



Aragonite neomorphism via intrafabric dissolution and calcite precipitation, not thin films

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Abstract: Since the 1970's, aragonite neomorphism (conversion of aragonite to calcite with partial retention of original internal structure) has been attributed to thin diagenetic films, often in meteoric water. Pleistocene material from Enewetak, the Bahamas and eastern Yucatan show the transition from aragonite to calcite "in progress". Original aragonitic material includes coral, *Halimeda*, molluscs (especially gastropods) and ooids. In all three areas, aragonite commonly shows partial intrafabric dissolution. In many cases, calcite crystals grew over that highly microporous aragonite to create calcite with partial retention of the original depositional fabric, creating neomorphosed (calcitized) aragonite. Geochemical data support this scenario. Carbon and oxygen isotopic compositions of the neomorphic calcites are similar to sparry meteoric calcite cements indicating crystals precipitated from similar waters as the cements. Stable carbon isotopes and Mg concentrations in neomorphic calcites are different from their aragonitic precursors and are not consistent with the thin-film model, which assumes a semi-closed system. Approximately 40 of the 95 Pleistocene Enewetak samples have aragonite with intrafabric dissolution adjacent to calcitized (neomorphic) aragonite. Neomorphosed (calcitized) aragonite was not observed immediately adjacent to unaltered aragonite (*i.e.*, separated by what would have been a thin film) in any Enewetak samples. This supports aragonite neomorphism by a two-stage process (intrafabric dissolution followed by calcite precipitation) rather than by thin films. Variations in concentration of inclusions in neomorphosed aragonite are similar to variations of relict material in aragonite with partial intrafabric dissolution and span a continuum from abundant aragonitic inclusions in neomorphic spar to inclusion-free calcite cement.

Keywords:

- carbonate diagenesis;
- aragonite neomorphism;
- calcitization;
- Pleistocene;
- Enewetak;
- Bahamas;
- Yucatan

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Résumé : Néomorphisme de l'aragonite par dissolution intra-structurelle et précipitation de calcite, et non par le biais de films diagénétiques minces.- Depuis les années 1970, le néomorphisme de l'aragonite, c'est-à-dire la conversion de l'aragonite en calcite avec une rétention partielle de la structure interne originale, a été attribué à des films diagénétiques minces, souvent dans des eaux souterraines météoriques. Des échantillons pléistocènes provenant d'Enewetak, des Bahamas et de l'est du Yucatán témoignent d'une transition diagénétique en cours entre aragonite et calcite. Ces matériaux, initialement aragonitiques, sont de natures variées : coraux, *Halimeda*, mollusques (notamment des gastéropodes) et oïdes. Dans ces trois régions, les allochèmes aragonitiques présentent fréquemment une dissolution partielle intra-structurelle. Souvent, des cristaux de calcite se développent au sein de cette trame aragonitique fortement microporeuse, formant une calcite qui conserve partiellement la texture originale et créant ainsi une aragonite néomorphisée (calcitisée). Les données géochimiques semblent valider ce scénario. En effet, les compositions isotopiques du carbone et de l'oxygène dans les calcites néomorphiques sont similaires à celles des ciments sparitiques météoriques, indiquant que les cristaux néomorphiques se sont formés à partir d'eaux semblables à celles ayant précipité les ciments sparitiques. Les isotopes stables du carbone et les concentrations de magnésium dans les calcites néomorphiques

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différent de celles de leurs précurseurs aragonitiques et ne sont pas cohérentes avec le modèle des films diagénétiques minces, qui suppose un système semi-fermé. Dans environ 40 des 95 échantillons pléistocènes d'Eniwetok, une aragonite présentant une dissolution intra-structurale est observée immédiatement adjacente à une aragonite calcitisée (néomorphisée). Dans ces mêmes échantillons, aucune aragonite néomorphisée (calcitisée) n'a été trouvée en contact direct avec une aragonite non altérée (c'est-à-dire qu'elles n'apparaissent jamais séparées par ce qui aurait été un film diagénétique mince). Ces observations suggèrent que le néomorphisme de l'aragonite résulte d'un processus en deux étapes (dissolution intra-structurale suivie de précipitation de calcite), plutôt que par le biais de films diagénétiques minces. Les variations de concentration des inclusions dans l'aragonite néomorphisée sont similaires à celles du matériau résiduel dans l'aragonite partiellement dissoute et forment un continuum, allant d'une calcite néomorphique riche en inclusions aragonitiques à un ciment de calcite sans inclusion.

Mots-clefs :

- diagénèse des carbonates ;
- néomorphisme de l'aragonite ;
- calcification ;
- Pléistocène ;
- Eniwetok ;
- Bahamas ;
- Yucatán

1. Introduction

In modern tropical carbonates, aragonite is one of the main minerals in reefs and shallow marine carbonate sediments. However, aragonite is very rare in pre-Cenozoic rocks though relicts have been found suggesting aragonite was depositionally common at many times in the past, for example in Ordovician-Silurian brachiopods (BALTHASAR *et al.*, 2011) and Archean stromatolites (LEPOT *et al.*, 2009). In some pre-Cenozoic limestones, the aragonite has been completely dissolved, and sometimes the molds are refilled with sparry calcite cement. In other cases, the aragonite has been converted to calcite with partial retention of an aragonite grain's original internal structure. The second process is commonly referred to as "neomorphism" (see photos in BATHURST, 1975, p. 488-489). FOLK (1965) defined and discussed the term "neomorphism" as "a comprehensive term of ignorance neomorphism for all transformations between one mineral and itself or a polymorph whether inversion or recrystallization whether the new crystals are larger or smaller or simply differ in shape from the previous ones".

The commonly accepted model for aragonite neomorphism to coarser crystalline calcite is that the conversion occurs across a thin aqueous film (~1 μm wide) with dissolution of aragonite on one side and precipitation of calcite on the other in response to calcite being a more stable mineral than aragonite, especially in fresh (meteoric) water (SANDBERG *et al.*, 1973; PINGITORE, 1976; WARDLAW *et al.*, 1978; SANDBERG & HUDSON, 1983; MALIVA, 1998). This was a theory to convert aragonite to calcite with partial retention of the depositional material's internal structure. This was a model that inferred from the starting and ending material without conclusive observations of the transition. This paper presents evidence from three Pleistocene localities that indicate that "neomorphism" or calcitization generally occurs by partial intrafabric dissolution of aragonite followed by precipitation of

calcite in those pores and over relicts of the original internal structure, not a process involving thin films.

SALLER (1992) presented this alternative earlier based on observations in Pleistocene carbonates in Eniwetok, the Bahamas and Yucatan. In those areas, much of the strata contain original aragonite, altered aragonite and neomorphosed (calcitized) aragonite, and hence, the process is observed "in progress". Petrographic and geochemical evidence supported the calcitization/neomorphism occurring by partial intrafabric dissolution of the aragonite followed by calcite crystals being precipitated within the partly to largely dissolved aragonite. Unfortunately, publication of color figures was difficult and expensive in 1992, and hence all photographs in SALLER (1992) are black and white. Color photographs of partially dissolved aragonite and calcite crystals overgrowing the partially dissolved aragonite creating neomorphosed or calcitized aragonite are much more compelling than black and white pictures. This paper presents color photographs of those Pleistocene carbonates to support the idea that aragonite generally converts to calcite with partial retention of structure through partial intrafabric dissolution of aragonite and later calcite precipitation rather than thin-film neomorphism. Geochemical data supporting that process are also shown here. This paper focuses on alteration and neomorphism of aragonitic grains and fossils, but not alteration of aragonitic muds (micrite).

2. Methods

Tropical Holocene and Pleistocene limestone samples were obtained from cores taken on Eniwetok, in the Bahamas and the Yucatan (Fig. 1). Most of the Pleistocene Eniwetok cores were acquired from wells drilled as a part of the EXPOE drilling project in the 1970's (COUCH *et al.*, 1975). Core samples from the Bahamas came from two wells (C-70 & C-73) on Cat Island and were kindly provided by Robert GINSBURG and the University of Miami in 1981. Samples of Pleistocene carbonates from eastern-most Yucatan are from wells (K-239 & K-274) and quarries and were provided by William (Bill) WARD of the University of New Orleans.

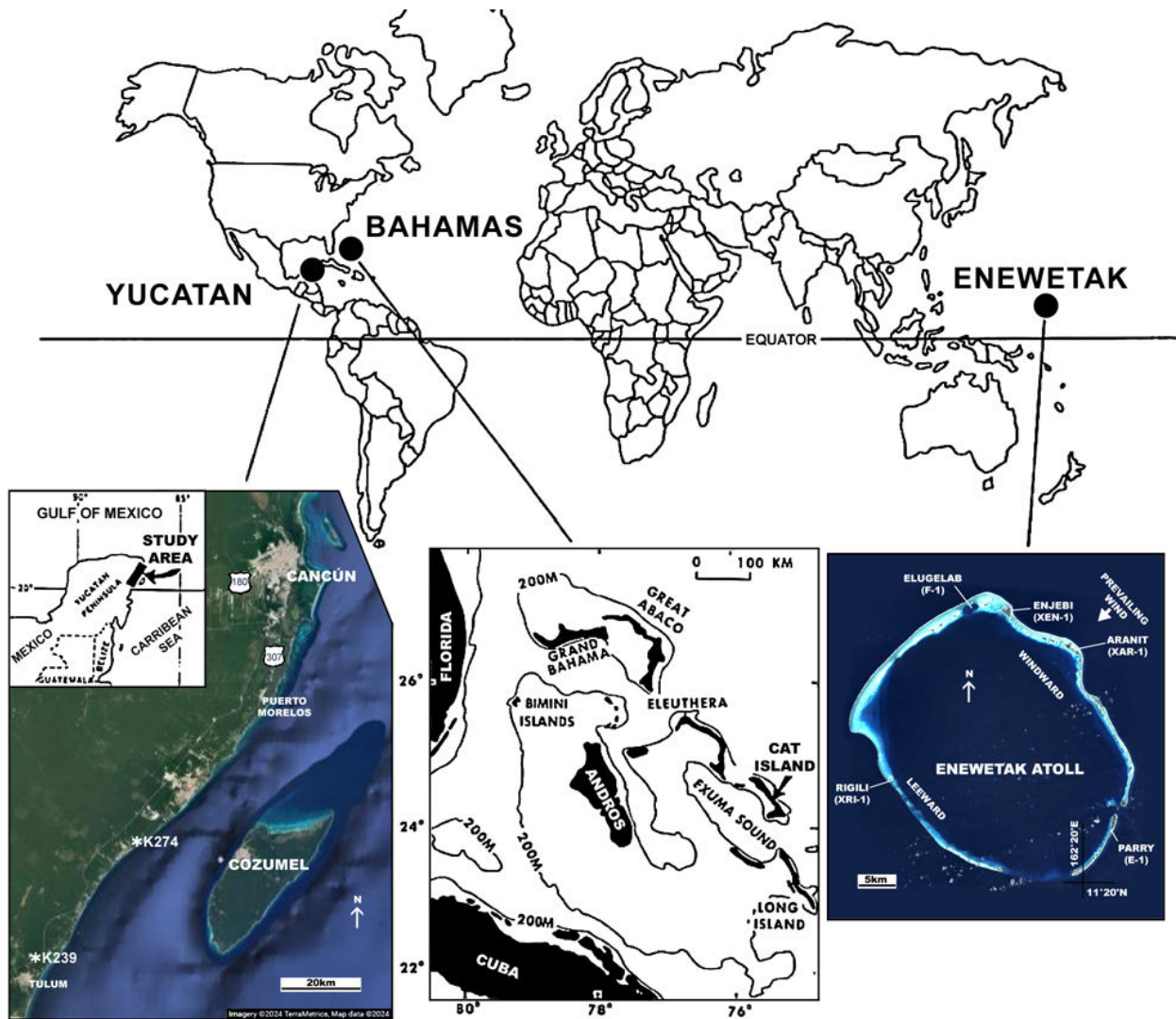


Figure 1: Location of study areas with Pleistocene limestones.

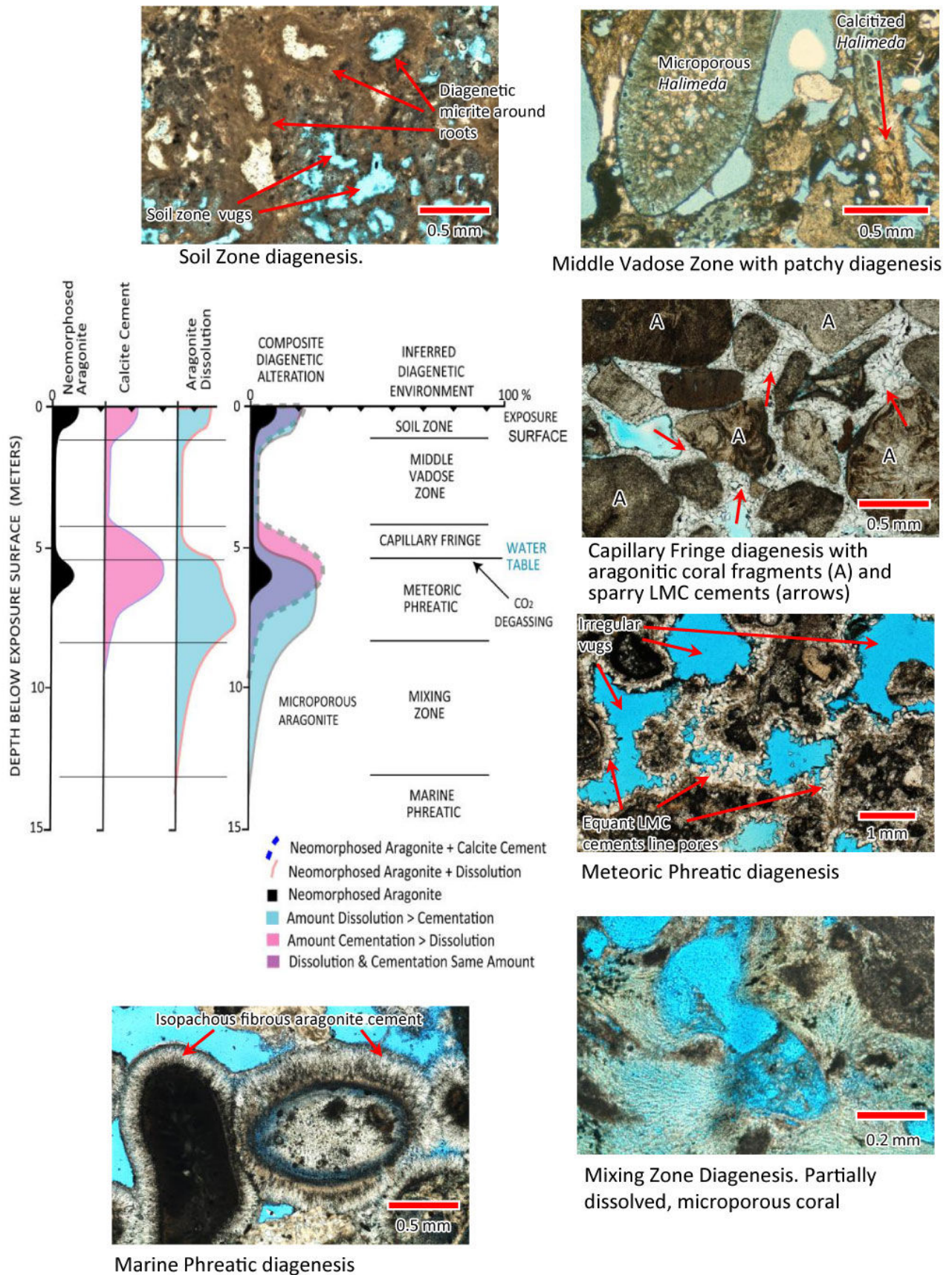
Samples used for thin sections were impregnated with blue epoxy while the samples were under a vacuum, and hence blue color on photomicrographs indicates porosity. All photomicrographs are under plane polarized light unless otherwise noted. Thin sections used for microprobe analysis were polished and coated with carbon. Results for Mg and Sr concentrations for each reported data point are the average of 9 or more different spot analyses. Accuracy and precision (2σ) of Sr for samples with greater than 1000 ppm Sr were approximately 10% of the reported value. Accuracy and precision (2σ) of Sr for samples with less than 1000 ppm Sr were approximately 100 ppm. Accuracy and precision of Mg concentrations were $\pm 10\%$ with a detectability limit of 0.02 wt % Mg. Elemental concentrations for two samples from a gastropod from the Yucatan were performed with atomic absorption spectrophotometry with accuracy and precision within 3% (see SALLER, 1984, for more details).

