BARIUM UPTAKE BY DIATOMS AND THE ^{226}RA - BA - SI SYSTEM IN THE OCEANS

BY

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A simple co-precipitation model of barium removal by siliceous organism via a Raleigh fractionation process was proposed, the fractionation ratio

$$\alpha = [Ba/Si]\ \text{plankton} : [Ba/Si]\ \text{water},$$

being constant. The validity of the model was tested on cultured diatoms, and on oceanic plankton samples. α was found to be a constant for the cultured diatom species, but varied with the different oceanic species. Shells of siliceous organisms are not the sole carrier of barium; calcareous and crustaceous organisms are also involved. Organic parts of the organisms may play an important role in barium transportation.

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INTRODUCTION

Since the pioneering work of Koczy [1], considerable investigative interests have been devoted to the study of radium-226 as a potential time tracer of oceanic circulation processes. Briefly, radium is produced by radio-active decay processes:

$$^{234}U \xrightarrow[\alpha]{2.48\times10^{5}\text{yrs}} {}^{238}Th \xrightarrow[\alpha]{7.5\times10^{4}\text{yrs}} {}^{226}Ra \xrightarrow[\alpha]{1622\text{yrs}} {}^{222}Rn$$

The half life for radium-226 is 1622 years [23]. In the ocean, radium is produced in sediments, introduced into the overlaying water, and subsequently diffuses and decays upward towards the surface. These properties are in complete contrast to the only other useful, long lived time-tracer, carbon-14. Carbon-14 is produced in the atmosphere by cosmic-ray interaction, it has a half life of 5,600 years, decaying to nitrogen-14 by β emission. Carbon-14 is introduced into the surface ocean, and subsequently diffuses and 'ages' toward the ocean bottom. Using radium as time-tracer will provide another independent dating system, which will put extreme constraints on modeling oceanic circulation processes.

From the earlier measurements of Koczy [1] and Broecker [4], models depending on carbon-dating and radium-dating show distinct inconsistencies. Depletion of radium is found in

the upper layers compared to the deep ocean. The residence time of the surface layer, calculated from the radium data, is too long as compared to those estimated by ^{14}C model of vertical mixing of bottom and surface water [3]. A non-decay process that scavenges radium from the surface layer must exist. From the similarity between radium and dissolved nutrient profiles, it has been suggested that radium is involved in the biochemical cycle in the ocean [3,5,7]. The cycle depends on the uptake of radium in surface waters by organisms, and transport across the thermocline mixing-barrier as the organism sinks. Radium is finally regenerated as the particles redissolve in the deep water column, or is removed to the sediments. These cyclic processes dominate the radium distribution in the ocean [12]. The effect of biological cycling has to be corrected before radium can be successfully used as a time-tracer. In the carbon-14 dating system, this is done by normalization to carbon-12. However, no stable isotope exists for radium. A chemical analogue is sought.

The success of an analogue system depends on the assumption that radium and its chemical analogue correlate systematically in all chemical and biological processes which alter their distribution. Barium, which is chemically similar to radium [6, 7], became a logical choice as chemical analogue for radium. Goldberg and Arrhenius [6] found high

concentration of radium in microcrystals of barium-bearing pellets; Szabo [7] reported that the surface sea-water radium:barium ratio is the same as the ratio in particulate phases formed within the sea. This evidence made barium a very plausible choice.

Barium distributions were measured in the ocean [9, 10] and several models were constructed in order to establish the radium-barium relationship [5, 10, 12]. Li et al [8] have established that ratio of radium-226 to barium is quite constant in Antarctic profiles. High precision measurements of barium and radium concentration in the ocean-water were performed on GEOSECS. Detailed profiles are available for comparison [2, 11, 13-16, 18, 19]. It is evident that Barium and Radium-226 correlate linearly in the South Pacific, Atlantic and Antarctic Oceans [2, 17, 18]. Li et al [8], Chung and Craig [2] observed that Ra-Ba relationship deviates from linearity in the Eastern Equatorial and North Pacific Ocean, with excess radium at greater depths. This deviation is generally attributed to the introduction of primary radium from sediments. The Ra/Ba ratio is not a constant, it varies significantly from location to location; a non-zero intercept of the Ra-Ba lines with the Ba-axis is also observed. The problem of why Ra-Ba show this particular relationship is not completely understood. It may merely be dis-

agreement in some analytical results among laboratories [17], or an indication of the difference in input mechanism between the two elements [2, 12, 17]. Radium has an areal source function, theoretically from all bottom sediments and the flux depends on sediment characteristics. Barium has a point source function, it is introduced through rivers. It will be necessary to make extensive studies on the variable source flux, before an exact correlation can be established between the two elements. However, the choice of Barium as chemical analogue for radium is a promising one.

Barium is now the most accurately determined trace metal in sea water. Its depth-distribution shows similar trends to alkalinity and silicate. Aside from potential use an an analogue system, studies of Barium distribution in the ocean may bring significant rewards to our understanding of the marine environment.

However, the mechanism governing the distribution of barium in the water column is not yet understood. Goldberg [5] proposed a non-biogenic model which states that the distribution is governed by the dissolution of barium sulfate, as the solubility product varies with depth. Church and Wolgemuth [20] later demonstrated that Ba is undersaturated with respect to the barite saturation value.

An alternate hypothesis is that barium is involved in the biochemical cycle. Revelle [24]; Goldberg and Arrhenius

[6] and Turekian and Tausch [25] observed high barium concentrations in pelagic sediments under high productivity regions. Bowen [21] reported that barium was concentrated in dry plankton samples, compared to sea water value, by factors of 450-4000. Bostrom [33], observed similar concentrations of barium. This leads to the conclusion that barium is involved with the biological cycle. Edmond [17], based on the evidence that the barium depth distribution profiles lack the depletion features which are characteristic of adsorption processes, such as those for Pb-210 [28], suggested that organisms are "actively" involved in barium transportation.

There is much dispute over the "carrier" organism for barium transportation. Among the choices proposed are calcareous foraminifera [24], radiolaria [6] and diatoms [26]. Goldberg [6], reported an extremely low, (0.02% of dry weight), content of barium in Miocene pelagic coccolith ooze. In more recent studies, Turekian and Tausch [25] and Thompson and Bowen [22] have come to the same conclusion: calcareous skeletons do not contribute significantly to the barium distribution picture. Bowen, [21] had reported enrichment, by factors of 16-78, of barium relative to calcium in littoral green algae. Arrhenius also reported concentrations of barium in protoplasm of live foraminifera. This suggested that if calcareous organisms are the carrier phases, barium will be

concentrated in the soft part. This is contrary to the findings of Broecker [12] and Edmond [17]. Comparing barium profiles with other hydrographic parameters, Broecker and Edmond found correlations of barium with alkalinity and silicate, but no resemblance to nitrate and phosphate. This led them to conclude that the "hard parts" rather than the "soft parts" of organisms are involved in barium transport.

Goldberg and Arrhenius [6] reported high concentrations of barium in siliceous fractions of pelagic sediment samples. Thompson [29] has also quoted a 0.25% dry weight barium content in diatomaceous cultures. A similarity between Ba and silicate profiles was reported by Chow and Patterson [9]. Based on these evidences and the excessively high Ra/Ba ratio in the deep ocean as compared to surface, Ku et al [30] suggested that silicious organisms, rather than calcareous organisms are the important carrier for radium. They further suggested that it is the test of siliceous organism that acted as carrier. Analyzing hydrographic data from the Antarctic Ocean, south of the polar front, where silicate effects diverge from alkalinity, Edmond [31] showed that silicate and radium have a linear correlationship, but radium and alkalinity diverge at the bottom. From these findings, he agreed with Ku's hypothesis.

These findings, however, do not necessarily exclude the

probability that the "organic part" of siliceous organism plays a role in barium transport. Plots of Ba vs Si in water columns show linear correlationship, but more than one linear region (different slopes) may exist within a single water column. A discontinuity is always observed aroung the region of 1 km. [Figure 3, 8]. Aside from cell-wall building [34, 35], silicate is also required for synthesis of macro-molecules in cytoplasm [37, 38]. It is also known that diatoms build up and maintain a large pool of silicic acid (up to 10% of total silicate) in cytoplasms [39]. The effect of organic transport may be small.

The various scattered lines of evidence all point to the vertical transport of barium and radium in the hard parts of organisms, probably in the silicious phases. However, given the complexity of observed Ba - Si relationships in the water column the process is not a simple one. The probability that zooplankton and other higher organisms which leave no simple trace of their activities also are important and cannot be ruled out [40, 41, 27].

MODEL

Edmond [17] has proposed a simple co-precipitation model of barium removal by siliceous organisms via a Raleigh fractionation process:

$$\frac{(Ba/Si)_t}{(Ba/Si)_{t=0}} = \left[\frac{(Si)_t}{(Si)_{t=0}}\right]^{[1-(Ba/Si)\ water/(Ba/Si)]}$$

Hence it is the Ba/Si ratio in the water that determines the effectiveness of barium removal. This may be extended easily to include all classes of organisms.

The dependence of elemental uptake on the concentration of the medium has been observed. Lund [49] has observed that phosphate uptake in lakes is dependent on concentration. Goldberg [48], through culture experiments, found a linear correlation between amount of uptake and phosphate concentration in the medium.

If model is valid, it implies that overall:

$$\left[\frac{\text{Barium}}{\text{Silicate}}\right]_{\text{plankton}} = \frac{[\text{Barium deep water} - \text{Barium surface water}]}{\text{Silicate deep water} - \text{Silicate surface}}$$

Edmond observed an anti-correlation between productivity and Ba/Si ratio in water column in the Arctic Ocean. [Fig. 5] The excess of silicate and barium between the Bering Sea bottom water at $\theta = 1.3$ and North Pacific deep water is 11 nm Ba/kg and 55 µm Si/kg. This gives a molar ratio for Ba/Si of 0.2×10^{-3}. The anomaly between the bottom water of Station 204 at 1.1° C and those at GIII is

about 40 nm Ba/kg and 40 μm Si/kg, giving a molar ratio of 1×10^{-3}. (From this calculation, the Ba composition of the carrier organism should vary 5 fold, from 400 ppm in the Arctic to 2000 ppm in the Tropics).

Since in silicate depleted water, (Si < 5μm/kg), barium is never less than 35 nm/kg, enrichment of deep water relative to surface water is approximately a factor of 5 for barium and 100 for silicate. The Ba/Si ratio in the water column can be approximated by: [17]

$$Ba = 36 + (5 \times 10^{-4})\ Si \qquad \text{[units in nm/kg]}$$

$$\text{i.e.} \quad \left(\frac{Ba}{Si}\right)_w = 36/Si + (5 \times 10^{-4})$$

Hence the Ba/Si ratio is a strongly decreasing function of the silicate concentration, especially at silica values <10μm/kg (Figure 6). Thus in tropical water, the ratio approaches 0.01 and in the Antarctic and North Pacific upwelling areas, the value drops below 0.001.

For a rough estimate of α - taking the value of surface water as being 3μm/kg silicate and 37 nm/kg barium and in North Pacific a deep water ratio of 100/170 - we have:

$$\alpha = (100/170) / (37/3) = 0.05$$

This represents a lower limit as $(Ba/Si)_{water}$ is much lower in Antarctic upwelling areas.

An independent estimate of α is proposed by Boyle (personal communication). He considers the ocean as being

in steady state:

$$\frac{dSi}{dt} = Ri^{Si} - R_R^{Si} = 0$$

$$\frac{dBa}{dt} = Ri^{Ba} - R_R^{Ba} = 0$$

R_i = rate of input

R_p = rate of removal by plankton

$$\frac{dBa}{dt} = Ri^{Ba} - \alpha\left[\frac{Ba}{Si}\right]_w R_P^{Si} = 0 \qquad \text{since } \alpha = \frac{\left[\frac{Ba}{Si}\right] \text{ plankton}}{\left[\frac{Ba}{Si}\right] \text{ water}}$$

$$\left[\frac{Ba}{Si}\right]_w = \frac{1}{2}\frac{Ri^{Ba}}{Ri^{Si}} = \frac{a}{\alpha}$$

where [Ba] = a [Si] + b shallow gradient.

Applying this model to various regions of the ocean gives $\alpha \sim 0.04$.

For Antarctic upwelling areas, assuming $\alpha = 0.1$, and observed surface sea-water values of 50 µm Si/kg, and 60 nm Ba/kg gives a molar ratio in diatoms of 1.22×10^{-4} = 100 ppm. For tropical silicate depleted water, surface water is 3µm Si/kg and 37.5 nm/kg giving a molar ratio of 1.23×10^{-3} = 2600 ppm. This is quantitatively in agreement with the mass balance in the water as discussed above.

In order to establish the validity of this simple model it is necessary to analyse oceanic plankton samples for their Ba:Si ratio and compare this with the ratio in the

waters in which they grow. It is unrealistic to analyze all species present. Three major classes of organisms, calcareous, siliceous and crustaceous should be collected in open ocean and subtropic upwelling areas. The Antarctic upwelling area where effect of calcareous organism is minimal, should also be sampled to give good comparison.

Laboratory plankton culture experiments may be used as a tool to test the validity of the fractionation model. From the previous discussion, silicious organisms may be the major carrier for barium. Studies on diatom cultures is the logical choice. Diatoms are the major group of primary producers in the ocean [48]. Diatoms require silica for normal growth and division [52, 42, 45]. Silica is taken up in the form of ortho-silicic acid $Si(OH)_4$ [34], polymerized and deposited as hydrated amorphous silicate to form the frustrule of the organism. [35, 36]. Silica is also required for the synthesis of macro-molecules inside the cytoplasm [37, 38]. The amount of silica in diatoms ranges from 25 - 60% of dry weight, and is lower in silicate starved cells [43, 49]. Efficiency of diatom utilization of silica is species dependent. Uptake of silicate conforms to a Michaelis-Menter type saturation kinetics [50]. The rate of uptake is dependent on the amount of Si in the growth medium [71]. In cultures where large amounts of silicate is present, the thickness of the silicified wall depends upon the

rate of cell division, more rapidly dividing cells deposit thinner shells [43]. However, in silicate depleted cultures, weakly silicified cells are observed. Plankton culture usually follow a characteristic growth pattern [44] (Fig. 9). The lag phase is a period for the innoculum to readjust to the new condition. If no limiting nutrient is observed, exponential growth can be sustained indefinitely. If there is a limiting nutrient, growth rate will decline, stabilize for a while and eventually stop. The amount of harvest depends on the initial concentration of the limiting nutrient. The Si content of cells from each step of the growth curve varies, cells retain their silicate content as long as they remain intact and viable [62].

By controlling the medium Si and Ba concentration, the rate and amount of uptake can be controlled. Also harvesting culture at different stages of growth will vary the ratio of the different cells. The uptake of silicate by diatom cells is not uniform with time, but takes place right before cell division is to occur. If the model is valid, the Ba/Si uptake by diatoms at that time is a constant proportional to the instantaneous Ba/Si ratio in medium.

$$\frac{\left[\frac{dBa}{dSi}\right]_{\text{diatom}}}{\left[\frac{Ba}{Si}\right]_{\text{medium}}} = \alpha$$

$$-\int \frac{dBa}{Ba} = \alpha \int -\frac{dSi}{Si}$$

$$\ln \frac{Ba^{\text{final}}}{Ba^{\text{initial}}} = \alpha \ln \frac{Si^{\text{final}}}{Si^{\text{initial}}}$$

$$\alpha = \frac{\ln \frac{Ba^{final}}{Ba^{initial}}}{\ln \frac{Si^{final}}{Si^{initial}}}$$

α can be calculated from initial and final conditions in the medium. If $\ln \frac{Ba}{Ba}^{f}_{i}$ is plotted against $\ln \frac{Si}{Si}^{f}_{i}$, the slope will give α. Excessive deviation from linearity implies α is not a constant. This model depends heavily on the assumption that:

$$[\frac{Ba}{Si}] \text{ plankton} = [\frac{Ba \text{ initial} - Ba \text{ final}}{Si \text{ initial} - Si \text{ final}}]$$

A plot of $[\frac{Ba}{Si}]$ plankton vs. $[\frac{\Delta Ba}{\Delta Si}]$ should give a line with slope = 1 passing through origin.

METHOD

Sample Collection -

Plankton samples were collected on two different research cruises. The first set was collected by the author in the South Atlantic Ocean, along the coast of West Africa, during Chain Cruise 115-2. (December 1972 - January 1973). Track and location of stations are shown on Map 1.

Sample collection was performed on station while large volume pumping for particulate matter was in process. Precautions were taken to prevent contamination from human activities.

Sampling was with a 30 cm diatom plankton net with a mesh aperture size of 56 µm. The net was attached to the hydrowire and slowly raised and lowered through the water column, covering a depth range of 0 - 50 meters. Each station was 1 to 2 hours long. Cells attached to the side of the net were washed down with surface sea water and concentrated in the collection jar at the cod end.

Upon harvest, samples were filtered through a 10 µm nylon net. The samples were not washed with distilled water to avoid elemental loss due to osmotic bursting of cells. The amount of barium and silicate contamination introduced by the left-over sea water should be negligible.

Immediately after filtration, the samples were dried on filters under heat lamps. Sample size ranged from 50 - 250 mg.

Water samples for silicate and barium analysis were collected, at the appropriate depths, between plankton tows. A few filtrates from the plankton concentration procedure were saved for analysis. Silicate was analyzed on ship board within a few hours upon collection. Barium samples were stored in pre-cleaned and pre-weighed polyethylene bottles. Barium analysis was performed at MIT within 6 months.

The second set of samples was collected by J.M. Edmond during a GEOSECS Cruise in the Antarctic Ocean, south of New Zealand, on board R/V Melville. The track and stations are shown on Map #2. Sampling was achieved by continuous pumping (5 - 10 hrs) of sea water from varying depths between 0 - 50 meters through 10μ nylon net. The samples were then harvested and dried immeditely in an oven on board ship. The sample size ranged from 1 - 5 gms. Silicate was analyzed on board, and barium was analyzed back at MIT.

Major species identification was performed on an Olympus POM microscope, equipped with a polarizer, at 400 x magnification. Samples were grouped into three categories: crustaceans, calcareous and silicous organisms, depending on the major species in the samples [63, 73].

