U^{234}/U^{238} AS A TOOL FOR DATING MARINE SEDIMENTS

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ABSTRACT

A method for dating the marine sediments using the decrease of U^{234}/U^{238} activity ratio in the calcium carbonate phase has been developed. A selective leaching agent $NH_4Ac\cdot HAc$ buffer is used which attacks only the calcium carbonate phase and very little of the other phases. The rate of sedimentation for the core, M–230 (Lat. 23° 10′N, Long. 67° 50′ E) from Indian Ocean is found to be 1·16 mm/1,000 yrs by this method. The calculated ionium value for the particular water column depth and for the typical composition of the top layer of the sediment 1·58 dpm/g, agrees very well with the actual value of 1·28 dpm/g observed, considering the uncertainties in the parameters used.

INTRODUCTION

POTRATZ (1955) and Barnes et al. (1956) observed increase of the ionium to uranium ratio with increasing depth in coral limestone cutting of Eniwetok atoll contrary to the decrease of ionium to uranium ratio found for deep sea sediments. Also, Barnes et al. (1956) reported that ionium is remarkably absent in freshly precipitated calcium carbonate deposits and suggested using the ionium growth for dating marine carbonates. Blanchard et al. (1967) concluded that dating by uranium disequilibrium measurements is applicable to fossil corals and other fossil marine carbonates that have formed and have remained in a marine environment. Further, the discovery of high U^{234}/U^{238} activity ratios in natural waters by Cherdyntsev' (1955) led to a serious study of the uranium isotopes disequilibrium in other media also, which resulted in the discovery of 15% excess of U^{234} over its parent U^{238} in sea-water by Thurber (1962). Later, Thurber et al. (1965 a) and Broecker and Thurber (1965) found excess U^{234} in recently-formed marine carbonates, oolites and corals and suggested the feasibility of using this excess 15% U^{234} for calculating the absolute ages of marine carbonates. Marine sediments from deep oceans contain several components : calcium carbonate, clays, detrital matter, etc., in varying amounts. The detrital uranium may have U^{234}/U^{238} ratio equal to or less than 1 (Ku-Teh-Lung, 1965). Thus, when measurements are made of U^{234}/U^{238} on total sediments, one obtains values nearer 1, if the detrital fraction is significant by weight. In the present work, an attempt is made to use the decrease in U^{234}/U^{238} activity ratio in the calcium carbonate phase of the marine sediments by developing a suitable leaching agent which does not attack the detri-tal phase. The material analysed is a core from Indian Ocean collected, on board R.V. Meteor.

ANALYTICAL PROCEDURE

The core sample of about 115 cm length was taken from the station Lat. 23° 10′ N, Long. 67° 50′ E (Gulf of Kutch). It was air-dried and sectioned at 10 cm intervals. The sample size was about 50 g for the uranium isotopes measurement in the calcium carbonate fraction and 5-10 g only for the same in the total sediment.

Calcium carbonate fraction of the sample was selectively attacked with 300 ml 4 N $NH_4 Ac$-2 N HAc buffer over a period of 24 hr. Leaching was repeated. Preliminary experiments with 50 g of molluscan shell pieces indicated that this amount of buffer solution was sufficient to dissolve the entire carbonate content. The buffer leach was evaporated to dryness, organic matter destroyed and the residue was taken up in 1 N nitric acid. It was oxidised with a little potassium bromate. Radiochemically pure uranium was isolated as per the procedure given by Sarma and Krishnamoorthy (1968).

The thin sources of plated uranium were counted in an alpha spectrometer consisting of a surface barrier detector coupled to an ORTEC low noise preamplifier unit and Nuclear Data 512 channel analyser for an average period of 2,000 minutes.

Sediment samples for total destruction were treated according to the chemical procedures described for the sample dissolution by Sarma (1964) and the rest of the procedure as described above was followed.

RESULTS AND DISCUSSION

Data on the U^{234}/U^{238} ratios in the carbonate fraction and in the total sediment along with per cent calcium carbonate and uranium activity in the carbonate phase are given in

TABLE I

Uranium data in different sections of the core M-230

(Station position : Lat. 23° 10′ N, Long. 67° 50′ E)

Depth cm	Calcium carbonate %	Uranium in leach dpm/g carbonate	Uranium in leach dpm/g sediment	U^{234}/U^{238} ratio In leach	U^{234}/U^{238} ratio In total sediment
Grab	13·36	4·08 ±0·12	0·54	1·136 ±0·029	..
0-10	15·71	3·29 ±0·15	0·52	1·128 ±0·023	1·005 ±0·033
10-20	5·59	9·64 ±0·24	0·54	1·105 ±0·026	0·989
20-30	9·50	4·10 ±0·13	0·39	1·078 ±0·036	±0·035 ..
30-40	13·89	4·67 ±0·08	0·65	1·067 ±0·036	1·008 ±0·047
80-90	10·90	3·36 ±0·11	0·58	1·035 ±0·019	..