Samples used for stable isotope analyses were separated from the bulk rock with an Exacto knife and then analyzed by Coastal Science Laboratories in Austin, Texas at 25° C using stand-

ard methods. Precision for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ were $\pm 0.2\text{‰}$ and reported relative to a VPDB standard.

3. Enewetak Atoll

Enewetak Atoll is at $\sim 11^\circ \text{N}$ latitude in the Marshall Islands in the Pacific Ocean (Fig. 1). It has a humid tropical climate with an average temperature of 28° C and average rainfall of 147 cm per year (EMERY *et al.*, 1954; WHEATCRAFT & BUDDEMEIER, 1981). Numerous geological studies have been published on Enewetak and surrounding atolls before and after nuclear tests in the late 1940's and early 1950's (for example, LADD *et al.*, 1948; EMERY *et al.*, 1954; COLE, 1957; SWARTZ, 1958, 1962; LADD & SCHLAGER, 1960; TODD & LOW, 1960; SCHLANGER, 1963; GROSS & TRACEY, 1966). Samples described here came from Holocene and Pleistocene limestones 1-75 m deep in the XAR-1, XEN-1 and XRI-1 wells obtained during project EXPOE (COUCH *et al.*, 1975). These wells are all on the elevated atoll rim. At time of deposition, sediments were dominated by aragonite and high-magnesium calcite (HMC) including abundant coral (aragonite), coralline algae (HMC), benthic forams (mainly HMC), and *Halimeda* (aragonite) with lesser amounts of molluscs (mainly aragonite) and echinoderm fragments (HMC).



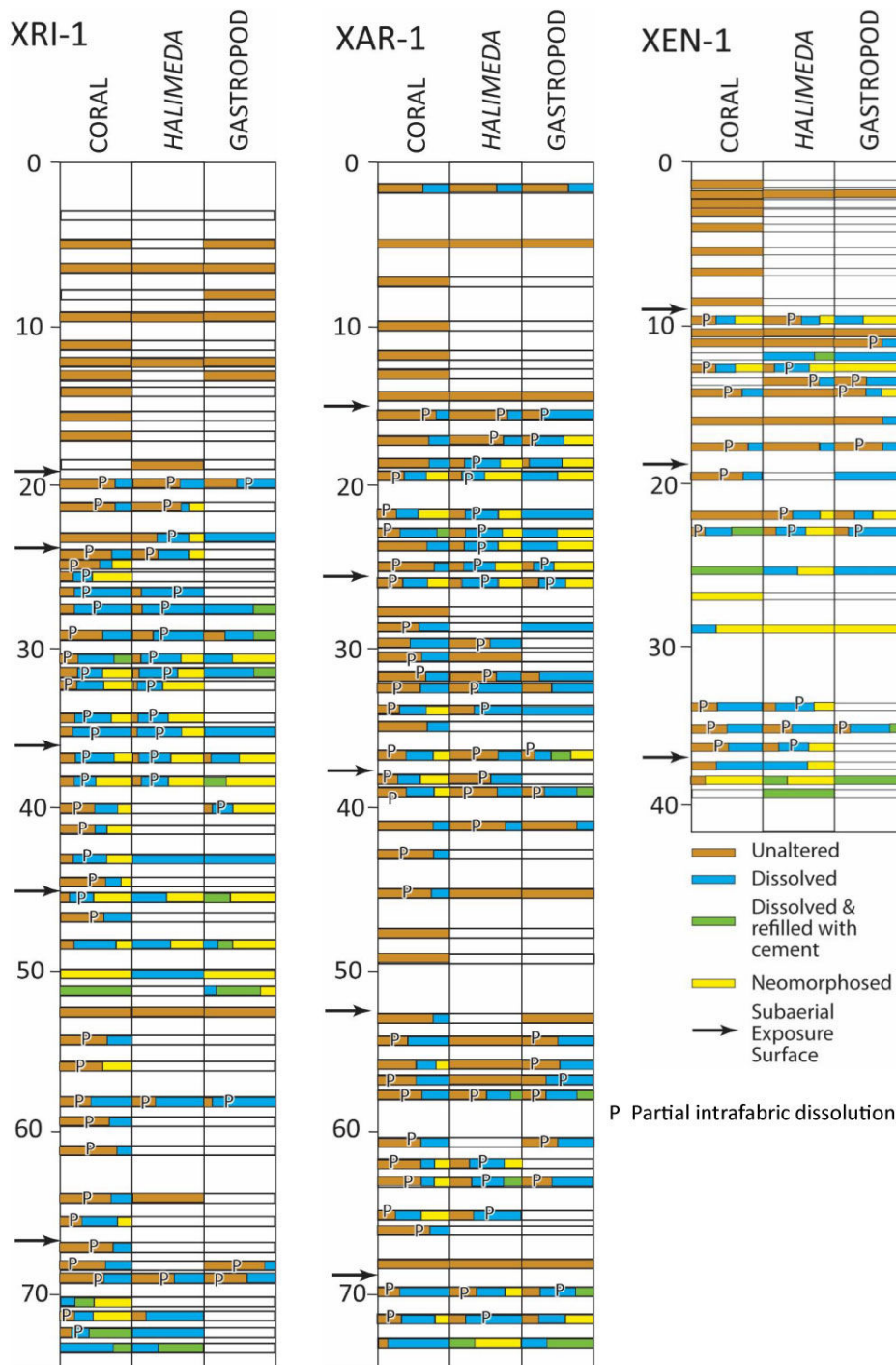


Figure 3: Plots showing relative amount of alteration of three major aragonitic fossil groups in the Pleistocene of three Enewetak wells. Subaerial exposure surfaces are from COUCH *et al.* (1975). The top exposure surface is approximately the top of the Pleistocene. Below that top subaerial exposure surface, samples contain intact aragonite (brown), pores where aragonite has been dissolved (blue), partially dissolved (partial intrafabric dissolution, P), and neomorphic (calcitized aragonite; yellow). Depths are in meters.

Five subaerial exposure surfaces were described and correlated through these wells by COUCH *et al.* (1975). Those were interpreted as representing the major falls in sea level (~100 m) that occurred during the Pleistocene at frequencies of ~110,000 years in association with MILANKOVITCH orbital cycles (SHACKLETON & OPDYKE, 1976; GÖTER & FRIEDMAN, 1988). Carbonate reefs and sediments were deposited during high sea levels and repeatedly exposed during sea level drops. Islands commonly developed when carbonate sediments built to and above sea level during time of high sea level, resulting in fresh-

water lenses and associated diagenesis 3-10 m below exposure surfaces (SALLER, 1984). As a result, freshwater diagenesis was highly variable in these Pleistocene samples with systematic variations related to paleo-subaerial exposure surfaces and paleo-freshwater lenses (Fig. 2). Some Pleistocene limestones had intense diagenesis and are now dominated by low magnesium calcite with little aragonite, whereas other intervals are still dominated by aragonite. Much of the Pleistocene contains both low-magnesium calcite (LMC) and aragonite (Fig. 3). Little HMC remains in the Pleistocene in these Enewetak cores.

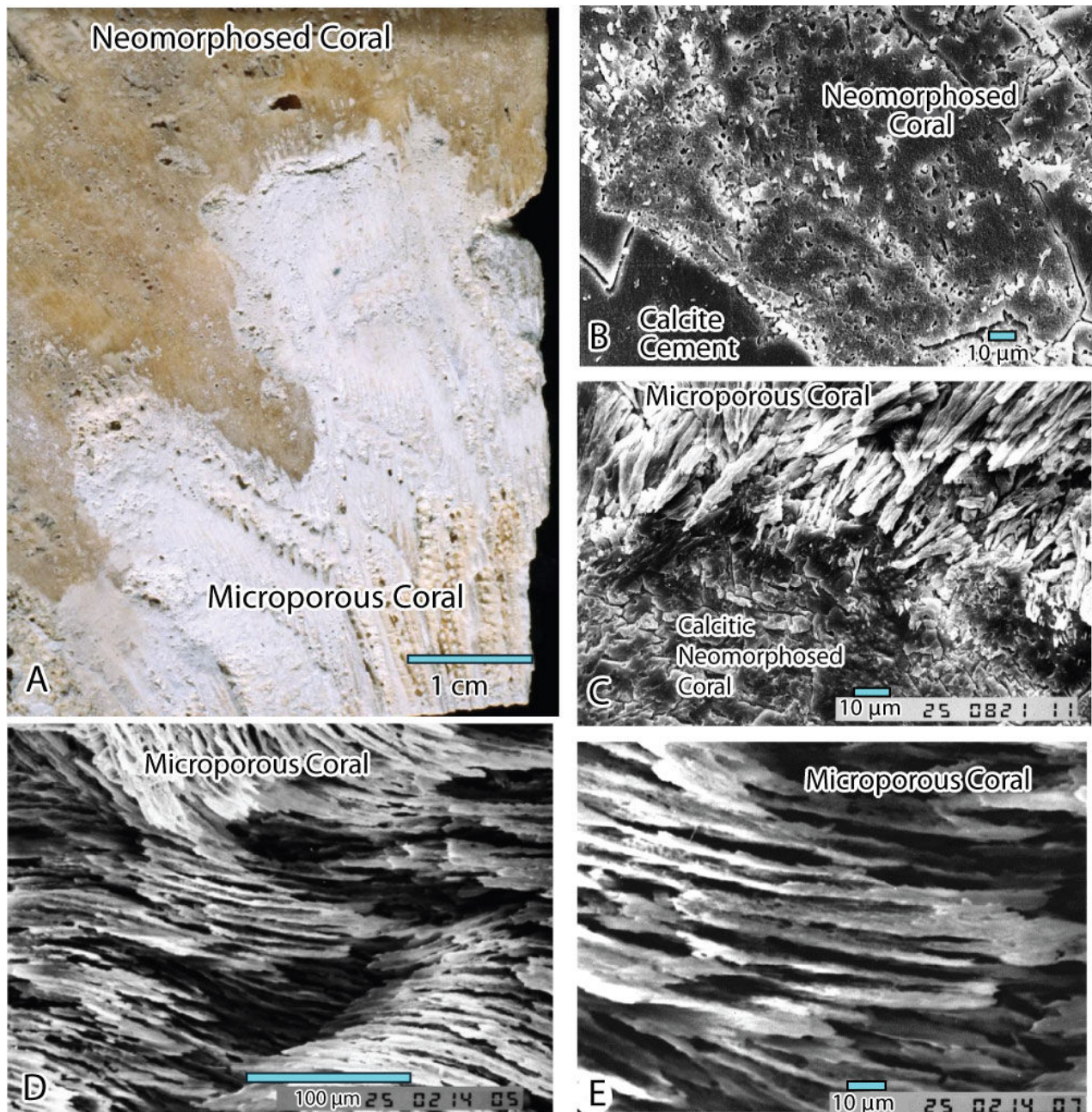


Figure 4: Enewetak samples. **(A)** Core photo showing neomorphosed (calcitized) coral adjacent to microporous (chalky) aragonitic coral. **(B)** SEM photo of a polished and etched surface. Neomorphosed coral is blocky calcite with inclusions of aragonite (white). Blocky calcite cement fills a depositional pore in the coral. **(C)** SEM photo of contact of calcitic neomorphosed coral and microporous aragonitic coral with intrafabric dissolution. **(D-E)** SEM photos of microporous aragonitic coral with intrafabric dissolution.

3.a. Petrography

Partially dissolved aragonite is very common in the Pleistocene succession of Enewetak and affects the three main originally aragonitic fossil groups: coral, *Halimeda* and molluscs (Fig. 3). This alteration product was called chalkified aragonite by SCHLANGER (1963) and GÖTER & FRIEDMAN (1988). It represented a partial intrafabric dissolution of commonly 70% or more of the fossil's original aragonite leaving many isolated patches of aragonite surrounded by porosity (Figs. 4-7; Appendices 1-4). Higher degrees of dissolution were probably present, but pores probably collapsed when cored. Commonly, cal-

cite crystals containing aragonite, organics, and relict wall structure (neomorphic calcite) occur adjacent to the highly dissolved aragonite (Figs. 4.A, C, 5.C, 6.D; Appendix 3). JAMES (1974) described very similar dissolution and calcitization of coral in the Pleistocene of Barbados.