Diatom Cultures -

Skeletonema costatum(Greville) Cleve, (Fig. 10), a neritic algae was chosen for the culture experiment. It is widely distributed in all seas. The cells are lens-shaped, elliptical or cylindrical with rounded ends. The diameter of the valve is 8μ - 15μ, pervalvar axis is 4μ - 12μ. Chain formation by means of spines interlocked midway between adjacent cells is very common, especially when the culture is dense. Auxospore formation is quite common, [47, 54]. An average of 30.6% Si to dry weight is reported [43]. The half-way saturation constant is 0.8 μm/ℓ and the species can take up silica from the medium down to a concentration of 0.2 μm/ℓ [51]. The stock of Skeletonema costatum was originally obtained from Dr. Gillard of Woods Hole Oceanographic Institute. Bacteria free stock cultures were maintained in "f/2" medium by Prof. Morel's research group. These cultures were the innoculum used throughout the experiment.

Medium -

It was originally intended to use enriched artificial sea water [56] as the culture medium. However, a large amount of Ba (≃360 nmoles/kg i.e. about 8 - 10 times surface ocean water values) was introduced with the chemicals, mainly from NaCl. Enriched sea water medium was therefore used instead.

Surface sea-water was obtained from Woods Hole Oceanographic Institute every month and was stored in polypropylene jugs. The medium used was a slight modification of Dr. Gillard's (Woods Hole Oceanographic Institute, personal communication) "f/2" culture medium [Table 1 - 5]. Ferric chloride and di-sodium EDTA was used as chelating agent in trace metal stock solution. Variable amounts of silica (as $Na_2SiO_3 \cdot 9H_20$) and barium (as $BaCl_2$) were added to some mediums to achieve variation of the Ba/Si ratio in the medium. The medium was made fresh every time.

Sterilization was achieved by filtration, Nucleopore filters 0.2μ , 47mn, and a Millipore Sterifil system were used. To check for contamination by filtration, pre-filtered and after-filtered medium were drawn for barium and silicate analysis.

Cultures were grown in polycarbonate Erlenmeyer flasks. 500 ml of medium was used for each culture. The medium was innoculated with ≃ 1 ml stock culture to give $\simeq 10^3$ cell/ml. All cultures were grown at 20°C, in white light supplied by 4 Sylvania "cool-white" fluorescent lamps. A 14-10 hrs light-dark cycle was used. A control was used to check for non-biological removal.

Cell density was measured by counting with a Zeiss phase contrast microscope. The whole field of the hemocytometer slides was counted. Average of 5 counts was taken. To

establish a silicate uptake, 30 ml culture was drawn daily from several flasks, and the sample was filtered and analyzed for silicate.

Cultures were harvested at variable times of growth. Cells were collected by centrifugation at 2000 rpm for five minutes. The supernant was filtered, and analyzed for barium and silicate. The diatom cell pellet was transferred into two 5 ml teflon beakers by distilled water and dried in an oven at 85°C.

Barium in Culture Medium and Sea-Water

Barium was analyzed by the isotope dilution technique described by Bacon and Edmond [11]. Isotopic analysis was performed on a 60°-sector, 6"-radius mass spectrometer. Peak heights were recorded by automatic digitizer. Barium 135-spike, which contained 95% of the isotope, was obtained from Oak Ridge National Laboratory. The spike was dissolved in 1x vycor distilled HCl and the concentration standardized with Optronic grade barium chloride. The isotope composition of the spike and common barium was determined.

Upon collection, barium samples were spiked with a known amount of Ba^{135} and stored in precleaned and preweighed polyethylene bottles.

A weight correction of 3.2 mg/day was used to account for losses by evaporation. An ion-exchange column packed with Dowex 50wx8, 2.5 cm diameter, 12 cm length was used to

separate the barium from sea salt. Approximately 200 ml sample was loaded on the column for each determination.

The ratio of 138/135 was calculated from 3 sets of peaks, and an average of 6 peak ratios was used.

Equation for the calculation:

$$\text{Ba-135} = \left[\frac{\text{Ratio}^{(138/135)\text{obsvd.}} - \text{Ratio}^{(138/135)\text{spike}}}{\text{Ratio}^{(138/135)\text{natl.}} - \text{Ratio}^{(138/135)\text{obsvd.}}}\right] \left[\begin{matrix}\text{conc of} \\ \text{Ba-135 in spike}\end{matrix}\right] \left[\begin{matrix}\text{amt of} \\ \text{spike}\end{matrix}\right]$$

$$\text{Ba total} = \left[\frac{\text{n mole Ba-135}}{\text{abundance of Ba-135}}\right]$$

Total Ba was normalized to weight and expressed in units of nmole Ba/kg. The precision of the analysis was established by duplicate analysis. The effects of different isotope ratios was determined by analyzing a set of samples from the same stock of sea-water, but with different amounts of spike. Blank determinations were determined periodically to ensure the system was free of contamination.

Barium in Plankton Samples

An attempt was made to analyze barium in diatom cells with Perkin-Elmer Atomic Absorption Spectro-photometer Model 403, equipped with graphite furnace. A standard calibration curve was successfully obtained (Fig. 11). However, there were problems in dissolving whole cell samples; a high background signal was observed, as a result of smoke produced by the cell remains. The technique is not quite desirable.

An alternate method employing isotope dilution technique and mass spectrometry proved to be more useful.

The whole reaction procedure to reduce barium in plankton cells to a nitrate form was performed in 5 ml teflon beakers. 15 - 20 mg of dried cells was spiked with Ba-135. 20 drops of ultra-pure HF (J.M. Baker - Ultrex) was added to decompose the silica frustrule. The beakers were left standing for 24 hours at room temperature. The sample was then dried under a heat-lamp. Another 10 drops of HF was added to complete the reaction, and it was taken to dryness again. 10 drops of perchloric acid was then added to drive off the remaining floride ions [57]. The perchloric acid was taken to dryness and heated until all fuming ceased. A charred residue was left. Approximately 1 ml of 6N HCℓ was added, and taken to dryness. 15 more drops of perchloric acid was added and let evaporate to dryness until all fuming ceased. A few drops of nitric acid, served to change the barium to nitrate state, was added and brought to dryness. The samples were then analyzed on the mass spectrometer. The precision of the technique and the effect of various isotope ratios was checked as described in the previous section. The total of barium was calculated as before and was expressed in nmoles/mg dry weight.

All oceanic samples were analyzed in duplicate. Two sets of samples, and 2 blanks were prepared each time. The

average of duplicates was used.

In an effort to find out where the barium was concentrated in the cell, a sample was soaked in 1:1 acetone: alcohol solution, which dissolves the outer membrane but will not lyze the cells, was used to dissolve the barium in the outer membrane. The suspension was filtered and filtrate saved for barium analysis. The cells were then soaked in 6N HCℓ for a day in an attempt to leach all barium from the organic matter. The sample was filtered and the filtrate saved for barium analysis. Barium in the filtrate was analyzed by atomic absorption, using a graphite furnace.

A similar experiment was constructed employing the isotope dilution technique. If HCl and HNO_3 were substituted for HF, the silicate frustrule wall remained intact. The sample went through all other steps in the method.

Silicate Analysis in Medium and Sea-Water

Dissolved silica was analyzed following the procedure of Strickland and Parsons [58] on a Beckman DU-2 spectrophotometer. Sodium floro-silicate at concentration 2.05 and 4.08 μm/ml was used as standards. Standard calibrations for both sea-water and distilled water were performed periodically. Artificial sea water was used for sea water blanks. A constant calculated from the ratio of the slopes of sea water: distilled water was used to correct for salt effects.

Silicate analyses were performed within one day. The

samples were refrigerated until analysis. Duplicates were analyzed on all samples. Distilled water standards, distilled water blank and synthetic sea water blank were included with each set of analysis. Average of duplicates were taken. Units expressed in μm Si/ℓ of sample.

Silica in Plankton Samples

A modification of the procedure described by Hurd [59] was used to extract silica from plankton cells. 15-20 mg dry cell samples were soaked with 5% Na_2CO_3 overnight in a 4 oz polypropylene bottle. The bottles were weighed and placed in a water bath at 85°C for 10 hours. The samples were cooled to room temperature and reweighed. Weight lost during heating was corrected. The sample was then filtered through 0.2 μ millipore filter. 1 ml of the filtrate, diluted to 25 ml with distilled water, was analyzed for silica content. The cells were washed twice with distilled water. The whole procedure was repeated once. Only 50 ml of 5% Na_2CO_3 was used. Silicate was analyzed following the procedure of Strickland and Parsons [58]; an extra amount (2ml) of HCl was added to the molybdate reagent to correct the pH. To ensure silica was stable throughout the extraction process, calibrated standards and controls were analyzed.

All oceanic plankton samples were analyzed in duplicate. Two sets of samples, with 2 blanks, and 2 standards were

prepared each time. The amount of silicate observed on second extraction was added to the first extraction. An average of the duplicates was used. The units were expressed in μm Si/mg dry wt.

Lab-ware Cleaning

It is important that contamination be kept to a minimum. Extreme care was taken to clean all the plastiware. All culture flasks and sterilfil filtration system were cleaned with distilled H_2O and then let soak in 1:1 nitric acid solution until used. Nucleopore filters were soaked in 2x distilled HCl for a few days, and washed with distilled water.

Teflon beakers were soaked in water and wiped clean of residue cells with Kimwipes. They were then boiled in 1:1 hydrochloric acid for 2 hours to oxidize the residue samples, and soaked in 1:1 nitric acid until used. Only 2x vycor distilled H_2O was used in final rinsing.

To avoid contamination of silicate from glass-ware only plastic-ware was used. Polypropylene bottles and filter systems were washed with detergent, rinsed with distilled H_2O and then soaked in 5% Na_2CO_3 until use. Filters were washed with 5% Na_2CO_3 before use.

RESULTS AND DISCUSSION

The isotopic abundance of barium for both natural and spike solutions was analyzed. A ratio of 138/135 of natural solution to spike solution was determined (Table 6).

Barium in the medium and seawater samples could be analyzed with high accuracy. Less than 0.87% error was introduced with duplicate samples (Table 7). Standards, with different isotope ratios, gave excellent agreements (Table 8). Blank determinations (Table 9) were low and stable with time, which showed the system was free from contamination throughout the year.

Precision for barium analysis in diatom cells was adequate for the purpose. Duplicates could be analyzed within 5% error (Table 10). Standard calibration with varying isotope ratio gave reasonable agreements, maximum error of 2.6% was introduced (Table 11). Analytical grade HF gave a high barium blank, approximately 5 nmole/ml; Ultrex-graded HF was used throughout the experiment. Blanks were stable and low, indicating a contamination-free system (Table 12). HCl and HNO_3 were substituted for HF in two sets of samples. The cells were then processed through the whole analytic-procedure as described in the methods section. An average

of 70% of total barium was found in these fractions (Table 13). This indicated barium uptake into the organic fraction. The results may not be conclusive as the vigorous treatment might have leached barium from the siliceous frustules. Radioactive tracing, using Ba-133 as tracer, may be the best solution.

The analytical error in determining dissolved silica is 2.5% (Figures 12 and 13). Variation of the standard slope with time was small. The correction factor for salt effects was calculated to be 0.914 (Table 14).

To assure there is no silicate loss during the extraction process, a set of standards were processed through the entire procedure (as described in the methods section), and another set was left as control. There were no significant differences in absorbance between these two sets of standards, showing no silicate loss during extraction (Figure 14). Each sample was extracted twice for silicate. The first extraction contained most of the silicate, an average of 2.6% was found in second extraction. The extraction technique was effective.

Results of analysis on duplicate samples show agreement within 5%. Determination using NaOH to extract silicate from diatom cells showed no significant difference (Jim Bishop, personal communication).

Diatoms were cultured over a period of twelve months. Silicate analysis and diatom cell count were made daily. The results were plotted (Figures 15, 16, 17). The small inversion point observed in culture A10 might be a result of slight synchronized division. Chains were commonly seen specially with dense cultures. Large cells, which might be auxospores, were frequently observed in exponentially growing cultures. The cultures were innoculated at concentrations of 5×10^3 to 5×10^4 cell/ml. Two to four days of lag phase were observed. Exponential growth was maintained for four to six days. Silicate was the only limiting nutrient in this medium. In culture A3, steady state was reached when silicate was depleted. Exponential growth was resumed when more silicate was added (Figure 17). The size of crop harvested and rate of growth was dependent on the initial concentration of silicate. Culture A15, which had initial silicate concentration of 33.3 µm/l, doubled itself in 48 hours and reached a cell concentration of 10^5 cell/ml at steady state growth (Figure 15). Culture A10 which had initial silicate concentration of 65.7µm/l, grew at 1 division/day and reached a cell concentration of 2×10^6 cell/ml at steady-state growth (Figure 16). These growth rates and cell-densities were lower than previously reported values (43, 45). This low growth rate was largely due to

insufficient lighting. Later cultures which received higher intensity illumination grew at a higher rate. An average of 30 mg dry weight of cells were harvested. A total of 25 cultures were grown. Barium and silicate content for diatom cultures is reported in Table 15. The barium content of the cells ranged from 0.02 to 0.26 nmol/mg. Results are in good agreement with Thompson's (29) reported value of 14ppm Ba/ash. A four-fold variation of Ba/Si ratio in cells was observed. This reflected the variation of the medium composition. Barium contamination was serious in the beginning. 5nm Ba/Kg contamination was observed for the filtration process only. This contamination was not observed after the cleaning procedure for all laboratory ware was adopted. Results of barium analysis on medium are listed in Table 16. Only the filtered sample value is included. Total removal of Ba from the medium is calculated.

There was no difference in silica concentration between filtered and unfiltered medium. Results of silicate analysis on medium and seawater are listed in Table 17. Only the filtered sample value average of the duplicates, are included. Total removal of Si from medium was calculated.

The ratio of barium:silica in cell was plotted against

ratio of removal of the elements (Fig. 18). Least square linear fit, with line passing through origin gave a slope of 0.83; by elimination of two points which were obvious departures from line gave a slope of 0.92, correlation coefficient was 0.66 (Table 18). Assuming that analysis of barium and silicate in plankton sample were accurate, the deviation of slope from unity implied that either silicate was added or barium was removed from medium. Since probability of silicate contamination was low, non-biological removal of barium from medium is the most probable solution.

Mass balance calculations are not feasible in this case, as only a fraction of the cells in the culture were collected. Indirect calculations can establish amount of non-biological removal; if no non-biological removal, total uptake of the element is equal to the total removed.

$$[Ba/Si]\ \text{cell} / [\Delta Ba/\Delta Si] = 1$$

Taking average silicate removed from medium $\Delta Si = 42\ \mu m/kg$, and (Ba/Si) plankton = 0.19. $\Delta Ba = 8$ nmole/kg. For a ratio of 0.92, $\Delta Ba = 8.7$ nmole/kg. Therefore 0.7 nm/kg barium was non-biologically removed. This number of course depends on culture conditions. Thompson [29] has observed 14ppm Ba in the medium precipitate. The precipitation only occurred occasionally and was in varying amount. Correction with a constant would have been biased. Inspecting the graph, aside from a few large departures, the data conformed to a line of

unit slope. Assuming all points conformed to this line, a maximum of 8% error was introduced. Mass balance calculations should be strictly followed in future experiments.

Ratios of $Ba_{(final)}/Ba_{(initial)}$ and $Si_{(final)}/Si_{(initial)}$ were computed (Table 19). ln $Ba_{(final)}/Ba_{(initial)}$ was plotted against ln $Si_{(final)}/Si_{(initial)}$. A least squares linear fit through the data gave a slope of 0.034. Correlation coefficient = 0.55 (Figure 19). Sample A14 deviated significantly from the curve; the point was rejected. Recalculation gave a slope = 0.03, correlation coefficient = 0.60. 18 points were involved in the calculation. α may be accepted as a constant. The scattering of data reflected the dynamics of the system.

8 stations and a total of 18 samples were collected during the Chain Cruise 115-2 to the South East Atlantic, along the coast of Africa. Station 1- sample 1 was rejected due to obvious sea-salt contamination. A total of 7 samples were collected in the Antarctic cruise. Silicate analysis for sea water was performed on board ship. Barium analysis was performed, back in the laboratory on stored sea-water and filtrate samples. Silicate in these bottles was redetermined. These laboratory rerun silicate values showed slight deviation from ship-board value. No special trend was observed. This was expected as nutrients are not stable with storage. All filtrates gave higher barium and silicate

values than their sea-water counterpart. The difference was much higher than could be accounted for by variation due to storage. Plankton ranged quite a lot in size and shape. Plankton smaller than 1 μ and larger than 150μ existing in the same water mass are not uncommon [63]. There might be a lot of plankton, <10μ, collected in the filtrate. The cells might have slowly decayed and released the Ba and Si content into the water. This will account for the high Ba/Si content in the filtrate samples. The ship-board value for silicate is used. Values for barium and silicate in sea water are recorded (Table 22, 23).

Only barium values from sea water analysis were used for subsequent calculations. Microscopic observation of the samples showed a diversity of species. Atlantic samples were separated into 3 groups (Table 20), crustaceous organisms, calcareous organisms, and siliceous organisms. In the Antarctic samples, only 2 types of major organisms were observed--siliceous diatoms and crustaceous organisms; calcareous organisms were not present. However the diatom samples show several distinct species (Table 21). Barium and silicate content of plankton samples are reported in tables 22, 23. Silicate was found to range from 0.1 μm/mg in crustaceous samples to 8μm/mg in Antarctic diatoms, representing a variation of 80 fold. Barium varied from 1.6 nm/mg in crustaceous organisms to 0.25 in calcareous

organisms, represented a six fold variation. This resembles the variation in the water column. It is important to note that it is the combination of different classes of organisms that produce this effect. This indicates more than one carrier phase is responsible for Ba transportation. By separating the plankton samples into groups observed under microscope, barium vs. silicate content in plankton was plotted by groups [Figure 20]. A linear least square fit on all data gave a negative slope of 0.118 and intercepted at barium concentration of 0.137. However, if least square fit was fitted for each group of data, crustaceous organisms give a slope of 2.39, correlation coefficient = 0.79; calcareous organisms give slope of 1.5;correlation coefficient = 0.8. The positive slopes indicated barium was concentrated. The siliceous organims, from the Atlantic Ocean or Antarctic Ocean gave negative slopes, indicating barium is excluded compared to silicate.

The ratios of Ba:Si in plankton and sea water were calculated [Table 22, 23]. The data was again separated into the grouping described by microscopic observation. [Ba/Si] plankton was plotted against [Ba/Si] water [Figure 21]. Three different lines are observed for Atlantic plankton samples. The Antarctic sample does not show specific trends. Straight lines, passing through the origin, were fitted through data of each group, by least square linear fitting method. A different

α is observed for each group. It is also shown that each group of organisms occupies a specific area in the graph of Si content in cell vs. [Ba/Si] cell [Figure 22]. The cultured diatom sample was concentrated in one small area [Figure 1] (note the difference in vertical scale). This necessarily implied that all the plankton species participated as carriers for barium. It is the addition effect that governed the barium distribution in the water column. In areas where not all classes of organisms are present (e.g. Antarctic Ocean), species variation dominate the barium distribution in the water column.

