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1 Facies and diagenesis distribution in an Aptian Pre-Salt carbonate
2 reservoir of the Santos Basin, offshore Brazil: a comprehensive
3 quantitative approach.

4

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16

17 **Abstract**

18 Aptian carbonate rocks of Santos Basin in the Brazilian southeastern continental margin show a highly
19 heterogeneous reservoir quality conditioned by many controlling factors. This study presents a
20 quantitative approach based on an integrated petrographic, mineralogical, and geochemical dataset
21 of the Barra Velha Formation (BVF) to understand the spatial and temporal distribution of depositional
22 and diagenetic aspects and the parameters controlling the nature and distribution of the diagenetic
23 phases in Santos Basin pre-salt carbonate reservoirs. In this formation 3 units can be differentiated.
24 The facies with higher Mg-clay content predominate in lower structural positions and regions with low
25 relative relief. Higher proportions of spherulites occur in the transitional zones, and fascicular calcite
26 occurs preferentially in the transitional and higher structural positions. Grainstones are observed in all
27 depositional environments, but with variations in their composition (intraclasts,
28 siliciclastic/volcanoclastic grain, and clay content). Stratigraphically, facies with higher Mg-clay content
29 predominate in Units 3 (base) and 2 (intermediate), whereas Unit 1 (top) is marked by a greater
30 proportion of grainstones and fascicular calcite. In Unit 1, fascicular calcite crusts tend to expand from
31 the structural high, toward lower areas. The distribution of the main diagenetic products and their
32 association with different facies highlight the role of depositional setting and primary constituents on
33 the diagenetic processes. The tectonic and climatic context of the BVF favored the preferential
34 precipitation and accumulations of Mg-clays in lower structural portions of the basin. The preservation
35 of Mg-clays is also strongly linked to the structural setting, with more intense diagenetic alterations in
36 higher structural areas. Dolomite is a major diagenetic phase in the studied samples, followed by silica.
37 These diagenetic phases are largely associated with Mg-clay alteration and predominate in Unit 1. Mg-
38 clays dissolution, as well as major alteration of carbonate phases, are concentrated in higher structural
39 positions. Given the higher occurrence of faults in these areas and the presence of saddle dolomite,
40 barite, celestine, and fluorite, which are typical products of hydrothermal alteration, part of the
41 dissolution processes may be related to hydrothermal alteration. The depositional and diagenetic

42 aspects indicate a close connection between the hydrochemical evolution of the lake waters with the
43 origin and diagenesis of these deposits.

44

45 **1. Introduction**

46 The Aptian Pre-salt carbonate section in the Brazilian Southeastern continental margin (Carminatti et
47 al., 2009; Carlotto et al., 2017) represents a very unusual sedimentary system in terms of composition
48 and dimension, raising questions about the environmental conditions that drove the sedimentation
49 and early diagenetic evolution of these deposits (Terra et al., 2010; Wright, 2012; Herlinger et al.,
50 2017). Given the occurrence of giant offshore reservoirs, this sedimentary formation has been recently
51 widely studied, producing several conceptual models about its tectonic, stratigraphic, and
52 sedimentological evolution (Karner and Gamboa, 2007; Lentini et al., 2010; Chaboureau et al., 2012;
53 Mercedes-Martín et al., 2019; Minzoni et al., 2020).

54 These deposits were firstly interpreted as formed in a marine setting (Dias, 2005; Moreira et al., 2007;
55 Gomes et al., 2009), then in an alkaline lacustrine environment (Wright, 2012; Muniz and Bosence,
56 2015; Tosca and Wright, 2015; Wright and Barnett, 2015; Herlinger et al., 2017; Tedeschi, 2017;
57 Pietzsch et al., 2018; Tosca and Wright, 2018; Artagão, 2018; Lima and De Ros, 2019; Wright, 2022).
58 Some of the first works analyzing the pre-salt deposits attributed their formation to microbial-
59 influenced processes, referring to them as microbialites and stromatolites (Dias, 2005; Moreira et al.,
60 2007; Terra et al., 2010, Muniz and Bosence, 2015; Mercedes-Martín et al., 2016), while others
61 proposed an abiotic origin (Wright and Barnett, 2015; Tosca and Wright, 2015; Herlinger et al., 2017;
62 Farias et al., 2019; Lima and De Ros, 2019; Gomes et al., 2020; Wright, 2022). These latter works
63 reported the scarcity of macrostructures and microstructures characteristic of microbial carbonates,
64 and the crystalline fabrics and isotopic composition indicative of an abiotic, chemogenic origin of the
65 pre-salt deposits. Herlinger et al. (2017) interpreted these deposits as due to syngenetic precipitation

66 controlled by changes of the lacustrine geochemistry, resulting essentially in encrustation and
67 replacement of stevensite deposits.

68 The existence of peculiar features and mineral phases in these deposits allows the interpretation of
69 different precipitation conditions and makes it difficult to find an ideal analogue (Mercedes-Martín et
70 al., 2017; Deschamps et al., 2020; Magalhães et al., 2020; Wright, 2022). Furthermore, the close
71 connection between the syngenetic and eodiagenetic processes highlights the importance of
72 disentangling the diagenesis suffered by the pre-salt deposits (Herlinger et al, 2017, Lima and De Ros,
73 2019; Sartorato et al., 2020; Wright and Barnett, 2020). Several studies emphasised the role of early
74 diagenesis on the evolution of the deposits, mainly related to the dissolution of Mg-clay substrates and
75 its replacement by calcite spherulites, dolomite and silica (Tosca and Wright, 2015; Wright and Barnett,
76 2015, 2020; Herlinger et al., 2017; Farias et al., 2019; Lima and De Ros, 2019). In fact, the Aptian
77 carbonate rocks of Campos and Santos Basins show that reservoir quality is strongly conditioned by
78 the characteristics of the depositional environment and the associated diagenetic alterations (Rezende
79 and Pope, 2015; Herlinger et al., 2017). The impact of diagenesis on the evolution of porosity and
80 permeability is, according to several authors, not restricted to early alteration processes (clay
81 replacement or dissolution, calcite cementation), but also to the circulation of hydrothermal fluids in
82 some locations of the basin (Vieira de Luca et al., 2017; Lima and De Ros, 2019; Lima et al., 2020,
83 Sartorato et al., 2020).

84 Thus, the combination of these sedimentary and diagenetic processes leads to the formation of
85 complex and heterogeneous reservoirs. Understanding the spatial distribution of the diagenetic
86 products is essential to determine the factors controlling the reservoir properties and to be predictive
87 (Morad et al., 2012; Whitaker and Frazer, 2018). Although previous studies have provided detailed
88 petrographic analyses and paragenetic relationships of the primary and diagenetic constituents of the
89 Barra Velha Formation (BVF) from the Santos Basin (Wright and Barnett, 2015; Farias et al., 2019;
90 Wright and Barnett, 2020; Carramal et al., 2022) and the coeval Macabú Formation from the Campos
91 Basin (Herlinger et al., 2017; Lima and De Ros, 2019), an integrated quantitative view of the spatial and

92 temporal distribution of the syngenetic and diagenetic phases is lacking. The characterization and
93 interpretation of these processes and products are still a matter of debate, and the definition of their
94 quantitative distribution will contribute to the understanding of the paleoenvironmental conditions
95 that drove the formation and modifications of these sediments.

96 Based on a huge database of petrographic descriptions, this study aims to present a comprehensive
97 quantitative characterization of the main depositional and diagenetic features of the lacustrine
98 carbonates of the Barra Velha Formation (BVF) from a key area of the outer high in the Santos Basin.
99 It also seeks to present spatial and temporal distribution patterns of facies and diagenetic products at
100 reservoir scale, based on petrography, mineralogical analyses and carbon and oxygen stable isotope
101 data. Finally, it discusses the different processes (syngenetic, eodiagenetic and late hydrothermal-
102 related) that control the reservoir heterogeneities of the South-Atlantic pre-salt succession. The results
103 will contribute to a better understanding of the origin and evolution of these carbonate rocks and
104 provide valuable constraints to reservoir characterization.

105

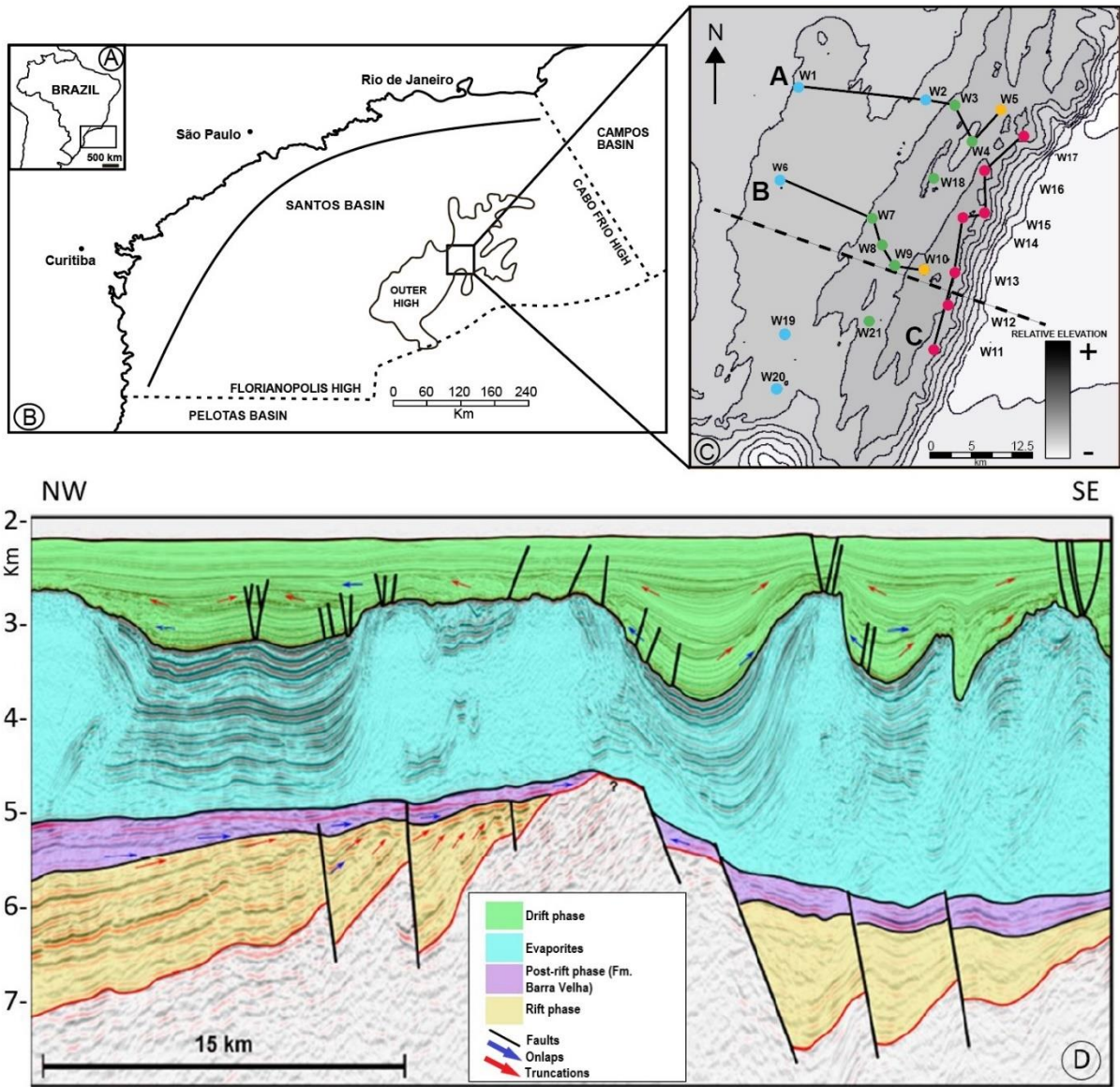
106 **2. Geological Setting**

107 2.1. Geodynamics

108 The Santos Basin, on the southeastern portion of the Brazilian continental margin, extends along the
109 coast of Rio de Janeiro, São Paulo, Paraná e Santa Catarina states, between parallels 23° and 28° South,
110 and covers a total area of approximately 350.000 km² (Figs. 1A and B). The basin is located between
111 the Pelotas Basin to the south, bounded by the Florianopolis high, and Campos Basin to the north,
112 bounded by the Cabo Frio high (Moreira et al., 2007).

113 The Santos Basin was formed during Early Cretaceous by the breakup of the Gondwana Continent. The
114 Mesozoic rifting started in the southern parts of the South American continent in the Late Jurassic,
115 reaching the equatorial margin by Late Aptian/Early Albian, culminating in the separation of South
116 American and African Plates (Rabinowitz and LaBrecque, 1979; Conceição et al., 1988; Chang et al.,
117 1992; Cainelli and Mohriak 1999; Moulin et al., 2010).

118 The South Atlantic Ocean can be divided into four long segments, from North to South: the Equatorial
119 segment, the Central segment, the Austral Segment and the Falkland Segment. The beginning of the
120 rupture, during the Jurassic, occurred in the southern portion of the Austral Segment (Popoff, 1988;
121 Torsvik et al., 2009; Moulin et al., 2010). In the Equatorial segment, the movement of the continent to
122 the north and northwest was impeded by the young oceanic lithosphere of the Central Atlantic Ocean,
123 Gulf of Mexico, and proto-Caribbean (Szatmari and Milani, 2016). As a result, from about 145 to 113
124 Ma, the South Atlantic rift remained closed in the northwest, along the Equatorial margin, but widened
125 wedge-like to the south, along the South America's eastern margin. As the rift widened, the basaltic
126 volcanism along the Ponta Grossa and Namibia dike swarms created the proto-Walvis Ridge, which
127 barred the access of ocean waters to the central South Atlantic rift from the South (Szatmari and
128 Milani, 2016).



129

130 Figure 1 – A) Location of the Santos Basin in the southeast region of the Brazilian continental margin.
 131 B) Location of the study area in the middle of the outer high in the Santos Basin (modified from
 132 Papaterra, 2010 and Ysaccis et al., 2019). C) Structural map of the top of the Barra Velha Formation
 133 (base of the evaporitic section), showing the location of the wells (colored dots) in the study area. The
 134 colors refer to the four paleogeographic sectors distinguished in the study area: blue wells located in
 135 the lower part of the depositional profile, green wells located in the transitional area, orange wells
 136 located in the western part of the structural high, and pink wells located in the southeastern flank of
 137 the high. The dashed line represents the approximate location of the interpreted seismic line (D). D)
 138 Interpreted seismic section of the study area, southward to transect B, oriented perpendicularly to the
 139 topographic high and showing the different tectono-stratigraphic formations of the Santos Basin
 140 (modified from Artagão, 2018).

141

142

143 Moulin et al. (2010), reviewing the kinematics of the opening of the South Atlantic, proposed that from
144 132 to 130 Ma, the opening occurred between the Walvis Ridge and Pelotas Basin. After 130 Ma and
145 until Aptian, the Santos block started to follow the general westward movement of the southern part
146 of South America, playing the role of a kinematic buffer between the movements that created the
147 northern Aptian basins. Since the rift was also barred from the Central Atlantic Ocean in the northwest,
148 where the Equatorial margin had not yet rifted, an endorheic lacustrine basin formed (Szatmari and
149 Milani, 2016).

150 Moreira et al. (2007) divided the tectono-stratigraphic evolution of Santos Basin into rift, post-rift and
151 drift supersequences (Fig. 2). The basement of the Santos Basin is composed of Precambrian
152 metamorphic rocks from the Mantiqueira Province, generated during the Neoproterozoic Brasiliano-
153 Pan African Orogeny (Almeida et al., 1981; Heilbron et al., 2004).

154 The rift phase spans from Hauterivian to Early Aptian time (Pereira and Feijó, 1994), comprising the
155 rocks of the Camboriú, Piçarras and Itapema Formations (Figs. 1D and 2). This phase is characterized
156 by the development of rotated tilted-blocks and half-graben basins filled with thick sedimentary
157 successions (Milani et al., 2007; Alves et al., 2017). The Piçarras Formation, deposited above the
158 basaltic rocks of the Camboriú Formation, comprises alluvial sediments in proximal areas and shales
159 of talc-stevensitic composition in lacustrine distal areas. In contrast, the Itapema Formation is
160 composed of bivalve bioclastic rudstones concentrated on structural high domains, and of lime
161 mudstones and organic-matter rich shales in the distal parts of the basin (Moreira et al., 2007).

My	GEOCHRONOLOGY			STRATIGRAPHY			TECTONIC
	EPOCH	STAGE	LOCAL STAGE	GROUP	FORMATION	UNCONFORMITIES	
110	EARLY CRETACEOUS	ALBIAN		CAMBURI	Guaruja		DRIFT
					Ariri	Salt base	
115		APTIAN	Alagoas	GUARATIBA	Barra Velha	Intra Alagoas	POST-RIFT
120						Pré-Alagoas	
125							
		BARREMIAN	Jiquia		Itapema		RIFT
			Buracica		Piçarras		
130	HAUTERIVIAN	Aratu		Camboriu	Top Basalt		
135							

162

163 Figure 2 – Lower Cretaceous stratigraphic chart of the Santos Basin, Brazil (modified from Moreira et
 164 al., 2007).

165

166 From Barremian to Aptian, in the Central segment, the rift development is characterized by
 167 lithospheric extension, with block tilting in the inner upper continental crust and formation of small
 168 grabens occupied by lakes (Dias et al., 1988; Karner et al., 2003; Carminatti et al., 2008). A regional
 169 unconformity, related to uplift and erosion of the rift section (Winter et al., 2007; Moreira et al., 2007),
 170 the so-called Pre-Alagoas Unconformity, marks the transition to the Aptian post-rift phase (Fig. 2). The
 171 latest phase is characterized in the Santos Basin by the sediments of Barra Velha Formation (BVF), main
 172 topic of this article.

173 A phase of thermal subsidence followed, marked by an extensive deposition of evaporites during the
 174 uppermost Aptian and lowermost Albian (Muniz and Bosence, 2015; Gomes et al. 2020). The first
 175 marine ingressions promoted the deposition of halite and anhydrite in both South America and West
 176 Africa margins (Asmus and Ponte, 1973; Cainelli and Mohriak, 1999; Mio, 2005). With the progression

177 of the South Atlantic opening, the evaporites were overlain by an Albian marine carbonate platform,
178 corresponding with the passive margin phase of the basin (Chang et al., 1992, Mio, 2005).

179

180 2.2. Case study

181 The study area is situated in the central portion of the Santos Basin, on the outer high, with the wells
182 studied distributed over a 45 km x 56 km rectangular area (Fig. 1C). The base of the evaporitic section
183 (that overlies the BVF) is marked by structural lows and highs with NE-SW direction, reflecting the
184 paleotopography at the end of the BVF succession (Fig. 1C). The study region is characterized by a tilted
185 fault block delimited by normal faults with SE dip; while the northwestern flank presents a ramp
186 morphology, with a low-angle slope, the SE region displays a steep faulted-flank (Fig. 1D). The sediment
187 thickness varies greatly towards the structural highs, where the basal part of the BVF can be absent
188 (Fig. 1D).

189 The BVF is bounded at the top by the evaporites of the Ariri Formation and at its base by the Pre-
190 Alagoas Unconformity. An internal unconformity called the Intra-Alagoas Unconformity separates the
191 post-rift phase into two stratigraphic units (Fig. 2). Previous stratigraphic and sedimentological studies
192 (Liechoscki de Paula Faria et al., 2017; Artagão, 2018; Gomes et al., 2020) allow the division of the BVF
193 into three stratigraphic units, informally named Unit 3 (base) to Unit 1 (top). The Intra-Alagoas
194 unconformity marks the top of Unit 3 (Fig. 2), whereas the stratigraphic surface that separates Units 2
195 and 1 is a major sequence boundary (Liechoscki de Paula Faria et al., 2017).

196 The BVF was initially interpreted as deposited in a transitional environment, from continental to
197 shallow marine settings (Moreira et al., 2007; Gomes et al., 2009). Later, several authors dismissed the
198 marine origin favoring the deposition of the BVF in an alkaline lacustrine environment (Wright, 2012;
199 Tosca and Wright, 2015; Wright and Barnett, 2015; Szatmari and Milani, 2016; Tedeschi, 2017; Pietzsch
200 et al., 2018). Based on petrographic descriptions from several wells of Santos Basin, Wright and Barnett
201 (2020) described the BVF as a highly heterogeneous combination of in-situ and re-worked grains, with
202 mineralogies comprising calcite, dolomite, magnesian silicates (stevensite and talc), and silica.

