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# **A STUDY OF THE WATER-MINERAL EQUILIBRIA IN THE RIVER GANGES**

Dissertation submitted to the Jawaharlal Nehru University, New Delhi,  
in partial fulfilment of the requirements for the Degree of  
MASTER OF PHILOSOPHY

29 p + appendix + tables + fig.

by

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PREFACE

This dissertation entitled A STUDY OF THE WATER-MINERAL EQUILIBRIA IN THE RIVER GANGES has been carried out in the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi-57. The work is original and has not been submitted in part or in full for any degree or diploma of any University.

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## ABSTRACT

Previous literature in the fields of river water chemistry and sediment chemistry has been reviewed. The longitudinal variation in the values of total dissolved salts has been explained in terms of changes in the concentrations of some of the major ionic constituents like, bicarbonate and chloride. The seasonal variation has been attributed to discharge effects. A few of the expected means of formation of bicarbonates from natural, as well as, man-made sources have been speculated. The saturation levels of some important carbonate minerals, like, Calcite, Aragonite, Magnesite and Dolomite, have been examined. The river is seen to be supersaturated with Dolomite. The phase study involving these minerals also suggests that the water is expected to be in equilibrium with Dolomite. Finally, the water composition is plotted in the alumino-silicate system, and it indicates, that Kaolinite and K-Mica can be expected to be present in the sediments. The discrepancies between the theoretically predicted composition of the sediments in the river and that reported by field investigations have been discussed.

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## INTRODUCTION

Our late Prime Minister, Jawaharlal Nehru, said of the Ganges, "The story of the Ganges from her source to sea, from old times to new, is the story of India's civilization and culture". Such a statement need not hold good for the River Ganges alone, but is also true of other rivers in the world, like the Amazon in South America, River Nile in Africa and River Volga in Russia. From time immemorial, rivers have been a witness to the growth of human civilization in various parts of the world. Hence, it is but natural, that rivers must attract the attention of scientific community around the world. In the course of the study of rivers by the scientists, principles of various disciplines have been used.

Thus, for example, a chemist, applies the principles of thermodynamics to study mass transfer and phase transformations that occur in the rivers during the course of many weathering reactions. A hydrologist concerns himself principally with the problems that rivers pose in the development of power and industries. Whereas, a geologist is usually interested in the mineralogy of the river bed.

But, when one surveys the literature, of all the approaches, the interdisciplinary approach to the study of rivers seems to be the most popular one. Therefore, it is not surprising that in the recent years increasing interest is paid in the application of oceanographic, biological and geochemical concepts to

the study of our aquatic environment. Since the present work falls in the domain of the Geochemistry of water, an effort will be made first to review some of the previous work in this field.

Water Chemistry of Rivers:-

Various aspects of water chemistry in the fresh water region and estuary region have interested the workers in this field. Gibbs (1967) and Reeder et al (1972) have shown for Amazon and Mackenzie rivers respectively that the geological diversity of the drainage basin is likely to be reflected in the river water chemistry. Gibbs (1967) has concluded that increased relief and physical weathering controlled the percentages of quartz, plagioclase, K-Feldspar, mica, chlorite and amphibole, and that, the percentage of calcic rocks in the upper portions of tributary basins controlled the amount of montmorillonite. Then, a combination of low-relief chemical weathering, and percentages of igneous and metamorphic rocks, controlled the percentages of kaolinite and gibbsite in the suspended particles in the Amazon river.

The presence of a large number of chemical elements in the natural waters has raised an interesting question about their origin. Garrels and Mackenzie (1967) have studied the origin of the chemical compositions of some springs and lakes. They have concluded that the compositions are consistent with a model in which the primary rock forming silicates are altered in a closed system to soil minerals plus a solution in steady state equili-

brium with these minerals. Edwards (1973) has examined the variation of the dissolved constituents in some Norfolk rivers with discharge. It was observed that Magnesium, bicarbonate and phosphorus were diluted by increase in discharge, whereas, nitrate and sulphate concentrations were positively correlated with discharge. The positive correlation was attributed to the possible leaching of the upper part of the soil profile.

As against the addition of chemical constituents to our aquatic environment by natural process, in the recent years, they have also been added artificially in the form of effluents from industries. Studies have been conducted to examine the effects of such wastes on the water quality and fisheries (Ganapathi and Chacko, 1951; Sreenivasan and Sounder Raj, 1967). Ganapathi and Chacko made a detailed study of the effects of the effluents discharged into the River Godavari from a paper factory. In this case, the discharge does not seem to have affected the indigenous fish population. But in the study conducted by Sreenivasan and Sounder Raj, the discharge from a paper factory into the Rivers Cauvery and Bhavani has proved harmful to the fishes.

The increasing pollution of natural waters has led to an awareness around the world, to keep a strict watch on the water quality of rivers and lakes. Accordingly, compilation of water quality data for many aquatic systems has been done. In our own country, an attempt to study the quality of water of



some rivers was made, and the information available in the form of a report (Govt. of India, 1955). In the United States, similar work on rivers and lakes has been published (Livingstone, 1960). Grove (1972) has compiled a table on the dissolved and solid load carried by the West African rivers: Senegal, Niger, Benue and Shari. In the case of South American River Amazon, chemical data are available throughout a yearly seasonal cycle (Gibbs, 1972).

The availability of extensive chemical data on water quality has led to several interpretative studies. For example, the increased salinity in the ground water and its harmful effects on irrigation has been reported (Jacks, 1973). In the case of the fresh water region of St. Lawrence, the water quality data are analysed graphically to show some of the inter-relationships among different variables and equilibrium composition of the suspended matter has been theoretically derived (Subramanian, 1974). In a study of different type, Subramanian (1976) has investigated some of the important factors, like pH and ionic strength, which control the concentrations of heavy metal ions in natural waters.

In the recent years, rivers have given place to estuaries as the subject of study (Borole et al in press; Subramanian and D'Anglejan, 1976). Borole et al have measured the concentrations of dissolved Uranium and Silicon in the Nerbada, Tapi and Godavari estuaries as a function of chlorosity by a radioactive

method. Their results suggest that Uranium behaves conservatively in all the three estuaries, whereas Silicon exhibits conservative behaviour in the Nerbada and Tapti estuaries, and behaves non-conservatively in the Godavari estuary.

The study of the chemistry of our aquatic environment has raised some questions about the probable mechanisms that control the world water chemistry, and secondly, as to how the chemical mass balance between rivers and oceans is maintained, given the fact that innumerable rivers and streams supply huge amount of dissolved constituents to oceans.

Garrels and Mackenzie (1966) have explained the constancy of the chemical composition of ocean waters by proposing a steady state model in which the excess stream derived solids are removed as minerals in marine sediments, as dissolved constituents in sediment pore waters, and as materials cycled through the atmosphere.

The mechanisms that control the world water chemistry have been discussed by Gibbs (1970). The author cites three main mechanisms - atmospheric precipitation, rock dominance and the evaporation crystallization process - as the major factors influencing the composition of the dissolved salts of the world waters.

#### Sediment Chemistry:-

Much work seems to have been done in the field of sediment chemistry by making use of the principles of thermodynamics and

kinetics. For example, Kramer (1967) has made a study of the Great Lakes by means of two equilibrium models. In the first, he has assumed constant temperature and pressure conditions, and in the second, he has considered them as variables. With these restrictions, he has examined the saturation levels of calcite, dolomite and apatite in the waters. He has also made a theoretical analysis (1968) of the mineral - water equilibria in Silicate weathering. In the field of kinetics, Helgeson (1971) has made a study of the kinetics of mass transfer among aluminosilicates and aqueous solution. Similarly, Denis Norton (1974), has defined equilibrium relationships between stream waters and weathering products, kaolinite and calcium montmorillonite, for the Rio Tanana system.

The increasing attention paid to the study of suspended matter in natural waters (Gibbs, 1974) has led to the development of a number of methods for studying the various aspects of the associated sediments (Cann and Winter, 1971; Pierce et al, 1973; Subramanian and D'Anglejan, 1976). Cann and Winter used a thin film technique for the chemical analysis of suspended sediments collected on membrane filters. Pierce et al have developed a technique for the mineralogical study of minute quantities of suspended matter on membrane filters and their technique has been successfully used for studying the mineralogy of the suspended matter in the St. Lawrence estuary (Subramanian and D'Anglejan, 1976). They have recently discussed a new method for estimation of weight per cent of elements in the suspended matter in the estuarine waters.

Nature of the Present Work:

The brief review that has been attempted above clearly brings out the fact that the study of natural waters has been diverse in nature. But, in these different approaches, the importance of reliable chemical data on water quality cannot be overemphasized. In fact, a meaningful study of any natural system is possible, only if water analysis data are available for the whole year. Therefore, before a worker in this field takes up a study of a natural system, at the first instance, he has to look for water analysis data recorded throughout the seasonal cycle. Since, such a work has been done by Handa (1972) on the River Ganges, his results have been used in the present work (Tables 1 - 3).

Prior to the publication of Handa's work, a detailed analytical data of any Indian river do not seem to have been published. Whereas, Livingstone (1963) quotes a partial analysis data of the Ganga river, Deb and Chadha (1964) carried out only a partial analysis (Ca, Mg, Na, K,  $\text{HCO}_3$ , Cl, pH and specific conductivity) for a number of rivers, which did not include Silicate, and neither the seasonal variations were recorded. Further, Morozov (1969) in his studies did not quote any analytical data from the Indian sub-continent.

Handa's paper records, among other things, a brief discussion on the dissolved salt content and mineral equilibria. In the case of the total dissolved solute, neither any interpretation is attempted graphically, nor the seasonal variations in their values

TABLE - 1  
[Handa (1972)]

Average monthly \*chemical composition of the Ganga river water at Rishikesh (1966-67).

Concentrations expressed in ppm.

