A Geochemical Model for the Formation of the Pre-Salt Reservoirs, Santos Basin, Brazil: Implications for Understanding Reservoir Distribution*

Paul Wright¹ and Nick Tosca²

Search and Discovery Article #51304 (2016)**
Posted October 10, 2016

Abstract

An evaporitic geochemical model is presented for the Aptian Barra Velha Formation reservoirs, Santos Basin, offshore Brazil. This has to explain the paucity of "normal" carbonate precipitates, the dominance of unusual calcitic morphologies and the presence or former presence of Mg-silicate matrices in the reservoir. The occurrence of metre-scale cyclothems with repetitive mineralogical, textural, micro-textural and early diagenetic changes is explained by invoking the evolution of highly alkaline lake waters with a high dissolved silica, Mg and Ca content. Several modern lakes provide partial indicators of how the evaporation of the Barra Velha lakes would have progressed in stages. Initially Mgsilicate precipitation, as a hydrous poorly crystalline gel, triggered by evaporation, produced a "chemical divide". This resulted in the near complete depletion of Mg, but allowed evaporative concentration of residual SiO₂ (aq), influencing the subsequent stages of brine development and sedimentation. The depletion of Mg limited the production of Mg-silicates but lowered the Mg/Ca favoring LMC precipitation, as is observed in some lakes such as Lake Chad. The nucleation of LMC within the gels led to the growth of spherulites. CO₂ degassing, driven by solubility decreases with evaporation, drove up pH and CO32- but coupled with low Ca2+, still favored CaCO₃ crystal growth, the kinetics of which were inhibited at very high pH. This favored an increase in crystal size over new nuclei, explaining the lack of other precipitates (e.g. micrite). The spherulites grew to large size and extended beyond their gel matrix producing crystal shrub cementstones with dendritic crystals reflecting high SiO2 (aq) in high pH fluids. The shrub units have the best reservoir quality. Continued evaporation led to increased levels of SiO (aq) but pluvial events caused a drop in the pH led to the growth of interstitial silica. This model predicts that even though the more porous shrub facies represents the shallowest facies, it was not restricted to the more proximal settings but to areas where lake waters ponded during evaporation, such as depositional lows as in the higher accommodation zones of half-grabens. Variations in the initial composition of the lake waters over the South Atlantic basins due to differences in catchment geology and hydrology would have resulted in significant differences in the final assemblage of carbonates and silicates.

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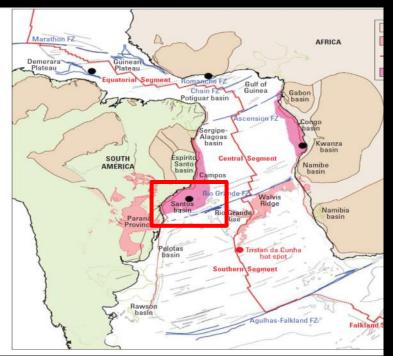


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Take away points -

- The key characteristics seen in the early Cretaceous Barra Velha Fm carbonates of Santos Basin (misnamed the "Microbialite" reservoir) can be reproduced by geochemical modelling
- This lends support for the interpretation that the reservoirs formed in hyper-alkaline shallow lakes, abiotically, and not as large, microbial carbonate platforms in deep lakes
- We emphasize that there are several different reservoir types in the South Atlantic Pre-Salt and that a clearer picture is now emerging of their diversity and of what was controlling their compositions, architectures, porosity types and diagenesis

South Atlantic Basins: Cretaceous lacustrine carbonates: the "Microbialite"

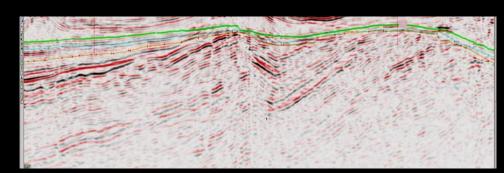


From: Aslanian et al. (2009). Tectonophysics v. 468, 98-112.

