only approximate due to the fewer observations in the first transition region.

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GROWTH RATE OF CALCITE CONCRETIONS

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ABSTRACT

Growth rates of two calcite concretions are calculated using a mathematical model and radiocarbon ages. The rates are within the range observed by earlier workers. Stable carbon isotope compositions of the nodules indicate precipitation under equilibrium with atmospheric carbon dioxide.

INTRODUCTION

CALCITIC concretions generally grow from supersaturated solutions often nucleating around a central body. Although it is realised that they grow very slowly in natural systems, their growth mechanism is still not quite certain. One process operative is probably diffusion controlled. Very few attempts have been made to experimentally measure the growth rates, perhaps due to the non-availability of suitable samples. This paper describes growth studies, using radiocarbon ages, on two calcitic concretions from a lake in Rajasthan, North Western India. The lake, Naliasar (75° 10′ E, 26° 55′ N), measuring about 4 km long and 2 km wide is one of the few freshwater lakes in the region. It lies very close to Sambhar, a large brackish lake. Naliasar gets filled during monsoon but remains as a playa for most other parts of the year. The lake sediments have in them concretions of several sizes. Two nearly spherical nodules containing more than 90% calcium carbonate, from depths of 5 cm and 12 cm respectively were collected for the present study.

MATERIALS AND METHODS

Since it was difficult to obtain layer-wise samples,

TABLE 1

Experimental and model-derived parameters of the calcite nodules

Fraction details	Equivalent radius in cm	^{14}C age in yrs* b.p. ($t_{1/2}$ = 57-30 yrs)	Growth rate in $\mu m/10^3$yrs	$\dagger^{13}C\%$ δ vs. PDB
Sample No. PRL-358 (depth below surface: 5 cm)				
Outer shell	1.81 (R$_2$)	13120±190	1745	+ 2.33
Inner core	1.61 (R$_1$)	16030±240		+ 2.65
Sample No. PRL-359 (depth below surface: 12 cm)				
Outer shell	1.981 (R$_3$)	16010±380	1600	+ 2.54
Middle shell	1.902 (R$_2$)	20580±580	812	+ 2.96
Inner core	1.104 (R$_1$)	22980±460	3100	+ 3.30

*Quoted with 1 sigma error. b.p. = before present.

$\dagger \ ^{13}C\% = (R_{sample}/R_{standard} - 1) \times 10^3$ where $R = \delta^{13}C/12c.$

successive acid leaches were used for radiocarbon measurements. The acid leaching produced carbon dioxide which was converted into methane for ^{14}C assay[1]. A portion of the CO_2^- was used for stable carbon isotope analysis. The ^{14}C data obtained for each fraction is given in table 1.

From the amount of Co_2 collected during each leaching, the fraction of $CaCo_3$ was calculated and equivalent 'spheres' of radius R and 'shells' dR constructed. Using a model employed by Peterson *et al.*[2] for dolomite growth, the rates of growth are calculated as follows.

The radiocarbon age obtained for an equivalent sphere of radius R is an average age of all the material in it. This average age t is given by

$$\langle t \rangle = \int_{0}^{R_1} t(r)dV \bigg/ \int_{0}^{R_1} dV$$

Similarly, the average age of the shell is given by

$$\langle t \rangle = \int_{R_1}^{R_2} t(r)dV \bigg/ \int_{R_1}^{R_2} dV$$

where r = radius of the sphere shell volume element dV at a given stage of growth

