the dominant species depending on the pH and pE. However, the system is not at thermodynamic equilibrium, so that some of the intermediate thermodynamically unstable species might be metastable for a sufficient period of time to be sampled and measured. Many variables, such as pH, initial concentration of reduced sulfur, catalysts and inhibitors, oxygen concentration, and relative reaction rates would influence the products found. Based on the experimental work of Nelson, et al., 1977, Cline and Richards, 1969, and Chen and Morris, 1972, the intermediate species that might be expected would include elemental sulfur, thiosulfate, polythionate (in particular tetrathionate and trithionate), and, possibly, sulfite. Therefore by measuring the concentrations of these species, as well as those of sulfide and sulfate, and, as a cross check, the species that react with iodine (H_2S, S_2O_3, SO_3, polysulfides, and possibly S^o stabilized by S_2O_3 or polythionates), greater insight into the sulfur cycle in the Galapagos hydrothermal waters would be obtained.

Figure 1.1

Hydrothermal Reduction and Oxidation of Sulfur

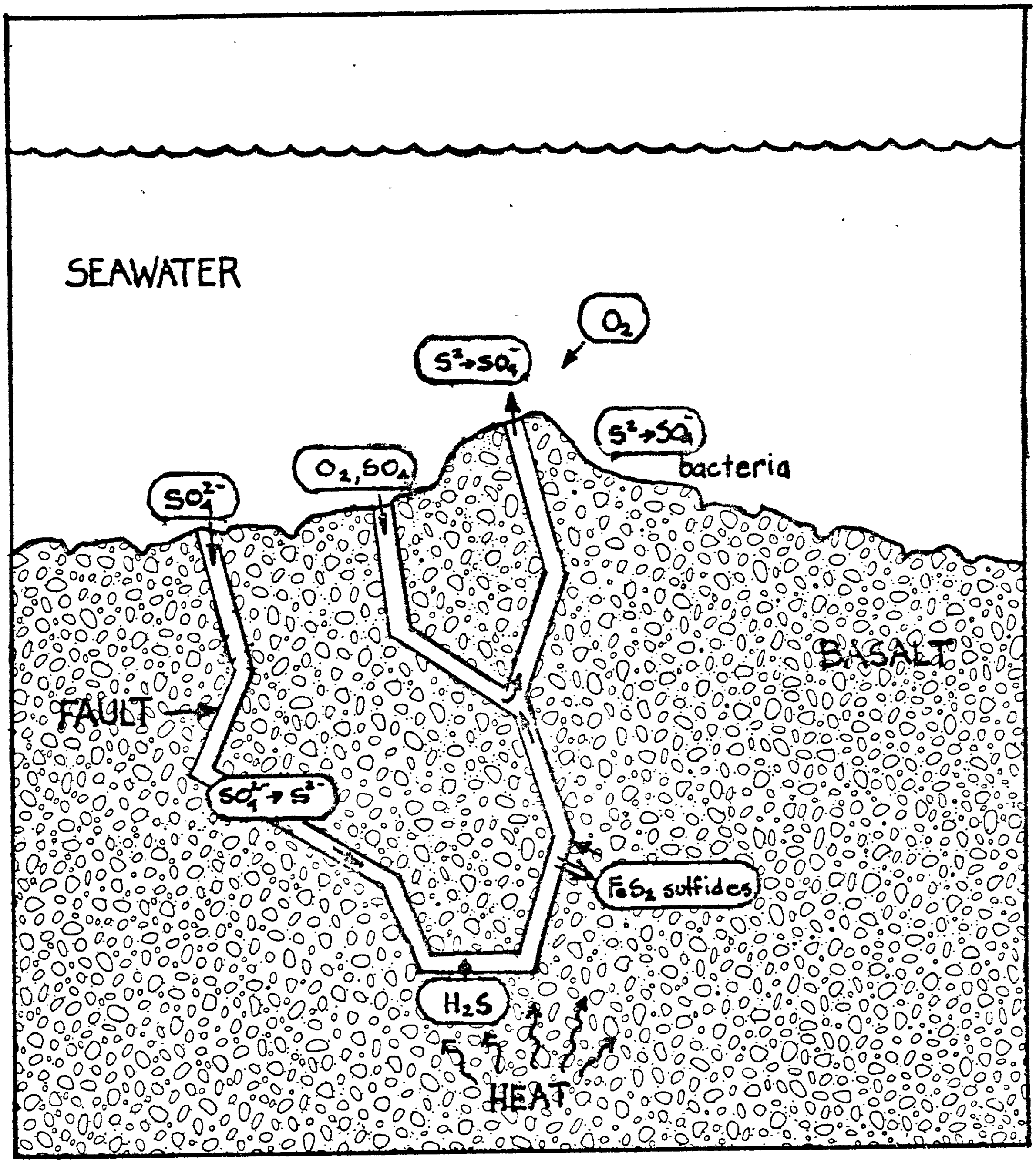
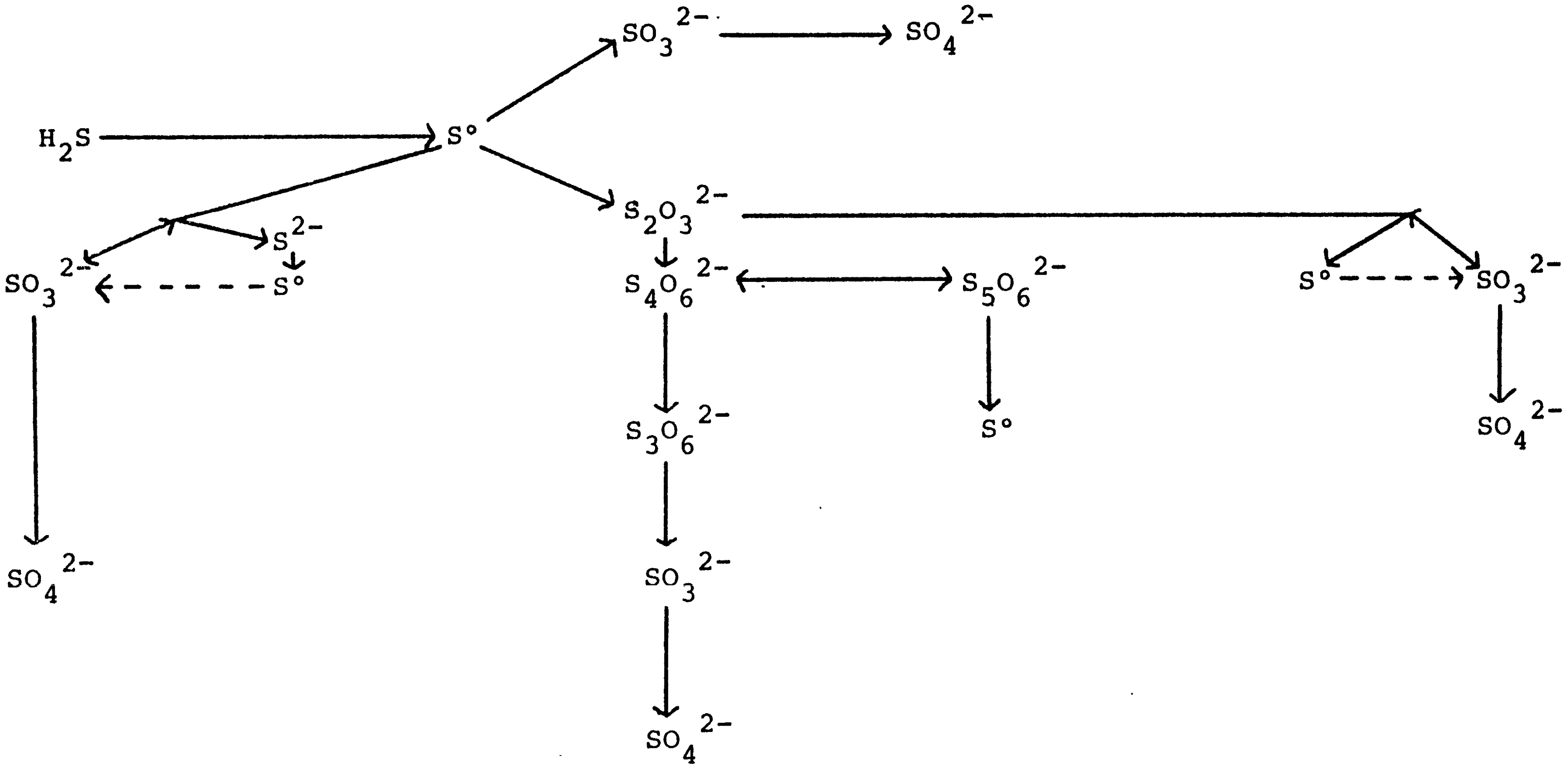

SEAWATER
O_2
$S^{2}\rightarrow SO_4^{-}$
$S^{2}\rightarrow SO_4^{-}$
bacteria
O_2, SO_4
SO_4^{2-}
BASALT
FAULT
$SO_4^{2-}\rightarrow S^{2-}$
FeS_2 sulfides
H_2S
HEAT

Figure 1.2

Oxidation Reaction Pathways - Acidic
and Neutral Solutions
(Nelson, et al., 1977)


SO_3^{2-}
SO_4^{2-}
H_2S
$S°$
$S_2O_3^{2-}$
S^{2-}
SO_3^{2-}
$S°$
$S_4O_6^{2-}$
$S_5O_6^{2-}$
$S°$
SO_3^{2-}
$S_3O_6^{2-}$
$S°$
SO_4^{2-}
SO_4^{2-}
SO_3^{2-}
SO_4^{2-}

CHAPTER 2

EXPERIMENTAL SECTION

Sampling

The Galapagos hydrothermal waters were collected using the sampling system described by J.B. Corliss, et al., 1979, mounted on the deep-sea submersible, Alvin. Three vent areas were sampled; "Rose Garden," "East of Eden," and "Mussel Beds" (Table 2.1).

Table 2.1

Vent area	Position		Dive #
	Lat.	Lon.	
Mussel Beds	0°47.5' N.	86°9.0' W.	898, 902, 904
Rose Garden	0°48.3' N.	86°14.3' W.	899, 900, 903, 905
East of Eden	0°47' N.	86°2.5' W.	901

The samplers were backfilled with nitrogen as samples were removed. Samples for sulfur species analyses were collected in ground glass stoppered reagent bottles using a plastic tube held at the bottom of the container. The sample was then allowed to flow into the bottle and overflow to avoid oxygen entrainment. Hydrocast samples from approximately the same area (Table 2.2) were collected using five liter OSU bottles.

