

AN ABSTRACT OF THE THESIS OF

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IN THE NORTHEASTERN PACIFIC OCEAN

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Reactive silicate concentrations in the area of the Columbia River Plume were measured on the July 1967 and January 1968 cruises of the R/V Yaquina by means of a Technicon Autoanalyzer[®]. Biological uptake, and three point mixing of river water, and surface and upwelled sea waters were found to be the mechanisms determining the distribution. Inorganic removal was found to be negligible. Agreement between the values obtained by the method of Mullin and Riley (1955) and the Autoanalyzer[®] was within 7% with little scatter. Freezing of samples was found to affect silicate values adversely.

Precise measurements of deep water silicate values enabled a qualitative explanation for the deep-sea silicate maximum in the North Pacific Ocean.

Processes Determining Silicate Concentrations
in the Northeastern Pacific Ocean

by

Stephen Warner Hager

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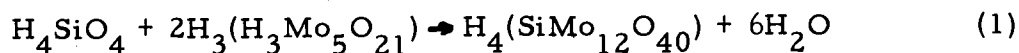
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PROCESSES DETERMINING SILICATE CONCENTRATIONS IN THE NORTHEASTERN PACIFIC OCEAN

INTRODUCTION

The nomenclature of dissolved SiO_2 is by no means consistent in the literature. "Silica" and "dissolved silica" are used frequently as are "silicate" and "dissolved silicate." "Reactive silicate" (Strickland and Parsons, 1965) is a more exact term, referring to that portion of the total SiO_2 in the solution which reacts with molybdate to form the colored silicomolybdate complex. The equation for the reaction is



where H_4SiO_4 is orthosilicic acid or silicic acid (Grasshoff, 1964). As it has been shown to be practically the only form of SiO_2 which is "reactive," it is synonymous with "reactive silicate." In the following work the word "silicate" will be used to refer to "reactive silicate."

Recent papers by Sillén (1961), Garrels (1965), Mackenzie and Garrels (1965, 1966a, 1966b), and Mackenzie et al. (1967) have drawn attention to possible roles of silicate in the physical chemistry of seawater. As an important plant nutrient, silicate also commands considerable attention. Redfield, Ketchum and Richards

(1963) summarized nutrient knowledge including silicate up to 1962. Harriss (1966) has since elaborated on the importance of silica-using organisms in determining oceanic silicate values. Armstrong (1965) has written a review of all aspects of silicon in the oceans.

Mechanisms which determine silicate concentrations have been studied by Stefánsson and Richards (1963, 1964) off the mouth of the Columbia River, by Rakestraw (1964) in the Indian Ocean, and by Schink (1967) in the Mediterranean Sea. Stefánsson (1966) made an interesting study of the effect of the Surtsey volcanic eruption on the nutrient content of the surrounding seawater.

Methods of measuring "reactive silicate" concentrations have centered mostly around the reduced silicomolybdate blue method of Mullin and Riley (1955). A significant advance has been the adaptation of automated analysis to silicate in seawater. Brewer and Riley (1966, 1967) and Armstrong, Stearns and Strickland (1967) have worked with the Technicon Autoanalyzer[®] and reported favorable results.

The sea off Oregon is a good place in which to study silicate because of the number of mechanisms operating. In addition to the mixing of the ocean and Columbia River waters and biological processes, upwelling along the adjacent coast provides an additional source of dissolved silicate. The wide range of silicate and salinity values also make the area well suited for testing instrumentation. The

6707A (5 July-15 July, 1967) and 6801F (29 January-2 February, 1968) cruises of the R/V Yaquina of Oregon State University were designed to provide exhaustive chemical studies of the plume. Additional deep water data was obtained on the April 1968 cruise of the USC&GSS Surveyor in the North Pacific Ocean. In each case, a Technicon Autoanalyzer[®] was on board and provided the opportunity to analyze silicate quickly and precisely. This thesis incorporates the results of those efforts in an attempt to provide better understanding of the processes which determine the distribution of silicate in the ocean.

THE ANALYSIS

Instrumentation

The analyses were carried out with a Technicon Autoanalyzer[®] by the method of Armstrong, Stearns and Strickland (1967). A slight modification was made to enable measurements of "reactive silicate" values up to 250 μ M. Details of the method are given in Appendix I. The apparatus consisted of a proportioning pump, voltage stabilizer, range expander, cuvette colorimeter, and a two-pen recorder (Figure 1). Sample introduction was done by hand as no automatic sampler was available.

The apparatus was set up in the forward hold of the ship. A sea water tap was located close to the apparatus, providing the opportunity for continuous profiling of the surface waters. From the tap a hose led to a one-liter reservoir into which the Autoanalyzer sampling tubes could be introduced. The flow rate was about three liters per minute. In areas with high particulate matter (c.f. in the river itself) flow-through filters were added which increased the delay time by about two minutes. A schematic of the filters used is shown in Figure 2. Whatman grade 50 paper was used. The filters are primarily useful in preventing large particles from obstructing the sampling tubes, although turbidity is also reduced with proper

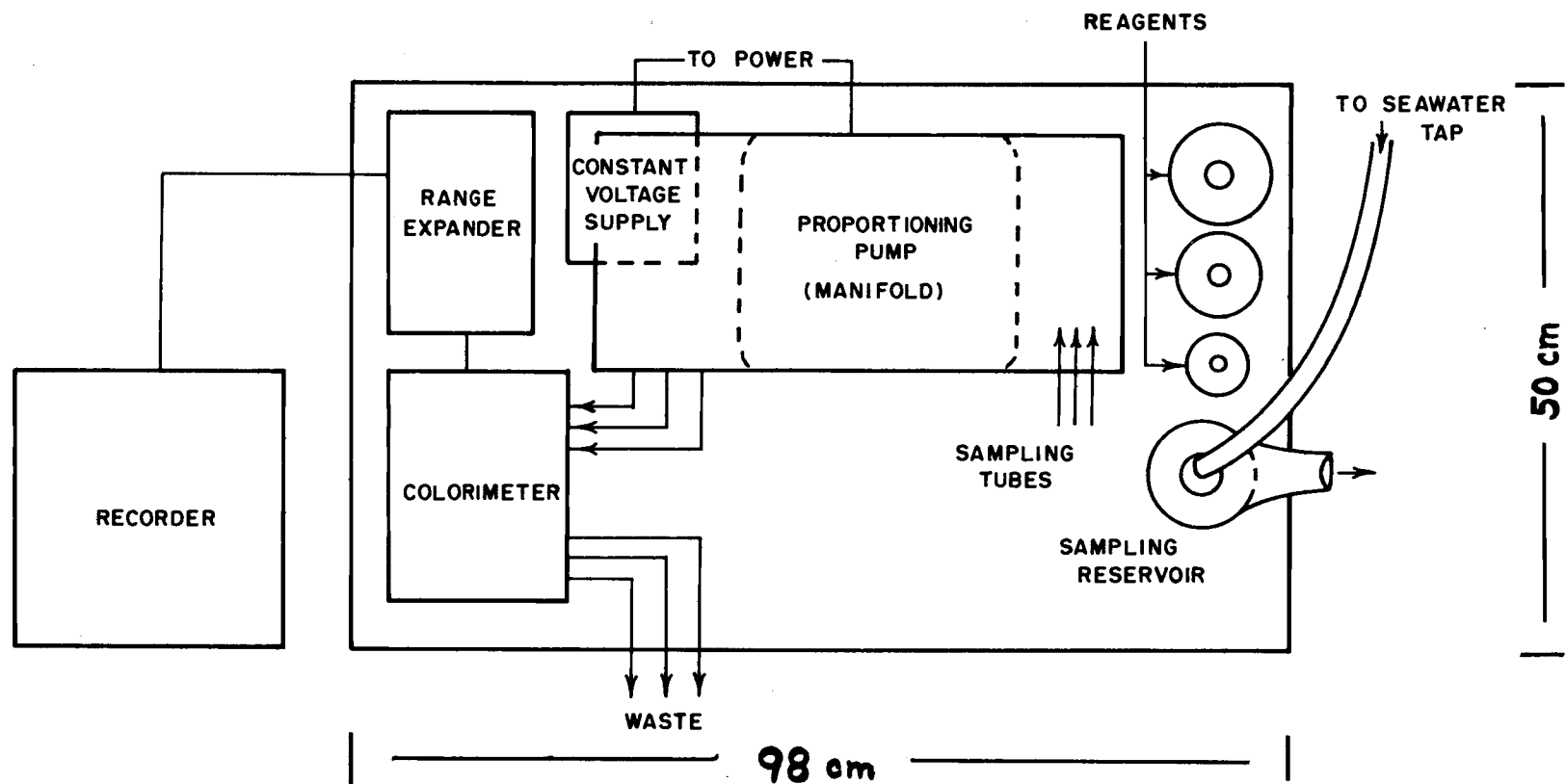


Figure 1. Schematic of the Technicon Autoanalyzer® used for the silicate analyses.

choice of filter papers. No rigorous testing of the effect of filtering system was undertaken. From observations made when removing or adding the filters we found that they are necessary only under extreme conditions.

Shipboard Use of the Technicon Autoanalyzer[®]

The Autoanalyzer[®] performed very well under all conditions encountered on cruises 6707A, 6801F of the R/V Yaquina and the April cruise of the USC&GSS Surveyor. On the R/V Yaquina, vibration due to the ship's engines was felt, but had no effect on the apparatus. Line voltage changes caused by the ship's hydrographic winch caused small identifiable variations in the recorder trace which had no effect on the data.

EVALUATION

Comparison of Methods

Adaptation of the Technicon Autoanalyzer[®] to the micronutrients in seawater will be a great time-saver for many analysts. However, it is important that we be able to correlate the data obtained by the Autoanalyzer[®] with that taken by the older manual methods. Brewer and Riley (1967) have done a preliminary work in this respect. Their conclusions with respect to the silicate analysis are different from those of this work. They state that the Autoanalyzer gives results "consistently lower (by 2.4% on average), " than the method of Mullin and Riley (1955). We find that the difference between the methods may be dependent on salinity.

Duplicate determinations were made on 26 randomly chosen samples from cruise 6707A. All analyses were done on shipboard, and 22 were repeated on the frozen samples brought to shore. The data are given in Table 1, and plotted in Figures 3, 4, and 5. The data are chronological and do not show any trends which could indicate drift in either of the methods. The Autoanalyzer[®] drift problem (discussed later) was of little significance relative to these data as is indicated by the lack of scatter shown in Figure 3.

Table 1. Comparison of the silicate values of samples analyzed at sea manually and with the Autoanalyzer[®], and after freezing by the manual method. Concentrations are in μM .

Sample	Manual (frozen)	Manual at sea	Autoanalyzer [®] at sea	Difference at sea, Autoanalyzer [®] minus manual
F-1	29	34.1	34.6	+0.5
F-7	7.6	7.07	6.26	-0.8
F-26	6.2	6.84	5.75	-1.1
F-15	6.6	6.13	5.26	-0.9
F-35	48	50.3	52.1	+0.8
B-41	-	95.3	101	+6
B-57	110	129	140	+11
B-75	45	38.3	44.8	+6.5
H-4	81	131	138	+7
79	95	120	128	+8
67	9	11.7	9.54	-2.2
84	6	1.30	1.27	0
217	70	150	154	+4
F-93	5	4.83	4.33	-0.5
F-105	-	1.53	1.44	-0.1
F-115	11	4.01	2.94	-1.1
G-85	-	24.9	23.6	-1.3
G-102	140	145	146	+1
G-115	-	7.55	7.06	-0.5
A-92	43	44.9	41.2	-3.7
E-16	3.8	3.42	3.16	-0.3
E-25	6.5	6.48	6.18	-0.3
N-11	36	42.9	42.8	-0.1
N-42	26	23.8	24.0	+0.2
N-47	30	28.2	28.4	+0.2
N-53	32	34.0	35.7	+1.7

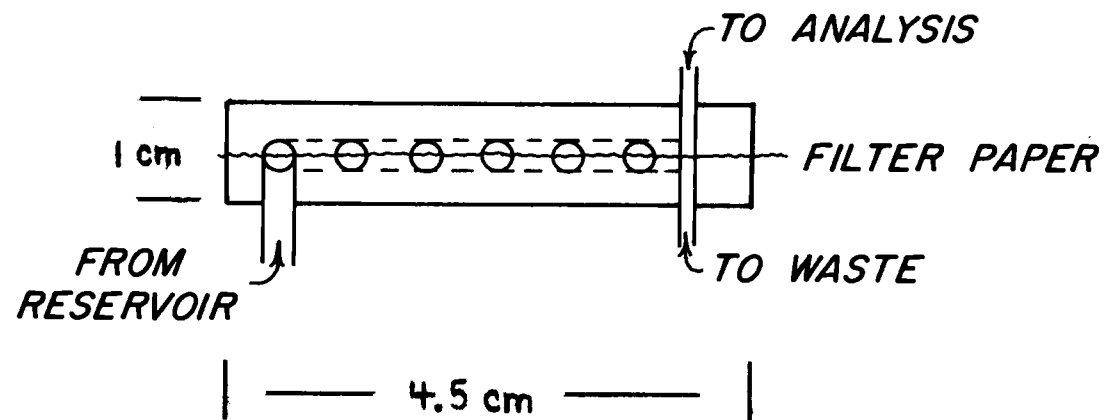


Figure 2. Schematic of the in-line filters used to reduce turbidity of waters prior to analysis.