$t(r)$ = age of the volume element

$R_1, R_2, \dots$, etc. = calculated equivalent radii (see figure 1). Assuming that the rate of growth of the radius has been constant with time
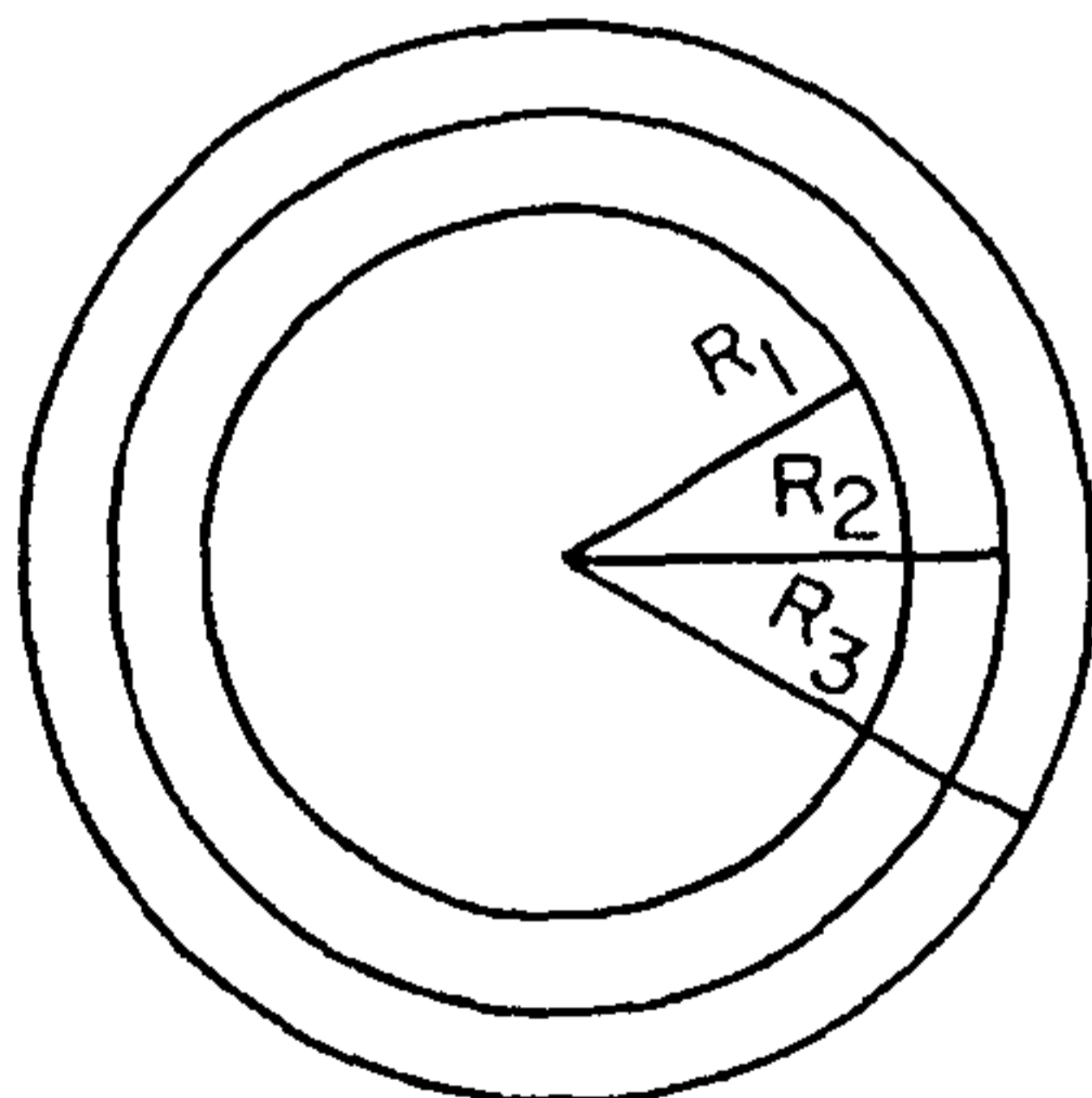

Figure 1. Schematic of the calcite nodule. The various R values (R_1, R_2, R_3) were calculated from the amount of CO_2 produced after acid leaching.

$$t(r) = T - kr$$

where T = total time since nucleation started and k = growth constant in time per microns.

Now $$dV = 4\pi r^2 dr$$

Integrating, the average age of the sphere is

$$t = T - \tfrac{3}{4}kR$$

and that of the first shell is

$$t = T - \tfrac{3}{4}k \left(\frac{R_2^{4} - R_1^{4}}{R_2^{3} - R_1^{3}} \right)$$

Similar expressions can be derived for the third, fourth, etc. 'shells' using appropriate R values.

DISCUSSION

The rate of growth calculated using the equivalent radius and above equations is shown in table 1. For sample No. PRL 359, the relatively large scatter could arise from even minor errors in the estimate of R values; the scatter being larger while employing closely placed R values such as R_3 and R_2. Therefore, greater reliability is placed on the growth rate 1600μ m per 10^3 yrs obtained using R_1 and R_3. This value also agrees well with that of the other nodule. Machette[3] has calculated the mean rates of calcrete nodule formation to be between 10 to 1μ m per year. Our values, which fall on the lower side, may suggest a growth under lees favourable conditions. Berner[4] had earlier calculated, theoretically, growth rates of spherical nodules by diffusion and obtained comparable values.

The per mil deviation of carbon isotopes (stable) with respect to PDB is also given in table 1. The range of carbon isotopic composition of the nodules fall within the range expected for $CaCo_3$, precipitated in equilibrium with atmospheric carbondioxide[5]. There is a noticeable enrichment in the lighter isotope towards the surface in both the samples. This could probably be due to a change in the concentration of carbon bearing species in solution and decreasing pH. Detailed work is required to explain such variation and to assess the suitability of these carbonates for palaeoclimatic information.

