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DOLOMITE AND ORGANIC MATERIAL

by

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Gebelein and Hoffman[1] drew attention to the co-occurence of dolomite with stromatolitic sequences, and suggested that the precipitation of dolomite is related to the site of organic material. Experiments by those authors confirmed previous results[2,3], that large quantities of magnesium may be absorbed from sea water by organic material. They also showed that magnesium rich algal filaments may form sites for the precipitation of high magnesium calcite with between 17-20 mole % $MgCO_3$, and although they failed to precipitate dolomite, they considered that the high-Mg calcite would be diagenetically altered to dolomite because of the high Mg/Ca ratio associated with the organic material.

The present writers would like to take up the story in two ways. Firstly, by reporting on both experimental and field studies, and secondly, by looking closely at the Gebelein and Hoffman experimental data in conjunction with other data from dolomite precipitating localities.

We have previously reported on sedimentary simulation experiments performed in a large tank [4,5]. In one experiment, a shallow water, organic rich, evaporitic carbonate environment was simulated and allowed to evolve over a period of eight to nine months. Mineralogical, chemical, and biological parameters of the supernatant and sediment environment were monitored regularly [5]. An important feature of the experiment was that a layer of decaying filamentous algae was placed between layers of crushed calcite and nesquehonite. At the end of nine months, samples of the decaying filamentous algae were collected, washed, dried, and X-rayed (Fig. 1). Dolomite had precipitated within the organic material. This is exceptionally important because for the first time a causal relationship between dolomite and organic material has been established. It is doubly important because Lippman[6] showed that dolomite did not precipitate from purely inorganic mixtures of calcite and nesquehonite, a fact verified within our laboratory. The X-ray diagram (Fig. 1) also shows that proto-hydromagnesite[7], and possibly huntite, also precipitated within the organic material.

One of us (Davies) has studied One Tree Reef, in the southern Great Barrier Reef. In the middle of the rubble cay at the southern end of the reef is a small semi permanent pool, in which carbonates are being precipitated. The sedimentary section within the pool is shown in Fig. 2. An algal mat (A) approximately 3-5 mm thick covers the surface, except near the edge of the pool where it is being grazed by land snails. Below the algal mat is a spongy pale pink to brown organic layer (B) which may be up to 75-100 mm thick. This rests on a white precipitate of aragonite and high magnesium calcite (C). Samples of the organic material were vacuum dried and X-rayed (Fig. 2). Dolomite occurs within the organic material. This therefore corroborates the laboratory experiments. It is pertinent also that no dolomite is found in any of the carbonates below the organic layer, and that magnesium increases away from the organic layer (Fig. 2). It is important also to point out that the dolomite is not present in great quantities, and is not ordered. However, the conclusion that organic material has formed a site for dolomite precipitation is inescapable.

The above reported experimental and field data appear to bear out the convictions of Gebelein and Hoffman[1] that dolomite formation is related to organic material. We also believe that is is so, but should like to offer explanations which are chemically different from those offered by Gebelein and Hoffman, explanations which are explicit within their own data, and which are borne out by previously published and unpublished field studies.

Data summarizing their experiments (Gebelein and Hoffman, p. 610), support two important conclusions not made by those authors. First, no precipitation occurred in the presence or absence of magnesium bearing sheath material, unless $(NH_4)_2 CO_3$ was added. Therefore magnesium present on organic material by itself is of little consequence, irrespective of the Mg/Ca ratios. Within their actual experiment, no organic decomposition occurred. Magnesium was therefore not made available for precipitation by organic decomposition, but was scavenged from its organic site by the introduction of $(NH_4)_2 CO_3$. Our second conclusion is therefore that the catalytic force in the crystallization of 17-20 mole % magnesium carbonates is the increase in alkalinity. The concentrations used by Gebelein & Hoffman was sufficient to markedly increase the alkalinity of the sample solutions. That this was meant to simulate organic decay is irrelevant. Organic decay did not occur. An insight into the true relationship between magnesium, alkalinity, and the crystallization of magnesium carbonates is explicit within the experimental data.

In most field studies, as in the experiments of Gebelein and Hoffman, the role of the Mg/Ca ratio has been stressed as critical in the formation of dolomite. Little is ever said of the CO_3 concentration. We believe that conditions for crystal precipitation depend on two parts of a solubility product. However, the importance attached to the Mg/Ca is not surprising when it is realized that with only one exception, no published alkalinity data exist for dolomite precipitating environments. Lippman[6] has also warned that too much importance has been attached to the Mg/Ca ratio. The solubility product of dolomite is exceeded in seawater (Garrels and Thompson[8], Hsu[9], Horne[10]) but dolomite does not form. Is it coincidental also that the carbonate concentration of seawater is low? The three modern dolomitic environments which have received most treatment are Bonaire, Netherlands Antilles; the Coorong, South Australia; and the Persian Gulf.

