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Silicification, flow pathways, and deep-seated hypogene dissolution controlled by structural and stratigraphic variability in a carbonate-siliciclastic sequence (Brazil)

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1 **Silicification, flow pathways, and deep-seated hypogene dissolution controlled by**  
2 **structural and stratigraphic variability in a carbonate-siliciclastic sequence (Brazil)**

3

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21

22 **Abstract**

23 Fractured and karstified carbonate units are important exploration targets for the hydrocarbon  
24 industry as they represent important reservoirs. Furthermore, large water reserves and geothermal

25 systems are hosted in carbonate aquifers. This paper documents the relationships between  
26 stratigraphy, structural patterns, silicification, and the spatial-morphological organization of a 3D  
27 multistorey cave system developed in a Neoproterozoic mixed carbonate-siliciclastic sequence. We  
28 found that the combination of lithology, silicification, fracture patterns (controlled by  
29 lithostratigraphic variability), and petrophysical properties control the formation of high or low  
30 permeability zones; their distribution was fundamental for the spatial organization of dissolution  
31 and the compartmentalization of the resulting conduit system in different speleogenetic storeys.  
32 We propose a deep-seated hydrothermal origin for the fluids involved in the main phases of karst  
33 formation. Warm and alkaline hydrothermal fluids caused silica dissolution, followed by chalcedony  
34 and quartz reprecipitation in pore space and fractures. Rising fluids concentrated along through-  
35 going vertical fracture zones in the lower storey, whereas sub-horizontal bedding-parallel fluid flow  
36 was focused on sedimentary packages containing highly silicified dolostones ( $\text{SiO}_2 > 80 \text{ wt\%}$ )  
37 characterized by high permeability. The Calixto Cave is an enlightening example for the complex  
38 speleogenetic history affecting a mixed carbonate-siliciclastic succession where the combined effect  
39 of silicification and hydrothermal karst dissolution can potentially generate high-quality reservoirs.

40

41 **Keywords:** deep hydrothermal karst; hypogene caves; fluid flow; karst reservoirs; speleogenesis

42

### 43 **1. Introduction**

44 Silicification and karst dissolution in carbonate reservoirs are crucial processes that modify textures,  
45 mineralogy, and petrophysical properties of the host rock (Hesse, 1989; Lima et al., 2020; Souza et  
46 al., 2021). Karst features may be the result of rising fluid flow (hypogene speleogenesis; *sensu*  
47 Klimchouk, 2007), whose recharge and solutional efficiency are not connected to meteoric water  
48 percolation (i.e., epigene or supergene speleogenesis). The aggressivity of this rising flow is usually

49 acquired from deep-seated sources, possibly associated with thermal processes, and is independent  
50 of soil or meteoric acids (Palmer, 2000; Audra and Palmer, 2015).

51 Many productive oil and gas deposits hosted in carbonate reservoirs are characterized by  
52 silicification and/or processes that can be assigned to hypogene karstification, like the Parkland field  
53 in Western Canada (Packard et al., 2001), the Tarim basin in China (Wu et al., 2007; Zhou et al.,  
54 2014; Dong et al., 2018; You et al., 2018), pre-salt reservoirs in Santos and Kwanza basins (Girard  
55 and San Miguel, 2017; Poros et al., 2017), and Campos Basin offshore Brazil (De Luca et al., 2017;  
56 Lima et al., 2020). Networks of deep-seated conduits formed by dissolution are often intercepted  
57 during drilling in hydrocarbon exploration within soluble rocks (Maximov et al., 1984; Mazzullo et  
58 al., 1996; Mazzullo, 2004). The result is loss of fluid circulation or borehole collapse (Xu et al., 2017).  
59 Furthermore, carbonate aquifers constitute the most significant geothermal water resources  
60 worldwide (Goldscheider et al., 2010; Montanari et al., 2017) and important groundwater reserves  
61 (Ford and Williams, 2007).

62 Even if less common than conventional carbonate-hosted karst, hypogene speleogenesis has also  
63 been documented in silicified carbonates, quartz sandstones, and quartzite rocks (Sauro et al., 2014;  
64 Souza et al., 2021; La Bruna et al., 2021). Cavities enlarged by solution in quartzites were also  
65 described associated with hydrothermal Sb–Hg mineralization in Kirghizstan (Leven, 1961; Kornilov,  
66 1978) and in Ukraine (Tsykin, 1989).

67 The presence of solutional voids and karst porosity in quartzites or highly silicified carbonates is  
68 thought to be common at depth where the solubility of silica is larger due to the high temperatures  
69 and alkalinity of circulating solutions (Lovering et al., 1978; Andreychouk et al., 2009; Klimchouk,  
70 2019; Sauro et al., 2014; Wray and Sauro, 2017). However, in the existing literature, only few  
71 publications addressed the link between silicification and the stratigraphic-structural control on  
72 karst development, with its relative implications in the study of carbonate reservoirs (Souza et al.,

73 2021; La Bruna et al., 2021). These studies focused on the main geological, diagenetic, and structural  
74 framework of the cave-hosting rocks, without exploring the speleogenetic mechanisms involved in  
75 the formation of solutional porosity.

76 In the past decades there has been a growing interest on the source of karst forming fluids,  
77 subsurface flow pathways, and geometry of the conduits' networks, with particular attention to  
78 deep hypogene speleogenesis (Klimchouk, 2007, 2009, 2019; Audra et al., 2009; De Waele et al.,  
79 2009, 2016; Audra and Palmer, 2015; Ennes-Silva et al., 2016; Klimchouk et al., 2016; Columbu et  
80 al., 2021; Spötl et al., 2021). Hypogene dissolution at depth has strong implications for carbonate  
81 reservoir properties and quality, given that the geometry of the conduits and their spatial  
82 distribution may focus fluid flow and generate strong heterogeneities in porosity and permeability  
83 (Klimchouk et al., 2016; Balsamo et al., 2020). The characterization of karst reservoir porosity is,  
84 therefore, a challenging task, also because most of the dissolution voids are below seismic  
85 resolution (Cazarin et al., 2019; Lyu et al., 2020; La Bruna et al., 2021). To fill this knowledge gap and  
86 optimize decision-making strategies in the conceptualization and characterization of karst  
87 reservoirs, detailed investigations on analog accessible caves are needed (Balsamo et al., 2020;  
88 Bertotti et al., 2020; La Bruna et al., 2021; Pisani et al., 2021; Pontes et al., 2021).

89 Karst porosity and permeability development can result from different processes. Several factors,  
90 such as lithology, hydrogeologic setting and source of aggressive fluids (epigene vs. hypogene),  
91 geological structures, stratigraphy, geochemistry, and climate contribute to the large variety of karst  
92 features, their morphologies, and the spatial organization of conduit networks (Klimchouk et al.,  
93 2000; Palmer, 2000; Ford and Williams, 2007). In carbonate sequences, fracture properties, pattern,  
94 and mechanical stratigraphy may affect hypogene karst development, given that fluid flow in low  
95 primary porosity rocks is mainly controlled by open discontinuities (i.e., joints) (Antonellini et al.,  
96 2014; Guha Roy and Singh, 2015; Lei et al., 2017; Lavrov, 2017; Giuffrida et al., 2019, 2020). The

97 spatial arrangement of bedding interfaces, stratabound fractures, stylolites, fault zones, and  
98 through-going vertical fracture-zones generates a complex tridimensional network that controls  
99 fluid flow in hypogene conditions. In this context, mechanical stratigraphy and fracture distribution  
100 cause a strong anisotropy in the tridimensional organization of flow pathways, speleogenesis, and  
101 conduit geometry (Klimchouk et al., 2009; Klimchouk et al., 2016; Klimchouk, 2019; Balsamo et al.,  
102 2020; La Bruna et al., 2021).