Month	TDS	H <sub>4</sub> SiO <sub>4</sub>	pH	Ca	Mg	Na	K	HCO <sub>3</sub>	Cl	SO <sub>4</sub>
Jan.	140	24	6.85	30	10	4.3	2.2	115	8	18
Feb.	125	22	6.80	28	13	4.6	2.5	117	9.5	23
Mar.	122	32	6.75	26	8.8	4.4	2.8	103	7.0	21
Apr.	110	23	6.90	23	5.8	2.6	2.1	86	7.3	9
May	120	32	6.95	27	5.9	2.1	2.8	89	7.5	15
June	100	26	7.00	21	5.7	2.0	2.1	83	5.7	8.5
July	105	24	6.95	21	5.2	2.0	3.6	84	3.5	9.0
Aug.	100	25	7.05	20	4.3	1.7	2.1	75	3.8	7.0
Sept.	105	30	6.85	20	5.4	2.0	2.2	80	3.6	7.5
Oct.	120	28	6.90	22	7.6	5.0	4.0	84	9.0	13.0
Nov.	115	24	6.95	25	7.7	3.2	2.1	90	8.0	16.0
Dec.	123	27	7.00	26	10.0	3.6	2.1	100	9.0	19

\*Since the concentrations of F, NO<sub>3</sub> and B were in fractions of one ppm, they have not been considered in the present work.

TABLE - 2  
[Handa (1972)]

Average monthly \*chemical composition of the Ganga  
river water at Rajmahal (1968-69).

Month	Concentrations in ppm.									
	TDS	pH	H <sub>4</sub> SiO <sub>4</sub>	Ca	Mg	Na	K	HCO <sub>3</sub>	Cl	SO <sub>4</sub>
June	155	7.45	12	35	6.6	9.0	4.0	158	7.0	19
July	126	7.25	18	26	4.9	5.6	3.5	100	5.5	11
Aug.	105	7.30	19	23	3.4	3.5	2.6	88	2.2	6.5
Sept.	100	7.15	22	19	3.9	3.2	2.4	84	1.4	3.4
Oct.	105	7.20	26	18	5.4	3.9	3.0	84	2.4	6.8
Nov.	145	7.25	22	3	8.5	5.0	4.0	140	3.7	12
Dec.	147	7.30	23	32	8.0	5.8	4.0	140	4.0	12
Jan.	165	7.35	20	30	8.7	7.5	4.8	153	6.0	11
Feb.	190	7.70	30	35	8.7	8.5	4.2	172	6.7	10
Mar.	225	7.50	35	37	11.0	12.0	4.5	197	9.2	14
Apr.	230	7.60	30	40	9.0	10.5	5.0	189	8.8	14
May	180	7.45	30	32	9.5	11.6	5.1	155	9.5	13

\*Since the concentrations of F, NO<sub>3</sub> and B were in fractions of one ppm, they have not been considered in <sup>3</sup> the present work.

TABLE - 3  
[Handa (1972)]

Average chemical composition of the Ganga  
river at Dakshineswar (1968-69).

Concentrations in ppm.

Month	TDS	pH	H <sub>4</sub> SiO <sub>4</sub>	Ca	Mg	Na	K	HCO <sub>3</sub>	Cl	SO <sub>4</sub>
Nov.	275	7.40	26	55	15	11	4.3	252	16	9.5
Dec.	390	7.35	32	71	21	20	5.3	329	22	12
Jan.	435	7.45	32	73	22	40	6.4	355	29	15
Feb.	485	7.55	29	72	26	47	8.0	365	60	21
Mar.	660	7.45	22	67	46	98	12.0	341	198	44
Apr.	1100	7.35	28	62	51	266	22.0	305	460	68
May	1900	7.80	27	68	79	498	31.0	305	862	133
June	205	7.50	27	30	14	30	6.3	165	25	13
July	198	7.40	30	28	12	20	1.8	152	13	9.5
Aug.	130	7.30	22	24	6	5	3.1	113	6	2.6
Sept.	150	7.35	15	34	6	8	3.8	147	7	5.8
Oct.	189	7.40	19	45	11	10	4.1	190	12	7.5

\*Since the concentrations of NO<sub>3</sub> were in fractions of one ppm,  
they have not been considered in the present work.

explained. The discussion on mineral equilibria does not record the longitudinal variations in the phases of the silicate and carbonate systems. No comments have been made on the carbonate system, whereas in the case of the Silicate system it has not been conclusively established that the river water is in equilibrium with Kaolinite.

A detailed study of the mineral equilibria of the Ganges system is necessary as it is one of the largest irrigating systems in the world, and, some new studies in the field of water - mineral equilibria will be of relevance. Secondly, the saturation levels of various carbonate minerals analysed here, can be used to examine the use of water from this system for industrial purposes. Finally, the study will also help in predicting whether the external supply of metal ions such as from industrial effluents can be removed by the expected precipitates.

Therefore, the above considerations led to the following study of the River Ganges by making use of the water quality data from, Handa (1972). First, the variation of the total dissolved solute has been examined to account for the seasonal and longitudinal variation. Then, the carbonate equilibria in the river water has been studied by considering the saturation levels of some important carbonate minerals, like Calcite, Aragonite, Dolomite and Magnesite. A phase diagram involving these minerals has been developed, and the appropriate analytical data from Handa (1972) plotted on it, to determine the carbonate mineral with which the water is in equilibrium.



In the case of the Silicate system, phase diagram involving the components  $K_2O-Al_2O_3-SiO_2$  was developed. Since, the variables  $\left[\frac{K^+}{H^+}\right]$  and  $[H_4SiO_4]$  fitted in the Kaolinite region for all the stations, diagrams involving other components, like MgO and CaO, were not developed. The phase diagram in the Kaolinite region has been enlarged to bring out the trend resulting from seasonal variation.

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snow-fed. The river leaves the mountains near Hardwar and flows across the Indo-Gangetic alluvials until it meets the Brahmaputra in Bangladesh (Raymahashay, 1970). The combined stream called the Padma together with the discharge from another tributary called The Meghna drains into the Bay of Bengal.

The Ganges basin has annual monsoon rains averaging from 1500 - 2120 mm. near the delta, 1000 mm. in the middle part, and 750 mm. towards the western end (U.N., 1966).

The drainage area of the Ganges is composed of highly weathered sediments and volcanics (Raymahashay, 1970), which results in a heavy clay load in the channel. According to Holeman (1968), in terms of sediment yield, Ganges is the second largest river in the world.

#### Selection of data:

It was pointed out in the last chapter that the main reason for selecting Handa (1972) for analysis was that it had recorded the water quality data for the entire seasonal cycle. Since the aim of the present work, is to bring out the changes in phase and total dissolved solids in terms of the seasons, water quality data typical

**FIGURE 1: The course of the Ganges from its source to the sea. Important tributaries have been shown. The three stations chosen for the present study have also been marked.**

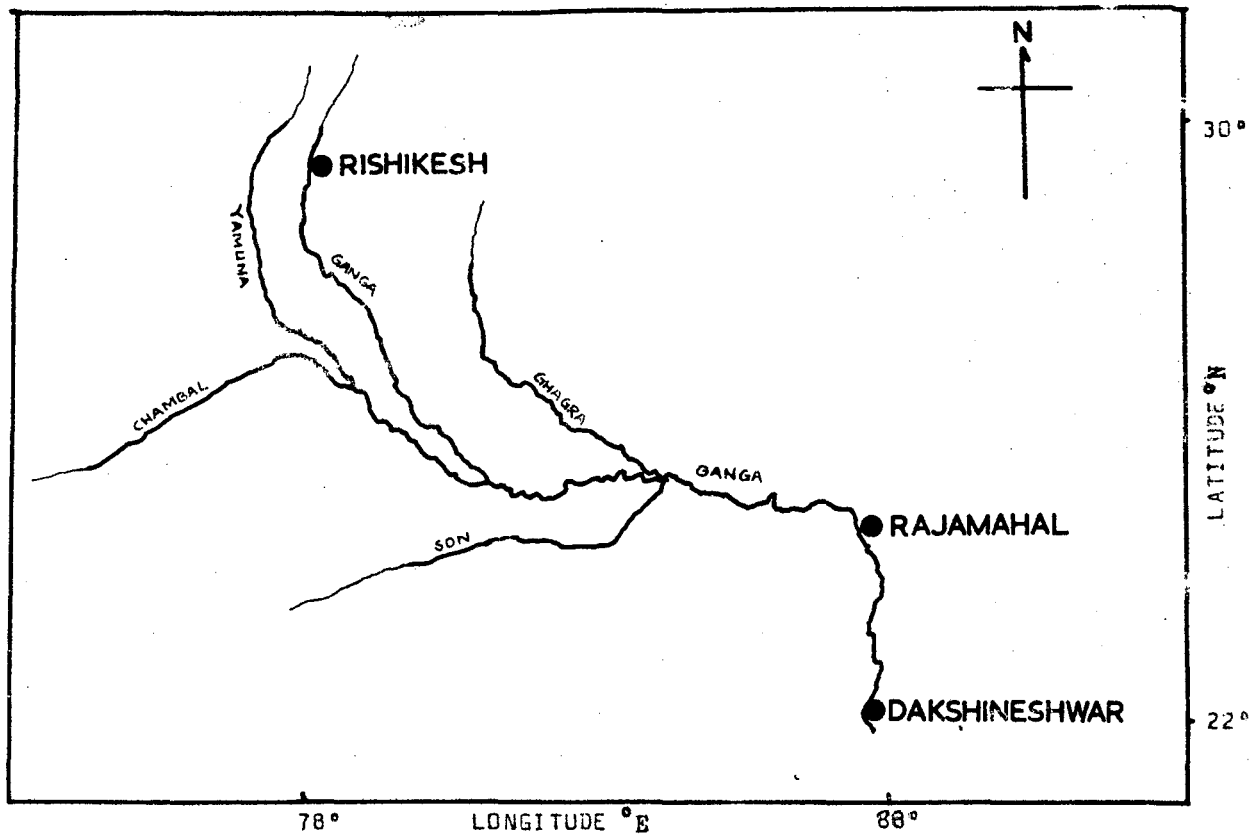


FIG. 1

Of the seasons were chosen. For example, for the total dissolved solids and carbonate equilibrium studies, the data for the months of January, April, August and November, each representative of a typical season in a year have been chosen. In the case of silicate equilibrium, the same consideration is applied with a slight difference. As it was found that there were appreciable differences in the values of Silicate ion concentrations around the year, to include all possible values, it was decided to choose six months in a year.