Bonaire is the only major locality from which alkalinity data are available. Deffeyes et al.[10] report that the alkalinity is markedly higher than seawater, but more importantly, the CO_3 concentration has increased markedly over the HCO_3 concentration.

No alkalinity data are published for the Persian Gulf localities, although it is known that salinities are high and the pH is low. The combination of these two factors results in a) the precipitation of $CaSO_4$, which leads to an increase in the solubility of previously precipitated metastable phases, and b) dissolution of these phases with a resulting increase in the alkalinity, also, c) a high CO_3/HCO_3 ratio is suggested by the high salinities.

Von Der Borch[11] does not report alkalinity from the Coorong, mentioning only bicarbonate rich pore waters associated with the hydromagnesite lake. However, recent data for Lake Fellmongery[12] show alkalinity values of up to 5-6 times that of seawater, while Taylor[12] reports Mg-calcites with 33 mole % $MgCO_3$ precipitating within the lake. Unpublished data obtained by officers of the Bureau of Mineral Resources show dolomite forming around the eastern shores of Lake Frome in South Australia. The only place where carbonate is precipitating coincides with the only place where groundwater alkalinities are high (eight times that of seawater).

We conclude therefore that high alkalinity is extremely important to the formation of dolomite. Organic material may play three different roles:

1. Living organic material, by virtue of photosynthesis, raises the pH and therefore raises the CO_3/HCO_3 ratio.

2. Living organic material can accumulate large quantities of magnesium ion [1,2,3].

3. Decaying organic material releases methane which may be used to reduce gypsum with concomitant production of CO_2. Similarly bacterial decay of organic material also produces CO_2. In both cases, the production of CO_2 will lead to an eventual increase in alkalinity. Various types of organic material, particularly some molecular fractions of humic acids inhibit the precipitation of aragonite. This inhibition may provide sufficient time to nullify the kinetic barriers inherant in dolomite formation.

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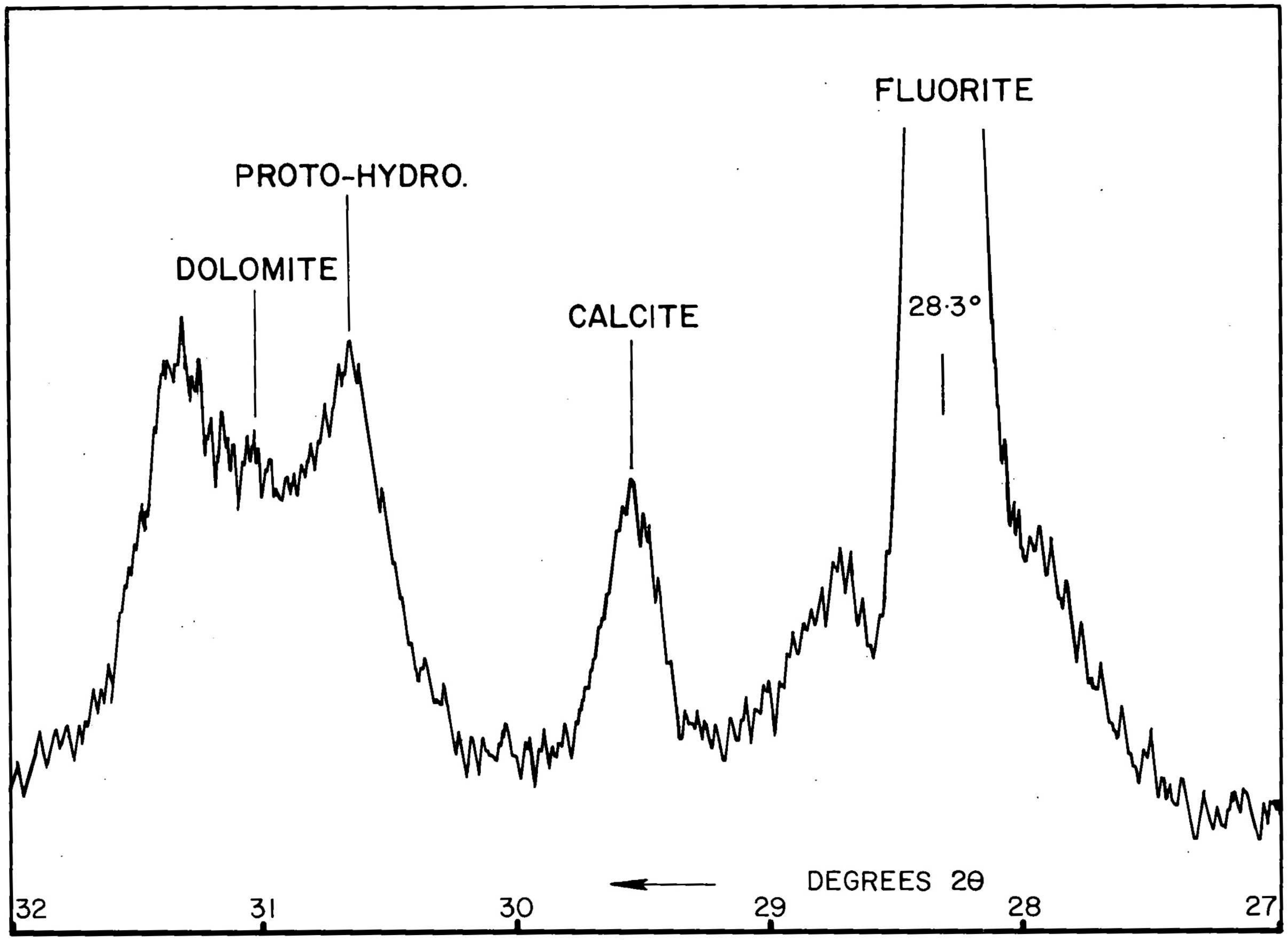