103 The objective of this work is to unravel the structural and stratigraphic controls on hypogene  
104 dissolution in a complex 3D cave network (Calixto Cave, Northeastern Brazil) characterized by  
105 silicification of carbonate layers. Following a multidisciplinary approach, quantitative structural  
106 analyses, stratigraphic, petrographic and petrophysical investigations on rock samples were used to  
107 characterize the sedimentary sequence in the cave. Furthermore, compositional analysis (XRD, XRF)  
108 and SEM-EDS investigations on cave mineral deposits and bedrock were performed to study  
109 silicification and solutional micro-textures. Combining this approach with a comprehensive  
110 geomorphological analysis of the conduit system, we assessed the role of structural-stratigraphic  
111 variability in controlling the karst-forming flow pathways and the resulting spatial-morphological  
112 organization of the conduit system. The results from this study may be of great interest for  
113 improving conceptual models of deep-seated hypogene dissolution in silicified carbonate units,  
114 allowing more reliable reservoir or aquifer reconstructions, and optimizing conceptual predictive  
115 models.

116

## 117 **2. Study area**

### 118 **2.1 Geological setting**

119 The Calixto Cave System (CCS) is a 1.4 km long and 55 m deep cave located in the Una-Utinga Basin  
120 in the São Francisco Craton (State of Bahia, Brazil) (Fig.1).

121

122 Figure 1. Simplified geological map showing the location of the Calixto Cave system (CCS) and the  
123 main structural lineaments of the São Francisco Craton (light blue color in the inset; modified after  
124 Almeida et al., 2000; Peucat et al., 2011, and Misi et al., 2011). Dike lineaments in the Bahia region  
125 were extracted from the 1:1,000,000 geological map of the State of Bahia  
126 (<https://rigeo.cprm.gov.br/xmlui/handle/doc/8665>).

127

128 The São Francisco Craton is the western portion of a large crustal block segmented during the  
129 Pangea breakup and the opening of the South Atlantic Ocean (Almeida et al., 2000; Misi et al., 2011).  
130 The Una-Utinga basin (Fig.2A) hosts a sedimentary succession of Neoproterozoic age (Una Group),  
131 which overlies the Archean and Paleoproterozoic basement composed of metamorphic and igneous  
132 rocks (Fig.2B). The Una-Utinga and the Irecê basins formed during rifting of the Rodinia  
133 supercontinent between 950 and 600 Ma (Condie, 2002). The Bebedouro *Fm*, composed of glacio-  
134 marine diamictites, marks the bottom of the Group (Misi and Veizer, 1998; Misi et al., 2011). The  
135 Salitre *Fm* overlies in stratigraphic unconformity the Bebedouro *Fm* and is characterized by a mostly  
136 carbonate succession with variable thickness (minimum 500 m), intercalated with siliciclastic or  
137 heterolithic beds (Misi, 1993; Misi et al., 2007, 2011; Santana et al., 2021).

138 Several geodynamic and tectonic events occurred in this area from ca. 740 to 560 Ma (Brito Neves  
139 et al., 2014). These events are broadly referred to as the Pan-African Cycle, or the *Brasiliano* Orogeny  
140 in South America (Teixeira et al., 2007). Strain in the Salitre *Fm* during the *Brasiliano* Orogeny  
141 resulted in a complex network of E-W- and NNE-SSW-trending deformed belts (Balsamo et al., 2020;  
142 Cazarin et al., 2021). These deformed belts include several fracture sets and a complex architecture  
143 of gentle folds characterized by fracture corridors localized in the hinge zone of the folds (Pontes et  
144 al., 2021). The most recent deformation events (540–510 Ma) were characterized by fissure

145 magmatism and associated hydrothermal fluid flow along faults and fracture zones (Almeida et al.,  
146 2000; Guimarães et al., 2011; Klimchouk et al., 2016).

147

148 Figure 2. A) Simplified geological map of the Una-Utinga basin. B) Simplified stratigraphic log of the  
149 main formations outcropping in the Una Group (modified from Santana et al., 2021). C) Topographic  
150 plan map of the CCS. The rose diagram in the right corner shows the frequency distribution of  
151 conduits' orientation. Red circles indicate study points and depth values are reported for different  
152 locations. Cave map acquired by *Grupo Pierre Marin de Espeleologia* (GPME) in 2008. The  
153 coordinates shown in the lower-right corner refer to the cave entrance.

154

## 155 **2.2 Hypogene caves and hydrothermal mineralization in the São Francisco Craton**

156 The Una-Utinga and the Irecê basins host hundreds of karst systems, some of which are among the  
157 longest known in South America, with a combined cumulative length of over 140 km (Auler, 2017).  
158 Some of these karst systems developed in hypogene conditions by rising hydrothermal fluids that  
159 migrated upward through the fractured basement and that were horizontally confined by low-  
160 permeability (seal) layers (Klimchouk et al., 2016; Cazarin et al., 2019; Balsamo et al., 2020; Pontes  
161 et al., 2021). Following this, late-stage supergene sulfuric acid speleogenesis developed in shallow  
162 aquifers due to oxidation of bedrock sulfides (Auler and Smart, 2003).

163 Other works focused on silicified carbonate units and hypogene speleogenesis in the São Francisco  
164 Craton. Bertotti et al. (2020) highlighted the local development of caves associated with strike-slip  
165 fault zones and late silicification of dolostone layers (Morro Vermelho Cave, Irecê basin). North of  
166 the study area, in the Mesoproterozoic carbonates of Cabloco *Fm*, the Crystal Cave karst system  
167 shows dissolution features controlled by stratigraphy, deep tectonic structures, fracture corridors  
168 in fold hinges, and highly silicified layers (Souza et al., 2021; La Bruna et al., 2021). Furthermore,



169 several cave systems in the Salitre *Fm* contain veins and deposits associated with hydrothermal  
170 mineral assemblages comprising quartz, chalcedony, barite, apatite, K-feldspar, hyalophane, iron  
171 oxides/hydroxides, iron-titanium oxides, and minor amounts of monticellite and diopside (Cazarin  
172 et al., 2019; Souza et al., 2021). Hydrothermal mineral assemblages and ore deposits have also been  
173 identified in the Una-Utinga and Irecê basins and their surrounding areas. These assemblages form  
174 Mississippi Valley-type (MVT) deposits containing quartz, sphalerite, barite, and galena (Kyle and  
175 Misi, 1997; Misi et al., 2012; Cazarin et al., 2021).

176 The Cambrian tectono-thermal event (~ 520 Ma) has been indicated as one of the probable drivers  
177 for hypogene speleogenesis in the Salitre *Fm* (Klimchouk et al., 2016). Late fracture reactivation and  
178 hydrothermal events during the Pangea breakup in the Jurassic-Cretaceous have also been  
179 proposed for the cave systems located in the northern part of the craton (Klimchouk et al., 2016;  
180 Cazarin et al., 2019). Other studies (Bertotti et al., 2020; Souza et al., 2021) proposed that the  
181 interplay between Si-rich fluids and karstification happened in mesodiagenetic deep-seated  
182 conditions during the late Proterozoic. If this is true, the solutional cavities in the silicified  
183 carbonates of the São Francisco Craton would be among the oldest known on Earth.

184

### 185 **3 Material and methods**

#### 186 **3.1 Cave morphological and topographic analysis**

187 Karst features are the result of mineral dissolution by fluid flow and fluid-rock interactions  
188 (Klimchouk et al., 2016). Morphologies and patterns of karst conduits, together with their infillings,  
189 are the fundamental attributes that reflect their origin and evolution. The spatial and morphological  
190 organization of the CCS conduits were analyzed by direct field investigation, detailed morphological  
191 observations, and the processing of a speleological topographic survey (Fig.2C) made in 2008 by the  
192 *Grupo Pierre Martin de Espeleologia* (GPME).

193 The CCS morphology and geological features were studied and mapped in 10 representative sites  
194 (Fig.2C) and systematically documented throughout the whole karst system. The morphological  
195 analysis of the CCS included the study of cave macro-morphology in plan, profile, and 3D view as  
196 well as the examination of spatial-temporal relationships between the identified morphological  
197 features and the local stratigraphy, structures, and former fluid flow pathways.

198 The cave survey was processed using the *cSurvey* software (<https://www.csurvey.it/>) to obtain a  
199 tridimensional, geographically referenced model corrected for the 2008 magnetic declination. The  
200 *cSurvey* software allows reconstructing the volumes of the cave by interpolation of azimuth,  
201 distance, and inclination measurements collected with a handheld modified Leica DISTOX laser-  
202 meter (Heeb, 2009). The *cSurvey* data were merged with the manually edited sketch maps drafted  
203 by the surveyor (Heeb, 2009; Lønøy et al., 2020; Pisani et al., 2021). With this approach, a raw 3D  
204 georeferenced model of the whole 1.4 km-long system was assembled. Following this step, the  
205 planimetry of the cave was processed in *ArcGis* software to manually measure the preferential  
206 direction of the conduits, normalized by the length of each cave segment (same method described  
207 in Pisani et al., 2019).