Table I for different sections of the core. From Fig. 1, which gives the decay of the excess
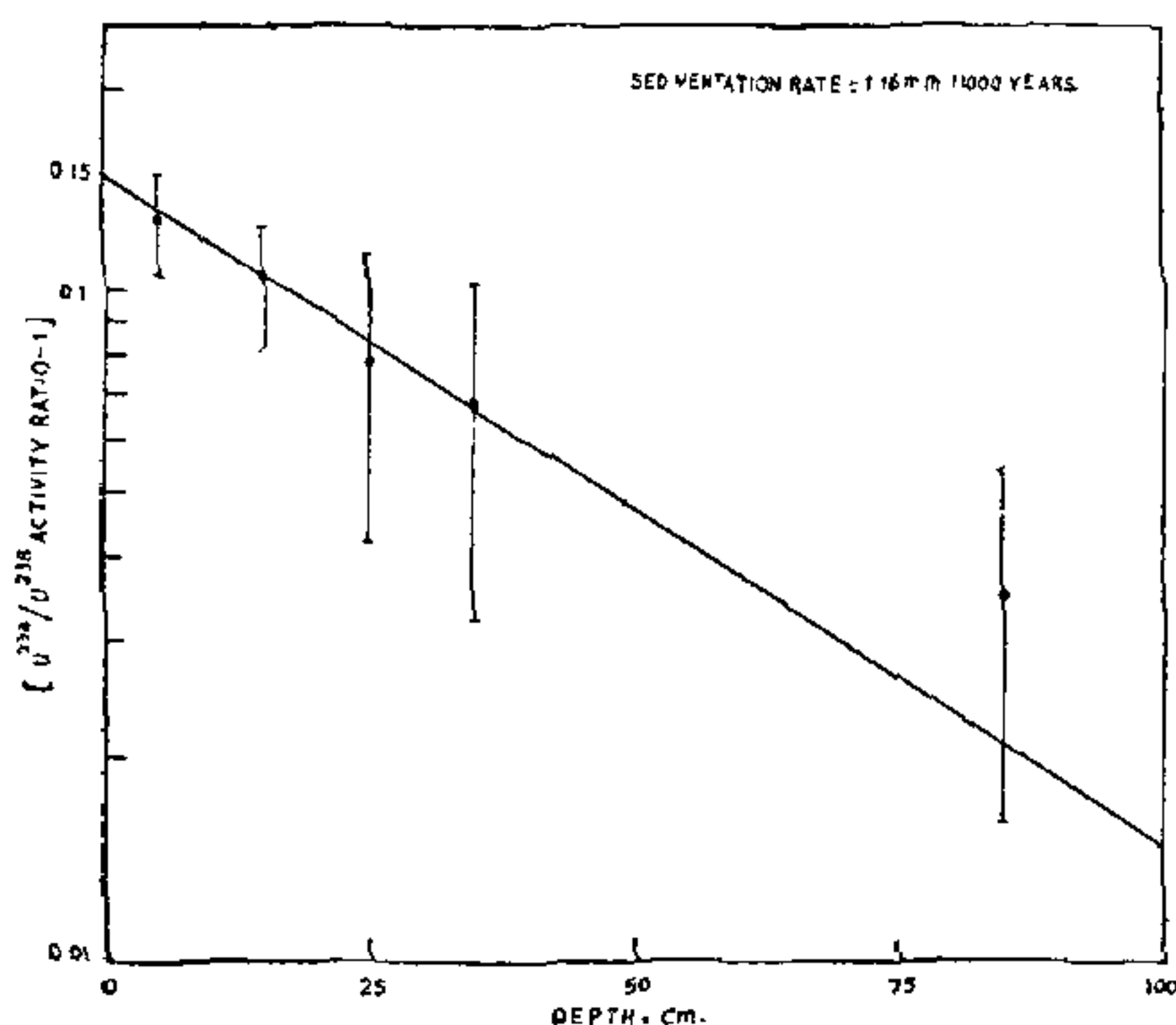

FIG. 1. Decay of excess U^{234} in different sections of the core M-230.

activity ratio of U^{234}/U^{238} over the equilibrium value against the mid-points of various sections, the rate of sedimentation is calculated to be 1·16 mm/1,000 years. Since the calcium carbonate in the sediment has oceanic origin, the U^{234}/U^{238} activity ratio in the top layer of the sediment (carbonate phase) should approach the value of 1·15. This is observed for the Grab sample as shown in Table I. Figure 2 represents the typical spectrum of uranium from the acetate buffer leach of 0-10 cm section of the core, M-230.