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FIG. 1

M(Pt) 227

CORE 4 — ONE TREE ISLAND

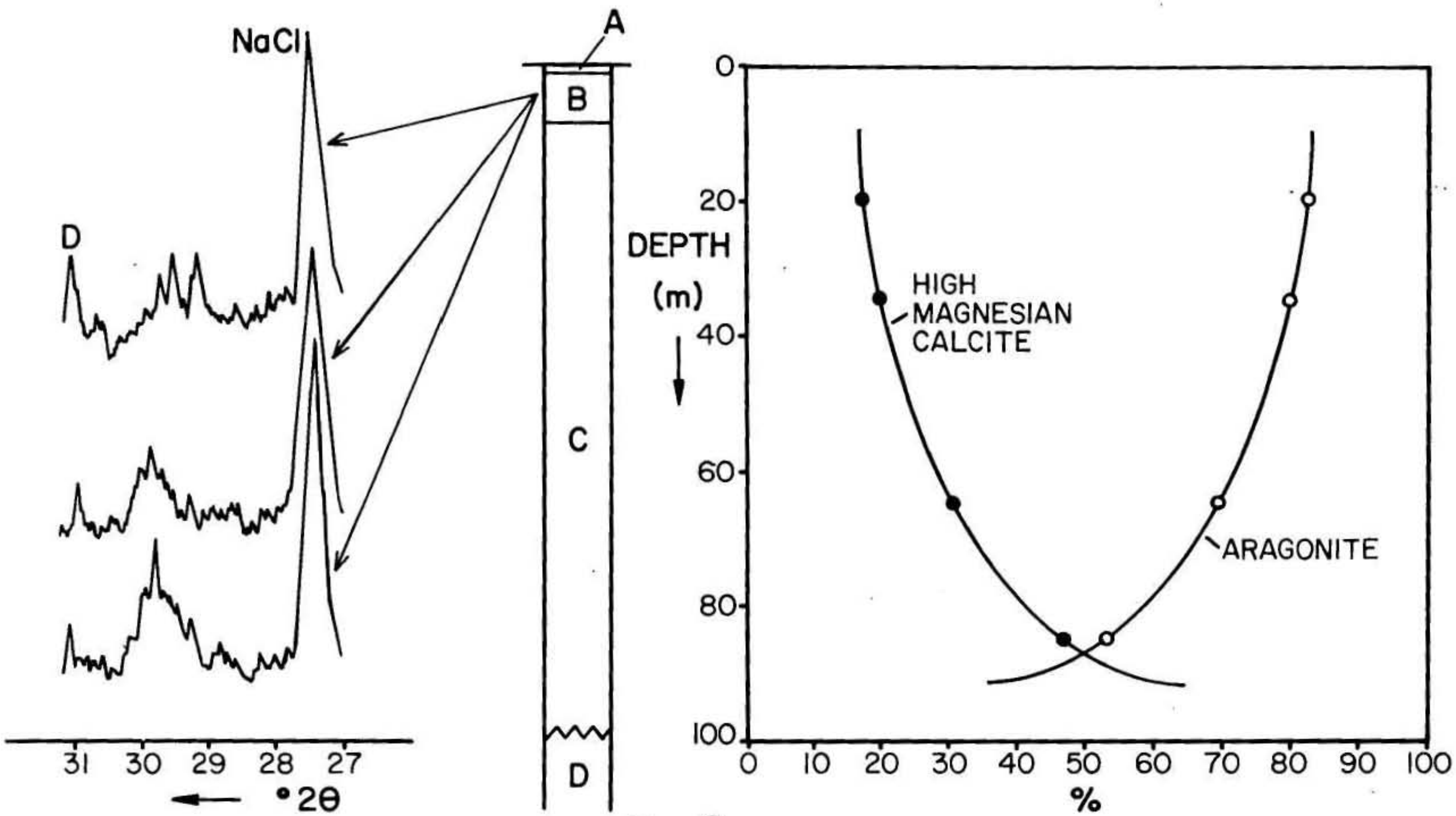

FIG. 2

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