208

### 209 **3.2 Stratigraphic and structural analyses**

210 We performed a detailed lithological and sedimentary facies description at several representative  
211 sites in the CCS (Fig.2C) using outcrop observations and thin section petrographic analysis. Rock  
212 samples were collected using a geological hammer or a handheld electric driller to extract mini drill-  
213 cores from the cave walls (3.8 or 2.5 cm in diameter). 23 standard-thickness polished thin sections  
214 stained with blue epoxy were prepared and analyzed with an optical petrographic microscope both  
215 under transmitted and reflected light. Following the field and petrographic observations, the  
216 sedimentary sequence hosting the cave was subdivided in units, grouped according to their

217 compositional and textural features. Carbonate rocks were classified based on their texture  
218 according to Dunham (1962) and Embry and Klovan (1971).

219 Structural measurements were collected in the survey points to unravel the nature, attitude, and  
220 kinematics of the observed fracture sets. Structural elements in the CCS were measured with classic  
221 geo-surveying tools (compass and clinometer) and classified according to their type: open-mode  
222 fractures (joints and veins), pressure solution seams (stylolites), faults, and fracture zones (FZ;  
223 defined as zones of through-going clustered fractures with an intensity larger than the background  
224 of the host rock). Joints, veins, and FZ include stratabound (bedding confined) and non-stratabound  
225 (through-going) structures. Statistical analysis of fracture sets was performed with the *DAISY3*  
226 software plotting lower-hemisphere equal-area stereograms, rose diagrams, and frequency  
227 histograms (Salvini, 2004). Grouping of the different fracture sets was performed by calculating the  
228 best-fit Gaussian-curves for each cluster of orientations (Salvini, 2004; Del Sole et al., 2020).

229 Furthermore, fracture attributes were measured along 12 linear scanlines in 5 representative  
230 transects (Marrett et al., 1999; Ortega et al., 2006) to estimate fracture permeability from field data  
231 (Giuffrida et al., 2019, 2020). The following parameters were measured for each discontinuity along  
232 the transect: attitude, distance from the origin of the scanline, type, mechanic aperture, height  
233 (when measurable), roughness, and infilling (if present). Along the transects, we also calculated  
234 fracture linear intensity  $P_{10}$  (Ortega et al., 2006) and the coefficient of variation (Cv), defined as the  
235 ratio between the  $\pm 1\sigma$  standard deviation and the mean value of fracture spacing of individual  
236 fracture sets (Odling et al., 1999; Zambrano et al., 2016; Pontes et al., 2021).

237 The mechanic aperture (B) and roughness coefficient (JRC) of the fractures were measured using  
238 analogical profile comparators developed by Barton and Choubey (1977), and Ortega et al. (2006).

239 Estimates for permeabilities of individual fractures were obtained using the parallel-plate model  
240 approximation (Taylor et al., 1999; Philipp et al., 2013; Giuffrida et al., 2020). Hydraulic aperture ( $b$ )

241 was computed by considering the JRC and by applying the following equation (1) (Barton and  
242 Choubey, 1977; Olsson and Barton, 2001; Giuffrida et al., 2020):

$$b = B^2 / JRC^{2.5} \quad (1)$$

243 Additionally, the real fracture spacing between individual features was calculated applying the  
244 Terzaghi method (1965).

245 The bulk permeability for each unit was then modeled as an Equivalent Porous Media (EPM; Taylor  
246 et al., 1999) combining the values of bedding-normal and bedding-parallel rock plugs permeability  
247 (considered equivalent to matrix permeability), fracture spacing, and estimated fracture  
248 permeability of individual sets. Bedding-parallel average permeability normal to the main fracture  
249 sets ( $K_N$ ) and bedding-normal average permeability parallel to the main fracture sets ( $K_P$ ) were  
250 calculated based on an elementary cubic volume of 1 m side using the equations described in Freeze  
251 and Cherry (1979) and reported in the Supplementary Material section of this article.

252 Given that natural fractures are neither smooth nor parallel, the reliability of applying the parallel-  
253 plate model to compute fracture permeability must be carefully considered (Zhang, 2019). Since our  
254 purpose was limited to evaluate the relative variability in fracture patterns and properties within  
255 the different sedimentary units, we did not perform any further analysis. Stochastic fracture  
256 aperture distribution and numerical modelling to upscale or calculate equivalent fracture  
257 permeability at confining pressure (Cacas et al., 1990; Flodin et al., 2004; Antonellini et al., 2014;  
258 Bisdorn et al., 2016; Zheng et al., 2020; Smeraglia et al., 2021) are beyond the scope of this work.

259

### 260 **3.3 X-ray analyses**

261 Eighteen rock samples from the sedimentary sequence exposed in the cave were collected and  
262 analyzed to measure the major (>1 g/100 g) and minor (0.1–1.0 g/100 g) compounds with X-ray  
263 fluorescence (XRF). The powdered samples were analyzed with a sequential wavelength dispersive

264 XRF spectrometer equipped on a Malvern Panalytical - model Zetium. The analyses were performed  
265 after STD-1 calibration and the values were normalized to 100 wt%. Finally, loss of ignition (LOI) was  
266 calculated heating the samples at 1020°C for 2 hours. The main mineral phases were also  
267 investigated with an Empyrean-Panalytical X-ray diffractometer mounting a Cu-anode ( $\lambda = 1.542\text{\AA}$ ;  
268 2.2 kW, range  $2\theta = 2.5\text{--}70^\circ$ , step size =  $0.02^\circ 2\theta$ ) at the *Laboratório de Caracterização Tecnológica*  
269 from the University of *São Paulo* (Brazil). The identification of crystalline phases was performed  
270 using the standard dataset of the PDF2 database from the ICDD (International Centre for Diffraction  
271 Data) and ICSD (Inorganic Crystal Structure Database). XRD analyses were also performed on  
272 selected samples of cave sediments at the *Laboratório do Centro de Tecnologias do Gás e Energias*  
273 *Renováveis-LTG-ER, Laboratório de Ensaios de Materiais* (Lagoa Nova, Brazil) with a Shimadzu XRD-  
274 6000 X-ray diffractometer mounting a Cu-anode (current: 20 mA, voltage = 40 kV, range  $2\theta = 5\text{--}80^\circ$ ,  
275 step size =  $0.02^\circ 2\theta$ ).

276

### 277 **3.4 SEM-EDS analyses**

278 SEM-EDS analyses were carried out on five selected polished thin-sections from highly silicified rocks  
279 with a Tescan Vega 3 LMU equipped with an Energy Dispersive Spectroscopy (EDS) EDAX Apollo-X  
280 SDD detector, at 20 kV accelerating voltage, 1.2 nA beam current, and 5-10  $\mu\text{m}$  beam diameter,  
281 operating at the DISTAV Department of the University of Genova. Additionally, *in situ* SEM analyses  
282 on eight silicified bulk rock fragments were performed at the BIGEA Department of the University  
283 of Bologna with a JEOL JSM-5400 equipped with an IXRF system for X-ray EDS spectroscopy to  
284 evaluate the microtexture and morphologies of quartz grains. All samples were prepared with gold  
285 coating and imaged both as backscattered electron (BSE) images or secondary electron (SE) images.

286

### 287 **3.5 Petrophysical properties**

288 Petrophysical analyses were performed to measure porosity, permeability, density, and pore  
289 volume on 50 rock plugs covering the whole stratigraphic sequence exposed in the cave. The  
290 analyses were performed using a *Coreval 700* unsteady-state gas permeameter and porosimeter at  
291 the *LABRES-Departamento de Engenharia de Petróleo* of the *Universidade Federal do Rio Grande do*  
292 *Norte*. Petrophysical properties were measured on 2.5 cm-diameter and 3 cm-high rock plugs cut  
293 from mini-drill cores extracted from the cave walls. For each unit, parallel and normal (or oblique)  
294 to bedding samples were collected to quantify the permeability tensor. The pore volume  
295 calculations were made in a N<sub>2</sub> gas injection porosimeter at a confining pressure of 600 psi.  
296 Additionally, the Klinkenberg correction was applied to calculate the permeability in mD  
297 (Klinkenberg, 1941; Araújo et al., 2021).