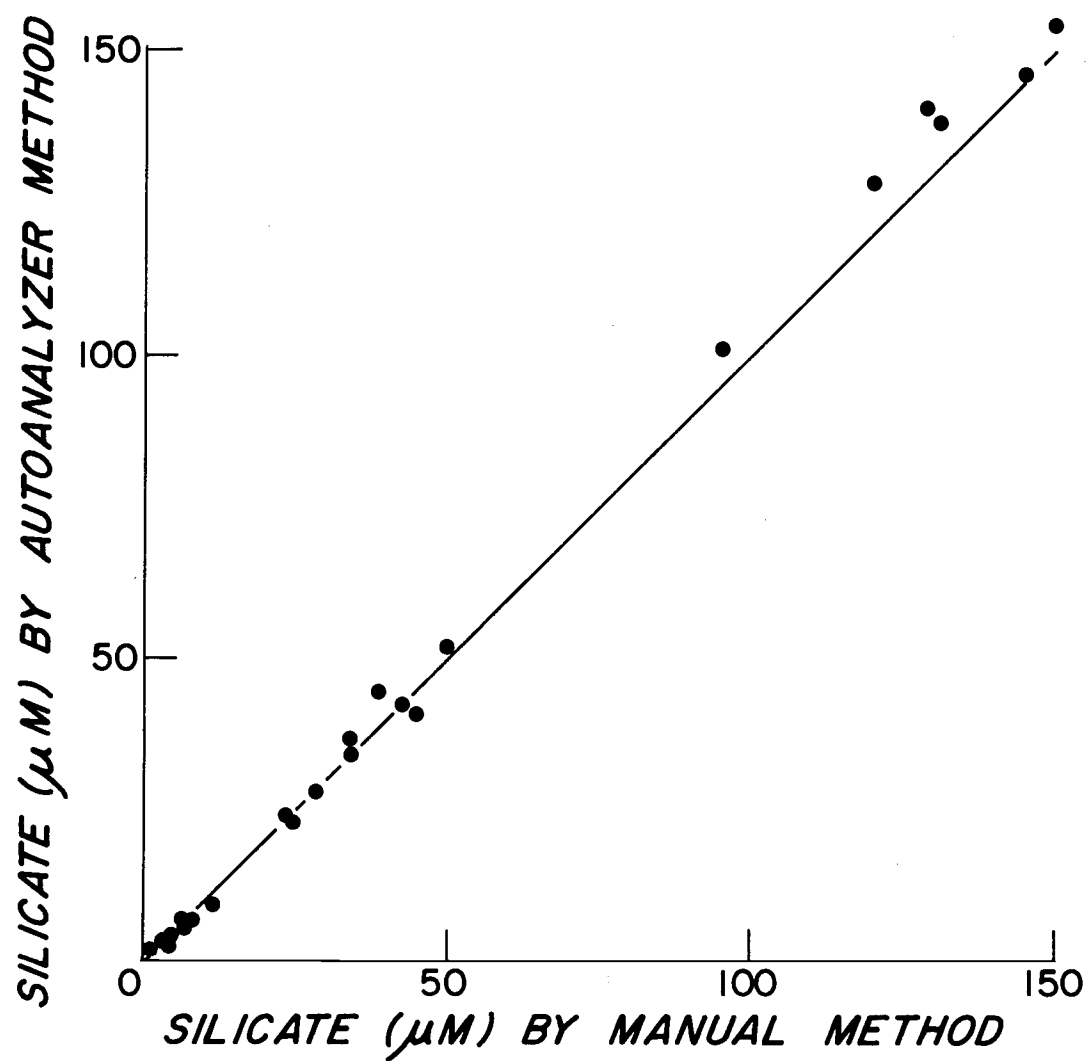


Figure 3. Comparison of manual and Autoanalyzer® methods of silicate analysis.

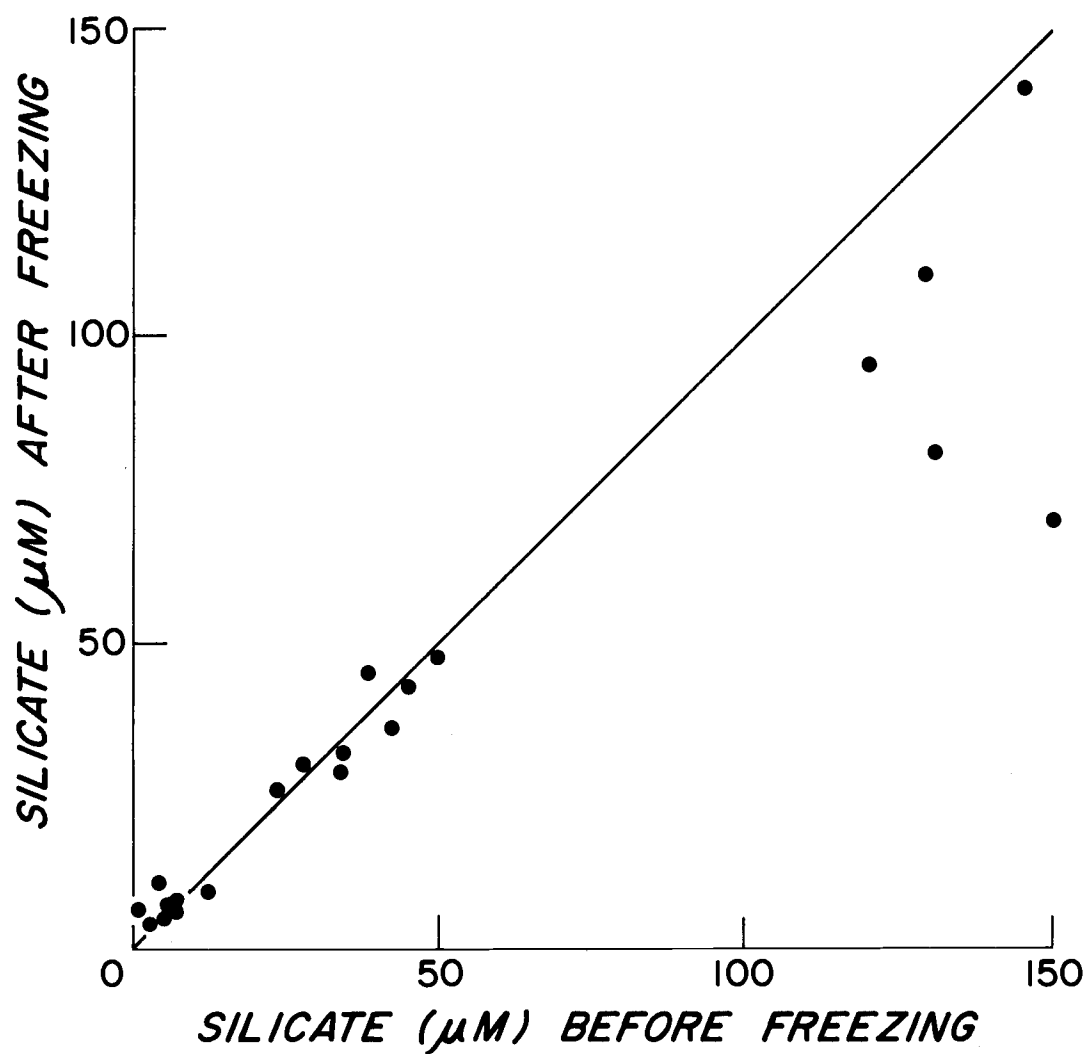


Figure 4. Comparison of silicate values before and after freezing. Samples were frozen for 3-5 months. Both analyses done by manual method.

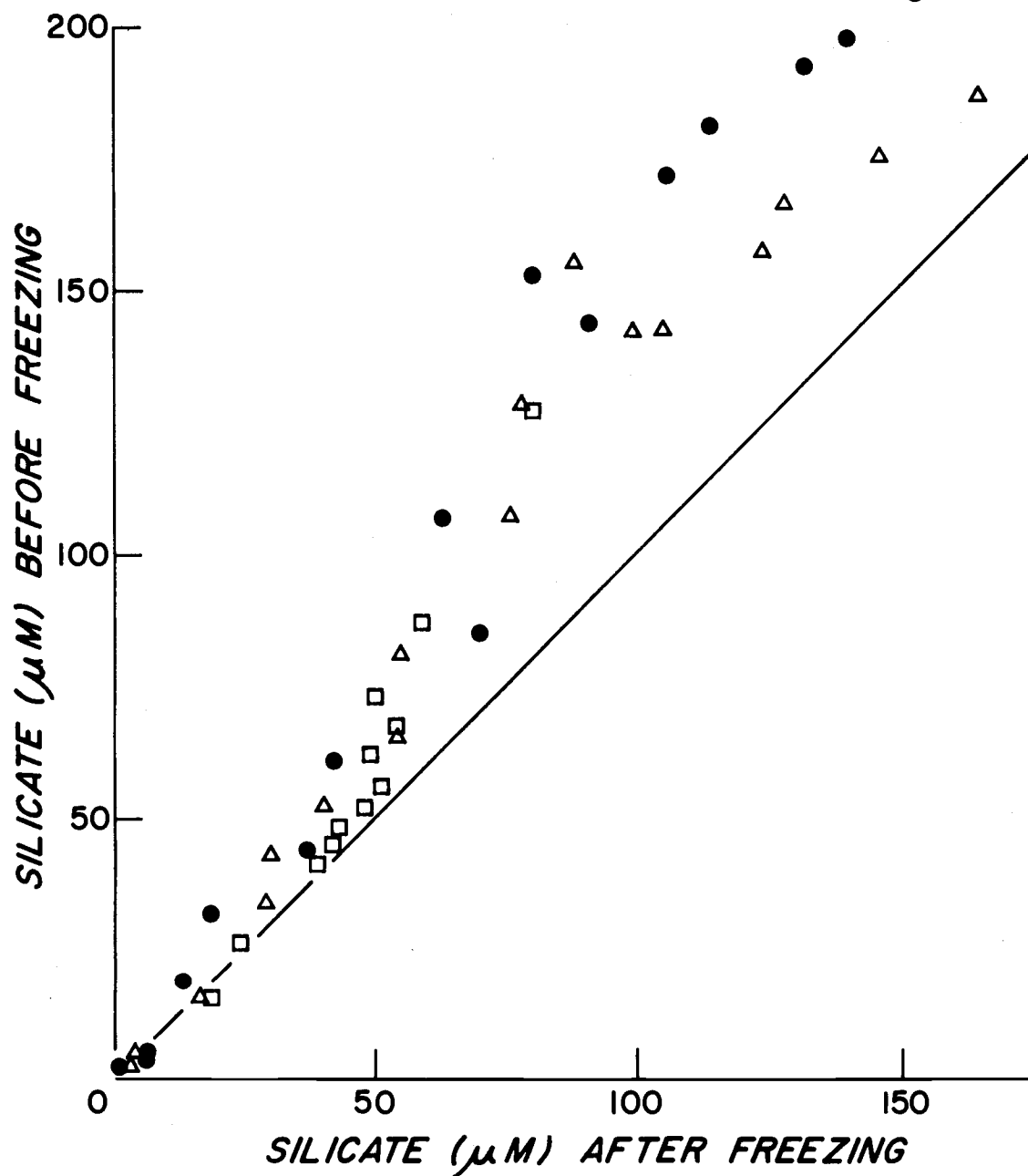


Figure 5. Comparison of silicate values before and after freezing. Samples were run before freezing on the Autoanalyzer® and after freezing by the manual method. Stations shown are NH-45 (□), KP-35 (Δ), and KP-51 (●).

Salt Error

The magnitude of the salt error in determinations with the Autocanalyzer[®] was measured in the laboratory. Fifty μM standards were made up in distilled water and in the artificial seawater, 28‰ S, of Strickland and Parsons (1965, p. 71). Using the intermediate range, 0.6 ml/min, sampling tube, the standards were alternated every six minutes until each had been run five times. The data show that the artificial seawater gives readings $1.1 \pm 0.3\%$ higher than the distilled water. Taking into account the nominal dilutions 0.6/3.2 and 0.1/3.2, salt errors for each range can be estimated (Table 2). Since the river water was run with the 0.1 tube, the salt error was negligible. The 2.5 ml/min tube was used mostly for normal surface sea waters with salinities greater than 28‰. The salt error should not be significant there either.

Table 2. Measured and calculated salt errors for silicate analysis by the Autoanalyzer[®].

Sampling tube	% Change/28‰
0.6 ml/min	1.1% measured
0.1 ml/min	0.2% calculated
2.5 ml/min	4.6% calculated

Effect of Freezing on Silicate Samples

Freezing of nutrient samples in polyethylene bottles is the most common method of preservation for later analysis. There are several modifications of the basic method being used today. These data show that the method used at Oregon State University affects silicate values greater than about 50 μM . These samples showed a marked decrease in reactive silicate with freezing, in agreement with the conclusions of Matson (1964). However, Stefánsson and Richards (1963) at the University of Washington had shown little change on values up to 160 μM .

A direct comparison of samples run manually at sea and again after freezing is shown in Figure 4. The same behavior is shown in Figure 5 with data from three stations on cruise 6707A. The stations are typical and were chosen without reference to the deviations observed but in an attempt to cover as large a range of silicate values as possible. Scatter may be attributed primarily to the frozen samples as Autoanalyzer[®] silicate profiles with depth are very smooth. Frozen samples often give erratic profiles.