Table 2.2

Stn #	Lat.	Lon.
86	2°12.1' N.	85°2.2' W.
135	0°38.8' N.	86°4.8' W.
139	0°47.7' N.	86°7.7' W.

Analysis

All colorimetric measurements were made using a Perkin-Elmer 55E spectrophotometer with a 1 cm. quartz cell, except for sulfide measurements in the 1 - 3 μ<u>M</u>. range which were made using a 4 cm. quartz cell.

Preparation of reagents is summarized on pages 28-32.

Sulfide

Hydrogen sulfide was determined using the spectrophotometric methylene blue method (Cline, 1969) with slight modifications. N,N-dimethyl-p-phenylenediamine-sulfate (Eastman Kodak No. 1333) and ferric chloride are reacted in 6 N. hydrochloric acid to produce the reagent.

The sample is added to the reagent. The procedure is optimized for a particular concentration range by changing the reagent concentrations and sample dilution (Table 2.3). The presence of sulfide is indicated by an intense blue color, the absorbance of which is measured at 670 nm. (Figure 2.1).

Figure 2.1

Sulfide Analytical Procedure

Figure 2.1

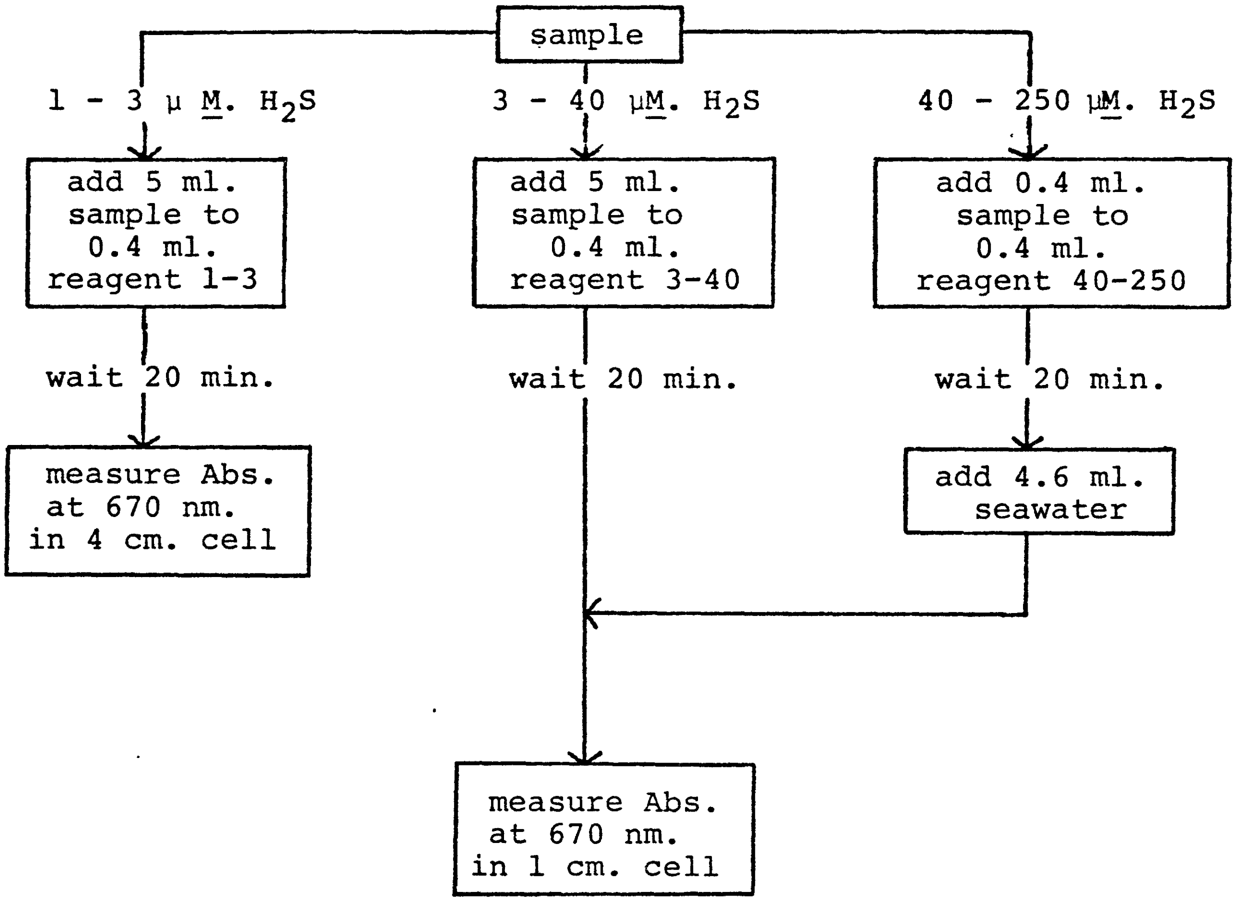

sample
1 - 3 μ M. H_2S
3 - 40 μM. H_2S
40 - 250 μM. H_2S
add 5 ml. sample to 0.4 ml. reagent 1-3
add 5 ml. sample to 0.4 ml. reagent 3-40
add 0.4 ml. sample to 0.4 ml. reagent 40-250
wait 20 min.
wait 20 min.
wait 20 min.
measure Abs. at 670 nm. in 4 cm. cell
add 4.6 ml. seawater
measure Abs. at 670 nm. in 1 cm. cell

Table 2.3

Sulfide conc. μmoles/liter	Diamine conc. g./500 ml.	Ferric conc. g./500 ml.	Dil. factor ml. : ml.	path length (cm.)
1 - 3	0.5	0.75	1 : 1	4
3 - 40	2.0	3.0	1 : 1	1
40 - 250	8.0	12.0	2 : 25	1

For sulfide concentrations expected to border on two ranges (e.g. 40 μ*M*. sulfide), samples were treated by both procedures. The concentration of the sample was then determined by comparing it with the standard curve covering the correct range.

The standards were prepared from sodium sulfide using distilled water that had been freshly boiled, cooled, and then bubbled with nitrogen gas to remove dissolved oxygen and carbon dioxide. The sulfide crystals were washed to remove oxidation products, dried, and dissolved in the water to give an approximately 0.1 N. concentration of sulfide. This solution was then standardized iodometrically (Budd & Bewick, 1952). Samples were compared to standard curves fitted by linear regression for the concentration ranges involved. The detection limit was 1 μ*M*. sulfide (Figure 2.2). The precision at the 95% level of confidence (Table 2.4) was constant over each of the concentration ranges used.

Figure 2.2

0-3 μ$\underline{M}$. Sulfide versus Absorbance

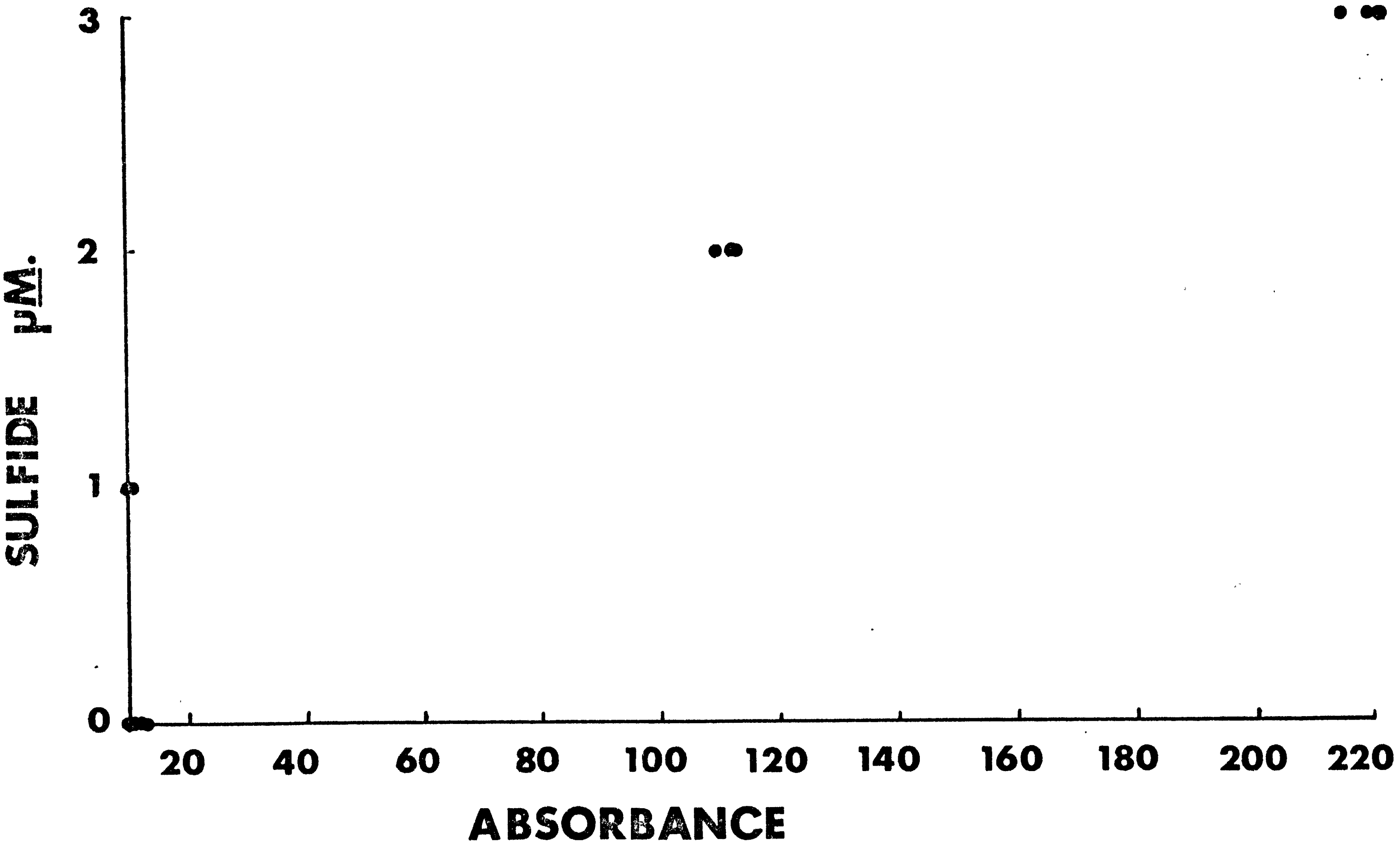

3
2
1
0
SULFIDE µM.
20
40
60
80
100
120
140
160
180
200
220
ABSORBANCE

Table 2.4

Sulfide conc. μmol/liter	Precision μmol/liter
1 - 3	± 0.05
3 - 40	± 0.9
40 - 250	± 29

Sulfate

Sulfate measurements were performed by Russ McDuff using the polarographic method of G.W. Luther and A.L. Meyerson (1975). The standard error was ± 0.2% at the 95% confidence level (2σ).