SUMMARY AND CONCLUSIONS

Radium 226 is a possible time-tracer for oceanic circulation processes. However, radium is known to be involved in the biochemical cycle, and it does not have a stable isotope to correct for the cyclic effects. The success of using radium as time-tracer hence depends on a good analogue system. Barium is presently the best prospect as a chemical analogue for radium.

Barium is also involved in the biochemical cycle in the ocean. Edmond has proposed a model which states that barium is removed by coprecipitate with silicate in tests of siliceous organisms. The efficiency of removal of barium depends on the barium:silicate ratio in the water. The ratio of [Ba/Si] plankton : [Ba/Si] medium is a constant, α. α is found to be equal to $\sim$ 0.05 by two separate sets of assumptions. The predicted molar ratio of barium:silicate in plankton is consistent with the observed variation in the ocean. As an attempt to establish the validity of the model, culture diatoms and oceanic planktons and the medium were analyzed for barium and silicate.

Skeletonema costatum (Greville) Cleve, a diatom, was cultured in batches over a period of one year, a total of nineteen samples were collected. Twenty-five plankton samples from Antarctic Ocean and South East Atlantic Ocean were collected during two separate cruises. Depending on the

major type of organisms found in each sample, the South Atlantic samples were separated into three groups. Mainly diatoms were found in the Antarctic Ocean samples, different species were observed.

From analysis of cultured diatoms and the medium, it is found that α is a constant for the species. Analysis of ocean plankton samples and seawater showed that barium uptake conforms to the fractionation model; however α is species dependent. Each of the different groups (calcareous, siliceous, crustaceous) of organisms had a different α . Evidence also supports the view that all these classes of organisms is involved in barium transport. Effect of each group of organism on barium removal depended on abundance of the particular carriers in the water.

Barium is currently the most accurately determined trace-metal, and it shows corelationship with other oceanic parameters. Investigations on barium distribution patterns and its carrier mechanisms will be beneficial to our understanding of the marine environment. Presently, data on elemental composition, especially barium, of oceanic planktons are too sketchy; more analysis should be performed before a firm conclusion can be made.

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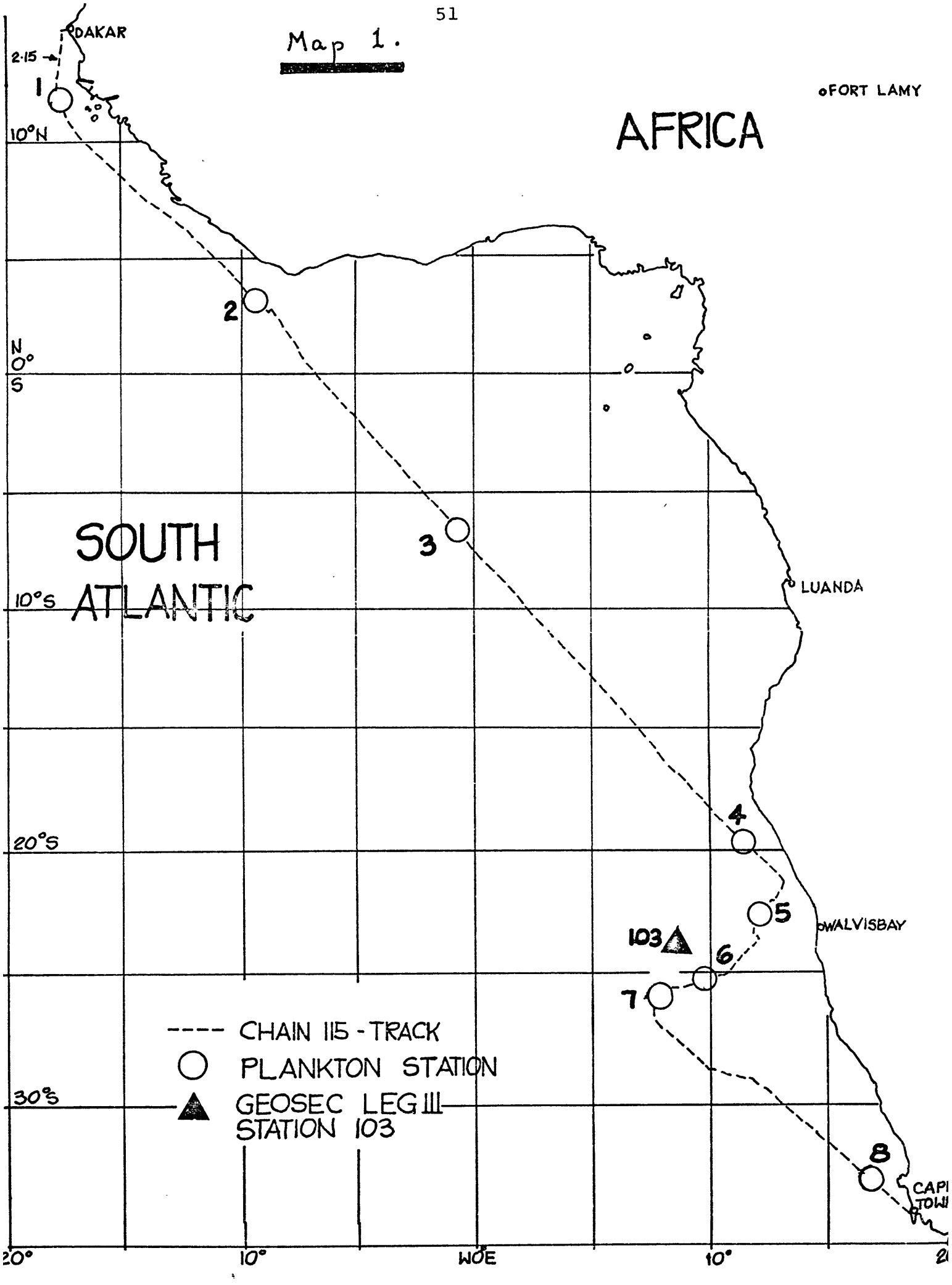
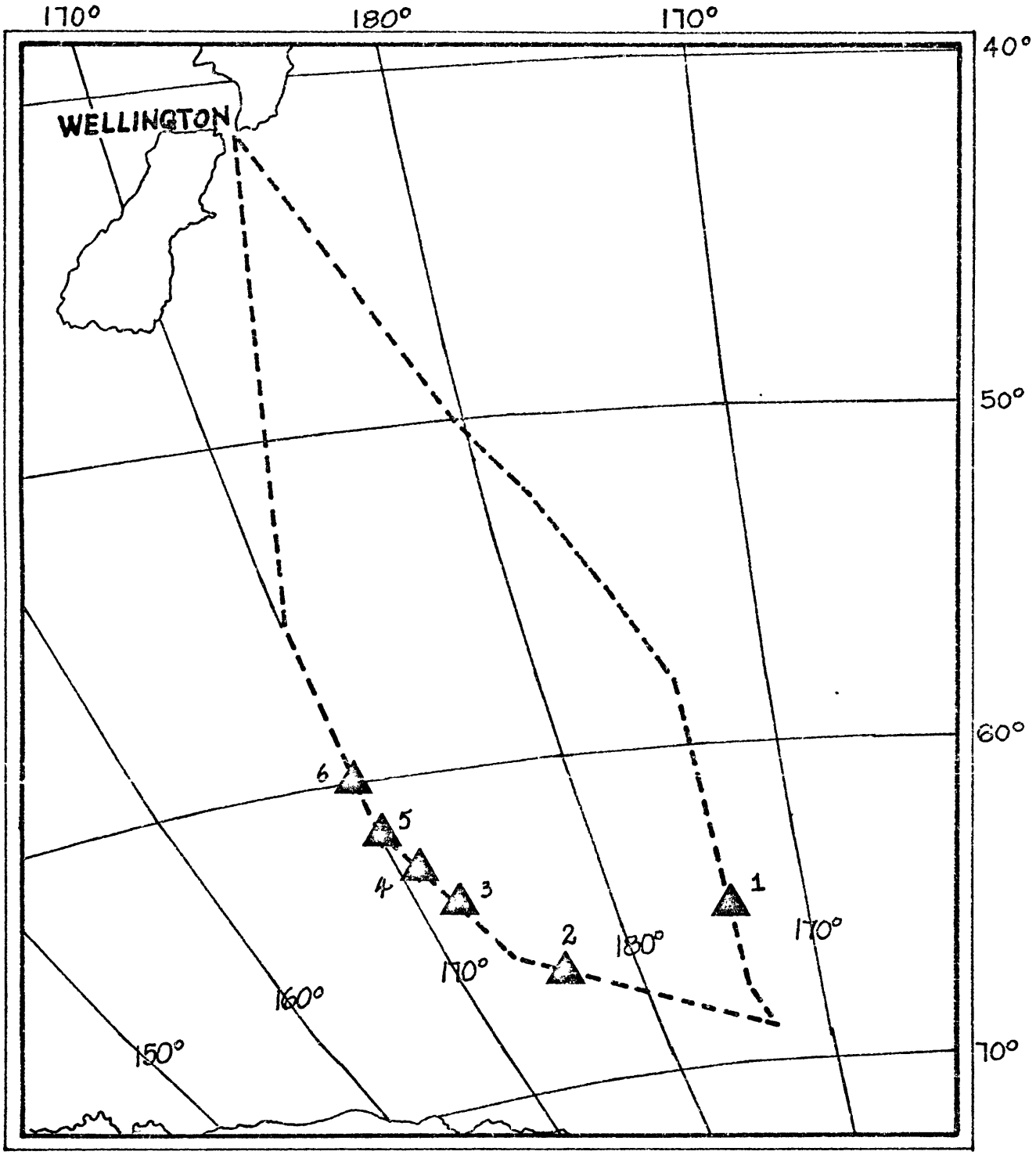

Map 1.
DAKAR
2·15
1
10°N
FORT LAMY
AFRICA
2
N
0°
S
SOUTH
ATLANTIC
3
10°S
LUANDA
4
20°S
5
WALVISBAY
103
6
7
CHAIN 115 - TRACK
PLANKTON STATION
GEOSEC LEG III
STATION 103
30°S
8
CAPE TOWN
20°
10°
W0E
10°



Track of R/V Melville
Geosec Leg 7

▲ Plankton Sampling Station
--- Track

Map 2

TABLE 1

Composition of enrichment "f/2"

Major nutrients (stock solutions are describe in Table 2)

$NaNO_3$	75 mg (883 µM)
$NaH_2PO_4 \cdot H_2O$	5 mg (36.3 µM)
$Na_2SiO_3 \cdot 9H_2O$*	varying

Trace metals (primary and working stock solution is given in Tables 3 and 4

$Na_2 \cdot EDTA$*	4.36 mg
$FeCl_3 \cdot 6H_2O^+$	3.15 mg (0.65 mg Fe or ca 11.7 µM)
$CuSO_4 \cdot 5H_2O$	0.01 mg (2.5 µg Cu or ca 0.04 µM)
$ZnSo_4 \cdot 7H_2O$	0.022 mg (5 µg Zn or ca 0.08 µM)
$CoCl_2 \cdot 6H_2O$	0.01 mg (2.5 µg Co or ca 0.05 µM)
$MnCl_2 \cdot 4H_2O$	0.18 mg (0.05 mg Mn or ca 0.9 µM)
$Na_2MoO_4 \cdot 2H_2O$	0.006 mg (2.5 µg Mo or ca 0.03 µM)
$BaCl_2 \cdot 2H_2O$	varying

Vitamins (working stock solution is given in Table 5)

Thiamin·HCl	0.1 mg
Biotin	0.5 µg
B_{12}	0.5 µg

Seawater † to one liter

Source - Dr. R. Gillard, Woods Hole Oceanographic Institute

TABLE 2

Stock solutions for major elements

(n% [W/V] means n grams brought to a volume of 100 ml with distilled water.)

The following are made 10^3 x more concentrated than in the final medium. Use 1 ml per liter of seawater to obtain medium "f/2", "h/2", or "f/2-Beta".

Material	Stock solution, % W/V
$NaNO_3$	7.5
$NaH_2PO_4 \cdot H_2O$	0.5
$NaSiO_3 \cdot 9H_2O$	3 (heat to dissolve if necessary)

Stock should be refrigerated and made fresh every month.

Source: Dr. R. Gillard, Woods Hole Oceanographic Institute

TABLE 3

Primary stock solutions for trace elements

(n% W/V means n grams brought to a volume of 100 ml with distilled water)

Salt	Primary Stock, % W/V
$CuSO_4 \cdot 5H_2O$	0.98
$ZnSO_4 \cdot 7H_2O$	2.2
or	
$ZnCl_2$	1.05
$CoCl_2 \cdot 6H_2O$	1.0
$MnCl_2 \cdot 4H_2O$	18
$Na_2MoO_4 \cdot 2H_2O$	0.63

It is convenient to make primary stocks of individual trace metals, with the elements 10^6 x more concentrated than in the final media "f/2" etc. A formulation is suggested above. Note that the sulfate salts are best because precipitation is minimized.

Source: Dr. R. Gillard, Woods Hole Oceanographic Institute

TABLE 4

Trace metal working stock solutions, EDTA chelated

Trace metal stock solution, using ferric chloride and di-sodium EDTA. Dissolve 3.15 g $FeCl_3 \cdot 6H_2O$ and 4.36 g Na_2 EDTA in ca 900 ml of distilled water; add 1 ml of each trace metal primary stock, (Table 5) and bring to one liter. pH is ca 2.0. The solutions remains clear if left at pH 2.0. If titrated to ca pH 4.5 (taking ca 7 ml of N NaOH), a precipitate will form, resembling that in the solution made with ferric sequestrene.

Use 1 ml/l of this stock solution to make medium "f/2" or "h/2". Even if the trace metal stock solution is left at pH 2.0, the effect on the pH of a sea water medium is negligible unless a large amount is used. (Eight time the usual amount [8 ml/l] lowered the pH of "f/2" from 7.8 to 7.2).

Source: Dr. R. Gillard, Woods Hole Oceanographic Institute

TABLE 5

Vitamin primary stock solutions and vitamin working stock solutions

Primary stock solutions.

Biotin is obtained in crystalline form; allow for about 4% water of crystallization. A primary stock solution is made containing 0.1 mg/ml by weighing about 10 mg and adding distilled water, 9.6 ml for each mg of biotin. Make the solution slightly acid if it is to be autoclaved. Keep the solution sterile and frozen.

Vitamin B_{12} is similarly obtained as crystals and 11% should be allowed for water of crystallization. Weigh (or buy in weighed amounts) and make a primary stock solution having 1 mg/ml. Acidify the solution if it is to be autoclaved, and keep sterile and frozen.

Primary stocks can be put up in ampoules or small screw-capped test tubes.

Vitamin working stock solution

To make the vitamin stock solution, bring 1.0 ml of biotin primary stock and 0.1 ml of B-12 primary stock to 100 ml and add 20 mg of thiamine HCl. No primary stock of thiamine is needed.

The vitamin stock solution is dispensed in 1, 2 or 5 ml lots in ampoules or in 10 ml lots in screw-capped test tubes, autoclaved, then stored in a refrigerator. Use 1/2 ml per liter of final medium, adding before autoclaving. One-tenth

this concentration is probably always adequate. If the ampoule is opened and the contents not completely used, freeze the remainder.

Source: Dr. R. Gillard, Woods Hole Oceanographic Institute

TABLE 6

Percent atomic abundances of isotopes measured in normal barium and in spike.

	130	132	134	135	136	137	138	132/135
Natural	0.11	0.11	2.45	6.56	7.85	11.24	71.69	10.928
spike	-	-	0.46	93.53	1.55	0.83	3.64	0.0389

TABLE 7

Replicate analysis of Woods Hole Surface Sea Water

Sample		Ba nm/kg
1		49.72
2		50.00
3		50.10
4		50.11
5		50.89
	mean	50.16
	Standard Deviation	0.87%

TABLE 8

Effects of varying isotopic - ratio on barium analysis of sea water samples

Standard	amount spike	Ratio 138/135	Ba content in sample nm/kg
blank	0.2	0.0651	0.254
1	0.1	3.7534	53.71
2	0.2	2.2867	55.67
3	0.3	1.6537	56.04
4	0.4	1.2941	56.17
5	0.5	1.0595	55.99
6	0.6	0.9097	56.13
7	0.7	0.7975	56.31
8	0.8	0.7010	55.96
9	1.0	0.5800	56.21
10	1.4	0.4270	56.29

Mean = 55.848

Stand. deviation = 0.774

= 1.4%

Mean of 4-S = 56.11

Stand. deviation = 0.14

= 0.25%

TABLE 9

Barium blank determinations on sea water samples

Date	Ba nm/kg
5/29/74	0.332
7/15/74	0.564
7/22/74	0.483
8/6/74	0.140
11/7/74	0.332
12/30/74	0.431
1/10/75	0.334
2/10/75	0.246
3/25/75	0.252
4/23/75	0.128
5/16/75	0.268
6/19/75	0.160
7/13/75	0.209
mean	0.298 $\pm$ 0.13

TABLE 10

Replicate analysis of GEOSECS plankton samples

Station		Ba nm/mg
GEOSECS #1	1.	0.606
	2.	0.613
	3.	0.635
	mean	0.618
	Standard deviation	2.4%
GEOSECS #3	1.	0.957
	2.	0.995
	3.	1.105
	mean	1.019
	Standard deviation	7.5%
GEOSECS #4	1.	1.017
	2.	1.035
	3.	1.041
	mean	1.031
	Standard deviation	1.2%

TABLE 11

Effect of varying isotopic ratio on barium analysis of plankton samples.

	amount of spike ml	Ratio 138/135	Ba nm/kg content in sample
Blank	0.2	0.076	0.36
1	0.1	1.3654	0.381
2	0.15	0.9845	0.382
3	0.2	0.7651	0.382
4	0.25	0.6250	0.381
5	0.3	0.5188	0.375
6	0.35	0.4900	0.404
		mean =	0.384
		S. D.=	2.6%

TABLE 12

Barium blank determination on plankton samples

Date	n mole Ba
4/28/75	0.157
4/28/75	0.151
5/18/75	0.305
7/15/75	0.216
8/13/75	0.556
8/13/75	0.163
8/25/75	0.04
8/26/75	0.051
	mean = 0.205 ± 0.17

TABLE 13

Barium in organic fraction of plankton

Sample	Treatment	Ba nm/mg	% of total
GEOSECS #4	HF	1.03	100%
	HCl	0.61	59%
	HNO_3	0.66	64%
GEOSECS #1	HF	0.62	100%
	HCl	0.48	77%
	HNO_3	0.52	84%

