PSClimate, Duration and Mineralogy Controls on Meteoric Diagenesis*

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Abstract

For subsurface prediction of porosity distribution in carbonates that have undergone subaerial exposure, it is critical to start to quantify the diagenetic effect of the following factors: rainfall/recharge, duration of subaerial exposure and original mineralogy. This project examines the diagenetic alteration associated with seven subaerial exposure surfaces in Miocene La Molata carbonates in SE Spain. For short-lived and/or arid events of subaerial exposure, and subaerial exposure of sediment with calcitic mineralogy, diagenetic alteration occur in the uppermost 0.5 to 2 m but not noticeably below it. Over this thin interval, there was minor dissolution (2-5%) and cementation (typically less than 3%). During the inception of end-Miocene subaerial exposure, mixing of freshwater with evaporated seawater led to dolomitization (greater than 90%) and dissolution (approximately 10-20%) over 83% of the carbonate system. Although short lived, this had the greatest impact on formation of secondary porosity. This surprising result suggests that a climate that allows for significant freshwater recharge and a hydrogeology that promotes mixing can have a profound impact on the creation of porosity, despite only incipient, short-lived, or updip subaerial exposure. During long-lived subaerial exposure after the Miocene, that included times of wet climate, calcite cement (25%) precipitated from fresh water in two different zones. This affected 53% of the overall carbonate system. Later dissolution in the vadose zone enhanced porosity as well. The amount of dissolution during and after calcite cementation is estimated to be 8% throughout the entire carbonate system. Although subaerial exposure has been thought to result in extensive alteration of carbonates, this study shows that some events of exposure have little affect and others have great affect. Short-lived subaerial exposure in an arid climatic setting is not likely to have great impact. Decreasing aridity and increased rainfall correlates to an increase in diagenetic alteration by meteoric waters. Carbonates composed of calcitic mineralogy are more resistant to alteration from meteoric diagenesis. During times of wet climate and high recharge, a hydrogeology promoting mixing between seawater and freshwater can promote great porosity enhancement, despite short duration. Given a long period of subaerial exposure during wet climate, volumetrically major amounts of cementation and dissolution are predicted.

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Zhaoqi Li (University of Kansas, currently ConocoPhillips), Robert H. Goldstein, and Evan K. Franseen (University of Kansas, Department of Geology)

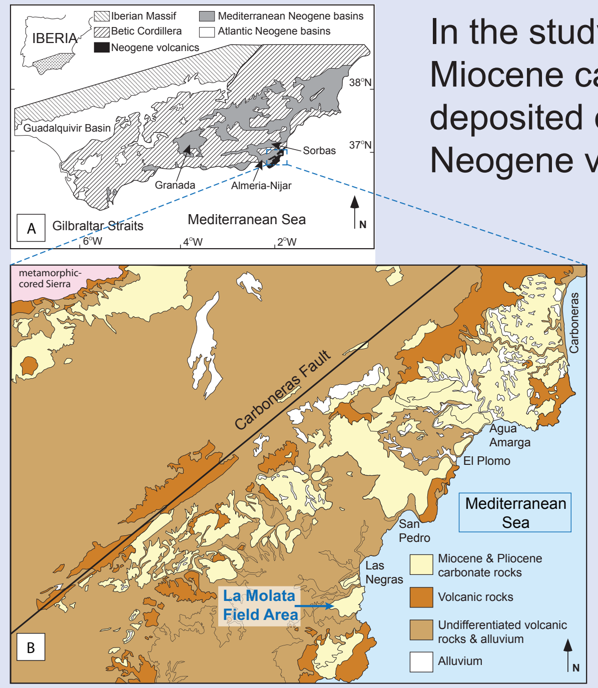
PURPOSE

- Study the record of carbonate diagenesis of Upper Miocene strata in SE Spain to refine understanding of diagenetic process and porosity-permeability response.
- Evaluate the effects of carbonate diagenesis associated with surfaces of subaerial exposure without the ambiguity of burial diagenesis.
- Quantify the diagenetic effect of rainfall/recharge, duration of subaerial exposure and original mineralogy.