203 According to these authors, the dominant primary calcite components are fascicular crusts and
204 spherulites, with some rare microbialites in the formation's uppermost 20–30 m. The carbonate
205 components associated with Mg-silicate phases and the paucity of fish remains suggest highly
206 restricted environments where mineral precipitation was dominantly controlled by the lacustrine
207 water geochemistry (Herlinger et al., 2017; Mercedes-Martín et al., 2019; Wright and Barnett, 2020).

208

209 **3. Material and methods**

210 This work is based on data from 21 wells located at different positions within the study area and
211 distributed on and from either side of a topographic, structural high (Fig. 1C). The use of “proximal”
212 and “distal” terminology, to refer to positions relatively closer and away from the structural high seems
213 inadequate as this terminology has a depositional significance, and criteria to confidently discriminate
214 between both environments are unclear. The study area was thus divided into four sectors, allowing
215 to delineate the distribution of sediments and diagenetic phases. The so-called higher area is
216 represented by two wells, northwest of the structural high (W5 and W10). Seven wells are located on
217 the southeastern steep flank (W11-W17). Six wells (W3, W4, W7, W8, W9, W18, and W21) are situated
218 in the transitional area of the northwestern low-angle slope, whereas six other wells (W1, W2, W6,,
219 W19, and W20) are located in the so-called lower area. The well data were also arranged in three
220 transects (named Transects A, B, and C), either along or perpendicular to the structural high (Fig. 1C).

221 The database consists of core and petrographic descriptions (1483 thin sections), bulk-sample C and O
222 isotopic analyses, quantitative evaluation of minerals by scanning electron microscopy and energy-
223 dispersive X-ray spectroscopy (QEMSCAN) and X-ray diffraction (XRD) analyses, performed at
224 Petrobras Research Center (CENPES) in Rio de Janeiro, Brazil.

225 The thin sections were prepared with blue epoxy resin impregnation and stained with alizarin red-S
226 and potassium ferricyanide solution, to differentiate carbonate minerals (Dickson, 1965). Petrographic
227 analyses were carried out with a Zeiss Imager A2 microscope, using both plane-polarized light (PPL)

228 and crossed-polarized light (XPL). A semi-quantitative visual estimation of primary and diagenetic
229 constituents, and pore types, has been done using the comparison chart of Terry and Chilingar (1955).
230 The petrographic analysis also focused on the description of texture, fabric and paragenetic
231 relationships. The results were documented using the Petroledge© knowledge-based system. A
232 statistical analysis was performed to evaluate the distribution and relationship between depositional
233 and diagenetic phases.

234 Stable C- and O- isotope analyses of bulk rocks were performed on 503 samples, derived from core
235 plugs and sidewall cores from 6 wells. For the analysis, a mass spectrometer Delta V Plus Advantage,
236 coupled to a device for extraction of CO₂ Kiel IV. 1 was used. The ¹⁸O/¹⁶O and ¹³C/¹²C ratios are
237 expressed in the conventional 'δ' notation, in parts per thousand (‰), relative to Vienna Pee Dee
238 Belemnite (VPDB).

239 Bulk-rock X-Ray Diffraction (XRD) analyses were obtained from 811 samples and clay fraction mineral
240 composition analyses were performed for 503 samples. For the clay fraction analyses, the samples
241 were fragmented using a Branson Cell Disruptor (Mod 350) and separated by several centrifuge steps.
242 The identification of the clay minerals was performed on the air-dried samples, solvated with ethylene
243 glycol, and subsequently heated at 490°C. The XRD analyses were performed in a RIGAKU D/MAX-
244 2200/PC diffractometer. The identification of bulk mineralogy was determined using the Jade software
245 (MDI) and the PDF-2 mineral database (ICDD). The quantitative analyses were performed using the
246 Rietveld method (Young, 1993) with FullProf software (Rodriguez-Carvajal and Roisnel, 1998).
247 Mineralogical maps of 92 samples from 5 wells were produced using the equipment QEMSCAN 650/FEI
248 with two EDS/Bruker coupled detectors.

249

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251

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253

254 **4. Results**

255 **4.1 Facies of the BVF**

256 A vast body of literature dealing with the BVF in the Santos Basin exists today, with a relative consensus
257 on its main components and textures, considered as a heterogeneous association of in-situ and re-
258 worked constituents (Wright and Barnett, 2015; Herlinger et al., 2017; Tanaka et al., 2018; Farias et
259 al., 2019; Basso et al., 2020; Gomes et al., 2020; Wright and Barnett, 2020). The in-situ facies
260 components are fascicular calcite (shrubs), spherulites, microcrystalline calcite, and clay minerals,
261 whereas the re-worked facies present different proportions of shrubs and spherulites intraclasts,
262 siliciclastic/volcanoclastic grains, with variable clay content. Based on the relative contributions of each
263 constituent, Gomes et al. (2020) proposed a consistent and rather exhaustive facies classification.
264 However, to understand the large-scale sedimentary and diagenetic characteristics of the study area
265 and simplify our data analysis, we have adopted the broader terminology of Lima and De Ros (2019).
266 Thus, the major facies recognized in the BVF are fascicular calcite crusts (shrubs), Mg-claystones with
267 spherulites, laminites, and intraclastic grainstones.

268

269 **4.1.1 Fascicular calcite crusts (shrubs)**

270 This facies consists of calcite crystals presenting fascicular-optical texture. These crystals grew
271 predominantly in a vertical to sub-vertical orientation, with an average height of 2 mm (Fig. 3A). The
272 crystal shrubs have a conical form in the longitudinal section that shows height greater than length
273 (Farias et al., 2019), or in certain layers, incipient forms with a height/width ratio of about 1:1. The
274 latter can be seen as morphologically intermediate forms between spherulites and crusts. The
275 fascicular calcite crusts show intercalations with millimetric to centimetric layers of spherulites, re-
276 worked particles (indistinct fragments of spherulites and shrubs), microcrystalline calcite, and
277 dolomite, creating a laminated macroscopic aspect, with locally low relief domical forms. Each layered
278 unit can reach 2 m in thickness.

279 The association with spherulites is frequent and can make up 30% of the samples. Minor constituents
280 comprise argillaceous peloids, ostracods bioclasts and Mg-clay laminations, which can be locally
281 incorporated into calcite aggregates (Fig. 3B). In 30 % of the samples, the Mg-clays appear as interstitial
282 sediment between the carbonate aggregates. The pore system is characterized by growth-framework
283 and inter-crystalline porosity types. The fascicular calcite crusts are not microporous.

284

285 **4.1.2 Mg-claystones with spherulites**

286 Mg-claystones are characterized by Mg-clays in association with different proportions of calcite
287 spherulites and dolomite (Figs. 3C-3E). For sake of clarity, the different clay minerals that constitute
288 these Mg-clays are characterized in part 4.3.2. The spherulites are spherical to sub-spherical calcite
289 crystal aggregates with a sweeping extinction and size generally less than 2 mm. It is possible to
290 categorize this facies into two distinct sub-facies, depending on the relative proportion of spherulites:
291 Mg-claystones with higher proportions of spherulites and Mg-claystones with minor proportions of
292 spherulites.

293 The Mg-claystones with higher proportions of spherulites (34% on average, 83% maximum) present
294 variable thickness, between 5 cm and 100 cm and display an irregular planar laminated structure,
295 marked by spherulites and clay laminae, showing a brownish color. The spherulites may occur
296 coalesced and recrystallized (Fig. 3C). The Mg-clays are present in 56 % of the samples and locally
297 represent 50 % of the sample constituents (Table 1). Silt- to sand-size siliciclastic grains of quartz and
298 muscovite are frequent and can occur as nuclei of the spherulites. Minor occurrences of ostracods are
299 also observed. The Mg-clays are commonly displaced by calcite spherulites (Fig. 3D) and frequently
300 show partial to total dissolution. The dissolution of the clay matrix and spherulites is the primary
301 process generating porosity in this facies, that initially possesses a low reservoir quality.

302 The Mg-claystones with minor proportions of spherulites exhibit a massive to layered structure (Fig.
303 3E), generally with centimetric bed thickness. Macroscopically it is characterized by centimetric
304 claystone layers and alternations of laminae with the sparse occurrence of spherulites. The spherulites

305 are observed in 30 % of the samples from this sub-facies, occurring as rare, isolated floating grains
306 representing around 3% on average (10 % maximum) of the constituents. Samples without spherulites
307 usually show intense dolomitization and replacement by microcrystalline calcite, resulting in the loss
308 of the original fabric.
309

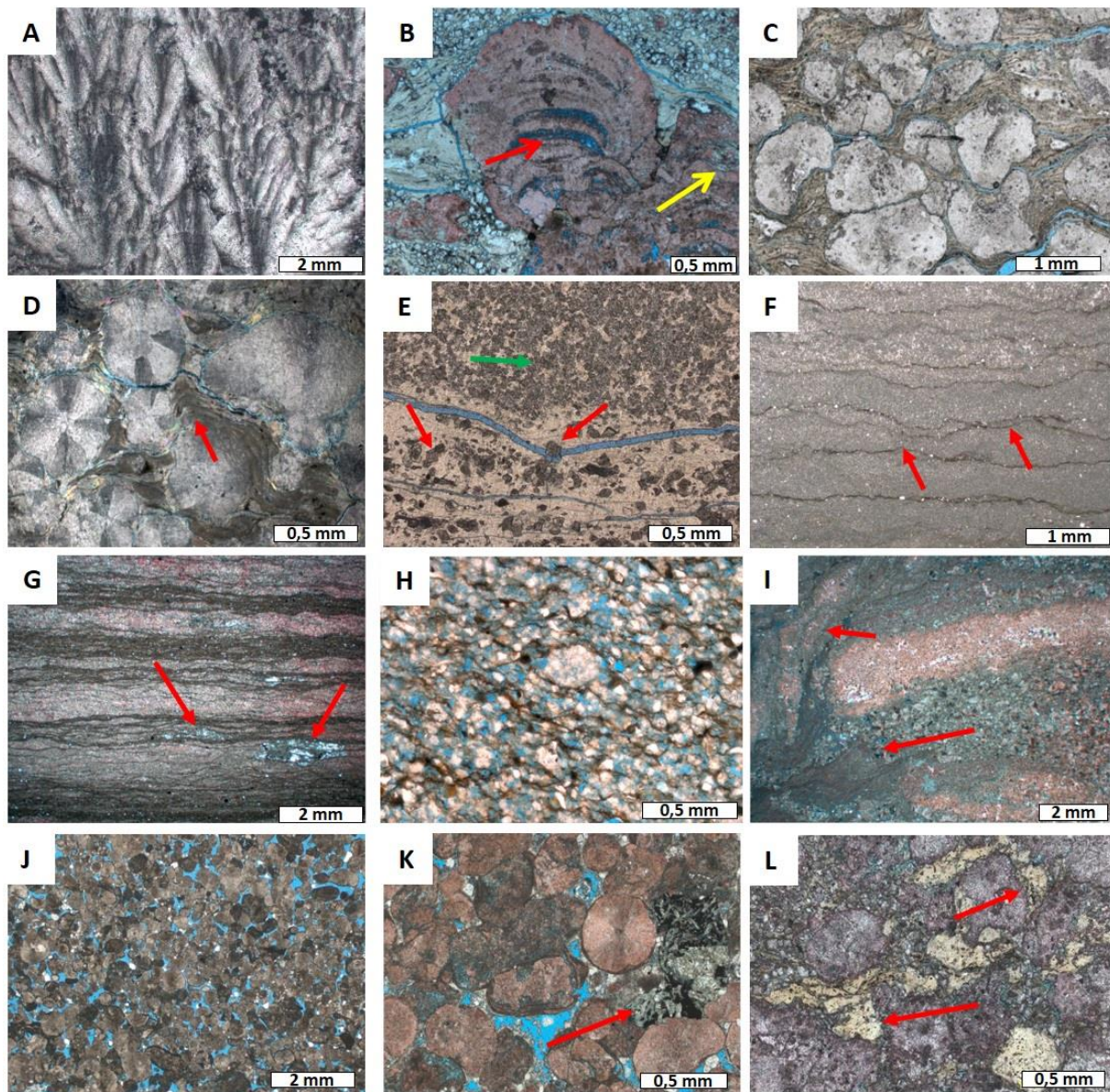
310

311 **4.1.4 Laminites**

312 This facies is composed of alternating laminae of microcrystalline calcite, microcrystalline dolomite,
313 Mg-clay, organic matter, and detrital components (quartz, feldspar, and micas). Macroscopically it is
314 characterized by plane-parallel flat or crenulated laminations (Figs. 3F and 3G) and frequent organic-
315 matter rich laminae. The colors vary between greenish and brownish, depending on the proportion of
316 siliciclastic mud, carbonate, and Mg-clay content. Ostracods, phosphatic fragments and micro-
317 spherulitic calcite are present in small quantities.

318 Fenestral and intercrystalline porosity are common across lamination. Microporosity is also frequent
319 and given the remains of organic-matter rich laminae in some samples (Fig. 3H), the porosity
320 generation could be related to organic matter degradation (Farias et al., 2019). The recrystallization of
321 calcite crystals is frequently observed, and occasional breccia and teepee structures occur, associated
322 with the crenulated laminites (Fig. 3I). The breccia is poorly sorted, made up of millimetric to
323 centimetric, subangular intraclasts of laminites, in a matrix of microcrystalline dolomite. Some of the
324 intraclasts are dolomitized and silicified.

325



326

327 Figure 3 – Photomicrographs highlighting main facies of the Barra Velha Formation: (A) Fascicular
 328 calcite crusts (crossed-polarized light; XPL); (B) Mg-clay matrix engulfed by shrubs (yellow arrow). Note
 329 the shrubs partially dissolved (red arrow) (plane-polarized light; PPL);16; (C) Mg-claystones with
 330 spherulites, showing coalesced and recrystallized spherulites (PPL); (D) Mg-claystones with spherulites
 331 showing a displacement aspect of the Mg-clay (red arrow) (XPL); (E) Mg-claystone with very fine
 332 dolomite crystals (green arrow) and dolomite rhombs (red arrows). Note the absence of spherulites in
 333 this sub-facies (PPL); (F) Laminites composed by microcrystalline calcite. Red arrows highlight
 334 dissolution seams (PPL); (G) Laminites with a crenulated morphology, composed by intercalations of
 335 very fine calcite crystals, dolomite, and organic matter. Red arrows highlight millimeter-scale silica
 336 nodules (XPL); (H) General aspects of organic matter remnants (PPL); (I) General aspects of breccia
 337 features in laminites. Red arrows highlight the intraclasts (XPL); (J) Intraclastic grainstone (Type-A)
 338 composed by fragments of fascicular calcite crusts and spherulites (PPL); (K) Type-B grainstone with
 339 volcanoclastic fragments (red arrow) (PPL); (L) Type-C grainstone (packstone) composed of carbonate
 340 and Mg-clay intraclasts (red arrows), with a minor fraction of siliciclastic grains (PPL).

341 Table 1 – Statistical summary of the average and maximum amounts of major constituents, Mg-clay
 342 and secondary porosity, in the main facies of the Barra Velha Formation. GST= intraclastic grainstones,
 343 SHR= fascicular calcite crusts, SPH= Mg-claystones with higher spherulites content, MGC= Mg-
 344 claystones with lower spherulites content, LAM= laminites.

Lithologic types		GST		SHR		SPH		MGC		LAM	
Constituents (%)		Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum
Calcite	Fascicular crusts	-	-	45.00	90.00	3.00	30.00	0.10	4.00	1.20	22.00
	Spherulites	-	-	6.50	32.00	34.00	83.00	3.00	10.00	1.60	33.00
Other Diagenetic phases											
Mg-clay	Syngenetic	1.00	38.00	2.00	30.00	5.00	50.00	14.00	83.00	3.00	35.00
Calcite	Replacing constituents	0.06	5.00	3.30	70.00	4.31	56.00	20.4	71.5	18.5	90.5
	Filling primary porosity	4.58	34.00	2.61	34.00	0.7	52.00	2.04	50.00	1.24	67.00
	Filling secondary dissolution porosity	0.04	3.00	0.5	25.00	0.34	8.00	0.03	1.00	0.27	10.00
	Filling fracture porosity	0.01	1.00	0.21	8.00	0.02	2.00	0.17	5.00	-	-
Dolomite	Replacing constituents	7.34	93.00	9.18	61.00	24.5	86.00	27.00	86.5	27.00	83.00
	Filling primary porosity	6.78	54.00	4.66	63.00	1.04	51.00	1.31	35.5	1.67	40.00
	Filling secondary dissolution porosity	0.15	29.5	0.71	35.00	0.94	25.00	0.32	7.00	1.00	35.00
	Filling fracture porosity	0.001	1.00	-	-	0.01	5.00	0.02	2.00	0.005	0.5
Quartz	Replacing constituents	2.68	70.00	4.25	65.00	5.65	97.00	6.71	55.00	8.91	72.00
	Filling primary porosity	2.08	53.00	1.73	58.00	0.62	33.00	0.39	15.00	0.32	10.00
	Filling secondary dissolution porosity	0.09	11.00	0.63	18.00	0.44	16.00	0.31	5.00	0.24	5.00
	Filling fracture porosity	0.01	2.00	0.09	8.00	0.03	10.00	0.08	6.00	0.07	3.00
Baryte	Replacing constituents/Filling porosity	0.07	5.00	0.08	5.00	0.05	4.00	0.13	0.47	0.03	2.00
Celestite	Replacing constituents/Filling porosity	0.004	2.00	-	-	-	-	-	-	0.01	2.00
Chalcedony	Replacing constituents/Filling porosity	0.35	17.00	0.78	30.00	1.15	80.00	0.4	10	2.1	45.00
Cryolite	Replacing constituents/Filling porosity	0.01	11.00	0.01	3.00	0.00	5.00	-	-	0.02	3.00
Dawsonite	Replacing constituents/Filling porosity	0.17	7.00	0.22	8.00	0.24	6.00	0.11	3.00	0.08	3.00
Fluorite	Replacing constituents/Filling porosity	0.002	1.00	-	-	-	-	-	-	0.03	5.00
Illite/smectite	Replacing constituents/Filling porosity	0.001	1.00	-	-	0.02	5.00	-	-	-	-
Kaolinite	Replacing constituents/Filling porosity	0.001	3.00	0.001	3.00	0.02	3.00	0.47	0.13	-	-
Magnesite	Replacing constituents/Filling porosity	0.15	15.00	0.73	27.00	1.59	46.00	0.42	22.00	0.8	25.00
Secondary dissolution porosity		5.00	31.00	5.00	40.00	5.00	24.00	2.00	25.00	4.00	30.00

345

346

347 4.1.5 Intraclastic grainstones

348 The intraclastic grainstones are the main facies in the study area, representing 44 % of the available
 349 samples. They are composed predominantly of fragments of fascicular calcite crusts, spherulites,
 350 laminites, and different proportions of siliciclastic/volcanoclastic grains and Mg-clay intraclasts (Fig. 3J-
 351 3L). The carbonate intraclasts are commonly rounded, moderately to well-sorted, with size ranging
 352 between fine- and coarse-sand (locally very coarse), with tangential to long grain contacts (Taylor,
 353 1950). Sutured and concave-convex contacts are observed but other compaction features (fractures,
 354 stylolithes, solution seams) are rare. This facies has a predominantly massive aspect but may present

355 a normal grading and cross-stratification. Intercalations with centimetre-thick layers of laminites and
356 fascicular calcite crusts are frequent.

357 The association of the different components allows to categorise the grainstones in three different
358 sub-facies, depending on the proportion of these components. Type-A grainstones are dominated by
359 carbonate fragments, with low content or absence of Mg-clays and siliciclastic/volcanoclastic grains.
360 They are the most common type (Fig. 3J). Type-B grainstones, composed of the most significant
361 content of siliciclastic/volcanoclastic grains, generally contain silt-sized detrital constituents (quartz,
362 feldspar, and mica) and sub-rounded to sub-angular basaltic volcanoclastic fragments (Fig. 3K). They
363 display inverse grading and concavo-convex to sutured grain contacts. Finally, type-C grainstones
364 range between a packstone to grainstone texture. They show the most prominent content of Mg-clays
365 (both as grains or matrix) and are characterized by the presence of ooids, peloids and clay intraclasts
366 (Fig. 3L). The Mg-clay content can be partially to totally replaced by calcite. They also show minor
367 amounts of ostracods, phosphatic fragments, siliciclastic grains, and volcanoclastic rock fragments.