TABLE 14

Least square linear fit for silicate standard calibration

	date	slope	intercept	standard error
dist H_2O	5/7/74	0.0117	0.001	0.001
	12/18/74	0.0117	0.001	0.002
	5/10/75	0.0118	0.003	0.004
	7/15/75	0.0112	0.002	0.003
mean		0.0116		
stand. dev.		2.3%		
Sea H_2O	5/27/74	0.0105	0.004	0.002
	12/28/74	0.0104	0.004	0.004
	5/3/75	0.0105	0.005	0.002
	8/6/75	0.0110	0.005	0.001
mean		0.0106		
stand. dev.		2.5%		

mean of sea water slope/mean of dist. H_2O slope = 0.914

TABLE 15

Barium and Silica Concentration in cultured diatom cells

sample	total sample harvest mg	Ba nm/mg	Si µm/mg	Ratio Ba/Si x 10^{-3}
A3	36.8	0.262	0.897	0.292
A4	30.2	0.131	0.641	0.204
A5	47.4	0.241	0.845	0.285
A7	16.4	0.093	0.816	0.114
A8	14.57	0.192	0.48	0.4
A9	25.6	0.059	0.367	0.161
A10	32.4	0.110	0.657	0.168
A11	36.7	0.069	0.516	0.134
A12	31.1	0.112	0.536	0.209
A13	35.0	0.061	0.740	0.082
A14	19.5	0.14	0.89	0.157
A16	26.0	0.062	0.597	0.104
A17	26.3	0.021	0.853	0.024
			mean =	0.1795
			S.D. =	55.8%

TABLE 16

Concentration of barium in before and after growth medium

Sample	Initial barium concentration nm/kg	Final barium concentration	ΔBa nm/kg
I	55.97	47.62	8.35
II	53.91	44.31	9.6
A1	55.31	43.29	12.02
A2	55.39	49.36	6.03
A3	52.25	42.80	9.45
A4	57.43	48.27	9.61
A5	63.54	48.16	15.38
A6	49.52	41.42	8.10
A7	70.64	60.00	10.64
A8	70.64	58.43	12.21
A9	62.74	57.3	5.44
A10	61.98	52.55	9.43
A11	62.55	54.81	7.74
A12	55.29	49.86	5.43
A13	56.54	51.19	5.35
A14	53.66	37.85	15.81
A15	53.66	44.62	9.04
A16	57.96	51.79	6.17
A17	54.60	49.26	5.34

TABLE 17

Concentration of silicate in before and after growth medium

Sample	Initial silicate concentration µm/kg	Final silicate concentration µm/kg	ΔSiµm/kg
I	38.8	2.07	36.73
II	41.91	1.23	40.69
A1	48.95	5.91	43.04
A2	41.77	3.24	38.53
A3	43.67	2.81	40.86
A4	48.24	1.32	46.92
A5	43.95	0.11	43.84
A6	39.63	4.5	35.13
A7	42.65	1.71	40.94
A8	42.65	1.22	41.43
A9	43.93	2.53	41.4
A10	65.73	0.89	64.84
A11	42.65	11.47	31.18
A12	62.25	6.15	56.1
A13	62.25	2.73	59.52
A14	33.78	0.93	32.85
A15	33.29	0.56	32.74
A16	73.74	17.60	56.14
A17	74.45	15.63	58.82

TABLE 18

Barium:Silicate ratio in diatom and ratio of total removal in medium

Sample	(Ba/Si) diatom	$\left[\frac{\text{Ba initial - Ba final}}{\text{Si initial - Si final}}\right]$
A3	0.292	0.231
A4	0.204	0.205
A5	0.285	0.351
A7	0.114	0.288
A8	0.40	0.295
A9	0.16	0.131
A10	0.168	0.145
A11	0.134	0.248
A12	0.209	0.097
A13	0.082	0.09
A14	0.157	0.481
A16	0.104	0.110
A17	0.024	0.048

TABLE 19

$\frac{\text{Ba final}}{\text{Ba initial}}$ vs. $\frac{\text{Si final}}{\text{Si initial}}$

Sample	$\frac{\text{Ba final}}{\text{Ba initial}}$	$\frac{\text{Si final}}{\text{Si initial}}$
I	0.851	0.053
II	0.822	0.029
A1	0.783	0.121
A2	0.891	0.078
A3	0.819	0.064
A4	0.841	0.027
A5	0.758	0.003
A6	0.836	0.114
A7	0.849	0.04
A8	0.827	0.029
A9	0.913	0.059
A10	0.848	0.014
A11	0.876	0.269
A12	0.902	0.099
A13	0.905	0.044
A14	0.705	0.028
A15	0.832	0.017
A16	0.894	0.239
A17	0.949	0.210

TABLE 20

Description of S. E. Atlantic Plankton Samples

Station	Description
1-2	Mostly birefringent material, mixed with crustaceous particles.
1-3	Crustaceous particles, fecal pellets, radiolaria, diatoms, only slightly birefringent.
1-4	Crustaceous skeletons mainly.
1-5	Birefringent materials mainly, whole crustaceans.
2-1	Birefringent materials and crustaceous particles mixed together.
2-2	Diatoms and few dinoflagellates, non-birefringent.
3-1	Crustaceous particles, no diatoms, non-birefringent material.
4-1	Crustaceous particles mainly, few foraminifera, slightly birefringent.
4-2	Mixed, crustaceous particles, diatoms and foraminifera.
4-3	Mixed crustaceous particles, diatoms and birefringent materials, whole foraminifera were collected.
4-4	Mixed crustaceous particles, diatoms and few foraminifera.
4-5	Diatoms, and few dinoflagellates, non-birefringent.
4-6	Diatoms and dinoflagellates, non-birefringent.
4-7	Diatoms, few foraminifera, birefringent only at sites of foraminifera.
4-8	Centric diatoms, crustaceous particles, non-birefringent.
5-1	Diatoms, birefringent (nylon) fibers.

Table 20 (continued)

6-1	Birefringent material
7-1	Crustaceous particles and and lots of birefringent materials.
8-1	Diatoms, non-birefringent.

TABLE 21

Description of Antarctic Ocean plankton samples.

Station	Description
GEOSECS 1	Diatoms, centric and pennate, non-birefringent.
GEOSECS 2	Linear shaped diatoms, non-birefringent.
GEOSECS 3	Disc shaped diatoms, non-birefringent.
GEOSECS 4	Diatoms, disc shaped, non-birefringent.
GEOSECS 5	Diatoms, disc and linear.
GEOSECS 6	Crustaceous particles, non-birefringent, no diatoms observed.

TABLE 22

Barium and silica data for S.E. Atlantic plankton samples.

group	sample	Ba nm/mg in cell	Si µm/mg in cell	$Ba/Six10^{-3}$	Ba nm/kg sea water	Si µm/kg sea water	$(Ba/Si)x10^{-3}$ water
Ca	1-2	0.751	0.403	1.864	41.0	1.2	34.27
Cr	1-3	1.087	0.4	2.715	42.3	3.28	12.89
Cr	1-4	0.404	0.12	3.37	45.79	1.9	24.1
Ca	1-5	0.430	0.284	1.515	42.1	1.23	34.17
Ca	2-1	0.339	0.206	1.647	38.0	0.967	39.3
Si	2-2	0.741	1.325	0.56	40.02	0.97	41.26
Cr	3-1	1.64	0.218	3.77	48.85	2.58	18.97
Cr	4-1	0.248	0.1025	2.416	54.31	4.01	13.54
Ca	4-2	0.30	0.451	0.665	42.08	3.56	11.82
Ca	4-3	0.539	0.881	0.612	64.47	5.0	12.9
Ca	4-4	0.445	1.290	0.345	44.90	3.7	14.0
Si	4-5	0.436	2.601	0.168	46.86	2.24	20.92
Si	4-6	0.695	2.213	0.314	42.96	1.6	26.85

TABLE 22 (continued)

group	sample	Ba nm/kg in cell	Si µm/kg in cell	Ba/Si $x10^{-3}$	Ba nm/kg sea water	Si µm/kg sea water	(Ba/Si)$x10^{-3}$ water
Si	4-7	0.605	1.185	0.510	42.73	1.13	37.8
Si	4-8	0.778	1.065	0.73	41.39	0.68	60.87
Si	5-1	2.023	1.416	1.429	38.92	0.34	114.47
Ca	6-1	3.653	2.01	1.815	33.66	0.751	43.49
Cr	7-1	1.914	0.681	2.81	41.57	2.295	18.07
Si	8-1	0.498	3.829	0.13	50.61	3.65	15.99

Group Ca = calcareous organisms

Cr = Crustaceous organisms

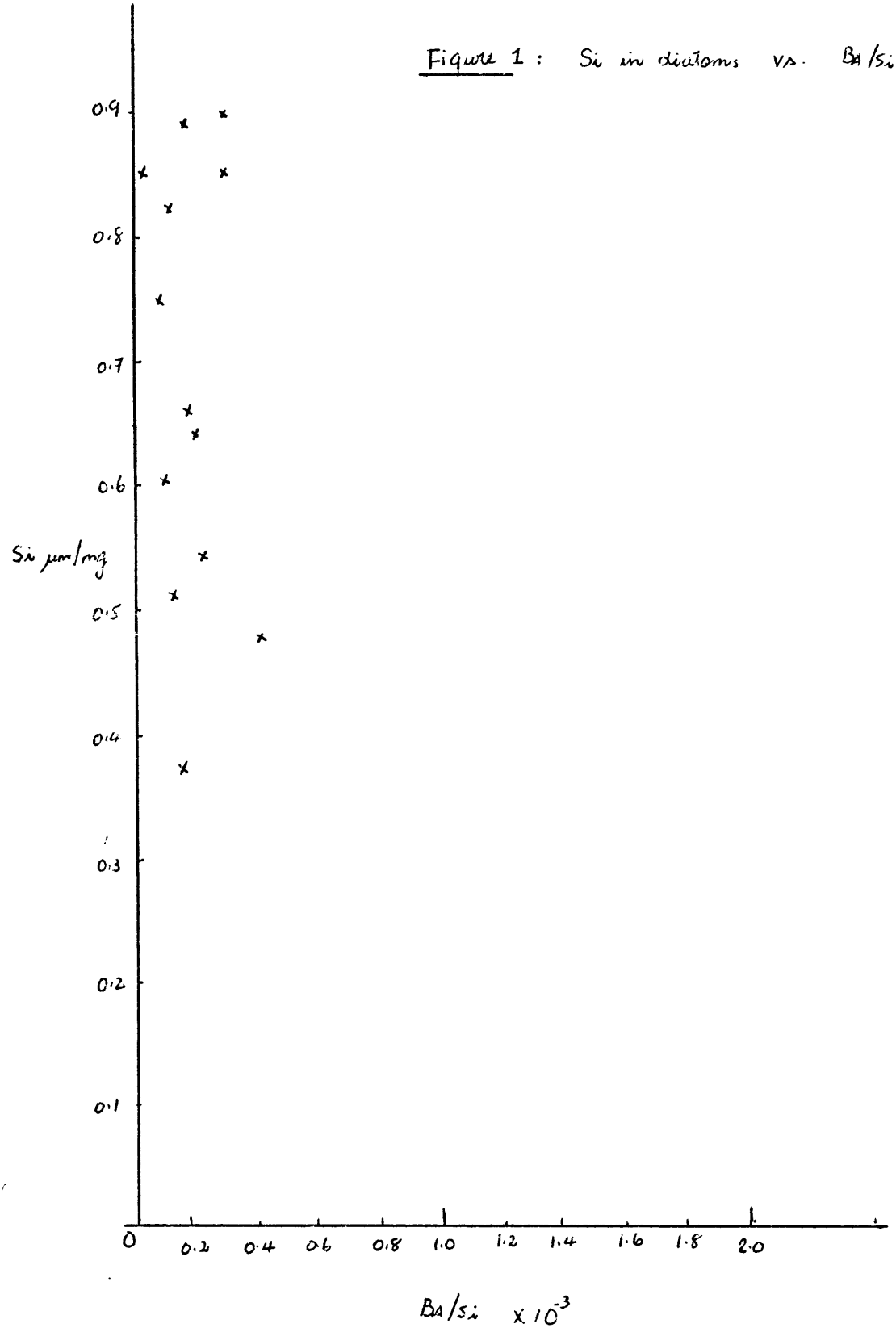
Si = siliceous organisms

TABLE 23

Barium and silicate in GEOSECS South Pacific samples

Sample	Ba nm/kg in cell	Si μm/kg in cell	Ba/Si $x10^{-3}$ in cells	Ba nmole/kg in sea water	Si μmole/kg in sea water	(Ba/Si) $x10^{-3}$ in water
1.	0.618	0.331	0.187	79.3	63.7	1.25
2.	0.531	5.70	0.093	80.1	47.0	1.7
3.	1.019	3.816	0.267	82.07	57.1	1.44
4.	1.031	3.006	0.329	73.5	15.7	4.68
5.	0.248	8.143	0.03	72.49	15.9	4.56
6.	0.175	0.291	0.602	72.18	3.6	20.05