298

## 299 **4 Results**

300 The results of our multidisciplinary study in the CCS are reported in the following sections. The  
301 sedimentary and speleogenetic units in the cave are presented moving from bottom to top of the  
302 sequence, describing their main sedimentary, petrographic, compositional, and geomorphological  
303 characteristics. Microtextural, and mineralogical data associated with the silicified units are  
304 illustrated. Finally, the structural and petrophysical properties of the different sedimentary and  
305 speleogenetic units are shown.

306

### 307 **4.1 Sedimentary and speleogenetic units in the CCS**

308 The sedimentary sequence exposed in the CCS includes the following sedimentary units (Fig.3A): (A)  
309 dolostones with tabular cross-stratification, (B1) highly silicified dolostones, (B2) heteroliths, (B3)  
310 siliciclastic tempestites, and (C) cherty dolostones. The bulk chemical and mineralogical  
311 compositions of 18 samples from the entire sedimentary succession and of four cave sediment

312 samples are reported in the Supplementary Material of this article. XRF results are also reported in  
313 the diagrams of Figure 4.

314 Based on its topography and tridimensional organization (Fig.3), the CCS can be classified as a 3D  
315 multistorey cave system (Audra et al., 2009; Audra and Palmer, 2015). The spatial organization of  
316 the conduit system and its morphology are strongly heterogeneous and reflect the vertical  
317 stratigraphic variations in the sedimentary column. Four speleogenetic units, grouped based on  
318 their morphological, geometric, and genetic characteristics, are defined from bottom to top as:  
319 lower storey (Fig.3B), middle storey (Fig.3C), upper storey (Fig.3D), and doline entrance (Fig.3E).

320 The network of conduits shows four clustered orientation trends in map view (Fig.2C): the NE-SW  
321 (N35E-N45E) and NW-SE (N125E-N135E) trends are the most frequent whereas the N-S (N0E-N10E)  
322 and E-W (N90E-N100E) are secondary trends. The cave does not show the typical geomorphic  
323 features deriving from epigenic speleogenesis (i.e., lack of surface-derived sedimentation, vadose  
324 speleogens, scallops or notches, etc.) and any link to surface geomorphology and drainage, except  
325 for the collapsed doline entrance. The typical cave sediments in the CCS are authigenic, deriving  
326 from block collapse or degradation by condensation-corrosion of the host rock. Secondary minerals  
327 resulting from guano-related processes (gypsum crystals and powders, phosphate crusts) are also  
328 present.

329  
330 Figure 3. A) Lithostratigraphic log of the sedimentary sequence exposed in the CCS, subdivided  
331 according to the units described in the main text. The 3D model extracted from the topographic  
332 survey of the cave is also shown. B) Lower storey typical morphologies, with phreatic spongework  
333 patterns, blind-ending passages, and rising conduits. White crusts covering the walls are calcite  
334 coralloids. C) Middle storey morphology with sub-elliptical or sub-rounded stratigraphically  
335 confined conduits. The longest and most developed sector of the CCS (expressed with green colors

336 in the 3D model) belongs to this unit. D) Typical shapes and dimensions of the upper storey conduits  
337 with small secondary passages. Condensation-corrosion features are commonly observed next to  
338 the entrance. E) Collapsed doline entrance. Red soil and debris are transported in the upper sector  
339 of the CCS by recent but ephemeral mudflows and streams. Bedding ( $S_0$ ) is shown with dashed  
340 yellow lines.

341

342 Figure 4. XRF bulk rock chemical composition of 18 representative hand samples collected in the  
343 cave and grouped according to their sedimentary unit. For the detailed description of the samples,  
344 the reader is referred to the Supplementary Material of the article.

345

#### 346 *4.1.1 Lower storey – Unit A*

347 The lower storey spans from the cave bottom to 35 m depth relative to the surface. The rocks  
348 exposed are medium to thick beds of dolostones with tabular cross-stratification (Fig.5A). Bedding-  
349 parallel stylolites are commonly observed, and they define the mechanical layering (spacing from a  
350 few cm up to 60-80 cm). This storey is characterized by vertical chambers with spongework  
351 morphologies (Fig.3B), rising conduits, cupolas, blind ending passages, and rift-like discharge  
352 feeders localized along the intersection of multiple fracture sets, faults, or FZ (Fig.5C). Such  
353 geomorphic features are typical (but not exclusive) of hypogene caves (Klimchouk, 2007, 2019;  
354 Audra et al., 2009; De Waele et al., 2009, 2016; Audra and Palmer, 2015). Fractures controlling the  
355 localization of feeders and rising conduits often present cm-wide reactive fronts (Fig.5B) and  
356 bleaching halos (whitening fabric due to fluid-rock interactions indicating mobilization of metal ions;  
357 Ming et al., 2016).

358 Dolostones have a crystalline texture (Fig.5D) deriving from the dolomitization of pristine ooidal  
359 grainstones (or less common wackestones) with terrigenous detrital clasts (mainly sub-rounded



360 quartz grains, Fig.5E) and fine pyrite crystals, often replaced by pseudomorphs of iron-oxides and  
361 hydroxides. The original ooidal texture is occasionally visible in thin sections (Fig.5E). Porosity is  
362 mainly represented by vuggy, moldic or intercrystalline pores, often filled by euhedral mega-quartz,  
363 K-feldspar (microcline) or apatite crystals (Fig.5D and 5F). White crusts of coralloid calcite growing  
364 on the dolostone rock characterize the cave walls at the bottom of the lower storey (Fig.3B).

365

366 Figure 5. Mesoscale (outcrop) and microscale (thin section) observations in the lower storey  
367 developed in unit A. A) Tabular cross-stratification with foresets occasionally preserved from the  
368 dolomitization process. B) Vertical-down view of a typical rift-like feeder localized on a NW-SE  
369 striking fracture zone composed of sub-parallel joints with bleaching reactive halos (pointed by the  
370 yellow arrows). C) Vertical-down view of a rift-like feeder localized at the intersection between NW-  
371 SE and N-S striking fracture zones. Nearby fractures are boxwork veins filled with quartz. D)  
372 Dolostone with crystalline texture and vuggy porosity filled with mega-quartz crystals (indicated by  
373 yellow arrows) and K-feldspar (microcline with typical cross-hatched twinning). Image under cross-  
374 polarized light. E) The original ooidal grainstone texture is occasionally preserved in the dolostone.  
375 Sub-rounded terrigenous detrital quartz is common in unit A. Image under parallel-polarized light.  
376 F) Detail of the dolomite grains and cement, with moldic porosity filled by quartz. Relict euhedral  
377 dolomite grains are included in the quartz cement. Image under parallel-polarized light. Label  
378 abbreviations: J (joint), V (veins), FZ (fracture zone), Qtz-f (mega-quartz fillings), Kfs-f (K-feldspar  
379 fillings), Qtz-cl (quartz detrital clast), Dol (dolomite).

380

#### 381 *4.1.2 Middle storey – units B1, B2 and B3*

382 The middle storey includes the most interesting and longest portion of the CCS, characterized by a  
383 maze network of sub-horizontal galleries developed between 35 and 31 m of depth from the

384 surface. This section contains a mixed carbonate-siliciclastic interval (~4 m-thick, Fig.6A) hosting  
385 ~80% of the entire cave passages.

386 The lower part of the middle storey is developed in unit B1, a 1.8 m-thick dolostone pack, with ooidal  
387 wackestone or mudstone (dolomicrite) textures, characterized by intense silicification ( $\text{SiO}_2 > 80$   
388 wt%, Fig. 4). Layering and ooidal structures are rarely preserved. Micro-crystalline quartz (defined  
389 as Qtz-A, forming chert) is concentrated in nodules or irregular layers replacing the dolomite grains  
390 (Fig.6B and 6C) and as cement between residual dolomite often associated with iron oxides and less  
391 frequently with pyrite. Residual dolostone and Qtz-A (chert) show abundant vuggy and fracture  
392 porosity. Open fractures and vuggy pores are partially filled with euhedral blocky mega-quartz (Qtz-  
393 B) and chalcedony quartz (Qtz-C), both having mineral inclusions that will be further described in  
394 the following sections.