368

369 **4.2 Facies distribution**

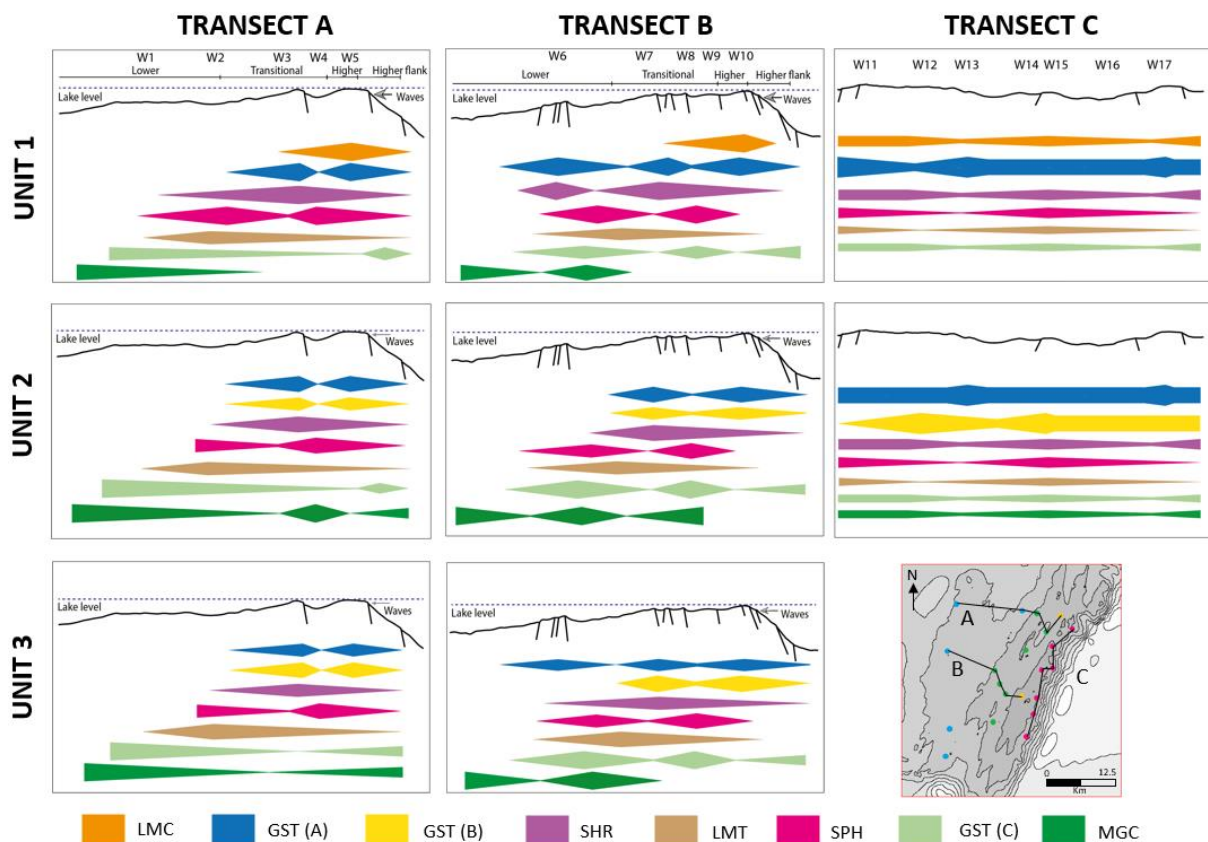
370 The well dataset enables the construction of correlation transects, which can help to define the facies
371 distribution and proportions, both in a spatial and temporal point of view (Fig. 4). These profiles were
372 reconstructed based on the basement topography assessed from seismic interpretation (Artagão,
373 2018). In the same way, schematic fault proportions are located on these profiles to represent a
374 simplified scheme of the fault network. These profiles show the existence of a topographic structural
375 high (wells W5 and W10), with a southeastern steep flank (wells W11 to W17) and a northwestern
376 low-angle slope (W1 to W4 and W6 to W9).

377 From a spatial point of view, the facies with a large Mg-clay content (grainstones with Mg-clays and
378 Mg-claystones with minor proportions of spherulites) predominate in lower areas, away from the
379 structural high, and in relatively low areas within the structural high, as in the case of well W4 (Fig. 4).

380 Furthermore, the wells situated in higher structural positions show very low preservation of the Mg-

381 clays, which occurs mainly as ooids and peloids, intensively affected by diagenetic processes (as
 382 previously reported by Carramal et al., 2022).

383 The Mg-claystones with high proportions of spherulites predominate in lower and transitional areas
 384 and fascicular calcite crusts occur preferentially in the transitional areas and some locations of the
 385 structural high (Fig. 4). Minor occurrences of spherulites and incipient forms of shrubs with Mg-clays
 386 are also observed in lower areas of the depositional profiles. In the studied wells, the proportion of
 387 laminites is generally scarce and preferentially distributed in the transitional areas, with minor
 388 occurrences in the lower areas. However, crenulated laminites occur in Unit 1 of BVF, and mostly on
 389 the structural highs. The grainstones are observed along the entire transects, but with variations
 390 depending on the grainstone sub-facies. The carbonate intraclastic grainstones occur preferentially on
 391 the structural highs, whereas the grainstones with the largest content of Mg-clay are more developed
 392 in the lower areas. Finally, the siliciclastic/volcanoclastic-dominated grainstones occur mainly in Units
 393 3 and 2, preferentially on the structural highs.



394

395

396 Figure 4 – Facies spatial and stratigraphic distribution over the three transects (A to C, located on the
397 map of the study area) and the three stratigraphic units labeled 3 (base) to 1 (top). No interpretation
398 was proposed for Unit 3 of transect C, as this unit pinches out on the basement. The scale of these
399 transects is given on the map. LMC= crenulated laminites, GST (A)= intraclastic grainstones, GST (B)
400 intraclastic grainstone with siliciclastic/volcanoclastic content, SHR= fascicular calcite crusts, LMT=
401 laminites, SPH= Mg-claystones with higher spherulites content, GST (C) intraclastic grainstones with
402 Mg-clay content, MGC= Mg-claystones with lower spherulites content.

403

404

405 Regarding the stratigraphic distribution, the most significant proportions of Mg-claystones with minor
406 proportions of spherulites occur in Units 3 and 2. The Mg-claystones with high amount of spherulites
407 predominates in Unit 1. Fascicular calcite crusts and intraclastic grainstones predominate in Unit 1. The
408 latter is marked by a more significant proportion of fascicular calcite crusts, particularly towards the
409 lower area of transect B. Some sites of the southeast flank show a high proportion of fascicular calcite
410 crusts in Unit 3, as in the case of well W11. Detrital content, mainly associated with laminites, Mg-
411 claystones with spherulites, and grainstones, generally occurs in low quantities. However, its
412 abundance shows a progressive decrease from Unit 3 to Unit 1 (Table 2). A slight decrease is observed
413 on the structural high (Table 3).

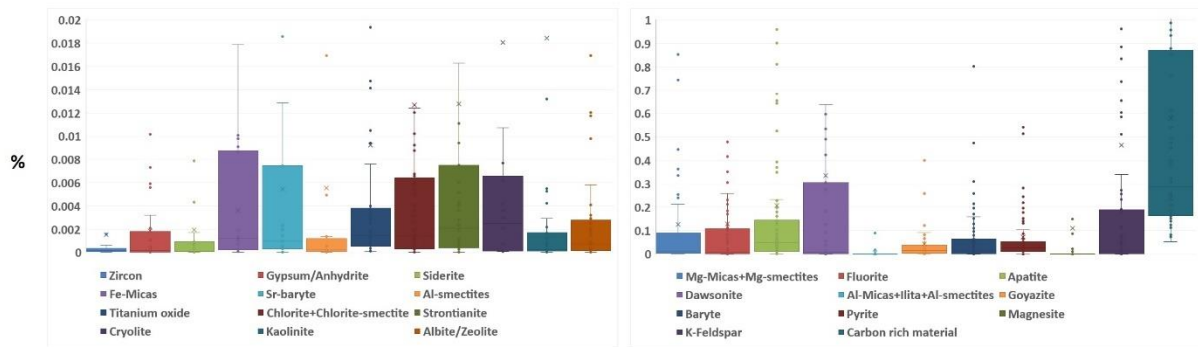
414

415 **4.3 Facies and clay mineralogy**

416 **4.3.1 QEMSCAN analysis**

417 The mineralogical composition of 92 samples from 5 wells located in different structural positions has
418 been mapped using the QEMSCAN system. The samples consist mainly of calcite, dolomite, quartz, and
419 Mg-clays, the latter varying significantly in proportion depending on the well position in the study area,
420 reaching a maximum of 50 % in distal wells. The sum of the trace minerals represents average
421 quantities of 3 % and the most common are presented in Figure 5.

422



423 Figure 5 – Boxplots showing the diversity and amounts of accessory minerals encountered in the Barra
 424 Velha Formation, based on QEMSCAN analyses. A) Proportions of trace minerals. B) Proportions of
 425 minor minerals.
 426

427

428 4.3.2 XRD analysis

429 Clay minerals occur in different proportions in the described facies, but also with different mineralogy.
 430 Bulk-rock X-Ray Diffraction (XRD) analyses show that the sum of calcite, dolomite, quartz, and clay
 431 minerals represent 90 % of the sample's composition. Among the secondary minerals Ca-dolomite, K-
 432 feldspar, and magnesite are the most representative. The larger and more complete sample dataset
 433 analyzed with XRD may explain some differences with the QEMSCAN analyses.

434 According to the XRD analyses, the clay minerals are composed chiefly of kerolite, mixed-layer
 435 kerolite/Mg-smectite, Mg-smectite, sepiolite, and minor amounts of non-magnesian clay minerals,
 436 such as Illite, illite-smectite, kaolinite and chlorite (Fig. 6A and 6B). Mg-smectite comprised stevensite
 437 and saponite (Netto et al., 2022) but their differentiation implies additional analyses that were not
 438 done for our dataset. Figure 6B shows the association between facies and the different clay species.

439 Kerolite and mixed-layer kerolite/Mg-smectite are the main Mg-clays observed in the case study (Fig.
 440 6A and 6B). The analyses show that kerolite and mixed-layer kerolite/Mg-smectite are present
 441 respectively in 73 % and 55 % of the Mg-claystones with high amounts of spherulites (Supplementary
 442 material Fig. A1). In the intraclastic grainstones, kerolite occurs in 82 % of the analyzed samples,
 443 whereas mixed-layer kerolite/Mg-smectite is only present in 50 % of the samples. Kerolite occurs in 70
 444 % of the fascicular calcite crusts, whereas mixed-layer kerolite/Mg-smectite is present in 40 % of the
 445 samples. Kerolite is also present in 67 % of the samples of laminites facies, but in low proportions (1-

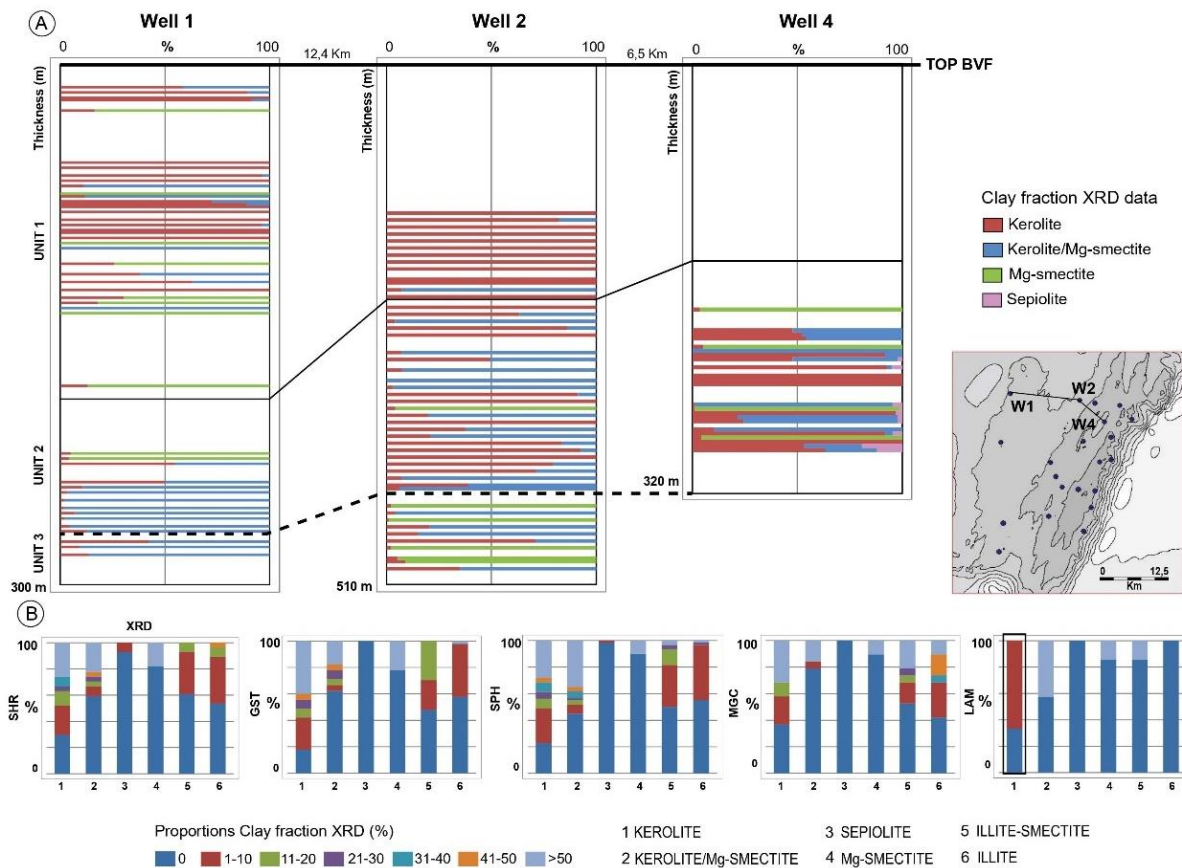
446 10 % of each sample), whereas the mixed-layer kerolite/Mg-smectite represents more than 50 % of
447 the clay fraction in 44 % of the samples.

448 Mg-smectites occur mostly related to intraclastic grainstones and fascicular calcite crusts, being
449 present in 20 % of the samples and in those cases representing more than 50 % of the clay fraction
450 (Fig. 6B). Sepiolite is rare, being present preferentially in fascicular calcite crusts (where it is present in
451 less than 10 % of the samples and representing 1 to 10 % of the clay fraction) or in Mg-claystones with
452 spherulites (present in less than 5 % of the samples and representing 1 to 10 % of the clay fraction). It
453 is absent in the other facies (Fig. 6B).

454 Non-magnesian clay minerals are mainly illite-smectite and illite. These clays occur in small quantities
455 in about 50 % of all the samples, except for the laminites where illite-smectite is only present in 15 %
456 of the samples but representing more than 50 % of the clay fraction (Fig. 6A). Other minor occurrences
457 of non-magnesian clays in the basin include kaolinite and chlorite.

458 In terms of stratigraphic distribution, Mg-smectite predominates in Unit 3 and in the lower areas (Fig.
459 6A). Kerolite and mixed layer kerolite/Mg-smectite contents increase in Units 2 and 1. The highest
460 proportions of kerolite occur in Unit 1, whereas the highest content of mixed-layer kerolite/Mg-
461 smectite occurs in Unit 2, mostly in wells situated in lower areas of the transects. Sepiolite occurs in
462 small quantities in Unit 2, in well W4 (higher domain) (Fig. 6A).

463



464

465 Figure 6 – (A) NW-SE transect showing the spatial and stratigraphic distribution of clay minerals (XRD).
 466 The dashed line represents the Intra-Alagoas unconformity. (B) Clay mineral composition per facies
 467 (SHR= fascicular calcite crusts, GST= intraclastic grainstones, SPH= Mg-claystones with high spherulite
 468 content, MGC= Mg-claystones with low spherulite content, LAM= laminites). The black rectangle on
 469 the last diagram is a reading example: for the samples identified as laminites facies, 33 % do not
 470 present kerolite, and 67 % present between 1-10 % of kerolite.

471

472 4.4 Other diagenetic constituents

473 In the studied carbonate succession, a complex interplay of sedimentary and diagenetic processes
 474 occurred, and it is somehow difficult to put a strict boundary between near-surface and burial
 475 diagenesis. We followed the diagenetic sequences proposed by Herlinger et al. (2017) and Lima and
 476 De Ros (2019), which considered fascicular calcite crusts as essentially syngenetic and spherulites as
 477 eogenetic products. Other post-depositional phases are also associated with early diagenesis or even
 478 late diagenesis.

479

480 **4.4.1 Dolomite**

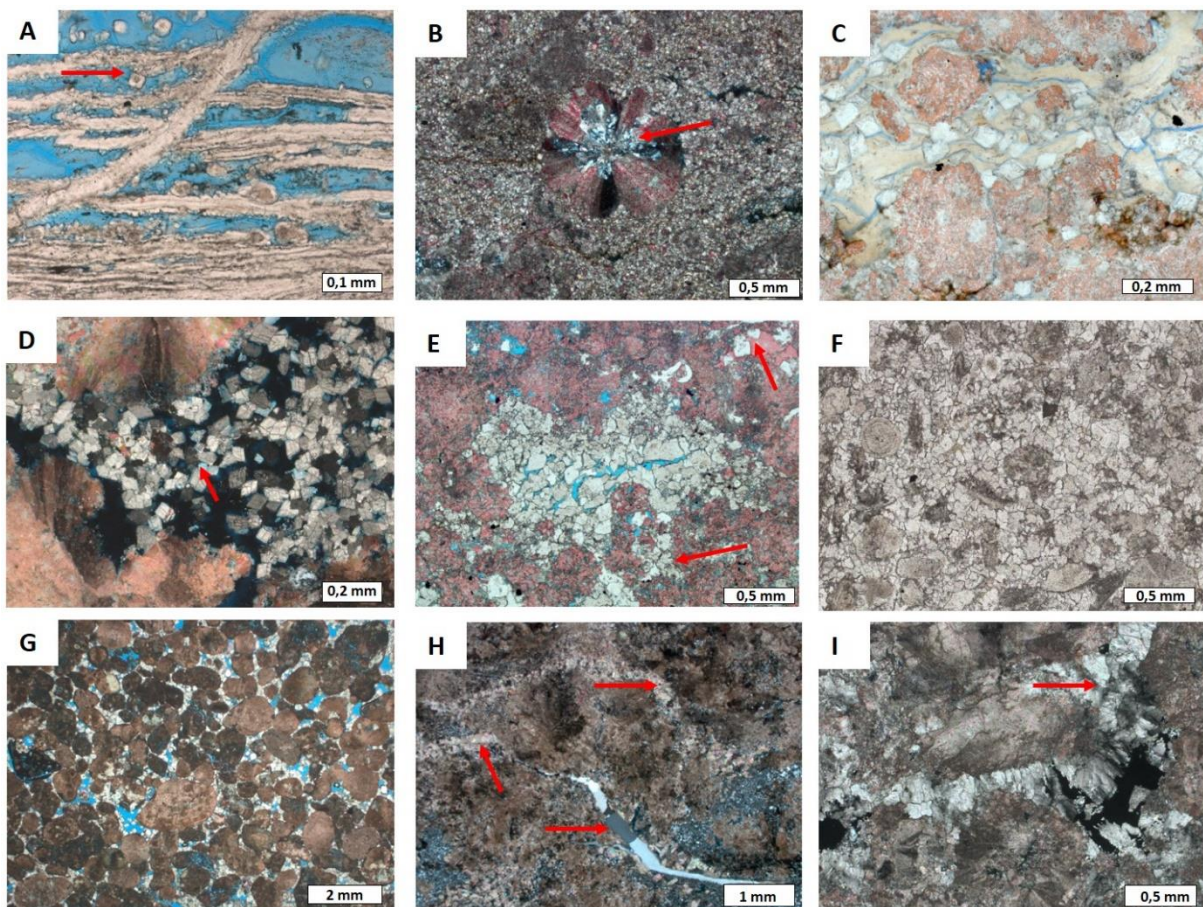
481 Dolomite is one of the most common diagenetic constituents observed in thin sections, occurring with
482 five main fabrics. The first type, only observed locally, forms lamellar aggregates (Fig. 7A), 30 to 50 μm
483 in thickness and composed of fibrous dolomite and magnesite. Some dolomite rhombs grew on the
484 lamellar dolomite. The second type is microcrystalline dolomite, which consists of very fine subhedral
485 crystals (15 to 60 μm) replacing spherulites and Mg-clays (Fig. 7B), as well as the laminites facies, giving
486 a recrystallized mottled aspect. The third type, called rhombohedral dolomite, occurs as well-
487 developed euhedral rhombs (25 to 100 μm in diameter) that can display concentric zonation, and that
488 are commonly arranged in a scattered floating pattern in Mg-clays, with evidence of displacive growth
489 (Fig. 7C). In a few samples, it occurs in the growth-framework porosity of fascicular crusts, showing a
490 tighter idiomorphic texture, with no or very rare remnants of clays and a secondary intercrystalline
491 porosity (Fig. 7D). The fourth type is granular mosaic dolomite, that consists of anhedral to subhedral,
492 fine to coarse crystals (0,25 to 1 mm) generally affecting pervasively the original facies, replacing
493 original calcite grains (spherulites, intraclasts...) and growing as a pore-filling cement in the primary
494 porosity (Fig. 7E-7G). This dolomite type also co-occurs with macrocrystalline quartz as fracture-infill
495 (Fig. 7H). Finally, the fifth type is coarse-crystalline saddle dolomite formed of anhedral to subhedral
496 prismatic crystals with sweeping extinction and curved crystal faces (Fig. 7I).