Figure 1 : Si in diatoms vs. Ba/Si ratio in diatoms



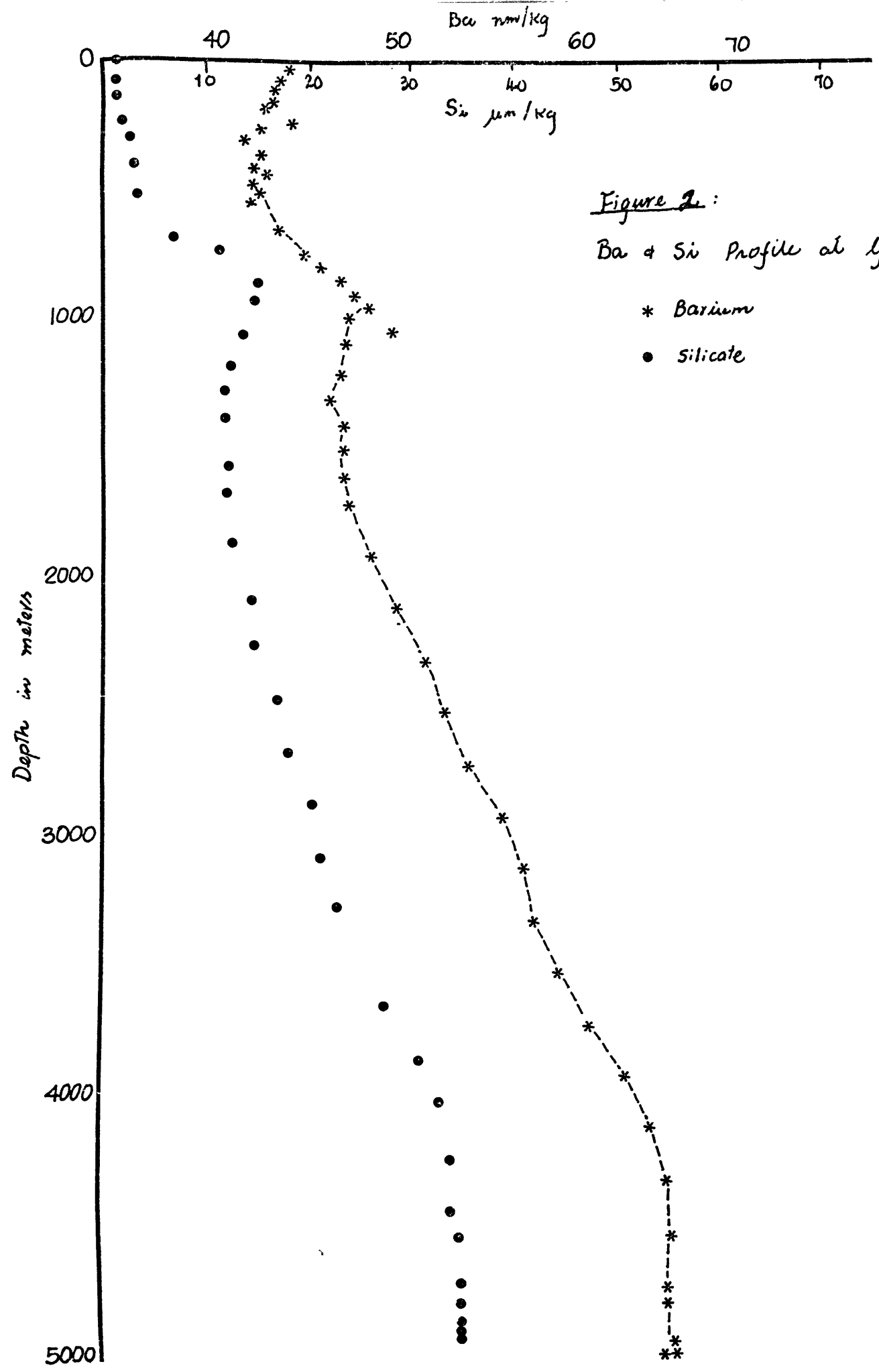
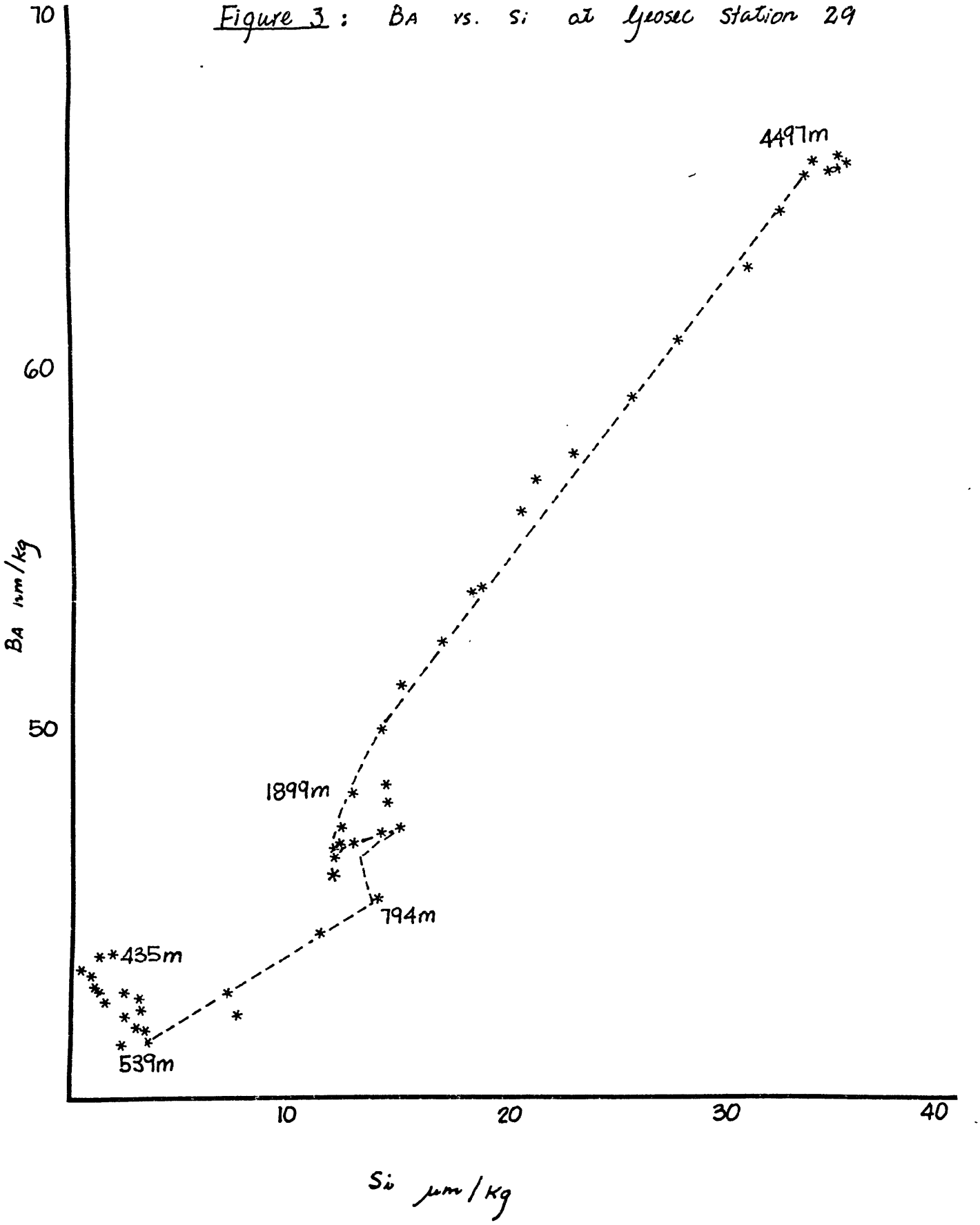
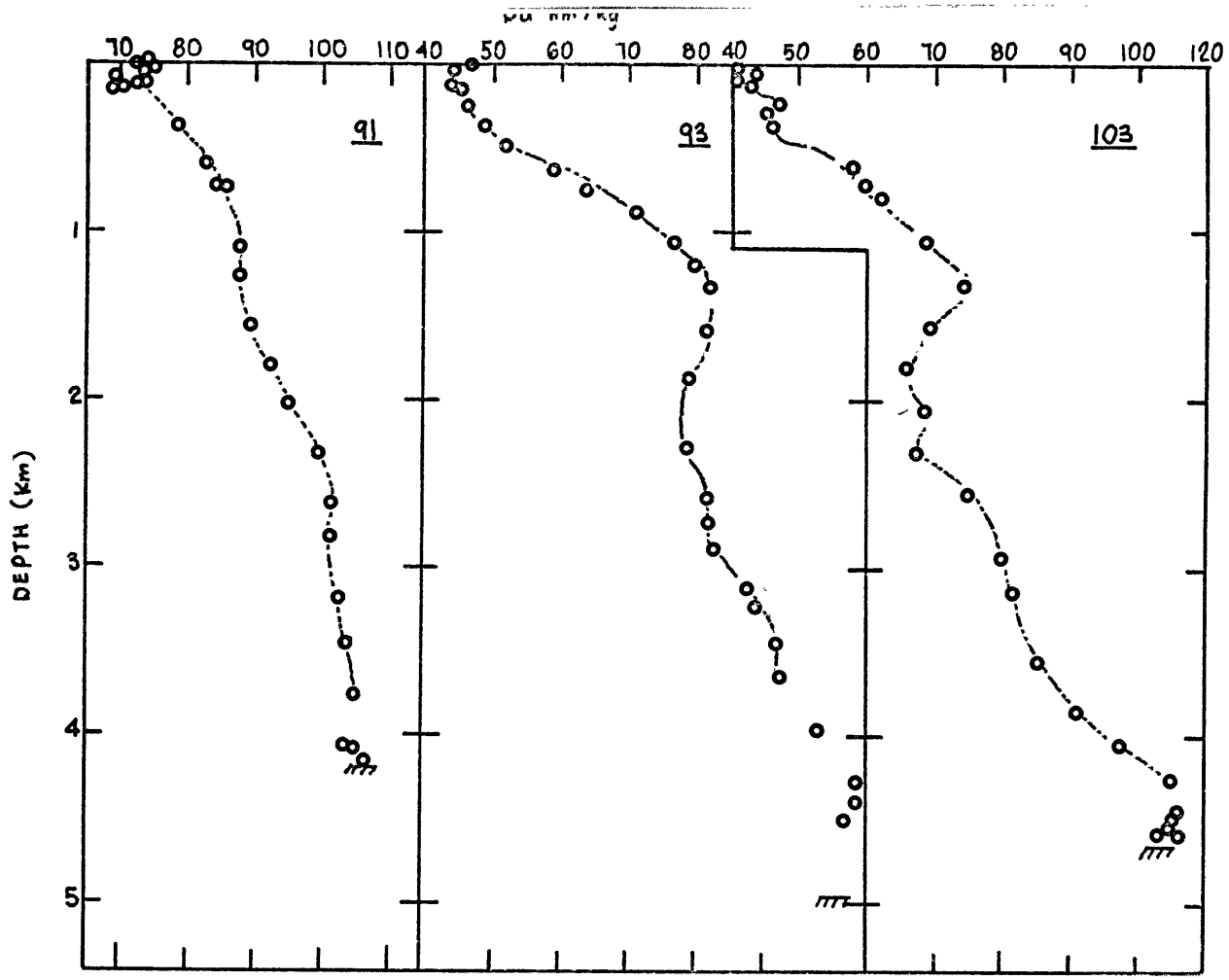


Figure 2:

Ba & Si Profile at Geosec #29

Figure 3 : B_A vs. Si at Geosec Station 29




70 80 90 100 110
40 50 60 70 80
40 50 60 70 80 90 100 120
91
93
103
DEPTH (km)
1
2
3
4
5

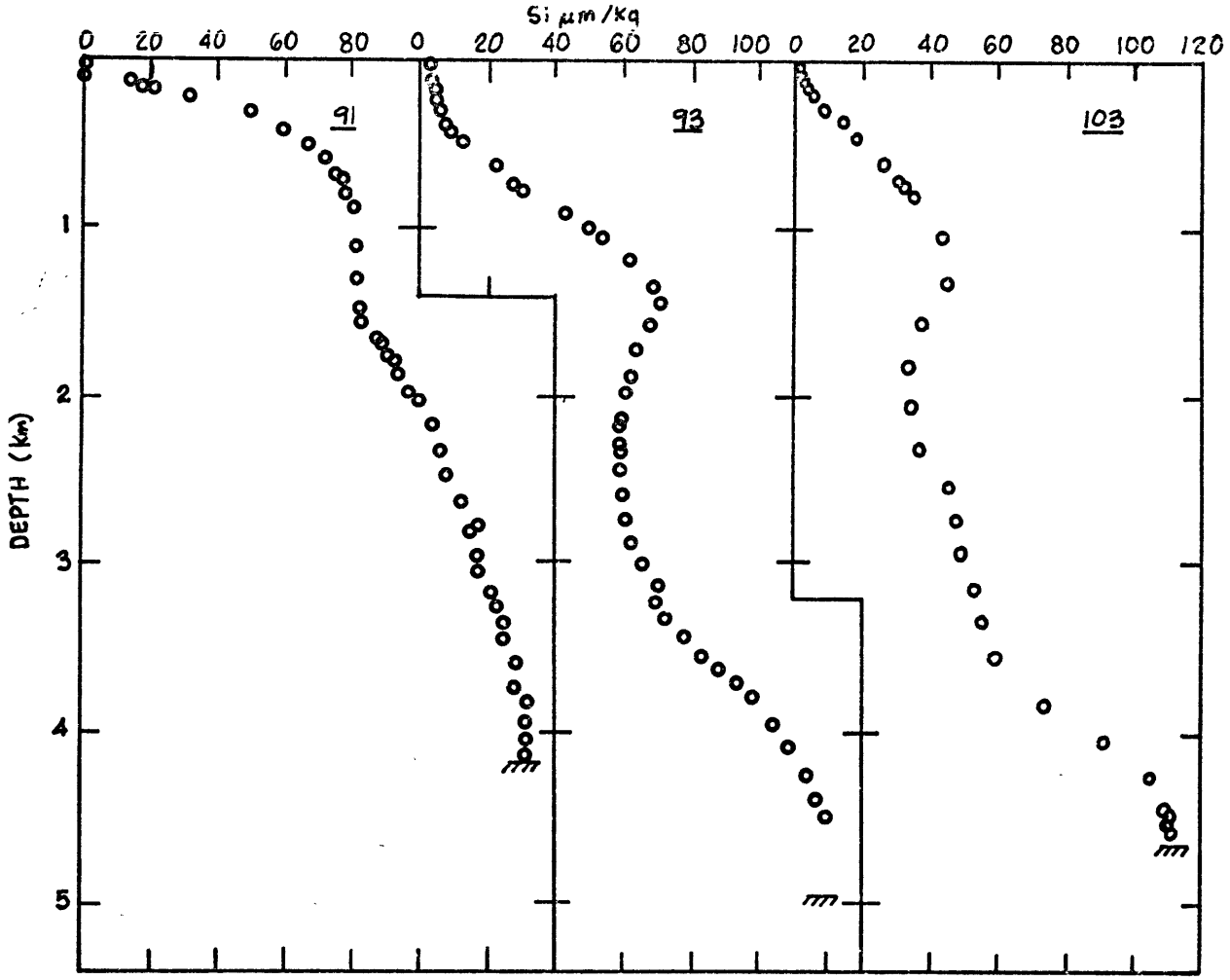

Si µm/kg
0 20 40 60 80
0 20 40 60 80 100
0 20 40 60 80 100 120
91
93
103
DEPTH (km)
1
2
3
4
5

Figure 4.

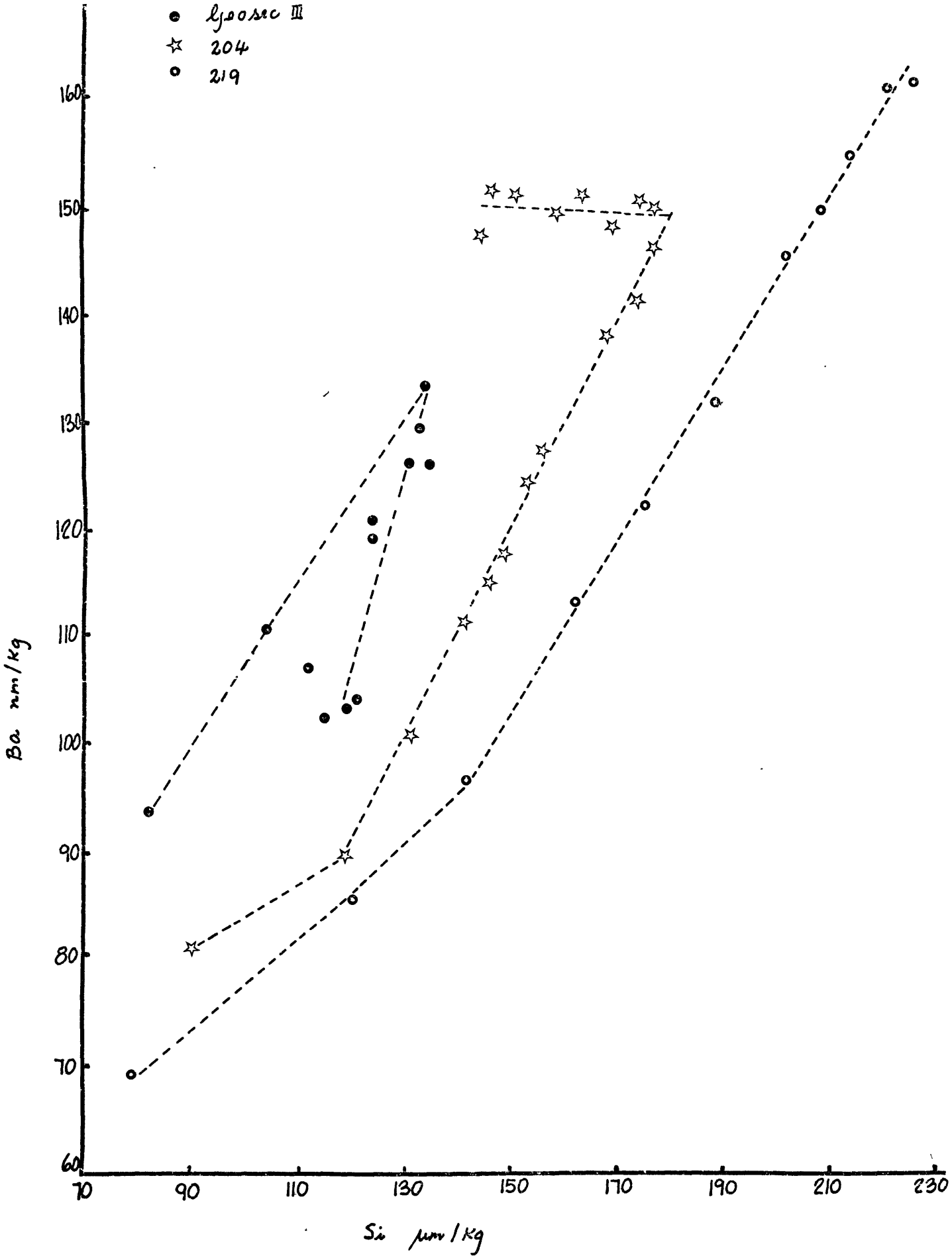


Figure 5 : Ba vs. Si at station 204, 219, Geosec III

Figure 6

Si vs. Ba/Si at Geosec South Atlantic Station 103

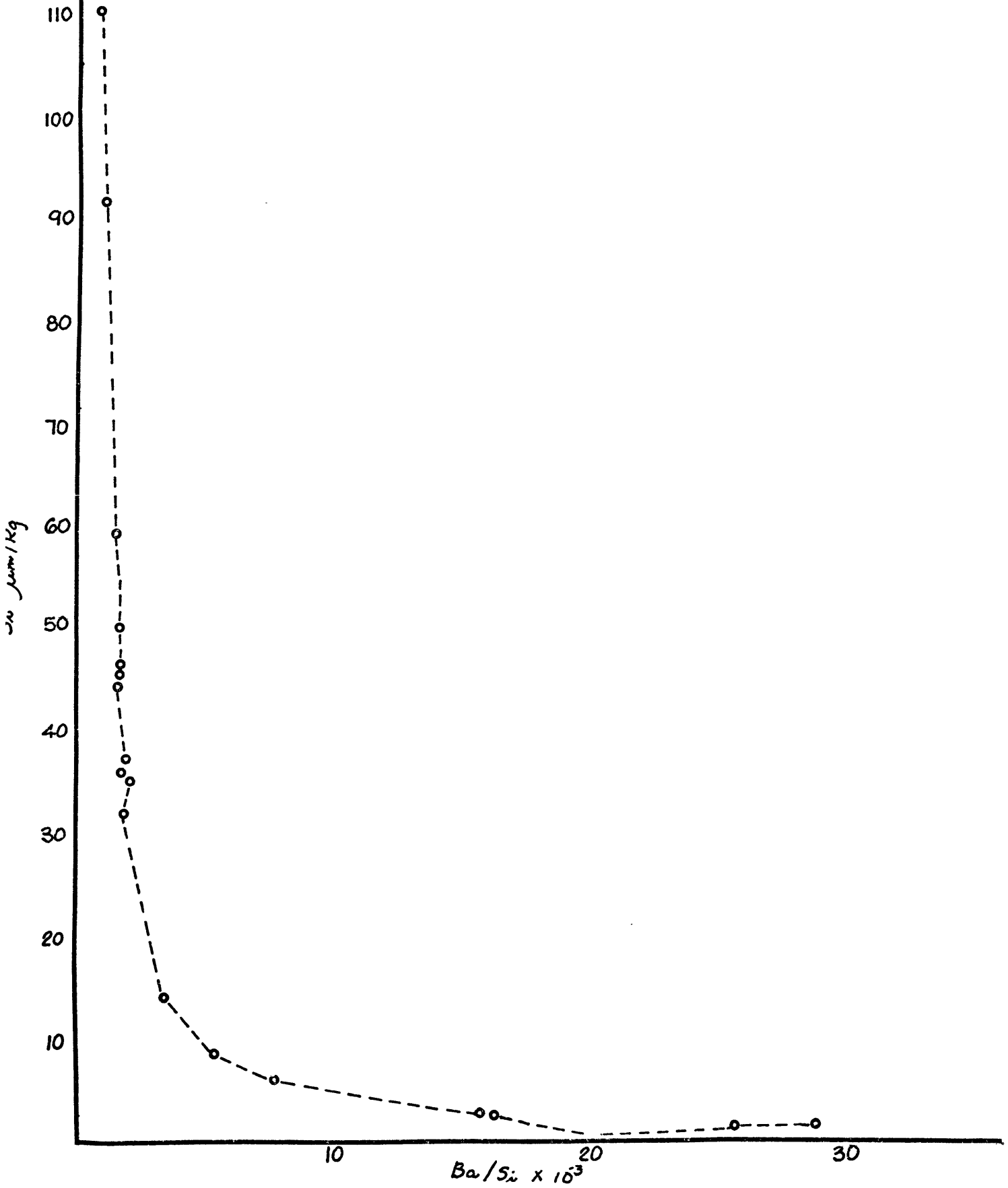


Figure 7:

Barium and Silicate Profile of Geosec Station 103

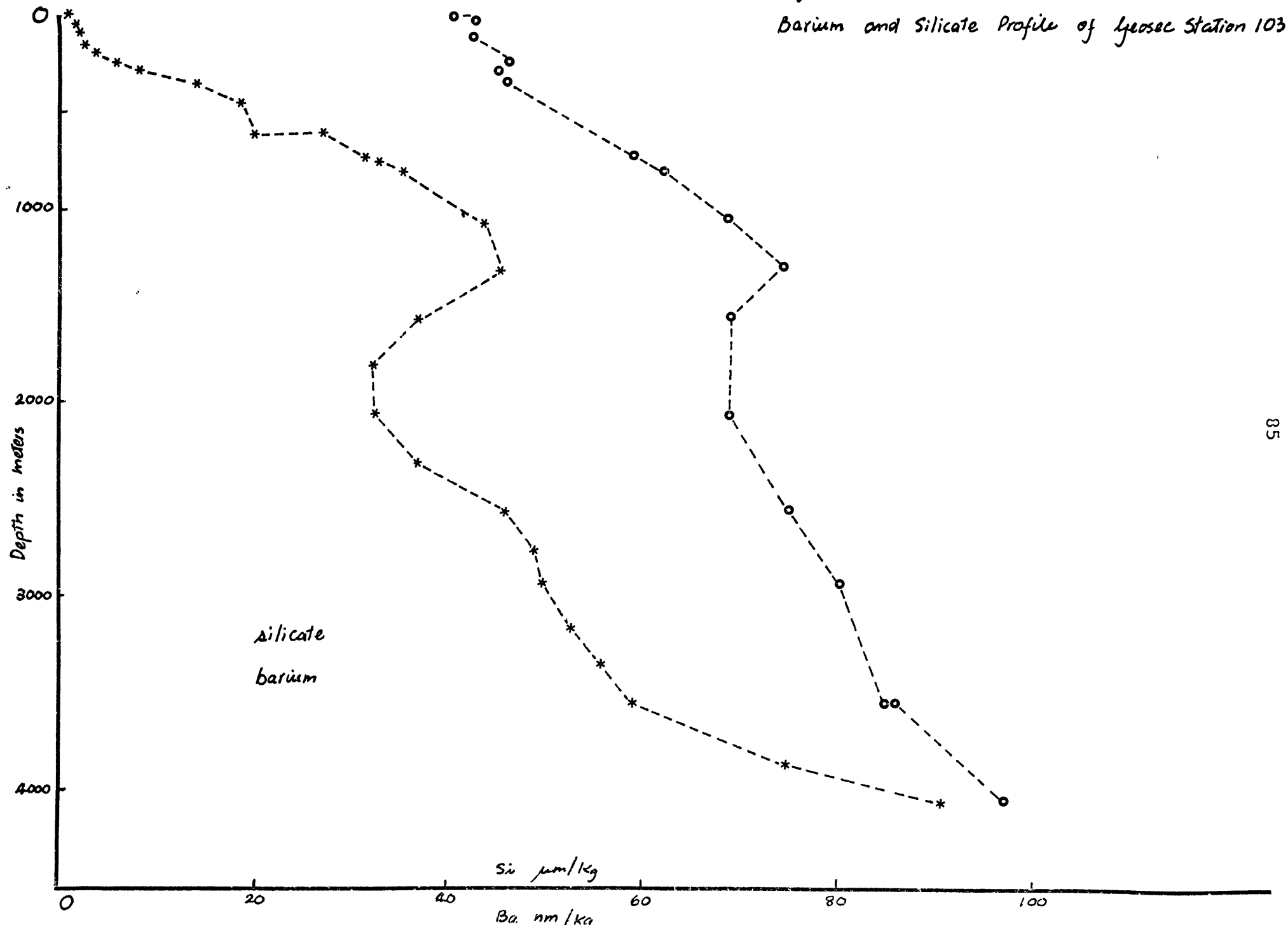


Figure 8 : Barium vs. Silicate at Yeasec Atlantic Station 103.

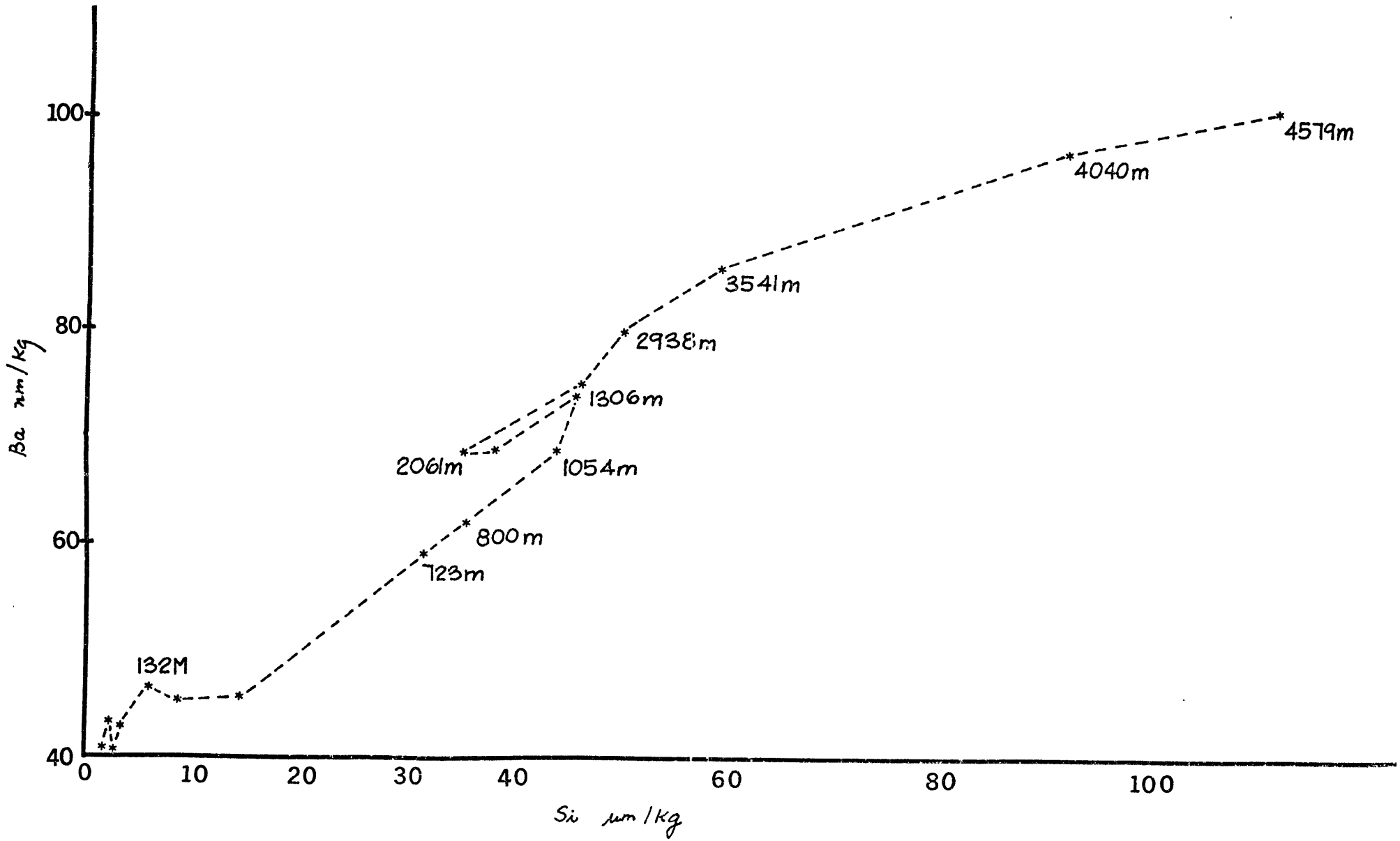
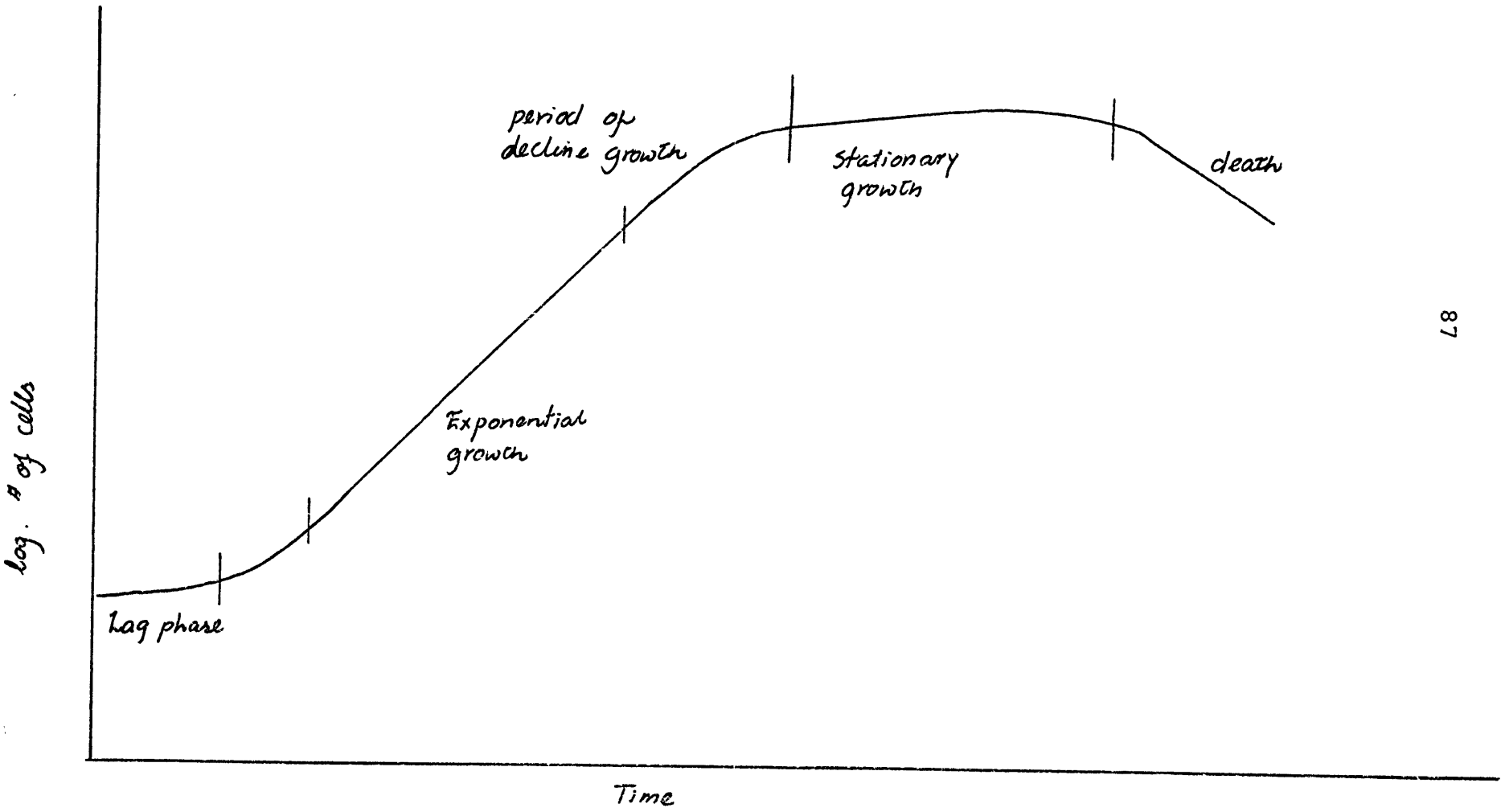
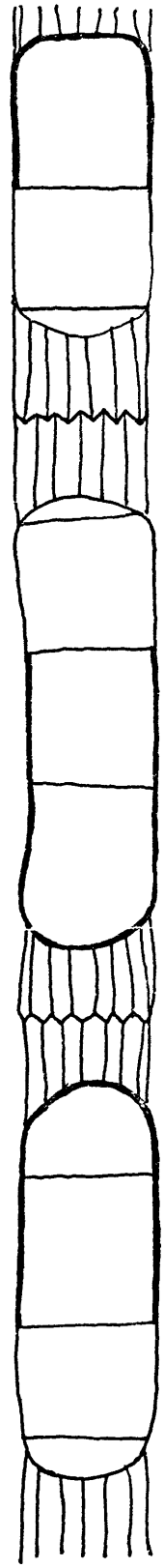


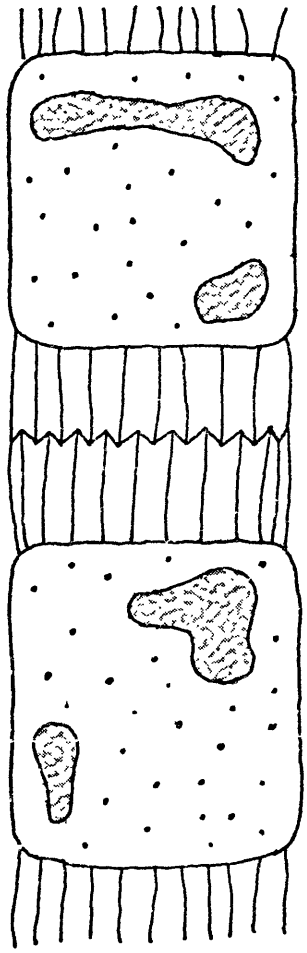
Fig 9: Growth Curve for limited volume cultures





10μ

dividing



13μ

resting spore formed

Figure 10 : Vegetative cells, Skeletonema Costatum

Figure 11: Calibration curve of Barium analysis by atomic absorbance.