395 The highly silicified package is sealed by unit B2, a 0.9 m-thick interval characterized by the  
396 alternation of thin heterolith layers (defined as a sedimentary structure made up of interbedded  
397 deposits of sand/silt and mud formed in a tidal environment; Reineck and Wunderlich, 1968), marly  
398 dolostones with detrital clasts, and dolomicrites with chert nodules (Fig.6D and 6E). Heteroliths are  
399 composed of mm-thick intercalations of mud and silt with wavy bedding (Fig.6D) or dolostones with  
400 ooidal grainstone texture with terrigenous detrital clasts and coarse silt grain size. Pyrite crystals  
401 and their iron oxides/hydroxides associated pseudomorphs are common in unit B2.

402 This heterolithic facies is capped by a 1.1 m-thick interval (unit B3) of graded coarse-to-fine  
403 siltstones (Fig.6F) organized in a rhythmic sequence with (from bottom to top) parallel lamination,  
404 hummocky-cross-stratification, and cross-lamination with climbing ripples, identified as a  
405 tempestite facies (Myrow and Southard, 1996). In the upper part of the unit, some hybrid  
406 carbonate-siliciclastic tempestites show massive, graded beds of intraclastic rudstones and coarse

407 sandstones with carbonate intraclasts and dolomitized ooids (Fig.6G). Iron oxide and hydroxide  
408 stains are commonly found in the tempestite facies (Fig.6F).

409

410 Figure 6. Mesoscale (outcrop) and microscale (thin section microphotographs) observations in the  
411 middle storey developed in units B1, B2, and B3. A) Outcrop view of the sedimentary interval  
412 between unit B1 and unit B3. Letters in the circles point to the locations of the microphotographs  
413 displayed in this figure. B-C) Micro-crystalline quartz (Qtz-A) replacing dolomite grains and cement  
414 in unit B1. Solutional pores and enlarged fractures are filled with euhedral blocky mega-quartz (Qtz-  
415 B) or chalcedony-spherulitic quartz (Qtz-C). Qtz-C is lining the solutional voids. Images under cross-  
416 polarized light. D) Heterolithic texture in unit B2, with sub-mm to mm-thick intercalations of clay  
417 and silt characterized by wavy-bedding. Image under parallel-polarized light. E) Marly dolostone  
418 with dolomicrite matrix and high content of terrigenous detrital grains composed of quartz and K-  
419 feldspar. Image under parallel-polarized light. F) Siltstone in the tempestite facies of unit B3.  
420 Siltstones have a high porosity at thin section scale and present disseminated iron oxides-  
421 hydroxides. Image under parallel-polarized light. G) Rudstone texture in unit B3 made of Intraclasts  
422 (highlighted in yellow) and detrital grains composed of quartz and K-feldspar. Image under parallel-  
423 polarized light. Label abbreviations: r-dol (relict dolomite), Qtz-V (quartz veins), Qtz-A (micro-  
424 crystalline chert), Qtz-B (euhedral blocky mega-quartz), Qtz-C (chalcedony), Kfs-cl (detrital K-  
425 feldspar clast), Qtz-cl (detrital quartz clast), Intra-cl (carbonate intraclasts).

426

427 The middle storey is a vast network of sub-horizontal passages with a maze pattern, connected to  
428 the lower storey by rising narrow feeders or conduits (Fig.7A). The main horizontal galleries are  
429 confined in the highly silicified unit B1, below the heterolithic/siliciclastic interval of units B2 and B3  
430 (Fig.7B). Just below unit B2, there are extensive mega-quartz (Qtz-B) or chalcedony (Qtz-C) mineral

431 deposits filling vuggy pores and veins (Fig.7A). Most of these quartz-rich mineral deposits are  
432 associated with pore space developed in the micro-crystalline quartz facies (chert, Qtz-A) or,  
433 secondarily, in the residual dolostone facies (Fig.7C).

434 The sub-horizontal galleries have a sub-elliptical or circular shape (Fig.3C and 7B) with a stepping  
435 roof profile, which reflects the collapse of layers in the ceiling above the silicified unit B1. Dolostones  
436 and marls in unit B2 have a cm-thick crushed texture at the contact with the cave walls. The  
437 pavements are made up of collapsed layers from the overlying units and soft white powders  
438 composed of gypsum and minor amounts of iron oxides/hydroxides or guano-derived phosphates.  
439 Secondary phosphates and iron-manganese oxides/hydroxides have also been found as  
440 overgrowths on the host rock. Calcite speleothems from percolation/evaporation of meteoric water  
441 decorate the walls and pavements in different sites of the middle storey.

442

443 Figure 7. A) Rising conduit localized in the dolomitized grainstones of unit A, at the top contact with  
444 units B1 and B2 where the middle storey (picture in box B) develops. Note the high concentration  
445 of quartz-rich mineral deposits in the upper part of unit B1. B) Sub-horizontal and rounded galleries  
446 in the middle storey. Galleries are organized in a maze network confined by units B2 and B3.  
447 Frequent collapses and evidence of dissolution by condensation-corrosion in the dolostone layers  
448 of units B2 and B3 contributed to the enlargement of the passages. C) Hand sample taken in the  
449 silicified unit B1 (location pointed in the picture in box B). Secondary guano-related phosphatic  
450 overgrowths (identified by SEM-EDS, Tab.1) form brown crusts on the mega-quartz crystals. Vuggy  
451 porosity (barren or filled) is concentrated in Qtz-A. Labels abbreviations: Qtz-f (undifferentiated  
452 quartz deposit), Qtz-A (micro-crystalline chert), Qtz-B (euhedral blocky mega-quartz), Qtz-C  
453 (chalcedony).

454

455 *4.1.3 Upper storey and doline entrance – unit C*

456 The upper part of the CCS, from the entrance at the surface down to a depth of approximately 31  
457 m, is characterized by isolated and small sub-horizontal galleries (Fig.3D) connected with the middle  
458 storey by inclined or vertical conduits developed along through-going fracture zones. These small  
459 and short galleries are hosted in cherty dolostone layers (Figs.8A, 8B, 8C) made up of thin- to  
460 medium-thick intercalations of dolomicrites and highly silicified ooidal grainstones/wackestones  
461 (unit C) and heteroliths (unit B2) (Fig.8C and 8D).

462 Unit C is composed of medium- to thick- layers of dolostones with mudstone texture (Fig.8E) or  
463 ooidal wackestone/grainstone texture with low content of detrital grains. Micro-crystalline quartz  
464 replacements of dolomite grains and cement are common (Qtz-A) and frequently associated with  
465 the ooid-rich facies (Fig.8F). Chalcedony (Qtz-C) or euhedral blocky mega-quartz (Qtz-B) filling vuggy  
466 pores and veins are also observed in this unit (Fig.8D). Vuggy pores and veins in the upper part of  
467 unit C may also be filled with calcite crystals (Fig.8E). Pressure solution by bedding parallel stylolites  
468 postdates the Qtz-A silicification episode both in thin-section and outcrop scale, causing apparent  
469 offsets and plastic deformation of chert nodules (Fig.8B).

470 Above the heterolith intercalations, the cave morphology consists of collapse halls and small  
471 chambers connected with the surface by a collapse. The entrance has a gentle slope covered with  
472 debris, boulders, and red soil coming from the surface (Fig.3E). The passages near the entrance  
473 present condensation-corrosion features.