497 Laminites and Mg-claystones with spherulites show the highest contents of dolomite (Table 1).
498 Dolomite is one of the major constituents in the laminites, being present in 93 % of the samples
499 (Supplementary material Fig. A2). Pore-filling, microcrystalline dolomite occurs in 22 % of the samples,
500 but only in small amounts. In the Mg-claystones with higher proportions of spherulites, the dolomite
501 occurs in 94 % of the samples showing an average amount of 25 %. In these samples, the main dolomite
502 fabric is rhombohedral, followed in relative order of importance by microcrystalline and lamellar
503 aggregates. As a pore-filling cement phase, dolomite is present in 22 % of the samples. Mg-claystones
504 with minor proportions of spherulites shows Mg-clay replacement by dolomite in 90 % of the samples,

505 representing average proportions around 27 % per sample, mainly of microcrystalline and
506 rhombohedral types.

507 In fascicular calcite crusts, dolomites occur mainly with its rhombohedral form (Fig. 7D) and as
508 microcrystalline mosaics, with minor occurrences of saddle dolomite. The amount of dolomite per
509 sample can reach 63 % (Table 1), with average values that vary around 13 % per sample. The main form
510 of dolomite occurrence is as replacement of interstitial Mg-clay and shrobs, being present in 66 % of
511 the samples, with average values of 9 % per sample.

512 Pore-filling dolomite cement predominates in the intraclastic grainstones and fascicular calcite crusts,
513 representing a key process of porosity reduction. Dolomite cement occurs in 73 % of the intraclastic
514 grainstone samples, with average quantities of 7 % per sample, and up to 54 % per sample (Table 1).
515 It is represented by rhombohedral and granular mosaic types, and locally by saddle dolomite. 44 % of
516 the fascicular calcite crusts display dolomite cement which may reach up to 63 % per sample.



517

518 Figure 7 – Photomicrographs highlighting different dolomite types of Barra Velha Formation: (A)
519 Lamellar aggregates. The red arrow highlights dolomite rhombs (plane-polarized light; PPL); (B) Very
520 fine dolomite crystals replacing calcite spherulites and possibly matrix (crossed-polarized light; XPL).
521 Note the spherulite partially replaced by quartz (red arrow); (C) Rhombohedral dolomite replacing Mg-
522 clay (PPL); (D) Fascicular calcite crusts with rhombohedral dolomite cement (XPL); (E) In-situ facies with
523 anhedral dolomite cement. The red arrows highlight the carbonate constituents replaced by dolomite
524 (PPL); (F) Grainstone with medium to coarse granular mosaic dolomite (indistinct cement and
525 replacement phase) (PPL); (G) Grainstone with fine granular dolomite cement (PPL); (H) Fascicular
526 calcite crusts intensely replaced by dolomite and quartz. The red arrows highlight the filling of the
527 pore-fracture by dolomite and quartz (XPL); (I) In-situ facies with saddle dolomite. Note the sweeping
528 extinction (red arrow; XPL).

529

530 **4.4.2 Calcite**

531 Even considered eodiagenetic in origin (Herlinger et al., 2017; Lima and De Ros, 2019), the spherulites
532 have been described in sections 4.1.2 and 4.2, as a main component of the Mg-claystones with
533 spherulites facies. Besides the fascicular and spherulitic aggregates, diagenetic calcite occurs also in
534 four various fabrics: 1) crypto- to fine crystalline form; 2) as rim cement; 3) as a coarse-crystalline,
535 granular mosaic; and 4) as a blocky cement mostly filling fractures.

536 Cryptocrystalline to fine crystalline calcite (Fig. 8A), is formed of inclusion-rich, subhedral crystals (10
537 to 20 μm) or crystal clusters, that mimic the original facies texture or allochems (lamination,
538 spherulites...), suggesting a replacement process. In some samples, this crystalline fabric is dominant,
539 leading to partial or total recrystallization of the original host. Rarely, calcite rims, 10 to 30 μm thick,
540 formed of prismatic to bladed crystals are observed as a coating around grains, in grainstones facies
541 (Fig. 8B). Rims are associated mainly with Mg-clay ooids (Fig. 8C). The coarse-crystalline calcite is
542 composed of medium to coarse (100 to 500 μm), anhedral to subhedral crystals, filling the porosity in
543 a granular, equant mosaic fabric (Fig. 8C). This calcite grows in facies that have previously undergone
544 compaction, attested by the concave-convex sutures between grains (Fig. 8D). Finally, minor amounts
545 of coarse euhedral crystals, poikilotopic and blocky calcites are also recognized, as a cement phase,
546 essentially filling fractures (Fig. 8E). This blocky calcite engulfs the saddle dolomite cement, thus
547 postdating it (Fig. 8F).

548 Diagenetic calcite occurs mainly in laminites, Mg-claystones, and grainstones facies (Table 1,
549 supplementary material Fig. A3). Cryptocrystalline to fine-crystalline calcite is present in about 40 % of
550 the laminites and claystones samples, with more than 30 % as a replacement phase. Calcite pore-filling
551 cement is common in grainstones (Fig. 8B and 8C), with 20 % of the samples presenting more than 10
552 % of calcite cement. Mosaic calcite occurs in 42 % of the samples, and calcite rims in 10 % of the
553 samples. In the fascicular calcite crusts, different types of diagenetic calcite are present in 47 % of the
554 samples, occurring similarly as a cement and a replacement phase. The most common fabrics observed
555 in the fascicular calcite crusts are, in order of relative importance, medium to coarse-crystalline mosaic
556 (cement phase), fine-crystalline calcite (replacement) and coarse euhedral blocky calcites (cement).
557 Minor occurrences of blocky calcite filling fractures and rims can be seen in up to 10% of the samples.
558

559 **4.4.3 Silica**

560 Silica is common in the BVF and displays four main different fabrics. Crypto- to microcrystalline silica
561 is the most frequent silica phase, forming drusy aggregates that partially to totally silicified calcite
562 spherulites (Fig. 7B), and mimetically replaced Mg-clay matrix. The silica replacement can be fabric
563 selective (e.g., it is confined within selected grains) or non-selective (Fig. 8G). This phase can also fill
564 growth-framework porosity between fascicular calcite crusts (Fig. 8H). Reworked silicified spherulites
565 and intraclasts in the grainstone facies tend to indicate an early process of silicification.
566 Microcrystalline silica is generally associated with microporosity. Quartz rims (20 to 50 μm thick) are
567 observed locally, forming coatings around grains made of prismatic to bladed crystals (Fig. 8C and 8I).
568 These rims predate the development of coarse-crystalline mosaic calcite (Fig. 8C). The similar
569 crystalline fabric, scale, occurrence in grainstone facies suggest a possible replacement of calcite rims
570 by silica. The third type is macrocrystalline quartz, composed of subhedral to anhedral crystals, 30 to
571 100 μm in diameter, that form a coarse mosaic cement filling pores (Fig. 8I) and also observed as
572 fracture infills. It is unclear if this phase may also be replacive. Last, a chalcedony phase with a fibrous

573 radiated fabric is observed and partially engulfs and replaces the coarse-crystalline mosaic and the
574 blocky calcites (Fig. 8E and 9A).

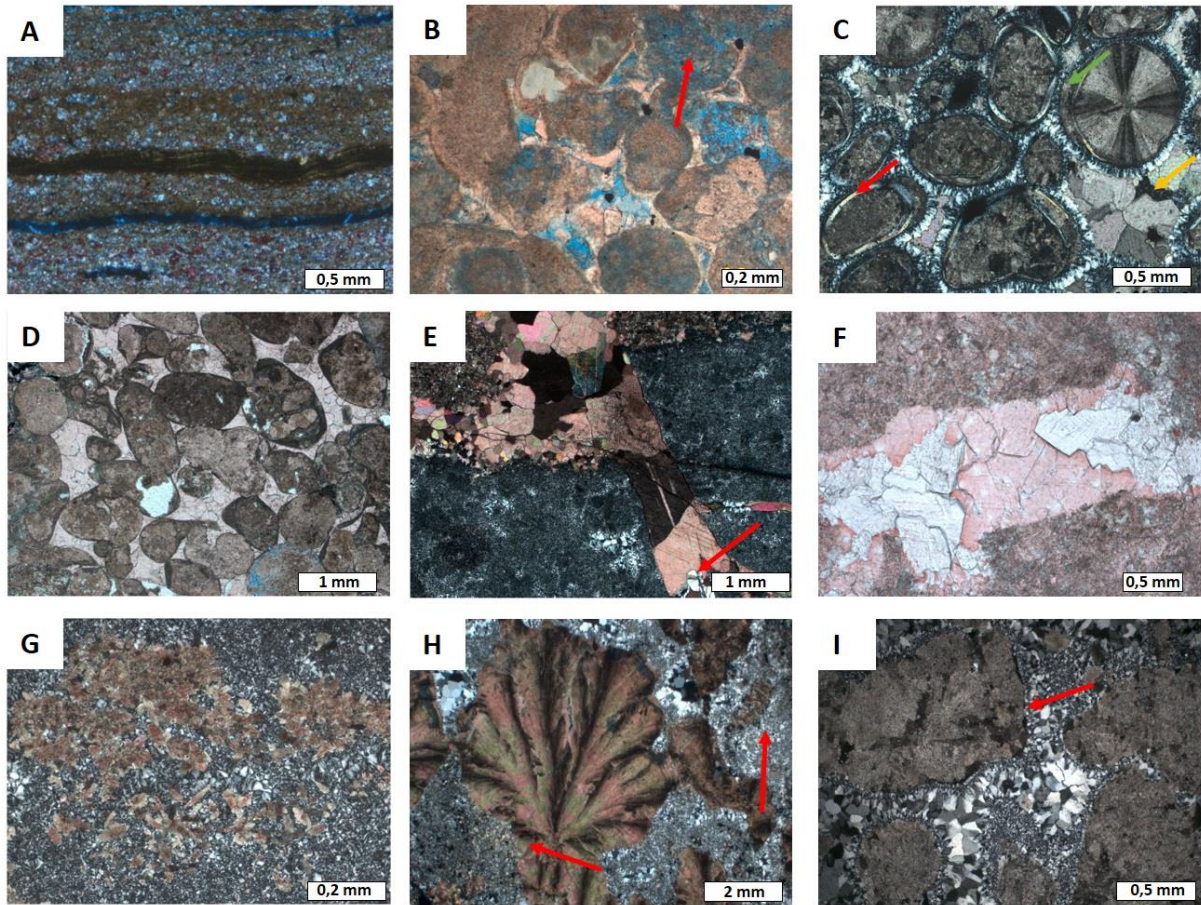
575 The laminites contains the largest amount of silica, primarily as a replacement phase, being present in
576 70% of the samples (Supplementary material Fig. A4). Centimetric tabular laminae and nodules of
577 silica, evolved in a few cases to pervasive silicification. Microcrystalline quartz is the most common
578 silica form in laminites, followed by chalcedony and macrocrystalline mosaic quartz.

579 The replacement of Mg-clays and calcite spherulites by silica is also frequently observed and occurs
580 mainly as microcrystalline and macrocrystalline mosaic quartz. In the Mg-claystones with higher
581 spherulite contents, silicification is observed in 75 % of the samples. In the fascicular calcite crusts, the
582 replacement reaches a maximum of 65 % of the samples, but in general, the proportion per sample is
583 low, with an average of 4 %. Chalcedony is accessory and mainly replaces spherulites and fascicular
584 calcite.

585 As for calcite, pore-filling silica is more important in the fascicular calcite crusts and intraclastic
586 grainstones (Fig. 8G and 8H). The proportions are similar in both facies (Table 1) and quartz as a pore-
587 filling phase is present in 40 % of the fascicular calcite crusts samples and in 35 % of the grainstone
588 samples.

589

590



591

592 Figure 8 - (A) Mg-clay partially replaced by very fine calcite and dolomite crystals (crossed-polarized
 593 light, XPL); (B) Grainstone constituents with calcite rims. Note the dissolution of the carbonate
 594 intraclasts (plane-polarized light, PPL); (C) Grainstone with fragments of shrubs, spherulites, showing
 595 silica rims and Mg-clay envelops (red arrow). The yellow arrow highlights mosaic calcite filling porosity,
 596 the green arrow highlights calcite coating around grains (XPL); (D) Grainstone with blocky calcite
 597 cement (PPL); (E) Poikilotopic calcite, filling fracture (XPL), partially replaced by chalcedony (red arrow);
 598 (F) In-situ facies with blocky calcite engulfing saddle dolomite cement (PPL); (G) In-situ facies with
 599 intense silicification (XPL); (H) Fascicular calcite crust with quartz cement. Note the quartz replacing
 600 the fascicular calcite (red arrows); (I) Grainstone with silica rims (red arrow) and macrocrystalline
 601 quartz cement (XPL).

602

603 4.4.4 Minor diagenetic phases

604 Minor occurrences of replacive and pore-filling minerals including barite, celestite, cryolite, dawsonite,
 605 fluorite, illite/smectite, kaolinite, and magnesite have been observed (Table 1). Magnesite, dawsonite
 606 and barite are the most frequent. Magnesite is present in 25 % of the Mg-claystones with spherulites
 607 and occurs as lamellar aggregates replacing and filling shrinkage pores in the Mg-clays. Dawsonite

608 occurs mostly associated with fascicular calcite crusts and spherulites (Fig. 9B) and barite occurs mainly
609 as a cement phase in intraclastic grainstones and fascicular calcite crusts (Fig. 9C).

610

611 **4.4.5 Dissolution and fractures**

612 Secondary porosity is generated by the dissolution of both Mg-clays and carbonate constituents.

613 Dissolution of carbonate intraclasts generated intraparticle and moldic porosity on intraclastic

614 grainstones (Fig. 8B). In fascicular calcite crusts, dissolution generated intra-framework porosity. In

615 these facies, the enlargement of interparticle and growth-framework pores is also common, creating

616 larger vugs (Fig. 9D). In laminites facies, a matrix microporosity is observed (Fig. 9E) as well as a

617 fenestral porosity, locally enlarged due to dissolution. In Mg-claystones, porosity formation is specially

618 related to Mg-clay dissolution (Fig. 9F), although the dissolution of spherulites is significant in some

619 samples. Dissolution of pore-filling calcite cement phase is common, generating intracrystalline

620 porosity. Porosity generated by dissolution is observed in different proportions in all the facies,

621 although preferentially affecting fascicular calcite crusts, Mg-claystones with spherulites, and

622 intraclastic grainstones (Table 1).

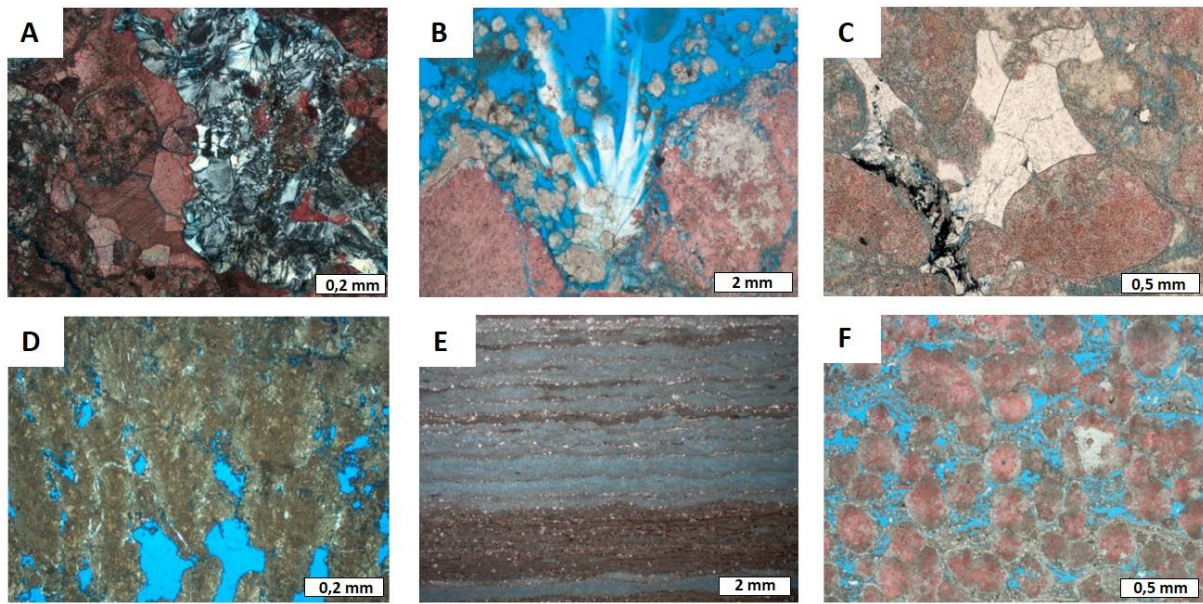
623 Late cement phases filling secondary dissolution pores are often observed, mainly in fascicular calcite

624 crusts and Mg-claystones with spherulites. In fascicular calcite crusts, late cements can consist of 35 %

625 of dolomite, and 25 % of calcite. Fractures are observed mainly in intraclastic grainstones and fascicular

626 calcite crusts and are frequently filled by a cement of quartz and calcite. However, the occurrence in

627 the samples is local.



628

629 Figure 9 – (A) Grainstone with coarse mosaic calcite, replaced by chalcedony (crossed polarized light;
 630 XPL); (B) Fascicular calcite crusts with cement of dawsonite and euhedral dolomite (plane-polarized
 631 light, PPL); (C) Cement of dawsonite and euhedral dolomite (PPL); (D) Growth-framework porosity
 632 enlarged by dissolution (PPL); (E) General aspects of dissolution in laminites; (F) General aspects of
 633 dissolution on Mg-claystones with spherulites (PPL).