Iodine Reactive Species

The iodine reactive species present were determined iodometrically by adding an excess of approximately 0.1 N. iodine and back titrating the excess iodine with 0.102 N. thiosulfate (Vogel, 1961). The iodine was standardized with thiosulfate daily. A seawater blank (approximately 46 μequiv./liter of iodine) was subtracted from the samples. The standard error was approximately ± 65 μeq/l of I_2 at the 95% confidence level. This large error could have been reduced by using less concentrated solutions of iodine and thiosulfate for the titration.

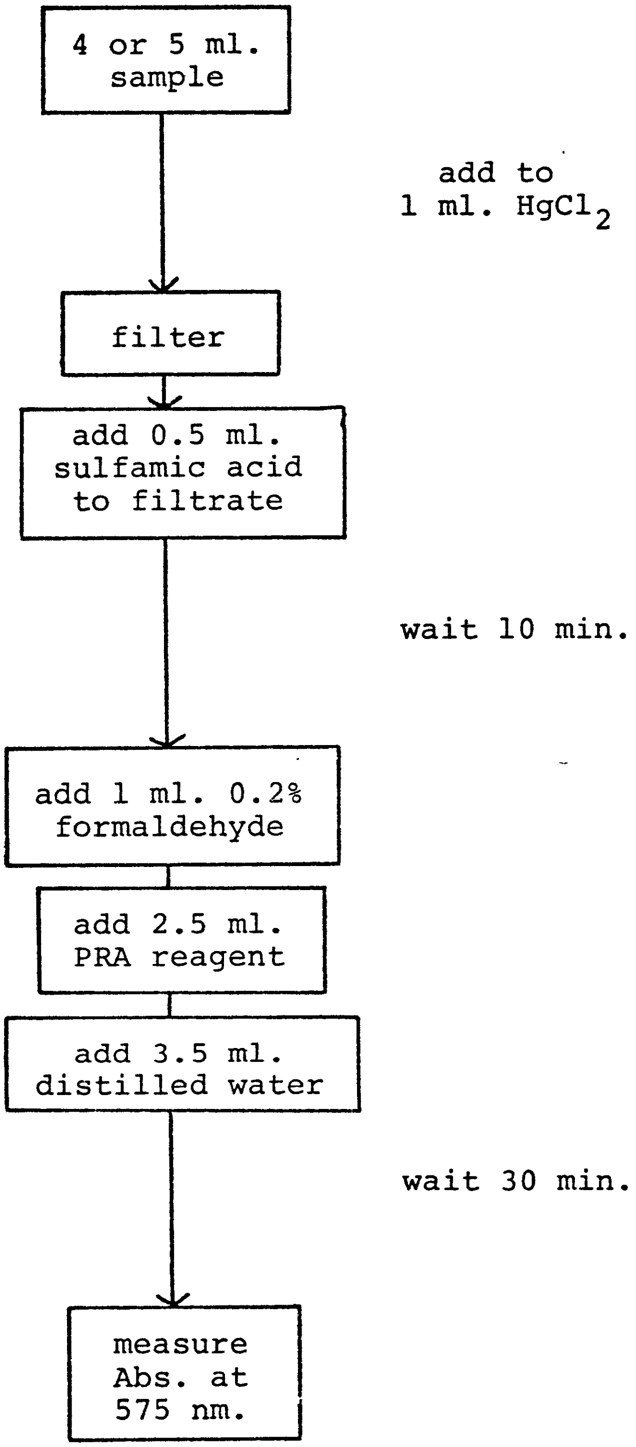
Sulfite

The colorimetric method of Scaringelli, et al., 1967, with modifications was used for sulfite determinations (Fig 2.3).

Figure 2.3

Sulfite Analytical Procedure

Figure 2.3


4 or 5 ml. sample
add to 1 ml. HgCl2
filter
add 0.5 ml. sulfamic acid to filtrate
wait 10 min.
add 1 ml. 0.2% formaldehyde
add 2.5 ml. PRA reagent
add 3.5 ml. distilled water
wait 30 min.
measure Abs. at 575 nm.

Sulfite reacts with formaldehyde and pararosaniline to form an intense violet color in acid solution. A 0.2 M. mercuric chloride solution (stabilizes sulfite from air oxidation by formation of dichlorosulfitomercurate) was used instead of 0.04 M. $HgCl_4$ because of the high chloride concentration in seawater. The $HgCl_2$ solution was made as concentrated as practical (0.2 M.) to maximize the sensitivity of the method. Millipore (0.45 μm.) filters were used for the filtrations.

Sulfite standards were prepared with sodium sulfite in distilled water treated as for the sulfide method. The solutions were standardized iodometrically. The standard error was ± 1 μM. at the 95% confidence level. The absorbances of the samples were then compared to the standard curves which had been fitted by linear regression. The detection limit was 1 μM. sulfite.

Thiosulfate, Trithionate, & Tetrathionate

The methods of T. Mizoguchi and T. Okabe (1975) were followed for thiosulfate, trithionate, and tetrathionate measurements. The three procedures are based on the reactions of these species with cyanide under different conditions (Table 2.5). The first procedure (A) is cupric ion-catalyzed cyanolysis of thiosulfate at a pH of 4.5. The second method (B) is the cyanolysis of tetrathionate at high pH, in the presence of acetone followed by cupric ion-catalyzed cyanolysis of thiosulfate. The last method (C)

Table 2.5

Procedure		Reaction	Equivalents of SCN^- expected (moles)
A	(1)	$S_2O_3^{2-} + CN^- \overset{Cu^{2+}}{=} SCN^- + SO_3^{2-}$	$S_A = (S_2O_3^{2-})$
B	(2)	$S_4O_6^{2-} + 2CN^- + 2OH^- \overset{Cu^{2+}}{=} 2SCN^- + SO_3^{2-} + SO_4^{2-} + H_2O$	$S_B = (S_2O_3^{2-}) + 2(S_4O_6^{2-})$
	(1)	$S_2O_3^{2-} + CN^- \overset{Cu^{2+}}{=} SCN^- + SO_3^{2-}$	
C	(3)	$S_3O_6^{2-} + CN^- + 2OH^- = SCN^- + SO_3^{2-} + SO_4^{2-} + H_2O$	$S_C = (S_2O_3^{2-}) + (S_3O_6^{2-}) + 2(S_4O_6^{2-})$
	(2)	$S_4O_6^{2-} + 2CN^- + 2OH^- \overset{Cu^{2+}}{=} 2SCN^- + SO_3^{2-} + SO_4^{2-} + H_2O$	
	(1)	$S_2O_3^{2-} + CN^- \overset{Cu^{2+}}{=} SCN^- + SO_3^{2-}$	

involves the cyanolysis of trithionate and tetrathionate in a boiling water bath at high pH, followed by cupric ion-catalyzed cyanolysis of thiosulfate.

Cadmium acetate was added to the samples (Figure 2.4) to eliminate interferences from sulfide and sulfite (B. Sorbo, 1957 and P.J. Urban, 1961). Pre combusted approximately 1 μm. glass fiber filters were used to remove the precipitate. The samples, where noted, were maintained at 19°C. in a thermostatically controlled water bath. The absorbances were measured at 460 nm. in a water cooled (19°C) 1 cm. quartz cell. Cupric sulfate was substituted for cupric chloride in the above reactions (A, B, & C) when the cupric chloride solution had been used up on board ship.

Standard curves for method A were prepared using a previously standardized 0.102 N. sodium thiosulfate solution (Vogel, 1961). The solution was made up following the sulfide procedure with $Na_2S_2O_3$ and standardized with potassium iodate. The error obtained from replicate standard curves fitted linearly was ± 15 μmoles/liter at the 95% confidence level.

Thiocyanate standards that had been previously compared to thiosulfate standards were used for methods B and C. The standards plotted in a parabolic curve (Figure 2.5), with a minimum of absorbance around 15 μmoles/liter of thiocyanate. Substitution of a less concentrated solution of cupric