Time (Ma)	System	Stage		Unconformities	Formation	Maximum thickness (m)
110 —		Albian (part)		evaporites	Guaruja	3800
1 1	T)			\rightarrow	Ariri	4100
120 —	us (part)	Aptian	Alagoas	Intra-Alagoas	Barra Velha	4200
1 4	lo:		Jiquia Buracica	Pre-Alagoas Top Basalt	Itapema	
130 —	асе	Barremian			Piçarras	
-	Cretaceous	Hauterivian	Aratu		Camboriú	
140 —		Valanginian Berriasian	Rio da Serra			

Main production from this interval is from the Santos Basin, with estimates of recoverable reserves in multi-billion barrels . Some wells produce >25K BLPD.

= Barra Velha Fm. Which is *up to* 550m



Carbonates developed during late rift to sag stage; Coquina reservoirs occur below

And discoveries in the conjugate Kwanza Basin

Facts

There are currently two different models for the depositional settings, seismic geometries, stratal architectures and porosity evolution in the Barra Velha reservoirs (so called "Microbialites") in Santos Basin

One published model invokes shallow evaporitic lakes, with the carbonates of largely abiotic origin produced with Mg-silicate gels, which later formed clay matrices, which later dissolved creating much of the porosity and impacting on later diagenetic events

The other model (unpublished) being used by several companies is of deep lakes, with seismically identified carbonate platforms with distinct margins and relief of up to several hundred metres, built by microbialites

Two end-member models? -

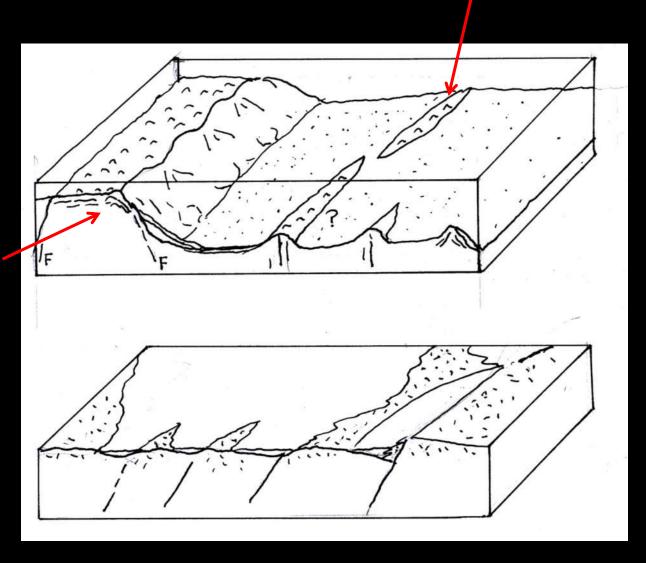
Microbial carbonate platform model

Deep (>300m?) perennial lakes with microbialite platforms on fault blocks and sub-lacustrine isolated buildups possibly along vents or around volcanoes

Carbonate platform margins rims and mounds and slope clinofroms

Abiotic shallow evaporite lake model

Linear buidlups along major faults with vents



Can we independently test the evaporite model?

How?

Isotopes – look for evaporation signals in the C & O isotopes

insufficient data in the public domain

Modelling - can geochemical modelling reproduce the key characteristics seen in the Barra Velha Fm

What are those characteristics?

Main components of the Barra Velha Fm

- Cm-scale "shrubs", in situ and reworked; when in situ form porous shrub framestones,
- Mm-scale spherulites, in situ and reworked; when in situ produce porous floatstone (quasi-boundstones)
- Laminated carbonate muds

These can be found in cyclothems

Various very mature grainstones/rudstones

The carbonates seem to have been originally LMC

See - Wright V P & Barnett 2014 Cyclicity and Carbonate-Silicate Gel Interactions in Cretaceous Alkaline Lakes. AAPG Search and Discovery Article #51011

Shrubs - Campos & Santos Basins



From: Diaz J L B. Geoci. Petrobras, Rio de Janeiro, v. 13, n. 1, p. 7-25, nov. 2004/maio 2005





Shrub-like growths

– Barra Velha Fm,
Cretaceous, Santos
Basin. From Terra et
al 2010, Boll.
Geosci. Petrobras,
18, 1, 9-29



