

with respect to control were measured after an incubation period of 24 hours at $35 \pm 1^\circ \text{C}$.

The bio-assay clearly shows that the activity of bis-(9-tetrahydrocarbazolyl) methane derivatives (IV, V and VI) is much lower than those of the corresponding tetrahydrocarbazole derivatives (I, II and III).

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HYDROTHERMAL SYNTHESIS OF OOLITHS

Introduction

HYDROTHERMAL phase equilibria studies were being carried out in this laboratory in the system $\text{Y}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-H}_2\text{O-CO}_2$ using oxalic acid and formic acid as source of CO_2 and H_2O , in the system. During the initial random runs made across the temperature range of $150\text{-}800^\circ \text{C}$ at low pressures (50-500 atmospheres), certain unusual development of oolitic textures were noticed, in addition to the development of several yttrium carbonate hydrates isostructural with natural minerals, when formic acid is used. The intention of the present note is to report for the first time, the synthesis of ooliths under hydrothermal condition and to discuss the probable mechanism of the development of oolitic textures.

Experimental

$\text{Y}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-H}_2\text{O-CO}_2$ system was studied by taking $\text{Y}_2\text{O}_3/\text{Fe}_2\text{O}_3$ in the ratio 3:5 and concentrated formic acid as the source of CO_2 and H_2O . About 100 mg of well ground $\text{Y}_2\text{O}_3/\text{Fe}_2\text{O}_3$ mixture is taken in platinum ampoules (5 cm length, 5 mm ID and 2 mm wall thickness). The ampoules are sealed by crimping the open end with 3 jaw chuck and welding with arc welding unit. Leak in the ampoules is checked through extended heating before the experiment and checking the weight after the run. Tuttle type cold seal vessels are used with Tempress Hydrothermal unit HR-IB-4. Runs were conducted for 90-100 hours, and the vessels are quenched after the run, to room temperature before venting out the pressure. The vessels are introduced in the pre-heated furnaces with distilled water as pressure trans-

mitting fluid. The product after the run is washed with hot distilled water and identified by X-ray powder diffraction method (114.6 mm camera with Co K α radiation).

Results and Discussion

Although a large number of experiments are conducted both with oxalic acid and formic acid, we are presently reporting only the results of a few selected experiments with formic acid. The formation of ooliths takes place at 200°C (Table I).

TABLE I
Details of hydrothermal experiments in
 $\text{Y}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-HCOOH}$ system

| Temperature ($^\circ \text{C}$) | Pressure (psi) | Product |
|--------------------------------------|-------------------|---|
| 150 | 1000 | $\text{C}_2\text{H}_2\text{FeO}_4 \cdot 2\text{H}_2\text{O} + \alpha\text{-Fe}_2\text{O}_3 + \text{Y}(\text{HCOO})_3$ |
| 200 | 4500 | $\text{FeCO}_3 + \text{Y}(\text{OH})\text{CO}_3\text{-A}$ (Ooliths) |
| 250 | 500 | $\text{Fe}_3\text{O}_4 + \text{Y}(\text{OH})\text{CO}_3\text{-A}$ |
| 485 | 6250 | $\text{Fe}_3\text{O}_4 + \text{Y}_2\text{O}_2\text{CO}_3\text{-Type II}$ |
| 680 | 4000 | $\text{YFeO}_3 + \text{Fe}_3\text{O}_4$ |
| 785 | 6500 | $\text{YFeO}_3 + \text{Fe}_3\text{O}_4$ |

At 780°C YFeO_3 (orthorhombic) and Fe_3O_4 (magnetite) are the stable phases, while at lower temperatures, Fe_3O_4 and $\text{Y}_2\text{O}_2\text{CO}_3\text{-II}$ (hexagonal) are the stable solids. Experiments below 300°C yield a stable carbonate phase, $\text{Y}(\text{OH})\text{CO}_3\text{-A}$ (orthorhombic) isostructural with natural mineral ancylite along with $\text{FeCO}_3\text{-siderite}$ phase. Good single crystals of these compounds have been obtained. Experiments below 200°C yield $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Y}(\text{HCOO})_3$ along with $\alpha\text{-Fe}_2\text{O}_3$ as stable phases. In addition to the carbonate phase, unusual, spherical ooliths are also formed. Some of them are loose while some are intimately clustered and joined (Figs. 1 and 2 respectively). Most of the ooliths are found broken into exact hemispheres (Fig. 3). X-ray analysis of the crushed ooliths showed the presence of siderite and ancylite. The core of the ooliths is either of ancylite or of siderite. In certain ooliths upto seven rhythmic layers can be clearly seen with sharp demarcation. Single crystals of ancylite-like phases are found to grow on the external surface of the outermost shell which, invariably, is of ancylite composition. Figure 4 shows a number of hollow broken shells made entirely of ancylite composition. Analysis of the sample was not possible for want of bulk material.



FIG. 1. Individual oolites with shell of ancyllite composition ($\times 55$).



FIG. 2. Clusters of oolites embedded in matrix of ancyllite composition ($\times 55$).



FIG. 3. Cross section of oolites showing concentric alternating growth of siderite (black) and ancyllite (white) layers ($\times 55$).