Figure 2.4

Thiosulfate, Tetrathionate, and
Trithionate Analytical Procedure

Figure 2.4

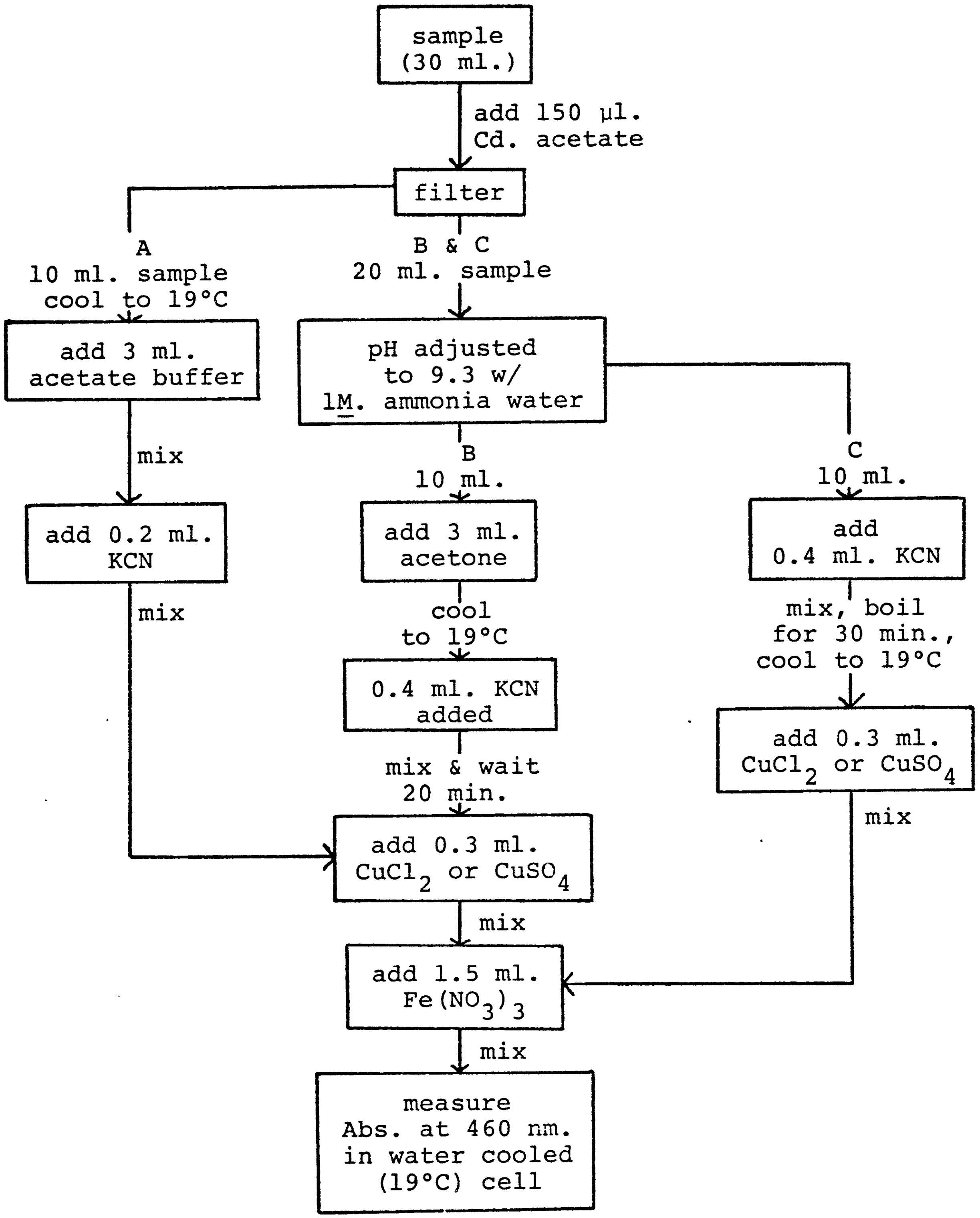
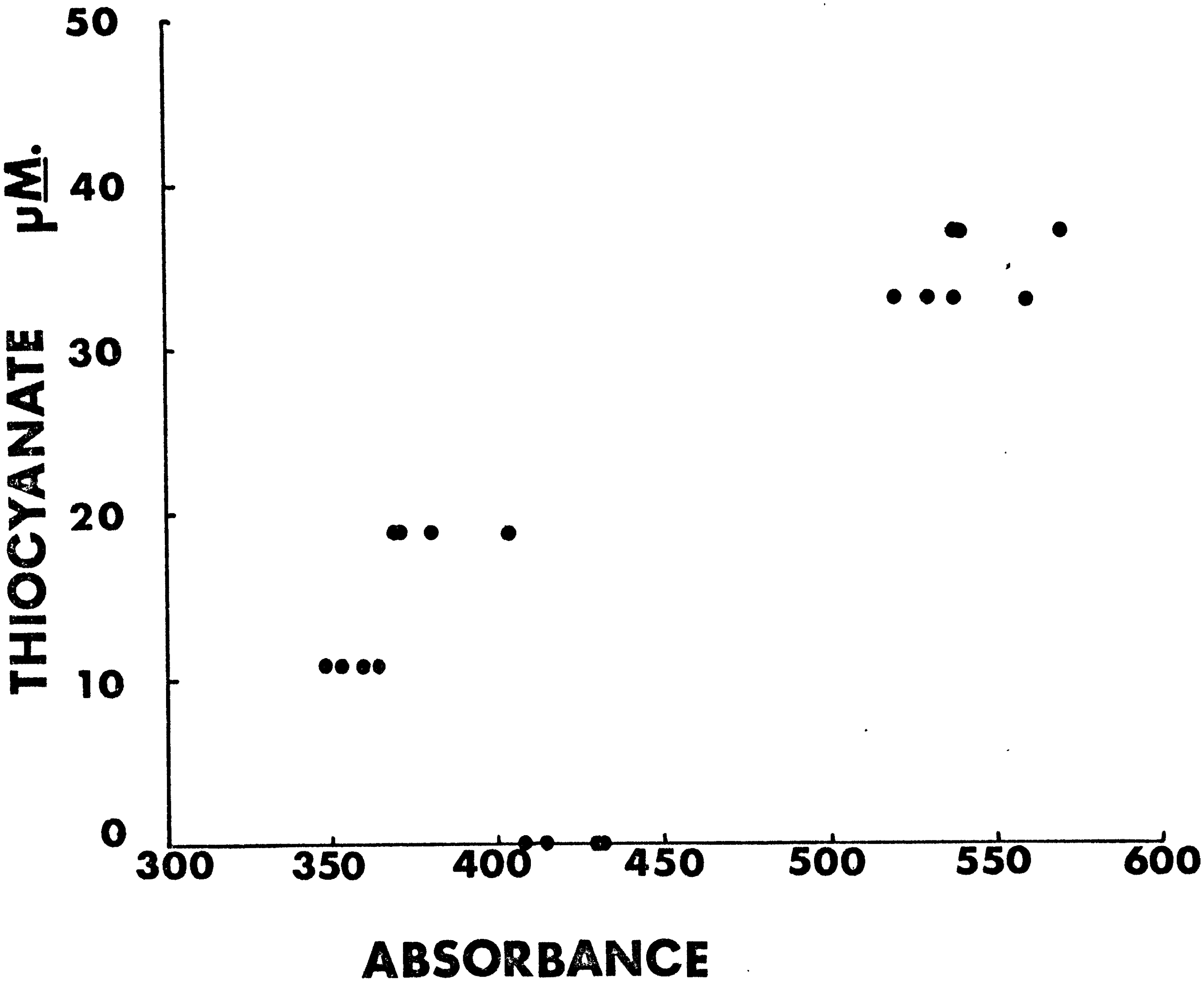

sample (30 ml.)
add 150 µl. Cd. acetate
filter
A
10 ml. sample
cool to 19°C
B & C
20 ml. sample
add 3 ml. acetate buffer
pH adjusted to 9.3 w/ 1M. ammonia water
mix
B
10 ml.
C
10 ml.
add 0.2 ml. KCN
add 3 ml. acetone
add 0.4 ml. KCN
mix
cool to 19°C
mix, boil for 30 min., cool to 19°C
0.4 ml. KCN added
add 0.3 ml. $CuCl_2$ or $CuSO_4$
mix & wait 20 min.
mix
add 0.3 ml. $CuCl_2$ or $CuSO_4$
mix
add 1.5 ml. $Fe(NO_3)_3$
mix
measure Abs. at 460 nm. in water cooled (19°C) cell

Figure 2.5

Thiocyanate, versus Absorbance,

Method C, ($CuSO_4$)


THIOCYANATE µM.
50
40
30
20
10
0
300
350
400
450
500
550
600
ABSORBANCE

sulfate for the cupric chloride in the procedure increased the standard error (Table 2.6). The parabolic shape of the standard curves in these procedures (B and C) may be due to an interference caused by the seawater medium since this phenomena is not observed in distilled water.

In general, errors on all the below procedures might have been further minimized if initial manipulation of the samples had been carried out under a nitrogen atmosphere. This, however, was not possible on board ship due to a shortage of nitrogen.

Table 2.6

		Std. error at 95% conf. (2σ) μM. thiocyanate
Method B	($CuCl_2$)	± 7
"	($CuSO_4$)	± 10
Method C	($CuCl_2$)	± 4.5
"	($CuSO_4$)	± 4.7

Table 2.7

Summary of Method Std. Errors

Method	Std. error at 95% confidence µM./liter
Sulfide (1-3 µM)	± 0.05
" (3-40µM)	± 0.9
" (40-250 µM)	± 29
Sulfate	± 0.2%
Iodine Reactive Species	± 65
Sulfite	± 1
S_2O_3(A)	± 15
SCN (B, $CuCl_2$)	± 7
SCN (B, $CuSO_4$)	± 10
SCN (C, $CuCl_2$)	± 4.5
SCN (C, $CuSO_4$)	± 4.7

REAGENTS

Sulfide:

N,N- Dimethyl-p-phenylene-diamine Sulfate; $[NH_2C_6H_4N(CH_3)_2]_2 \cdot H_2SO_4$, Eastman Kodak Co., No. 1333.

Ferric Chloride; $FeCl_3 \cdot 6H_2O$, A.C.S. Reagent grade, Matheson Coleman & Bell.

6 N. Hydrochloric Acid; A.C.S. Reagent grade, Fisher Scientific Co..

Sodium Sulfide; $Na_2S \cdot 9H_2O$, A.C.S. Reagent grade, Mallinckrodt, Inc..

Iodine Reactive Species:

0.1 N. Iodine; A.C.S. Reagent grade, J.T. Baker Chem. Co., (standardize daily).

Starch soln. - Make a paste of 1.0g. of Soluble Starch; A.C.S. Reagent grade, Merck and Co., Inc., with a little distilled water, and pour the paste with constant stirring, into 100 ml. of boiling distilled water, and boil for one minute (A.I. Vogel, 1961).

0.1 N. Sodium Thiosulfate; $Na_2S_2O_3 \cdot 5H_2O$, A.C.S. Reagent grade, Mallinckrodt, Inc..

Potassium Iodate; KIO_3, A.C.S. Reagent grade, Allied Chem., Specialty Chemicals Division.

Potassium Iodide; KI, A.C.S. Reagent grade, J.T. Baker Chem. Co..

2 N. Sulfuric Acid, H_2SO_4, A.C.S. Reagent grade, Mallinckrodt, Inc..

Sulfite:

3 M. Phosphoric Acid; H_3PO_4, A.C.S. Reagent grade, 85%, Fisher Scientific Co..

0.2 M. Mercuric Chloride; $HgCl_2$, A.C.S. Reagent grade, Mallinckrodt, Inc..

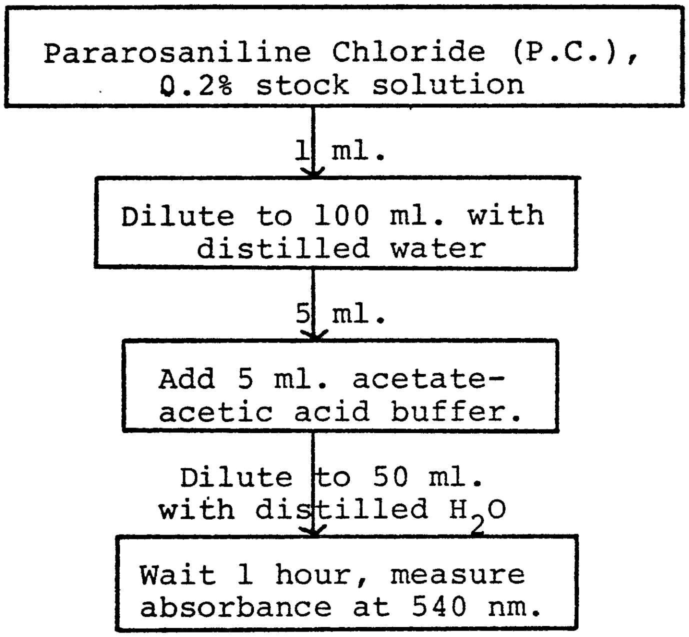
0.6% Sulfamic Acid; NH_2SO_2OH, Assay 99.90-100.10%, G. Frederick Smith Chemical Co (Prepare daily).