Spherulites

Range up to 16mm in diameter



Source – ANP Pre-Salt Libra Geological Assessment : 17/9/2013

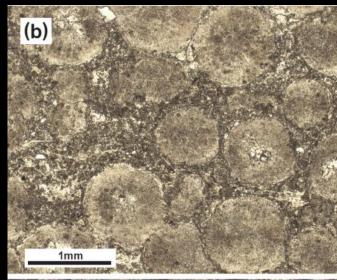


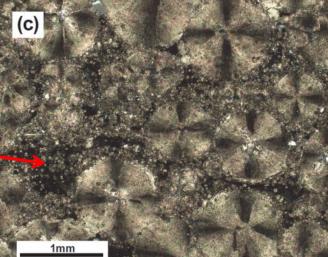
Terra G J S et al. B. Geoci. Petrobras, Rio de Janeiro, v. 18, n. 1, p. 9-29, nov. 2009/maio 2010

Dolomite matrix

Cpl

Ppl





Facies 3



Laminated carbonate muds – Barra Velha Fm, Cretaceous, Santos Basin. From Terra et al 2010, Boll. Geosci. Petrobras, 18, 1, 9-29



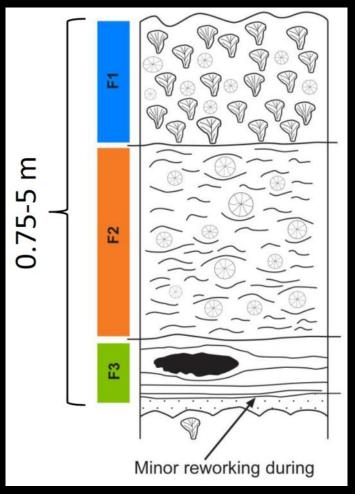
Source – ANP Pre-Salt Libra Geological Assessment : 17/9/2013



Depositional origin of Facies 3:

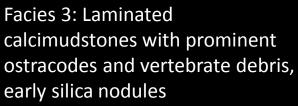
- Detrital, finer grained lower energy, deeper (lakes commonly have shallow wave base cf marine basins) with some desiccation cracks, no paleosols
- Elevated concentrations of ostracodes suggest lowered salinities/alkalinities
- Influx of phosphatic debris vertebrates invade during lowered salinity/alkalinity phases
- Early silica nodule growth suggests lowered pH triggering silica precipitation

The Cyclothems in the Lacustrine Barra Velha Fm

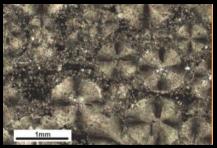


Facies 1: Calcite shrub framestones, with Mgsilicates or patchy traces of former Mg-silicates

Facies 2: Calcite spherulite floatstones, with Mg-silicates or traces of former Mg-silicate matrices







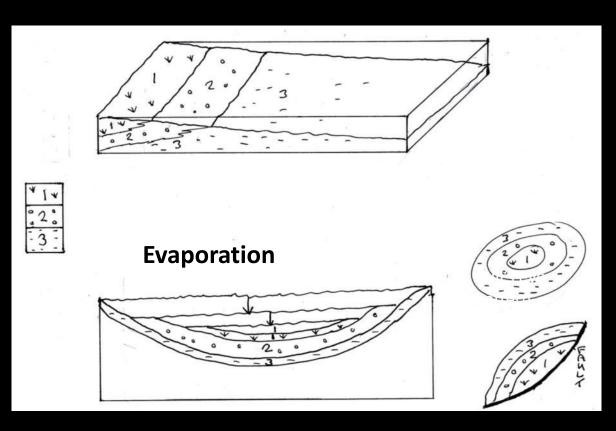


Photos from Terra et al 2010, Boll. Geosci. Petrobras, 18, 1, 9-29

From - Wright, V. P. & Barnett, A. J. 2015 An abiotic model for the development of textures in some South Atlantic early Cretaceous lacustrine carbonates. In Bosence, D. W. J. et al. (eds) Microbial Carbonates in Space and Time: Implications for Global Exploration and Production. Geological Society, London, Special Publications, 418, 209–219.