Instrument Drift Problem

The behavior of the 50 μM standards over the duration of cruise 6707A is plotted in Figure 6. Similar behavior was observed for

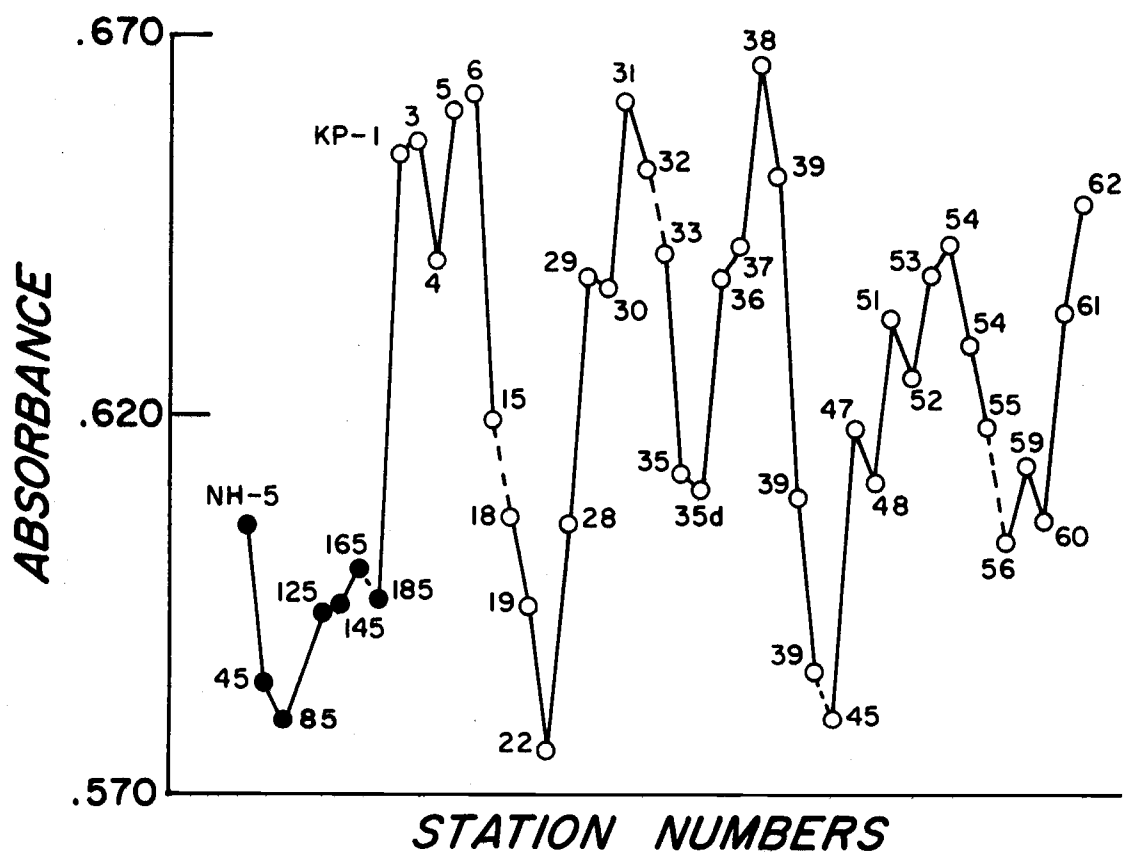


Figure 6. Absorbances of 50 μ M standards over the duration of cruise 6707A. Time from NH-5 to KP-62 is ten days. Station positions are shown in Figure 8a.

the 10 μ M and 100 μ M standards. The drift observed was shown to be not due to reagent drift. It was also shown in later laboratory tests that it is not a function of the age of the pump tubing or of the particular colorimeter used on the cruise. Behavior observed in the laboratory following cruise 6707A is shown in Figure 7. It was run using new pump tubing and a new colorimeter from the Technicon Corporation. The colorimeters had temperature compensation circuits built into them, but the regularity of the drift suggests that this is not the problem. The effectiveness of the compensation is at present unknown.

On later cruises, the problem was minimized by the running of more frequent standards and blanks. It was also shown in the laboratory that the samples can be normalized to a consistent value for the standard if the colorimeter gain is maintained at the same value. It is now thought then that by running standards every half hour, and blanks every hour the overall precision can be 1% or better. Sample to sample precision was shown to be generally better than 1%. Estimates of drift error for cruise 6707A show 80% of the samples to have a precision of better than 5%. For cruise 6801F, 90% had a precision of better than 3%.

In general the Autoanalyzer[®] provides a rapid analysis that is free from the influences of Mal de Mer. The possible precision of 1% is a great improvement over other commonly used methods, and,

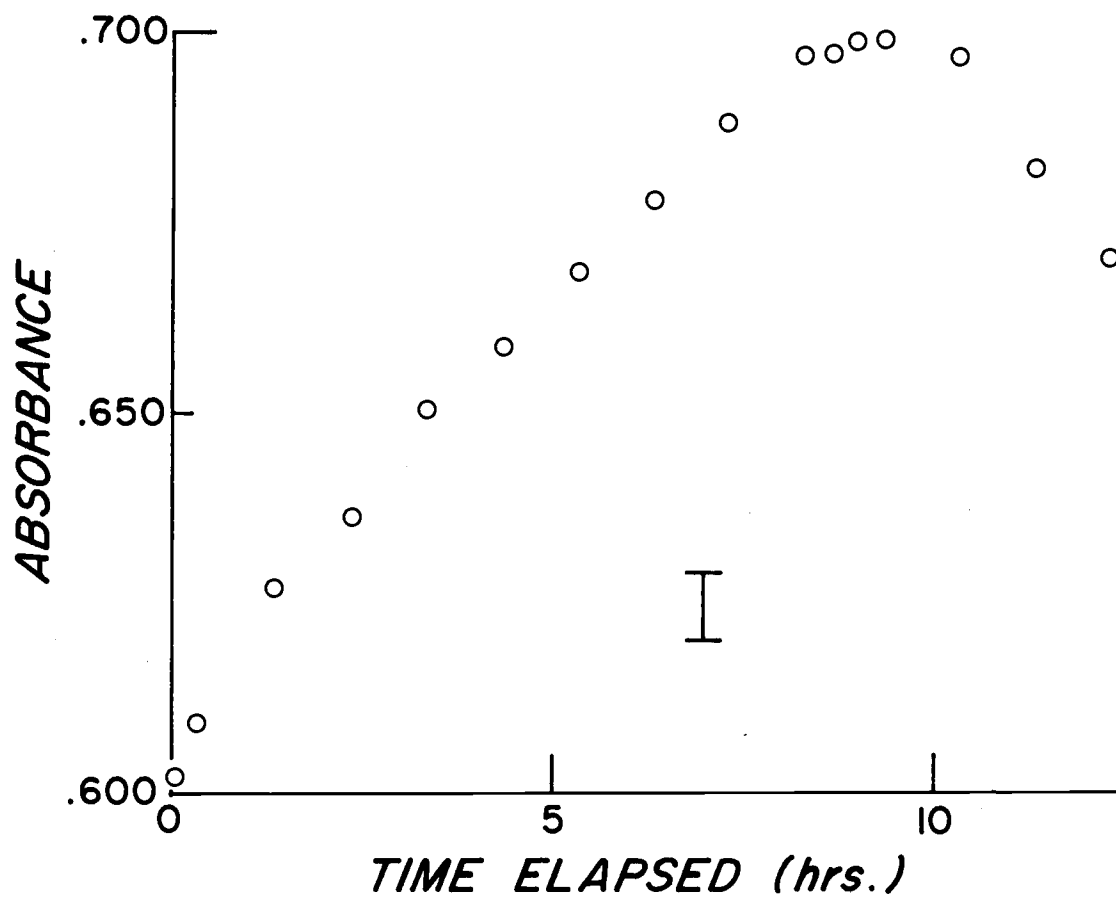


Figure 7. Behavior of a 50 μ M standard in the laboratory. Colorimeter was different from that used on cruise 6707A, and new pump tubes were used. Net baseline drift is shown at the bottom.

particularly, over analyses from frozen samples. This should enable us to make considerably more use of silicate data.

COLUMBIA RIVER PLUME

The horizontal distribution of nutrients off the mouth of the Columbia River has been studied by Stefánsson and Richards (1963, 1964), and Hobson (1966). Because of the wide concentration differences in the river and ocean waters, silicate is well suited for a study of processes leading to observed distributions. Cruises 6707A and 6801F of the R/V Yaquina enabled a fairly detailed determination of silicate distributions from which processes will be inferred. Station positions and surface contours are given in Figures 8 and 9.

The behavior of the Columbia River Plume in the winter is markedly different from that in the summer. While the summer plume extends to the south and southwest of the river mouth, the winter plume proceeds north remaining close to the coast. This is due to the prevailing winds which are southerly in the summer and northerly in the winter.

The area and depth of influence also differ with season. The former is mostly a function of the seasonal variation in the flow volume of the river. Depth of mixing is predominantly affected by the meteorological conditions, the weather being much more rough in the winter months. The relative stabilities of the thermoclines also play a part.

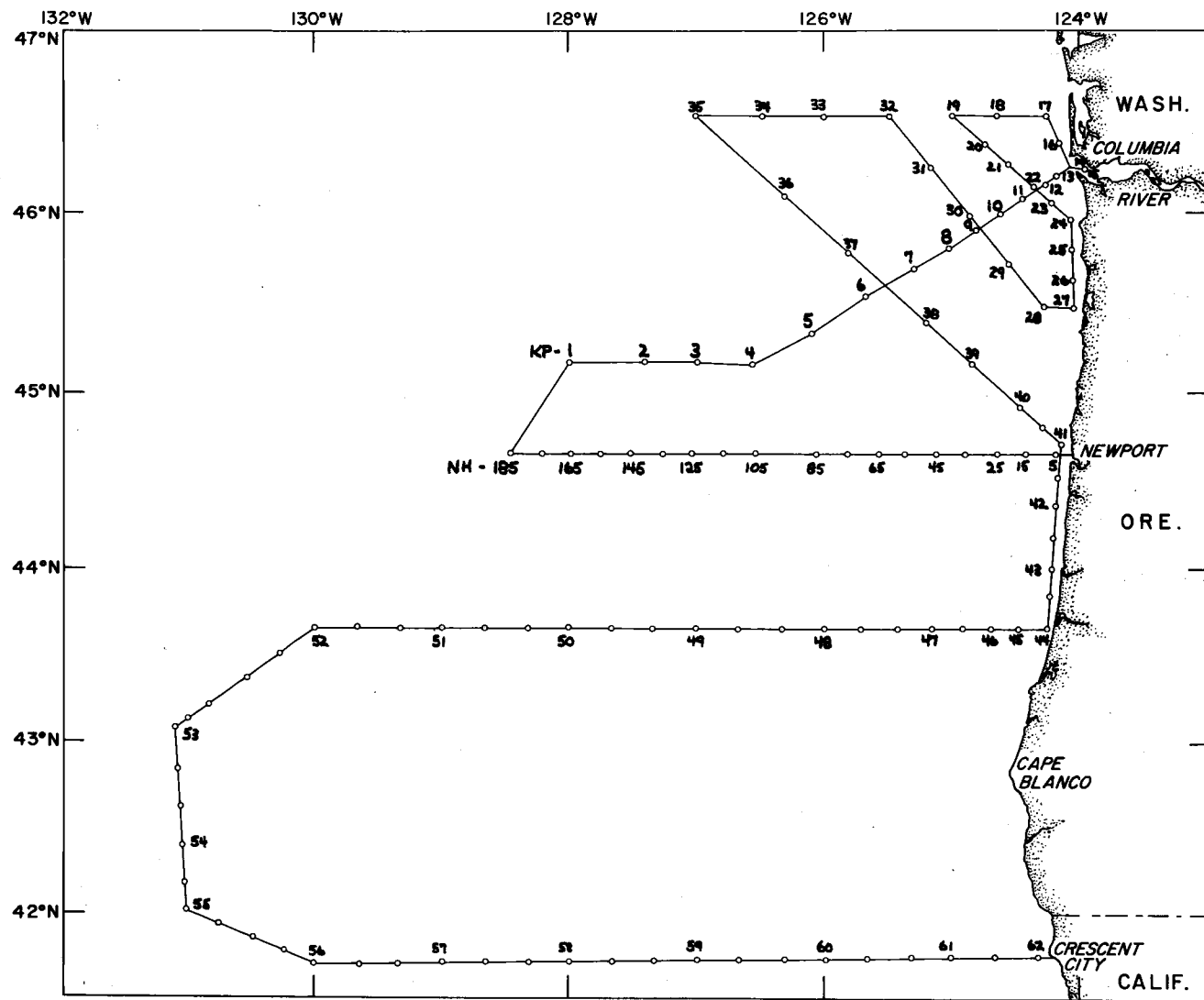


Figure 8a. Surface contours for cruise 6707A. Station numbers.

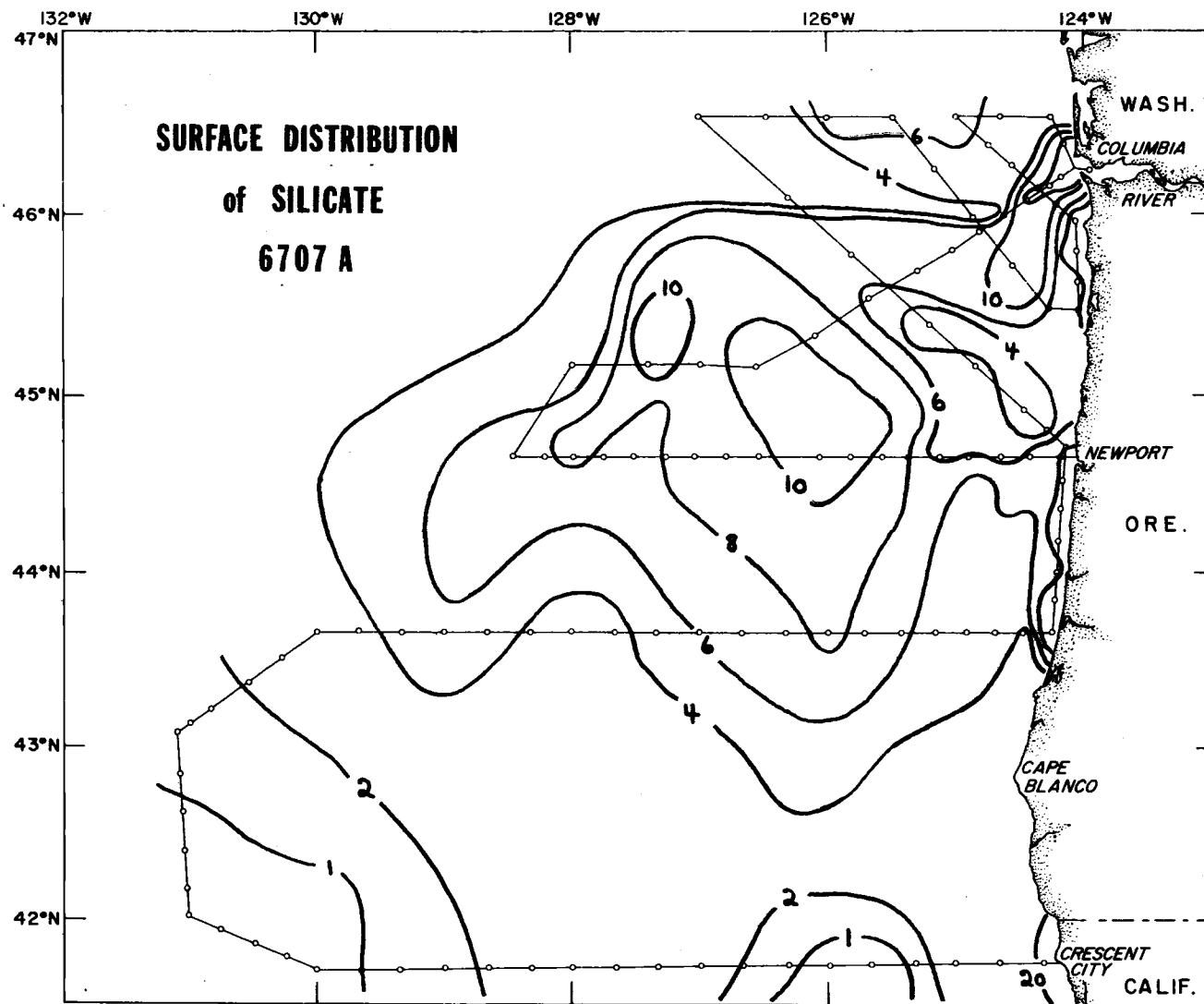


Figure 8b. Surface contours for cruise 6707A. Silicate (μM).