IMPLICATIONS

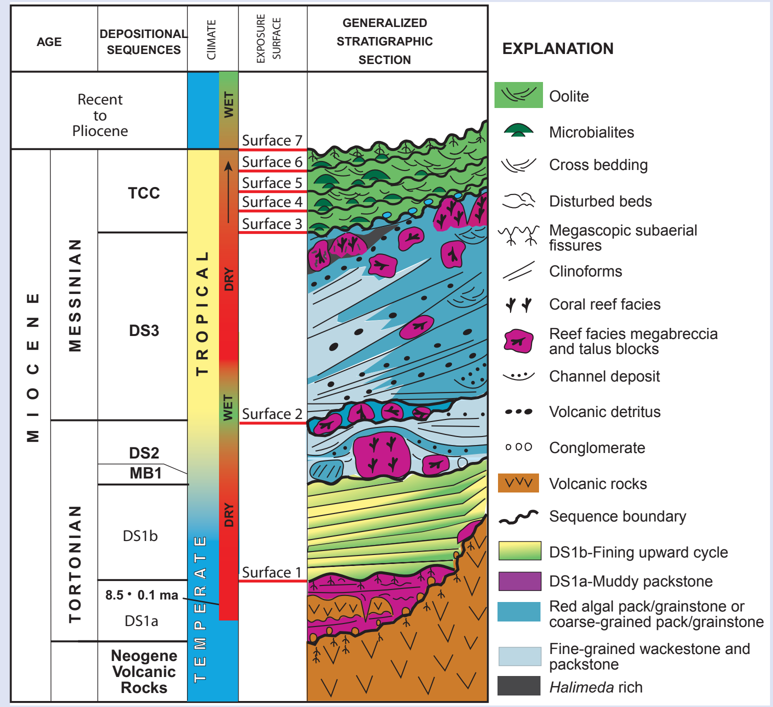
- Although subaerial exposure commonly is thought to result in extensive alteration of porosity in carbonates, this study many events of exposure have little impact and others have great impact.
- Short-lived subaerial exposure in an arid climatic setting is not likely to have great impact. Decreasing aridity and increased rainfall correlates to an increase in some forms of diagenetic alteration by meteoric waters. Carbonates composed of originally calcite mineralogy are more resistant to some forms of alteration from meteoric diagenesis than originally aragonite.
- During times of wet climate and high recharge, a hydrogeology promoting mixing between seawater and freshwater can promote great porosity enhancement, despite short duration. Given a long period of subaerial exposure during wet climate, volumetrically major amounts of cementation and dissolution are predicted.

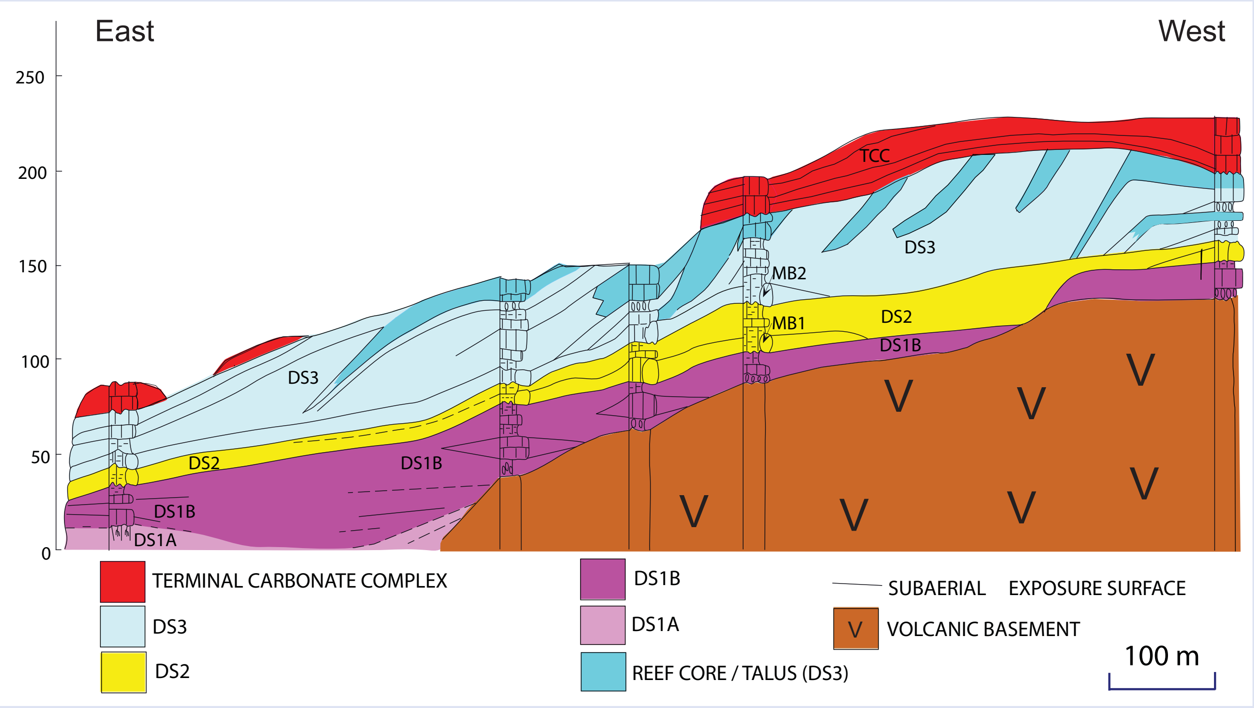
LOCATION



In the study area, Upper Miocene carbonates were deposited on the flanks of Neogene volcanic highs.