The process of neomorphosing aragonite to calcite is clearly in progress at Enewetak. Of the 95 Pleistocene samples examined, 65 have partial intrafabric dissolution of aragonite (Fig. 3). Neomorphic calcite replacing at least some aragonitic fossils occurs in 57 of the samples. Of those 57 samples, 53 also have unaltered aragonite, and 40 have aragonite with intrafabric dissolution adjacent to the cal-

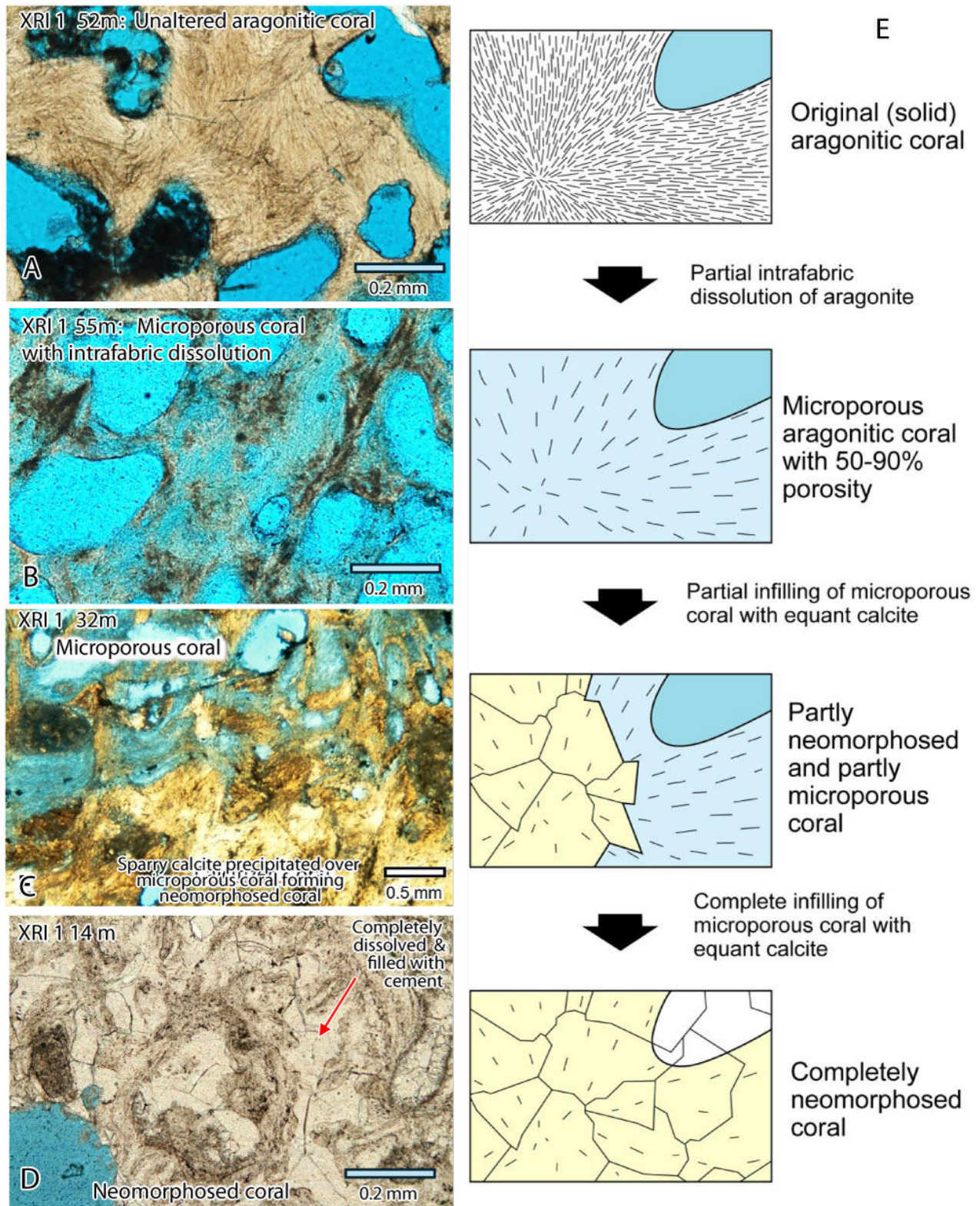


Figure 5: Sequential model for aragonite neomorphism in Enewetak starting with **(A)** unaltered coral followed by **(B)** microporous coral to **(C)** partially neomorphosed coral to **(D)** completely neomorphosed coral. **(E)** Schematic of the model for neomorphism.

citized (neomorphic) aragonite (Fig. 3). Six samples had petrographically "unaltered" aragonite separated by less than a 1 mm thick zone of partially dissolved aragonite, but calcitized (neomorphic) aragonite was never observed juxtaposed with intact aragonite (*i.e.*, separated by what could have been a thin film).

Commonly, sparry calcite crystals appear to have been precipitated into an aragonite grain with partial intrafabric dissolution (Appendix 3). This is also observed under a SEM (Fig. 4). Aragonitic grains can be traced from partially dissolved areas to completely open pore space (Fig. 7.B; Appendices 2.D, 4.A-B). Similarly, calcite crystals with

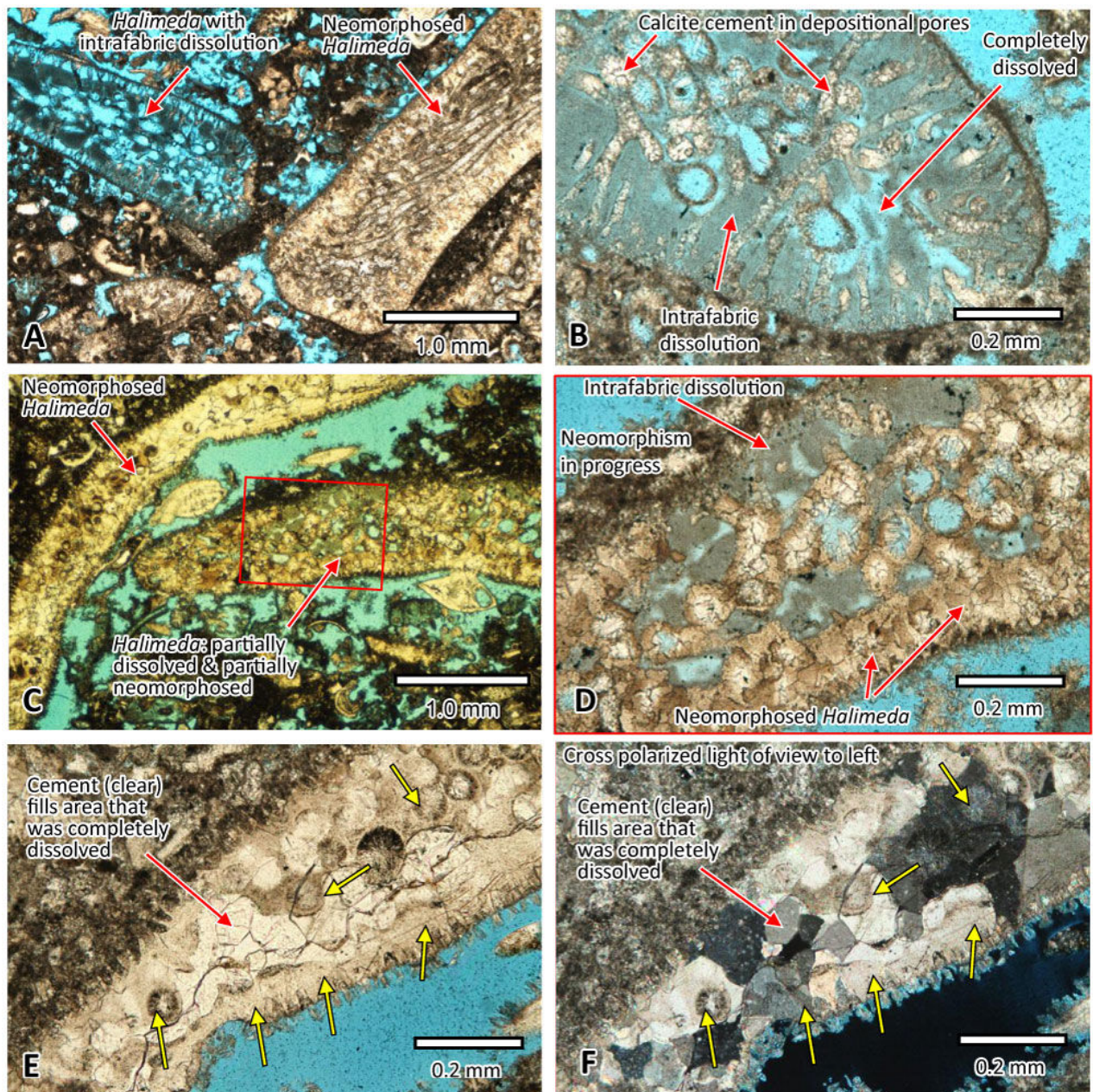


Figure 6: *Halimeda* with partial intrafabric dissolution and neomorphism (Enewetak, XRI-1, 45 m). **(A)** Two *Halimeda* flakes, one microporous and one neomorphosed with brownish sparry calcite. **(B)** Microporous *Halimeda* that is completely dissolved in places. **(C)** Neomorphosed *Halimeda* and partly neomorphosed *Halimeda*. **(D)** Close-up of rectangle in **(C)** showing microporous *Halimeda* passing to neomorphosed *Halimeda* (light brown). **(E)** *Halimeda* that has neomorphic spar (light brown) and areas filled with calcite cement. Many calcite crystals (yellow arrows) have parts that are clear (cement) and light brown (neomorphic spar). **(F)** Same view as **(E)** in cross polarized light.

partial retention of structure (calcitized/neomorphosed aragonite) can be traced into clear calcite cements (Figs. 5.D, 6.E-F; Appendix 1.F-H).

Interpretation:

Aragonite in Pleistocene carbonates in Enewetak is in the process of being either dissolved or replaced by calcite. Key petrographic observations supporting neomorphism by partial intrafabric dissolution followed by calcite precipitation into extremely microporous aragonite are: (1) widespread microporous aragonite, (2) patches of sparry calcite with aragonitic inclusions (neomorphosed aragonite) within microporous aragonite, (3) microporous aragonite passing to completely

dissolved aragonite on a microscopic scale, and (4) patches of sparry calcite with aragonitic inclusions (neomorphosed aragonite) passing laterally into sparry calcite cements [which could be formed by sparry calcite precipitating into situation shown in (3)]. The simplest explanation for these observations is neomorphism of aragonite by partial intrafabric dissolution followed by calcite precipitation into that microporous aragonite. A simple argument against thin film neomorphism in Enewetak Pleistocene limestone is that a narrow zone <10 microns wide does not separate unaltered aragonite from calcitized (neomorphic) aragonite in any of these Enewetak samples.

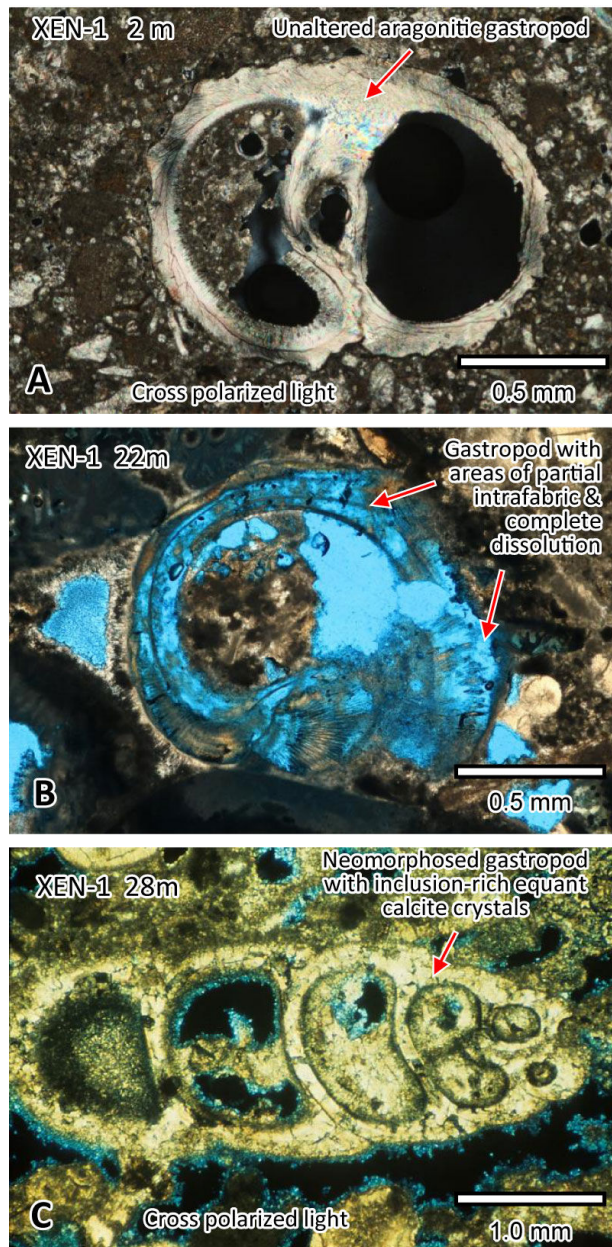


Figure 7: Stages of gastropod neomorphism in Enewetak XEN-1 well. **(A)** Original aragonitic gastropod. **(B)** Gastropod with areas of partial intrafabric and areas of complete dissolution. **(C)** Neomorphosed gastropod.

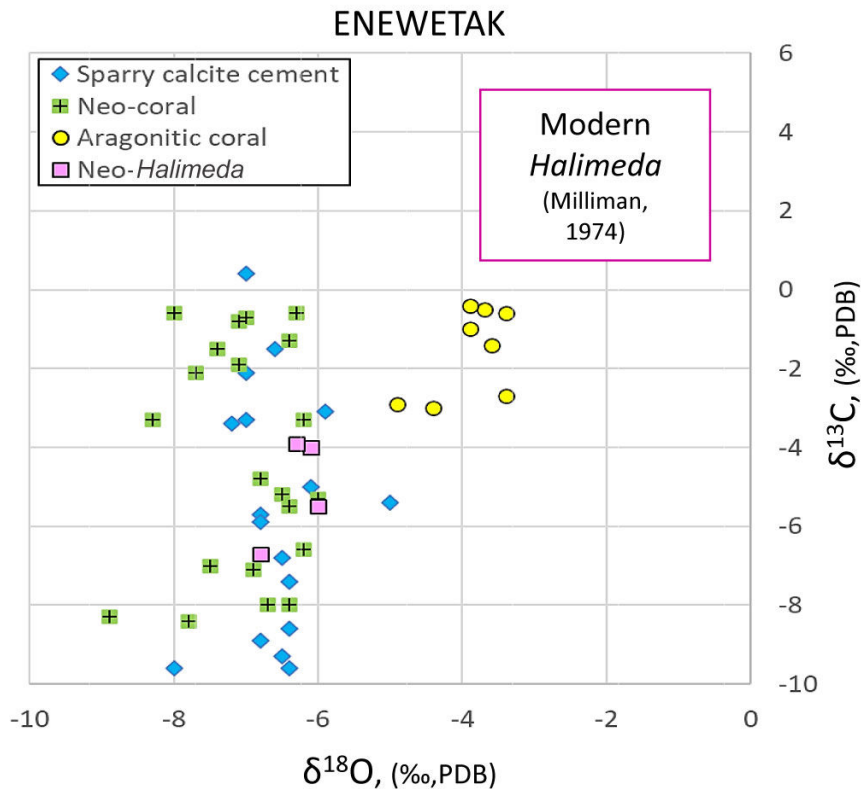
The consistent occurrence of (1) microporous aragonite and (2) neomorphosed (calcitized) aragonite that is adjacent to microporous aragonite supports a two-stage process of partial intrafabric dissolution followed by calcite precipitation, both occurring during periods of sub-aerial exposure and freshwater diagenesis. Aragonite dissolution probably occurred repeatedly (1) in vadose and phreatic meteoric environments during and immediately following storm and high-rainfall events and rainy seasons and (2) in mixing zones below freshwater phreatic zones (Fig. 2). During storm events and high-rainfall seasons, CO_2 charged waters originated in soil zones and moved through the vadose zone and into the upper meteoric phreatic zone (WHITAKER & SMART, 1997, 2007). CO_2 can come from the

atmosphere, plant respiration and decay of organic, especially plant material. Those CO_2 -charged waters form carbonic acid that preferentially dissolves metastable aragonite more rapidly than the original rainwater (JAMES & CHOQUETTE, 1984; BUDD, 1988). Dissolution events in meteoric vadose and phreatic environments may have been short-lived and only dissolved part of the aragonite before the waters became saturated with respect to calcite and precipitated calcite.