0.2% Formaldehyde; HCHO, A.C.S. Reagent grade, Approximately 37%, Mallinckrodt, Inc., (Prepare daily).

1 M. Sodium Acetate-Acetic Acid buffer; $Na_2C_2H_3O_2 \cdot 3H_2O$, A.C.S. Reagent grade, Matheson Coleman and Bell. Acetic Acid Glacial; CH_3COOH, A.C.S. Reagent Grade, 99.7%, Fisher Scientific Co..

Pararosaniline Chloride; $C_{19}H_{18}ClN_3$, (0.2% ± 0.03 in 1 M. hydrochloric acid), Eastman Kodak Co., A 14051.

P.C. concentration (Figure 2.6)



The actual pararosaline concentration as a percentage of the nominal concentration is determined by the formula:

$$(1)\ \%\ \text{P.C.} = \frac{\text{Abs x k}}{\text{grams of dye taken}}\text{, where k} = 21.3$$

to allow for correction of P.C. in reagent.

$$(1A)\ \%\ \text{P.C.} = \frac{(.458)\ (21.3)}{(.1)} = 97.5\%\ \text{P.C.}$$

Procedure B (Scaringelli, et al., 1967) was used because this method covered a wider range of sulfite concentrations. PRA reagent for method B is prepared by adding 200 ml. of 3 M. phosphoric acid to 20.5 ml. stock P.C. and diluting to 250 ml. with distilled water (PRA reagent). An additional 0.2 ml. of stock P.C. was added for each one percent that the stock P.C. assays below 100% (0.2 ml. x 2.5% = 0.5 ml.).

Sodium Sulfite Anhydrous; Na_2SO_3, A.C.S. Reagent grade, Merck and Co., Inc..

Thiosulfate, Trithionate, and Tetrathionate:

0.75 M. Potassium Cyanide; KCN, A.C.S. Reagent grade, Matheson Coleman and Bell.

0.3 M. Cupric Chloride; $CuCl_2 \cdot 2H_2O$, Analytical Reagent grade, Mallinckrodt, Inc. OR 0.2 M. Cupric Sulfate; $CuSO_4 \cdot 5H_2O$, A.C.S. Reagent grade, J.T. Baker Chem. Co..

0.2 M. Cadmium Acetate; $(CH_3CO_2)_2$ $Cd \cdot 2H_2O$, Reagent grade, Matheson Coleman and Bell.

2 M. Sodium Acetate - Acetic Acid buffer; (see above).

1 M. Ammonium Hydroxide; A.C.S. Reagent grade, Assay 28.0-30.0% NH_3, Fisher Scientific Co.

1.5 M. Ferric Nitrate - Perchloric Acid Reagent- 303 g. of Ferric Nitrate; $Fe(NO_3)_3 \cdot 9H_2O$, A.C.S. Reagent grade, Mallinckrodt, Inc. was dissolved in a small volume of distilled water containing 186 ml. of conc. Perchloric Acid; $HClO_4$, A.C.S. Reagent grade, 70 wt.%, G. Frederick Smith Chemical Co., and diluted to 500 ml. with distilled water.

0.1 N. Thiosulfate; (see above).

Potassium Thiocyanate; KCNS, A.C.S. Reagent grade, Fisher Scientific Co..

CHAPTER 3

RESULTS AND DISCUSSION

Sulfur species in the Galapagos hydrothermal waters show linear trends versus temperature in the data (passing through the ambient sea water temperature and composition) which were interpreted as dilution lines. Dilution of the concentration of the species was due to a combination of mixing below the seafloor, in the vents, and during sampling with ambient sea water (J. B. Corliss, et al., 1979 and J. M. Edmond, et al., 1979a,b). Problems with the sampling system leaking led to further dilution (0-89% hydrothermal water collected) and possible oxidation of the reduced sulfur species present in the samples.

Sulfide concentrations in the vents increased with increasing temperature (Table 3.1, Figure 3.1). East of Eden had the highest gradient (2.6 x 10^{12} mol/yr) with Mussel Beds changing the least (Table 3.2). These trends indicated that hydrogen sulfide was being produced in the hydrothermal system, either by reduction of seawater sulfate, leaching sulfide from the basalt or primary hydrogen sulfide from magmatic sources (Bonatti, 1975). Sulfide concentration versus oxygen concentration (Figure 3.2) showed a decreasing trend. Oxygen was absent in the samples with hydrogen sulfide concentrations above 120 $\mu\underline{M}$, which differs substantially from data previously published (Edmond, 1979b) where oxygen disappeared at approximately 50 $\mu\underline{M}$ sulfide. This difference is due to the entrainment of oxygenated

Table 3.1

Concentrations of Sulfide, Sulfite,
Thiosulfate, Trithionate, Tetrathionate,
Iodine Reactive Species, Oxygen,
and Silica for the Galapagos Vents

Table 3.1

Dive #	Vent #[1]	Bottle #[2]	Si μM.	O_2 μM.	H_2S μM.	$S_2O_3^{2-}$ μM.	SO_3^{2-} μM.	I_2[3] μeq.	SO_4^{2-} μM.	$S_4O_6^{2-}$ μM.	$S_3O_6^{2-}$ μM.
898	1	207	275	84	1.4	1	-1	336		11	-5
898	1	204	259	114	1.6	9	-1	312		9	-5
898	1	103	402	48	10.5	2	0	581	28.16	12	1
898	1	202	400	60	16.7	2	1	589		12	-3
898	1	203	457	36	19.7	8	1	581	28.24	12	-8
898	1	206	201	106	0.3	7	-1	450		10	-3
899	2	105	619	0	147.0	5	1	216		12	-4
899	2	106	596	0	144.0	11	1	277		6	7
899	2	107	587	0	165.0	18	1	314		5	-6
899	2	101	513	4	75.0	9	0	335	27.88	9	0
899	2	109	550	0	145.0	27	0	220		1	
899	2	113	479	0	67.0	8	1	196		10	-6
899	2	112	395	19	44.0	7	1	167		11	-6
899	2	102	303	58	49.0	6	1	151		11	2
900	2	202	854	0	177.0	14	1	453	27.42	7	-4
900	2	206	846	0	285.0	18	1	510			

Table 3.1 (cont'd.)

Dive #	Vent #	Bottle #[2]	Si µM.	O_2 µM.	H_2S µM.	$S_2O_3^{2-}$ µM.	SO_3^{2-} µM.	I_2[3] µeq.	SO_4^{2-} µM.	$S_4O_6^{2-}$ µM.	$S_3O_6^{2-}$ µM.
900	2	103	625	0	190.0	14	0	369		8	-5
900	2	207	348	34	93.0	14	2			8	-7
900	2	204	608	0	162.0	17	0	379		7	-7
900	2	203	322	54	98.0	13	3	188		9	-7
900	2	205	279	66	80.0	11	3	183		10	-6
901	3	109	161	117	0.5		4	198			
901	3	102	161	119	0.4		1	288			
901	3	107	160	115	0.9		1	288			
901	3	112	167	109	0.7		1	300			
901	3	106	336	0	142.0	3	1	316		13	
901	3	105	360	0	182.0	-7	1	406	28.30	18	-10
902	1	204	605	0	31.5	15	1	77		8	-7
902	1	203	626	0	35.8	21	1	98	27.78	5	2
902	1	104	490	43	21.9	4	1	73		12	-6
902	1	207	575	0	31.5	18	1	57		6	0

Table 3.1 (cont'd.)

Dive #	Vent #	Bottle #^{2}	Si μM.	O_2 μM.	H_2S μM.	$S_2O_3^{2-}$ μM.	SO_3^{2-} μM.	I_2^{3} μeq.	SO_4^{2-} μM.	$S_4O_6^{2-}$ μM.	$S_3O_6^{2-}$ μM.
902	1	202	486	13	22.4	29	0	-20		1	-1
902	1	205	486	10	19.1	14	0	82		8	2
902	1	103	443	55	12.9	0	1	16		15	-6
903	2	102	558	0	137.0	11	1	143		10	2
903	2	107	837	0	140.0	5	1	384	27.47	9	5
903	2	106	927	0	221.0	4	1	633		13	-5
903	2	101	636	0	138.0	5	1	45	27.78	12	-4
903	2	109	724	0	169.0	5	1	294		12	2
903	2	302	420	26	118.0	6	1	62		11	0
904	1	205	588	0	28.1	28	-1	132	27.81	0	-1
904	1	207	561	3	24.5	28	0	120		0	0
904	1	204	507	15	20.7	25	0	59	28.02	2	0
904	1	202	595	0	33.0	25	0	140	27.84	2	-2
904	1	303	574	11	28.6	27	0	112	27.87	1	-1
905	2	113	1007	0	336.0	18	1	446	27.14	4	-1

Table 3.1 (cont'd.)

Dive #	Vent #	Bottle #^{2}	Si µM.	O_2 µM.	H_2S µM.	$S_2O_3^{2-}$ µM.	SO_3^{2-} µM.	I_2^{3} µeq.	SO_4^{2-} µM.	$S_4O_6^{2-}$ µM.	$S_3O_6^{2-}$ µM.
905	2	106	238	33	31.9	15	2	60		5	1
905	2	112	372	28	70.0	15	2	82		6	-5
905	2	101	627	0	190.0	15	1	233	27.64	5	1
905	2	109	596	0	148.0	15	1	184		5	-3
905	2	304	343	317		7	1	-11			
0	4	0	165	120	0.0	0	0	0	28.62	0	0

1. Vent #: 1: Mussel Beds; 2: Rose Garden; 3: East of Eden

2. Bottle #: 1 : A; 2 : B; 3 : H; (e.g. 105 ≡ A 5).

3. Iodine Reactive Species

Table 3.2

Gradients and Fluxes for Sulfide and Sulfate

Table 3.2

	H_2S	SO_4^{2-}	Iodine Reactive Species
Range	0.0-336 μM.	27.14-28.62 mM.	-20-633 μeq.
Gradient $(\frac{\text{moles}}{\text{Cal.}})$	(1) 5.14×10^{-9} (2) 1.83×10^{-8} (3) 5.24×10^{-8}	-1.06×10^{-7}	(1) 6.08×10^{-8} (1A) 3.27×10^{-8} (2) 3.65×10^{-8} (3) 3.13×10^{-8}
Flux $(\frac{\text{moles}}{\text{yr.}})$	(1) 2.6×10^{11} (2) 9.2×10^{11} (3) 2.6×10^{12}	-5.3×10^{-12}	(1) 3.04×10^{12} (1A) 1.63×10^{12} (2) 1.83×10^{12} (3) 1.56×10^{12}

For the above calculations, 5×10^{19} cal/yr. was taken as the global hydrothermal heat transport from accreting plate boundaries.