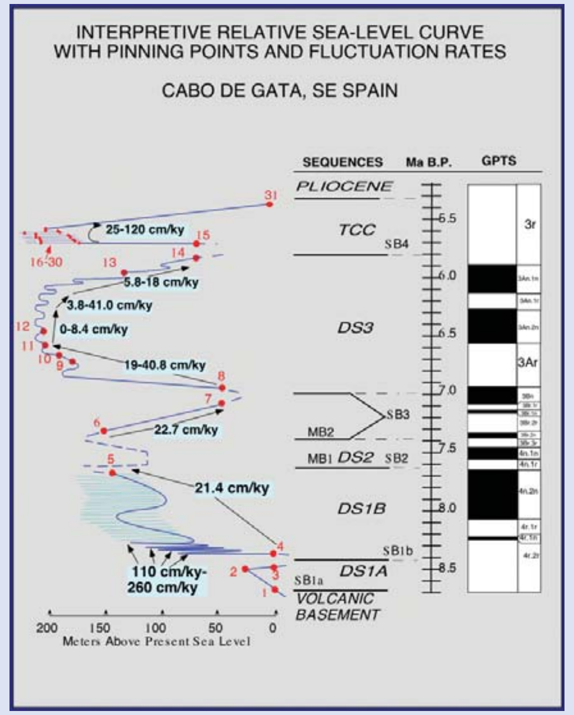
STRATIGRAPHY





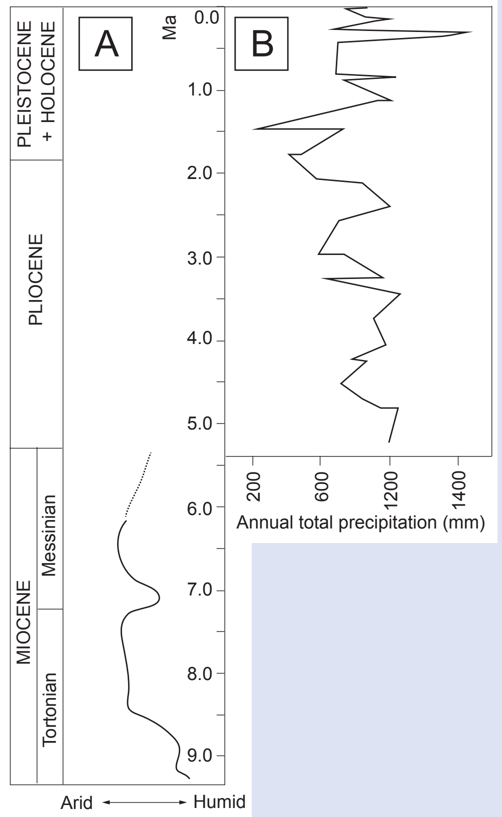
2D cross section of La Molata constructed on the basis of measured outcrop sections. Modified from Franseen et al. (1998)