Mixing of freshwater and seawater results in waters with lower aragonite and calcite saturations (BADIOZAMANI *et al.*, 1973; BACK *et al.*, 1986; WHITAKER & SMART, 2007) causing more rapid dissolution of aragonite than the original rainwater. The Pleistocene of Enewetak contains some thick intervals with partially dissolved aragonite and little other diagenesis (Figs. 2-3). These are commonly well below an exposure surface and just below interpreted paleo-freshwater phreatic zones where the strata show increased dissolution and calcite cementation. For example, the section between 57 and 65 m in the XRI 1 well is dominated by partial, intrafabric dissolution of aragonite with no significant calcite cement or neomorphism (Fig. 3). This is 12 m below the nearest overlying exposure surface at 45 m, and hence is interpreted as a mixing zone dissolution. These mixing zones are interpreted to occur below islands formed during relatively high sea level. BUDDEMEIER and OBERDORFER (1986) describe modern mixing zones that are >15 m thick on the island of Engebi and in the XEN-1 well. If the diagenetic environment subsequently changed from mixing zone to an upper meteoric or capillary fringe zone, calcite could be precipitated over microporous aragonite, forming neomorphosed/calcitized aragonite. Calcite precipitation occurs in meteoric environments that experienced evaporation of meteoric water and/or degassing of CO_2 during drier periods of time (JAMES & CHOQUETTE, 1984; WHITAKER & SMART, 2007). Water evaporation is most pronounced in soil zones during dry intervals of time. CO_2 degassing is common in (1) soil zones, (2) other vadose zones, (3) capillary fringe zones immediately above the water table, and (4) the upper meteoric phreatic zone. If CO_2 -charged waters dissolve calcium carbonate and become saturated with respect to calcite, CO_2 degassing will increase the supersaturation and result in precipitation of calcite (HANOR, 1978).

3.b. Geochemistry

Different components of Pleistocene limestone on Enewetak were analyzed geochemically for $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and concentrations of Sr and Mg (SALLER & MOORE, 1991; SALLER, 1992). Neomorphic (calcitized) aragonites (1) have very similar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions as sparry calcite cements and (2) are very different from Pleistocene aragonitic coral and modern *Halimeda* described by MILLIMAN (1974) (Fig. 8). Pieces of aragonitic *Halimeda* and aragonitic molluscs in our samples were generally not big enough to be analyzed separately for stable isotopes.



◀ **Figure 8:** Stable carbon and oxygen isotopic compositions for Pleistocene and Holocene Enewetak samples. Neomorphosed coral (Neo-coral) and neomorphosed *Halimeda* (Neo-*Halimeda*) plot in a field similar to sparry, meteoric calcite cements, but distinctly different from aragonitic coral from Enewetak and modern aragonitic *Halimeda* (from MILLIMAN, 1974). These data support neomorphism by intrafabric dissolution and sparry calcite precipitation, not thin films.

Neomorphosed (calcitized) coral, *Halimeda* and molluscs have Sr concentrations that are generally above sparry calcite cements, but far below their aragonitic precursor (Table 1). Microprobe traverses show erratic high Sr spots in

the calcitized aragonites (Fig. 9). Mg concentrations in calcitized aragonites are similar to sparry calcite cements and distinctly above their aragonitic precursors (Tables 1-2).

Table 1: Strontium and magnesium concentrations from Electron Microprobe Analyses.

		Sr (ppm)	Sr (ppm)		Mg wt %	Mg wt %
	n	Mean	σ		Mean	σ
Pleistocene, Enewetak						
Aragonitic Coral	32	7,800	780		0.082	0.023
Aragonitic <i>Halimeda</i>	7	8,340	1,520		0.036	0.036
Neomorphosed Coral	36	1,550	450		0.221	0.030
Neomorphosed <i>Halimeda</i>	21	1,920	430		0.231	0.070
Neomorphosed Molluscs	18	1,120	160		0.286	0.078
Sparry Calcite Cement	147	600	170		0.236	0.061
Cat Island, Bahamas						
Neomorphosed Molluscs	17	1,350	860		0.130	0.033
Sparry Calcite Cement	93	1,200	980		0.210	0.130
Northeast Yucatan, K-274 well						
Neomorphosed Coral	11	2,330	990		0.430	0.077
Sparry Calcite Cement	54	730	410		0.603	0.150

"n" is the number of samples analyzed. Each sample analyzed is the mean of 9 or more spot analyses. σ is the standard deviation.

**Table 2:** Geochemistry of Neomorphosed Coral and Optically Continuous Intracoraline Calcite Cements in Enewetak cores.

		Neomorphosed Coral			Optically Continuous Intracoraline Cement			
		Sr (ppm)	Sr (ppm)	Mg wt %		Sr (ppm)	Sr (ppm)	Mg wt %
Well/Depth	Points	Mean	σ	Mean	Points	Mean	σ	Mean
XAR-1	34 m 45	1,650	840	0.17	45	930	220	0.19
	38 m 72	1,890	400	0.15	45	1,320	320	0.14
	56 m 27	1,930	620	0.27	36	1,080	240	0.29
	65 m 63	1,120	650	0.24	45	190	130	0.15
XRI-1	24 m 27	1,470	360	0.27	36	1,170	310	0.29
	25 m 81	2,980	1310	0.25	36	2,230	890	0.24
	41 m 45	1,700	750	0.14	36	1,090	900	0.25
	50 m 99	1,800	680	0.33	63	960	450	0.32
		$\delta^{13}\text{C}$	$\delta^{18}\text{O}$			$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	
XRI-1	50 m	-3.3	-6.2			-3.1	-5.9	

Average of Enewetak Coral Analyzed in this study.

n	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
8	-1.5	-3.9

Sr and Mg analyses were by electron microprobe.

"Points" are the number of spot analyses for Sr and Mg concentrations.

"n" is number of coral samples analyzed for stable carbon and oxygen isotopes and are reported in ‰, VPDB.

Interpretation:

The geochemistry of neomorphosed (calcitized) aragonite relative to calcite cements and original aragonite is consistent with meteoric calcite precipitating within an extremely microporous aragonite, but not consistent with neomorphism along a thin film in a semi-closed environment. The stable carbon and oxygen isotopic compositions of the neomorphosed (calcitized) aragonite are very similar to sparry meteoric cements in these Pleistocene strata, but are different from the original aragonitic fossils (Fig. 8). Oxygen isotopes of neomorphic (calcitized) aragonite that formed by dissolution and reprecipitation along a thin film might be expected to be nearly in equilibrium with the meteoric waters because original water in that thin film contains many oxygen atoms compared to oxygen atoms from the dissolved aragonite. In contrast, the carbon isotopes in the neomorphosed (calcitized) aragonite should reflect a semi-closed system where it would be difficult to get allochthonous carbon atoms into the interior parts of the thin film. The observed stable carbon isotopes not being controlled or even significantly influenced by the aragonitic precursor is not consistent with neomorphism along a thin film, but it is consistent with calcite crystals growing within a microporous aragonitic precursor.

The observed Sr concentrations are consistent with both mechanisms of aragonite neomorphism, but Mg concentrations are not. Sr

concentrations of the neomorphosed (calcitized) aragonites are intermediate between the original aragonitic fossils and sparry calcite cements, though closer to the cements (Table 1). Those Sr concentrations in the neomorphic spars could be a consequence of (1) a thin-film causing a semi-closed system resulting in elevated values due to concentrating Sr from the dissolving aragonite (with some Sr escaping from the margins of the thin film) (DAVIES, 1977), or (2) high Sr concentration in the neomorphic calcite due to aragonitic inclusions in the neomorphic spars. Microprobe traverses of neomorphosed aragonites have high spikes (Fig. 9) which is more consistent with calcites overgrowing Sr-rich aragonitic inclusions (or their relicts) rather than neomorphism along a thin film where Sr might be generally concentrated within a front, but not at a point.

Mg concentrations in calcitized aragonites are similar to sparry calcite cements and generally substantially greater than their aragonitic precursor. The distribution coefficient of Mg in calcite varies from 0.012 at 10° C to 0.040 at 50° C (OOMORI *et al.*, 1987); hence Mg should be preferentially excluded from the neomorphic calcite. As a result, Mg concentrations caused by neomorphism along a thin film, should be lower rather than substantially higher than the aragonitic precursor. Mg concentrations being similar to sparry calcite cements is again consistent with neomorphism by calcite crystals precipitating over a microporous precursor.

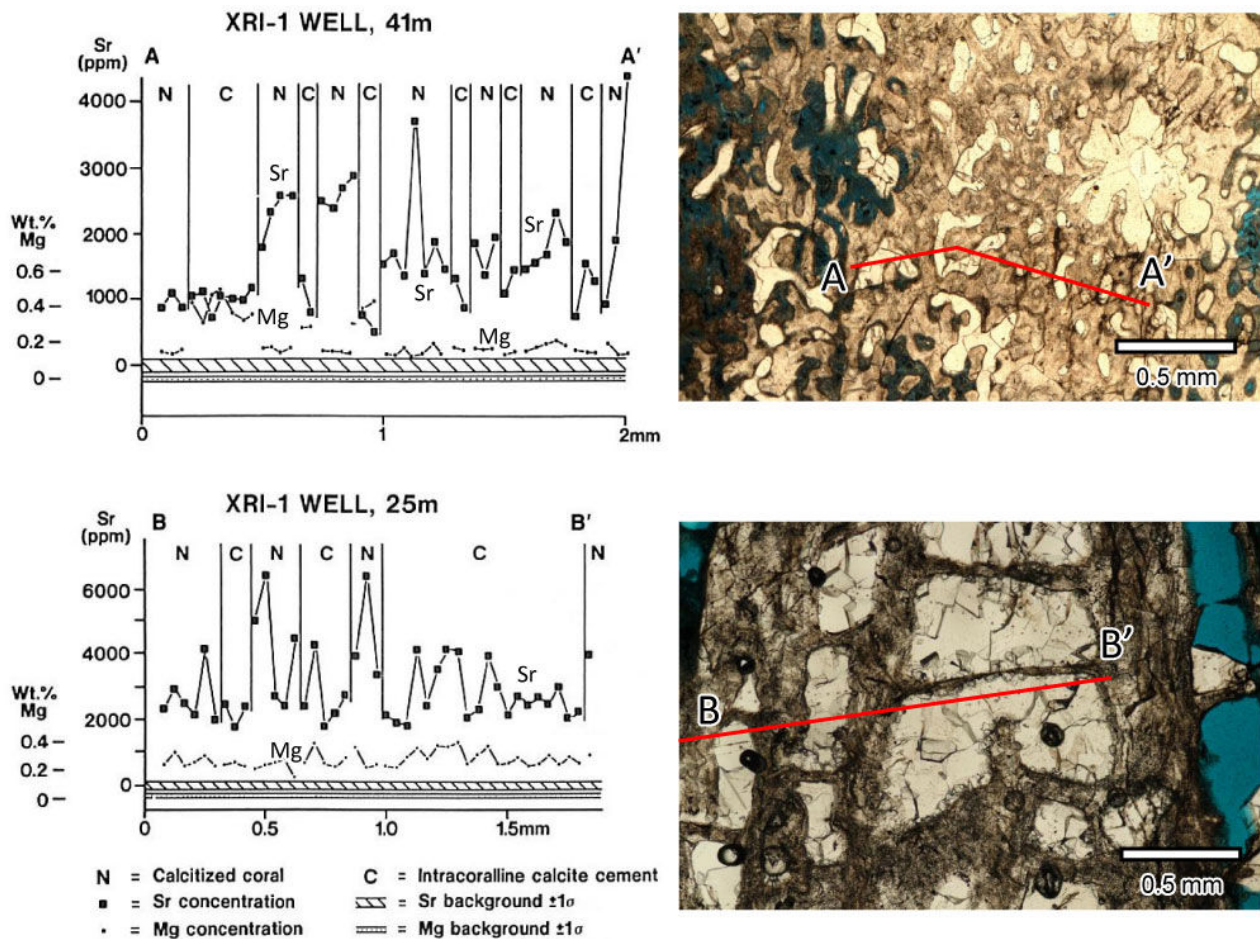


Figure 9: Electron microprobe traverses for Enewetak corals showing variations in strontium and magnesium concentrations in neomorphosed coral (N) and intracoraline calcite cement (C). Sr concentrations in neomorphosed coral are generally higher than cements. Spikes in Sr concentration in neomorphosed coral are interpreted as inclusions of the original coralline aragonite remaining after partial intrafabric dissolution and being overgrown by calcite crystals.

4. Bahamas

The Bahamas is one of the world's largest modern carbonate provinces, stretching more than 1300 km from northwest to southeast. The Bahamas has islands scattered across numerous platforms. During the Pleistocene, platforms were repeatedly flooded during high sea level and subaerially exposed during low sea level (BEACH & GINSBURG, 1980; GINSBURG, 2001). In addition, carbonate sediment accumulated locally above sea level forming islands during some periods of high sea level, resulting in subaerial exposure and meteoric diagenesis locally during some periods of high sea level. Cat Island is on the eastern side of the Great Bahama Bank, near the center of the Bahamas (Fig. 1). Robert GINSBURG generously allowed us to sample cores from two wells (C-70 and C-73) on Cat Island. These cores were studied by BEACH and GINSBURG (1980) and BEACH (1995). These cores are thought to include the entire Pleistocene and uppermost Pliocene successions. Limestones above a depth of 10 m are dominated by ooid and peloid grainstones, whereas limestones at 11-30 m are wackestone, packstones and grainstones with peloids, miliolid forams, mollusc fragments and *Halimeda*.

4.a. Petrography

Limestones above a depth of 12 m commonly consist of 10-50% aragonite with unaltered and partially dissolved aragonitic grains. Some complete dissolution of aragonitic grains occurs (Fig. 10.C-D), but partial intrafabric dissolution is very common (Figs. 10.A-B, 11.B; Appendix 5.A) similar to that observed on Enewetak. At 12-30 m, most originally aragonitic grains (molluscs and peloids) have been dissolved or neomorphosed (Figs. 10.C-F, 11.A; Appendix 6.A-F). In samples from 2-30 m deep, partial intrafabric dissolution and neomorphism to coarser calcite was observed in ooids (Fig. 11.B-D), gastropods (Fig. 10.A-B, E-F; Appendices 5.A, C-F, 6) and *Halimeda*.

Neomorphic calcite was observed adjacent to microporous aragonite in mollusc shells and adjacent oolitic cortices (Fig. 11.B-D; Appendix 5.C-D). Areas with partial intrafabric dissolution of aragonite were adjacent to areas with complete dissolution (Figs. 10.B, 11.B). Neomorphic calcite in mollusc shells was observed passing laterally into clear sparry calcite cement in many mollusc shells (Figs. 10.E-F, 11.A; Appendices 5.G, 6.A-B). Unaltered aragonite was not observed separated from adjacent neomorphosed aragonite by an ultra-thin zone.