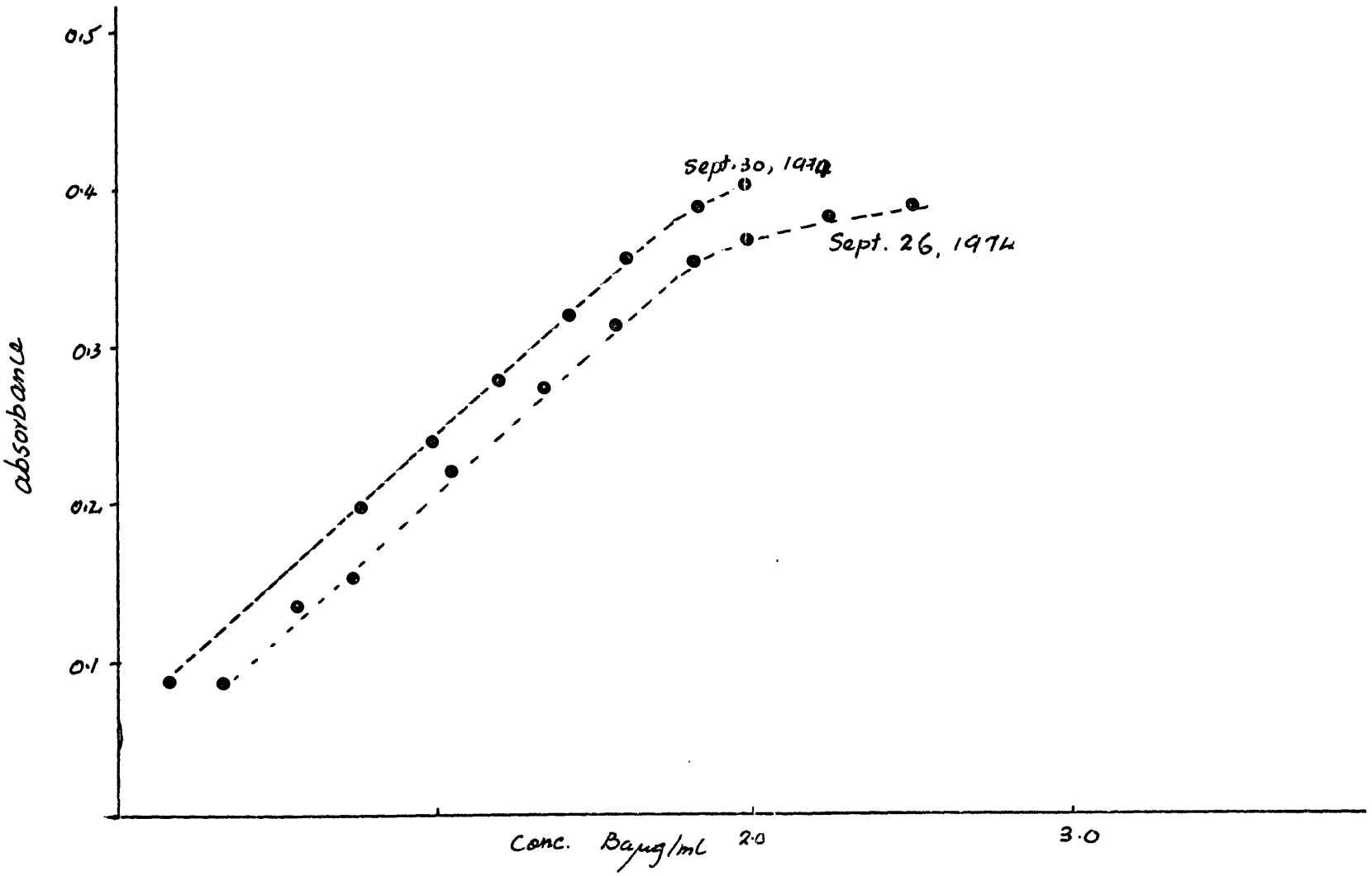


Figure 12 : Calibration curve for silicate analysis in distilled water

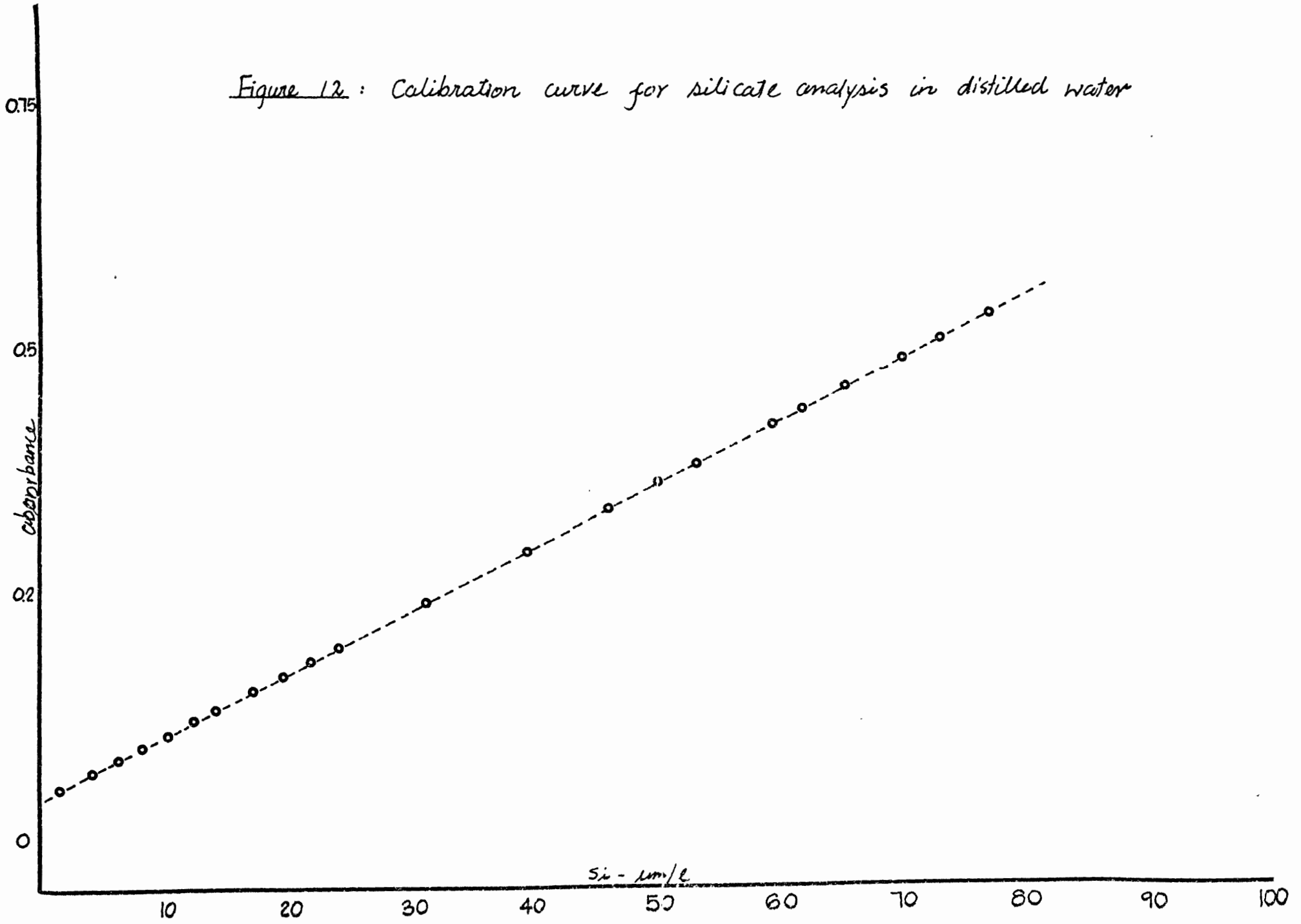


Figure 13. Standard calibration curve for Si - analysis in sea-water

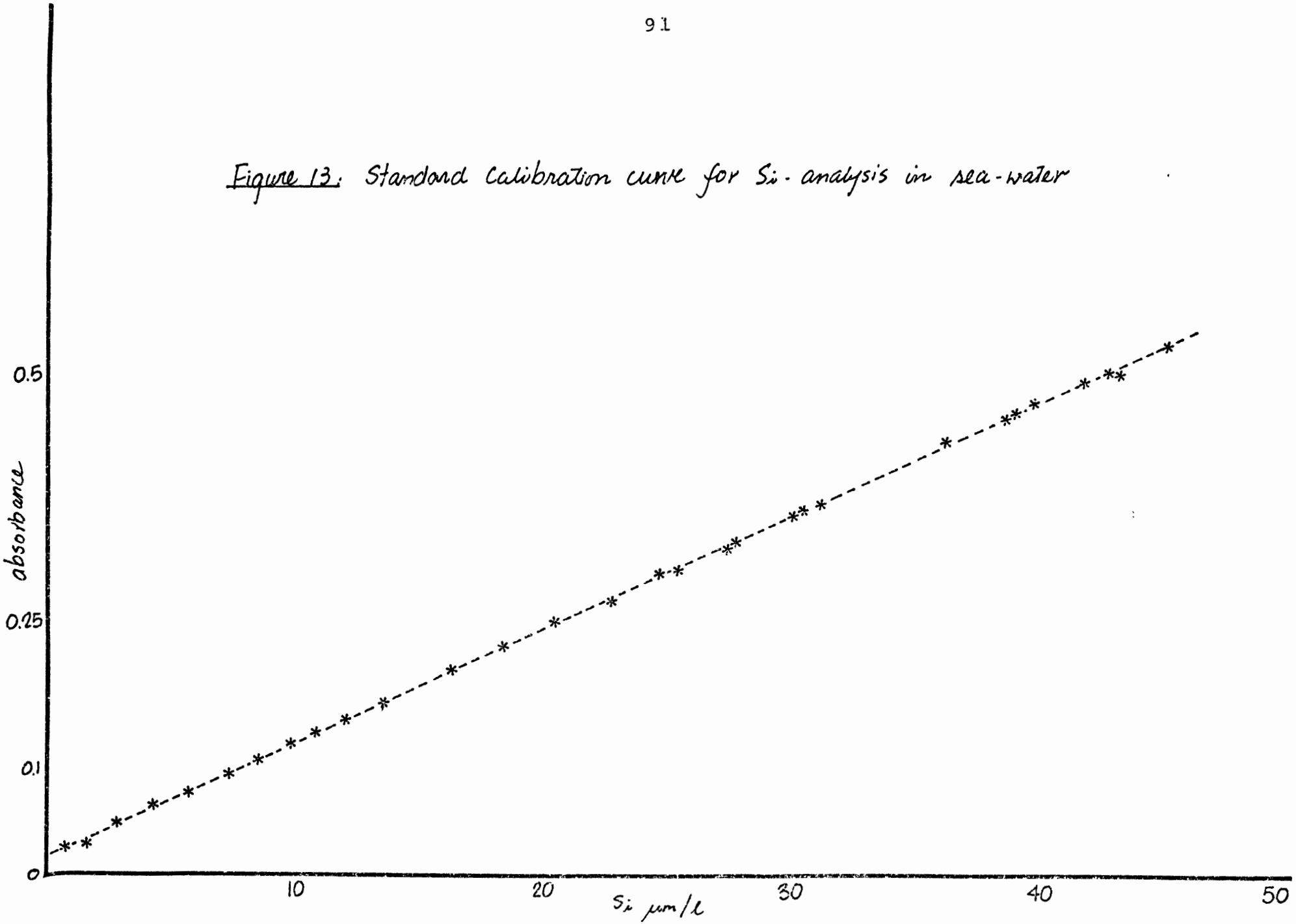


Figure 14: Standard Calibration for silicate extraction technique and control.

* extraction

o control

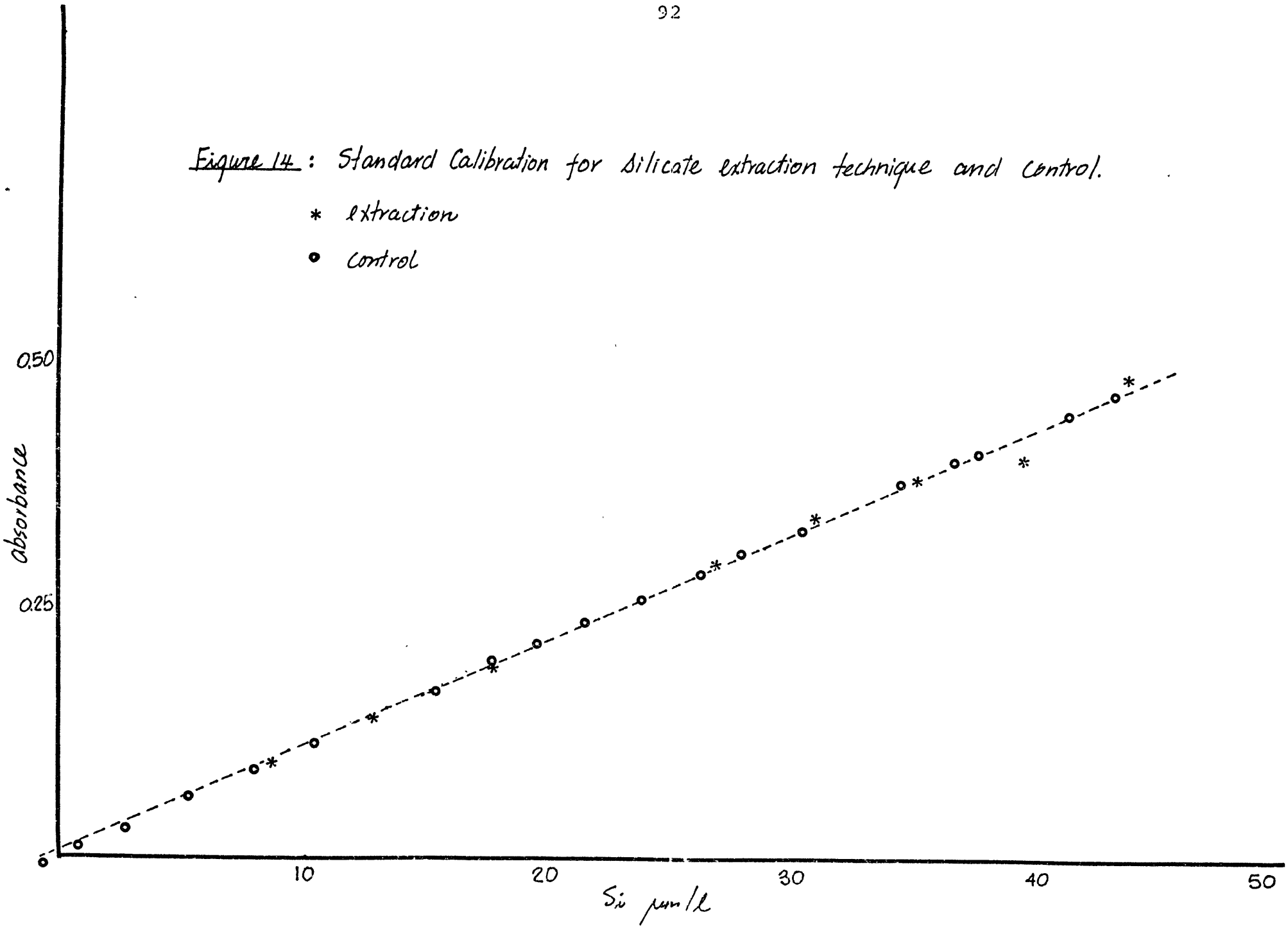
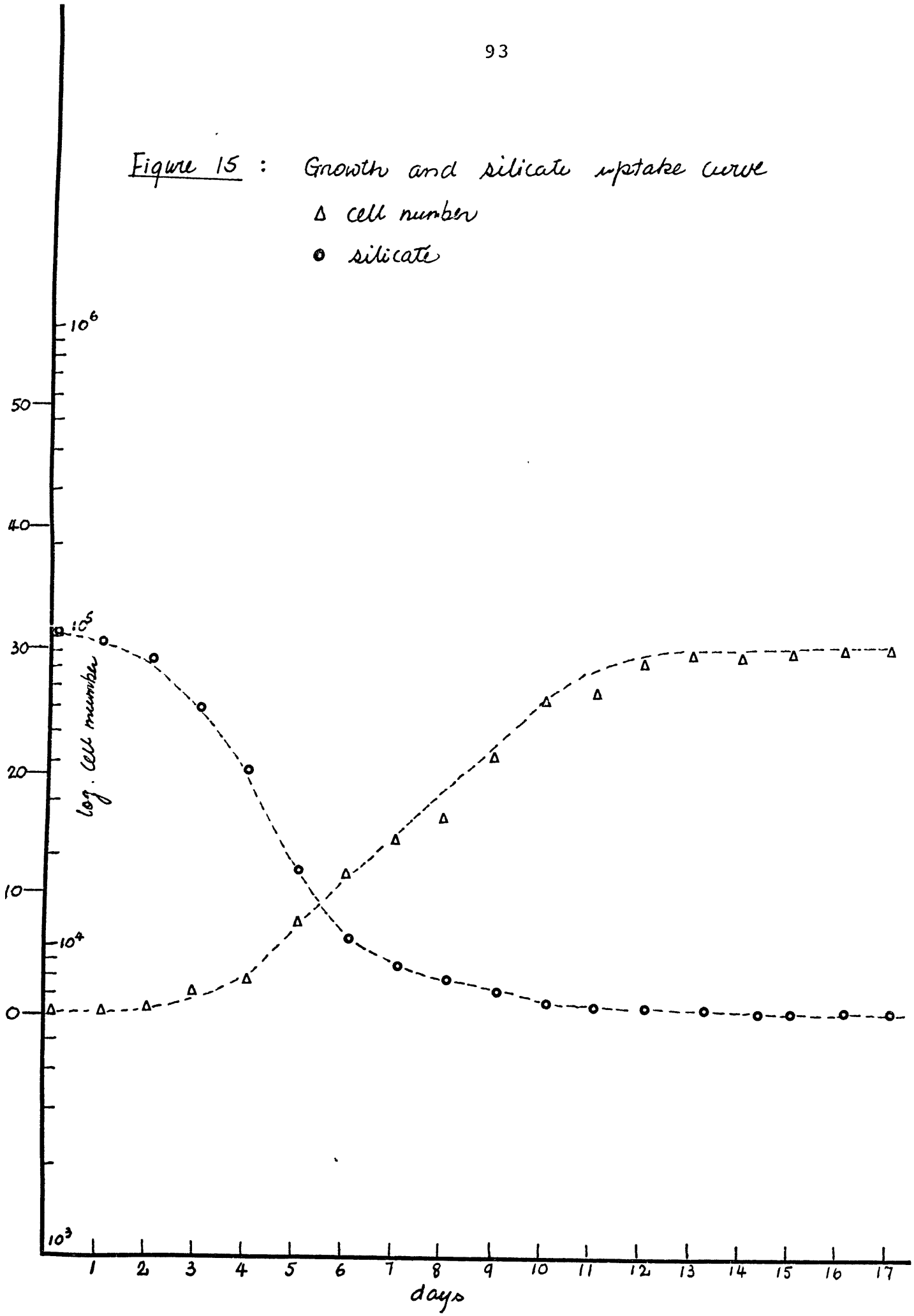


Figure 15 : Growth and silicate uptake curve

Δ cell number

⊙ silicate



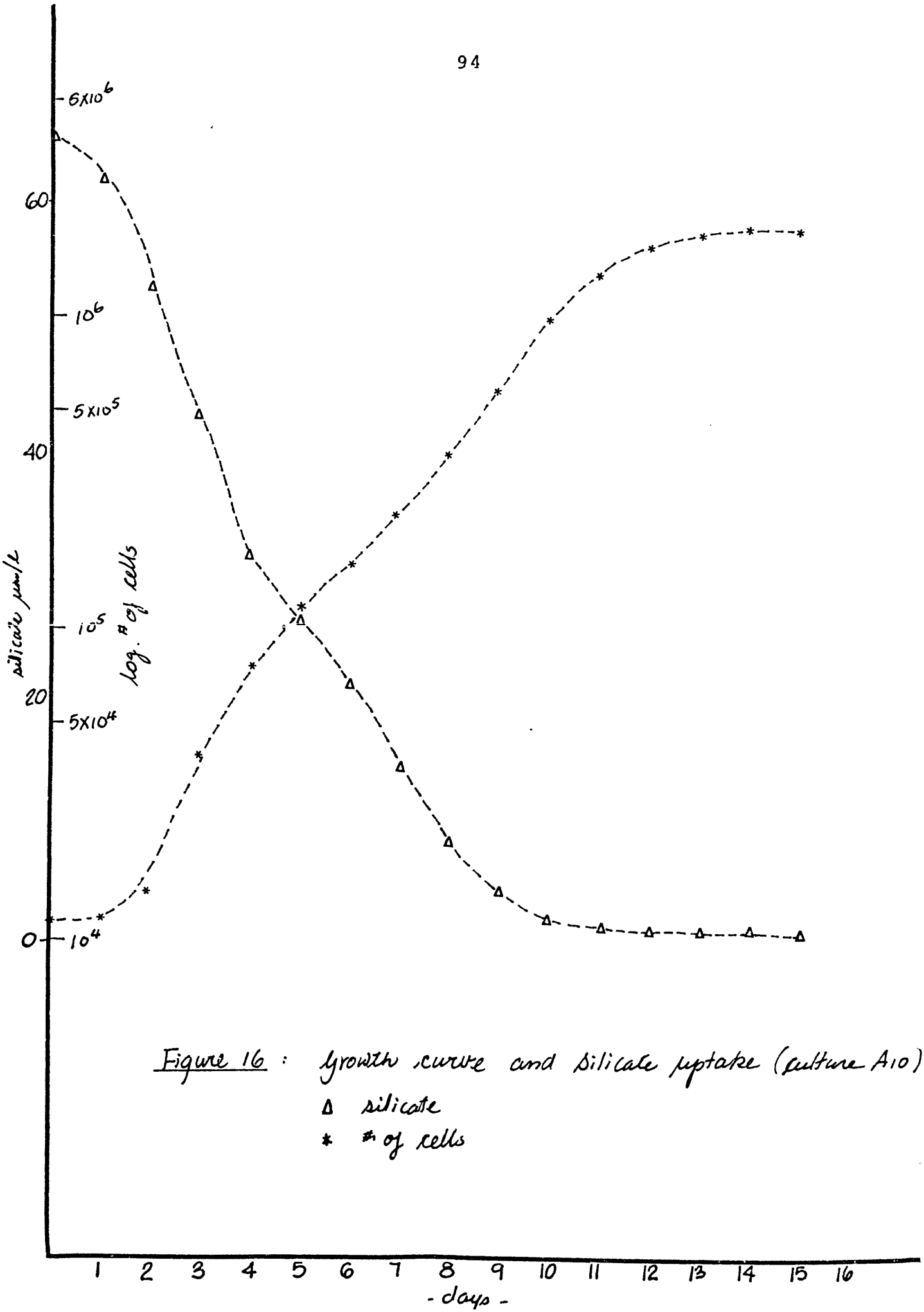


Figure 16 : Growth curve and silicate uptake (culture A10)

Δ silicate

* # of cells

Figure 17 : Growth & Silicate Uptake (sample A3)