DURATION AND SUBAERIAL EXPOSURE



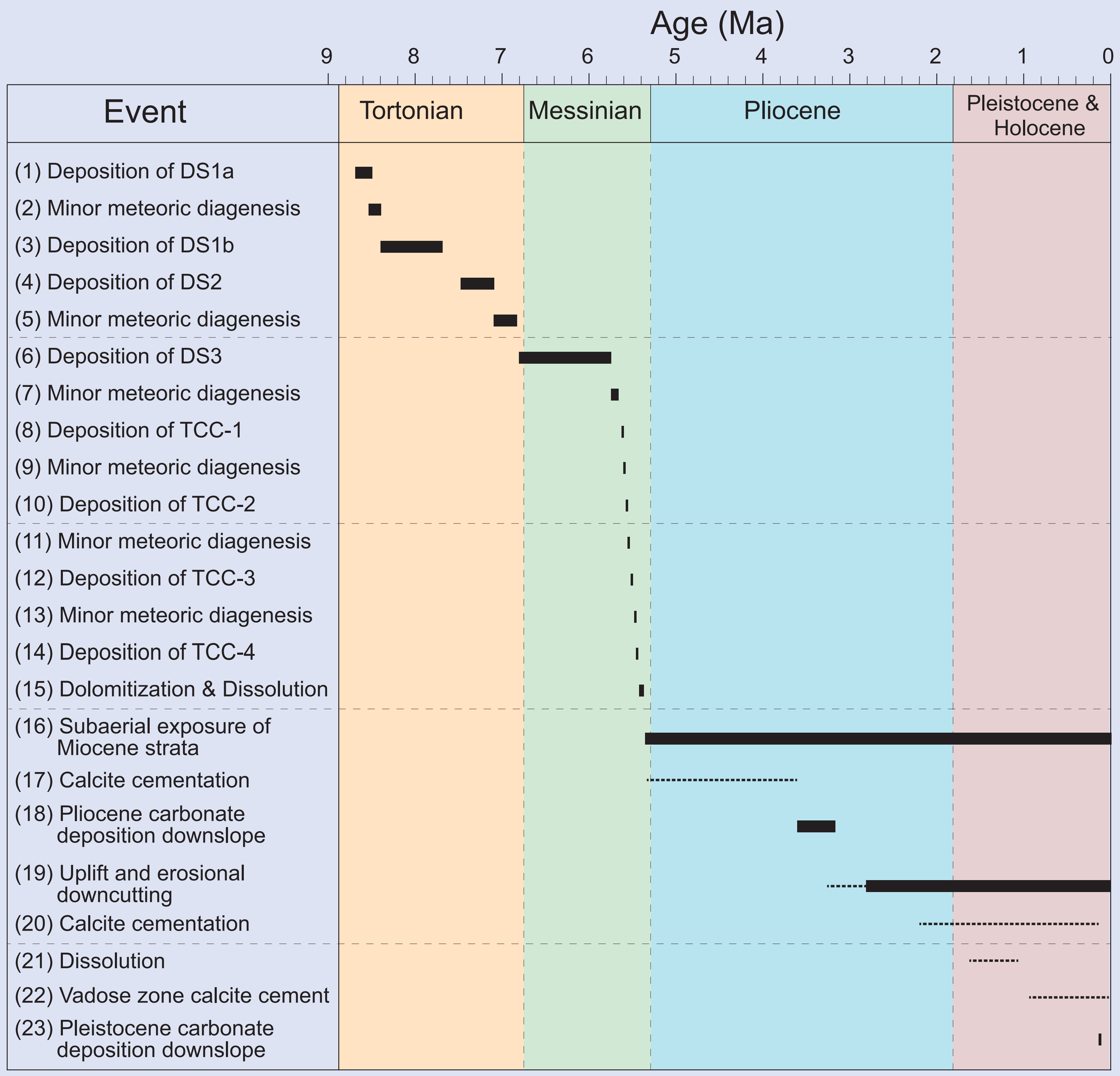
Interpretive relative sea-level curve constructed with pinning points for the Miocene depositional sequences at La Molata, and calibrated to the GPTS of Cande and Kent (1995). Solid dots and numbers on the relative sea-level curve are the pinning points, known positions of relative sea level identified from outcrops. This sea-level curve is used to constrain duration of subaerial exposure on each sequence boundary (after Franseen et al., 1998).

CLIMATE



Plot showing climatic evolution in Spain relative to age. (A) Curves of humidity and aridity (solid line) from rodent data of van Dam and Weltje (1999). Dotted line of increasing rainfall is suggested by transition from evaporites to Lago-Mare freshwater-to-brackish water sediment (Bourillot et al., 2010). (B) Annual total meteoric precipitation curves from rodent data of Hernández Fernádez et al. (2007) implying variations of arid and humid climate in which Pliocene starts off with high rainfall. Rainfall deceases through time and then becomes highly variable during the Pleistocene.