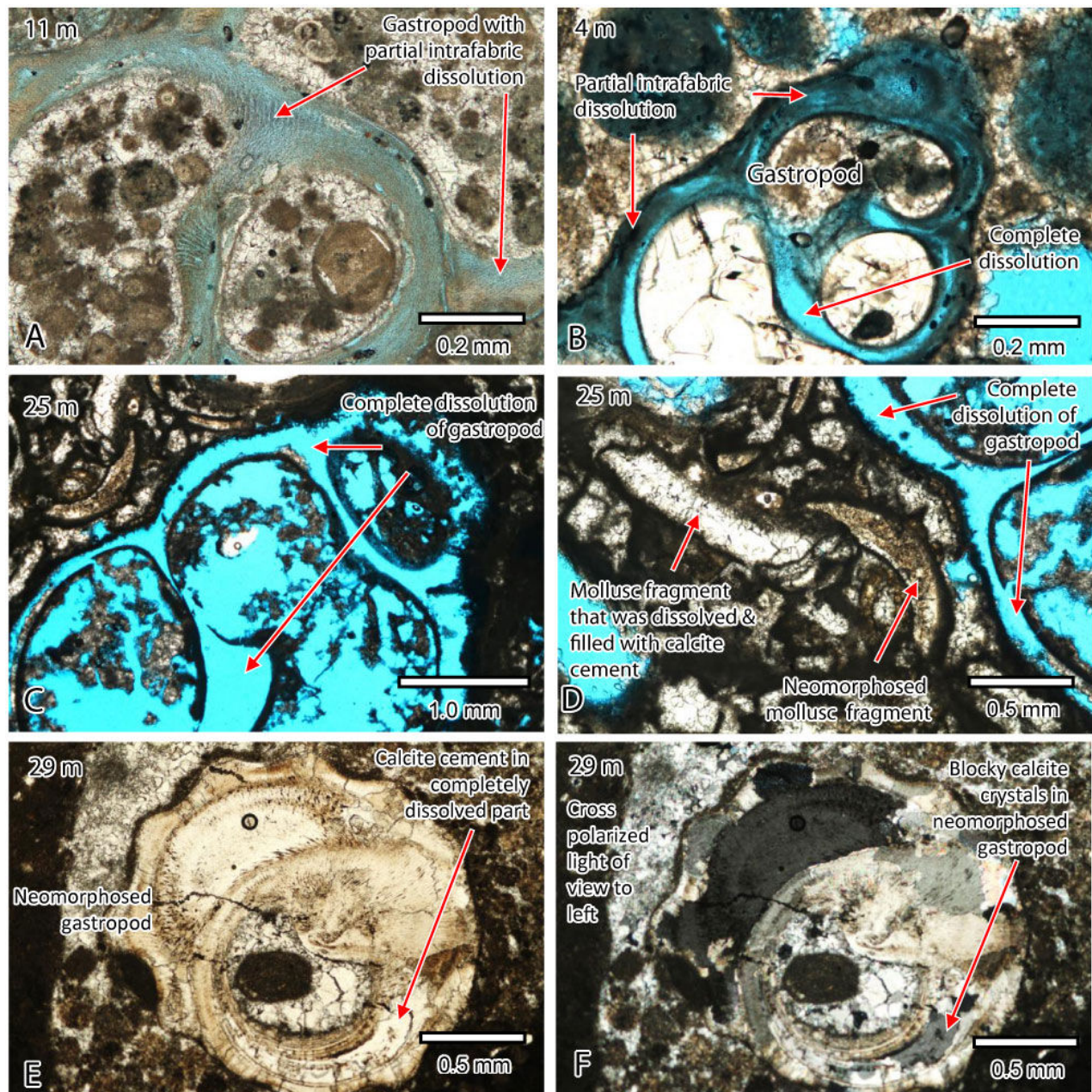


Figure 10: Alteration of gastropods in Cat Island, Bahamas, well C-73. **(A)** Gastropod with partial intrafabric dissolution. **(B)** Gastropod with partial intrafabric and complete dissolution. **(C)** Largely dissolved gastropod. **(D)** Dissolved gastropod, neomorphosed mollusc fragment, mollusc fragment that was completely dissolved and infilled with calcite cement. **(E)** Neomorphosed gastropod (light brown) with areas that were completely dissolved and refilled with cement (clear, white). **(F)** Same as (E) under cross polarized light showing blocky calcite crystals in the neomorph spar.

Interpretation:

Similar to Enewetak, petrographic observations support aragonite neomorphism by intrafabric dissolution of aragonite followed by precipitation of calcite crystals over that partially dissolved aragonite. Those observations include (1) neomorphosed (calcitized) aragonite adjacent to aragonite with partial intrafabric dissolution, (2) partially dissolved aragonite adjacent to completely dissolved aragonite, and (3) neomorphic calcite crystals passing laterally into clear calcite cements, as would be expected with calcite crystals precipitated into pore systems observed in (2). Unaltered aragonite was not observed adjacent to neomorphic spar separated by an ultra-thin zone, arguing against thin-film neomorphism.

4.b. Geochemistry

Results of analyses of stable carbon and oxygen isotopes are shown in Figure 12 and Table 1. Molluscs were the only originally aragonitic grain type in Bahamian samples in big enough pieces to separate and analyze for stable carbon and oxygen isotopes. Stable isotope fields of neomorphosed (calcitized) aragonitic molluscs and sparry (meteoric) calcite cements are similar and distinctly different from aragonitic molluscs in the area (Fig. 12; Table 3). The average concentrations for strontium and magnesium in neomorphosed molluscs and sparry calcite cements are shown in Table 1.

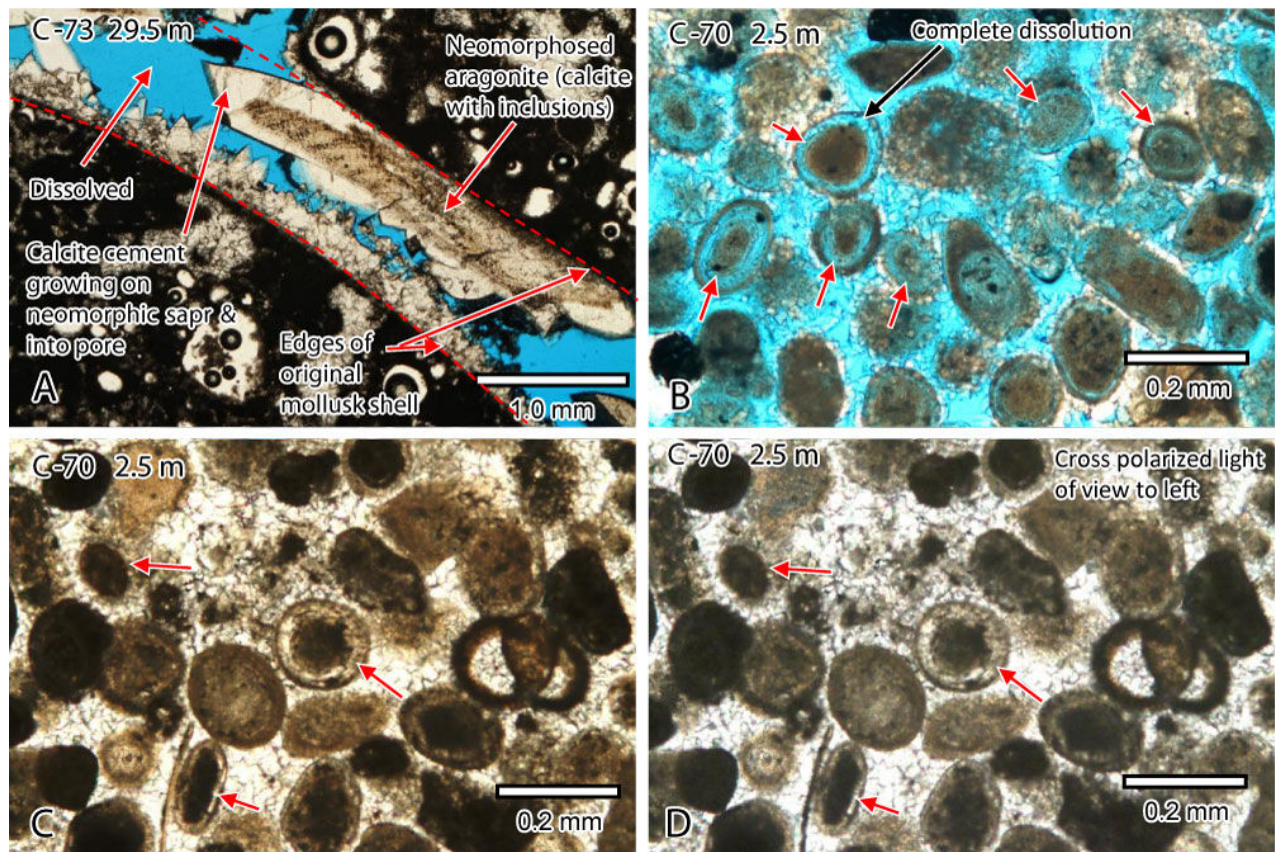


Figure 11: Diagenesis of Cat Island, Bahamas samples. **(A)** Mollusc that likely was completely dissolved in places and had areas with partial intrafabric dissolution. Sparry calcite then precipitated into both creating the observed fabric. **(B)** Ooids with partial intrafabric dissolution (red arrows). **(C)** Neomorphosed ooids (arrows) likely created by sparry calcite precipitated into microporous ooids similar to those in another part of the thin section and shown in (B). **(D)** Same area as (C) but under cross polarized light.

Table 3: Carbon and oxygen stable isotopic compositions of Aragonite, Neomorphosed Aragonite and Sparry Calcite Cements.

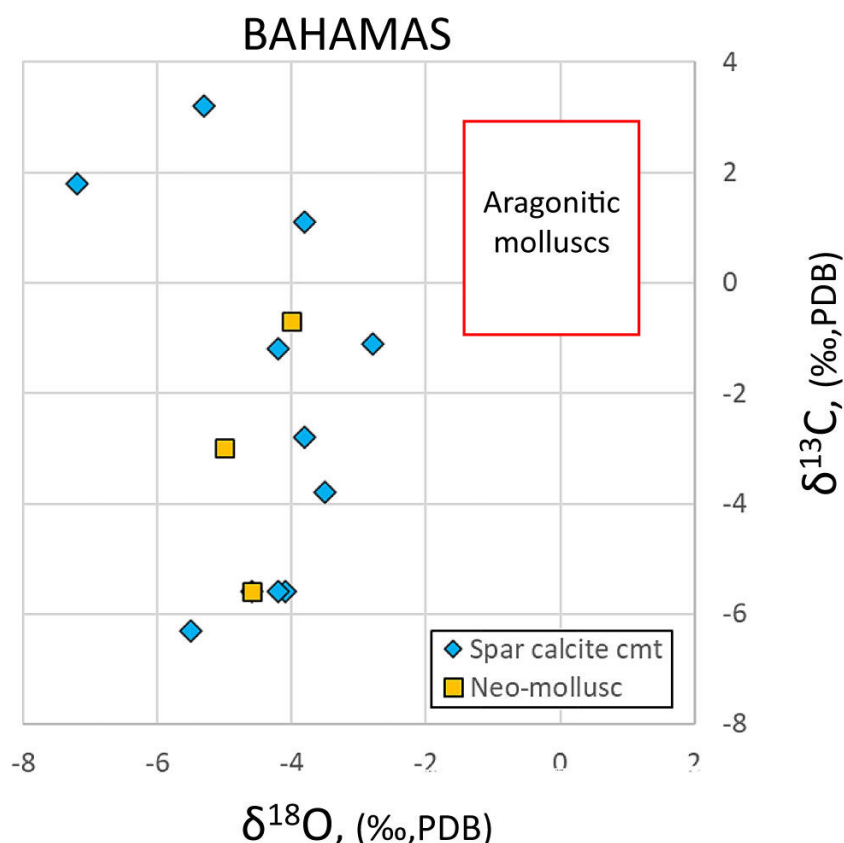
			$\delta^{13}\text{C}$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	$\delta^{18}\text{O}$
		n	Mean	σ	Mean	σ
Pleistocene, Enewetak	Coral	8	-1.5	1.1	-3.9	0.5
	Neomorphosed Coral	22	-4.3	2.9	-6.9	1.2
	Neomorphosed <i>Halimeda</i>	5	-4.8	1.2	-6.3	0.3
	Sparry Calcite Cement	20	-5.1	3.1	-6.5	0.6
Plio-Pleistocene, Cat Island, Bahamas	Neomorphosed Molluscs	3	-3.1	2.4	-4.5	0.5
	Sparry Calcite Cement	9	-3.4	2.6	-4.1	0.7
Pleistocene, Yucatan	Neomorphosed Coral	4	-4.1	2.3	-4.8	0.4
	Sparry Calcite Cement	5	-4.8	1.8	-5.0	0.8

"n" is number of samples. All data are in ‰, VPDB. σ is the standard deviation.

Interpretation:

Similar to Enewetak, the geochemistry of samples from Cat Island in the Bahamas supports neomorphism by partial intrafabric dissolution followed by calcite precipitation, not thin-film neomorphism. The stable carbon and oxygen isotopic compositions of neomorphosed molluscs are similar to sparry calcite cements in the Cat Island samples (Fig. 12; Table 3), and hence the simplest explanation is neomorphism by precipitation of meteoric calcite within a highly dissolved aragonitic precursor. As with Enewetak samples, oxy-

gen isotopes could be controlled by the meteoric waters of a thin film, resulting in similar oxygen isotopic compositions; however, the carbon isotopes should be controlled by the aragonite being dissolved on the one side of the thin film and then precipitated as calcite on the other side. The stable carbon isotopic compositions of the neomorphic calcite are very different from molluscs in modern tropical carbonates (Fig. 12; MILLIMAN, 1974), which is not consistent with thin-film neomorphism.



◀ **Figure 12:** Stable isotopic data from the Pleistocene material from Cat Island, Bahamas. Neomorphosed molluscs (Neo-mollusc) have distinctly different compositions than aragonitic molluscs in the area, but stable carbon and oxygen isotopes that are similar to meteoric calcite cements from the same wells. Red rectangle shows the composition of aragonitic gastropods from south Florida and the Bahamas (STRAUSS *et al.*, 2014).

Molluscs have Mg and Sr concentrations that are more consistent with formation of neomorphic spar by partial intrafabric dissolution followed by calcite precipitated into the microporous aragonite, rather than along a thin film. Sr concentrations in the neomorphic spars are intermediate between original mollusc aragonite and sparry calcite cements, although aragonitic molluscs have substantially lower Sr concentrations than coral (Table 1). Hence, Sr concentrations are consistent with both mechanisms of neomorphism. Aragonite gastropods in modern tropical carbonates generally have Mg concentrations of 0.01–0.10 wt % Mg (MILLIMAN, 1974). The Mg concentrations in our Bahamian neomorphic molluscs (Table 1; average Mg of 0.13 wt %) are generally above aragonitic molluscs, suggesting an open system relative to Mg, and not a thin film origin for neomorphic spars. The Mg concentrations of the neomorphosed molluscs are different enough from sparry calcite cements, that they do not support neomorphism by intrafabric dissolution and sparry calcite precipitation either.

5. Yucatan

Carbonates studied in the Yucatan came from two wells and samples collected from quarries along the eastern side of the Yucatan peninsula (Fig. 1). All samples are Pleistocene in age. Those samples were kindly loaned from W.C. (Bill) WARD's collection. Each of the two wells acquired approximately 10 m of core. Strata included three depositional packages bounded by two subaerial exposure surfaces. The upper depositional pack-

age had a coral dated as 122,000 year BP (SZABO *et al.*, 1978).

5.a. Petrography

Diagenetic alteration was intense and continued until the cores were taken out of the ground because they were in active meteoric and mixing zones. Dolomite was also present in these cores (WARD & HALLEY, 1985). Only minor aragonite remained in these cores and that was mainly in the upper package. Original aragonite grains and fossils were mainly coral with some molluscs (mainly gastropods) and minor *Halimeda*. A few samples had unaltered aragonite (Fig. 13.A, 14) and aragonite with partial intrafabric dissolution (Fig. 13.B; Appendix 4C-E). A few neomorphosed molluscs were observed (Fig. 13.C-D). Most aragonitic material was dissolved, and then some of the resulting pores were refilled with equant calcite cement (Fig. 13.E-F). A gastropod from a quarry sample had neomorphic calcite juxtaposed to unaltered aragonite where a thin film could have been (Fig. 14). Neomorphosed corals were present at 1–4 m in the K-274 core (Fig. 13.G-H), but were not observed in the K-239 core.