Analysis of water has been carried out with samples from three stations, namely, Rishikesh, Rajmahal and Dakshineshwar. The first station, Rishikesh, lies near the source, and the second station is Rajmahal. Before the main river reaches Rajmahal many of the important tributaries, like Yamuna, Chambal and Son, joins up with it. The last station is Dakshineshwar which lies almost at the mouth.

In a work of this nature, when reliance is placed upon another author's work, it is bound to suffer from limitations. First of all, the choice of stations is too few to give a real picture. In fact, it would have been much more meaningful, if water quality data were available for at least a dozen stations situated all along the river at regular intervals. Secondly, the analysis does not seem to have been carried out immediately after the collection of samples, especially, pH and Silicate determinations. It is well known that changes in their values could occur due to storage. Finally, the biggest limitation is the temperature factor. In none of the data,

temperature has been quoted. As is well known, in any work of equilibrium studies, it is one of the most important factors (Kramer, 1967). In the present work, therefore, the standard temperature of 25°C is considered while analysing the data.

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Total Dissolved Salts:

Figure 2 shows the values of total dissolved load at the three stations, namely, Rishikesh, Rajmahal and Dakshineshwar. The vertical bars in the figure represent seasonal variations. Because of discharge effects, total dissolved load can be expected to vary seasonally (Edwards, 1973; Gibbs, 1967, 1972; Grove, 1972; Livingstone, 1960).

Longitudinal variations, in general, can be explained by two reasons depending upon, whether the amount of total dissolved salts increases or decreases. The decrease in the dissolved salts may be due to inorganic precipitation occurring along the course, or removal of salts by the ecosystem, or by dilution caused by a river entering with a small dissolved load (Subramanian, 1974). On the other hand, increase in the amount of total dissolved salts can be due to the dissolution of some of the inorganic phases in the sediments such as  $\text{CaCO}_3$ , or by addition of water from a tributary draining a soft rock basin. Furthermore, if the bank is heavily urbanised or industrialized, then salts can be expected to be added to the river in the form of urban and industrial effluents.

In the case of the Ganges river, the variation of total dissolved salts records an increase all along the river. But the increase is not uniform in nature. Whereas, the amount of total

**FIGURE: 2: The longitudinal variations of total dissolved solute values have been represented graphically. The Arithmetic Means of the seasonal variations for each station has been joined by the dotted line. The vertical line represents the seasonal variations.**



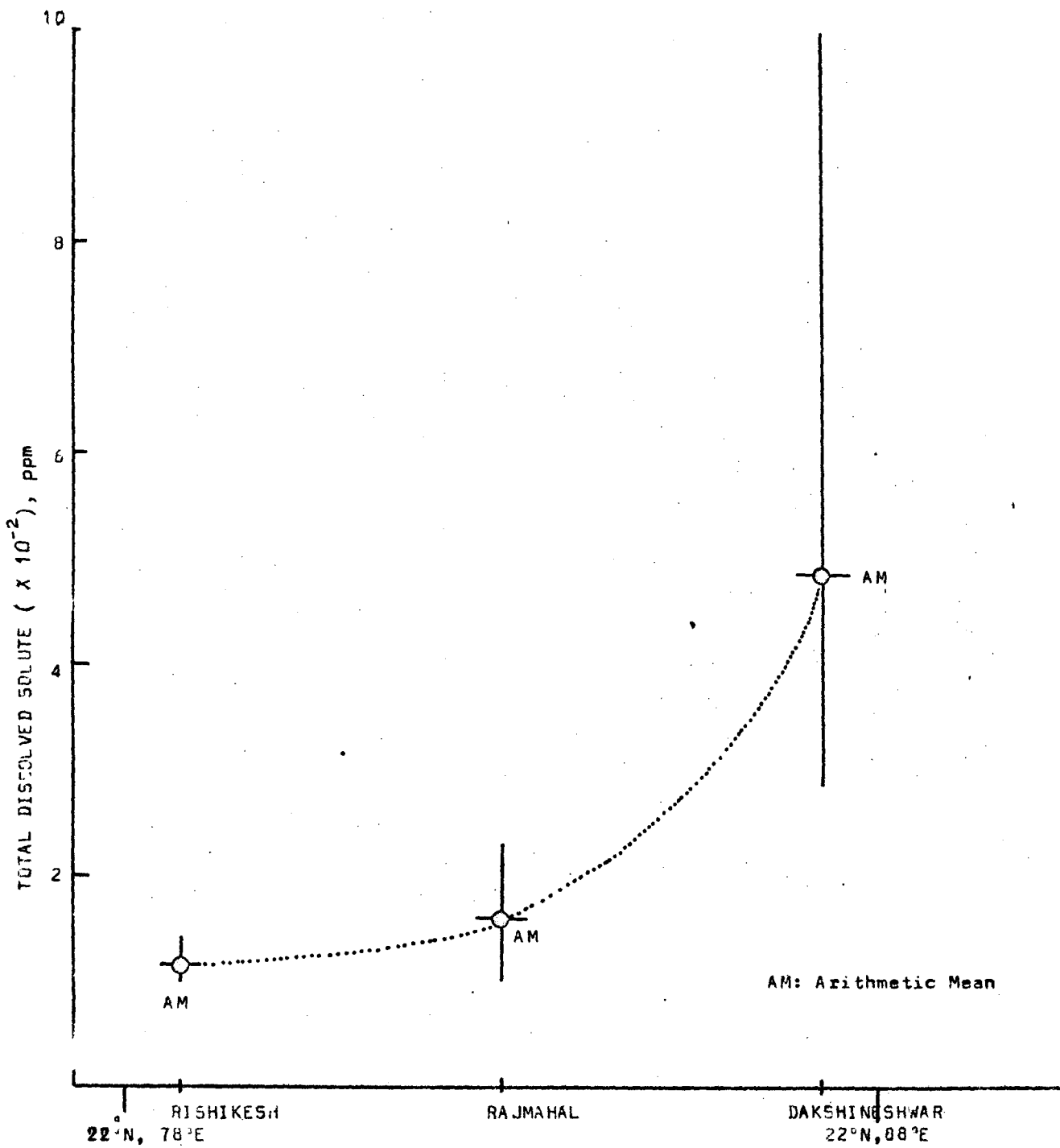


FIG. 2

dissolved salts gradually increases between Rishikesh and Rajmahal, the variation is sharp in between Rajmahal and Dakshineswar. Since Dakshineswar is situated in the estuarine region, it may represent a region of mixing of sea water from Bay of Bengal with the Ganges river water.

From the discharge effect point of view, normally a decrease in the value of total dissolved solute is expected at Rajmahal as compared to that in Rishikesh as was shown for some African rivers by Grove (1972). This is because some of the major tributaries like Yamuna, Son and Chambal join the main river before it reaches Rajmahal. Their combined effect should have diluted the waters and a decrease in the total dissolved salts value must have occurred. Hence, the increase has to be explained as either due to constituents being derived from the leaching of the upper part of the soil profile, or due to salts being added from industry. It is pertinent to point out here that this belt is one of the major industrial regions in the country.

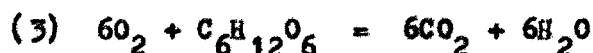
The other important argument that goes in favour of the observed increase in total dissolved salts is the increase in the atmospheric precipitation all along the course of the river (U.N. 1966). Gibbs (1970) has proposed atmospheric precipitation, as one of the major factors that control the world river water chemistry. He has observed that precipitation is a significant source of dissolved constituents in world rivers.

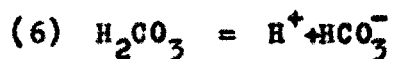
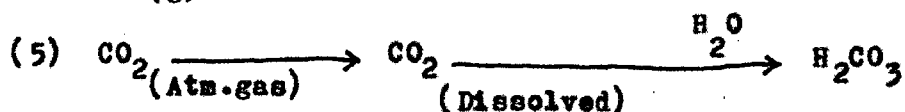
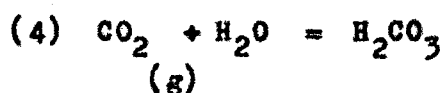


In the first reaction calcite is being leached to bicarbonate and in the second reaction albite weathers to kaolinite. Such reactions offer a possible natural source for bicarbonate. It has also been observed from the data, that the concentrations of bicarbonate are higher in Rajmahal and Dakshineswar than in Rishikesh. As temperature is an important factor controlling the rate of a reaction (Zumberge and Nelson, 1972), increased rates for the above weathering reactions may be observed in Rajmahal and Dakshineswar than in Rishikesh, because the former places are situated in the plains whereas Rishikesh lies at the foothills of Himalayas. The second reaction assumes added relevance when it is combined with the observation that kaolinite is the common constituent of the Ganges river sediments, as reported by Handa (1972). This observation has also been verified theoretically through the concept of phase diagram discussed later in this work.

In the light of the fact that the banks of the river are highly industrialized and urbanized, an explanation from this point of view could also be offered.

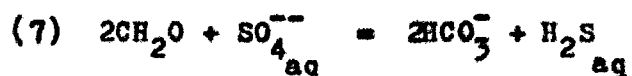
Organic matter, a very common constituent of agricultural effluents, can break down to release  $\text{CO}_2$  which may hydrolyse to give excess  $\text{HCO}_3^-$  to the river water; further the atmospheric  $\text{CO}_2$  will also hydrolyse to give  $\text{HCO}_3^-$  to the river water. The above two situations can be explained in terms of the following reactions:



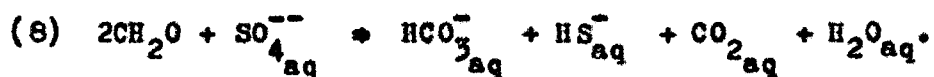


Such an organic decay to produce  $\text{HCO}_3^-$  and alter the pH has been experimentally demonstrated by Berner (1971).