PARAGENESIS

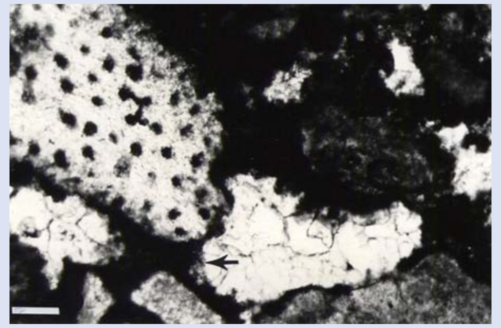


SUMMARY OF DIAGENETIC ALTERATION

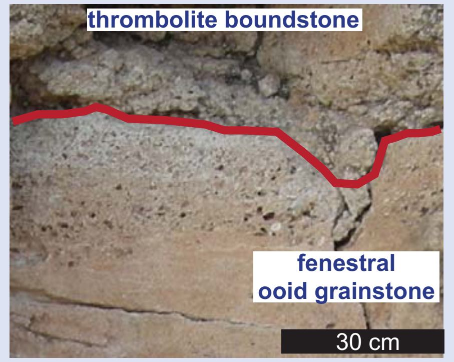
Surfaces	Duration	Climate	Mineralogy	Meteoric dissolution		Meteoric cementation	
				Extent	Amount	Extent	Amount
1	120-130 kyrs	Arid	primarily calcitic	upper 1.5 m	Less than 1%	upper 1 m	1 to 15%, averaging 2%
2	250 kyrs	More humid	calcitic and aragonitic	upper 2 m	up to 20%, averaging 5%	upper 2 m	less than 1%
3	233-533 kyrs	Arid	primarily aragonitic	upper 1.2 m in updip areas	4 to 6%	upper 1.2 m in updip areas	2%
4	Less than 25-100 kyrs	Arid	primarily aragonitic	localized in the upper 1 m	2%	upper 0.5 m	less than 3%
5	Less than 25-100 kyrs	Less arid	primarily aragonitic	upper 1 m	less than 3%	upper 2 m in updip areas	3%
6	Less than 25-100 kyrs	More humid	primarily aragonitic	upper 2 m in updip areas	7%	upper 1 m	2% for downdip areas, 5% for updip areas
7	Greater than 5.3 myrs	Both arid and humid	primarily dolomite	the entire carbonate complex	2 to 27%, averaging 8%	53% of the carbonate system	In the two cemented zones, less than 10% to more than 60%, averaging 25%. Outside the two zones, less than 1%.

•Short-lived exposure in arid climate has little impact (Surfaces 1, 3, 4).
•Decreasing aridity and increased rainfall correlates to an increase in diagenetic alteration by meteoric waters (Surfaces 4-6).
•Long periods of subaerial exposure during wet climate produce volumetrically major amounts of cementation and dissolution (Surface 7).

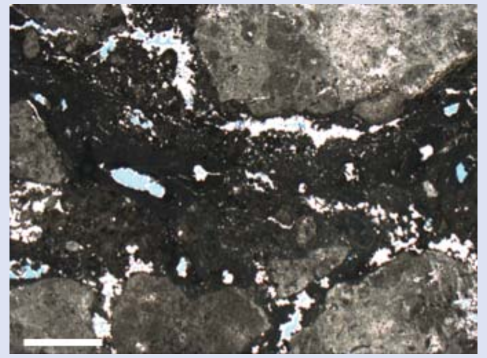
EXPOSURE SURFACES 1 - 3



Photomicrograph showing meniscus cement M-1 (arrow). Scale is 100 µm. Photo by Whitesell (1995).



Facies succession and erosion surfaces indicate multiple events of subaerial exposure



Transmitted light photomicrograph showing autoclastic breccia and rhizoliths. Scale is 1 mm

- Thin (less than 1.5 meter) zones below surfaces 1 - 3 contain caliche laminated crust, rhizoliths, and autoclastic breccia, all indicating periods of paleosol formation.
- Cement stratigraphic analysis shows only minor vadose calcite cementation and minor (less than 1 to 6%) dissolution of aragonite below surfaces 1 and 3.
- Surface 2 shows greater amount of cementation and dissolution, most likely due to longer duration and more humid climate.

EXPOSURE SURFACES 4 - 6

SURFACE 4

- Pendant and meniscus cement is minor, less than 3%, and is restricted to the top 0.5 meter of TCC1 (Whitesell, 1995).
- Localized patches in the upper 1 m of this sequence show minor dissolution of ooids and other aragonitic skeletal fragments, including gastropods and bivalves, creating approximately 2% moldic porosity