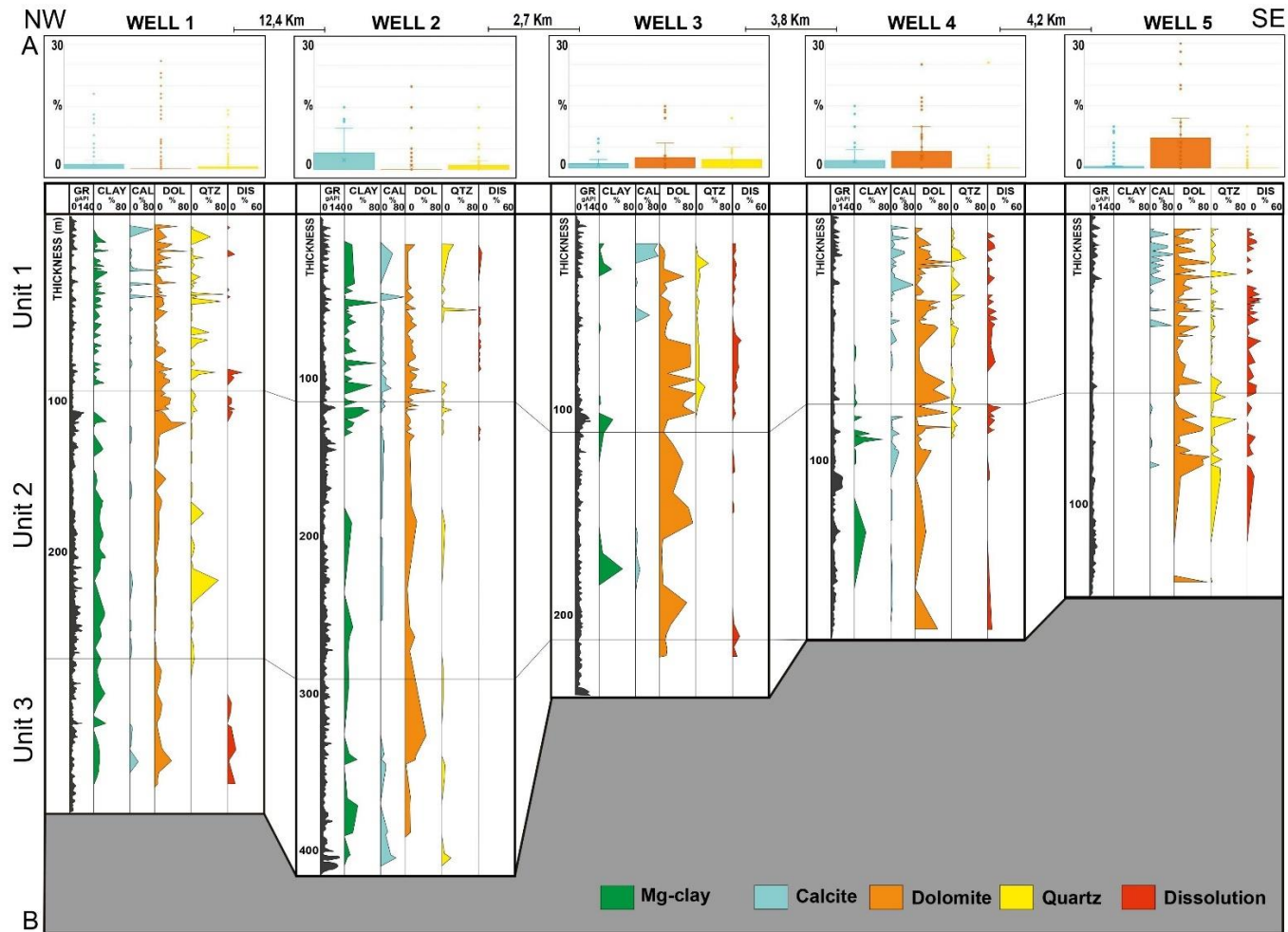
634

635 4.5 Distribution of the diagenetic phases and dissolution

636 The results of petrographic observations and quantification were set in the studied wells, organized
 637 along two dip transects, perpendicular to the structural high (Figs. 10 and 11) and one strike transect
 638 along the SE flank, parallel to the structural high (Fig. 12). Vertical sampling spacing varies from 30 cm
 639 to 5 m, with an average spacing of 50 cm. The dataset enables the characterization of the lateral and
 640 vertical distribution of the main diagenetic phases (Fig. 13).

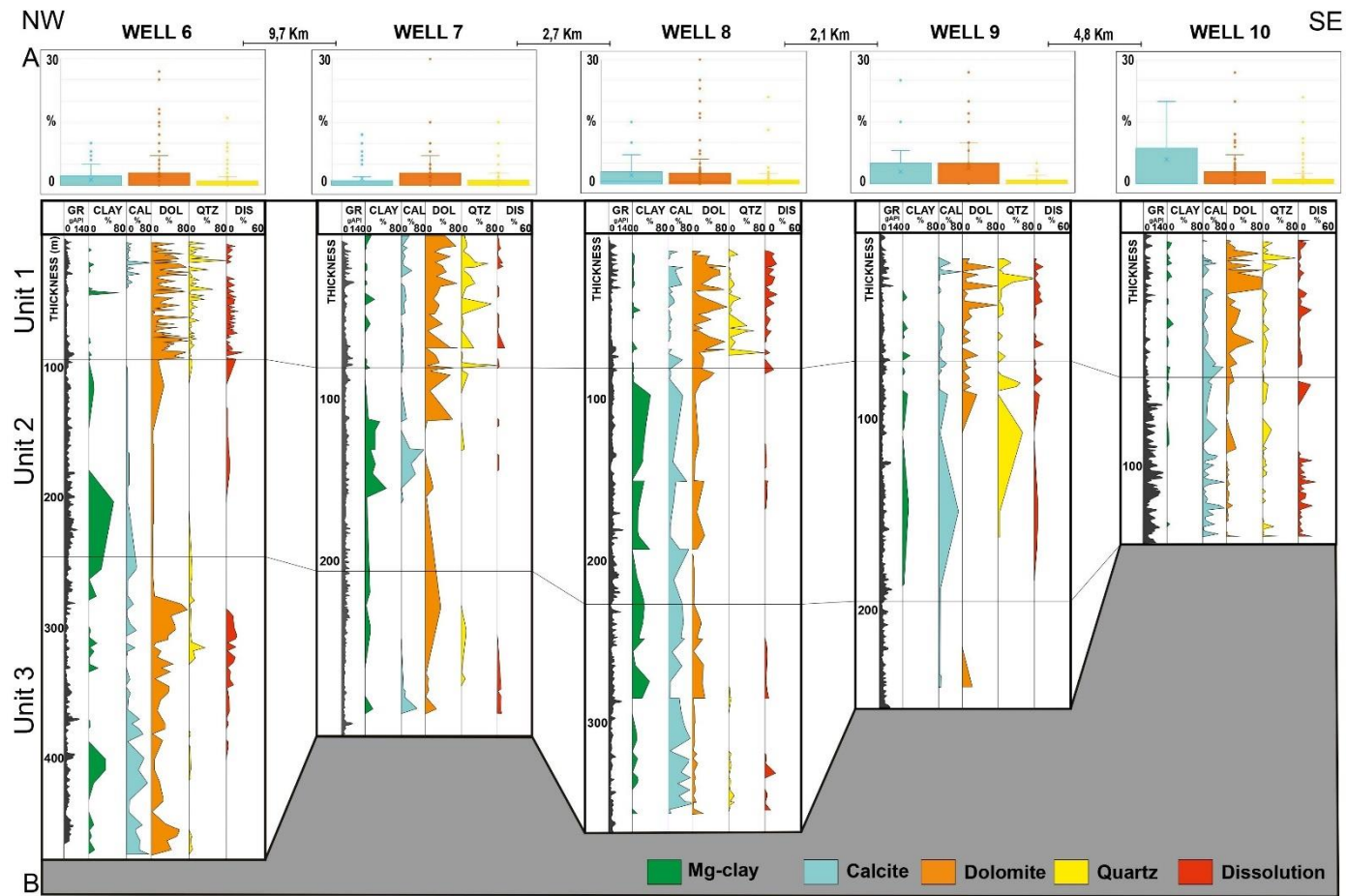
641 The northeastern region of the study area (transect A, Fig. 10) shows a higher proportion of dolomite
 642 in the transitional zone and towards the structural high. This increase is associated with the
 643 replacement of the constituents, and partially with a pore-filling cement phase (Fig. 10A and B).
 644 Conversely, in the central portion of the study area, represented by transect B, dolomitization
 645 increases towards the lower area, especially in Unit 1 (Fig. 11B). Dolomitization is also intense in the
 646 wells of the southeast flank, both in Units 2 and 1 (Fig. 12B). In this area, dolomite cement is frequent

647 (Fig. 12A), mostly in intraclastic grainstones. The increase of dolomite in lower sites, as observed in
648 transect B (Fig. 11), may be related to differences in the structural pattern of the study area. The region
649 of well W6 is marked by a higher relief bounded by faults (Fig. 1C and Fig. 11), creating a distinct
650 depositional setting compared with the northwest portion.



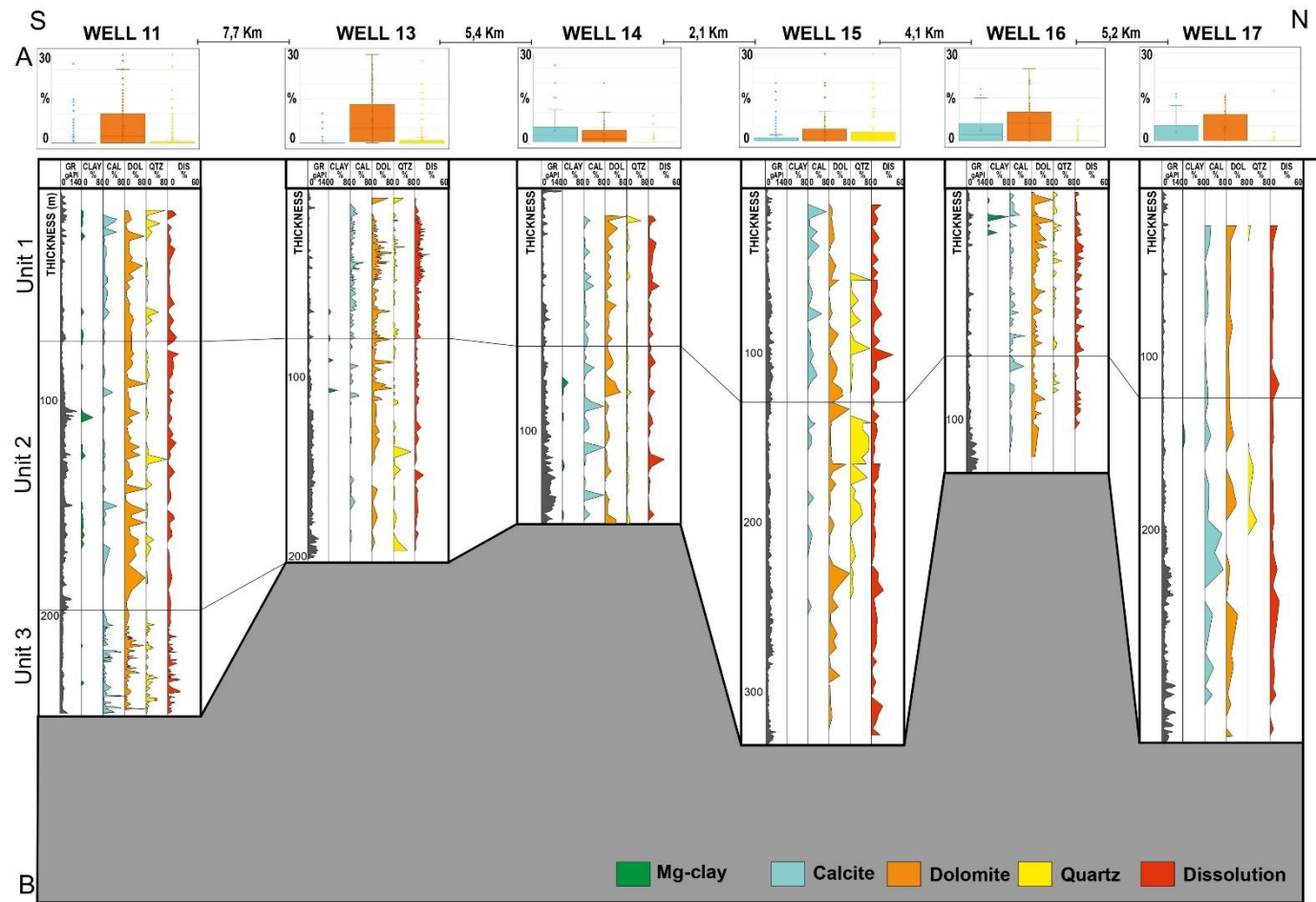
651

652 Figure 10 – NW-SE correlation along transect A showing the quantitative distribution of the main diagenetic minerals in the study area. A) Boxplots of calcite,
 653 dolomite, and quartz pore-filling cement proportions. B) Vertical distribution of Mg-clay, diagenetic minerals (sum of the replacement and cementation) and
 654 dissolution. Values vary between 0 and 80% per sample for the Mg-clay and diagenetic minerals and between 0 and 60% for the dissolution process. The
 655 gamma ray log (GR) is also plotted. The profile morphology was reconstructed based on the BVF basal boundary assessed from seismic interpretation (Artagão,
 656 2018), corroborated with the well data that reach the BVF boundary.



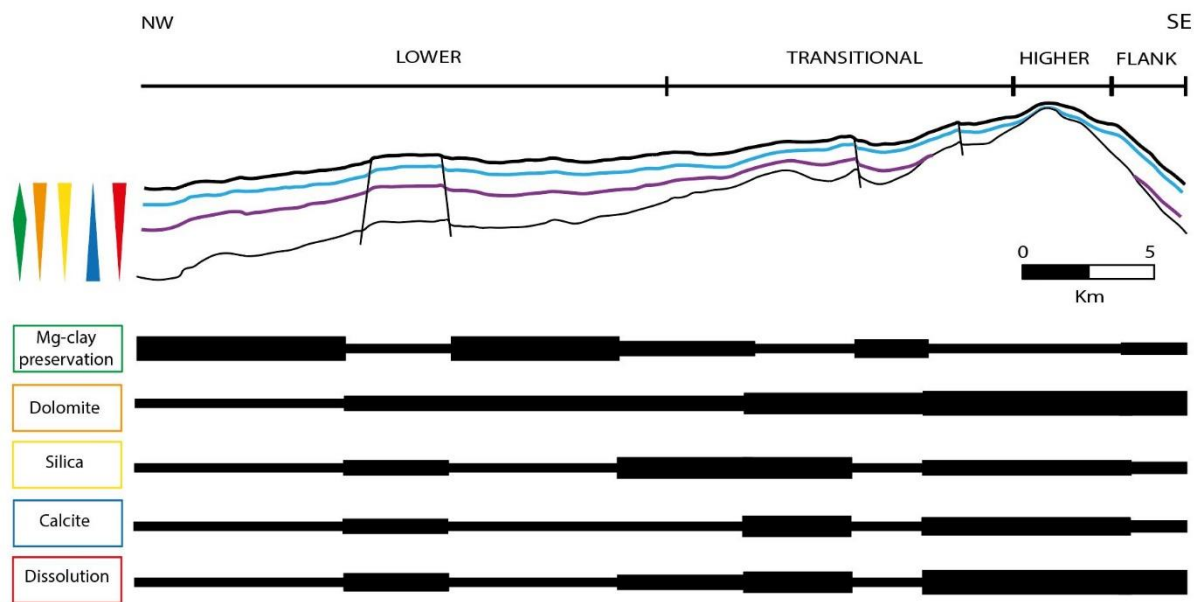
657

658 Figure 11 – NW-SE correlation along transect B showing the quantitative distribution of the main diagenetic minerals in the study area. A) Boxplots of calcite,
 659 dolomite, and quartz pore-filling cement proportions. B) Vertical distribution of Mg-clay, diagenetic minerals (sum of the replacement and cementation) and
 660 dissolution. Values vary between 0 and 80% per sample for the Mg-clay and diagenetic minerals and between 0 and 60% for the dissolution process. The
 661 gamma ray log (GR) is also plotted. The profile morphology was reconstructed based on the BVF basal boundary assessed from seismic interpretation (Artagão,
 662 2018), corroborated with the well data that reach the BVF basal boundary.



663

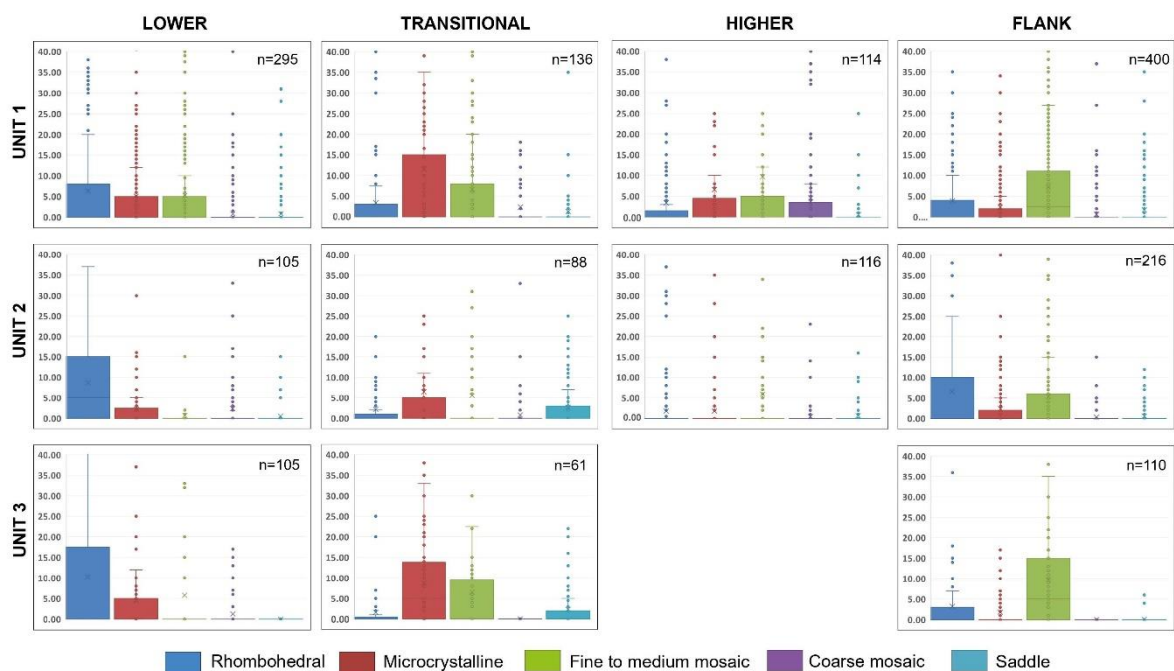
664 Figure 12 – NW-SE correlation along transect C showing the quantitative distribution of the main diagenetic minerals in the study area. A) Boxplots of calcite,
 665 dolomite, and quartz pore-filling cement proportions. B) Vertical distribution of Mg-clay, diagenetic minerals (sum of the replacement and cementation) and
 666 dissolution. Values vary between 0 and 80% per sample for the Mg-clay and diagenetic minerals and between 0 and 60% for the dissolution process. The
 667 gamma ray log (GR) is also plotted. The profile morphology was reconstructed based on the BVF boundary assessed from seismic interpretation (Artagão,
 668 2018), corroborated with the well data that reach the BVF boundary.



670
 671 Figure 13 – Scheme showing the lateral and vertical distribution of the main diagenetic phases in the
 672 study area. Purple line represents the Intra-Alagoas unconformity (between Unit 3 and 2) and the blue
 673 line represents the boundary between Units 2 and 1.

674
 675 Dolomite fabrics also spatially vary. The highest amounts and proportion per sample of rhombohedral
 676 dolomite are observed in lower areas (Fig. 14). Rhombohedral dolomite is widely found associated
 677 with Mg-claystones with spherulites and fascicular calcite crusts facies. Medium-crystalline mosaic
 678 dolomite has similar proportions in all the facies and is most common on the structural highs. An
 679 important increase of mosaic dolomite is observed in Unit 1. Microcrystalline dolomite is also
 680 abundant, prevailing in the laminites, and transitional areas (Fig. 14). The other dolomite types occur
 681 locally but can reach 90 % in some samples, as in the case of saddle dolomite. The proportion of
 682 lamellar dolomite/magnesite is in general, very low, but it is possible to observe a preferential
 683 association of lamellar aggregates with fascicular calcite crusts and spherulitic facies.
 684 Calcite cementation generally occurs in the highest structural parts, and on the southeastern flank
 685 (Figs. 11A and 12A). It is also more abundant in Units 2 and 3, in the central region (transect B; Fig. 11),
 686 associated with reworked facies (intraclastic grainstones). Other major occurrences are observed in
 687 Unit 1, associated with crenulated laminites. The coarse-crystalline mosaic and blocky calcites are

688 more developed in the southeast flank. Although the calcite rims occur in small proportion, they are
 689 also more frequent in the southeast flank and on the structural high.
 690 Silica does not present any peculiar spatial distribution, although it is possible to observe higher
 691 proportions in Unit 1 (Fig. 12), preferentially in the laminites facies, and along the southeastern flank,
 692 essentially as a cement phase (Fig. 11B). Chalcedony is found mainly in Mg-claystones with spherulites
 693 and in fascicular calcite crusts on the southeastern flank and the structural high, and occasionally in
 694 the lower areas (Table 3). Among other diagenetic phases, dawsonite and barite are the most frequent,
 695 both occurring as replacement and cement. Dawsonite follows the same distribution pattern as
 696 chalcedony, while barite occurs primarily as a cement phase on the southeastern flank, mainly in Unit
 697 1.



698
 699 Figure 14 – Boxplots showing the distribution of the different types of dolomite, in different parts of
 700 the study area and stratigraphic units. No data was collected for Unit 3 in the higher area, as it pinches
 701 out. The data of Unit 3 in the flank region are from well W11.