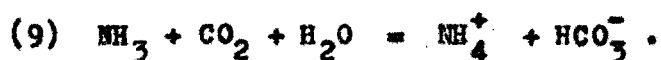
The above mentioned cases are examples, where  $\text{HCO}_3^-$  ions can be produced under aerobic oxidation of effluents. With the increasing pollution of natural waters by organic wastes from urban areas, the possibility of production of bicarbonates under anaerobic conditions also exists. For example, sulphates which are an important constituent of wastes from petrochemical and coal industries (Subramanian, 1974) could lead to bicarbonates, as shown by the generalized overall reactions, using carbohydrates.



or



The other major element in the effluents is Nitrogen principally from the farmlands, which could also produce bicarbonate, following reaction such as,



Mineral Equilibria in the System CaO-MgO-CO<sub>2</sub>-H<sub>2</sub>O

Chemical equilibrium concepts are valuable in considering a dynamic fresh water regime for several reasons: (1) relating actual conditions to equilibrium model results help to isolate important biological, physical and chemical processes; (2) the lack of fit of equilibrium model predictions to actual situations emphasizes areas for further investigation; (3) organization of systems allows for generalization and simplification of empirical water chemistry data (Kramer, 1967).

In the study of carbonate system, two chemical equilibrium concepts have been used to analyse the water quality data and determine the nature of sediment with which the water is expected to be in equilibrium. By means of Ion Activity Product (I.A.P.) and the Solubility Product values (K), the saturation levels of some of the important carbonate minerals like Calcite, Aragonite, Dolomite and Magnesite have been examined. Also, phase diagram involving these minerals was developed and the appropriate data plotted on it to predict the expected assemblages in the system under consideration.

Study of Saturation Levels:

The Ionic Activity Product (I.A.P.) of a salt is defined as the product of the activities of the ions in solution at that temperature which in all the cases has been taken to be 25°C. The activity coefficients of the ions throughout the work have been

calculated by making use of the Debye - Huckel equation (Garrels and Christ, 1965). Then they were compared with the Solubility Product constant for each mineral at each of the months by taking the ratio  $\frac{I.A.P.}{K}$ . The ratios have been tabulated in the appendix (Table 4).

According to Edwards (1973), when the ratio is 1.0, the water is in equilibrium with respect to that mineral. Ratios higher than 1.0 indicate supersaturation and those lower unsaturation. The observed saturation level on the basis of the ratio has also been mentioned in the table. Longitudinal variations of the  $\frac{I.A.P.}{K}$  values for all the stations have been represented graphically (Figure 3 to 6) for all the above mentioned minerals.

Three important conclusions about the saturation levels are worth mentioning: (1) With respect to Aragonite and Magnesite, the mean value of the saturation levels of the water lies below the equilibrium value of 1. (2) In the case of Dolomite, the river is highly saturated and in fact, the ratio records extremely high values in Dakshineshwar. (3) In all the cases, there is a trend towards increasing saturation for all minerals.

#### Phase Study:

If the assumption is made that carbonate minerals are in equilibrium with the waters, the interrelations of the minerals can be shown as functions of the activities of the ions dissolved in the water. Hence, it is possible to develop qualitative diagrams that are useful, if only to provide a graphic summary of the mineral

FIGURE 3 to 6: The saturation levels  $\frac{I.A.P.}{K}$  for the carbonate minerals, Calcite, Aragonite, Dolomite and Magnesite and their variations seasonally as well as longitudinally have been represented. The  $\frac{I.A.P.}{K}$  corresponding to 1 represents the equilibrium value. Values higher than 1 indicates saturation and below 1 undersaturation.