(1) Mussel Beds , (1A) Mussel Beds, Dive 898

(2) Rose Garden

(3) East of Eden

Symbols Used in Figures in Chap. 3

◇ - Mussel Beds

✚ - East of Eden

▲ - Rose Garden

Figure 3.1

Sulfide versus Silica

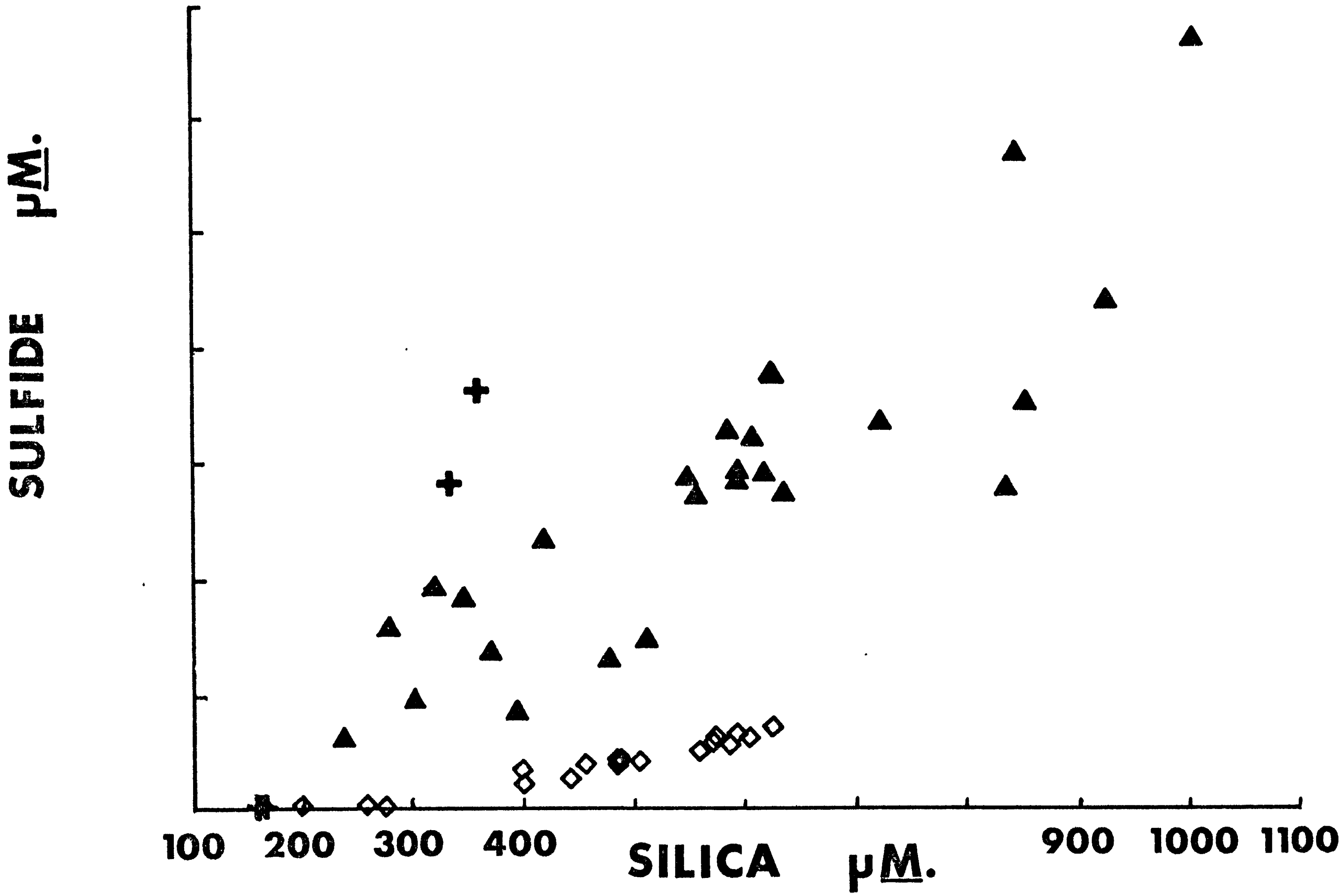
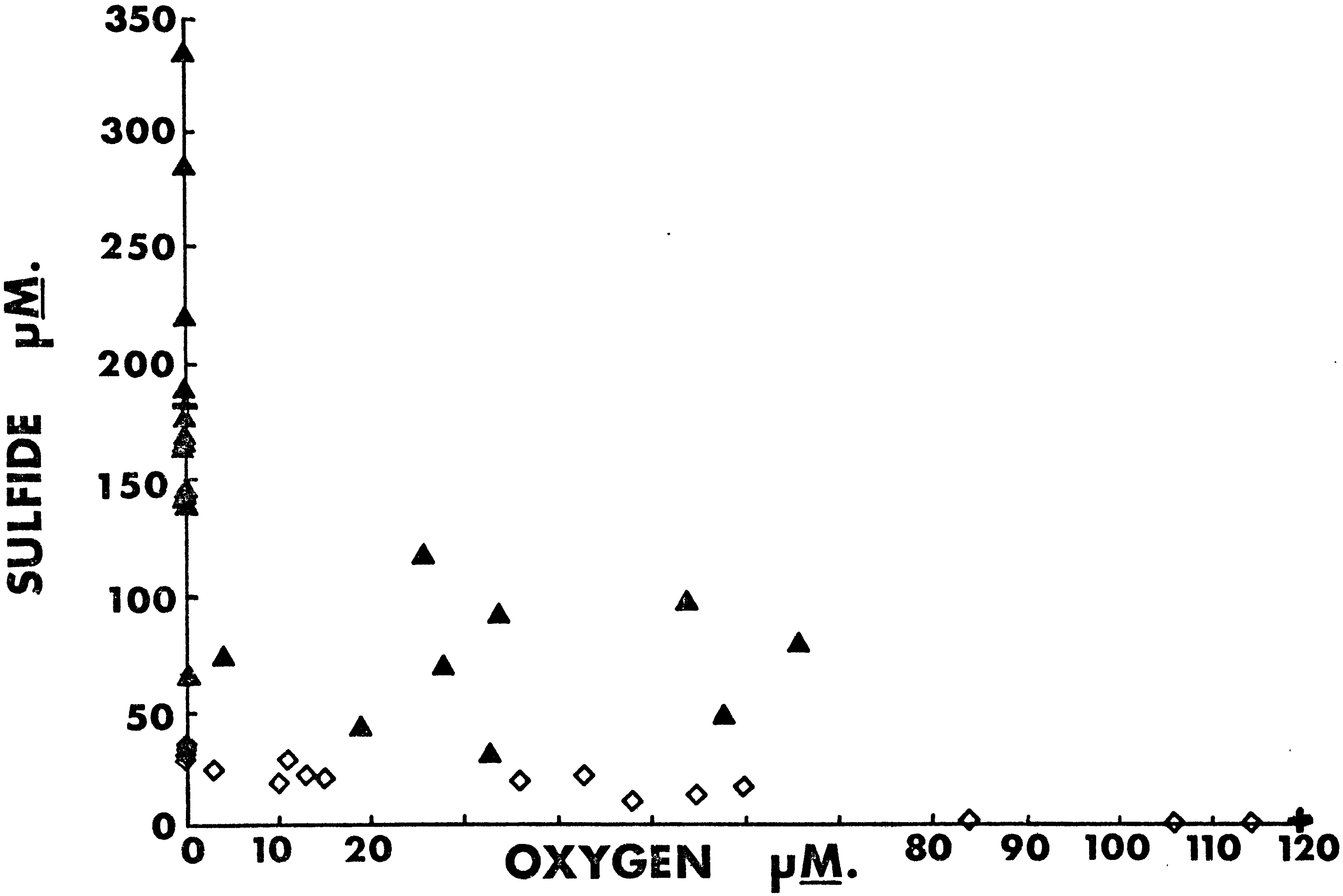

SULFIDE µM.
SILICA µM.
100
200
300
400
900
1000
1100

Figure 3.2

Sulfide versus Oxygen


SULFIDE μM.
350
300
250
200
150
100
50
0
0
10
20
80
90
100
110
120
OXYGEN μM.

ambient water during sampling with the leaky samplers and the relatively slow oxidation of sulfide. (Sulfide oxidation is inhibited at pH values below 7, presumably because of the protonation of the HS^- molecule, Chen and Morris, 1972).

Sulfate decreased uniformly in all vent fields (Figure 3.3, Tables 3.1, 3.2).

Sulfite was constant with temperature at about 1 μM (the detection limit), (Figure 3.4), though in East of Eden and Rose Garden some of the concentrations at low temperature were above 1 μ_M_ sulfite.

Thiosulfate, trithionate, and tetrathionate were also constant with temperature within the limit of resolution (Figure 3.5, Table 3.1). Cyanolysis of any elemental sulfur present (only particles <1 μm as the samples were filtered) should interfere positively to some extent in the tetrathionate method and to a greater degree in the trithionate procedure (Nelson, et al., 1977), though this interference has not been quantified.