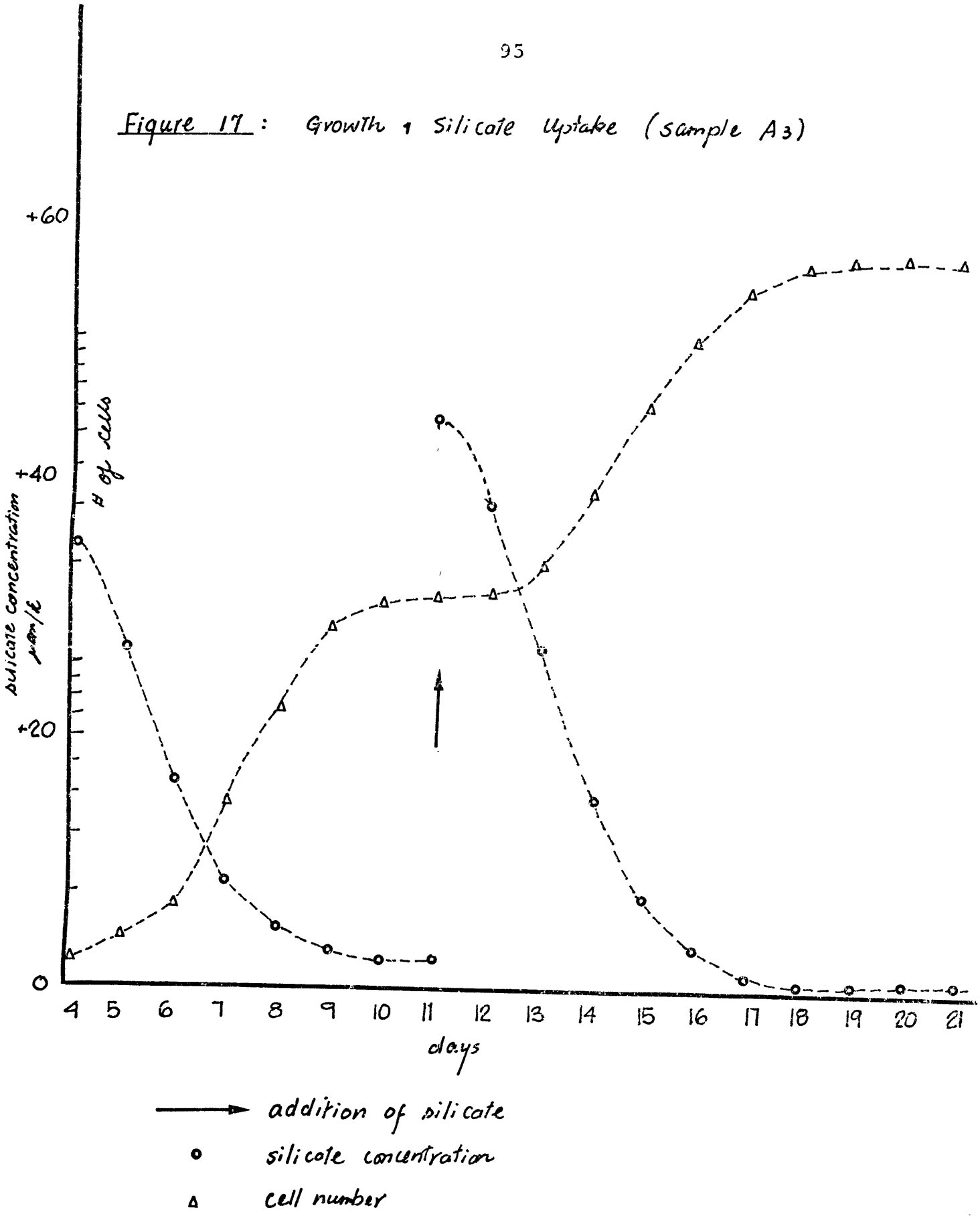


Figure 18 : B_A/S_i cell culture vs. $\Delta B_A/\Delta S_i$ medium

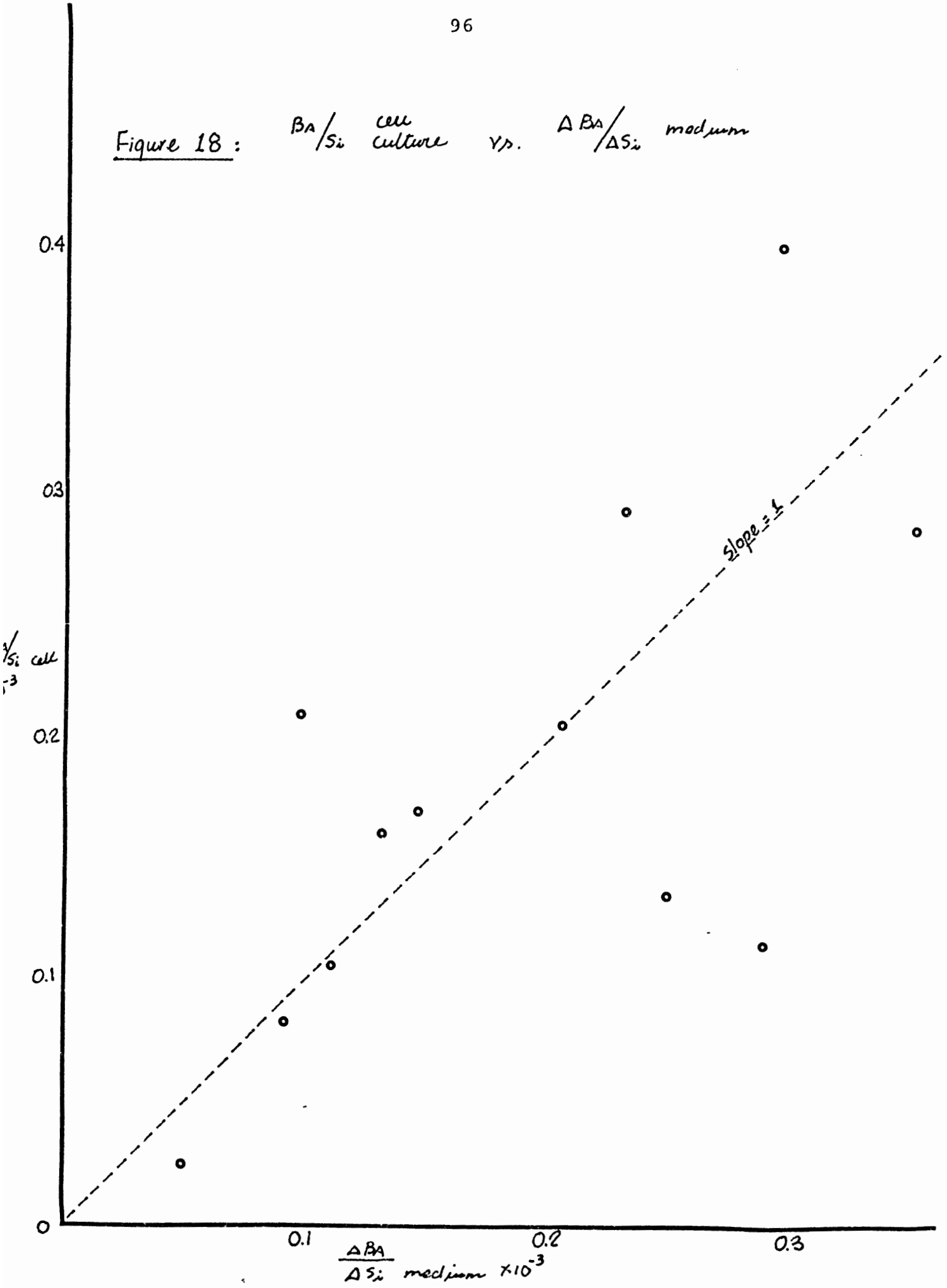
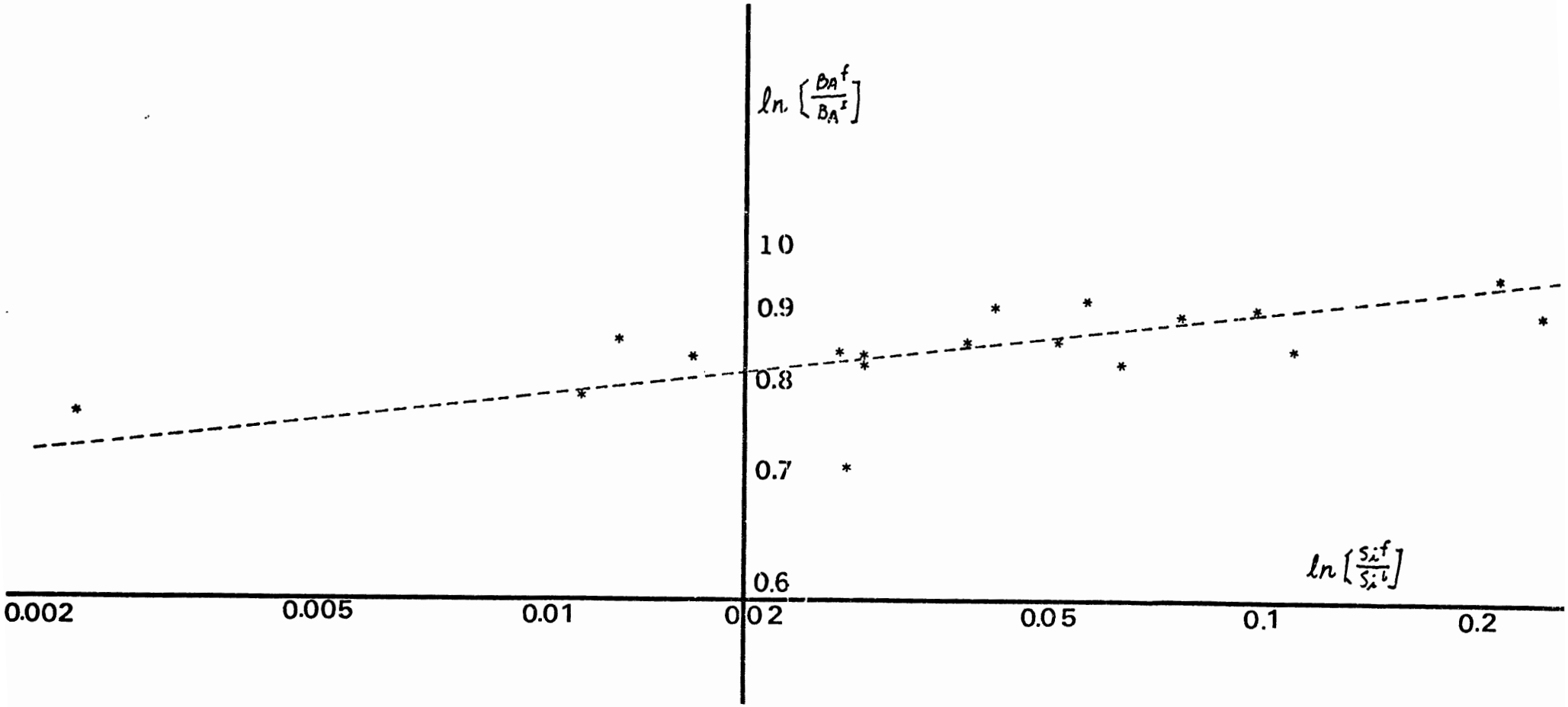


Figure 19 : Plot of $ln\left[\frac{BA\ final}{BA\ initial}\right]$ vs. $ln\left[\frac{Si\ final}{Si\ initial}\right]$ in culture medium.



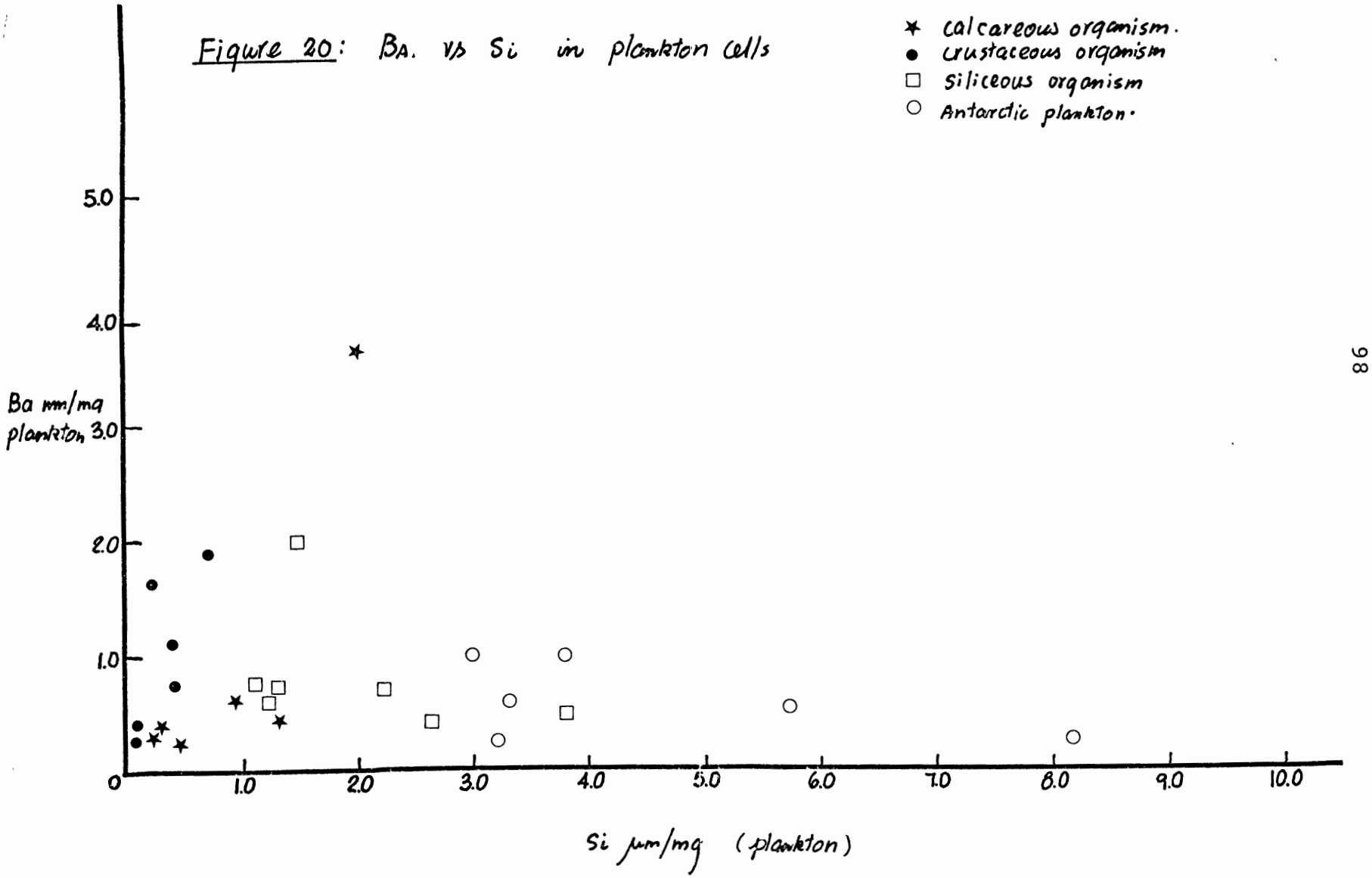


Figure 20: Ba. vs Si in plankton cells
★ calcareous organism.
● crustaceous organism
□ siliceous organism
○ Antarctic plankton.
Ba mm/mg plankton
5.0
4.0
3.0
2.0
1.0
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
Si μm/mg (plankton)

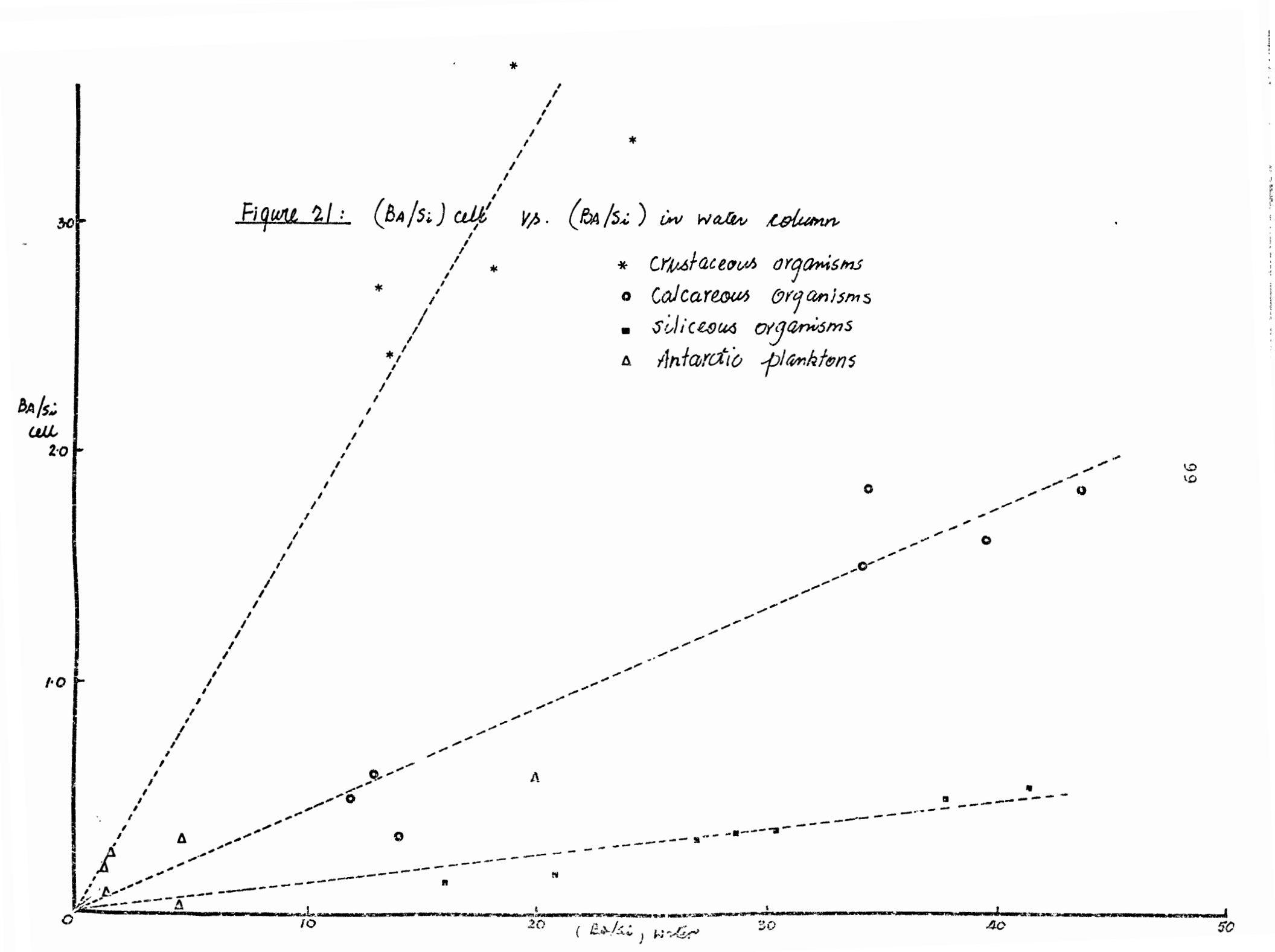


Figure 21: (Ba/Si) cell v/s. (Ba/Si) in water column
* Crustaceous organisms
o Calcareous organisms
■ Siliceous organisms
Δ Antarctic planktons
Ba/Si cell
30
2·0
1·0
0
10
20
30
40
50
(Ba/Si) water
99

Figure 22 : Si in cell v/s. Ba/Si in cells of oceanic planktons.