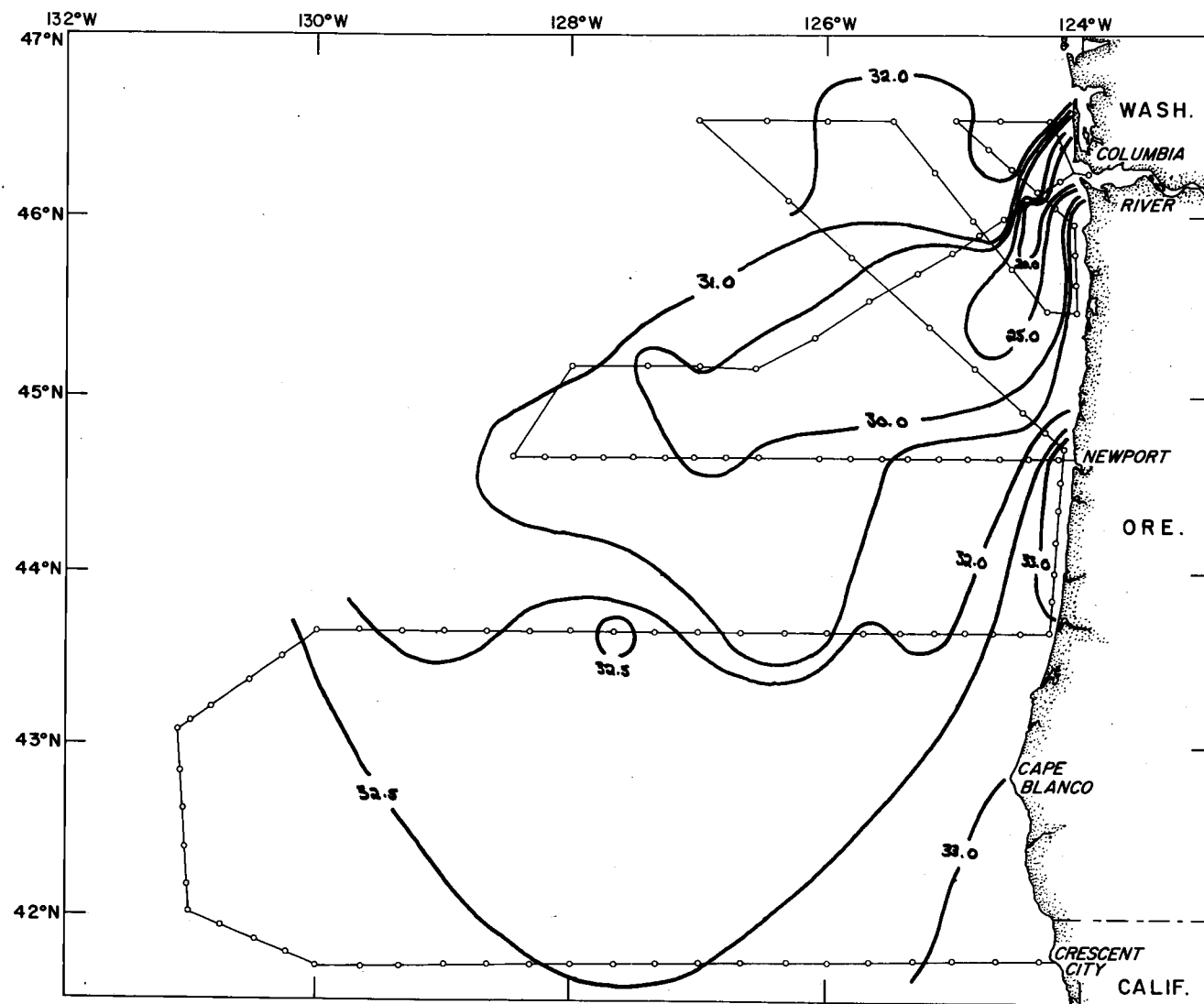


Figure 8c. Surface contours for cruise 6707A. Salinity (‰).

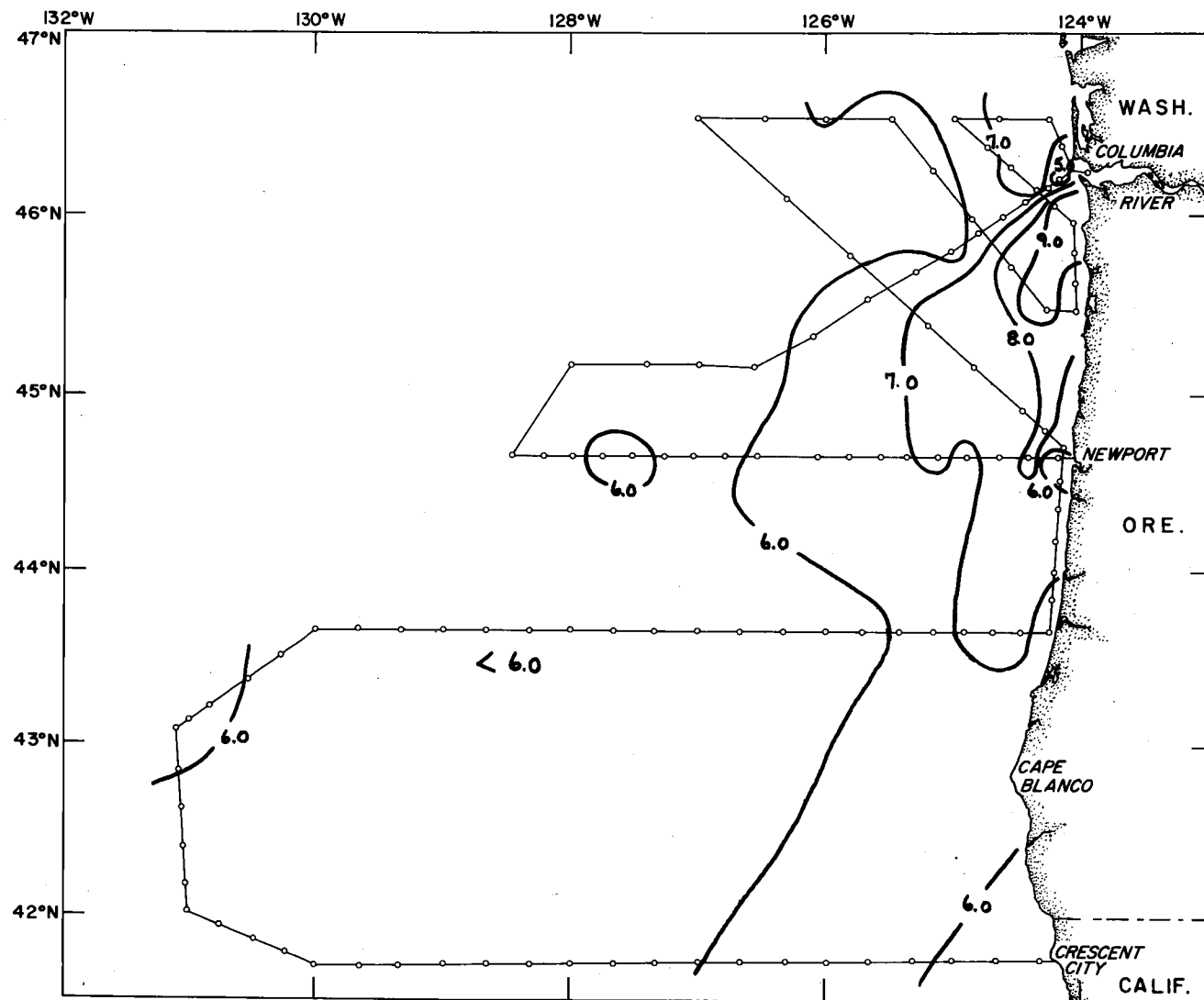


Figure 8d. Surface contours for cruise 6707A. Dissolved oxygen (ml/liter).

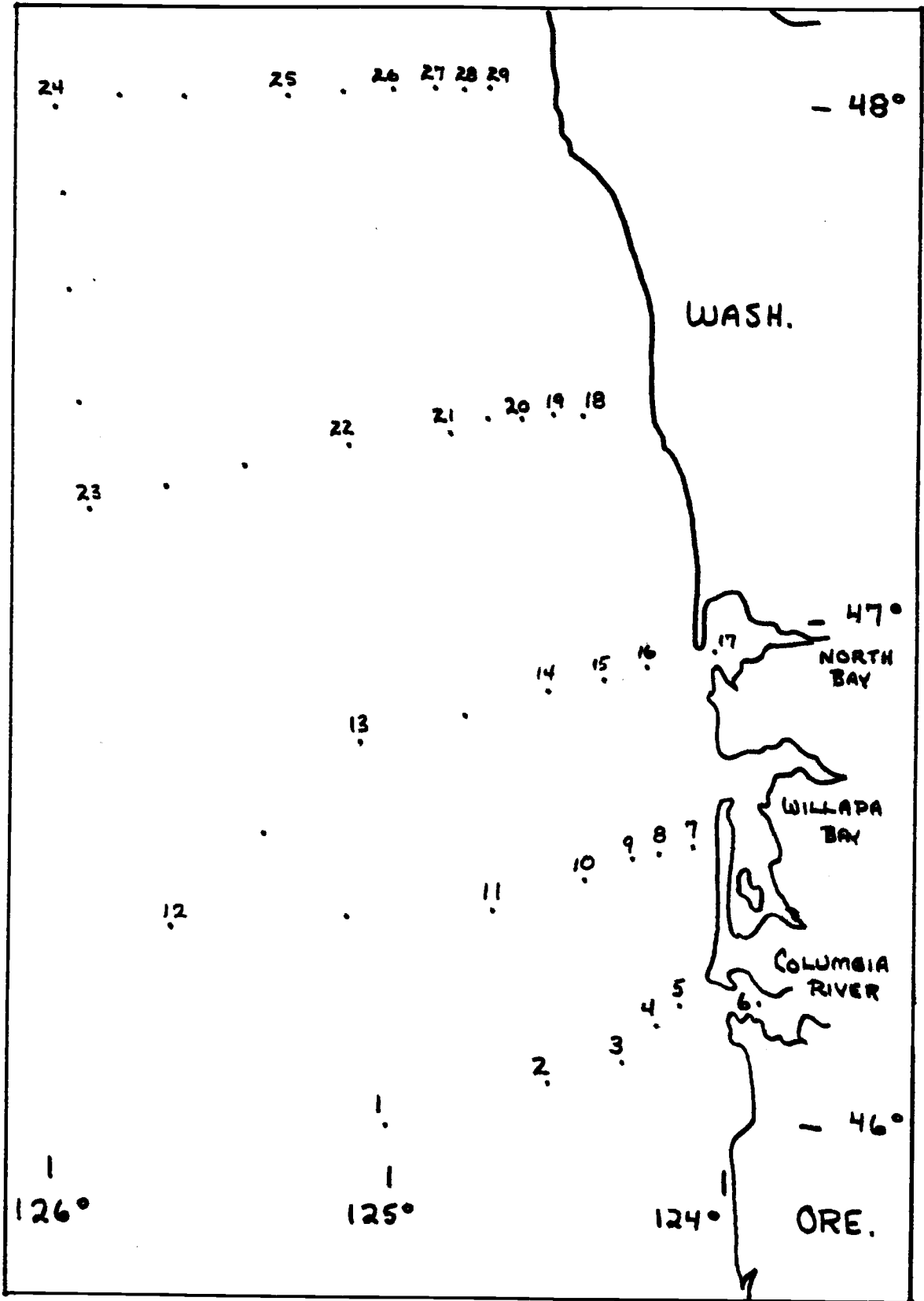


Figure 9a. Surface contours for cruise 6707A. Station numbers.