Two possible explanations for the cyclothems

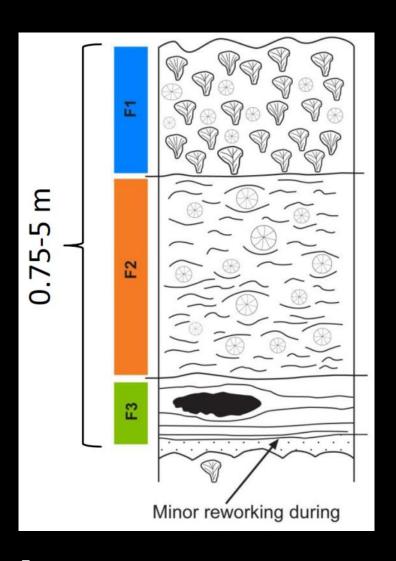
Waltherian



Implies that the facies see in a stratigraphic sequence were time equivalents and the cyclothem represents lake level change

Each facies type represents a different stage of brine evolution caused by evaporation – the facies are not time equivalents and likely occupy different sized areas

Evaporitic interpretation of the lacustrine cyclothems in the Barra Velha Fm



No sulphates and no chlorides!

Facies 1: Reduction of gel precipitation allows rapid growth of calcite crystal shrub framestones by asymmetric growth of spherulites into lake waters

Facies 2: Evaporation triggers Mg-silicate gel precipitation; pH >9.5. Mg rapidly depleted. = low Mg/Ca. Spherulites grew in Mg-silicate gels, in low densities.

Facies 3: flooding phase; reduced alkalinity-salinity allows influx of ostracodes and vertebrates; also triggers silica precipitation as pH drops

From - Wright, V. P. & Barnett, A. J. 2015 An abiotic model for the development of textures in some South Atlantic early Cretaceous lacustrine carbonates. In Bosence, D. W. J. et al. (eds) Microbial Carbonates in Space and Time: Implications for Global Exploration and Production. Geological Society, London, Special Publications, 418, 209–219.

What is missing?

Typical carbonate features are rare or absent –

- Such as ooids, intergranular cements, carbonate muds and microbialites
- Something suppressed these common types of precipitate, and microbes were likely present
- Sulphates and chlorides are absent
- BUT Mg-silicates (now talc-stevensite) are/were widespread

Is there a geochemical explanation to support this model?

Lake water evaporation: Thermodynamic modelling

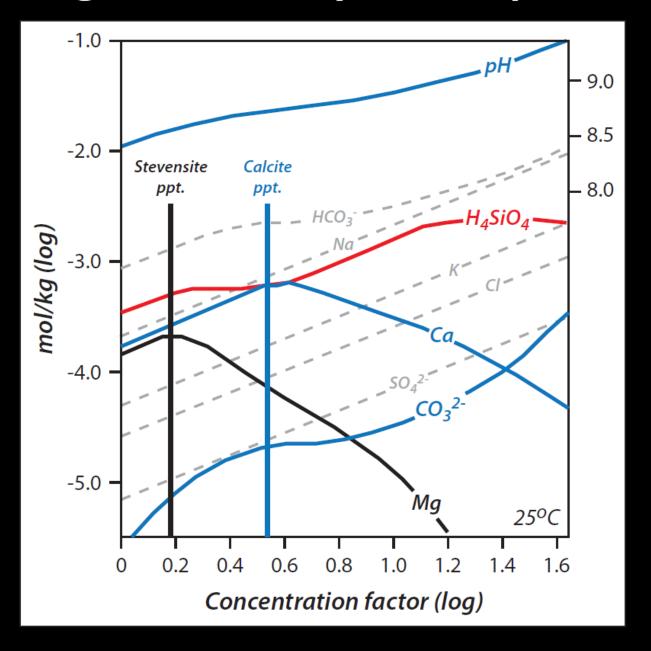
- Begin with dilute water from Lake Chad (Gac et al., 1977)
- Remove H₂O through evaporation at 25°C
- Activities calculated with Pitzer ion interaction model for high ionic strength
 - Mg-silicate solubility estimated from Tosca (2015)
- Assume no "back-reaction" between precipitated minerals & evaporating fluid