The formation of oolites and oolitic textures in the natural ores of Fe, Mn, Al and siliceous sedimentary cherts has been a subject of controversy. The formation of such textures in the present experiments are explained by assuming that at low temperatures, carbon monoxide evolved from the formic acid forms bubbles. Such gas bubbles become the chemically active centres for the precipitation and crystallization of the substrate material. This is evidenced from

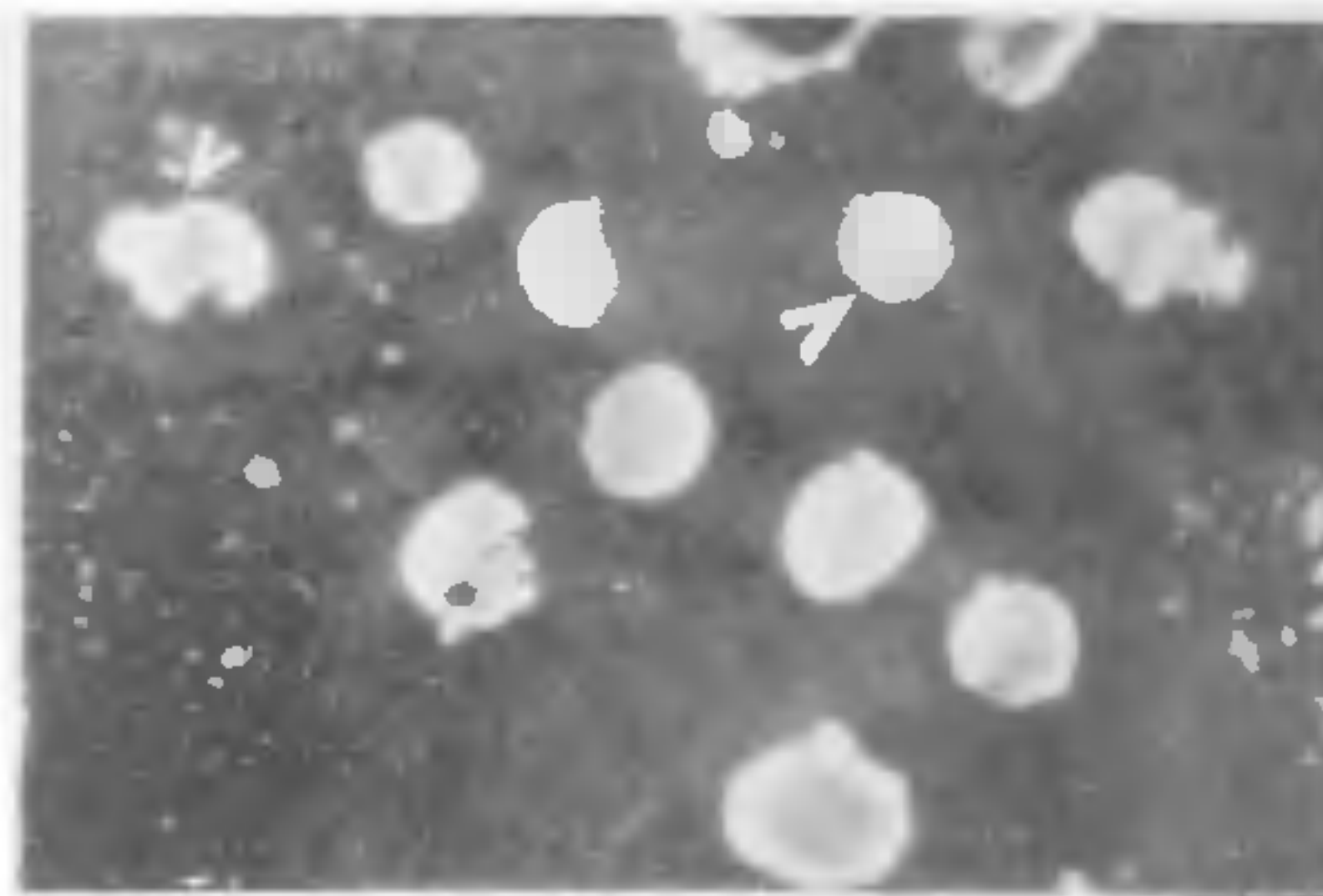


FIG. 4. Hollow broken shells of ancyllite composition ($\times 55$).

several hollow hemispherical shells noticed (Fig. 4). Alternate depletion of yttrium and iron in the substrate material with the progressive precipitation of yttrium carbonate-ancyllite and iron carbonate-siderite, could be the probable explanation for the rhythmic layering observed. The authors are investigating the formation of such oolitic textures in other systems, $\text{Fe}_2\text{O}_3\text{-MnO-HCOOH}$, $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-HCOOH}$, etc., to find out if this could possibly be the mechanism of vast development of oolitic textures found in nature.

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A RECORD OF HOLOTHURIAN SCLERITES FROM THE TRIASSIC OF MALLA JOHAR, KUMAUN HIMALAYA

THE present note records for the first time the presence of holothurian sclerites from the Middle Triassic Kalapani Limestone of Malla Johar, Kumaun Himalaya, from the samples brought by one of us (S. K.) as a member of the Second Expedition of Wadia Institute of Himalayan Geology to Malla Johar area in the year 1972. Kalapani Limestone is exposed in Kiogar Valley and the samples were collected at a place 5 km east of Sumna in the Chamoli district of Uttar Pradesh. Holothuroids were recovered by acid etching in connection with search for conodonts. Although a sample (T55) yielded large number of well-preserved conodont elements but only a few moderately preserved holothurian sclerites could be recovered. The present material of sclerites includes exclusively wheel type forms that have been assigned to the single species of *Acanthothellia anisica*. Similar material of sclerites has already been described by