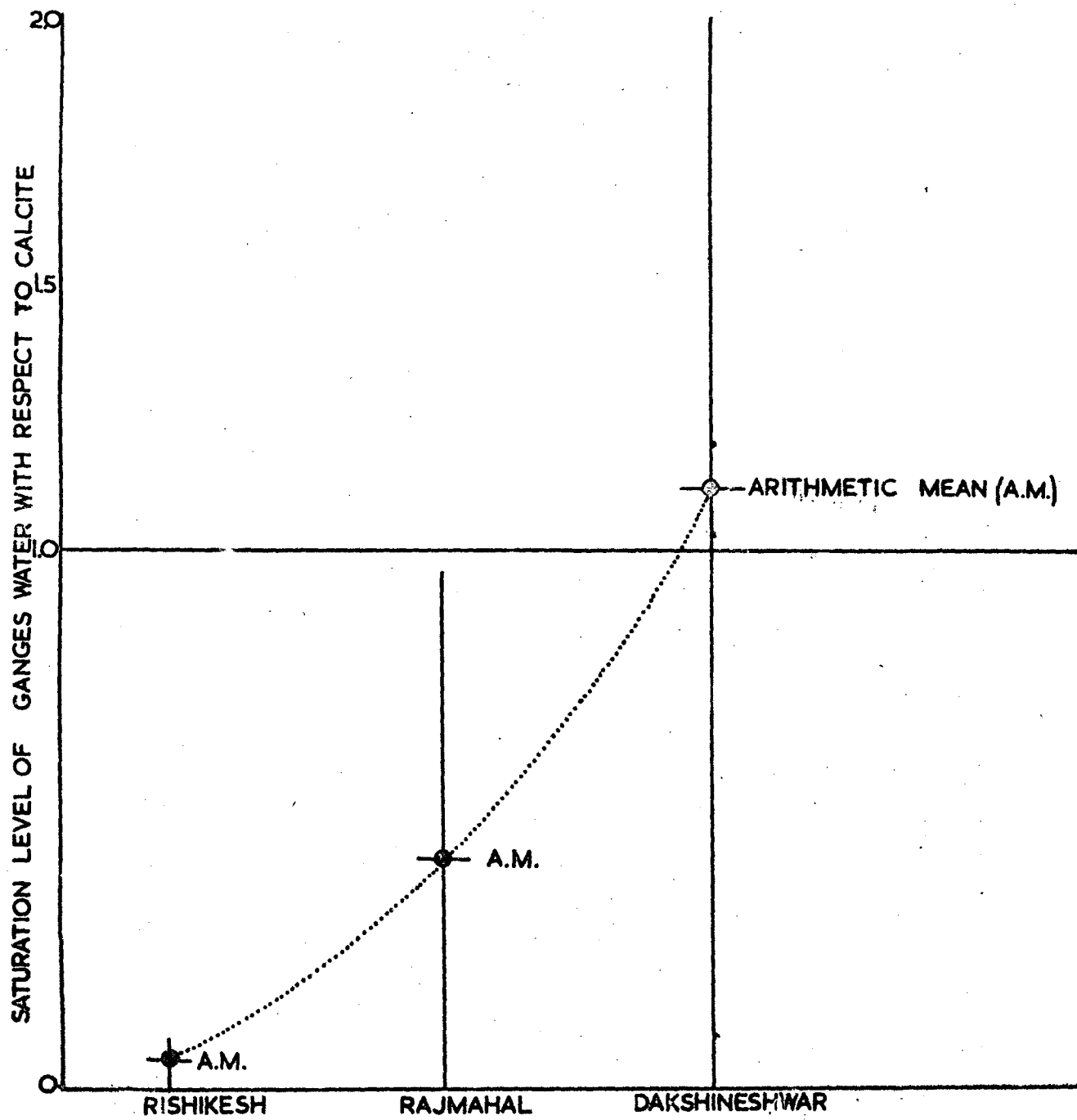


Fig. 3

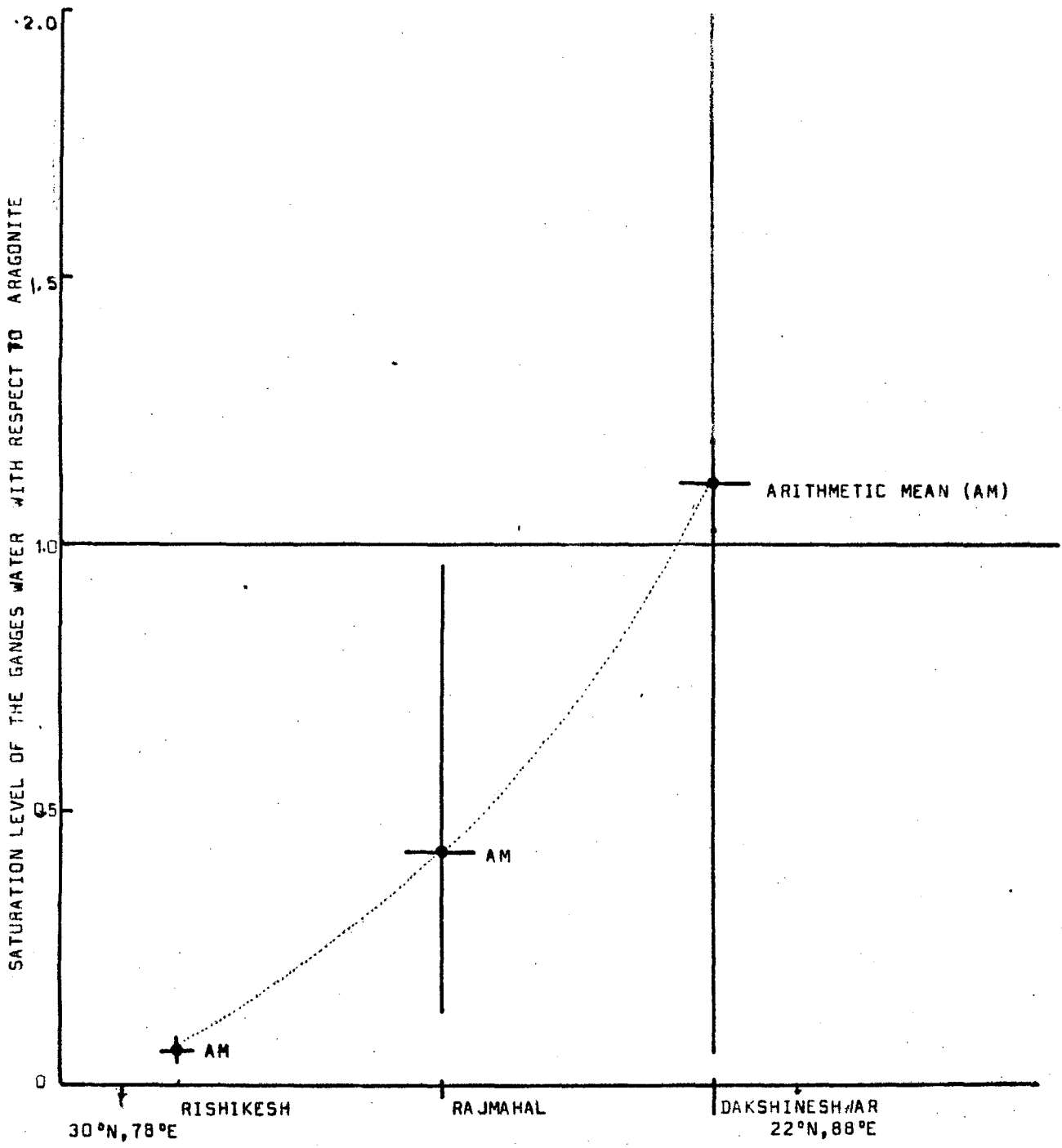


Fig. 4

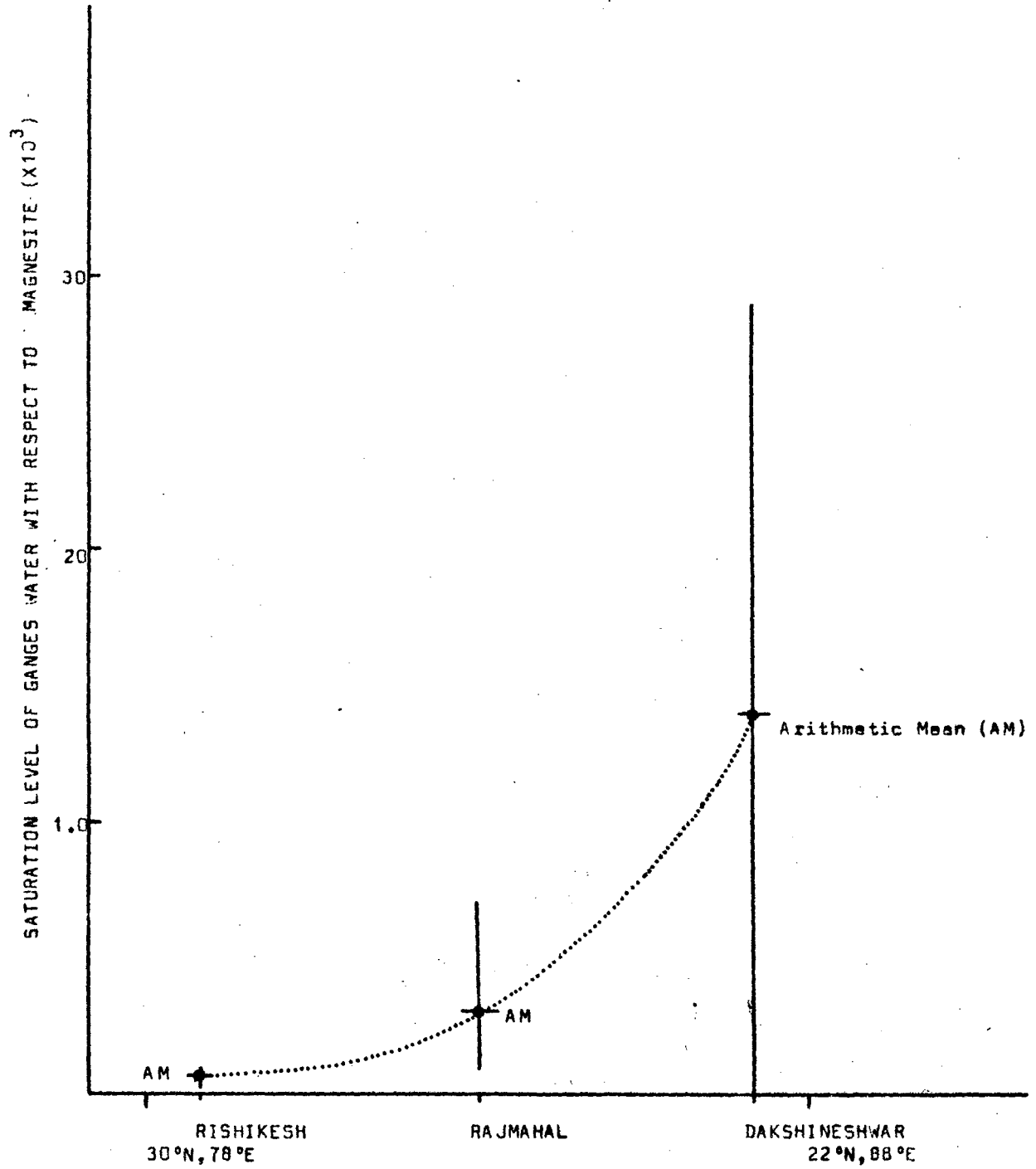


Fig. 5

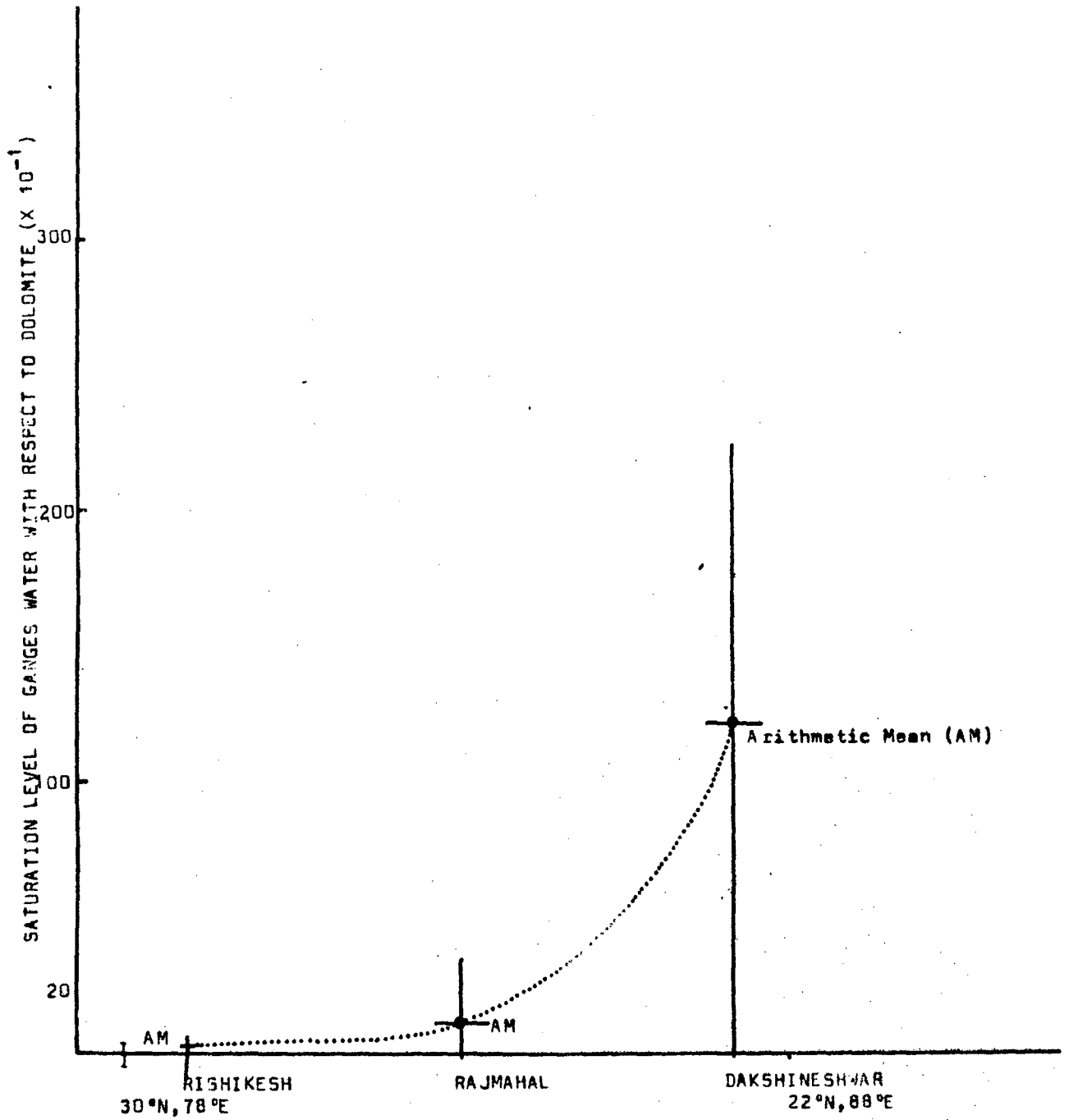
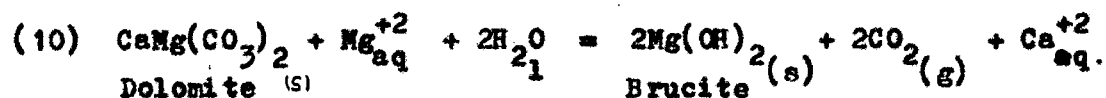


FIG. 6

sequences that might be expected if equilibrium were attained (Garrels and Christ, 1965).