702
 703 Dissolution increases towards the structural high (Fig. 10 and 11) and is widely observed in the
 704 southeastern flank (Fig. 12). In the lower areas, dissolution is important only in Unit 1. In this
 705 stratigraphic unit, Mg-claystones with spherulites show major dissolution features, as well as the

706 laminites. The largest occurrences of vuggy pores are also concentrated in Unit 1, mainly associated
 707 with fascicular calcite crusts in the higher area of the depositional profile. In the southeastern flank,
 708 dissolution frequently occurs in both Units 1 and 2. A punctual increase in Unit 3 of well W6 is also
 709 observed (Fig. 11). Post-dissolution cementation is localized and occurs mainly in the transitional and
 710 higher areas.

711 Average porosity values generated by dissolution are low (Tables 2 and 3), but this represents only the
 712 dissolution porosity quantified by petrography. At a larger scale, core description shows that
 713 dissolution is intense and pervasive in the wells situated in the structural highs, where it can be
 714 associated with fracturing. The statistical analysis of the petrographic data indicates this general trend
 715 of dissolution.

716

717 Table 2 – Statistical summary of the average and maximum amounts of major diagenetic constituents,
 718 Mg-clay, and secondary porosity, in the stratigraphic units of Barra Velha Formation.

Stratigraphic unit		Unit 1		Unit 2		Unit 3	
Constituents (%)		Average	Maximum	Average	Maximum	Average	Maximum
Calcite	Fascicular crusts	17.90	90.00	16.10	87.00	22.30	84.00
	Spherulites	17.60	86.00	20.20	85.00	14.90	76.00
Other diagenetic phases							
Mg-clay	Syngenetic	9.00	83.00	10.00	93.00	7.00	77.00
Calcite	Replacing constituents	4.50	90.50	3.85	75.00	10.20	85.00
	Filling primary porosity	2.52	34.00	2.82	78.00	4.17	52.00
	Filling secondary dissolution porosity	0.25	10.00	0.27	25.00	0.33	25.50
	Filling fracture porosity	0.09	8.00	0.02	5.00	0.07	5.00
Dolomite	Replacing constituents	16.70	86.50	10.70	90.00	11.40	93.00
	Filling primary porosity	4.65	52.00	4.00	63.00	4.30	55.00
	Filling secondary dissolution porosity	0.68	35.00	0.37	35.00	0.24	15.00
	Filling fracture porosity	0.01	5.00	0.001	1.00	-	-
Silica	Replacing constituents	5.80	97.00	2.90	78.00	1.60	25.00
	Filling primary porosity	1.70	33.00	1.03	58.00	1.60	52.00
	Filling secondary dissolution porosity	0.30	16.00	0.24	15.00	0.50	18.00
	Filling fracture porosity	0.04	8.00	0.004	1.00	0.10	10.00
Secondary dissolution porosity		5.00	40.00	4.00	30.00	3.00	22.00
Detrital grains		3.00	30.00	4.00	18.00	6.00	34.00

719

720 Table 3- Statistical summary of the average and maximum amounts of major diagenetic constituents,
 721 Mg-clay, and secondary porosity of Barra Velha Formation, in different portions of the study area.

Regions		Lower		Transitional		Higher		Flank (section C)	
Constituents (%)		Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum
Calcite	Fascicular crusts	12.5	83.0	13.4	87.0	17.5	90.0	20.0	84.0
	Spherulites	26.7	86.0	14.5	72.0	14.0	66.0	12.8	62.0
Other diagenetic phases									
Mg-clay	Syngenetic	10.0	75.0	6.0	51.0	1.0	39.0	1.0	42.0
Calcite	Replacing constituents	5.2	90.5	10.48	75.0	5.8	70.0	3.0	85.0
	Filling primary porosity		30.0	1.51	52.0	3.5	67.0	4.12	78.0
	Filling secondary dissolution porosity	0.39	8.0	0.77	25.5	0.25	10.0	0.05	5.0
	Filling fracture porosity	0.08	5.0	0.01	1.5	0.04	3.0	0.09	8.0
Dolomite	Replacing constituents	17.5	86.0	19.0	93.0	13.6	86.5	10.2	90.0
	Filling primary porosity	2.08	45.0	2.6	30.0	3.4	51.0	6.5	63.0
	Filling secondary dissolution porosity	0.2	10.0	0.79	30.0	0.76	35.0	0.5	35.0
	Filling fracture porosity	0.006	2.0	0.004	0.5	0.02	5.0	0.001	1.0
Silica	Replacing constituents	3.82	97.0	4.76	78.0	3.09	70.0	4.8	72.0
	Filling primary porosity	0.64	27.0	1.07	53.0	0.76	15.0	2.3	58.0
	Filling secondary dissolution porosity	0.5	16.0	0.38	12.0	0.29	15.0	0.21	18.0
	Filling fracture porosity	0.03	3.0	0.04	3.0	0.12	8.0	0.03	10.0
Baryte	Replacing constituents/Filling porosity	0.03	3.5	0.06	4.0	0.12	7.0	0.07	5.0
Chalcedony	Replacing constituents/Filling porosity	0.5	40.0	1.0	35.0	2.4	70.0	0.9	80.0
Dawsonite	Replacing constituents/Filling porosity	0.03	4.0	0.07	5.0	0.05	3.0	0.3	6.0
Secondary dissolution porosity		3.0	25.0	3.0	17.0	5.0	28.0	6.0	40.0
Detrital grains		4.0	34.0	4.0	30.0	3.0	13.0	3.0	30.0

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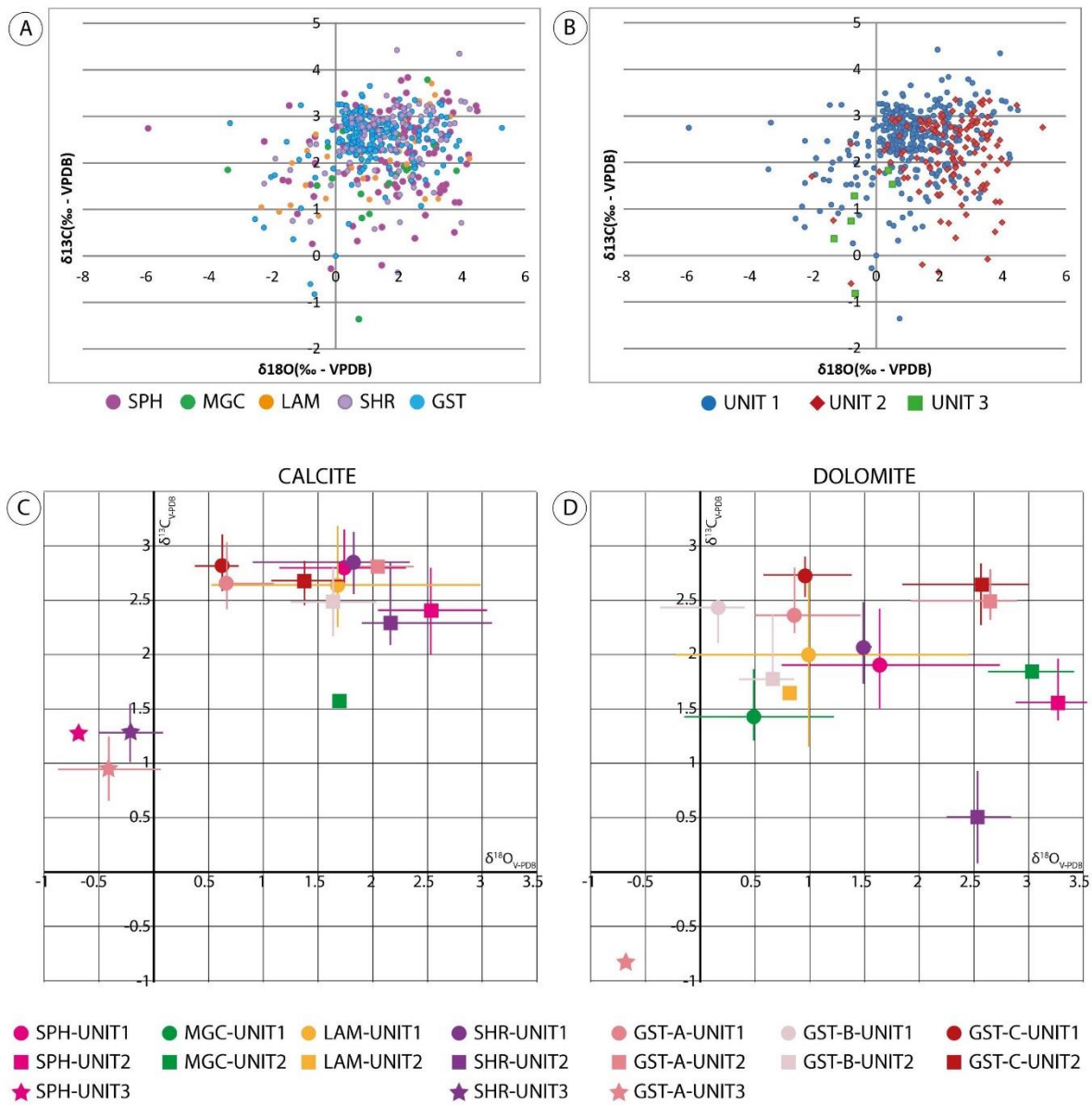
723

724 4.6 Geochemistry

725 4.6.1 Bulk oxygen and carbon isotopic analysis

726 The bulk sample values of $\delta^{13}\text{C}$ vary between -1.35 and +4.42 ‰, with median and average values of
 727 +2.51 and +2.36 ‰ respectively, and most of the data presenting positive values. The values of $\delta^{18}\text{O}$
 728 vary between -5.93 and +5.26 ‰, with median and average values of +1.39 and +1.42 ‰, respectively.
 729 In contrast to the $\delta^{13}\text{C}$ data, the $\delta^{18}\text{O}$ displays more negative values, especially in well W6. The bulk
 730 sample values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, categorized by facies and stratigraphic units are shown in Figures 15A
 731 and 15B. As bulk analyses are problematic to interpret, data were sorted given their dominant
 732 mineralogy, and a selection of samples were realized (Table 4): samples with more than 70 % of the
 733 carbonate phase being calcite (mostly fascicular calcite or spherulites) and samples with more than 70

734 % of the carbonate phase being dolomite (mostly microcrystalline and rhombohedral dolomite). The
 735 isotopic data do not show any good covariant trend, whatever the facies, the dominant mineralogy, or
 736 the stratigraphic unit (Table 4).
 737



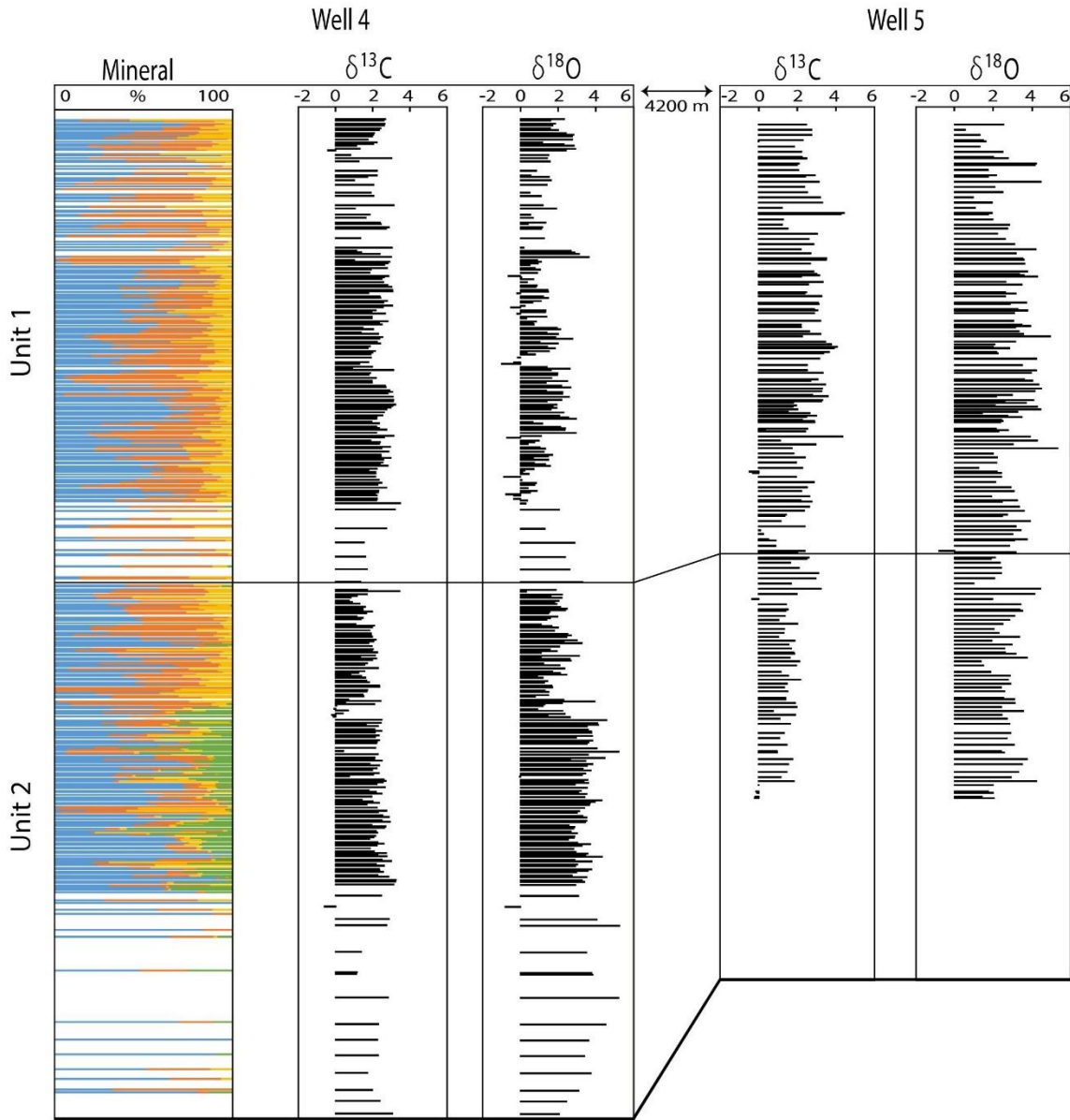
738
 739 Figure 15 - $\delta^{18}\text{O}$ vs. $\delta^{13}\text{C}$ crossplots. (A) Bulk values per facies; (B) Bulk values per stratigraphic units; (C)
 740 Samples dominated by calcite; (D) Samples dominated by dolomite. For (C) and (D), points correspond
 741 to the average values of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ for the different facies and stratigraphic units. The horizontal
 742 and vertical bars correspond to the first and third quartile of each dataset (when available). SPH= Mg-
 743 claystones with higher spherulite content, MGC= Mg-claystones with lower spherulites content, LAM=
 744 laminites, SHR= fascicular calcite crusts, GST= grainstones of different types (A, B, C).

745

746 Concerning the calcite values, no specific pattern is observed between the stable isotopes and the
747 different facies (Fig. 15C). The data show lower variation ranges for $\delta^{13}\text{C}$ than for $\delta^{18}\text{O}$ values. A good
748 correlation is observed with stratigraphic units. In Unit 3, at the base of the succession, the low number
749 of samples precludes to make an accurate evaluation of the data, although a few samples show the
750 lowest values with average $\delta^{18}\text{O}$ values ranging from -0.69 to -0.21 ‰ and average $\delta^{13}\text{C}$ from 0.95 to
751 1.28 ‰. Unit 2 displays the highest $\delta^{18}\text{O}$ values (up to 2.53 ‰) and moderate to high average $\delta^{13}\text{C}$
752 (from 1.56 to 2.80 ‰). Finally, Unit 1, at the top of the succession is characterized by significantly lower
753 $\delta^{18}\text{O}$ values compared to Unit 2 (from 0.62 to 1.82 ‰) but with the highest average $\delta^{13}\text{C}$ values (2.63
754 to 2.84 ‰). In this latter unit, it must be noted that a slightly increasing trend of both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$
755 average values is observed between the laminites, Mg-claystones with spherulites and shrubs facies.
756 Nevertheless, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ patterns depend on the location of the wells on the depositional profile
757 (Fig. 16). In well W4, situated on a lower area within the structural high, the $\delta^{13}\text{C}$ values are relatively
758 constant, while the $\delta^{18}\text{O}$ values present significant differences between the Units 1 and 2. Relative to
759 mineralogy, the highest values of $\delta^{18}\text{O}$ are associated with the intervals with high Mg-clay content. In
760 well W5, situated on a higher structural position, a change in $\delta^{13}\text{C}$ pattern is observed, with higher
761 values in the Unit 1, whereas $\delta^{18}\text{O}$ data show a minor variation. The amount of XRD data in well W5 is
762 insufficient to correlate the isotopic data with mineralogy.

763 The dolomite values show a more scattered distribution (Fig. 15D). As for calcite, no clear relationship
764 is observed between the isotopic signatures and the different facies. The laminites and the type-B
765 grainstones, dominated by microcrystalline dolomites, shows relatively lower $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ average
766 values, compared to the other facies, both in Units 1 and 2. The other facies, rather dominated by
767 rhombohedral dolomite show the same stratigraphic trends than for calcite. Thus, Unit 2 shows the
768 highest $\delta^{18}\text{O}$ values (up to 3.28 ‰) and highly variable average $\delta^{13}\text{C}$ (from 0.50 to 2,64 ‰), while Unit
769 1 is characterized by lower $\delta^{18}\text{O}$ values (from 0.17 to 1.64 ‰) but with the highest average $\delta^{13}\text{C}$ values
770 (1.42 to 2.72 ‰).

771



772 ■ Calcite ■ Dolomite ■ Quartz ■ Clay mineral

772

773 Figure 16 – Schematic transect showing profiles of bulk mineralogy, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ of the wells W4 and W5.

774 The well W5 does not have sufficient mineralogy data for correlation.

775

776

777

778

779

780 Table 4 - $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (Avg.=average value, Q1=first quartile, Q3=third quartile) for each facies and
 781 stratigraphic units (when available), for samples dominated by calcite and dolomite. Correlation
 782 coefficients are calculated for each series when number of samples (n) are sufficient.

	Name	n	d18O - Avg.	Q1	Q3	d13C - Avg.	Q1	Q3	Correl. coef.
CALCITE	SPH - UNIT 1	24	1.73	1.15	2.29	2.81	2.64	3.15	-0.14
	SPH - UNIT 2	12	2.53	2.07	3.02	2.40	2.00	2.79	0.65
	SPH - UNIT 3	1	-0.69	--	--	1.28	--	--	--
	STV - UNIT 2	1	1.69	--	--	1.56	--	--	--
	LAM - UNIT 1	10	1.67	1.04	2.99	2.63	2.25	3.19	0.34
	SHR - UNIT 1	44	1.82	0.90	2.33	2.84	2.56	3.13	-0.34
	SHR - UNIT 2	13	2.16	1.90	3.09	2.28	2.09	2.85	-0.02
	SHR - UNIT 3	2	-0.21	-0.51	0.08	1.28	1.01	1.56	--
	GST-A - UNIT 1	11	0.66	0.71	1.09	2.65	2.42	3.03	0.26
	GST-A - UNIT 2	2	2.04	1.73	2.35	2.80	2.75	2.85	--
	GST-A - UNIT 3	2	-0.42	-0.88	0.05	0.95	0.65	1.24	--
	GST-B - UNIT 2	2	1.63	1.24	2.02	2.48	2.17	2.79	--
	GST-C - UNIT 1	17	0.62	0.38	0.77	2.81	2.51	3.10	0.51
	GST-C - UNIT 2	6	1.37	1.07	1.74	2.67	2.46	2.87	-0.84
	DOLOMITE	SPH - UNIT 1	23	1.64	0.75	2.73	1.90	1.51	2.43
SPH - UNIT 2		7	3.28	2.88	3.60	1.55	1.39	1.94	-0.21
STV - UNIT 1		12	0.49	-0.15	1.29	1.42	1.22	1.86	-0.13
STV - UNIT 2		2	3.03	2.64	3.43	1.84	1.84	1.85	--
LAM - UNIT 1		15	0.99	-0.42	2.43	1.99	1.16	2.69	0.66
LAM - UNIT 2		1	0.82	--	--	1.92	--	--	--
SHR - UNIT 1		3	1.50	1.42	1.56	2.05	1.73	2.49	-0.99
SHR - UNIT 2		2	2.54	2.25	2.82	0.50	0.07	0.93	--
GST-A - UNIT 1		30	0.87	0.51	1.47	2.35	2.20	2.80	0.28
GST-A - UNIT 2		9	2.65	1.92	2.89	2.48	2.33	2.79	0.28
GST-A - UNIT 3		1	-0.67	--	--	-0.82	--	--	--
GST-B - UNIT 1		5	0.17	-0.86	0.88	2.42	2.16	2.31	-0.62
GST-B - UNIT 2		5	0.67	0.36	0.86	1.77	1.86	2.38	0.89
GST-C - UNIT 1		35	0.96	0.58	1.38	2.72	2.53	2.90	-0.16
GST-C - UNIT 2		21	2.57	1.84	3.00	2.64	2.27	2.84	-0.11

783

784

785

786 5 Interpretation and discussion

787 The BVF is mainly constituted by a limited mineral assemblage, composed essentially of calcite,

788 dolomite, silica, and Mg-clays. Different biological or chemical controls on mineral precipitation may

789 have exerted a strong influence on the diagenetic pathways of these sediments (Herlinger et al., 2017).