Initial fluid composition

рН	8.2	
log P _{CO2}	-3.5	
Ca	0.3 mmolal	
Mg	0.2 mmolal	
SiO2	0.5 mmolal	
SO ₄	0.04 mmolal	
CI	0.08 mmolal	

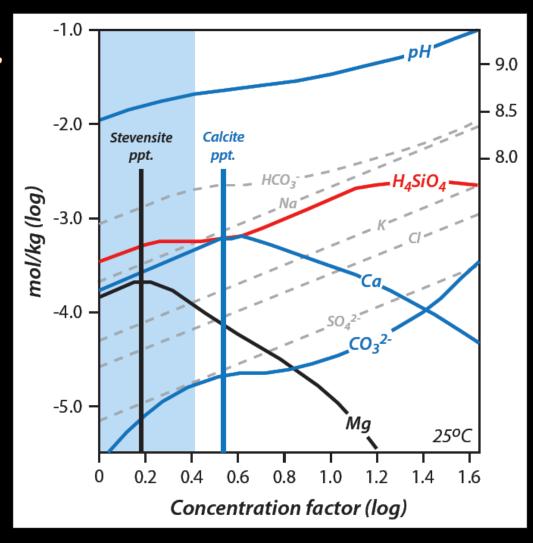
There are 4 key stages of evaporation that <u>sequentially</u> influence Mg-silicate / carbonate sedimentation

Changes in chemistry with evaporation



Stage I: Mg-silicate nucleation & crystal growth

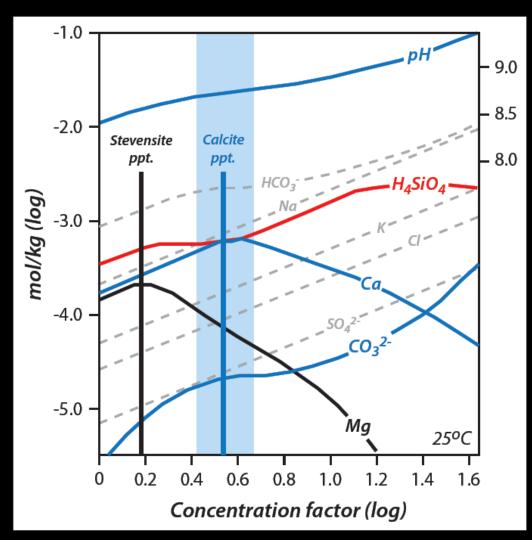
- Al-free Mg-silicates (i.e., stevensite, kerolite, sepiolite) are common in lacustrine carbonates
- Laboratory syntheses constrain solubility / stability
- In modern lakes, evaporation triggers regional-scale precipitation
- Precipitates initially as hydrous, poorly crystalline "gel"



Mg-silicate precipitation acts as a "chemical divide"

Stage 2: Mg-consumption & LMC nucleation

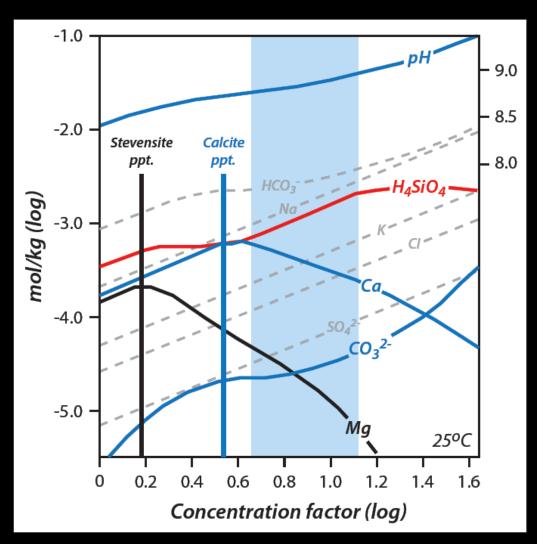
- Mg-silicates remove Mg & lower Mg/Ca ratio (SiO₂(aq) increases)
- Low-Mg calcite nucleates
- Mg-silicate → LMC sequence observed in several modern systems (e.g., Lake Chad)
- Consistent w/ LMC spherulitic growth in Mg-silicate gel (Barra Velha Fm)
 - Rapid nucleation of ACC?