Carpenter (1962) has constructed an interesting diagram that shows metastable and stable equilibria among the Calcium and Magnesium carbonates (Figure 7). The boundaries between the phases are calculated from  $\Delta G_f^\circ$  values. As a means of illustration, the equilibrium between Brucite and Dolomite is considered. The equilibrium between these two minerals can be represented by the following chemical reaction:



The equilibrium constant (K) will be given by

$$(11) \quad K = \frac{[\text{Mg}(\text{OH})_2]^2 [\text{Pco}_2]^2 [\text{Ca}^{+2}]}{[\text{CaMg}(\text{CO}_3)_2]_s [\text{Mg}^{+2}] [\text{H}_2\text{O}]^2}$$

By making the assumption, that the activities of Brucite, Dolomite and water are equal to unity\*, the above equation reduces to

$$(11a) \quad K = \frac{[\text{Pco}_2]^2 [\text{Ca}^{+2}]}{[\text{Mg}^{+2}]}$$

The K value is calculated by making use of the change in free energy for the reaction in the following equation

$$\Delta G^\circ = -RT \ln K$$

and at STP,  $\Delta G^\circ = -1.364 \log_{10} K$ .

---

\*This assumption is not strictly valid for Dolomite, since it is a solid solution. However, for the purpose of this discussion, the Dolomite is taken to represent an ideal pure composition and its activity considered unity.

**FIGURE: 7: Relations among Calcium and Magnesium carbonates at 25°C and 1 atmosphere total pressure, as a function of  $[P_{CO_2}]$  and  $[Ca^{+2}/Mg^{+2}]$ . Solid lines show equilibrium relations between stable phases; dashed lines show equilibrium relations between metastable phases, and between metastable and stable phases (Enlarged from Garrels and Christ (1965) p 376).**

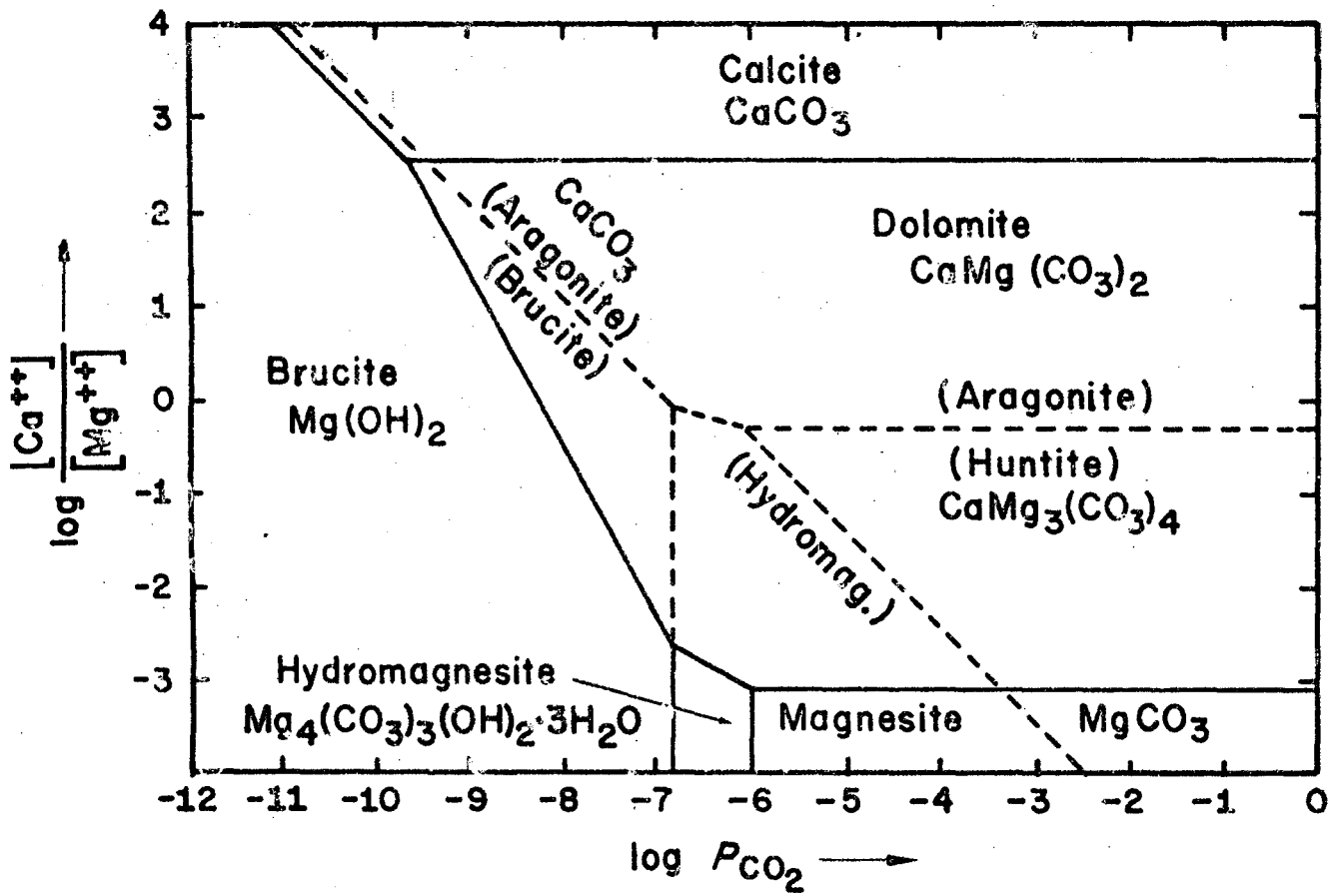


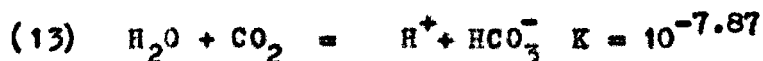
FIG. 7

If we take the logarithm of both sides of the equation (11a), it is reduced to a form that resembles the equation of a straight line:

$$(12) \quad \log \left[ \frac{Ca^{+2}}{Mg^{+2}} \right] = - 2 \log [P_{CO_2}] - \log K.$$

This equation in turn can be represented on a diagram. Similarly, the chemical equation between other phases, like Dolomite/Calcite, Calcite/Brucite and Magnesite/Dolomite can be considered and the phase diagram developed with  $\log [P_{CO_2}]$  and  $\log \left[ \frac{Ca^{+2}}{Mg^{+2}} \right]$  as two variables.

In order to plot the observed water analysis data on the developed phase diagram, the activity coefficients of Calcium and Magnesium ions were computed as described above. The partial pressure of  $CO_2$  was calculated as follows. For this purpose, the chemical reaction (Garrels and Christ, 1965):



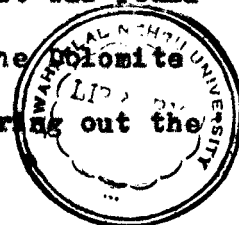
was considered to represent the interaction of the atmospheric  $CO_2$  with the natural waters. The partial pressure of the  $CO_2$  can be written in terms of the activities as follows:

$$P_{CO_2} = \frac{[H^+][HCO_3^-]}{K} \quad \frac{549(540)(282.253 \cdot 21)}{J334 \cdot 8T}$$

The data provided the concentrations of  $H^+$  and  $HCO_3^-$  and from these the activities were calculated.

When the logarithm of the observed  $[P_{CO_2}]$  and  $\left[ \frac{Ca^{+2}}{Mg^{+2}} \right]$  (Appendix, Table 5) were plotted on the developed phase diagram, it was found that all the points clustered around a small area in the Dolomite region and the seasonal variation was not clear. To bring out the

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seasonal variation clearly, the Dolomite region of the phase diagram has been enlarged (Figure 8).

The phase diagram for the carbonate system shows that the expected mineral to be in equilibrium with the water is Dolomite. The seasonal trend here is interesting. For Rishikesh and Rajmahal, the mineralogy exhibits a cyclic trend; the variation in the mineralogy moves in the direction of Brucite phase till August and afterwards the trend is reversed. For Hakshineswar, there is no such trend, and here, probably the mixing of sea water with fresh water complicates the mineralogy, since sea water is also supersaturated with respect to Dolomite (Garrels and Thompson, 1962).

The conclusion reached on the basis of solubility product concept as well as the phase study is that the expected mineral should be Dolomite.

In this connection, it will be interesting to examine the precipitation of Dolomite in the natural systems. Holland et al (1964) gave an activity product higher than  $10^{-15}$ , as against the K value of  $10^{-17}$  to  $10^{-19}$  for Dolomite, but no precipitation of Dolomite occurred in the sea water. This indicates that supersaturation with respect to Dolomite can exist for long periods. Similarly, in the laboratory experiments under simulated conditions carried out by Kranskopf (1965) indicates no precipitation of Dolomite from sea water.

To explain the anomalous behaviour of Dolomite, Kranskopf (1965) has come out with some explanations. According to the author, the

**FIGURE 8:** The plot of carbonate mineral equilibria in the River Ganges. As all the water quality data lie in the Dolomite region, to bring out the seasonal variations clearly, this area has been enlarged.