474

475 Figure 8. Mesoscale (outcrop) and microscale (thin-section microphotographs) observations in unit  
476 C. A) Thick dolostone layer composed of dolomicrite (microphotograph in box E) with chert nodules.  
477 B) Close-up view of chert nodules deformed by bedding-parallel pressure solution (stylolites).  
478 Differential dissolution produced an apparent offset in the chert nodules, indicating that it postdates

479 the formation of the chert nodules in the dolostone. C) Typical cave passage in the upper storey  
480 with the greatest widening localized in the cherty dolostone layers. D) Heterolith layers with wavy  
481 bedding and quartz-rich mineral deposits in unit B2. E) Dolomicrite with bedding-parallel stylolite in  
482 unit C. Image under parallel-polarized light. F) Silicified dolostone layer in the upper storey (see  
483 picture in box C) with ooidal grainstone texture and abundant detrital quartz grains. Silicification is  
484 represented by Qtz-A replacing dolomite grains and cement. Image under cross-polarized light.  
485 Label abbreviations: TG-J (through-going joint), J (joint), Qtz-f (mega-quartz filling porosity), Cal-V  
486 (calcite vein), Qtz-cl (quartz clast).

487

#### 488 **4.2 Silicification textures**

489 Quartz and silicified textures occur in all sedimentary units outcropping in the CCS. However, the  
490 highest concentration of silica and quartz-rich facies is observed in unit B1, associated with the sub-  
491 horizontal maze network of the middle storey (Fig.7). Silicification occurs mainly as diagenetic  
492 replacement of dolomite grains and cement by micro-crystalline quartz (Qtz-A; Fig.6A and 9). Qtz-A  
493 forms nodules and irregular layers, mainly localized in the dolomitized ooidal wackestone or  
494 mudstone textures and associated with small size (< 20  $\mu\text{m}$ ) iron- and iron-titanium oxides or, less  
495 commonly, pyrite. The replacement process is shown by micron-sized ghosts of the precursor  
496 carbonates (Maliva and Siever, 1989). Ghosts resemble the typical rhombohedral dolomite grains  
497 and are mostly composed of fluid inclusions or microcavities that were not completely replaced by  
498 micro-crystalline quartz (Fig.9B and 10B). At the meso-scale, different tones of chert (from light  
499 yellow to dark grey, Fig.7C) reflect the amount of associated iron oxides, rhombohedral-shaped  
500 inclusions, grain size, and porosity.

501 Chert nodules are often characterized by high porosity textures (up to 10-15%), occasionally filled  
502 with euhedral mega-quartz (Qtz-B; Figs.6B, 9A, 9E, 9F, 9G), chalcedony/spherulitic quartz (Qtz-C;

503 Figs.6B, 9E, 9F) or apatite (Fig.10E). The contact between Qtz-A and Qtz-B/Qtz-C fillings is usually  
504 sharp with irregular rims (Fig.9E and 9F). These mega-quartz and chalcedony deposits are  
505 characterized by several mineral inclusions illustrated in the SEM images of Figure 10. Mineral  
506 inclusions in Qtz-B/Qtz-C are composed of Ca-sulfates (anhydrite and gypsum), barite, K-feldspar,  
507 Fe-Ti oxides and hydroxides, muscovite, apatite, and accessory Fe-Cr spinels (chromite group),  
508 sphalerite (very small crystals found in association with Ca-sulfates), and pyrite. Furthermore, Qtz-  
509 B occasionally displays colloform-plumose textures and undulose extinction.

510 Silicification expressed by Qtz-B and Qtz-C is mainly concentrated in the middle and lower storeys,  
511 below the heterolithic and tempestite facies of units B2 and B3. Quartz-filled veins are observed  
512 also in the upper storey, near faults and through-going FZ (Fig.8D). Furthermore, mm- to cm-thick  
513 lenses of hydraulic breccias have been observed in thin sections from the middle storey (Figs.9H, 9I,  
514 10H). These hydraulic breccias are composed of sub-euhedral grains and fragments of quartz, K-  
515 feldspar, and phosphates (apatite, monazite; Fig.10I) supported by a matrix of weathered host rock  
516 (mostly clay minerals and feldspars altered in muscovite, and pseudomorphs of hematite-goethite).  
517 Due to their small size and irregular textures, it was not possible to clearly establish if the REE-  
518 phosphates found in the alteration zones are relict detrital grains or authigenic.

519 The mineral list identified with SEM-EDS combined with petrographic analyses in the highly silicified  
520 unit B1 are summarized in Table 1.

521

522 Figure 9. Silicification microtextural observations at optical microscopy. A) Microcavity and veins in  
523 Qtz-A (chert) filled by euhedral blocky mega-quartz (Qtz-B). Image under cross-polarized light. B)  
524 Qtz-A replacing dolomite crystals. Ghosts of relict rhombohedral dolomite crystals are still visible.  
525 Image under parallel-polarized light. C) Mosaic of multiple microphotographs showing silicification  
526 features plastically deformed by bedding-parallel pressure solution in an intraclastic rudstone of

527 unit B3. Images under cross-polarized light. D) Secondary mineral inclusions in a mega-quartz crystal  
528 (Qtz-B). Minerals with high interference colors are anhydrite, barite, or muscovite crystals. Image  
529 under cross-polarized light. E) Detail of spherulitic-chalcedony quartz (Qtz-C) and micro-crystalline  
530 quartz (Qtz-A). In the upper right corner, there are euhedral blocky quartz crystals (Qtz-B) with  
531 mineral inclusions. Image under cross-polarized light. F) Qtz-A with sharp rims and Qtz-B and Qtz-C  
532 crystallizations. Image under cross-polarized light. G) Association of Qtz-B with undulose extinction  
533 and K-feldspar with perthitic texture. On the left side, there are residual non-silicified dolomite  
534 crystals. Image under cross-polarized light. H) Micro-scale hydraulic breccia textures with quartz and  
535 K-feldspar fragments supported by a matrix composed of muscovite, iron-oxides/hydroxides, and  
536 altered clay or feldspar minerals. Images under parallel-polarized light. Quartz crystals have iron-  
537 titanium oxides inclusions. I) Same picture of box H under reflected light microscope with crossed  
538 nicols. Label abbreviations: Qtz-A (micro-crystalline quartz), Qtz-B (euhedral blocky mega-quartz),  
539 Qtz-C (chalcedony/spherulitic quartz), Qtz (quartz), Ms (muscovite), Anh (anhydrite; high  
540 interference colors), Kfs (K-feldspar), intracl (intraclasts), Fe (hydro)ox (iron-oxides and iron-  
541 hydroxides), Ti ox (titanium oxide, rutile), r-Dol (relict dolomite).

542

543 Figure 10. Silicification micro-textures observed at SEM. A) Contact between Qtz-A and Qtz-B. Note  
544 the vuggy and intercrystalline porosity (~15-20%) in the Qtz-A texture. B) Rhombohedral-shaped  
545 dolomite ghost inclusions in Qtz-A. C-D) Micro-textures typical of slow dissolution kinetics (Mecchia  
546 et al., 2019) in Qtz-A, like: "V"-shaped notches, corrosion holes and etch pits. E) Qtz-A associated  
547 with iron-oxide crystals and intercrystalline voids filled with Fe-Cr spinel and apatite crystals. F) Qtz-  
548 B with inclusions of anhydrite, iron oxides, and barite crystals. G) Qtz-B with inclusions of Fe-Cr spinel  
549 and sulfates (mostly anhydrite). H) Hydraulic breccia micro-texture with associated alteration zone  
550 in a heterolith layer of unit B2. The orange arrows point to iron oxide-hydroxide aggregates



551 disseminated in the alteration zone. I) REE (Ce, La, Nd, Th)-phosphate (monazite) in the hydraulic  
 552 breccia alteration zone. From A to D: SE images; from E to L: BSE images. Label abbreviations: Qtz-  
 553 A (micro-crystalline quartz), Qtz-B (euhedral blocky mega-quartz), Qtz (quartz), Kfs (K-feldspar), Anh  
 554 (anhydrite), Brt (barite), Py (pyrite), Chr (Fe-Cr spinel group), Fe-ox (iron oxides), Fe-(hydro)ox (iron-  
 555 oxides and iron-hydroxides), Ap (apatite), Mnz (REE-phosphate, monazite).

556

557 Table 1. List of the mineral phases associated with silicification identified by combined SEM-EDS and  
 558 petrographic microscopy.