Species reduced by iodine showed a general increase with temperature (Figure 3.6). The vent fields differed in their gradients (Table 3.2) with Mussel Beds exhibiting two different trends associated with two different days of sampling. In water with a neutral or acidic pH (hydrothermal waters--pH 6 to 7) only sulfide, sulfite,

Figure 3.3

Sulfate versus Silica

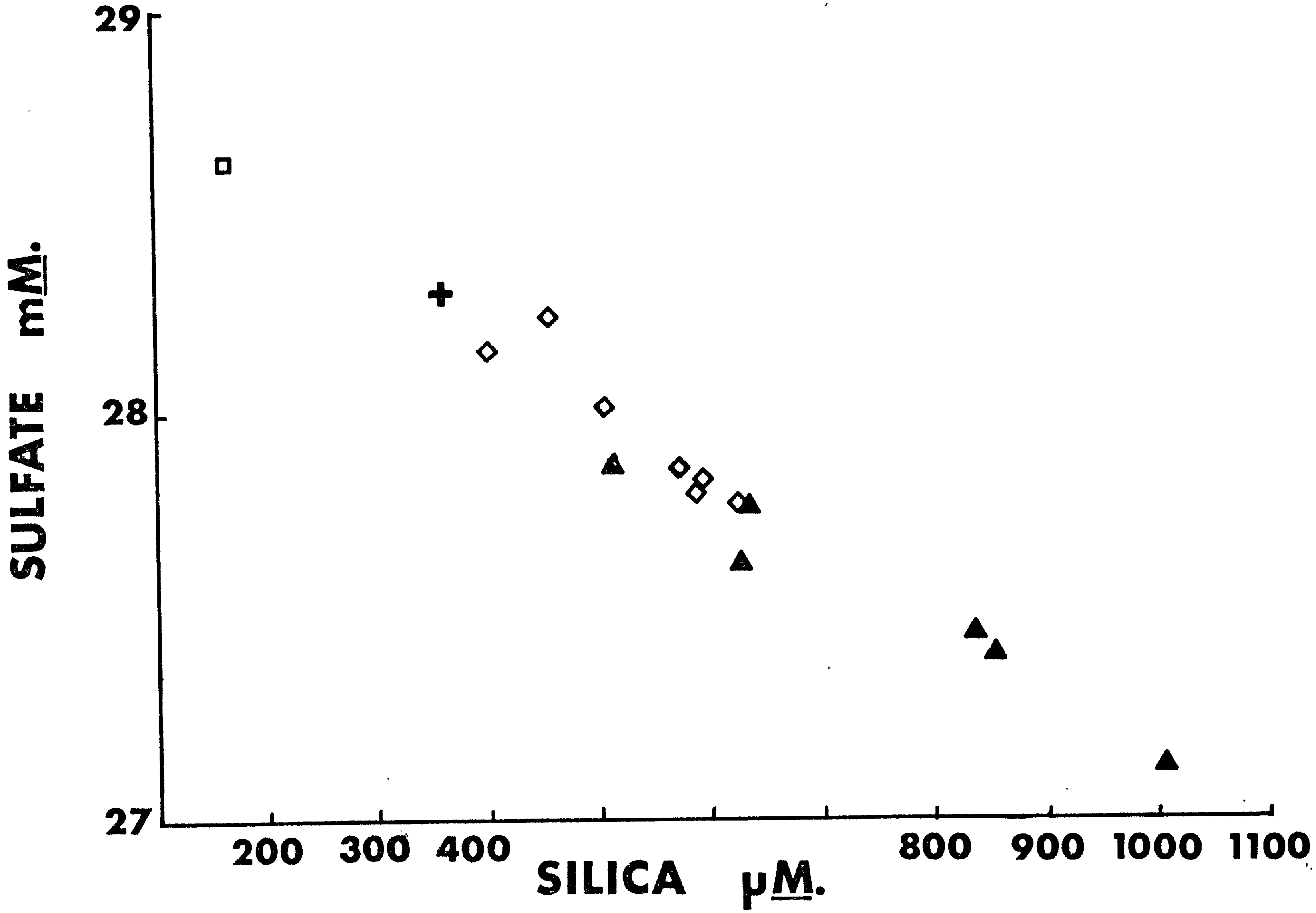

29
28
27
SULFATE mM.
200
300
400
800
900
1000
1100
SILICA μM.