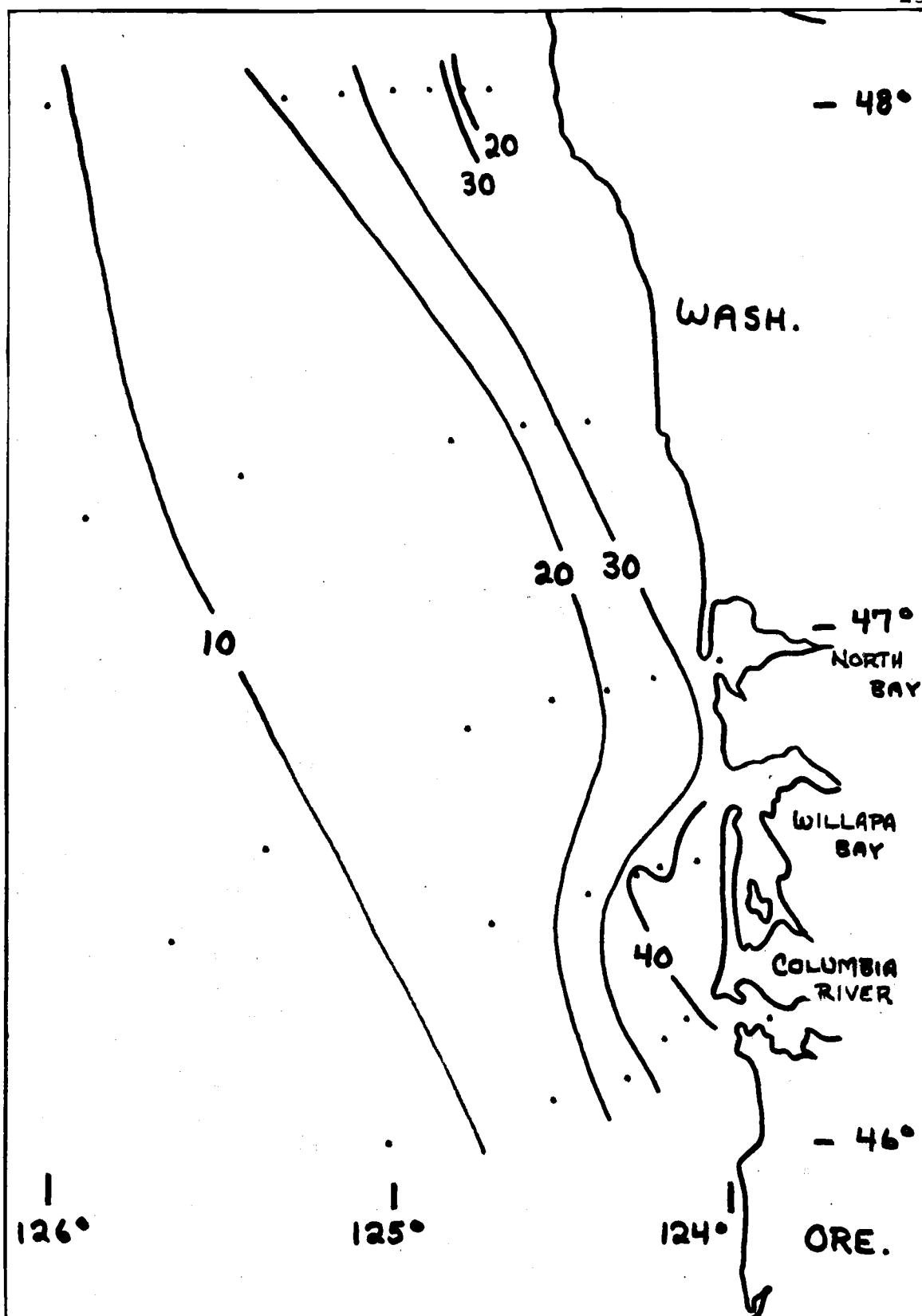


Figure 9b. Surface contours for cruise 6801 F. Silicate (μM).

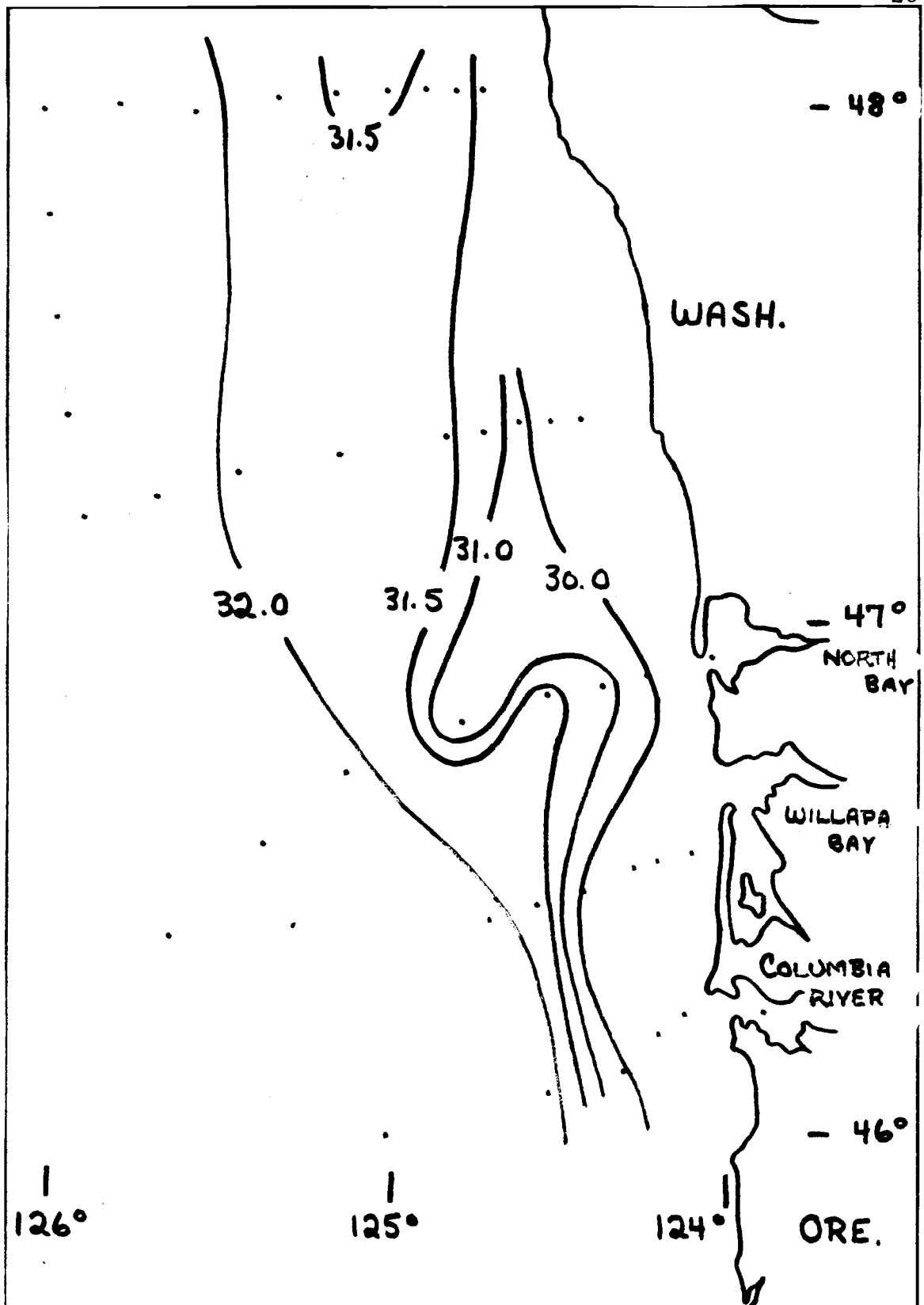


Figure 9c. Surface contours for cruise 680 F. Salinity (‰).

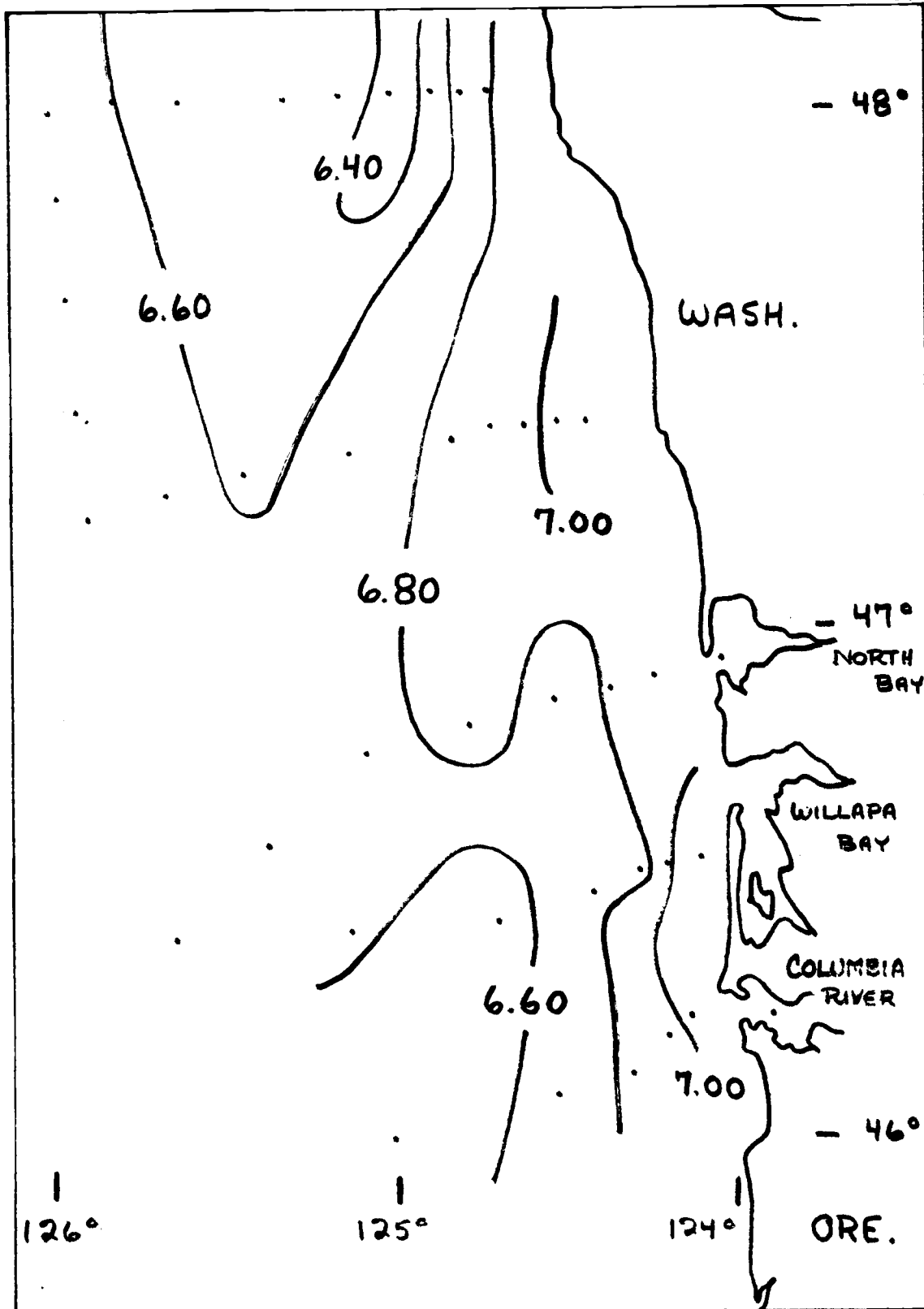


Figure 9d. Surface contours for cruise 680 F. Dissolved oxygen (ml/liter).

There are two major processes and several minor ones which contribute to the observed silicate distribution. Mixing of water types and biological uptake are the main processes, although the latter is less significant in the winter. Minor influences include lens formation, and proximity to the coast and/or bottom. Inorganic removal of silicate was shown not to occur under the prevailing conditions in agreement with the findings of Stefánsson and Richards (1963).

Mixing

The chief influence observed on the silicate distribution off the mouth of the river is mixing. In the summer (6707A) three point mixing of river water, upwelled water and ordinary surface seawater is observed (Figure 10). In the winter (6801F) when there is no upwelling, straight line mixing of river and ocean waters occurs (Figure 11). Deviations in the summer are mostly due to the vigorous biological uptake present at the time of measurement. The winter plume is contributed to quite significantly by outflow from the Strait of Juan de Fuca.

Biological Activity

The effect of biological uptake in the summer is marked. The high oxygen and low silicate values observed off the northern Oregon

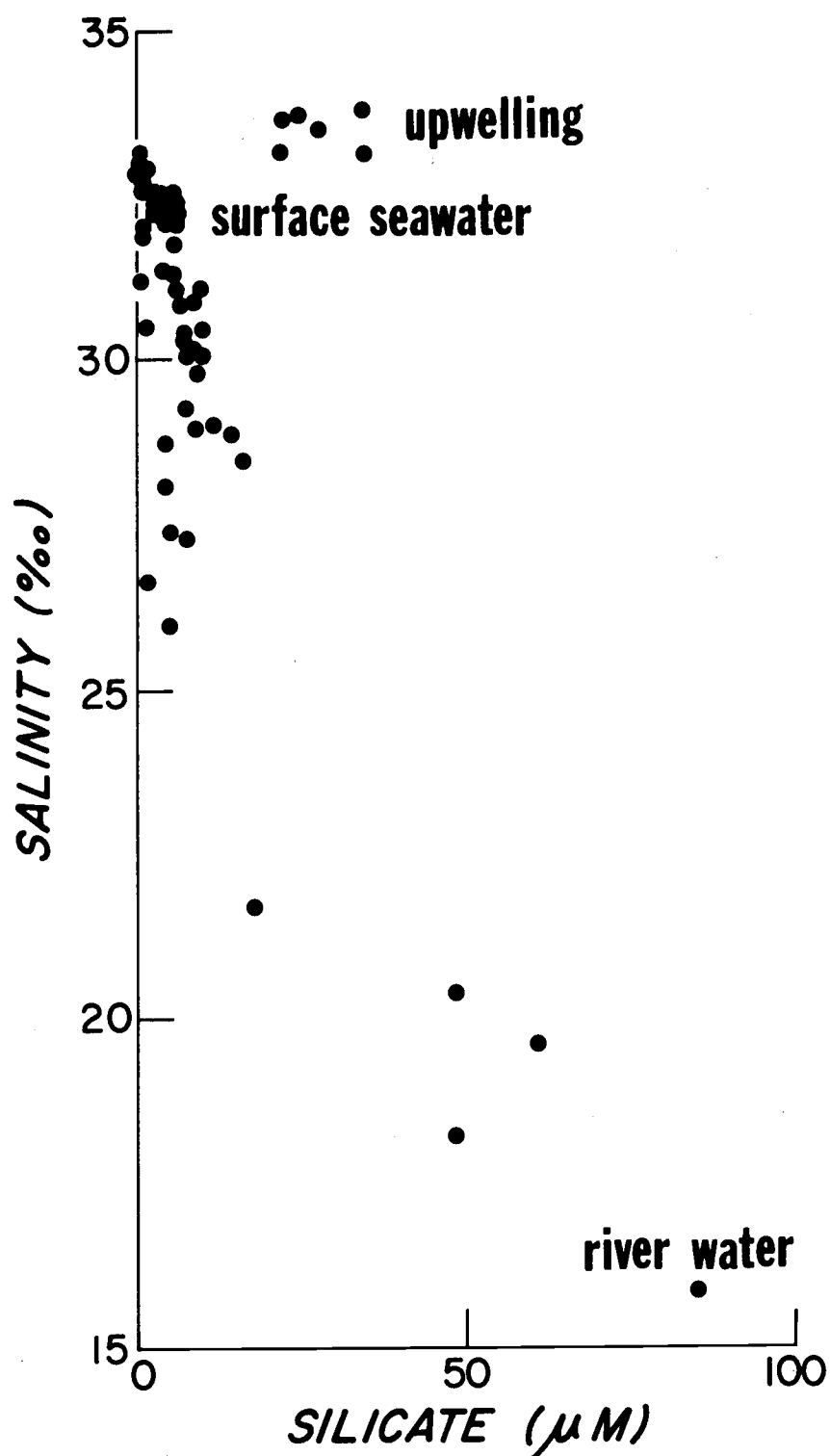


Figure 10. Silicate versus salinity for surface samples on cruise 6707A. Biological activity caused points to move to the left. Note that salinities start at 15‰.