790 For example, the role of biological factors related to Mg-clays and dolomite precipitation has been

791 addressed by Burne et al. (2014), Pace et al. (2016), or Kirkham and Tucker (2018) both in the pre-salt
792 formation or in other cases. Other studies considered part of the dolomite as a product of
793 neomorphism of a microbially-influenced metastable precursor (Gomes et al., 2020) or formed within
794 extracellular polymeric substances (EPS) (Sartorato, 2018). However, for other authors, the lack of
795 direct textural or isotopic evidence for microbial deposits in most of the BVF, except for the uppermost
796 meters of the formation, is evidence of dominant abiotic processes. The abiotic models emphasized
797 not only the scarcity of microbial features but the role of Mg-clay as a source of elements, essentially
798 for dolomite and silica precipitation (Wright and Barnett, 2015; Tosca and Wright, 2015; Farias et al.,
799 2019). Although these processes have been extensively described and interpreted, very few papers
800 (Wright and Barnett, 2020; Gomes et al., 2020; Carramal et al., 2022) have integrated a quantitative
801 approach combined with spatial and stratigraphic distribution and elaborated on the relations
802 between this distribution and the depositional or structural setting. This will be developed in the
803 following discussion.

804

805 **5.1 Syndepositional processes**

806 **5.1.1 Mg-clays**

807 In our study area, Mg-clays are abundant, and rocks essentially constituted by them can reach 150 m
808 in thickness in some wells, being in line with the extensive Mg-clay occurrences described in the
809 West African and eastern Brazilian Margins (Wright and Barnett, 2015; Tosca and Wright, 2015; Saller
810 et al., 2016; Sabato Ceraldi and Green, 2016; Herlinger et al., 2017; Farias et al., 2019; Lima and De Ros
811 2019; Gomes et al., 2020; Wright and Barnett, 2020). Moreover, the current Mg-clay content only
812 represents a fraction of the original content, considering the extent of its replacement by
813 microcrystalline and cryptocrystalline calcite, dolomite, and silica, as well as their dissolution (Herlinger
814 et al., 2017; Lima and De Ros, 2019).

815 Jones and Gálan (1988) and Tosca and Wright (2015) suggested that the factors controlling the
816 formation of Mg-rich clays are pH (alkalinity), pCO₂, and salinity; and that the specific chemical

817 conditions required for their precipitation could be achieved rapidly and with large lateral extensions
818 through evaporative concentration. Biological materials, such as microbial cells or extracellular
819 polymeric substances (EPS), could also act as substrates for Mg-silicate nucleation by lowering the
820 interfacial energies for Mg-silicate precipitation (Tosca and Wright, 2015). The identification of Mg-
821 clays in association with biofilms and microbial carbonate is reported in some works (Tosca et al., 2011;
822 Burne et al., 2014; Perri et al., 2018).

823 In our case study, the facies with the highest preserved Mg-clay content (Mg-claystones with minor
824 proportions of spherulites) occurs in Unit 2. Moreover, it seems that high $\delta^{18}\text{O}$ values measured on
825 carbonates are associated with samples in which the highest Mg-clay content is found (i.e., well W4).
826 The high isotopic values, both in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ may suggest: 1) a lesser diagenetic alteration, as
827 diagenesis would tend to decrease $\delta^{18}\text{O}$ values (Lima and De Ros, 2019); 2) evaporitic conditions
828 (Talbot, 1990; Farias et al., 2019) and correlative evaporative concentrations of the water, also favoring
829 Mg-clay precipitation and preservation (Pozo and Calvo, 2018; Galán and Pozo, 2011). Vertical
830 partitioning is also observed for the clay mineralogy, with Mg-smectite dominant in Unit 3 passing
831 upward to dominantly mixed layer kerolite/Mg-smectite and kerolite in Units 2 and 1. This Mg-clay
832 distribution suggests a gradual change in the water chemistry as the genesis of the different types of
833 Mg-clays is conditioned by variations in pH, salinity, and Si/Mg ratio (Jones and Galán, 1988; Carramal
834 et al., 2022; Netto et al., 2022). Netto et al. (2022) recognized a similar vertical trend of the Mg-clay
835 minerals in samples from a well located in the Outer High structure of the Santos Basin. They
836 interpreted the predominance of Mg-smectite (stevensite) in the lower part of the stratigraphic
837 succession as due to early evaporative conditions while the precipitation of kerolite in the upper part
838 would be related to the presence of relatively more diluted waters. Stevensite stability is favored by
839 high salinity and pH and low to moderate Si/Mg ratios, while the kerolite stability is favored by
840 moderate salinity, pH between 8 and 8.5, and low Si/Mg ratio, with transitions from one to the other
841 represented by kerolite-stevensite interstratified minerals (Galan and Pozo, 2011). Tosca and
842 Masterson (2014) even suggested a broader range of pH for kerolite formation, reaching higher values

843 of 9.4. In this case, the Si/Mg ratio would be one of the main factors for kerolite precipitation.
844 According to these observations, the Mg-clays trend could indicate a variation in the detrital
845 contribution in the basin, since kerolite formation is favored in environments with low detrital
846 sediment input (Deocampo, 2015). This hypothesis is supported by the detrital grain abundance
847 increase in Unit 3 and distribution of the grainstones with siliciclastic/volcanoclastic grains that are
848 observed in Units 3 and 2, in the vicinity of the structural high, directly overlying the fractured
849 substratum (explaining the abundance of volcanoclastic/siliciclastic material). The sources of solutes
850 in the pre-salt lake are not evident, with potential sources including leaching and erosion of flood
851 basalts outside the rift, enhanced by hydrothermal activity (Szatmari and Milani, 2016; Farias et al.,
852 2019); intrabasinal magmatism (Szatmari et al., 2016; Wright, 2022); felsic rocks from the basement,
853 in contact with groundwaters (Pietchz et al., 2018); marine seepage through the Walvis Ridge volcanic
854 barrier (Farias et al., 2019); mantle exhumation and serpentization (Tosca and Wright, 2015; Pinto et
855 al. 2017; Lima et al., 2020). Despite the low proportion of terrigenous input in the basin, the higher
856 contribution of detrital grains in Unit 3 and its progressive decrease indicates a change in the lake's
857 water recharge pattern that could influence the Mg-clays type precipitation. A higher amount of non-
858 magnesian clay minerals observed in laminites, intraclastic grainstones, and Mg-claystones with
859 spherulites can also be associated with areas and periods characterized by higher detrital input.

860 From a spatial point of view, the facies with the largest preserved Mg-clay content predominate in
861 lower areas, away from the structural high, and in relative lows within the high, as in the case of well
862 W4. In these areas, Mg-clay occurs as very fine laminated fabrics, associated with a low amount of
863 spherulites. On the contrary, the wells of transects A and B located on the structural high, as well as
864 on its eastern flank (transect C), are characterized by very low content of Mg-clays, which occurs mainly
865 as intraclasts and ooids. Such differences could be due to a system of different small and isolated lakes
866 with no or only episodic lateral connection (Farias et al., 2019). However, the lateral continuity of the
867 different seismic reflectors and stratigraphic units of the BVF (Wright and Barnett, 2017) point to a
868 unique large lake, at least at field scale. Changes in hydrodynamic conditions are supported by the very

869 fine laminated fabrics deposited and well-preserved in low-energy environments, localized in lower
870 areas, and ooids associated with high-energy conditions, predominating in higher areas of the
871 depositional profile (Lima and De Ros, 2019; Basso et al., 2020; Carramal et al., 2022). The scarcity of
872 Mg-clays in these settings could also be related to lesser preservation and a stronger diagenetic
873 alteration, owing to variable physico-chemical conditions in such places. The high sensitivity of Mg-
874 clays to pCO₂ and pH, their high reactive surface area, and their Al-free composition can lead to their
875 destabilization, replacement, and dissolution during early diagenesis (Deocampo, 2005; Tosca, 2015;
876 Tosca and Wright, 2015).

877 Fluctuations in environmental conditions probably favored distinct Mg-clay minerals in time and
878 variable types and degrees of alterations (Carramal et al., 2022). The decrease of Mg-clays amounts in
879 the high areas of the depositional setting (and particularly in Unit 1) coincides with an increase of
880 dolomite and magnesite amounts, which suggest more intense replacement processes. The diagenetic
881 alterations of Mg-clays and their relationship with other minerals will be discussed below.

882

883 **5.1.2 Fascicular calcite crusts**

884 Fascicular calcite crusts (or shrubs) from the Barra Velha and Macabu Formations have been illustrated
885 in several publications (Herlinger et al., 2017; Farias et al., 2019; Gomes et al., 2020; Lima and De Ros,
886 2020; Wright and Barnett, 2020) and are interpreted by these authors as products of abiotic
887 precipitation. According to Herlinger et al. (2017), the fascicular calcite aggregates are syngenetic
888 precipitates resulting from encrustation and replacement of other sediments, mainly stevensite.
889 Wright and Barnett (2015), Farias et al. (2019), and Lima and De Ros (2019), based on petrographic
890 characteristics, rather indicate a rapid vertical growth of crystals, directly at the sediment-water
891 interface or right below it, from highly carbonate-saturated solutions.

892 As the main constituent of the in-situ facies, the fascicular calcite crusts form mainly in transitional and
893 higher areas of the depositional profile. In higher sites, these carbonates are abundant, mostly devoid
894 of Mg-clays, and grew on top of each other. They may have formed directly at the water-sediment

895 interface as syngenetic precipitates (Lima and De Ros, 2019). In contrast, in lower areas of the studied
896 depositional profile, fascicular calcite crusts are mostly observed as incipient forms, being commonly
897 associated with spherulites and interstitial Mg-clays. In this case, the frequent engulfment of Mg-clays
898 in the calcite aggregates and their displacive crystal growth indicate that part of the shrubs precipitated
899 as a result of an early diagenetic process (Carramal et al., 2022), replacing and deforming the Mg-clays
900 (Lima and De Ros, 2019; Farias et al., 2019).

901 The preferential location of these crusts in shallow environments and the dominantly high $\delta^{13}\text{C}$ and
902 $\delta^{18}\text{O}$ isotopic values, observed for these carbonates in Units 2 and 1, suggest precipitation under the
903 influence of evaporative concentrations (Wright and Barnett, 2015; Sabato-Ceraldi and Green, 2016;
904 Barnett et al., 2018; Farias et al., 2019). For Saller et al. (2016), the morphology of these calcite crusts
905 is dependent on depositional energy, degree of supersaturation, and substrate. The development of
906 incipient forms in deeper and less energetic environments is in line with the previous observations of
907 Lima and De Ros (2019) or Basso et al. (2020), who also described “hybrid forms” between spherulites
908 and fascicular crusts. The interlayering between fascicular calcite crusts and intraclastic grainstones
909 point to rapid changes in hydrodynamic conditions. In the same way, the centimetric alternation of
910 fascicular calcite, spherulites, and Mg-clays observed in this study, seems to reflect local and rapid
911 changes in the lake chemistry and hydrodynamism (Gomes et al., 2020; Lima and De Ros, 2019;
912 Mercedes-Martín et al., 2019).

913 An alternative hypothesis based on sedimentological observations suggests that shrubby carbonate
914 formation might arise from the combination of changes in the hydrodynamic conditions and microbial
915 influence either in natural hot-spring deposits (Erthal et al., 2017) but also in anthropogenic
916 hyperalkaline, saline environments (Bastianini et al., 2019). Experimental data suggest that the
917 incipient formation of vertically stacking spherulitic calcite resembling pre-salt fascicular calcite habits
918 requires both the intervention of highly supersaturated waters and the presence of microbial-derived
919 polymers (Mercedes-Martín et al., 2021a, b). It was not possible to decipher such microbial influence
920 in our study.

921 At field scale, fascicular calcite crusts are observed in the three successive units, in quite similar
922 proportions (Table 2), with a slight increase in Unit 1. They also gradually expand away from the
923 structural high, from base to top of the succession (Fig. 4). This observation can be compared with the
924 aggrading and subsequent prograding geometries with a gradual flattening outward geometry of
925 clinoforms observed on seismic by Minzoni et al. (2020). They interpreted these features as a basal
926 shallowing-upward, with the filling of accommodation and the development of laterally extended,
927 shallow high-energy settings. The moderate to high $\delta^{18}\text{O}$ values observed for fascicular calcite crusts
928 in Units 2 and 1 are also suggestive of a progressive increase of the evaporitic conditions toward the
929 end of the BVF deposition, which would lead to highly carbonate-saturated lake-waters. The rather
930 constant $\delta^{13}\text{C}$ values compared to the larger range of $\delta^{18}\text{O}$ values (Fig. 16) indicates long water
931 residence times in the paleolake, equilibrium between atmospheric and lake water CO_2 , and
932 evaporative conditions (Pietzsch et al., 2020).

933

934 **5.2 Early diagenetic phases**

935 Syngenetic and eogenetic processes occur in close association in the pre-salt deposits. The initial
936 composition, constituted mainly by Mg-clays and fascicular calcite, is one of the factors influencing the
937 diagenetic modifications and resulting products (Herlinger et al., 2017).

938

939 **5.2.1 Spherulites and Mg-clay preservation**

940 Spherulites are very common and abundant in the BVF, throughout the entire basin. The formation of
941 calcite spherulites is a subject of discussion, having been interpreted as a result of: (1) biotic primary
942 precipitation associated with microbial processes (Chafetz et al., 2018; Kirkham and Tucker, 2018), and
943 (2) eodiagenetic products, replacing and/or displacing the laminated Mg-clays (Wright and Barnett,
944 2015, 2016; Herlinger et al., 2017; Lima and De Ros, 2019; Carramal et al., 2022).

945 In our study, spherulites appear in three sub-facies: Mg-claystones with low and with high proportions
946 of spherulites; and grainstones. These facies are characterized at certain locations of the depositional

947 profile by moderate to intense dissolution of the clay matrix (Fig. 9F), generating porosity. This is in
948 line with the observations of Wright and Barnett (2020), who recognized three different associations
949 of spherulites in the BVF: 1) in association with Mg-clays; 2) with fenestral porosity, lacking Mg-clay;
950 and 3) as re-worked deposits. Moreover, the spherulites observed in our study frequently display
951 inclusions of Mg-clay, with a displacive growth that locally deformed the Mg-clay laminations. These
952 observations support a secondary diagenetic origin for the spherulites rather than primary syngenetic
953 precipitation. The similar $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ range of values than for fascicular calcite also indicate long
954 water residence times in the paleolake and evaporative conditions (Pietzsch et al., 2020).

955 The exact timing of spherulite formation relative to Mg-clay precipitation is also debated. Wright and
956 Barnett (2015, 2020) proposed the precipitation and deposition of an initial Mg-silicate gel, its
957 subsequent crystallization to different types of Mg-clay, in which the spherulites would grow and be
958 potentially re-worked. Based on the strong parallel orientation of the laminated deposits, on their
959 common association with siliciclastic particles and mud, and on the deformation of the Mg-clay
960 laminae by the very early precipitation of the spherulites, we interpreted that they precipitated within
961 an already formed Mg-clay fabric, following the work of Carramal et al. (2022). It must be noted that,
962 based on experimental observations, Mercedes-Martín et al. (2016) suggested that silicate gels might
963 not be required to encourage the formation of polycrystalline calcite grains which otherwise can be
964 the product of interference with organic acids.

965 The amounts of calcite spherulites, shrubs, and Mg-clays in the different facies are apparently
966 controlled by the intensity of the Mg-clay alteration processes in the higher and lower areas, related
967 to different hydrodynamic conditions and intensive dissolution processes. Indeed, we observe that the
968 transitional and higher areas of the depositional profile show low or absence of Mg-clays content and
969 a higher proportion of spherulites. In this setting, the dissolution of Mg-clays could be related to lake
970 level fluctuations, with rare potential subaerial exposure suggested by the flat-pebble breccia and
971 teepee structures observed in laminites facies, or to the dilution of lacustrine waters by meteoric influx
972 (Lima and De Ros, 2019; Carramal et al., 2022). Mg-clays dissolution is also important in the wells

973 located on the flank and in well W6, locations characterized by the presence of faults (Fig. 12). Such
 974 areas would be more prone to CO₂ input by magmatic and hydrothermal activity (Herlinger et al., 2017;
 975 Lima and De Ros, 2020) and to early diagenetic dissolution. Conversely, greater accumulation and
 976 preservation of Mg-clays is observed in the northwest area, characterized by a lower structural position
 977 and by rare faults.

978 Dissolution is a critical process of porosity generation in BVF deposits (Tosca and Wright, 2015),
 979 especially in the Mg-claystones with spherulites, that originally presented a poor reservoir quality. In
 980 addition, the Mg-clay dissolution could play a key role in later diagenesis (Tosca and Wright, 2015;
 981 Carramal et al., 2022). The release into the system of Mg²⁺, SiO₂ and minor Na⁺ would favor the
 982 precipitation of dolomite, silica, and Na-silicates (Tosca and Wright, 2015). This is supported by the
 983 diagenetic features observed in the study area. The distribution of dissolution and dolomite in the Mg-
 984 claystones share a similar increasing trend (Table 5) towards transitional and higher areas. In particular,
 985 medium-crystalline mosaic dolomite is the most common dolomite fabric on the structural high, with
 986 a maximum observed in Unit 1.

987 Table 5 – Statistical summary of the average and maximum amounts of Mg-clay, dolomite, and
 988 secondary dissolution porosity in the Mg-claystones with spherulites.

Regions		Lower		Transitional		Higher		Flank (section C)	
		Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum
Constituents (%)	Diagenetic phase								
Mg-clay	Syngenetic	11.5	55.0	5.0	30.0	1.2	13.0	2.4	42.0
Dolomite	Replacing constituents/Filling porosity	17.5	70.0	34.0	88.0	27.0	80.0	31.0	83.0
Secondary dissolution porosity		1.5	24.0	3.7	19.5	6.5	24.0	7.6	22.0

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997 **5.2.2 Dolomite**

998 After the calcite spherulites and shrubs, dolomite is an important diagenetic mineral phase identified
999 in the BVF sediments, occurring more as a replacement phase than as a pore-filling cement. The
1000 different fabrics observed can be associated with distinct timings.

1001 The lamellar dolomites/magnesites, which mimic shapes of Mg-clays laminations plates are one of the
1002 specificities of the pre-salt sag deposits (Wright and Barnett, 2020; Carramal et al., 2022). These
1003 lamellar aggregates were associated with highly evaporative conditions, as attested by the presence
1004 of magnesite, which requires highly concentrated waters (Farias et al., 2019). Carramal et al. (2022)
1005 suggested that they initially formed filling shrinkage pores generated by Mg-clays dehydration or by
1006 its replacement by kerolite. The well-expressed pseudomorphosis of the Mg-clay laminae suggests very
1007 early diagenesis prior to any significant compaction that would have closed the shrinkage porosity.

1008 Another recurrent form of dolomite is the microcrystalline dolomite, occurring mainly in the transition
1009 zones and Unit 1, largely associated with laminites facies. It is often observed as a replacement of Mg-
1010 clays and commonly occurs in association with crypto- to fine crystalline calcite. Dolomite samples of
1011 the laminites facies show lower ranges of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, compared to calcites sampled in the
1012 same facies and to dolomites sampled in other facies. This may point to episodic changing
1013 environmental conditions and more diluted waters, leading to Mg-clays replacement. In our case
1014 study, the microcrystalline dolomite is precisely observed in the uppermost part of the BVF, and
1015 associated with crenulated laminites, generally interpreted as microbial in origin (Sartorato, 2018;
1016 Artagão, 2018). Given these two points, the role of biological processes in its formation cannot be
1017 totally discarded.