SURFACE 5

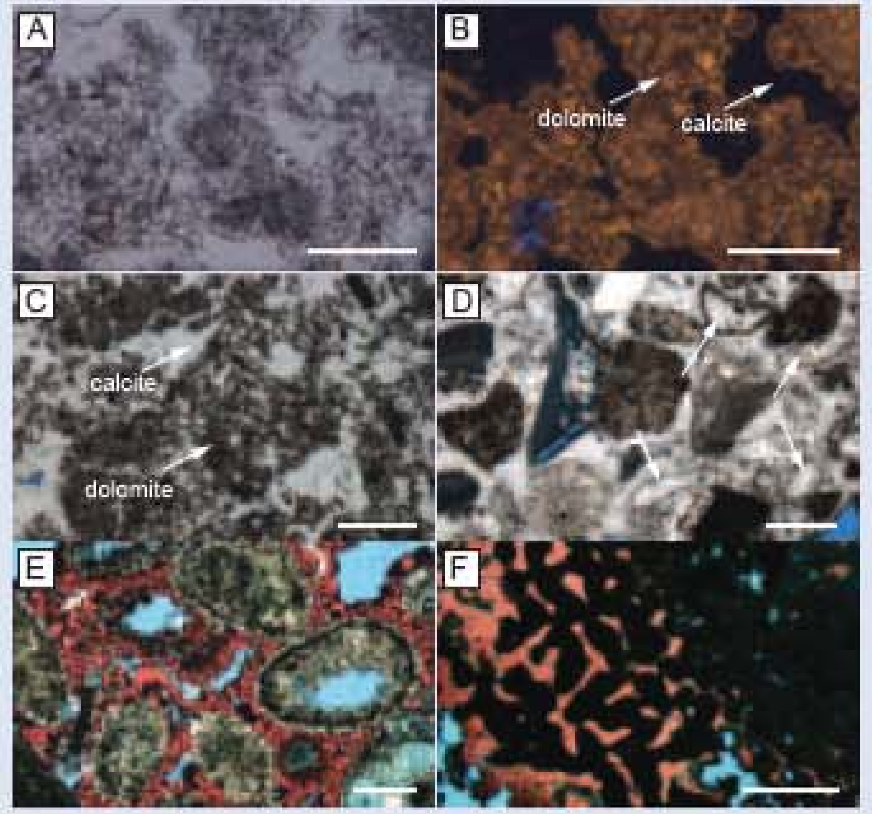
- Meniscus cement, associated with this surface only occurs in the top 2 meters of updip TCC 2, and does not extend into the overlying sequence TCC 3. It is estimated that such meniscus cement averages 3% where it is found.
- Secondary porosity formed before the deposition of TCC 3 includes fractures, molds, and vugs, and is most abundant in the top 1 meter of TCC 2. The amount of secondary porosity appears to be minor, and is less than 3%.

SURFACE 6

- Downdip areas along the paleotopography of TCC 3 have minor amounts of calcite cement that range from 1 to 5% (average of 2%) in the uppermost 1 m. In contrast, updip areas have greater amounts of vadose calcite cement that range from 1 to 15% (average of 5%) in the uppermost 1 m.
- The top 2 meters of TCC3 have secondary porosity (approximately 7%), including vugs, solution-enlarged fractures, and molds of ooids.

Surfaces 4, 5 and 6 have the same duration of exposure, however, show increased diagenetic alteration from 4 to 6. The greater diagenetic alteration is most likely due to the increased humidity/rainfall. In addition, more diagenetic alteration in updip areas as compared to downdip areas is most likely because updip areas have longer duration of subaerial exposure than downdip areas.

SURFACES 7 - cementation

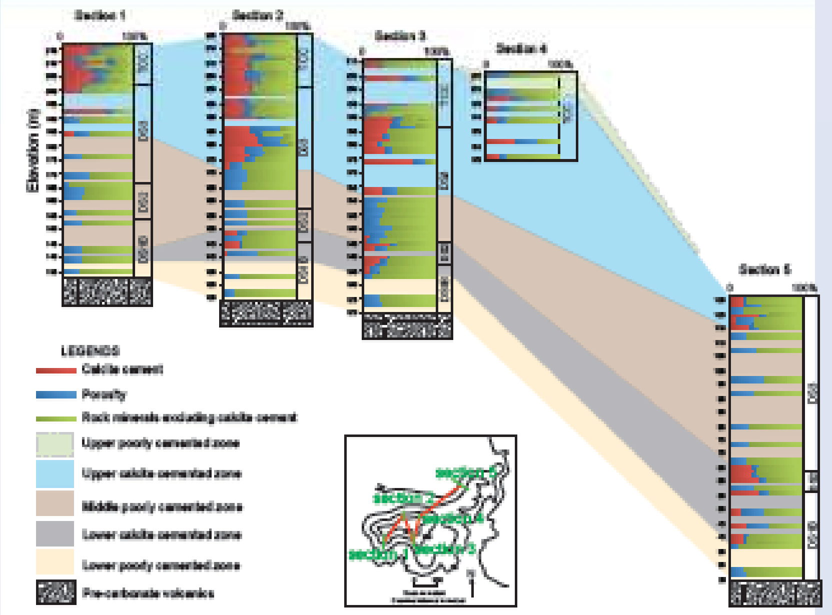


(A & B) Paired transmitted light and CL photomicrographs show poikilotopic non-luminescent calcite cement, scale bars are 100 μm.