Name	Simplified formula	Description
Quartz	SiO <sub>2</sub>	microcrystalline (Qtz-A) chert as diagenetic replacement of dolomite; blocky mega-quartz (Qtz-B) or chalcedony (Qtz-C) filling porosity and fractures; fragments in hydraulic breccias
Hematite	Fe <sub>2</sub> O <sub>3</sub>	pseudomorphs of pyrite; associated with silicification and hydraulic breccias; inclusions in hydrothermal quartz; overgrowths and coatings
Pyrite	FeS <sub>2</sub>	disseminated in dolomitized carbonate, mainly replaced by hematite-goethite; inclusions in hydrothermal quartz
Sphalerite	ZnS	rare inclusions in hydrothermal quartz
Goethite	FeO(OH)	alteration of hematite crystals; coatings
Pyrolusite	MnO <sub>2</sub>	alteration of bedrock
Gypsum	CaSO <sub>4</sub> · 2H <sub>2</sub> O	lamellar gypsum filling porosity and as overgrowths; soft powders on cave floors; inclusions in hydrothermal quartz
Anhydrite	CaSO <sub>4</sub>	inclusions in hydrothermal quartz
Barite	BaSO <sub>4</sub>	inclusions in hydrothermal quartz
K-feldspar	K(AlSi <sub>3</sub> O <sub>8</sub> )	inclusions in hydrothermal quartz and filling pores; fragments in hydraulic breccias
Muscovite	KAl <sub>2</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub>	inclusions in hydrothermal quartz; alteration zones associated with hydraulic breccias
Calcite	CaCO <sub>3</sub>	Vein fillings
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	primary dolomitization of calcite grains and cement
Montmorillonite	(Na,Ca) <sub>0.33</sub> (Al,Mg) <sub>2</sub> (Si <sub>4</sub> O <sub>10</sub> )(OH) <sub>2</sub> · nH <sub>2</sub> O	residual clay minerals in bedrock
Taranakite	K <sub>3</sub> Al <sub>5</sub> (PO <sub>3</sub> OH) <sub>6</sub> (PO <sub>4</sub> ) <sub>2</sub> · 18H <sub>2</sub> O	crusts on cave walls and overgrowths on quartz deposits; guano-related phosphates

Robertsite-Mitridatite series	$\text{Ca}_2(\text{Mn}^{3+}, \text{Fe}^{3+})_3\text{O}_2(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$	crusts on cave walls and overgrowths on quartz deposits; guano-related phosphates
Brushite	$\text{Ca}(\text{PO}_3\text{OH}) \cdot 2\text{H}_2\text{O}$	crusts and acicular overgrowths on quartz deposits; guano-related phosphates
Apatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	inclusions in hydrothermal quartz deposits and filling pores, or guano-related overgrowths on quartz deposits
Berlinite-Variscite group (?)	$\text{Al}(\text{PO}_4) - \text{Al}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$	guano-related phosphates
Hematite-Ilmenite series	$\text{Fe}_2\text{O}_3 - \text{FeTiO}_3$	inclusions in hydrothermal quartz
Rutile	$\text{TiO}_2$	inclusions in hydrothermal quartz
Chromite group	$\text{FeCr}_2\text{O}_4$	inclusions in hydrothermal quartz
REE-phosphates (Monazite Group)	$\text{REE}(\text{PO}_4)$	small grains in the alteration zones of hydraulic breccias or detrital (?)
Ni-phosphate (?)	?	small grains in the alteration zones of hydraulic breccias or detrital (?)

559

#### 560 **4.3 Deformation and fracture patterns**

561 The structural elements observed in the CCS were classified as: stylolites, open-mode fractures  
562 (joints/veins), through-going fracture zones (FZ), and faults (Fig.11A).

563 Bedding in the CCS is sub-horizontal to gently dipping to the NW (< 5-15°) (Fig.11B). Bedding-parallel  
564 stylolites due to burial were observed in all carbonate units and, especially, in units A and B1.

565 Open-mode fractures are joints and veins (Fig.11B and 11C). Infilling of veins is made up of  
566 carbonates (mostly dolomite) or quartz. Boxwork quartz veins (Fig.6B and 6C) are common in the  
567 lower and middle storey and are composed of Qtz-B or Qtz-C assemblages (Fig.5C). Open-mode  
568 fractures are commonly bed-perpendicular or high angle to bedding, and either stratabound  
569 (confined to bedding interfaces) or shorter than single bed thickness. Based on the statistical  
570 analysis of fracture orientations, four sets of open-mode fractures were identified: NW-SE, N-S to  
571 NNE-SSW, NE-SW, and E-W (Fig.11F). Non-stratabound (through-going) fracture zones (FZ), on the  
572 contrary, are formed by cm-spaced joints, veins, or sheared joints organized in connected arrays,  
573 which cut across bedding (Fig.11D). Through-going FZ include NW-SE and N-S to NNE-SSW sets  
574 (Fig.11G). These structures are mostly developed in the lower storey (unit A).

575 The dolomitized grainstones in unit A are also affected by rare small-scale faults (Fig.11E)  
576 interpreted as sheared through-going fracture zones (Myers and Aydin, 2004), which display similar  
577 characteristics and orientation to the previously mentioned FZ sets. In these faults, kinematic  
578 indicators are rarely observed, so that slip sense is generally evinced from the vertical throw of  
579 bedding interfaces or bedding-parallel stylolites. These small-offset (< 1 m) faults have oblique-slip  
580 kinematics: right-lateral on the NW-SE trend and left-lateral on the NNE-SSW trend (Fig.11A and  
581 11E). Furthermore, secondary E-W-striking low angle reverse faults are observed; they cause small-  
582 scale detachments (throws up to 1-5 cm) of heterolith layers in the middle storey.  
583 Fracture properties of open mode stratabound fractures measured along linear scanline are shown  
584 in Table 2.

585

586 Figure 11. A) Structural features measured in the CCS displayed with lower-hemisphere equal-area  
587 stereographic projections and classified by type. B) Example of bedding-parallel stylolites and  
588 stratabound veins in the dolostones of unit A. C) Example of open-mode stratabound fractures  
589 (joints) in the dolomicrites and marly dolostones of unit B2. D) Karst dissolution along a through-  
590 going FZ composed of clustered open-mode fractures (joints) in unit A. E) Example of a small-scale  
591 fault along a NW-SE through-going fracture zone reactivated in shear (oblique-slip). F-G) Statistical  
592 analysis by Gaussian-best fit calculated from the normalized frequency distribution histograms for  
593 both the open-mode fracture dataset (F) and the through-going FZ dataset (G). Azimuth data are  
594 given in  $\pm 90^\circ$ . RMS: root mean square error; SD: standard deviation.

595

596 Table 2. Scanline properties and quantitative fracture attributes measured for the open-mode  
597 fracture sets identified in the CCS.

Scanlines properties							
Sedimentary unit	Study site	Lithology	Scanline trend	Scanline length (m)	Layer thickness	n	Linear intensity $P_{10}$ (m <sup>-1</sup> )
A	point H	Crystalline dolostone	N12E	0.8	36 cm	15	18.75
	point A	Crystalline dolostone	N120E	0.75	41 cm	14	18.67
B1	point G	Highly silicified dolostone	N50E	0.35	8 cm	13	37.14
	point F	Highly silicified dolostone	N107E	0.9	6 cm	27	30.00
B2	point F	Marly dolostones	N107E	1.8	8 cm	19	10.55
	point G	Dolomicrite	N50E	0.8	10 cm	15	18.75
	point G	Marly dolostones	N50E	1.4	18 cm	9	6.43
B3	point F	Coarse laminated siltstone	N90E	3	20 cm	11	3.67
	point G	Mixed carbonate-siliciclastic coarse sandstones	N40E	3	36 cm	14	4.67
C	point J	Dolomicrite	N120E	0.6	28 cm	8	13.33
	point J	Dolomicrite	N35E	1.8	100 cm	18	10.00
C (chert)	point J	Silicified cherty dolostone	N35E	0.5	9 cm	23	46.00
Structural analysis							
Sedimentary unit	Fracture Set	Type of fractures	Mean normal spacing (mm)	Cv	Mean mechanic aperture (mm)	Mean hydraulic aperture (mm)	
A	NW-SE N122E	Stratabound joints/veins	65.67±0.51	1.07	1.06±0.74	0.053±0.072	
	N-S N177E	Stratabound joints/veins	29.71±0.31	0.73	0.48±0.27	0.010±0.011	
	NE-SW N33E	Stratabound joints/veins	56.92±0.22	0.56	0.92±0.60	0.037±0.054	
	N-S N2E	Fracture zones (n=2)	-	-	-	-	
	NW-SE N128E	Fracture zones (n=9)	-	-	-	-	
B1	NW-SE N118E	Stratabound joints	12.92±0.41	1.29	0.31±0.12	0.042±0.038	
	N-S N12E	Stratabound joints	53.19±0.35	0.68	0.46±0.15	0.043±0.039	
B2	NW-SE N130E	Stratabound joints/veins	92.38±0.26	0.71	0.56±0.29	0.016±0.019	
	NE-SW N55E	Stratabound joints/veins	129.86±0.20	0.42	0.71±0.35	0.005±0.004	
	E-W N94E	Stratabound joints/veins	22.94±0.41	0.70	0.73±0.35	0.004±0.002	
B3	NW-SE N131E	Stratabound joints	210.8±0.24	0.47	1.16±0.56	0.029±0.030	
	NE-SW N21E	Stratabound joints	196.05±0.21	0.52	0.9±0.30	0.028±0.017	
C	NW-SE N134E	Stratabound joints/veins	95.28±0.54	1.43	0.15±0.11	0.001±0.001	
	N-S N4E	Stratabound joints/veins	51.35±0.31	0.79	0.17±0.08	0.001±0.001	
C (chert)	NW-SE N128E	Stratabound joints	53.92±0.45	1.01	0.08±0.03	0.003±0.001	
	N-S N178E	Stratabound joints	16.76±0.38	0.97	0.09±0.03	0.003±0.002	