The sedimentation rate 1·16 mm/1,000 years is an extremely low value for the Indian Ocean

region. For such low precipitation rates, a high amount of Th^{230} activity of the order of 50 dpm/g is observed in the top layer of Pacific cores (Goldberg and Koide, 1958). The Th^{230} activity observed in the top segment of this core, 1·28 dpm/g is understandable as the depth of the water column at this point is only 25 metres whereas the depths in deep oceans are 3-4 km which increases the production of ionium. Sarma (1964) made model calculations of the expected Th^{230} activity in the top layers of the ocean sediments as a function of the water depths, sedimentation rate
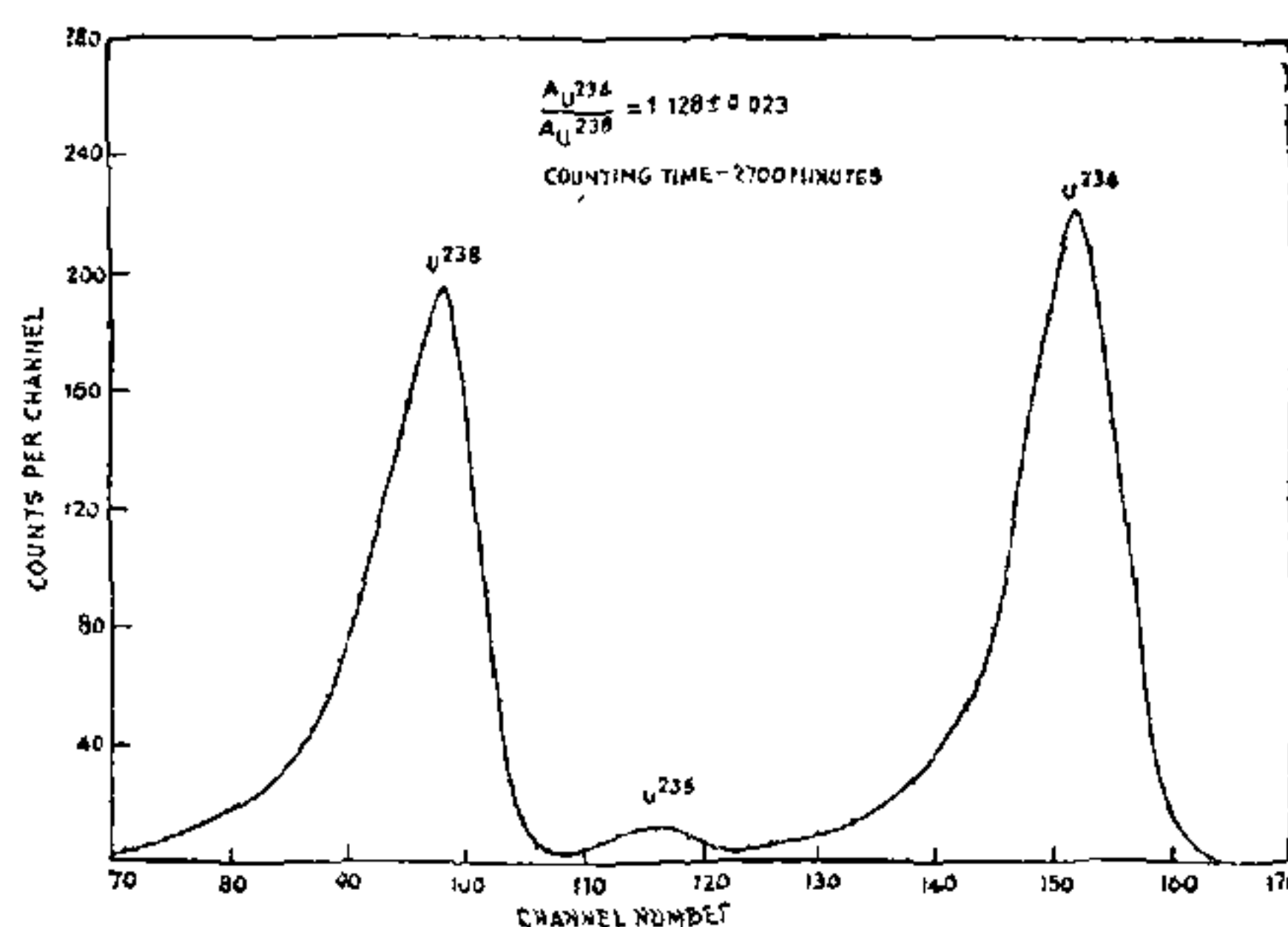