Interpretation:

Petrographic data from Yucatan carbonates do not provide as much evidence for the mechanism of aragonite neomorphism as samples from Enewetak and the Bahamas. These wells are at the eastern edge of the Yucatan peninsula, and hence, vast amounts of meteoric water from the interior of the Yucatan peninsula could have moved through these carbonates causing the in-

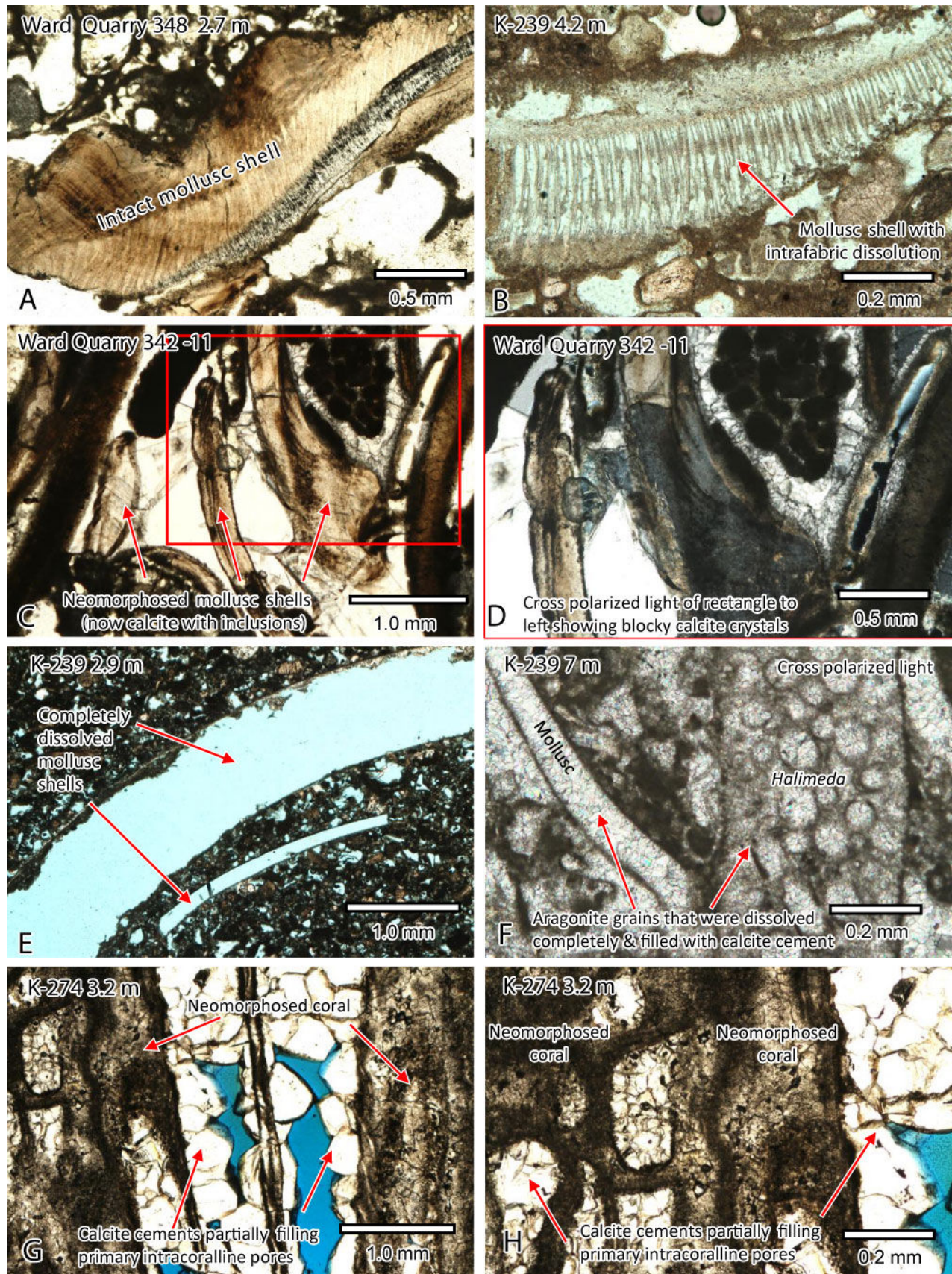


Figure 13: Thin section photomicrographs of Pleistocene Yucatan samples. (A) Aragonitic mollusc fragment. (B) Mollusc fragment with partial intrafabric dissolution. (C) Neomorphosed mollusc fragments. (D) View of rectangle in (C) in cross polarized light. (E) Completely dissolved mollusc shells. (F) Mollusc and *Halimeda* that were dissolved filled with calcite cement. (G-H) Neomorphosed coral with depositional pores partially filled with calcite cement.

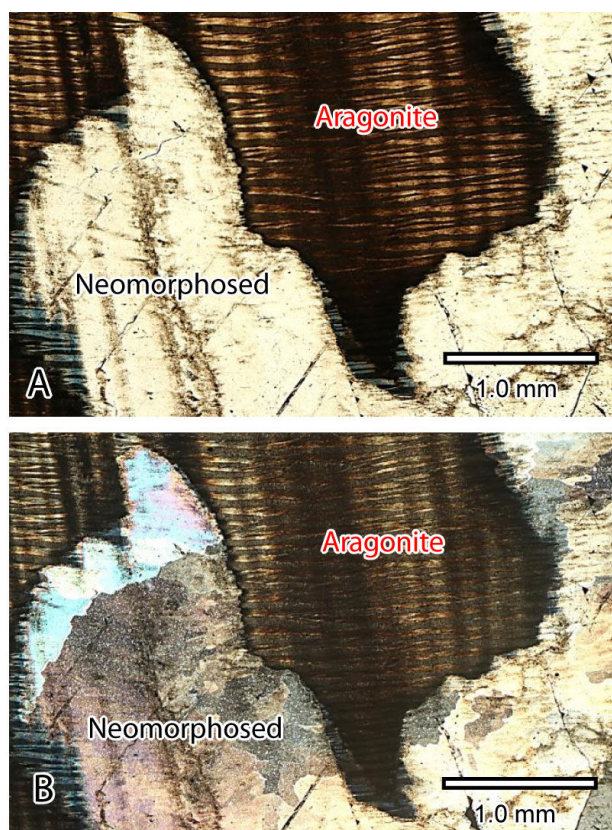


Figure 14: Yucatan gastropod from quarry. (A) Plane polarized light. (B) Cross polarized light. Neomorphous calcite is separated from original aragonitic gastropod by a very narrow zone. Although apparently separated by something that could have been a "thin-film", the geochemistry of the neomorphous calcite ($\delta^{13}\text{C} = -0.7\text{‰}$ VPDB, $\delta^{18}\text{O} = -6.2\text{‰}$ VPDB, Sr = 0.20 wt %, Mg = 0.024 wt %) is different from the aragonitic gastropod ($\delta^{13}\text{C} = +3.2\text{‰}$ VPDB, $\delta^{18}\text{O} = -0.7\text{‰}$ VPDB, Sr = 0.24 wt %, Mg = 0.008 wt %) and, hence, not compatible with neomorphism in a semi-closed "thin-film" system.

tense diagenetic alteration that was observed in these cores. Some aragonitic molluscs show partial intrafabric dissolution, and neomorphism of aragonite has occurred. The juxtaposition of neomorphous calcite and aragonite in a gastropod from the quarry would support thin-film neomorphism, but the geochemistry of the original and neomorphosed aragonite are very different arguing strongly against it.

5.b. Geochemistry

Yucatan samples analyzed geochemically include the aragonitic part of a gastropod, neomorphosed part of the same gastropod, neomorphosed coral and sparry calcite cements (Fig. 15). As with material from Enewetak and the Bahamas, the stable carbon and oxygen isotopic compositions of the neomorphous calcite were similar to sparry calcite cements, though the neomorphous material had higher $\delta^{18}\text{O}$ values than the sparry calcite cements, but they were within the variability of both types of samples (Fig. 15; Table 3). The $\delta^{13}\text{C}$ values for the neomorphosed coral are distinctly different from modern coral in the area (Fig. 15). The neomorphous part of the quarry

gastropod was greatly different in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ than the aragonitic part of the gastropod.

The Sr and Mg concentrations of neomorphosed coral and sparry calcite cements have the same pattern as Enewetak and Bahamian samples (Table 1). Sr concentrations of neomorphosed coral are intermediate between the aragonitic coral (7,000-9,000 ppm, MILLIMAN, 1974) and sparry calcite cement (Table 1). Mg concentrations of neomorphosed coral (average 0.43 wt %) overlap the field of sparry calcite cements, though their average value is between modern coral and sparry calcite samples. Modern corals have concentrations of 0.08-0.22 wt % Mg (MILLIMAN, 1974).

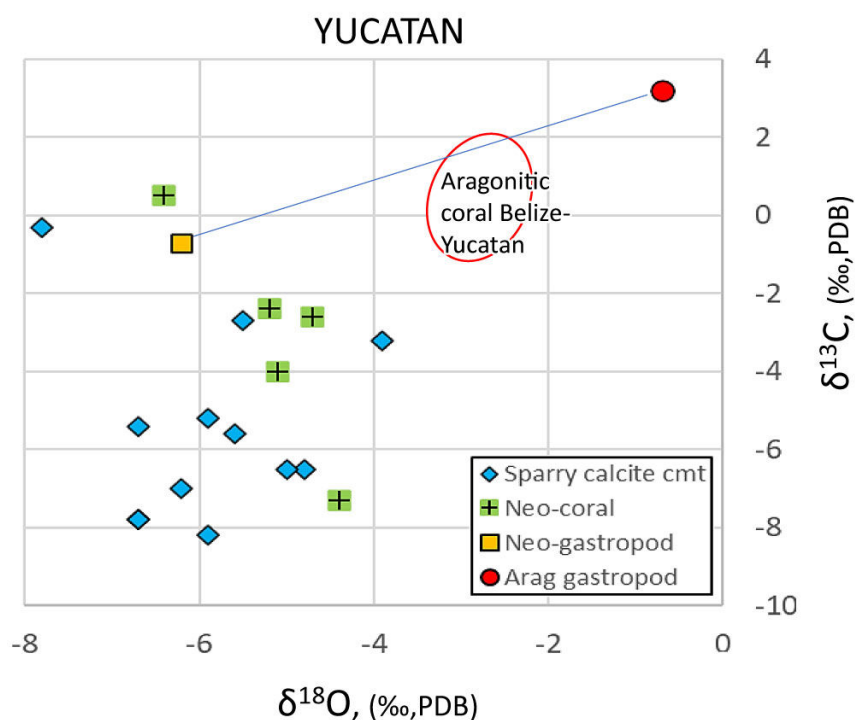
Geochemistry of the aragonitic and neomorphosed parts of the gastropod from a quarry shows substantial differences in isotopes and Mg concentrations. The aragonite part of the gastropod had $\delta^{13}\text{C}$ of +3.2‰ (VPDB), $\delta^{18}\text{O}$ of -0.7‰ (VPDB), Sr concentration of 0.24 wt % and Mg concentration of 0.008 wt %. In contrast, the neomorphous calcite part of the gastropod had $\delta^{13}\text{C}$ of -0.7‰ (VPDB), $\delta^{18}\text{O}$ of -6.2‰ (VPDB), Sr concentration of 0.20 wt % and Mg concentration of 0.024 wt % (Sr and Mg concentrations were from atomic absorption analyses; Fig. 14).

Interpretation:

As in the other study areas, the stable isotopic compositions of neomorphosed coral and neomorphosed gastropod are similar to sparry calcite cements (Fig. 15), suggesting a similar origin which is consistent with intrafabric dissolution followed by sparry calcite precipitation. The $\delta^{13}\text{C}$ of the neomorphosed coral is significantly different from aragonitic coral in the area (Fig. 15) which argues against thin-film neomorphism.

The Sr concentrations of the neomorphosed coral samples are consistent with either Sr being concentrated along a thin film or from aragonitic inclusions in a sparry meteoric calcite. Mg concentrations (average 0.43 wt %) are substantially higher than aragonitic coral (0.08-0.22 wt % Mg, values from MILLIMAN, 1974). It is difficult to explain how Mg could be added to the neomorphous spar in a semi-closed system (which is required for a thin-film origin), especially for an ion that should be preferentially excluded (OOMORI *et al.*, 1987). The Mg concentrations in the cements and neomorphous calcites are consistent with meteoric calcites precipitating within microporous aragonite to form neomorphous spars.

The geochemistry of the aragonitic part and neomorphosed part of the quarry gastropod separated by a thin zone (Fig. 15) indicates that the conversion did not occur by a thin film in a closed or semi-closed system. The higher Mg concentration in the neomorphosed part is unlikely from the originally aragonitic gastropod, especially since Mg ions should be preferentially excluded from calcite (OOMORI *et al.*, 1987). The difference in $\delta^{13}\text{C}$ between the original aragonitic gastropod and neomorphous gastropod (~4‰) also argues against thin-film neomorphism, even though it is



◀ **Figure 15:** Stable isotope plot of Yucatan data. The field of neomorphosed aragonitic fossils (Neo-coral and neo-gastropod; now calcite) is different from their aragonitic precursors, but similar to meteoric calcite cements. Red oval is field of modern coral from data in GISCHLER *et al.* (2009). The "Arag. gastropod" and "Neo-gastropod" connected by a blue line are from the sample shown in Figure 14.

the only sample examined in this study that is separated by a very thin zone (Fig. 14). The dissolved carbon in a thin film should have been similar to the original gastropod, making the substantial difference between the aragonitic and neomorphosed parts of the gastropod incompatible with thin-film neomorphism.

6. Discussion

Several items merit further discussion.

Role of CO₂ in aragonite neomorphism: A question regarding neomorphism of aragonite to calcite is- what is timing and main process responsible? The theory behind thin-film neomorphism is that a water (freshwater) can be undersaturated with respect to aragonite and supersaturated with respect to calcite; hence, aragonite could dissolve on one side of a thin film and then Ca²⁺ and CO₃²⁻ could precipitate as calcite on the other side of the thin film (PINGITORE, 1976). All that is required is freshwater, and hence neomorphism should be occurring at a significant rate wherever there is freshwater to start the thin-film process. This is not observed in Holocene and Pleistocene freshwater systems. Diagenesis and especially aragonite diagenesis in those systems is heterogeneous (BUDD, 1988; SALLER & MOORE, 1989, 1991; Fig. 2 in this paper). Data presented here indicate that most aragonite dissolution and calcite precipitation forming neomorphic spar did not occur at exactly the same time, rather aragonite dissolution alternates with calcite precipitation with a separation in time of variable duration (minutes to many millennia?), and hence the difference in aragonite and calcite stability is not the only factor involved.

Temporal variations in CO₂ and pCO₂ of diagenetic waters are thought here to be a critical part of neomorphism of aragonite. Influxes of rainwater and organic material (and their decay) cause changes in pCO₂ and can occur related to storm events, seasons and longer scales climatic changes (BUDD, 1988; WHITAKER & SMART, 2007; GULLEY *et al.*, 2015, and others). As a result, aragonite and calcite saturations in groundwaters change frequently (BUDD, 1988). Subsurface, meteoric waters could have lower calcium carbonate saturations after recharge events and increases in pCO₂ causing dissolution during and after storms. During subsequent dry periods, waters could become more saturated and precipitate calcite associated with CO₂ degassing (HANOR, 1978; WHITAKER & SMART, 2007; GULLEY *et al.*, 2015). These wetting and drying events would allow partial intrafabric dissolution of aragonite to alternate with calcite precipitation, and neomorphose aragonite to calcite in the same rock and same diagenetic environment.