Result is spherulite growth in gels

Stage 3: pH increase & decline in LMC saturation

- CO₂ degassing w/ evaporation drives pH up (Eugster & Jones, 1979)
- High pH & CO₃²⁻ but low Ca²⁺ lowers saturation, still favouring CaCO₃ crystal growth
- CaCO₃ nucleation kinetics inhibited at high pH (Ruiz-Agudo et al., 2011)
- Favours increase in crystal size over new nuclei (consistent w/ lack of micrite in Barra Velha Fm)



In the meantime, SiO₂(aq) is still increasing...

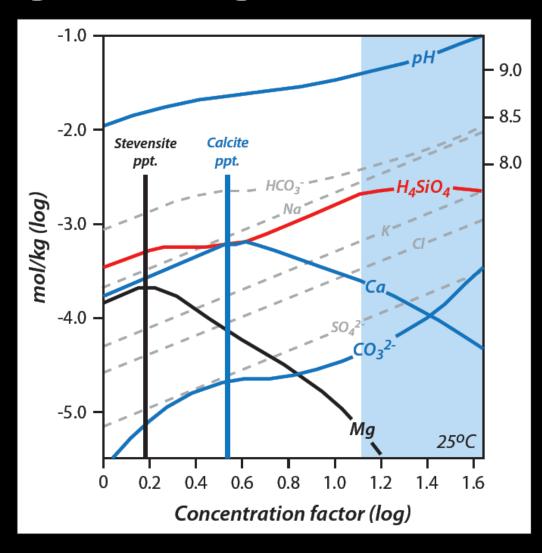
Result is carbonate precipitation limited to earlier sites = shrubs

Stage 4: pH increase & growth in high-SiO₂ solution

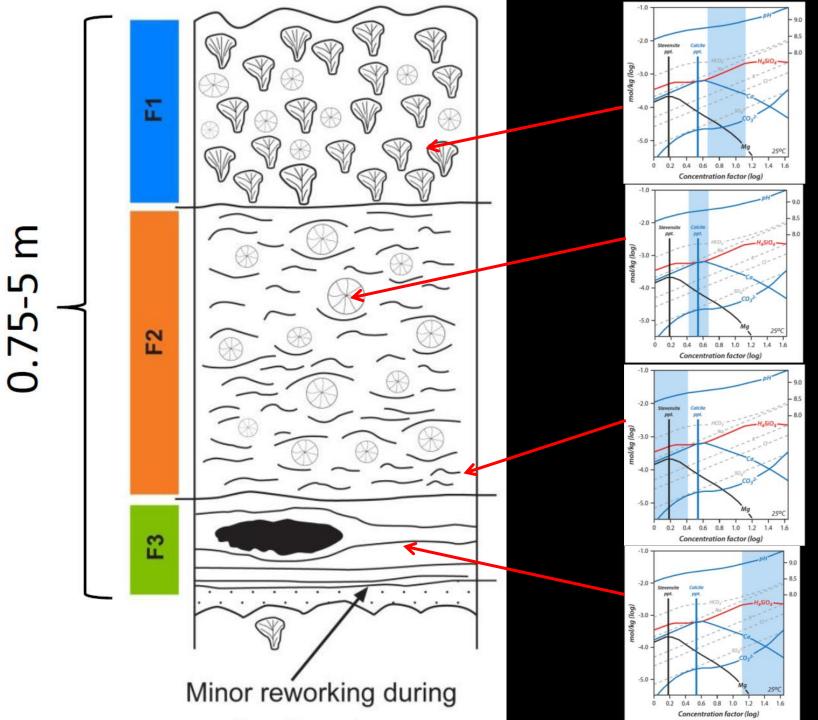
High pH retains SiO₂(aq)

 CaCO₃ growth at high pH & SiO₂(aq) produces multibranched dendritic crystals (Garcia-Ruiz, 2000)