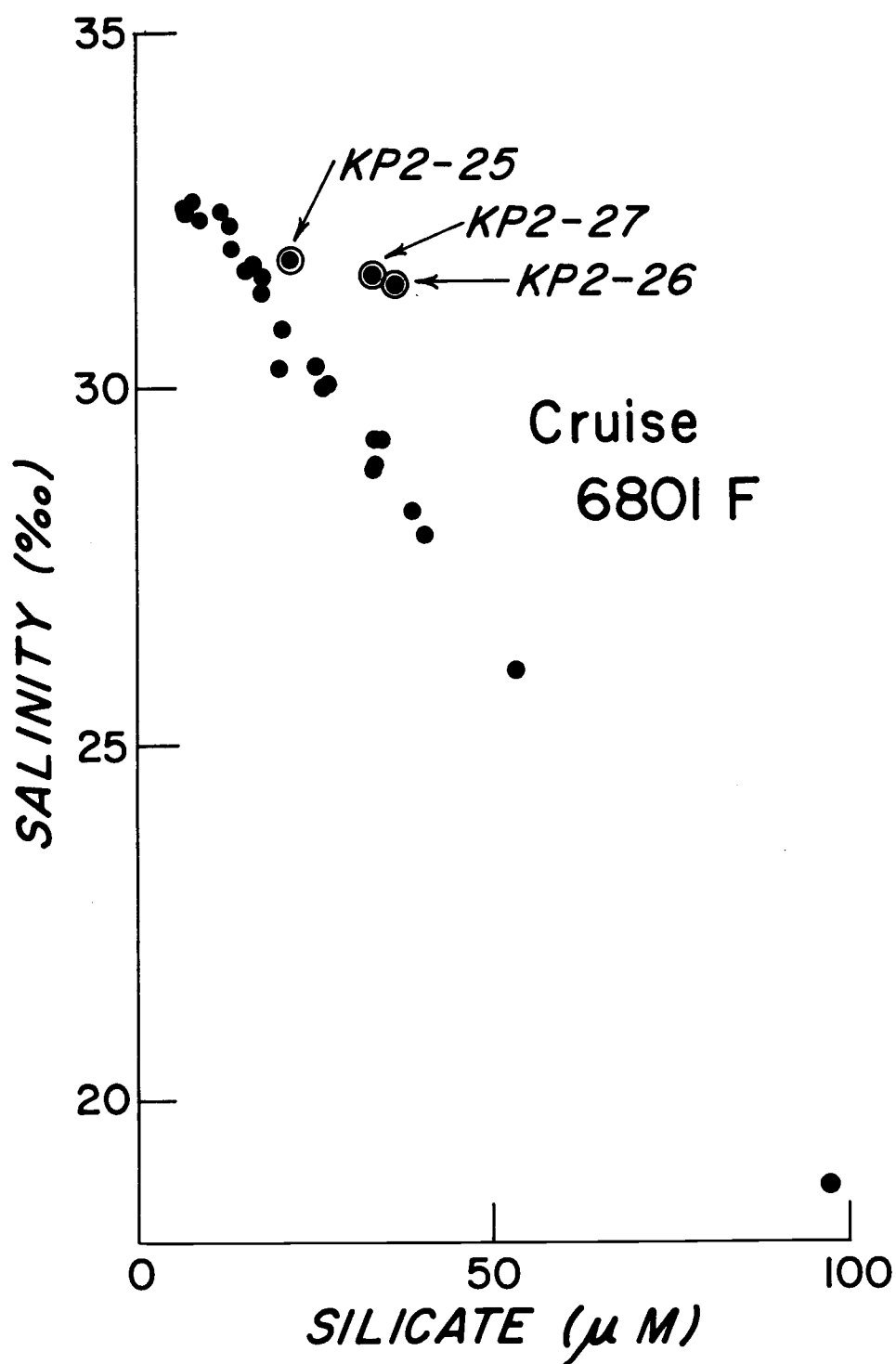


Figure 11. Silicate versus salinity for surface samples on cruise 6801A. Stations KP2-25, KP2-26, and KP2-27 are significantly affected by the outflow from the Strait of Juan de Fuca. Note lack of biological activity.

coast indicate areas of intense photosynthetic activity, or phytoplankton blooms. In addition to the blooms, there is generally high production taking place throughout the area studied. The most striking evidence of this comes from observations of the silicate minimum that occurs at about 30 meters off the Oregon coast. Although the plume water mixes to depths of 50 meters or more, the 30 meter contours show almost no relief (Figure 12).

The combined influences of the plume and biological uptake and release produce the observed minimum. Ordinarily, the phytoplankton maintain a fairly constant silicate concentration in the upper layers. The river, however, provides large amounts of silicate at the surface. Due to the limitations of the quantities of the other nutrients, nitrate and phosphate, added by the river, the phytoplankton are only able to remove a fraction of the added silicate. The remaining high surface values, combined with the increasing silicate values as the thermocline is approached, produce a relative minimum.

That the minimum was not erased by intensive biological activity was seen at Stations KP-38 and KP-39 of Cruise 6707A. Minima of $0.6 \mu\text{M}$ and $3.9 \mu\text{M}$ were observed although oxygen saturations were high. Upwelling does generally erase the minimum due to relatively rapid vertical transport of water and more favorable nutrient ratios. In surface waters affected by the plume, the

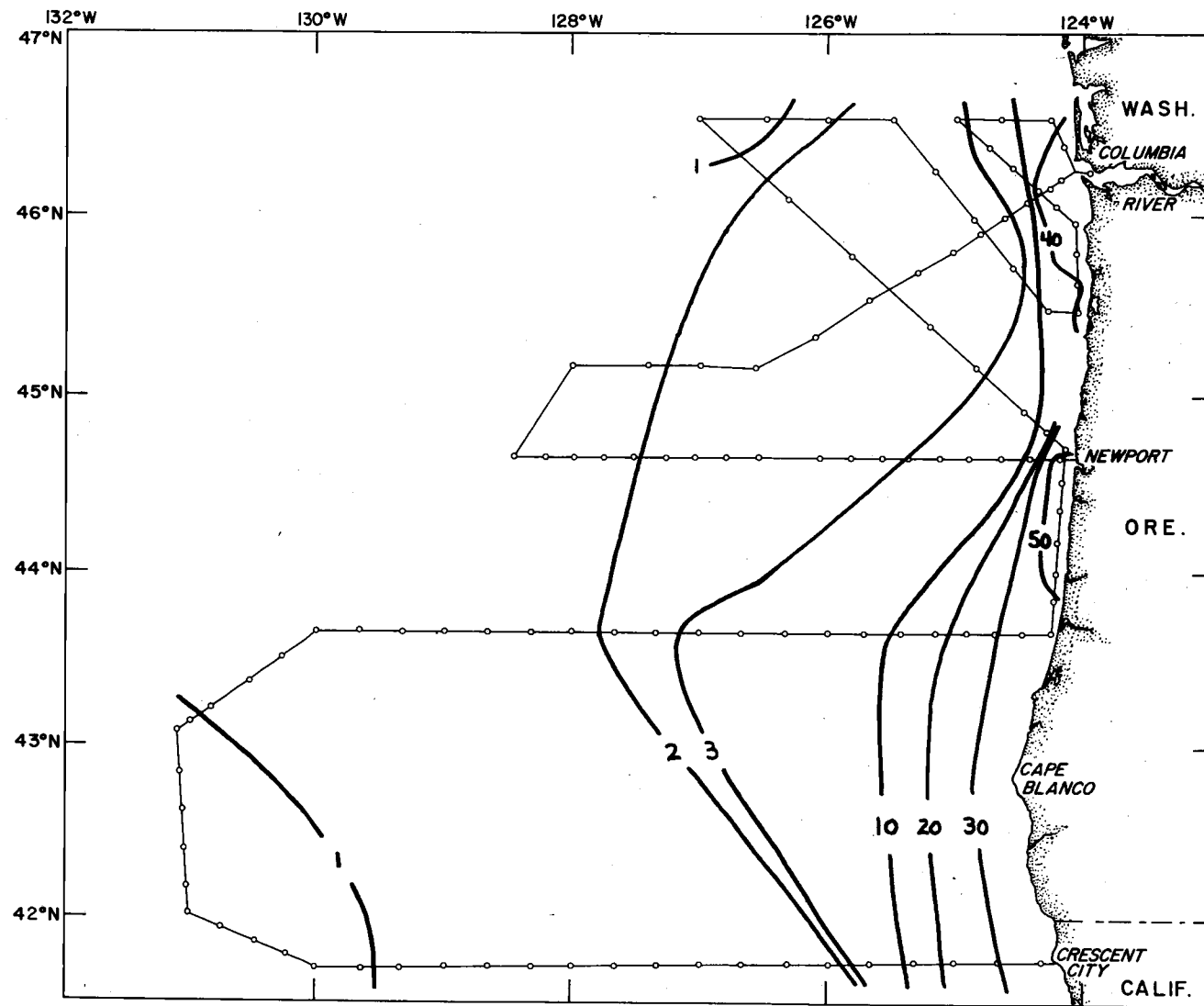


Figure 12. Silicate contours at 30 meters on cruise 6707A.

silicate:nitrate:phosphate ratios may be about 50:1:1. This is quite different from the oxidation ratios of 23:16:1 (Park, 1967). In upwelled waters, however, the ratios become about 50:20:2, much more favorable for a depletion of the silicate present.

Correlation of the minimum with the edge of the plume was attempted on cruises 6707 A and 6801 F. Results, although inconclusive, suggest that the disappearance of the minimum indicates the edge of the plume. On 6707 A, only stations KP-55, 56, 57 of the stations unaffected by upwelling demonstrated no significant minimum. Stations KP-54 and KP-58 showed significant minima. Surface salinities for the stations are shown in Table 3. On the basis of this table, the salinity contour delineating the plume was estimated to be 32.7 ‰. This is roughly in agreement with the value of about 32.5 ‰ determined by Park (1966).

On cruise 6801 F, the minimum was more easily correlated due to the lack of upwelling. The winter plume remained near the Washington Coast (Figure 8) and the shallow water affected the near-shore stations. The surface salinities (Table 4) correlated with the existence of the minimum give a salinity delineation of 32.5 ‰.

The monthly inputs of silicate into the surface waters of the northeast Pacific Ocean by the Columbia River are shown in Table 5. The high values in the late spring and early summer are conducive to phytoplankton blooms, although without similar

Table 3. Delineation of the plume on the basis of the silicate minimum and surface salinities for cruise 6707A.

Station	Magnitude of minimum	Surface S ‰	Comments
KP-54	0.8 μ M	32.616	Plume
KP-55	No	32.787	Seawater
KP-56	0.1 μ M	32.774	Seawater
KP-57	No	32.844	Seawater
KP-58	0.2 μ M	32.669	Plume

Delineation: 32.7 ‰

Table 4. Delineation of the plume on the basis of the silicate minimum and surface salinities for cruise 6801 F.

Station	Magnitude of minimum	Surface S ‰	Comments
KP2- 1	No	32.517	Seawater
2	20 μ M	32.269	River water
12	0.4 μ M	32.459	Seawater
18	No	28.832	River--too shallow (9 m) to have min.
23	0.3 μ M	32.399	Seawater
24	0.5 μ M	32.324	River
28	0.6 μ M	31.651	River
29	No	31.300	River--too shallow (12 m) to have min.

Delineation: 32.35 ‰

Table 5. Monthly flows, silicate concentrations, and total silicate inputs for the Columbia River, measured at Astoria, Oregon, April 1967 to April 1968. Data are from Park, Osterberg and Forster (1969).

Year	Month	Averaged river flow $\times 10^{12}$ liters/month	Silicate μM	Total silicate input $\times 10^9$ moles/month
1967	April	15.3	172	2.63
	May	21.6	168	3.63
	June	42.4	142	6.02
	July	30.9	92	2.84
	August	13.1	62	0.81
	September	9.2	75	0.69
	October	12.2	132	1.61
	November	13.2	177	2.34
	December	15.9	198	3.15
1968	January	16.1	215	3.46
	February	23.4	207	4.84'
	March	20.8	198	4.12
	April	13.9	177	2.46

high supplies of the other nutrients this will not be so. It should be noted also that diatoms have been found to be capable of utilization of silicate other than that measured as "reactive silicate" (Schutz and Turekian, 1965). Thus the silicate values in Table 5 must represent a lower limit of the net contribution of nutrient silicate by the river.

Lens Formation

On cruise 6707A, we observed that lenses of river water were being formed by the influence of the tides on the estuary. The closed 10 μM silicate contour we observed at about 105 nautical miles from the coast (Figure 8) suggests this. Additional indication is taken from data of the intersecting cruise tracks off the river mouth. On the inbound track, the value was 49 μM . On the cross-track, 2.6 tide cycles (32.5 hours) later, the value was 16 μM .