Alternatively, Pleistocene sea-level fluctuations can cause large shifts of diagenetic environments. Aragonitic sediments might be in a mixing zone and experience widespread partial intrafabric dissolution of aragonite, and then sea level falls and those sediments could be in a meteoric vadose or upper phreatic environment with precipitation of sparry calcite. This would also result in calcite being precipitated into extremely microporous aragonite forming neomorphosed (calcitized) aragonite.

Formation of neomorphosed aragonite without freshwater: Neomorphosed aragonitic fossils occur in limestones that were not subjected to freshwater (HENDRY *et al.*, 1995; MELIM *et al.*, 2002). MELIM *et al.* (2002) proposed neo-



morphism in seawater during burial. MELIM *et al.* (2002) did not show stable isotope data for separates of the neomorphosed (calcitized) aragonite making it difficult to show whether thin-film neomorphism was likely, or whether those could have formed by intrafabric dissolution alternating with calcite precipitation. HENDRY *et al.* (1995) proposed a model for neomorphism occurring during shallow and deeper burial with waters affected by reactions involving organic material. The stable carbon and oxygen isotope compositions of the neomorphic spar were significantly different from the postulated aragonitic precursor and similar to calcite cements that varied through time. This is difficult to reconcile with thin-film neomorphism, but could be compatible with calcite precipitation into microporous aragonite forming at various times.

JAMES *et al.* (2005) observed loss (dissolution) of aragonite in cool-water carbonates in south Australia and proposed that the undersaturated seawater was produced by bacterial decay of organics causing undersaturation with respect to aragonite. Interestingly, no neomorphosed aragonite was produced (or at least mentioned). This might be because the diagenetic system did not alternate between aragonite dissolution and calcite precipitation at the needed frequency.

Role of organisms and organic matter: The relation of organisms and carbonate diagenesis is well documented and falls into two categories. (1) Biochemical processes associated with bacteria and other organisms affecting the diagenetic water as the organisms live (DIAZ *et al.*, 2023) and (2) decay of organic material affecting microenvironments. Organic material is present within coral skeletons after death (PERRIN & SMITH, 2007). The decay of that material associated with bacteria and other organisms may elevate local $p\text{CO}_2$ causing localized dissolution and microporosity within coral (JAMES, 1974; PINGITORE, 1976). It has also been recognized that microorganisms can facilitate thin alteration zones by creating localized supersaturation conditions around grains (REID *et al.*, 1990). However, the extent to which biogenic processes drive neomorphism versus abiotic pathways is still debated (LEPOT *et al.*, 2008), and live organisms were not apparently involved in aragonite neomorphism in this study.

Has neomorphism of aragonite fossils and grains occurred via a thin film: Thin-film neomorphism has been an accepted process for more than 50 years, and hence publications have not needed to prove it or even rigorously support it. Clearly, aragonite can be transformed to calcite, and this transformation can be accelerated or slowed by temperature, porosity and dissolved ions (HASHIM & KACZMAREK, 2021). I am not aware of a study that "proves" that an aragonite fossil has been transformed to calcite with partial retention of its internal structure by a "thin-film". A "thin-film" process should be a relatively closed system, and hence trace elements and stable carbon isotopic compositions should be very similar

to the original aragonite. Many published examples of advocating thin-film neomorphism show significant geochemical differences between the original aragonite and neomorphic spar (for example WEBB *et al.*, 2009), and hence are not semi-closed systems. Thin-film neomorphism is possible, especially at higher temperatures, but strong supporting data is needed to demonstrate it.

7. Conclusions

For many decades, neomorphism by thin-films ($\sim 1 \mu\text{m}$ wide) has been the accepted mechanism for the conversion of aragonite to calcite with partial retention of original wall structure (SANDBERG *et al.*, 1973; PINGITORE, 1976; WARDLAW *et al.*, 1978; SANDBERG & HUDSON, 1983; MALIVA, 1998). In only a very few Pleistocene localities have samples of neomorphosed (calcitized) aragonite separated from unaltered aragonite by a thin-film been found (PINGITORE, 1976; JAMES & CHOQUETTE, 1984). However, many of those studies describe chalkified aragonite (aragonite with intrafabric dissolution) being common.

In this study, Pleistocene limestones in three different localities contain both aragonite and neomorphosed (calcitized) aragonite indicating that these intervals are in the process of transitioning from metastable aragonite to stable, low-magnesium calcite. Aragonite has commonly undergone partial intrafabric dissolution at these locations. In many of those cases, calcite crystals with inclusions partially retain the aragonitic precursor's internal fabric (neomorphosed aragonite) in or adjacent to aragonite with partial intrafabric dissolution. Out of more than 200 samples examined in this study, only one contains unaltered aragonite separated from neomorphosed (calcitized) aragonite by a thin zone, and in that single sample, the geochemistry of the neomorphosed material is not consistent with thin-film neomorphism. These observations support a two-stage process with partial intrafabric dissolution of aragonite followed by precipitation of sparry calcite as the main process for aragonite neomorphosing into calcite. If intrafabric dissolution proceeds to completion before calcite precipitation, an aragonite mold is formed instead of neomorphosed spar.

Geochemical data also support aragonite neomorphism by partial intrafabric dissolution followed by calcite precipitation and refute thin-film neomorphism. Stable carbon isotope values from neomorphosed fossils are generally different than their aragonitic precursors and closer to sparry calcite cements in these strata. Stable carbon isotopes should be very similar to their aragonitic precursor if neomorphic spar formed by a semi-closed, thin-film process. Mg concentrations in neomorphosed aragonitic fossils are generally higher than their precursors and closer to sparry calcite cement, which is also inconsistent with thin-film neomorphism that should be in a semi-closed system. Stable carbon and oxygen isotope



values from neomorphosed aragonite are similar to meteoric calcite cements, supporting a similar origin for the calcite. Higher strontium concentrations generally observed in neomorphic calcites are probably associated with aragonite inclusions. Higher Mg concentrations in the neomorphic spars than the original aragonite require a more open system and import of magnesium from formation waters interacting with other depositional material like coralline algae (originally HMC).

Many scenarios are available for partial intra-fabric dissolution of aragonite to alternate with calcite precipitation and form neomorphic spar. Although many waters, especially freshwaters are capable of dissolution of aragonite, dissolution is more volumetrically important in certain diagenetic environments and at certain times. Likewise, calcite precipitation into partially dissolved aragonite could occur in different diagenetic environments and at different times. In Holocene and Pleistocene meteoric systems, increases in $p\text{CO}_2$ related to influxes of water and decay of organic material during storms are a common way to increase undersaturation and dissolve aragonite in many freshwater environments (soil zone, vadose, phreatic) (BUDD, 1988). Degassing of CO_2 from those same waters during times with little rainfall is a simple way to precipitate calcite in those same environments resulting in neomorphic spars (HANOR, 1978; WHITAKER & SMART, 2007; GULLEY *et al.*, 2015). Alternatively, widespread intra-fabric dissolution without much calcite precipitation occurs in mixing zones below water tables (as opposed to coastal mixing zones). A shifting of diagenetic environments could allow that microporous aragonite to be in an environment with some calcite precipitation, and hence form calcitized (neomorphic) aragonite.

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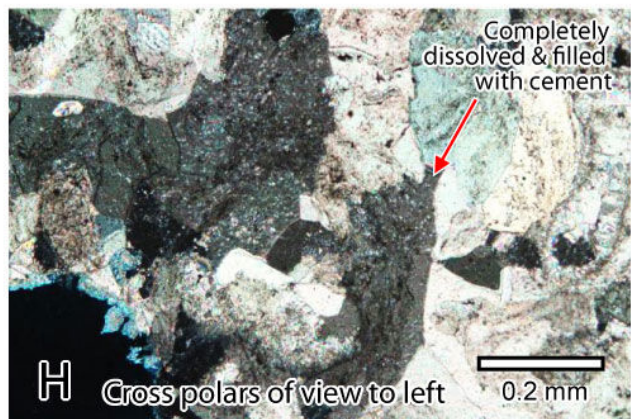
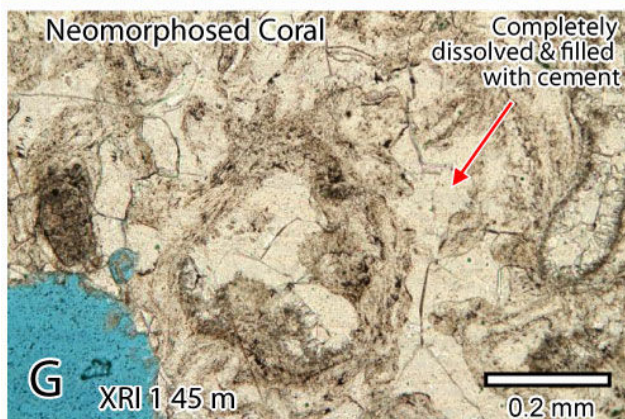
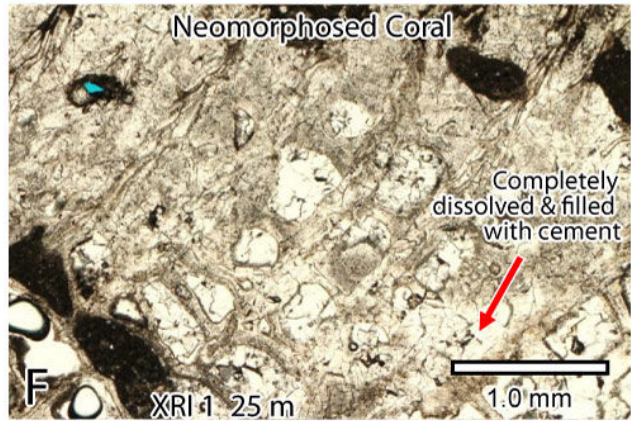
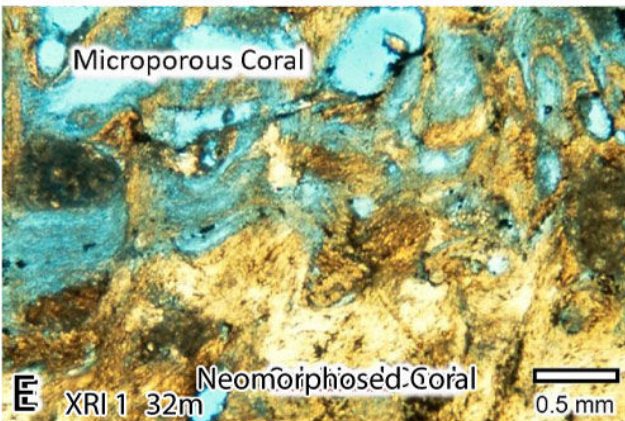
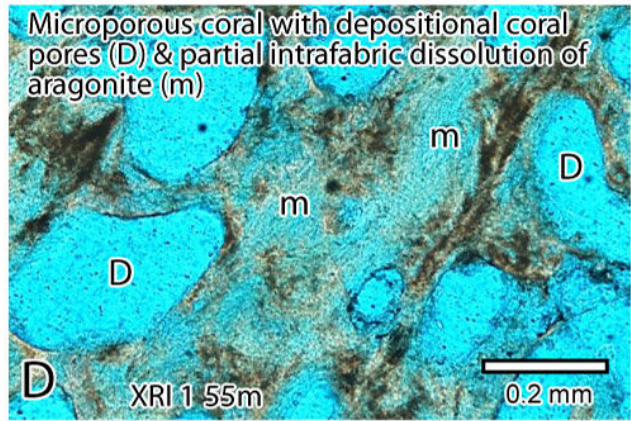
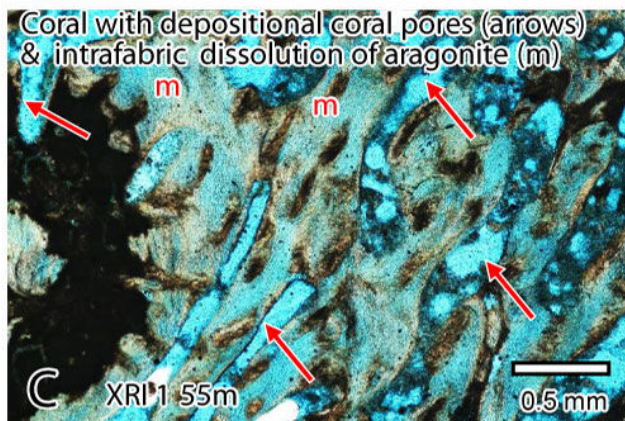
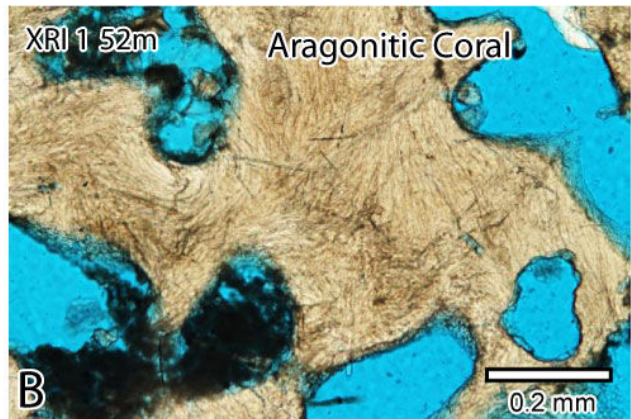
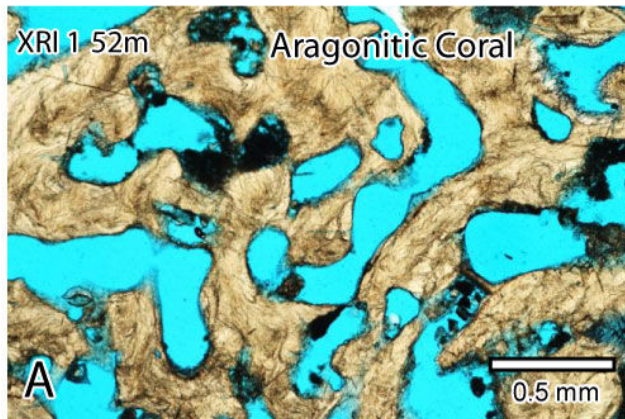