 Consistent with crystal shrub growth morphology in Barra Velha Fm



Freshening will lower pH & trigger silicification



Evaporation

Influx and freshening

Porosity development – dissolution of Mg-clays Si tetrahedra Deprotonation Mg octahedra Octahedral vacancies Interlayer cations (e.g., Mg2+, Li+) **Burial diagenesis** Stevensite (Mg-rich smectite) Overpressure? extensive silica dissolution of cementation calcite & replacement Mg-silicate Minor precursor Mg^{2+} ? Cryolite Cannabilisation of Ca2+ (Al source?) & replacement dolomitization

Tosca N & Wright V P 2014 The formation and diagenesis of Mg-clay minerals in lacustrine carbonate reservoirs. AAPG Search and Discovery Articl #51002

Tosca N & Wright V P, in press 2016 Diagenetic pathways linked to labile Mg-clays in lacustrine carbonate reservoirs: A model for the origin of secondary porosity in the Cretaceous Pre-Salt Barra Velha Formation, offshore Brazil. In Armitage, P et al (eds) Reservoir Quality of Clastic and Carbonate Rocks: Analysis, Modelling and Prediction. Geological Society, London, Special Publication 435, doi.org/10.1144/SP435.1

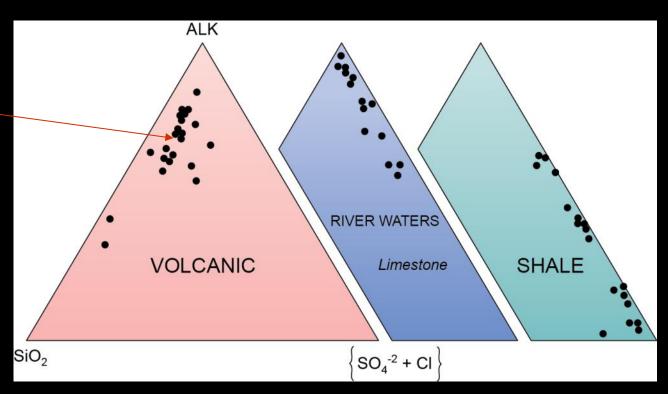
What is special about the Barra Velha Fm?

It required highly alkaline conditions and probably a catchment geology dominated by basic igneous rocks

" calcite, tri-octahedral smectite, analcime (& Na bicarbonates & carbonates) etc...form in lakes where volcanic terrains predominate."

Stevensite -

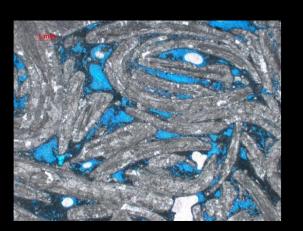
Ca, Mg, Na, K, Fe, & Li silicate...over 30% Mg



Cerling T 1994 Global Geological Record of Lake Basins Vol 1, page 29

Wright. V.P. 2012 Lacustrine carbonates in rift settings: the interaction of volcanic and microbial processes on carbonate deposition. In Garland, J., Neilson, J E, Laubach S E & Whidden K J (eds) Advances in Carbonate Exploration and Reservoir Analysis. Geological Society Special Publicaion 370, 39-47.

We know there are other types of lacustrine reservoirs in the South Atlantic – but why?