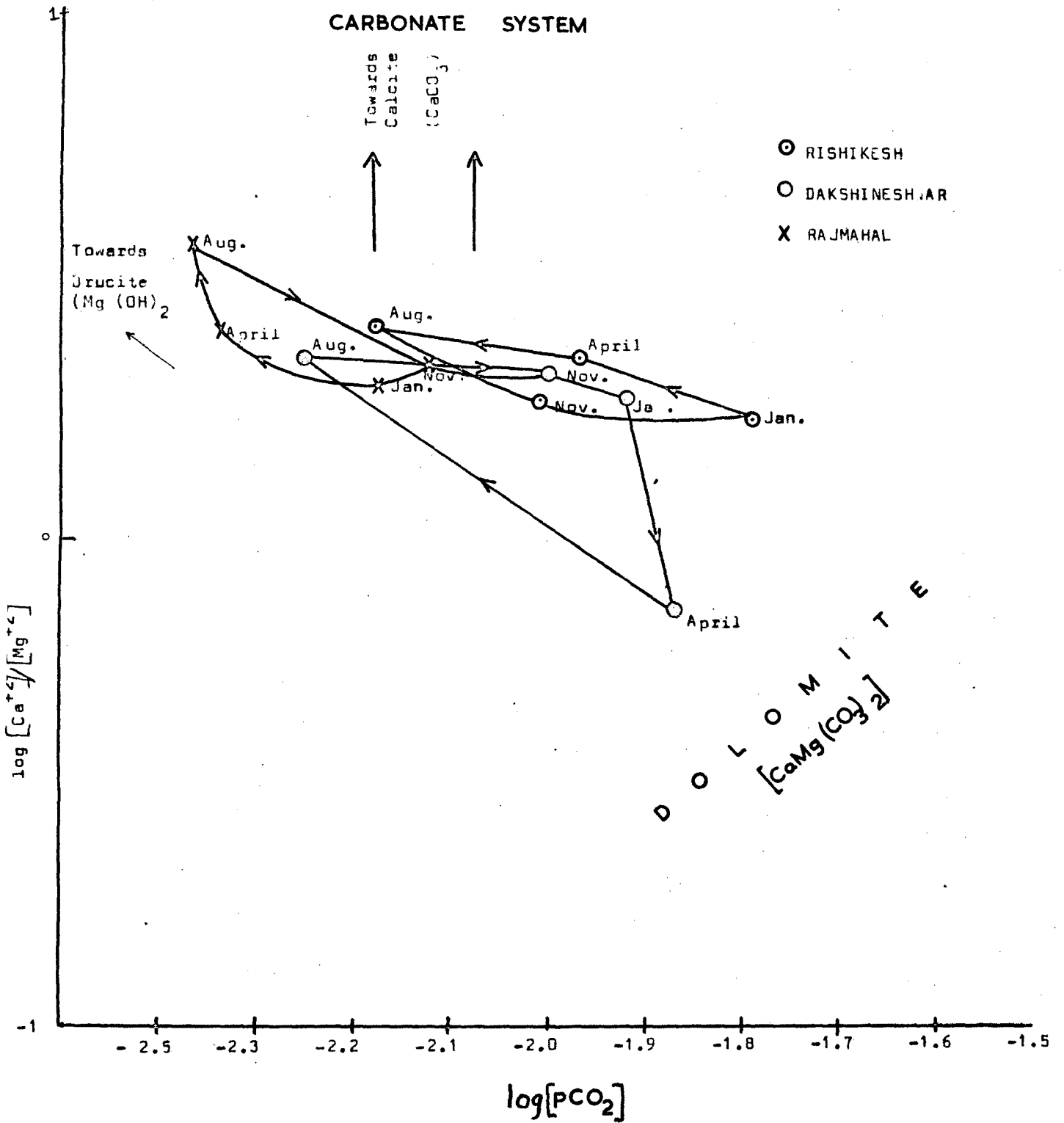


FIG. 8

main reason could be the peculiar crystal structure of Dolomite, which forbids its formation quickly at low temperatures. It has been found by the same author that the precipitation of Dolomite is hastened at higher temperatures. The second explanation given is that Dolomite is not precipitated as  $\text{Ca Mg} (\text{CO}_3)_2$  in natural water but as Calcite which in turn is converted to Dolomite. In other words, the formation of Dolomite is not the result of the combination of  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  and  $\text{CO}_3^{--}$  ions, but results from the combination of  $\text{Ca CO}_3$  (Calcite) with  $\text{Mg}^{+2}$  following a reaction of the type,



Mineral Equilibria in the System  $\text{Na}_2\text{O}-\text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$

Water composition plotted on activity - activity diagrams of the aluminosilicate system has been used by several workers to successfully predict the composition of sediments in equilibrium with the water (Kramer, 1967; Garrels and Mackenzie, 1971; Jacks, 1973; Subramanian, 1974). The water composition can be studied as a function of pH, concentration of  $\text{H}_4\text{SiO}_4$  and the concentration of one particular cation such as  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$  or  $\text{K}^+$ . A number of two dimensional plots can be prepared with the above variables and an equilibrium water composition for the silicate minerals can be derived for each set of variables (Jacks, 1973). Such an analysis for the St. Lawrence river and estuary water indicates that the waters should be in equilibrium with chlorite, illite, gibbsite and kaolinite (Subramanian, 1974). Similar observations have also been made by Jacks (1973) for waters from various igneous rocks.

In the present work, such an analysis has been attempted. It was decided to develop a phase diagram for some of the silicate minerals like gibbsite, kaolinite, chlorite and K-Feldspar. Accordingly, three variables  $\text{K}^+$ ,  $\text{H}^+$  and  $\text{H}_4\text{SiO}_4$  were considered and an orthogonal plot consisting of two variables  $\log\left[\frac{\text{K}^+}{\text{H}^+}\right]$  and  $\log\left[\text{H}_4\text{SiO}_4\right]$  was developed for the mineral systems consisting of gibbsite, kaolinite, K-Mica and K-Feldspar. On plotting the appropriate data, that is,  $\log\left[\text{H}_4\text{SiO}_4\right]$  and  $\log\left[\frac{\text{K}^+}{\text{H}^+}\right]$  (Appendix Table 6) from the water quality data, it was found that for all analysis the

water fell in the Kaolinite region. Therefore, other components like MgO, CaO and Na<sub>2</sub>O were not considered, and the stability diagram involving K<sub>2</sub>O - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> - H<sub>2</sub>O at 25°C and 1 atmp. pressure was developed (Figure 9). To bring out the seasonal trend clearly, the Kaolinite region of the diagram has been enlarged (Figure 10).

The stability diagram leads to two important conclusions. First, as against the case of carbonate system, there is no clear seasonal trend in the waters at each station. But there is a definite longitudinal trend and as the river flows towards the ocean, there is a gradual shift of the mineralogy in the direction of K-Mica occurs.

If the actual mineralogy of the sediments had been known it would have been interesting to compare that with the predicted one. No information of this nature except an observation that the water is expected to be in equilibrium with Kaolinite is available. In case of other river systems like St. Lawrence such an exercise to determine the actual mineralogy has been attempted (Subramanian and D'Anglejan, in press). In some cases the observed mineralogy has proved different than the predicted one. For example, on the basis of water chemistry data Subramanian (1974) predicts the minerals to be composed of gibbsite and chlorite in the case of St. Lawrence. Rutherford (1972) has reported only illite, chlorite and mixed layer clays in the bottom sediments of the St. Lawrence river, but gibbsite has not been reported any-

FIGURE 9: Stability relations of some phases in the system  $K_2O - Al_2O_3 - SiO_2 - H_2O$  at 25°C and 1 atmosphere, as functions of  $\left[\frac{K^+}{H^+}\right]$  and  $[H_4SiO_4]$ . Numbers in boundary lines refers to equations in text (Garrels and Christ, 1965).

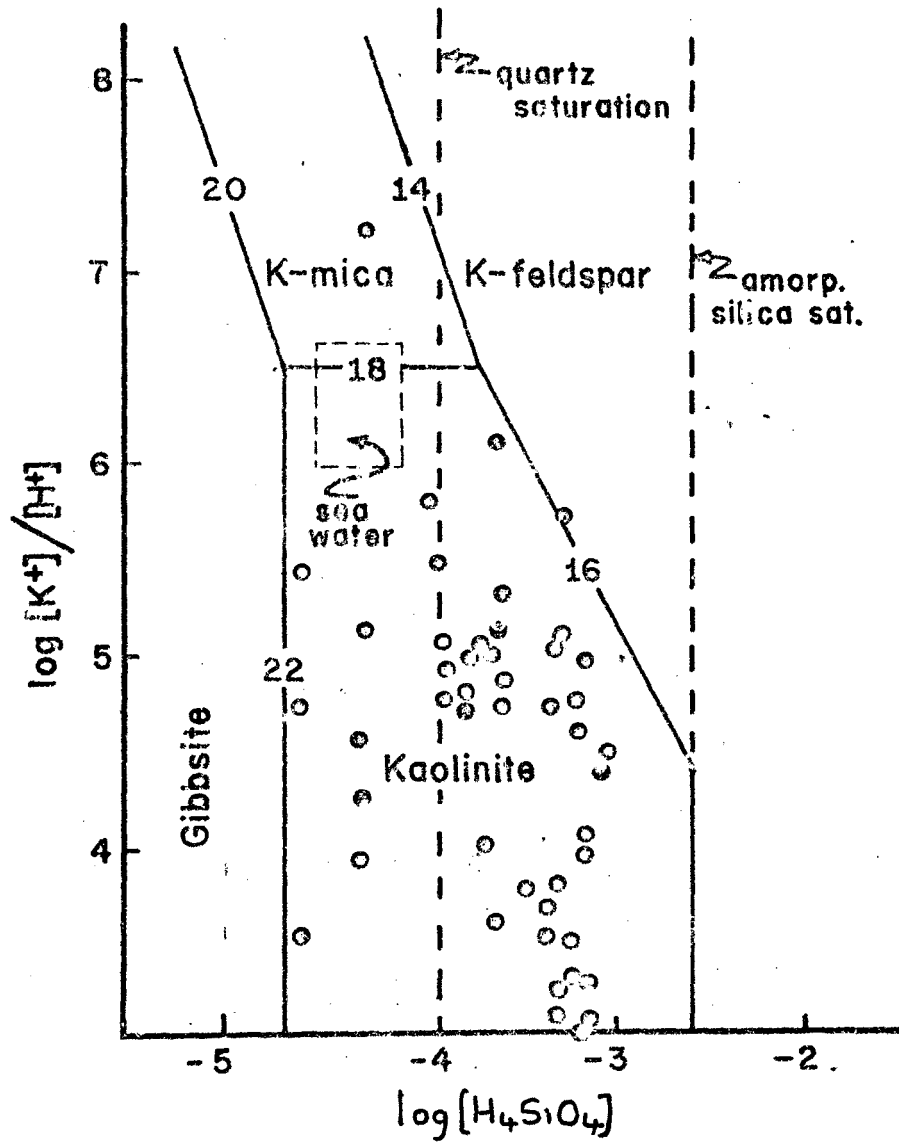


FIG. 9



**FIGURE: 10:** The plot of water composition of River Ganges at the three stations in the aluminosilicate system. Since, all the plots fell in the Kaolinite region, it has been enlarged. A longitudinal shift towards K-Mica is observed.