FIG. 2. Alpha spectrum of the uranium from C_aCO_3 phase of the 0-10 cm section of the core M-230

and the fraction of detrital and calcium carbonate phases.

$$S_{230} = Q_d F_d S_{238\ d} + QHNU\lambda_{238}\ \lambda_{232}/rA_u D$$

where

S_{230}, specific activity of ionium, dpm/g

Q_d, U^{234}/U^{238} ratio in the detrital fraction, assumed 1

F_d, detrital fraction

$S_{238, d}$, U^{238} activity in the detrital fraction, dpm/g

Q, U^{234}/U^{238} in sea-water

H, depth of the water column, cm

N, Avogadro number

U, uranium content of sea-water, g U/cm³

λ_{238} and λ_{230} decay constants of U^{238} and Th^{230}

A_u, atomic mass of uranium

D, density on dry basis, g/cm³, and

r the rate of sedimentation in cm/year.

Using the above formula, for M-230 core, the expected Th^{230} activity works out to be 1·58 dpm/g taking $S_{238, d}$ as 1·25 dpm/g of the top segment and F_d as 0·85, whereas the observed value is 1·28 dpm/g which are in good agreement considering the uncertainties in the parameters used for the calculation.

Under anaerobic conditions, high ratios for U^{234}/U^{238} have been reported by Veeh (1967) even in total sediments of the upper continental slope in the eastern Pacific, Gulf of California, when the uranium content is high (4·8 to 39·0 ppm U). In such cases, the decay of excess U^{234} can be followed even in total sediments to determine the sedimentation rates. However, as already pointed out, we are observing U^{234}/U^{238} activity ratios very near 1. This ratio of 1, as well as the consistently small amounts of uranium in the ammonium acetate-acetic acid leach (0·5 dpm/g total sediment) compared to that of uranium from totally destroyed sediment (2·5 dpm/g in the top segment of the core) indicate the selective attack of the authogenic carbonate phase by the buffer. Hence, the method of attacking authogenic carbonate phase as the one reported here above, is of general utility for determining the sedimentation rates using the excess U^{234}/U^{238} activity.

ACKNOWLEDGEMENT

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EVALUATION OF ANTIBACTERIAL AND ANTITOXIC IMMUNITY IN CHOLERA*

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WITH the realization that current cholera vaccines confer only short-term immunity to the disease, research has been stepped up in various laboratories of the world towards identifying more effective immunizing agents. There are two aspects to be considered, both dependent on the pathogenesis of the disease. While the infecting organism, *Vibrio cholerae*, is strictly confined to the gut where it proliferates, the pathological manifestations of the disease such as severe dehydration and electrolyte imbalance are due to an enterotoxin (choleragen) released by the organisms during growth.[1] Consequently, immune mechanisms should be operative either against the invader restricting its capacity to multiply in the gut or towards the toxin by neutralizing its activity before any harm results.[2] Thus, one has to think in terms of either antibacterial or antitoxic immunity or both in cholera immunology.

Sero-epidemiological evidence obtained from cholera endemic areas has provided clues for further research in this field. One of the features observed in East Pakistan was the inverse relationship between age and susceptibility to the disease, children being more susceptible than adults. Correlated with this were higher titres of a complement dependent vibriocidal antibody in the sera of individuals of older age-groups.[3] It was also seen that the frequency of clinical cholera in familial contacts of cholera cases was lowest among individuals with high vibriocidal antibody levels and increased progressively among persons with lower titres.[4] However, the association of this antibody with immunity to the disease is not yet proved as high titres have been observed in healthy individuals never exposed to cholera antigens and in certain other diseases like brucellosis. Passive protection experiments in mice with antibrucella sera showed that there was no correlation between protection and vibriocidal titres.[5] Further,

2