Coquina reservoirs of Brazilian Lago Feia & Itanema Formations



Coquinas and microbialites in West African: Toca Fm

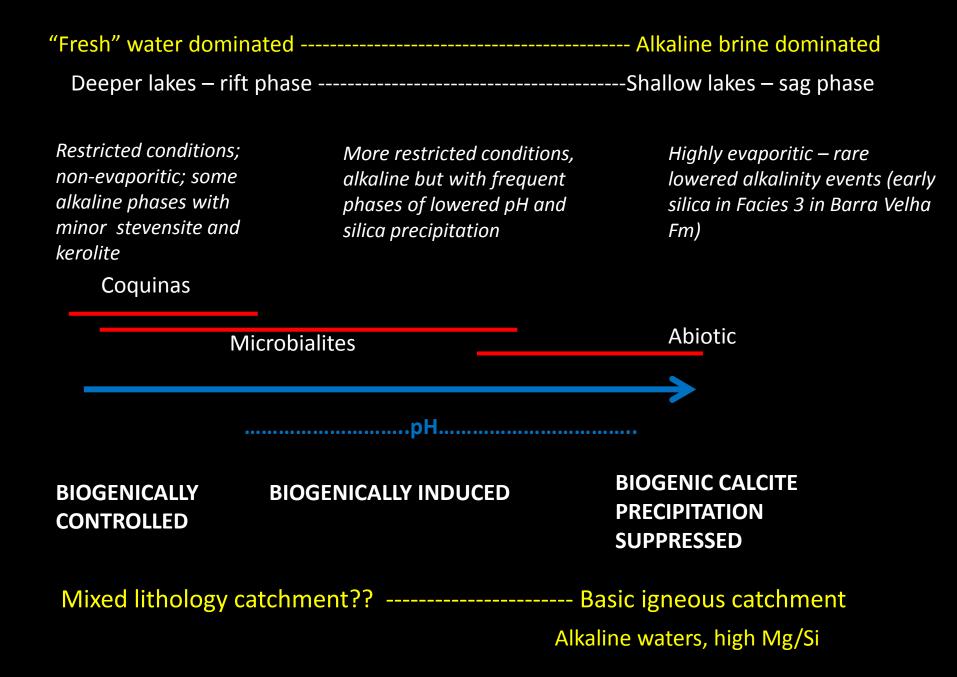


Microbialite cherts, Aptian of Kwanza Basin; Sallet et al. 2016. Bull. AAPG, 100, 1135-1164

Tectonics – rift versus sag (controls water depth, circulation etc)

Climate/Hydrology – fresher (lower pH) versus evaporitic and alkaline (high pH)

Catchment – mixed solutes versus basic igneous source



Lake Turkana waters

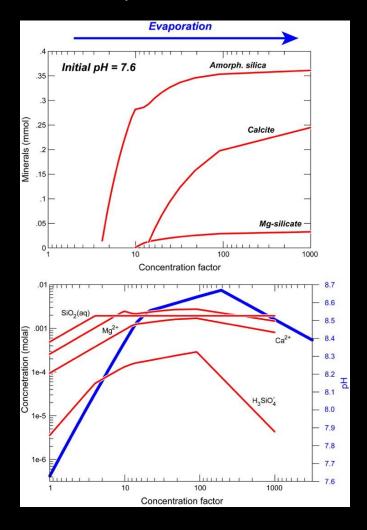
Evaporation Initial pH = 8.8Mg-silicate Calcite Minerals (mmol) 0.4 100 1000 Concentration factor H₃SiO 9.6 9.5 9.4 9.3 T 9.2

100

Concentration factor

10

Lowered pH



In modern rift lakes waters such as Lake Turkana (E Africa) changes in pH can favor Mg-silicate precipitation (as In the Barra Velha of Santos Basin) or silica precipitation (microbialite cherts of Kwanza Basin?).

9.0

8.9

1000

South Atlantic Pre-Salt Factories Coquinas – importance of physical processes (internal waves and **BIOGENICALLY** seiches?) **CONTROLLED** +/moldic and integranular pore systems Meteoric dissolution Lagoa Feia Fm, Campos Basin HTD & corrosion Itanema Fm, Santos Basin Late silica cements Aragonite loss & and calcite cementation Biogenic calcite precipitation Toca Fm, suppressed Congo, Cameia Cabinda Prone to early Field, Mgsilica silicates Kwanza precipitation Barra Velha Fm **Santos Basin** pН **BIOGENICALLY INDUCED ABIOTIC** Microbialites; constructional Evaporitic, partly cyclic, sheet-like. margins, buildups, clinoforms Porosity evolution Calcitic and siliceous Framework porosity *influenced by stevensite* decay

Take away points -

- The key characteristics seen in the early Cretaceous Barra Velha Fm carbonates of Santos Basin (misnamed the "Microbialite" reservoir) can be reproduced by geochemical modelling
- This lends support for the interpretation that the reservoirs formed in hyper-alkaline shallow lakes, abiotically, and not as large, microbial carbonate platforms in deep lakes
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