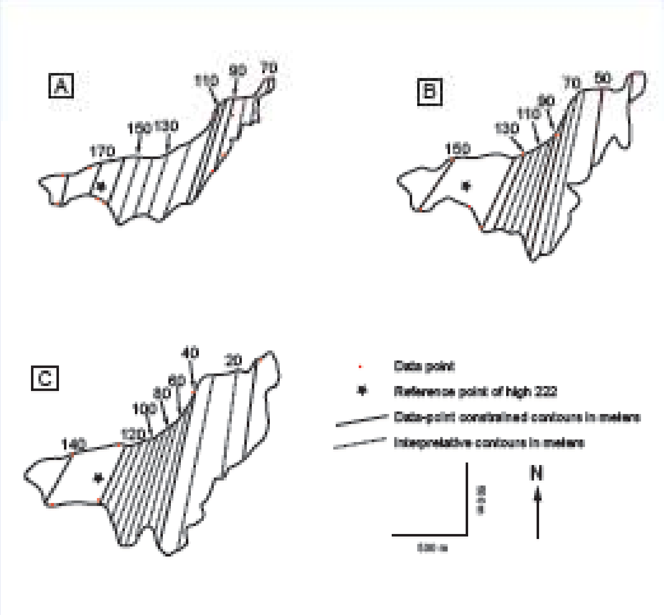
(C) Poikilotopic calcite cements in microbialite, scale is 1 mm. (D) Calcite cements precipitate in both primary intergranular pores and secondary moldic pores (arrows), scale is 1 mm. Scale is 1 mm.

(E) Equant calcite cements grow symmetrically around dolomitized ooids and take alizarin red-S stain. Scale is 0.5 mm. (F) Precipitation of poikilotopic calcite cement in Porities boundstone. Calcite is pink and takes alizarin red-S stain.

TWO CEMENTED ZONES

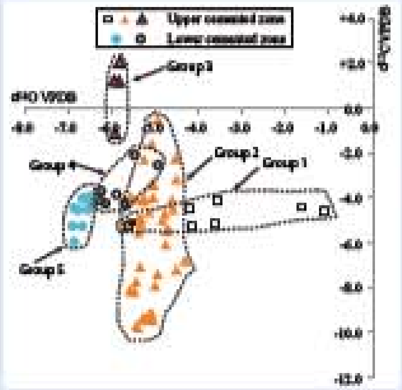


In cross section, there are two laterally continuous calcite-cemented zones. A zone between them mostly lacks calcite cement. Cemented zones cut across stratigraphic surfaces

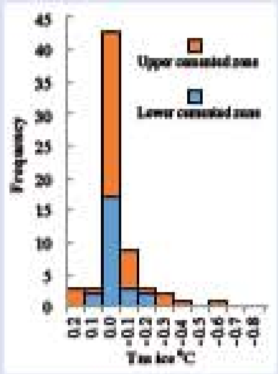


Contour maps represent the basal surface of the upper cemented zone (A), top surface of lower cemented zone (B), and basal surface of the lower cemented zone (C)

GEOCHEMISTRY OF CEMENT



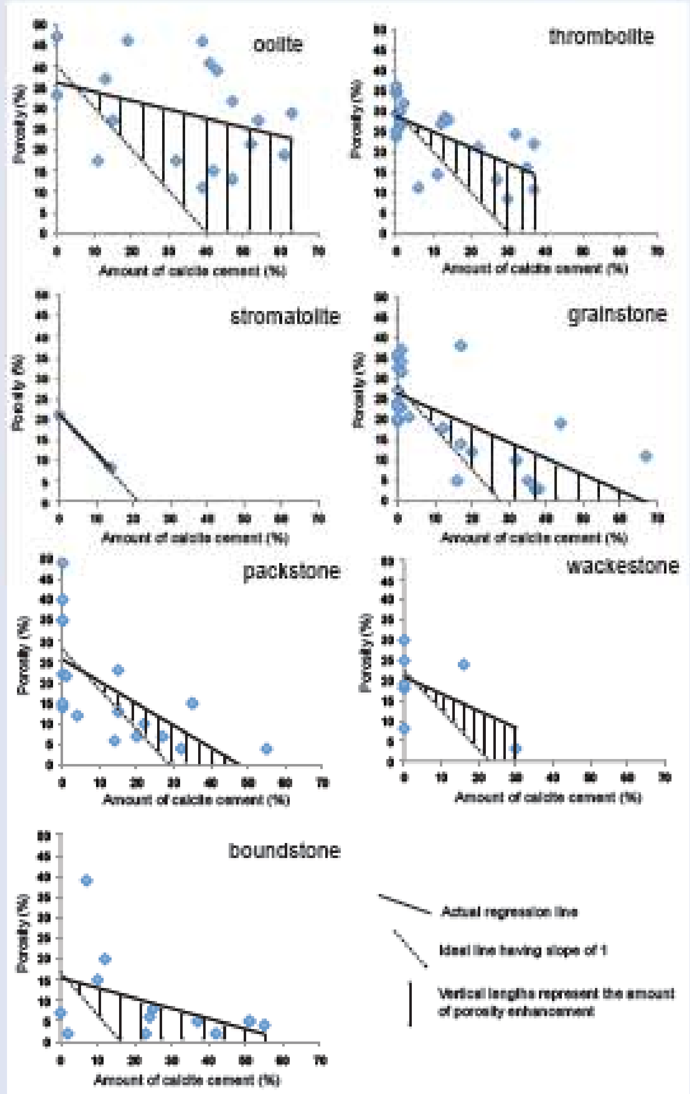
Carbon and oxygen isotopes of calcite powders, microsampled from large pores, range from - 7.0 to - 1.1‰ PDB for $\delta^{18}O$, - 10 to + 2.0‰ PDB for $\delta^{13}C$. Negative oxygen and negative carbon isotope values are consistent with meteoric waters