Coastal Influence

Summer and winter profiles of silicate show a general increasing trend as they near the coast. The summer behavior can be definitely attributed to circulation related to upwelling. Winter upwelling has also been reported along the Oregon coast (Burt et al., 1959). It is possible, however, that the trend shown in Figure 13 is due to interaction with the bottom in the form of nutrient

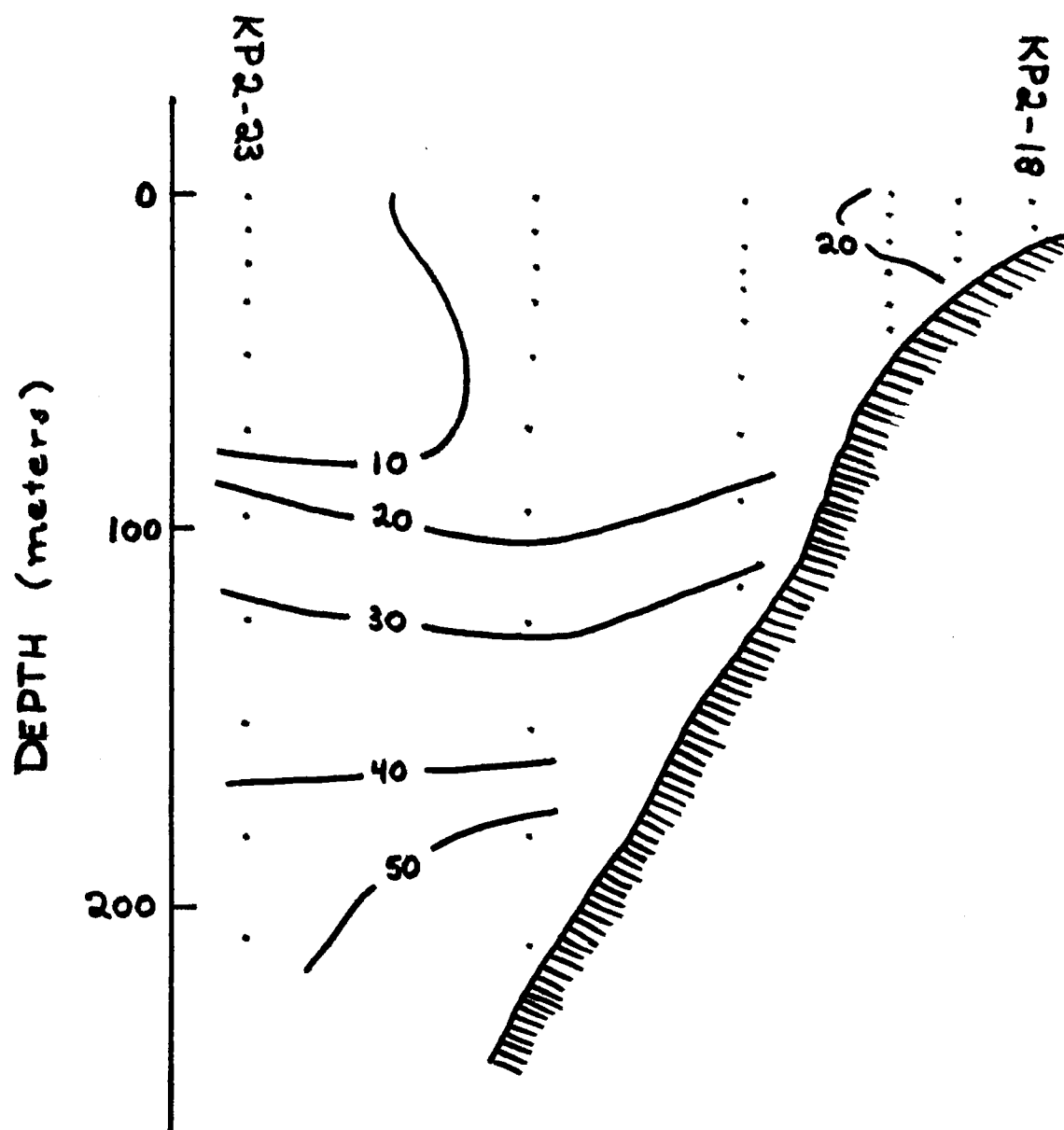


Figure 13. Vertical cross-section between stations KP2-18 and KP2-23 of cruise 6801F.

regeneration.

Inorganic Removal

Plots of salinity versus silicate from cruise 6707A for the mouth of the Columbia River seem to support the conclusion of Stefansson and Richards (1963) that inorganic uptake is negligible. Laboratory tests of a preliminary nature were run with the Auto-analyzer[®] using Columbia River water and ordinary surface seawater. The data (Table 6) showed that the effect was undetectable if it existed at all. Release of silicate may even be suggested. This does not by any means negate the results of Bien et al. (1958) or of Mackenzie et al. (1967). The quantity of suspended material in both of those studies was probably much higher than that found in the Columbia River at the time of these measurements (Stefansson and Richards, 1963).

Table 6. Results of laboratory tests on the removal of silicate upon mixing of river and ocean waters. Concentration is in μM .

	Test #1	Test #2
River water concentration	73.5	72.8
Ocean water concentration	5.2	3.2
500 ml of each mixed together and refrigerated 24 hours	41.7	39.3
Calculated mixture concentration	39.4	38.0
Difference, observed minus calculated	+2.3	+1.3

DEEP SEA SILICATE

Biogenic Silicate

Observed silicate values contain two components: that associated with the oxidation of organic matter, and that of non-oxidative origin.

$$\text{Si}_{\text{obs}} = \text{Si}_{\text{ox}} + \text{Si}_{\text{non-ox}} \quad (2)$$

Oxidative silicate may be related to the apparent oxygen utilization (AOU) by the equation

$$\text{Si}_{\text{ox}} = 7.4 (\text{AOU}) \quad (3)$$

where Si_{ox} is in μM and AOU in ml/liter (Park, 1967). This value was derived using the laboratory results of Grill and Richards (1964) on silicate:phosphate ratios in decomposing phytoplankton and is comparable to an averaged model with $\text{O}_2:\text{Si}:\text{P}$ of 138:23:1.

Unlike the non-oxidative fractions of phosphate and nitrate, non-oxidative silicate is a result of the interplay of two processes. An equation for this can be written:

$$\text{Si}_{\text{non-ox}} = \text{Si}_{\text{inorg}} + \text{Si}_{\text{pre}} \quad (4)$$

where $\text{Si}_{\text{(inorg)}}$ is the quantity due to the inorganic (non-oxidative) dissolution of silicious remains of diatoms and radiolaria. $\text{Si}_{\text{(pre)}}$

is preformed silicate, analogous to the preformed nutrients of Redfield, Ketchum and Richards (1963) and affected only by the mixing of water masses. Park (1967) made the first attempt to separate these two components in the intermediate waters off the Oregon coast.

The validity of Equation (3) or any equation of the form

$$Si_{ox} = k (AOU) \quad (5)$$

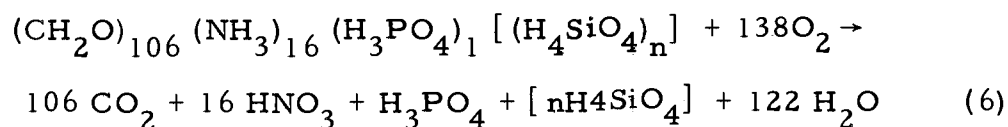
is open to question. The release of silicate upon the decomposition of phytoplankton has not been well characterized. Even if we assume that a quantitative fraction of the silicon in an organism is released concurrent with the oxidation of the organism we face the problem of phytoplankton population variations both geographical and seasonal.

Use of field data of silicate and oxygen to obtain the constant in Equation (5) has several complications. From Equation (2), we can see that a silicate/oxygen plot will only produce a straight line if the quantity Si_{non-ox} is constant. Thus, the calculation must be carried out in relatively shallow waters, above the level where inorganic dissolution of diatoms begins. In some areas, this may be as shallow as 100 meters (Kozlova and Mukhina, 1967), although 200 meters seems possible for the Oregon coast (Park, 1967). The calculation also assumes a single process, decomposition, since the uptake and oxidation ratios are different and would cancel each other

to some extent. This limits how near the surface we can get, leaving a very narrow, perhaps nonexistent depth band where such calculations would be meaningful. The assumption of concurrent release of silicate has some support, however. Grill and Richards (1964) found in their laboratory experiment that regenerative release of orthosilicate and orthophosphate produced an approximately linear relationship following an initial period of continued silicate uptake. After about 100 days, the phosphate being released went approximately to zero while the release of silicate continued at a decreased rate. This would seem to indicate that the early regenerative kinetics of silicate and phosphate are approximately parallel.

The amount of silicate released following the leveling off of the phosphate value was approximately equal to that taken up at the start of the light-free decomposition period. This uptake was thought by Grill and Richards (1964) to be used in silicification of existing cells. This assimilation process during the dark oxidation period might be considered to be a counterpart to the non-oxidative release on decomposition.

In the model for the oxidation of phytoplankton, the phosphate and silicate are also "similar" in that the oxidation state of phosphorus is unchanged in the process as is that of silicon. The equation for the model is generally written:



Thus, although the biochemistry of phosphate is complicated and may bear no relationship to that of silicate, the elementary parallelism of silicate and phosphate in the model and in the laboratory makes the assumption a good jumping off point. Inspection of the quantity $\text{Si}_{\text{non-ox}}$ as calculated from the above assumption may give us insight as to the processes which do determine silicate concentrations.

The kinetics of silicate release and dissolution are quite complicated and not well understood. The rate of release of silicate concurrent with the oxidation of the organism may vary as the oxidation process progresses as was indicated in the laboratory study of Grill and Richards (1964). As the relatively hard skeletal material of the diatom is exposed to seawater by the decomposition of its organic protective coating, the kinetics of silicate release change markedly. The outer layers of the test may dissolve quite rapidly, leaving a less soluble fraction behind. This decreasing solubility may also be reinforced by the adsorption of metals or development of other protective films on exposed surfaces. In general, then, the rate of release of inorganic silicate from diatoms appears to go through a maximum at some time in their fall through the water

column.

The existence of two groups of diatoms, the "easily soluble" found in coastal areas and the "sparingly soluble" found in open ocean areas introduces an additional factor. In general, the easily soluble diatoms dissolve appreciably in the upper 100 meters, whereas the sparingly soluble ones may reach the bottom with only small amounts of silicate removed (Kozlova and Mukhina, 1967). It is thought that the diatoms used in the Grill and Richard (1904) experiment were of the easily soluble kind in which "non-oxidative" dissolution plays only a small role.

There will be, therefore, some level of the water column where the rate (mg/day/organism) times the number of organisms will be a maximum. We would expect to find, then, a maximum in non-oxidative silicate in the water column.

Data

Observed silicate, AOU, oxidative silicate, non-oxidative silicate, and salinity values for the Surveyor stations SU-91-68 (25 April 68) and SU-105-68 (27 April 68) are shown in Tables 7 and 8. Oxidative silicate is calculated from equation (3); $Si_{ox} = 7.4 \text{ AOU}$, and non-oxidative silicate from equation (2); $Si_{non-ox} = Si_{obs} - Si_{ox}$. Silicate values are estimated to be $\pm 1\%$ precision. AOU values are considered to be $\pm .03 \text{ ml/liter}$.

Table 7. Chemical oceanographic data for SU-91-68, 37°01.8'N 179°54.8'E.

Depth (m)	Obs. Si (μ M)	AOU (ml/liter)	Si ox (μ M)	Si non-ox (μ M)	T (°C)	S (‰)
1	8.69	-0.22			12.89	34.409
20	8.64	-0.05			12.79	34.412
50	8.62	-0.07			12.71	34.408
100	9.27	+0.16	1.18	8.1	12.12	34.387
150	9.75	0.14	1.04	8.8	11.94	34.372
200	10.4	0.16	1.18	9.2	11.78	34.360
250	10.5	.48	3.55	6.9	11.36	34.342
300	13.0	.84	6.22	6.8	10.70	34.261
400	22.4	1.76	13.0	9.4	8.82	34.107
503	38.0	3.05	22.6	15.4	6.83	33.997
600	58.5	4.33	32.0	26.5	5.47	34.010
809	84.9	5.81	43.0	42	4.15	34.130
1003	108	6.64	49.1	59	3.42	34.303
960	109	6.70	49.6	59	3.35	34.316
1536	133	6.90	51.1	82	2.45	34.500
1836	140	6.55	48.5	91	2.13	34.560
2530	141	5.56	41.1	100	1.68	34.634(2)
2836	139	5.13	38.0	101	1.59	34.653(2)
3105	137	4.82	35.7	101	1.50	34.668(2)
4130	129	4.42	32.7	96	1.45	34.679(2)
4315	129	4.32	32.0	97	1.47	34.682(2)
4818	131	4.23	31.3	100	1.53	34.682(2)
5330	131	4.22	31.2	100	1.60	34.685(2)

Table 8. Chemical oceanographic data for SU-105-68, 41°47.8'N, 179°54.9'W.

Depth	Obs. Si	AOU	Si ox	Si non-ox	T	S
1	11.6	-0.03			9.89	34.164
19	11.6	+0.02			9.87	34.161
47	11.6	0.00			9.86	34.161
95	12.3	.16	1.18	11.1	9.48	34.134
143	12.5	.23	1.70	10.8	9.22	34.127
190	13.1	.23	1.70	11.4	8.87	34.073
238	14.5	.38	2.81	11.7	8.53	34.046
286	15.1	1.95	14.4	0.7	8.18	33.996
353	28.5	3.72	27.5	1.0	7.07	33.949
478	49.2	4.74	35.1	14.1	5.50	33.970
574	66.9	4.86	36.0	30.9	4.85	34.030
668	93.9	6.23	46.1	47.8	3.79	34.194
966	110	6.70	49.6	60	3.27	34.319
1052	116	6.74	50.1	66	3.06	34.371
1244	124	6.84	50.6	73	2.75	34.367
1535	134	6.85	50.7	83	2.37	34.506
2020	141	6.35	47.0	94	2.00	34.584
2510	141	5.55	41.1	100	1.76	34.625
3000	136	5.09	37.7	98	1.60	34.654
3765	131	4.50	33.3	98	1.50	34.674
3990	130	4.42	32.7	97	1.49	34.677
4490	130	4.29	31.7	98	1.52	34.682
4990	131	4.29	31.7	99	1.56	34.684
5490	131	4.24	31.4	100	1.63	34.682
5990	131	4.20	31.1	100	1.70	34.686

The existence of the maximum in observed silicate at about 2300 m is definite (Figure 14). The existence of a secondary minimum at about 4000 m deserves some attention. The minimum is thought to be real because the data for deep stations SU-91-68 and SU-105-68 both show the same behavior, including the same depths for the feature. It is highly improbable that the same behavior would occur due to random errors in the analyses. Systematic errors would probably not produce extrema.