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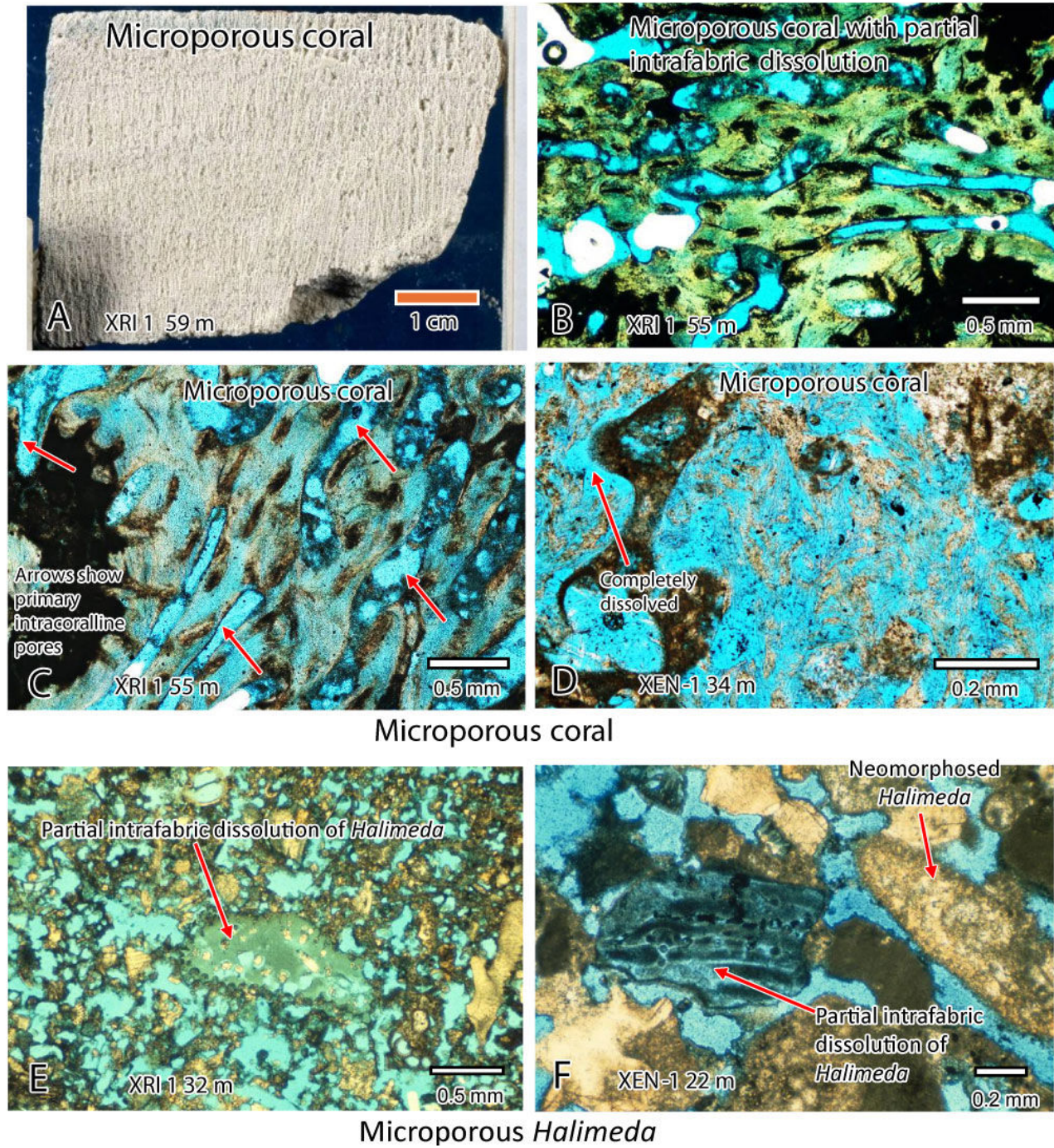
Appendices

Appendix 1: Enewetak. Progression from original aragonitic coral (**A-B**) through partial intrafabric dissolution (**C-E**) to neomorphosed coral (**F-H**).



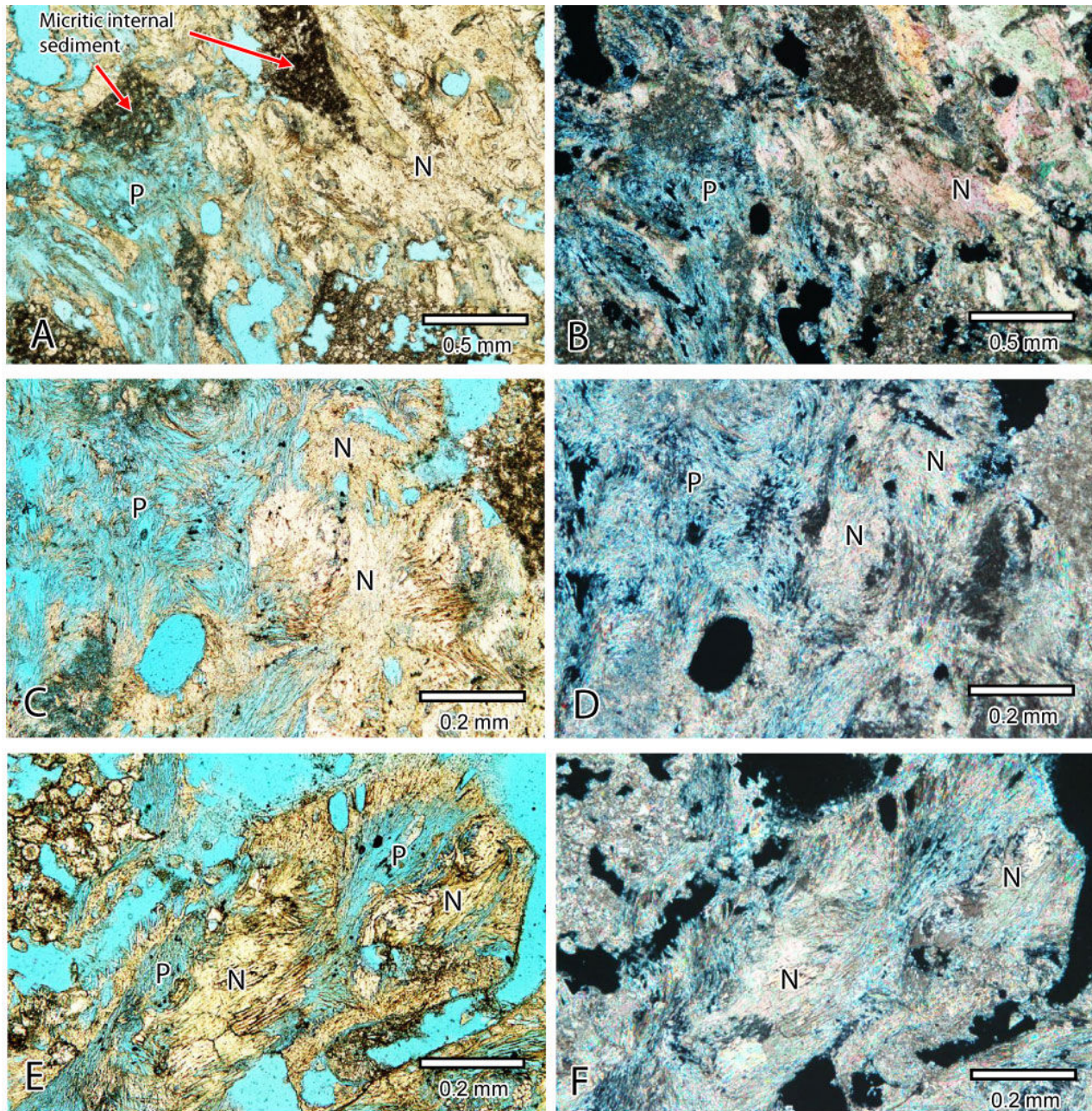


Appendix 2: Partial intrafabric dissolution of aragonite.



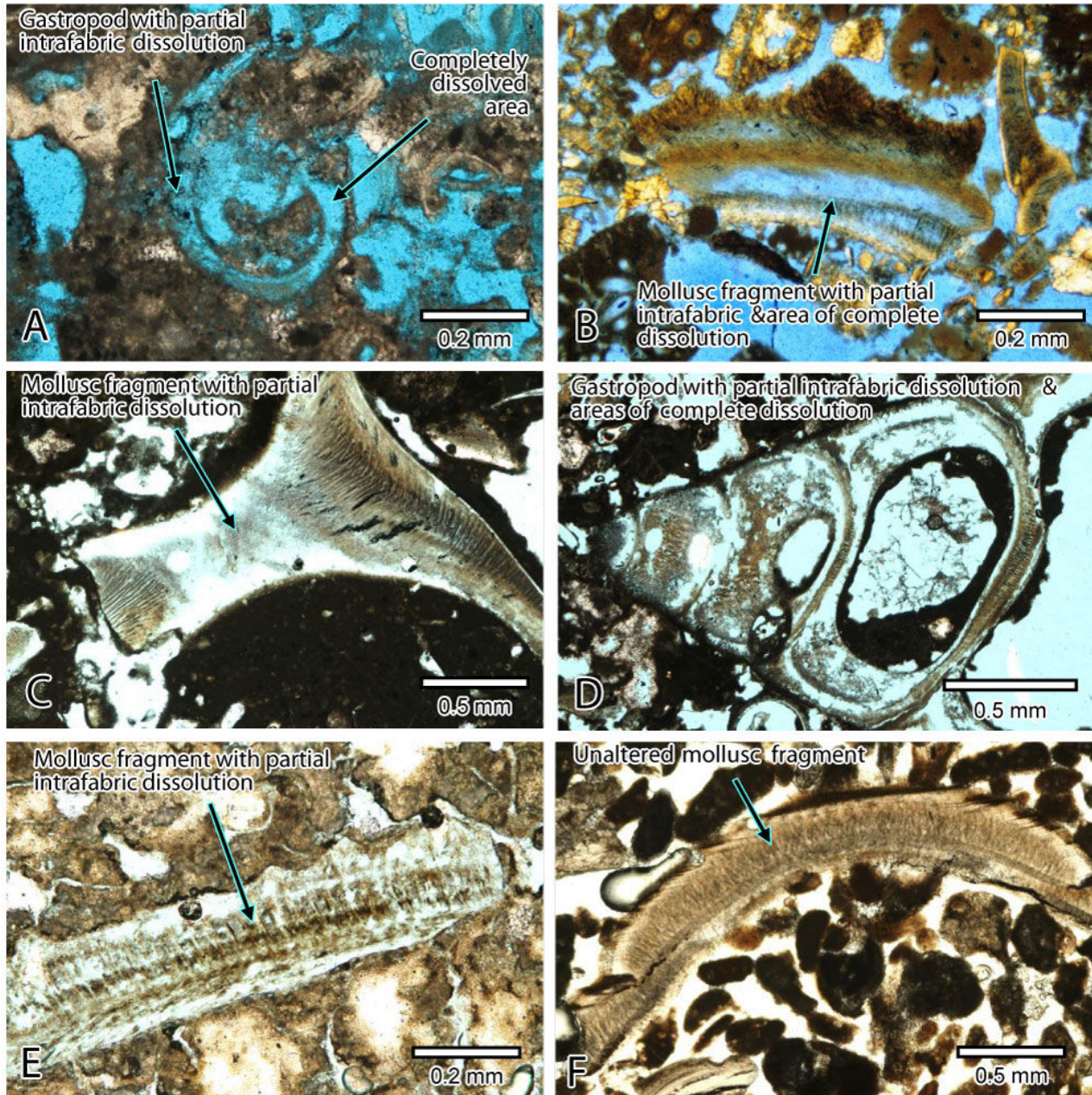


Appendix 3: Neomorphism in progress. Enewetak XRI-1 well at 32 m. Calcite crystals precipitated over microporous coralline aragonite with partial intrafabric dissolution result in neomorphic fabric (N) adjacent to areas with partial intrafabric dissolution of aragonite (P). Photos on left are plane polarized light (PPL). Photos on right are crossed polarized light (XPL).



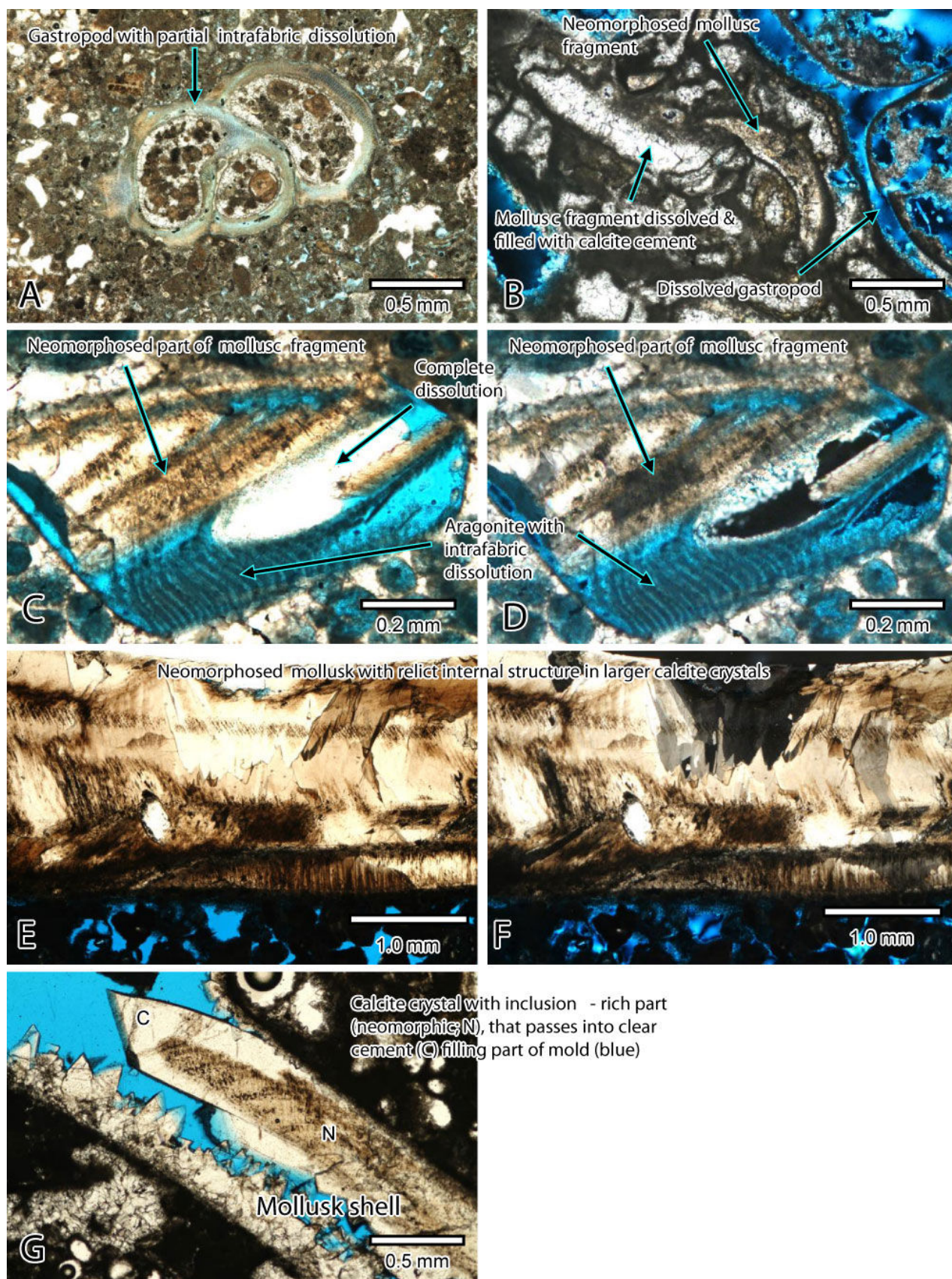


Appendix 4: Mollusc diagenesis. **(A-E)** Partial intrafabric dissolution of mollusc shells. **(A)** Enewetak, XRI-1, 45 m. **(B)** Enewetak Pleistocene, well & depth unknown. **(C-D)** Yucatan K-239, 4.3 m. **(E)** Yucatan K-239, 6.7 m. **(F)** Unaltered shell, Yucatan quarry sample 355, 2.7 m.





Appendix 5: Molluscs, Pleistocene, C-73 well Bahamas, depth in meters. **(A)** 11 m, **(B)** 25 m, **(C-D)** 29 m, **(E-F)** 16 m, **(G)** 30 m. Photos on left are plane polarized light (PPL). Photos on right are crossed polarized light. **(C & D)** are the same view. **(E & F)** are the same view.





Appendix 6: Neomorphosed molluscs, Pleistocene, C-73 well, Bahamas. **(A-B)** 21 m, **(C-F)** 13 m. Photos on left are plane polarized light (PPL). Photos on right are crossed polarized light of image to left (XPL). Crystal size and shape are apparent where crystals are at partial extinction in XPL. **(E-F)** are the enlarged middle of **(C-D)**.