1018 The rhombohedral dolomite is predominantly found associated with fascicular calcite crusts and
1019 spherulites, often “floating” in the interstitial space among the calcite shrubs and spherulites. This
1020 dolomite fabric concentrates mainly in lower areas and Unit 2, reflecting their close association with
1021 Mg-clays. In their depositional model for the BVF, Farias et al. (2019) proposed an alternative model
1022 for the formation of dolomite rhombs. According to them, the beginning of the evaporation process

1023 would result in precipitation of fascicular calcite at the sediment-water interface and precipitation of
1024 rhombohedral dolomites at the brine-air interface, which would then accumulate at the bottom of the
1025 saline lake. With progressive evaporation of the CaCO₃-rich waters increasing the Mg/Ca ratio into the
1026 systems, the dolomitization of the Mg-clay matrix occurred (Farias et al. 2019). This would result in
1027 the deposition of levels of fascicular calcite crusts alternated with levels of dolomite rhombs, and not
1028 in the observed distribution of rhombs “floating” in the interstitial spaces among shrubs. Moreover,
1029 this would not explain the dolomite distribution associated with the spherulites. Finally, in these facies,
1030 the isotopic values observed for dolomite show a similar range of δ¹⁸O values but lower δ¹³C values
1031 compared to calcite of the same facies, which is not the expected behavior for a continuous increasing
1032 evaporation of the lake waters. Given these observations, the rhombohedral dolomite likely results
1033 from the partial replacement of Mg-clays before their subsequent dissolution (Herlinger et al., 2017).

1034

1035 **5.2.2 Silica**

1036 Early diagenetic silica occurs mainly as nodules (Fig. 3G), layers, and pervasive microcrystalline quartz.
1037 Despite the limited amounts of silica observed in the petrographic descriptions, it is more common in
1038 Unit 1, where it is a relevant component in XRD analyses (Fig. 16).

1039 The origins and timing of silica in the BVF are debated. Various forms of silica have been identified in
1040 the pre-salt formations of the conjugate South Atlantic margins, in Brazil (offshore Santos and Campos
1041 Basins) and Angola (Kwanza and Namibe Basins). In the Kwanza Basin, the original carbonate deposits
1042 suffered important diagenesis where silica metasomatism plays a key role with: 1) early replacement
1043 and cementation by silica at relatively low temperature (< 100°C); 2) a second silica generation linked
1044 to high-temperature hydrothermal processes (Tritlla et al., 2018; Teboul et al., 2019). In the Campos
1045 Basin (Pão de Açúcar), pervasive silicification of the original carbonates attributed to a late
1046 hydrothermalism phase, that generated corrosion, porosity formation, and silica replacement and
1047 precipitation (Vieira de Luca et al., 2017). Finally, eogenetic silica precipitation has been interpreted as

1048 Mg-clays replacement (Lima and De Ros, 2019; Wright and Barnett, 2020), linked to freshening lake
1049 periods when relatively lower alkalinity values would favor its precipitation (Wright and Barnett, 2020).
1050 The higher proportions of silica in Unit 1 (and especially within laminites) associated with the presence
1051 of replacive microcrystalline dolomite or calcite and their respective isotopic signatures (see above)
1052 also suggest the alternation of freshening-evaporation lake conditions (Wright, 2022) or reduced
1053 infiltration to sub-bottom aquifers (Mercedes-Martín et al., 2019). Alternatively, a hypothesis of
1054 precipitation as a syngenetic phase is addressed in Sartorato et al. (2020), with the cryptocrystalline
1055 silica resulting from organo-mineralization processes. However, in the study area, this silica phase is
1056 rarely found.

1057

1058 **5.3 Mesogenetic phases and hydrothermal processes**

1059 In our case study, the higher areas and southeast flank show a significant dolomitization process,
1060 evidenced by the increase of pervasive mosaic dolomite, especially within in-situ facies (Mg-claystones
1061 with spherulites, laminites, and fascicular calcite crusts). The higher occurrence of dolomite associated
1062 with a decrease in the amount of Mg-clay may again suggest the replacement of Mg-clay by dolomite.
1063 However, petrographic observations (i.e., Fig. 7E – 7H) showed that the granular mosaic dolomite can
1064 also replace pervasively fascicular calcites and spherulites, grow as a pore-filling cement in the primary
1065 porosity (mostly associated with grainstones) or also co-occur with macrocrystalline quartz as fracture-
1066 infill. This indicates a late eogenetic to mesogenetic timing.

1067 Total replacement of the original carbonate fabrics is frequently observed. Moreover, intervals with
1068 macrocrystalline quartz and coarse blocky calcite cement, are recurrent. The depositional texture
1069 exerted a strong control on the diagenetic modifications (Herlinger et al., 2017). Grainstones and
1070 fascicular calcite crusts exhibit heterogeneous cementation, and more dissolution features, as the
1071 initial porous systems of these sediments may have facilitated fluid circulation. As faults are more
1072 common in those areas, the structural pattern apparently acted as a major controlling factor. The

1073 greater intensity of such diagenetic alterations, as well as the presence of saddle dolomite, could be
1074 related to the circulation of hydrothermal fluids along those fractured zones.

1075 However, extensive hydrothermal processes, like those reported in other portions of the Santos and
1076 Campos Basin (Vieira de Luca et al., 2017; Lima et al., 2020), were not found in the study area.
1077 Silicification has no peculiar spatial distribution and does not exhibit features indicative of
1078 hydrothermal events, as described in the coeval succession of the Pão de Açúcar area of Campos Basin
1079 (Vieira de Luca et al., 2017), or the Parque das Baleias area of Northern Campos Basin (Lima et al.,
1080 2020). Isotopic ratios do not point either to an important hydrothermalism diagenetic overprint, given
1081 the relatively high and positive values. Mineral phases such as macrocrystalline calcite, saddle
1082 dolomite, barite, celestine and fluorite, characteristic of hydrothermal alteration of the pre-salt
1083 formation in the Campos Basin (Lima and De Ros, 2020), have been only observed in a very low
1084 proportion in the study area. The QEMSCAM and XRD analyses also show that these minerals occur
1085 only as minor or even trace amounts. Among the mentioned minerals, saddle dolomite is the most
1086 prominent, and although it is not by itself indicative of hydrothermal processes, it is often associated
1087 with wells located in fault zones, suggesting hydrothermal influence (Herlinger et al., 2017).
1088 Hydrothermal activity contributed only locally to the alteration of the pre-salt carbonates and to the
1089 precipitation of specific mineral assemblages.

1090

1091 **6 Conclusions**

- 1092 • The integrated analysis of sedimentary facies, geochemistry data, and diagenetic features of
1093 the BVF in a key area of the Santos Basin highlighted the roles of depositional setting and
1094 primary constituents on the diagenetic processes. The quantitative characterization of
1095 diagenetic products allowed to recognize spatial and stratigraphic trends of syngenetic and
1096 diagenetic phases, indicating the Mg-clays as an initial substrate.

- 1097 • The pattern of Mg-clays preservation indicates that the structural setting was a strong
1098 determinant of the diagenetic changes, with stronger diagenetic alterations along structural
1099 highs and fault zones.
- 1100 • The precipitation of fascicular calcite was much more developed in higher areas, and their
1101 alternation with Mg-clay precipitates suggests local fluctuations of evaporative conditions of
1102 the basin. The gradual lateral expansion of fascicular calcite away from the structural high
1103 during Unit 1 is associated with a large-scale basinal shallowing upward trend.
- 1104 • The data from the present study suggest that evaporative conditions prevailed in the Aptian
1105 pre-salt succession with some fluctuations in environmental conditions favoring different Mg-
1106 clay minerals in time, distinct isotopic signatures, and variable types and degrees of diagenetic
1107 alterations. In Unit 3 (base), low isotopic ratios, higher detrital siliciclastic/volcanoclastic
1108 grains, and dominance of Mg-smectite suggest relatively dilute waters, with high detrital input
1109 and low to moderate Si/Mg ratios. In Unit 2, the high isotopic values, the progressive increase
1110 of mixed layer kerolite/Mg-smectite and kerolite, the decrease of detrital grains (apart from
1111 the structural high) are indicators of more evaporative conditions and lesser input of water.
1112 Finally, in Unit 1 (top), lower $\delta^{18}\text{O}$ values but high $\delta^{13}\text{C}$, the dominance of kerolite, the
1113 occurrence of silica and dolomitic replacement phases may point to evaporative conditions
1114 but with frequent fluctuations and freshening of the water, explaining the stronger diagenetic
1115 imprint.
- 1116 • Dolomite is one of the most relevant diagenetic phases in the BVF, largely associated with Mg-
1117 clays replacement, developing in several fabrics. Lamellar dolomite/magnesite aggregates,
1118 microcrystalline and rhombohedral dolomite are early diagenetic phases, strongly dependent
1119 on the environmental conditions and variations of the lake water composition. Given its
1120 pervasive aspect and its co-occurrence with macrocrystalline quartz as fracture-infill, mosaic
1121 dolomite is a mesogenetic product. Its preferential occurrence in higher structural positions
1122 and flank regions may suggest a structural control.

- 1123 • The dissolution features indicate an important process of secondary porosity generation,
1124 mainly associated with diagenetic Mg-clays destabilization.
- 1125 • The presence of macrocrystalline calcite, saddle dolomite, barite, celestine and fluorite are
1126 typical products of hydrothermal alteration. Their distribution in the higher structural positions
1127 and in the southeast flank may be related to minor hydrothermal fluids circulation, also having
1128 an impact on the alteration of carbonate phases.

1129

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1414 **8 Figures captions**

1415 Figure 1 – A) Location of the Santos Basin in the southeast region of the Brazilian continental margin.

1416 B) Location of the study area in the middle of the outer high in the Santos Basin (modified from

1417 Papaterra, 2010 and Ysaccis et al., 2019). C) Structural map of the top of the Barra Velha Formation

1418 (base of the evaporitic section), showing the location of the wells (colored dots) in the study area. The

1419 colors refer to the four paleogeographic sectors distinguished in the study area: blue wells located in

1420 the lower part of the depositional profile, green wells located in the transitional area, orange wells

1421 located in the western part of the structural high, and pink wells located in the southeastern flank of

1422 the high. The dashed line represents the approximate location of the interpreted seismic line (D). D)

1423 Interpreted seismic section of the study area, southward to transect B, oriented perpendicularly to the

1424 topographic high and showing the different tectono-stratigraphic formations of the Santos Basin

1425 (modified from Artagão, 2018).

1426 Figure 2 – Lower Cretaceous stratigraphic chart of the Santos Basin, Brazil (modified from Moreira et

1427 al., 2007).

1428 Figure 3 – Photomicrographs highlighting main facies of the Barra Velha Formation: (A) Fascicular

1429 calcite crusts (crossed-polarized light; XPL); (B) Mg-clay matrix engulfed by shrubs (yellow arrow). Note

1430 the shrubs partially dissolved (red arrow) (plane-polarized light; PPL);65; (C) Mg-claystones with

1431 spherulites, showing coalesced and recrystallized spherulites (PPL); (D) Mg-claystones with spherulites

1432 showing a displacement aspect of the Mg-clay (red arrow) (XPL); (E) Mg-claystone with very fine
1433 dolomite crystals (green arrow) and dolomite rhombs (red arrows). Note the absence of spherulites in
1434 this sub-facies (PPL); (F) Laminites composed by microcrystalline calcite. Red arrows highlight
1435 dissolution seams (PPL); (G) Laminites with a crenulated morphology, composed by intercalations of
1436 very fine calcite crystals, dolomite, and organic matter. Red arrows highlight millimeter-scale silica
1437 nodules (XPL); (H) General aspects of organic matter remnants (PPL); (I) General aspects of breccia
1438 features in laminites. Red arrows highlight the intraclasts (XPL); (J) Intraclastic grainstone (Type-A)
1439 composed by fragments of fascicular calcite crusts and spherulites (PPL); (K) Type-B grainstone with
1440 volcanoclastic fragments (red arrow) (PPL); (L) Type-C grainstone (packstone) composed of carbonate
1441 and Mg-clay intraclasts (red arrows), with a minor fraction of siliciclastic grains (PPL).

1442 Figure 4 – Facies spatial and stratigraphic distribution over the three transects (A to C, located on the
1443 map of the study area) and the three stratigraphic units labeled 3 (base) to 1 (top). No interpretation
1444 was proposed for Unit 3 of transect C, as this unit pinches out on the basement. The scale of these
1445 transects is given on the map. LMC= crenulated laminites, GST (A)= intraclastic grainstones, GST (B)
1446 intraclastic grainstone with siliciclastic/volcanoclastic content, SHR= fascicular calcite crusts, LMT=
1447 laminites, SPH= Mg-claystones with higher spherulites content, GST (C) intraclastic grainstones with
1448 Mg-clay content, MGC= Mg-claystones with lower spherulites content.

1449 Figure 5 – Boxplots showing the diversity and amounts of accessory minerals encountered in the Barra
1450 Velha Formation, based on QEMSCAN analyses. A) Proportions of trace minerals. B) Proportions of
1451 minor minerals.

1452 Figure 6 – (A) NW-SE transect showing the spatial and stratigraphic distribution of clay minerals (XRD).
1453 The dashed line represents the Intra-Alagoas unconformity. (B) Clay mineral composition per facies
1454 (SHR= fascicular calcite crusts, GST= intraclastic grainstones, SPH= Mg-claystones with high spherulite
1455 content, MGC= Mg-claystones with low spherulite content, LAM= laminites). The black rectangle on

1456 the last diagram is a reading example: for the samples identified as laminites facies, 33 % do not
1457 present kerolite, and 67 % present between 1-10 % of kerolite.

1458 Figure 7 – Photomicrographs highlighting different dolomite types of Barra Velha Formation: (A)
1459 Lamellar aggregates. The red arrow highlights dolomite rhombs (plane-polarized light; PPL); (B) Very
1460 fine dolomite crystals replacing calcite spherulites and possibly matrix (crossed-polarized light; XPL).
1461 Note the spherulite partially replaced by quartz (red arrow); (C) Rhombohedral dolomite replacing Mg-
1462 clay (PPL); (D) Fascicular calcite crusts with rhombohedral dolomite cement (XPL); (E) In-situ facies with
1463 anhedral dolomite cement. The red arrows highlight the carbonate constituents replaced by dolomite
1464 (PPL); (F) Grainstone with medium to coarse granular mosaic dolomite (indistinct cement and
1465 replacement phase) (PPL); (G) Grainstone with fine granular dolomite cement (PPL); (H) Fascicular
1466 calcite crusts intensely replaced by dolomite and quartz. The red arrows highlight the filling of the
1467 pore-fracture by dolomite and quartz (XPL); (I) In-situ facies with saddle dolomite. Note the sweeping
1468 extinction (red arrow; XPL).

1469 Figure 8 - (A) Mg-clay partially replaced by very fine calcite and dolomite crystals (crossed-polarized
1470 light, XPL); (B) Grainstone constituents with calcite rims. Note the dissolution of the carbonate
1471 intraclasts (plane-polarized light, PPL); (C) Grainstone with fragments of shruvs, spherulites, showing
1472 silica rims and Mg-clay envelops (red arrow). The yellow arrow highlights mosaic calcite filling porosity,
1473 the green arrow highlights calcite coating around grains (XPL); (D) Grainstone with blocky calcite
1474 cement (PPL); (E) Poikilotopic calcite, filling fracture (XPL), partially replaced by chalcedony (red arrow);
1475 (F) In-situ facies with blocky calcite engulfing saddle dolomite cement (PPL); (G) In-situ facies with
1476 intense silicification (XPL); (H) Fascicular calcite crust with quartz cement. Note the quartz replacing
1477 the fascicular calcite (red arrows); (I) Grainstone with silica rims (red arrow) and macrocrystalline
1478 quartz cement (XPL).

1479 Figure 9 – (A) Grainstone with coarse mosaic calcite, replaced by chalcedony (crossed polarized light;
1480 XPL); (B) In-situ facies with cement of dawsonite and euohedral dolomite (plane-polarized light, PPL);

1481 (C) Cement of dawsonite and euhedral dolomite (PPL); (D) Growth-framework porosity enlarged by
1482 dissolution (PPL); (E) General aspects of dissolution in laminites; (F) General aspects of dissolution on
1483 Mg-claystones with spherulites (PPL).

1484 Figure 10 – NW-SE correlation along transect A showing the quantitative distribution of the main
1485 diagenetic minerals in the study area. A) Boxplots of calcite, dolomite, and quartz pore-filling cement
1486 proportions. B) Vertical distribution of Mg-clay, diagenetic minerals (sum of the replacement and
1487 cementation) and dissolution. Values vary between 0 and 80% per sample for the Mg-clay and
1488 diagenetic minerals and between 0 and 60% for the dissolution process. The gamma ray log (GR) is also
1489 plotted. The profile morphology was reconstructed based on the BVF basal boundary assessed from
1490 seismic interpretation (Artagão, 2018), corroborated with the well data that reach the BVF boundary.

1491 Figure 11 – NW-SE correlation along transect B showing the quantitative distribution of the main
1492 diagenetic minerals in the study area. A) Boxplots of calcite, dolomite, and quartz pore-filling cement
1493 proportions. B) Vertical distribution of Mg-clay, diagenetic minerals (sum of the replacement and
1494 cementation) and dissolution. Values vary between 0 and 80% per sample for the Mg-clay and
1495 diagenetic minerals and between 0 and 60% for the dissolution process. The gamma ray log (GR) is also
1496 plotted. The profile morphology was reconstructed based on the BVF basal boundary assessed from
1497 seismic interpretation (Artagão, 2018), corroborated with the well data that reach the BVF basal
1498 boundary.

1499 Figure 12 – NW-SE correlation along transect C showing the quantitative distribution of the main
1500 diagenetic minerals in the study area. A) Boxplots of calcite, dolomite, and quartz pore-filling cement
1501 proportions. B) Vertical distribution of Mg-clay, diagenetic minerals (sum of the replacement and
1502 cementation) and dissolution. Values vary between 0 and 80% per sample for the Mg-clay and
1503 diagenetic minerals and between 0 and 60% for the dissolution process. The gamma ray log (GR) is also
1504 plotted. The profile morphology was reconstructed based on the BVF boundary assessed from seismic
1505 interpretation (Artagão, 2018), corroborated with the well data that reach the BVF boundary.

1506 Figure 13 – Scheme showing the lateral and vertical distribution of the main diagenetic phases in the
1507 study area. Purple line represents the Intra-Alagoas unconformity (between Unit 3 and 2) and the blue
1508 line represents the boundary between Units 2 and 1.

1509 Figure 14 – Boxplots showing the distribution of the different types of dolomite, in different parts of
1510 the study area and stratigraphic units. No data was collected for Unit 3 in the higher area, as it pinches
1511 out. The data of Unit 3 in the flank region are from well W11.

1512 Figure 15 - $\delta^{18}\text{O}$ vs. $\delta^{13}\text{C}$ crossplots. (A) Bulk values per facies; (B) Bulk values per stratigraphic units; (C)
1513 Samples dominated by calcite; (D) Samples dominated by dolomite. For (C) and (D), points correspond
1514 to the average values of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ for the different facies and stratigraphic units. The horizontal
1515 and vertical bars correspond to the first and third quartile of each dataset (when available). SPH= Mg-
1516 claystones with higher spherulite content, MGC= Mg-claystones with lower spherulites content, LAM=
1517 laminites, SHR= fascicular calcite crusts, GST= grainstones of different types (A, B, C).

1518 Figure 16 – Schematic transect showing profiles of bulk mineralogy, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ of the wells W4 and W5.
1519 The well W5 does not have sufficient mineralogy data for correlation.

1520 Table 1 – Statistical summary of the average and maximum amounts of major constituents, Mg-clay
1521 and secondary porosity, in the main facies of the Barra Velha Formation. GST= intraclastic grainstones,
1522 SHR= fascicular calcite crusts, SPH= Mg-claystones with higher spherulites content, MGC= Mg-
1523 claystones with lower spherulites content, LAM= laminites.

1524 Table 2 – Statistical summary of the average and maximum amounts of major diagenetic constituents,
1525 Mg-clay, and secondary porosity, in the stratigraphic units of Barra Velha Formation.

1526 Table 3- Statistical summary of the average and maximum amounts of major diagenetic constituents,
1527 Mg-clay, and secondary porosity of Barra Velha Formation, in different portions of the study area.

1528 Table 4 - $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (Avg.=average value, Q1=first quartile, Q3=third quartile) for each facies and
1529 stratigraphic units (when available), for samples dominated by calcite and dolomite. Correlation
1530 coefficients are calculated for each series when number of samples (n) are sufficient.

1531 Table 5 – Statistical summary of the average and maximum amounts of Mg-clay, dolomite, and
1532 secondary dissolution porosity in the Mg-claystones with spherulites.

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