Figure 3.4

Sulfite versus Silica

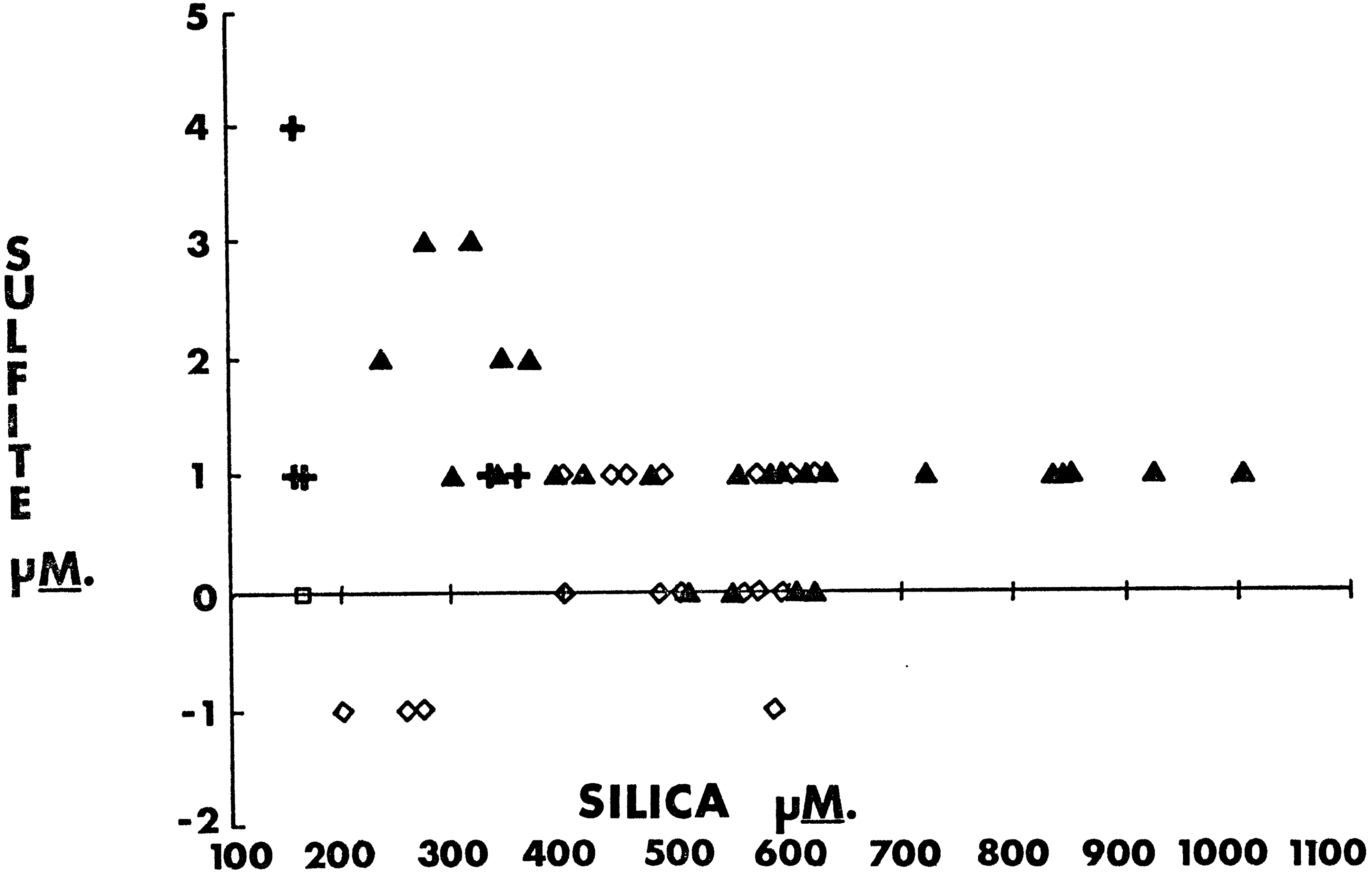

SULFITE µM.
5
4
3
2
1
0
-1
-2
SILICA µM.
100
200
300
400
500
600
700
800
900
1000
1100

Figure 3.5

Thiosulfate versus Silica

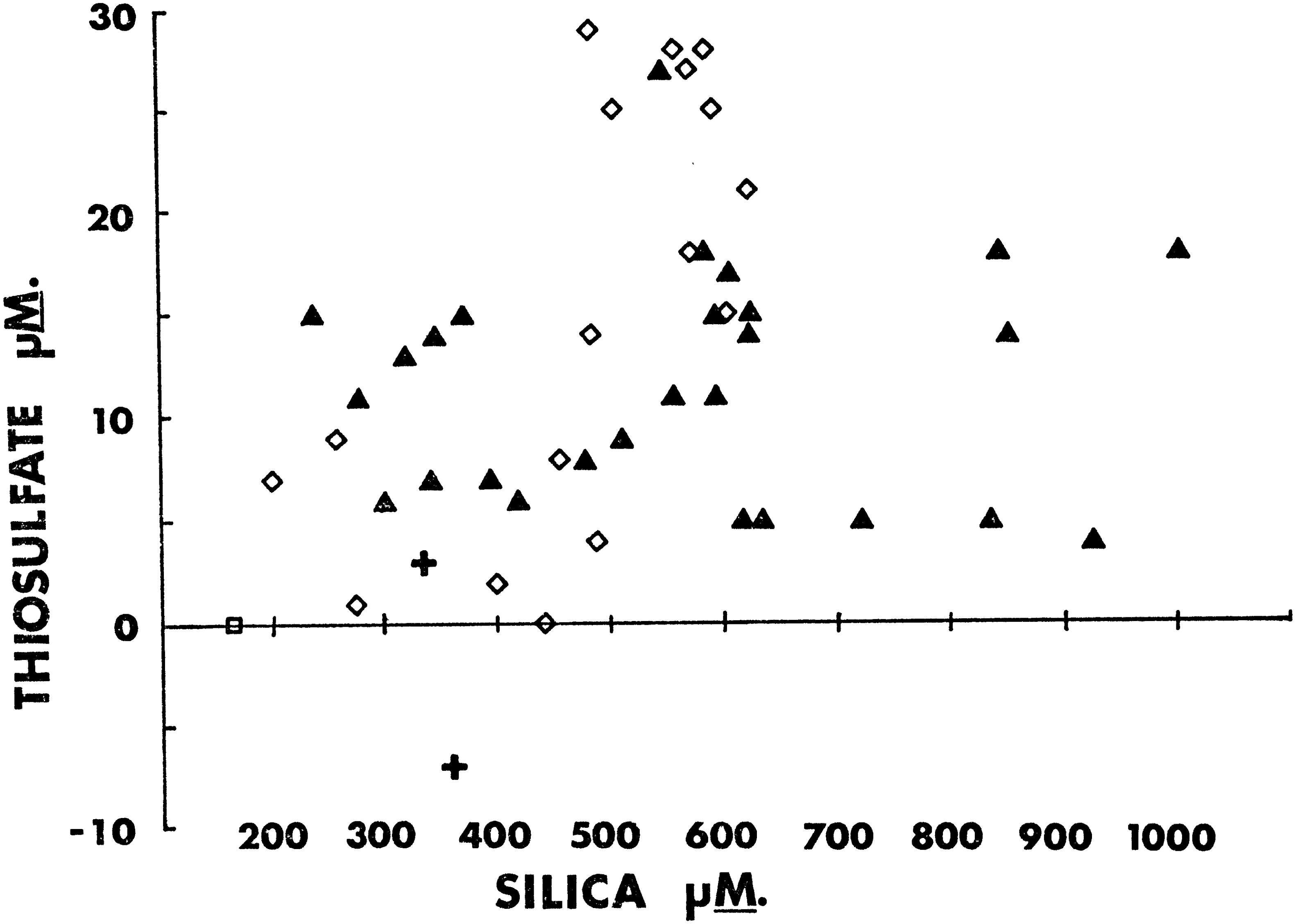
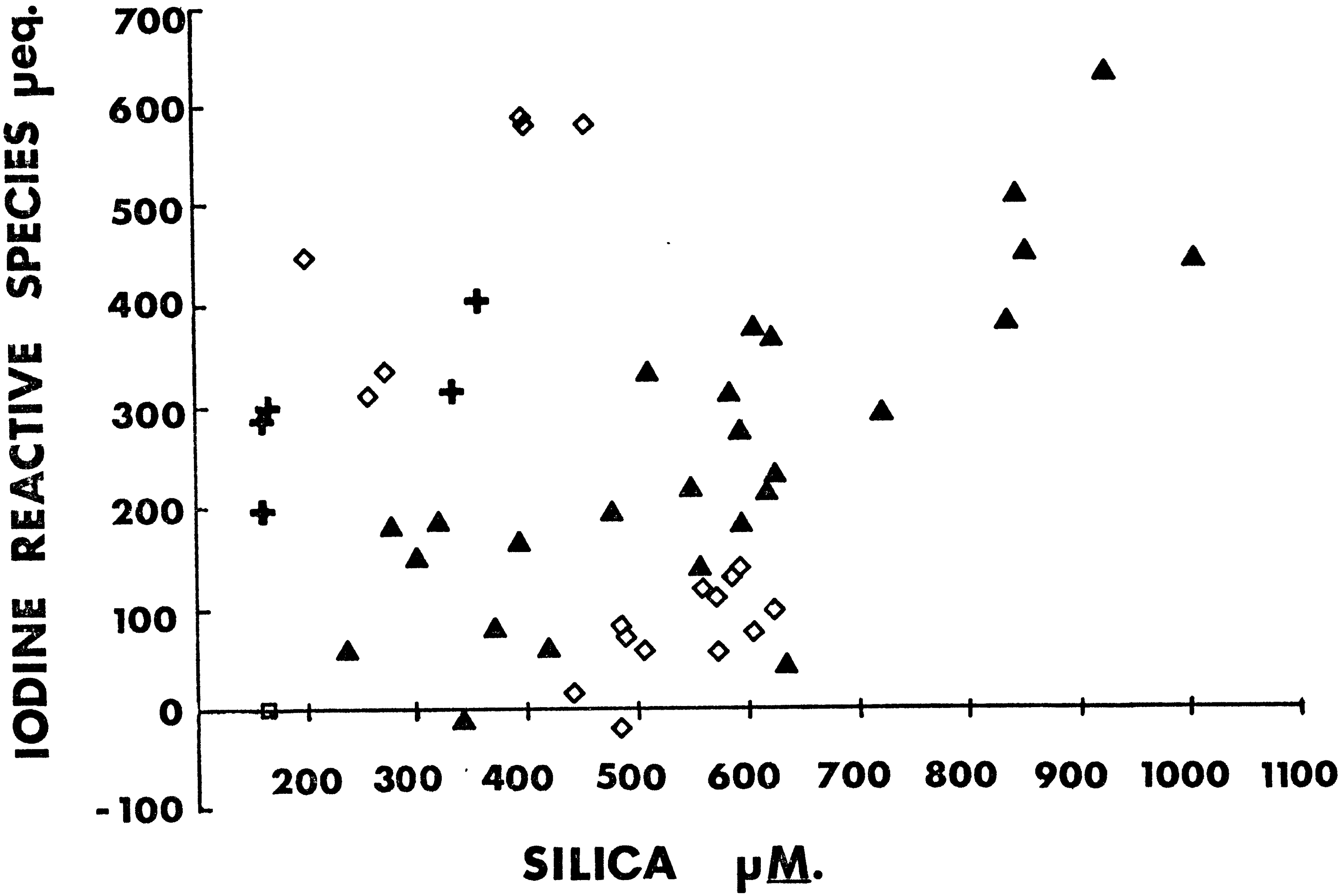

30
20
10
0
-10
THIOSULFATE μM.
200
300
400
500
600
700
800
900
1000
SILICA μM.

Figure 3.6

Iodine Reactive Species versus Silica


IODINE REACTIVE SPECIES μeq.
700
600
500
400
300
200
100
0
-100
200
300
400
500
600
700
800
900
1000
1100
SILICA μM.

and thiosulfate should be expected to be reactive with iodine. The concentrations of these sulfur species leaves a large amount of reacted iodine unaccounted for (Figure 3.7). A possible explanation for this is suggested by experiments by Nelson, et al. (1977); colloidal sulfur suspensions stabilized by thiosulfate or polythionates may lead to iodine reactivity, unlike other sulfur suspensions. This reactivity may be due to a surface charge mechanism resulting from slow hydrolysis or oxidation upon the surface of the sulfur crystals, whereby charge sulfoxy groups react. The hypothesis that these unaccounted for iodine reactive species are in fact colloidal sulfur is further supported by the observation that the major component of suspended material filtered in situ from the hot springs is native sulfur (Corliss, unpublished data).

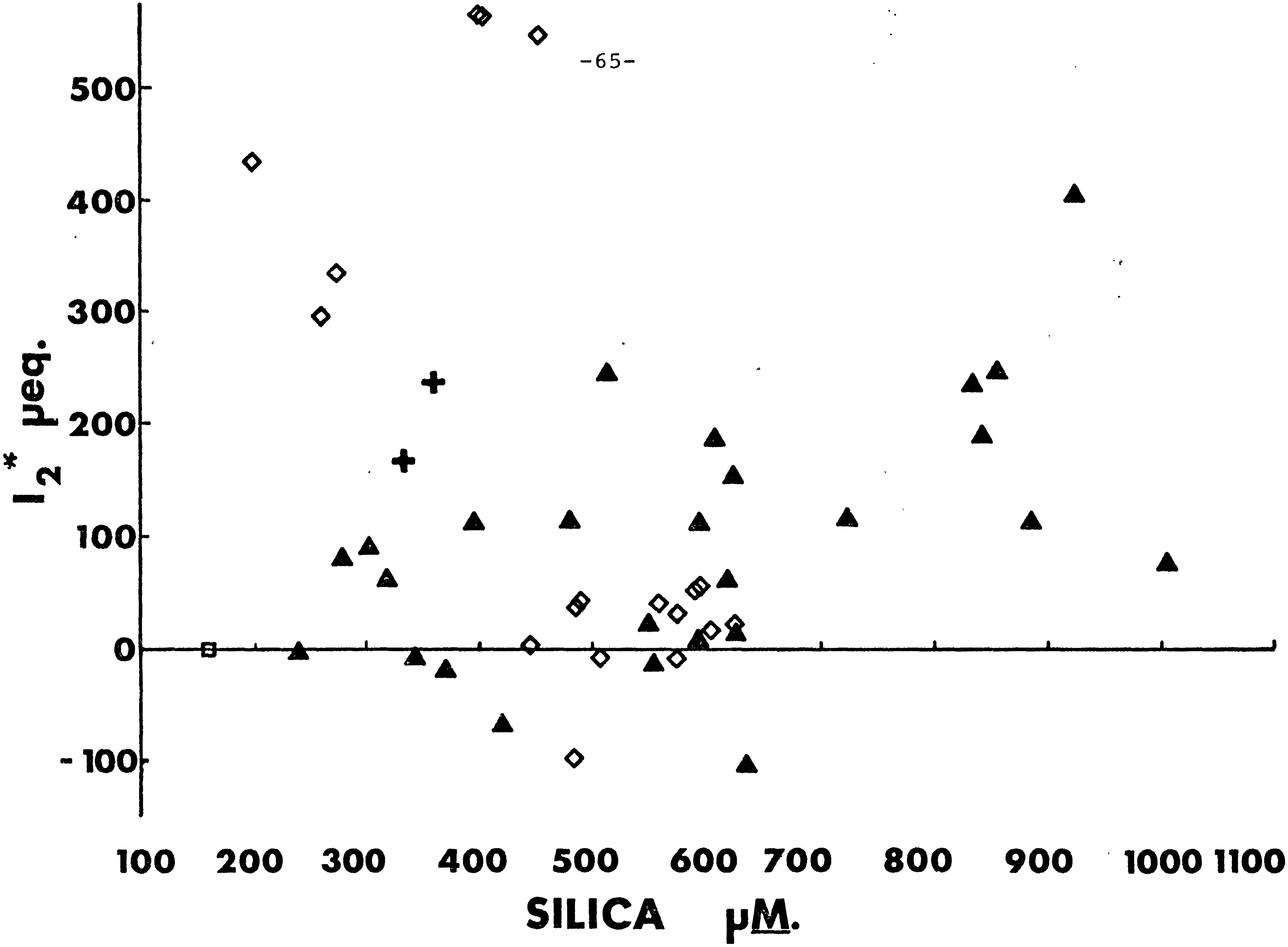
Polysulfides, while also iodine reactive, were not measured since their presence is unlikely due to the low pH conditions present in the hydrothermal solution.

In a profile of the overlying waters (stations 86, 135 and 139), reduced sulfur species were not found.

The sulfur chemistry of the Galapagos hydrothermal vents suggest that hydrogen sulfide and possibly elemental sulfur are the principal reduced sulfur species. Sulfite, thiosulfate, and polythionates are observed in low

Figure 3.7

Iodine Reactive Species Minus
Sulfide, 2x Thiosulfate, and
Sulfite (I_2^*) versus Silica


500
400
300
200
100
0
- 100
I_2^* μeq.
100
200
300
400
500
600
700
800
900
1000
1100
SILICA μM.

concentrations implying that sulfur is not oxidized beyond the zero valence state to any significant extent. The flux of sulfide from the hydrothermal system is large, 2.6×10^{11}-2.6×10^{12} mol/yr, which is consistent with previous observations (Edmond, et al., 1979b).

Sulfate is reduced in the vents (flux = -5.3×10^{12} mol/yr) suggesting that this is an important sink in the oceanic sulfate budget (Edmond, et al., 1979a).

The observed concentrations of sulfur species in the hydrothermal vent waters suggest that elemental sulfur and possibly polysulfides should be examined in more detail as the measurement of these species will give additional insight into the sulfur chemistry of seafloor hydrothermal systems.

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