Similar reasoning can be applied to the existence of a maximum in non-oxidative silicate at about 2500 m, and a secondary minimum at about 4000 m.

Part of the original data trace for SU-105-68 is shown in Figure 15 to show the detectability of the deep-sea maximum and secondary minimum.

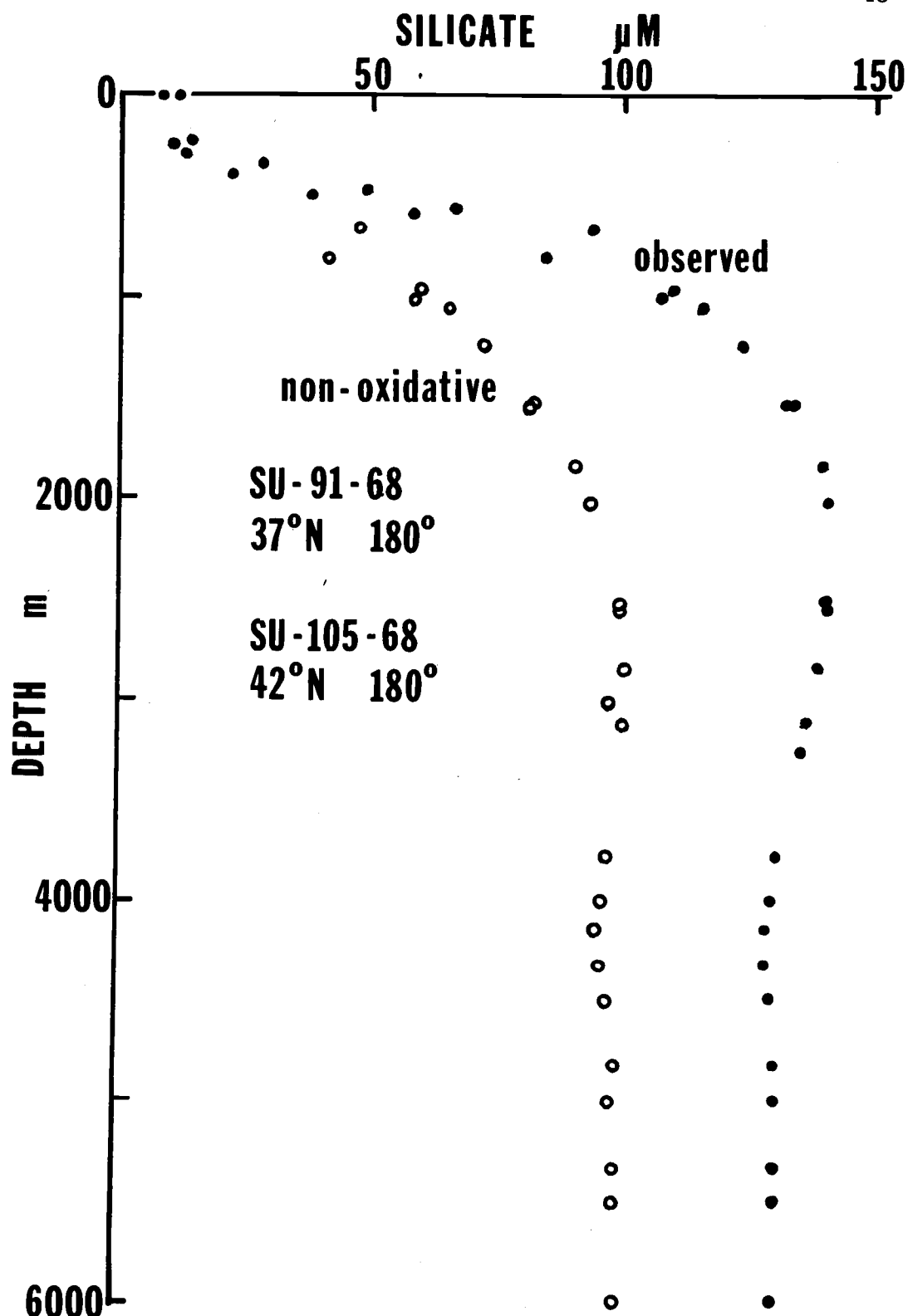


Figure 14. Observed silicate and non-oxidative silicate for stations SU-91-68 and SU-105-68. Data from Tables 7 and 8.

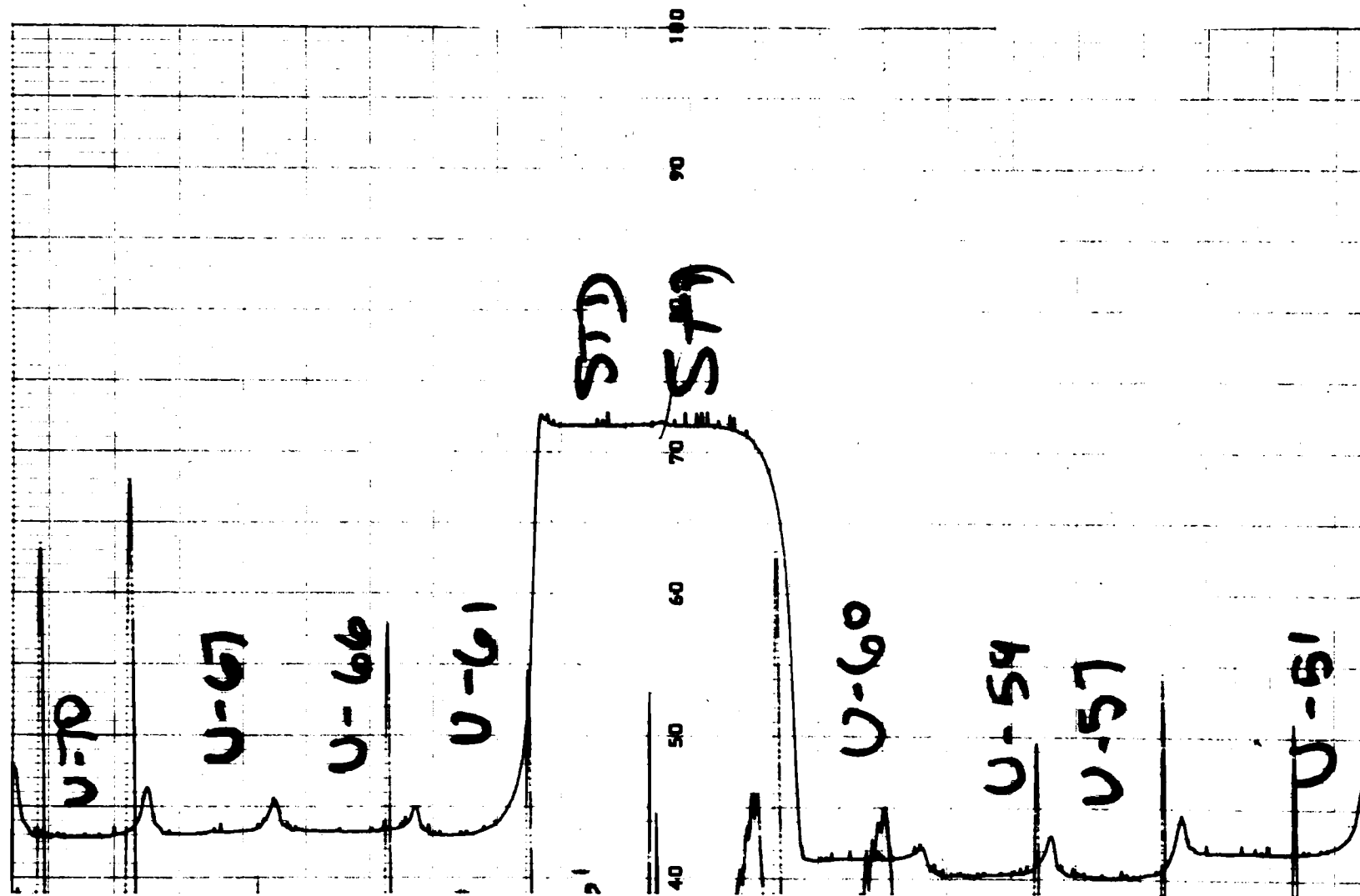


Figure 15. The original data trace for SU-105-68. Phosphate trace has been blocked out. Note maximum (sample U-57) and secondary minimum (samples U-66 and U-67). Values are in percent transmission.

DISCUSSION

The maximum in observed silicate occurs at about 2200 meters in the North Pacific Ocean (Table 7). This is about 800 meters deeper than the maximum in oxidative silicate (1400 m), and 300 meters shallower than the maximum in non-oxidative silicate (2500 m).

The depth of the maximum is determined by the crossing of increasing and decreasing components; non-oxidative and oxidative silicate, respectively. At 1400 meters, the rate of increase of non-oxidative silicate is considerably larger than the rate of decrease of oxidative silicate. As non-oxidative silicate approaches its maximum at 2500 m, its rate of increase becomes less. At 2200 meters, an equivalence is reached. Below 2200 meters, the decrease in oxidative silicate is more rapid than the increase, if any, in non-oxidative silicate (Figure 14).

The maximum in non-oxidative silicate represents the level of maximum contribution of inorganic silicate. It would be the level at which the integral over the number of diatom tests and their rates of release (non-oxidative dissolution) is maximized. The contribution of inorganic resolution might be expected to tail off at a slower rate than does the oxidative release curve, since the former represents primarily a decrease in the rate of solution of the material as

opposed to an actual significant decrease in the amount of material being acted upon.

The secondary minimum can be explained in either of two ways. Like the observed maximum, it may represent the crossing of two contributions, in this case the decreasing rate of inorganic dissolution and an increase in preformed silicate due to bottom water. An alternative explanation comes from the integral approach. At the sediment-water interface there will be an accumulation of diatoms still exposed to seawater. Resuspension of diatoms on the bottom could, then, contribute noticeably to the silicate concentrations of waters in contact with the bottom. Looking at the density (σ_t) structure of the bottom waters, we find that σ_t is essentially constant from 3800 meters to the bottom. Mixing over this column would be energetically not difficult, and the Si could have mixed upward to the observed level of 4000 meters.

The rate of release on the bottom can be assumed to be quite slow if we consider that earlier solution processes will attack and remove the more easily soluble parts of the organism. Thus the magnitude of the observed increase is reasonable.

In simplified form, the deep waters of the Pacific Ocean move northward and are over-ridden by the North Pacific Intermediate waters which flow south and east. South of the Antarctic convergence, the deep waters undergo a relatively dense rain of diatoms.

North of the convergence, the diatom activity falls off very rapidly and does not become appreciable again until north of the subarctic boundary. We can neglect the influence of dissolving radiolaria since they are found primarily in the eastern equatorial parts of the Pacific Ocean (Sverdrup et al., 1942).

We have at 50° a water column with high concentrations of fairly reactive diatoms throughout. At 40°N, however, much of the water column has very low or zero concentrations and more resistant diatoms (Kozlova and Mukhina, 1967). We would expect, then, that a maximum would be formed in the south and be considerably altered to the north by mixing and lack of supply in the upper layers.

The effect of the North Pacific intermediate waters will be to provide a supply of diatom tests to the waters immediately south of the subarctic boundary. This is shown clearly in the data of Kozlova and Mukhina (1967, Figure 3, p. 1325). At 180°, between 35° and 45°N, the area of our measurements, this supply is thought to be significant. The net effect would be to intensify the maximum in the deep water, or, if that maximum has been erased due to mixing, to contribute to one.

Further studies using precise silicate analyses along North-South tracks in the Pacific are needed to ascertain the relative contributions of the diatoms from the southern parts of the Pacific and those added in the northern parts.

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APPENDIX

APPENDIX I

The Method of Analysis:

The Technicon Autoanalyzer® method is built around a proportioning pump which delivers reagents or sample at a rate determined by the diameter of the pump tubings. Mixing coils placed between the addition points of the various reagents assure a homogenous sample-reagent mixture.

A schematic of the analysis is given in Figure A-1. The numbers represent nominal addition rates in milliliters per minute. Use of sampling tubes delivering 2.50, 0.60, and 0.10 ml/min produces usable ranges of 0-12, 0-60, and 0-250 μ M.

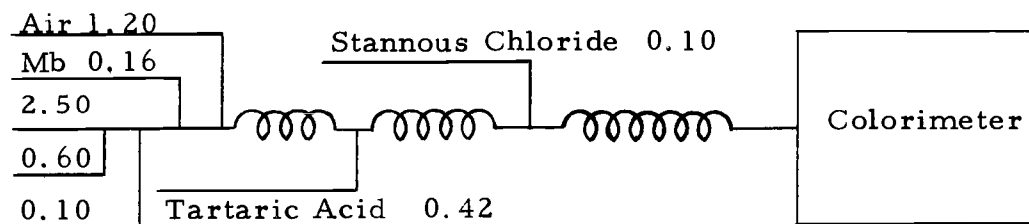


Figure A-1

Reagents were as follows:

Molybdate: 80 ml 5% w/v ammonium molybdate solution plus
120 ml 1.2 N hydrochloric acid.

Tartaric Acid: 10% w/v in distilled water.

Stannous Chloride: Stock solution: 40% w/v $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 5N hydrochloric acid. Dilute 5 ml to 200 ml with 1.2 N hydrochloric acid for daily use. This is 1% w/v in 1.2 N hydrochloric acid.

Standards: Primary standard (5000 μM) was made by dissolving 0.9403 gms of Na_2SiF_6 , dried at 105°C and desiccated, in distilled water and making to one liter. Standards of 10 μM , 50 μM , and 100 μM concentrations were made up using the artificial seawater of Strickland and Parsons (1965, p. 71).

Blanks: Blanks were run using doubly distilled water.

The data were treated in the following manner. Transmittancies were recorded and converted to absorbancies using the relationship

$$A = -\log T$$

Standards were treated as samples. Blanks were recorded and were subtracted assuming a linear drift between the initial and final blanks. This procedure was shown in the laboratory to be justified provided the time interval between blanks is not too large.