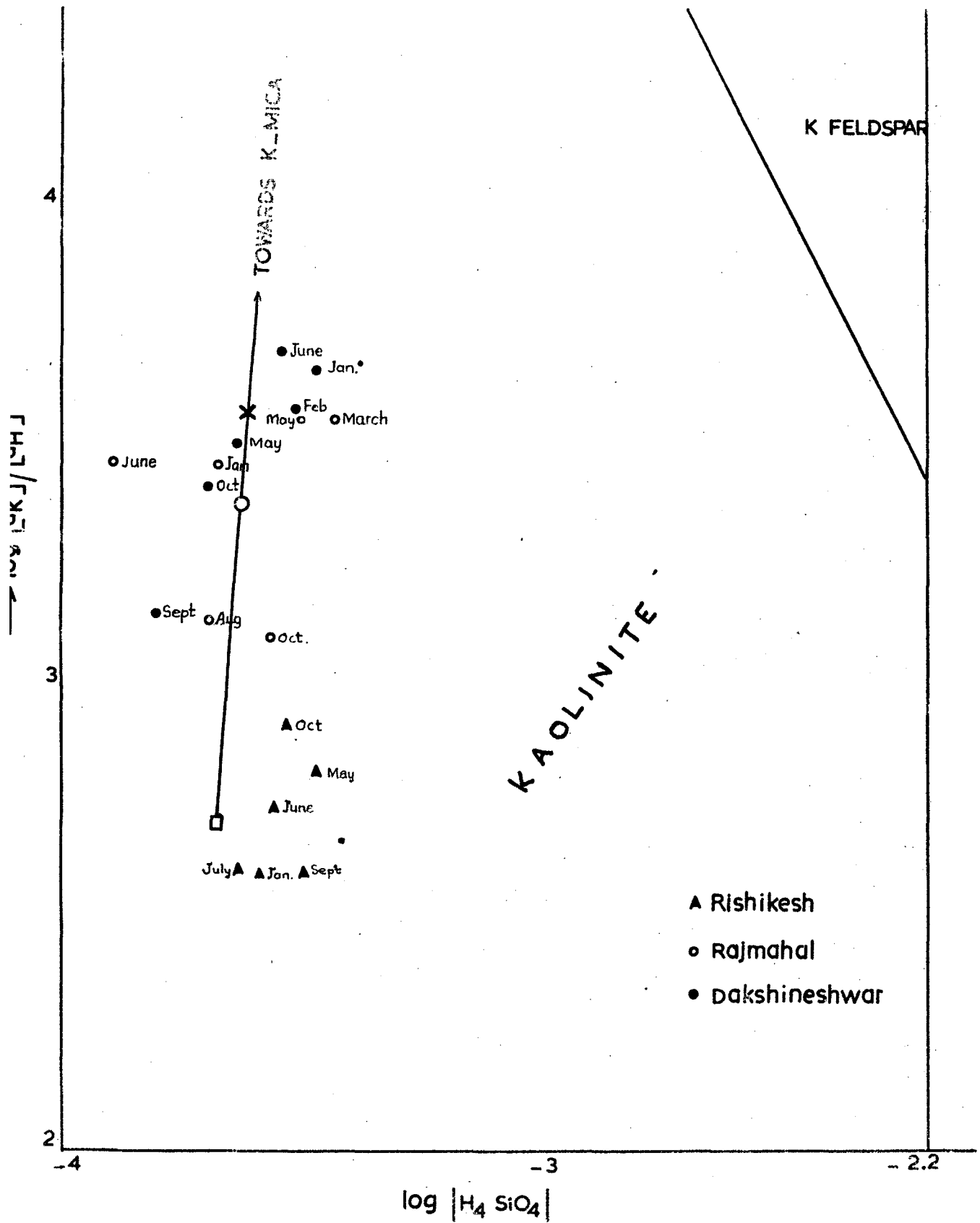


Fig. 10

where (Subramanian, 1974). Therefore, in the case of the River Ganges too, study on the actual mineralogy of the sediments is essential to make useful interpretations. Nevertheless, the present study has shown that the expected mineralogy must be in the Kaolinite region, a longitudinal trend clearly exists, and the equilibrium shifts in the direction of K-Mica, which is the stable phase expected to be in equilibrium with sea water (Helgeson and Mackenzie, 1970).

The above trend in mineralogy that has been observed in the case of the River Ganges agrees well with the study that has been carried out by Garrels and Mackenzie (1971). The authors have shown that the plot of river water generally falls in the Kaolinite region and that of sea water in the K-Mica region. Similarly, here it has been shown, that the progressive change from a fresh water to sea water regime is reflected in the change in mineralogy from Kaolinite to K-Mica. Since, all the water analysis fall in the aluminosilicate system, it raises a question about the complete absence of gibbsite phase in the water. The answer probably lies in the explanation provided by Garrels and Mackenzie (1971) that gibbsite forms only in soils that are continually drained by water deficient in silicate and bicarbonate. However, even in Rishikesh, where the bicarbonate concentration is comparatively less, none of the water analysis falls in the gibbsite region. Therefore, the silica concentration in the waters must be responsible for the



### CONCLUSION

In the course of the present study, three main conclusions have been reached:

- 1) The total dissolved solute in the Ganges river exhibits a longitudinal as well as a seasonal trend;
- 2) The river water is supersaturated with the mineral Dolomite; in respect of Calcite and aragonite, along the course, the water gets increasingly saturated, and
- 3) the water composition in the aluminosilicate system plots in the Kaolinite region, but a longitudinal trend towards K-Mica region has been observed. Thus, it is significant, that on the basis of field investigations in the fresh water region, Handa (1972) suggests the presence of Kaolinite, and Mallik (1976) has observed Kaolinite and K-Mica in the mouth of the Hooghly river.

Raymahashay (1970) has mentioned the predominance of mechanical weathering over chemical weathering in the case of the Ganges river. However, an analysis of the carbonate equilibria, suggests that chemical weathering to a great extent is responsible for the practical role the river plays in the environment. For example, the increasing pH arising out of an increase in  $\text{HCO}_3^-$  ion concentration all along the river, may help to precipitate some of the toxic heavy metals as hydroxides. Further, the usefulness of the river water is also dependent upon the saturation levels of carbonate minerals. It has been shown that the river is highly super-

saturated with respect to dolomite and no precipitation of this mineral has yet been reported. Therefore, the use of such waters in industries without modifications can lead to corrosion problems.

The analysis of silicate mineral equilibria is of academic interest. However, in the geological time scale, as has been discussed in the text, the weathering reactions assume importance.

A.P.P.E.N.D.I.X

TABLE - 4

I.A.P.  
K Solubility Product

Ratios for Calcite, Aragonite, Dolomite and Magnesite.

Stations	Months	<u>I.A.P.</u> K <sub>Cal.</sub>	<u>I.A.P.</u> K <sub>Ar.</sub>	<u>I.A.P.</u> K <sub>Dol.</sub>	<u>I.A.P.</u> K <sub>Magnesite</sub>	Explanations
Rishikesh	January	0.0816 (U)	0.0621 (U)	4.0200 (S)	0.00008 (U)	
	April	0.0557 (U)	0.0406 (U)	1.3300 (S)	0.00004 (U)	<u>Values of Solubility Used (From Berner (1971)).</u>
	August	0.0562 (U)	0.0440 (U)	1.3240 (S)	0.00004 (U)	
	November	0.0670 (U)	0.0499 (U)	2.396 (S)	0.00006 (U)	
Rajmahal	January	0.3366 (U)	0.2540 (U)	5.8050 (S)	0.0003 (U)	K Aragonite = $6.0 \times 10^{-9}$
	April	0.9576 (U)	0.7100 (U)	368.800 (S)	0.0007 (U)	K Dolomite = $1.91 \times 10^{-20}$
	August	0.1400 (U)	0.1070 (U)	5.200 (S)	0.0001 (U)	K Magnesite = $2.51 \times 10^{-6}$
Dakshineshwar	January	2.0488 (S)	1.5360 (S)	2265.1 (S)	0.0018 (U)	(U) - Undersaturated
	April	1.1890 (S)	0.8904 (U)	2039.7 (SS)	0.0029 (U)	(S) - Saturated
	August	0.1911 (U)	0.1433 (U)	16.20 (S)	0.0001 (U)	(SS) - Supersaturated.
	November	1.037 (S)	0.7875 (U)	537.7 (SS)	0.0009 (U)	



TABLE - 5

Tabulation of  $\log \frac{\text{Ca}^{+2}}{\text{Mg}^{+2}}$  and  $\text{Pco}_2$  values.

Station	Months	$\log \text{Pco}_2$	$\log \text{Ca}^{+2}/\text{Mg}^{+2}$
Rishikesh	January	-1.7931	0.2601
	April	-1.9706	0.3820
	August	-2.1808	0.4502
	November	-2.0105	0.2945
Rajmahal	January	-2.1797	0.3201
	April	-2.3375	0.4314
	August	-2.3605	0.6128
	November	-2.1165	0.3579
Dakshineswar	January	-1.9237	0.3032
	April	-1.8700	1.8692
	August	-2.2508	0.3856
	November	-2.0234	0.3464

TABLE - 6

Tabulation of  $\log H_4SiO_4$  and  
 $\log \frac{H^+}{H^+}$  values.

Station	Months	$\log H_4SiO_4$	$\log \frac{K^+}{H^+}$
Rishikesh	January	4.3962	2.5743
	February	4.3598	2.5752
	May	4.5224	2.7825
	June	4.4330	2.7076
	September	4.4942	2.5824
	October	4.4639	2.8823
Rajmahal	January	4.3181	3.4255
	March	4.5611	3.5253
	May	4.4942	3.5328
	June	4.0969	3.4412
	August	4.2967	3.1062
	October	4.4330	3.0692
Dakshineswar	January	4.5224	3.6318
	February	4.4800	3.5456
	March	4.3598	3.4753
	June	4.4487	3.6732
	September	4.1931	3.1209
	October	4.2967	3.3868

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