Measured fluid inclusions within calcite give Tm-ice of 0 °C, indicating fresh water, 0 ppt salinity (seawater salt equivalent).

Fluid inclusion measurements, together with C & O isotope data, shows calcite cement precipitated from meteoric water.

SURFACES 7 - dissolution



Plots showing how to quantify minimum porosity enhancement from dissolution that took place during and after calcite cementation. Black solid lines represent actual regression lines between porosity and the amount of calcite cement for each lithofacies. Dotted lines represent ideal lines with slope of 1 and y intercept at mean value for low or no calcite cement. Ten estimates of the difference are made at even spacing, and the average is used to represent the minimum amount of dissolution during and after cementation. Stromatolite values were undersampled, and thus are likely poor estimates.

Summaries of the minimum amount of dissolution during and after calcite cementation for each lithofacies. Percent values are as porosity of the total rock volume.

Lithofacies	Regression (y-porosity, x-amount of calcite cement)	Ideal porosity without calcite cement	Amount of dissolution
Oolite	y = -0.2127x + 36.064	40%	5 to 27%, averaging 19%
Thrombolite	y = -0.3825x + 28.606	30%	3 to 17%, averaging 10%
Stromatolite	y = -0.9214x + 21.2	21%	less than 1%
Grainstone	y = -0.3942x + 26.245	28%	3 to 14%, averaging 9%
Packstone	y = -0.5331x + 25.586	28%	2 to 10%, averaging 6%
Wackestone	y = -0.4224x + 20.918	22%	2 to 11%, averaging 7%
Boundstone	y = -0.2475x + 15.524	16%	2 to 12%, averaging 6%

Meteoric alteration associated with subaerial exposure surface 7 was extensive. This meteoric diagenesis led to reduction of the porosity in cemented zones by 25%, and these zones covered 53% of the cross sectional area of the stratigraphy. In addtion, later vadose dissolution enhanced porosity during and after cementation by an estimated amount of 8% throughout the entire carbonate system.

CONCLUSIONS

1. For short-lived and/or arid events of subaerial exposure, and subaerial exposure of sediment with calcitic mineralogy (surfaces 1-6), diagenetic alteration took place in the uppermost 0.5 to 2 m but not noticeably below it. Over this thin stratigraphic interval there was minor dissolution (2-5%) and cementation (typically less than 3%).

2. During long-lived subaerial exposure after the Miocene, that included times of wet climate, calcite cement (25%) precipitated from fresh water in two different zones. This affected the 53% of the overall carbonate system . Later dissolution in the vadose zone enhanced porosity as well. The amount of dissolution during and after calcite cementation is estimated to be 8% throughout the entire carbonate system.

3. Although subaerial exposure has been thought to result in extensive alteration of carbonate sediments, this study shows that some events of exposure have little affect and others have great affect. Short-lived subaerial exposure in an arid climatic setting is not likely to have great impact on porosity. Decreasing aridity and increased rainfall correlates to an increase in diagenetic alteration by meteoric waters. Carbonates composed of calcitic mineralogy are more resistant to alteration from meteoric diagenesis.

4. Given a long period of subaerial exposure during wet climate, volumetrically major amounts of cementation and dissolution are predicted.