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SOLID SOLUTION SERIES OF HYDROXYL AND CHLORAPATITES OF ARSENIC— PREPARATION AND CHARACTERIZATION

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ABSTRACT

Hydroxylapatite, $Ca_{10}(AsO_4)_6(OH)_2$, and chlorapatite, $Ca_{10}(AsO_4)_6(Cl)_2$, of arsenic and a series of their solid solutions over the entire range of compositions were prepared by appropriate solid state reactions. The samples were characterized by chemical, x-ray and infrared studies. While chemical analyses could establish the stoichiometry of the samples, the other studies could confirm their homogeneity.

INTRODUCTION

THE toxicity of elemental arsenic[1] and its salts[2] leading to arsenic poisoning is well known. The mechanism of such a poisoning can be attributed to incorporation of arsenic in the human skeletal system through a precipitation from body fluid of Ca_{10}-$(AsO_4)_6(OH)_2$, $(AsHA_1)$ and isomorph of calcium hydroxylapatite, $Ca_{10}(PO_4)_6(OH)_2$ the principal inorganic constituent of human bones and teeth[3]. The availability of Cl^- ions in the body fluids as well as in human dental enamel and bone and the ability of these ions to replace OH^- ions[4,5] in the apatite lattice suggest that another isomorph arsenic chlorapatite, Ca_{10}-$(AsO_4)_6(Cl)_2$, (AsClA) likely to be formed at the bone-body fluid interface helps in arsenic poisoning. The present investigation aims at arriving at an optimum set of conditions to prepare a series of solid solutions of AsHA and AsClA over the entire compositional range and to characterize them.

EXPERIMENTAL

A sample of AsHA was prepared by a wet method, investigated in detail earlier[6], using calcium nitrate and diammonium hydrogen arsenate as starting materials. A solid state reaction between AsHA and $CaCl_2$ given below was employed to prepare AsClA and a series of its solid solutions with AsHA over the entire compositional range:

$$2Ca_{10}(AsO_4)_6(OH)_2 + nCaCl_2 \rightarrow 2Ca_{10}(AsO_4)_6$$
$$(OH)_{2-n}Cl_n + nCa(OH)_2$$
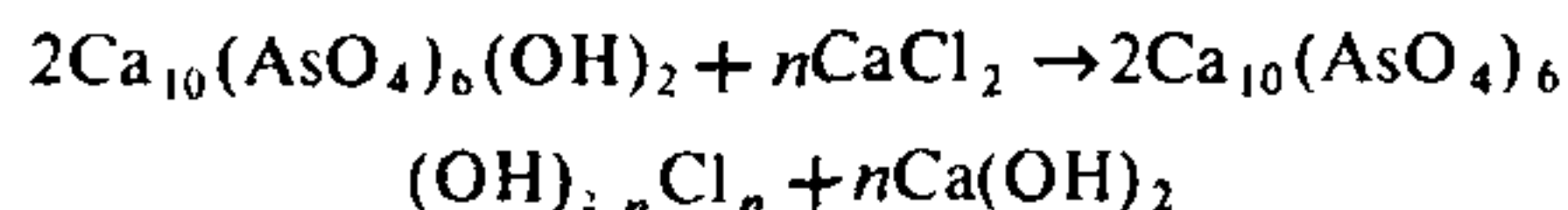
where n was varied from 0.2 to 2.0. A stock solution of calcium chloride in double distilled water and ethanol was standardised by estimating the calcium content by the complexometric titration[7]. Stoichiometric amounts of calcium chloride in the form of its aqueous solution s and AsHA, sieved previously to 200 (BSS) mesh, required for preparation of 10 g samples of a solid solution of AsHA and AsClA were taken. The mixture was heated gradually over a period of 9 hr at 1060°C. The sample was cooled and suspended in a mixture of 5% EDTA and a buffer solution of NH_4Cl and NH_4OH to maintain a pH of 10 and was subjected to a rigorous mechanical shaking for about 6 hr. The colloidal solution was filtered through a sintered G-3 glass filter and washed with ammonium hydroxide till the washings were free calcium and chloride ions. The residue was dried at 110°C for 12 hr, powdered and sieved to 200 (BSS) mesh.

The samples were analyzed for calcium, arsenic and chloride[9,10]. The infrared absorption spectra in the range, 650–4000 cm^{-1}, of the samples were recorded in nujol mulls with a Parkin Elmer infrared spectrometer (model 720) equipped with NaCl optics. X-ray diffraction patterns of the samples were recorded using an x-ray generator equipped with a Guinier camera under $Cu-K_\alpha$ radiation, the voltage, current and the time of exposure being 36 kV, 20 mA and about 3 hr respectively.

RESULTS AND DISCUSSIONS

Based on chemical analyses, the weight of calcium, arsenic and chloride of AsClA was found to be 30.53, 34.15 and 5.41% respectively which amounted to a g