598

599

600 NW-SE, N-S, and NE-SW sets were measured in unit A. The NW-SE set shows a mean fracture spacing  
601 of 65-66 mm and a Cv value of 1.07. The N-S set has a mean spacing of 29-30 mm and a Cv value of

602 0.73. Finally, the NE-SW set shows a mean spacing of 56-57 mm and a Cv value of 0.56. In unit A,  
603 NW-SE and N-S through-going FZ were encountered along the linear scanlines; their real properties,  
604 however, were not measured due to the intense karst weathering.

605 The highly silicified layers in unit B1 (middle storey) show a high intensity of stratabound fractures  
606 ( $P_{10}$  ranging from 30 to 37  $m^{-1}$ ) with respect to the surrounding carbonate layers. Two main joint  
607 sets were recognized: NW-SE, with a mean spacing of 12-13 mm, and N-S, with a mean spacing of  
608 52-53 mm. The Cv values are respectively 1.29 and 0.68. These two closely spaced fracture sets are  
609 organized in well-connected clusters.

610 In the scanlines through the marly dolostones and mudstones of unit B2, three main sets of  
611 stratabound open-mode fractures were identified: NW-SE, NE-SW and E-W. The NW-SE set shows a  
612 mean fracture spacing of 92-93 mm and a Cv value of 0.71. The NE-SW set has a mean spacing of  
613 129-130 mm, and a Cv value of 0.42. Finally, the E-W set shows a mean spacing of 22-23 mm, and a  
614 Cv value of 0.7.

615 In the tempestite facies of unit B3, a minor intensity of brittle deformation ( $P_{10}$  ranging from 3.7 to  
616 4.7  $m^{-1}$ ) is observed with two main joint sets striking NW-SE and NE-SW. Both sets show mean  
617 spacing around 20-21 cm and Cv values of 0.47 and 0.52, respectively.

618 In unit C, scanlines were measured both on chert nodules and carbonate layers (dolomicrite). The  
619 main sets measured are NW-SE and N-S. In the dolomicrite layer, the NW-SE set shows a mean  
620 spacing of 95-96 mm and a Cv value of 1.43, whereas the N-S set shows a mean spacing of 51-52  
621 mm and a Cv value of 0.79. The NW-SE and N-S joint sets in the chert nodules result respectively in  
622 mean fracture spacing of 53-54 mm and 16-17 mm, and Cv values of 1.01 and 0.97, respectively.

623 The silicified and cherty dolostone facies show the closest-spaced fracture sets, as well as the  
624 highest degree of fracture connectivity noticed by field observations both in map (Fig.12A) and  
625 section view (Fig.12B). On the contrary, in the carbonate-dominant and siliciclastic facies (Fig.12C

626 and 12D) fractures are mainly constituted of stratabound veins with variable apertures and wide  
627 spacing. In the lower storey, localization of through-going FZ and faults can produce volumes of  
628 channelized fracture permeability testified by their association with feeders (Fig.5B and 5C), rising  
629 conduits (Fig.7A), and karst development (Fig.11D). The fracture intensity ( $P_{10}$ ) was calculated for  
630 each scanline and is reported in Fig.12E and Tab.2.

631

632 Figure 12. Fracture patterns highlighted by line drawing in the different sedimentary units of the  
633 CCS. A) Example of fracture development in dolostone (low connectivity, low fracture density) and  
634 chert (high connectivity, high fracture density) in the highly silicified layers of the middle storey.  
635 Note that the picture represents a planimetric view of the ceiling. B) Different fracture patterns in  
636 the cherty dolomicrites of unit C (upper storey). Chert nodules localize brittle deformation and  
637 fracturing. C) Example of widely spaced and stratabound fractures in unit B2 (middle storey).  
638 Occasional through-going but poorly connected fractures are observed. D) Stratabound and  
639 clustered through-going fractures in unit A (lower storey). E) Fracture linear intensity ( $P_{10}$ ) calculated  
640 for each scanline. Chert nodules in the highly silicified layers localize the highest values of  $P_{10}$  (30-  
641  $40 \text{ m}^{-1}$ ).

642

#### 643 **4.4 Petrophysical properties**

644 The fracture properties collected from different scanlines in the cave allowed to characterize the  
645 variations in fracture normal spacing and to estimate individual fracture permeability for the whole  
646 sedimentary sequence outcropping in the CCS (Philipp et al., 2013; Giuffrida et al., 2020). The results  
647 are displayed in  $\log_{10}$  scale as box-plot diagrams (Fig.13), subdivided by fracture sets and grouped  
648 according to the different sedimentary units described in the previous sections. The crosses in the  
649 boxplots refer to mean values, whereas the left and right box sides are the 1st and 3rd quartiles,

650 respectively. The box whiskers define the minimum and maximum values in the data range  
651 excluding outliers. Estimated individual fracture permeability in unit A ranges from  $10^3$  to  $10^5$  mD,  
652 with a mean value around  $10^4$  mD. In unit B1, stratabound fractures are closely spaced (mean values  
653 around  $10^1$  mm), and they have a fracture permeability with mean values between  $10^4$  and  $10^5$  mD  
654 for each individual set. Unit B2 has variable permeability values, with means around  $10^3$  mD. In the  
655 siltstones of unit B3, fracture spacing is wide (up to  $10^2$  -  $10^3$  mm) and the mean fracture permeability  
656 is around  $10^4$  –  $10^5$  mD. Finally, in unit C fracture permeability is higher in the silicified zones with  
657 chert nodules (means between  $10^2$  and  $10^3$  mD) than in the dolomitic facies (means between  $10^0$   
658 and  $10^1$  mD).

659 On the right side of Figure 13, the rock plug measurements of porosity (expressed in %) and  
660 permeability (expressed in mD) are displayed in a  $\log_{10}$  scale. Rock plug permeability values are  
661 subdivided into horizontal and vertical permeability. The colored dots represent the mean values,  
662 whereas the whiskers refer to the 1st and 3rd quartiles of the datasets. The results from the analyses  
663 are displayed in a  $\log_{10}$ - $\log_{10}$  diagram in Figure 14, where trendlines represent the best fit power-  
664 law distribution of the datasets subdivided by sedimentary units. All  $R^2$  values are  $> 0.7$  except in the  
665 silicified unit B1, where alteration and karst dissolution are intense and permeability values are  
666 scattered ( $R^2$  value is 0.48). The mean  $R^2$  value ( $R^2=0.72$ ) of the trendlines confirms a good fit of the  
667 power-law distribution for the datasets.

668 Figure 13 graphically describes the variations of petrophysical properties relative to the CCS  
669 lithostratigraphic profile and the spatial organization (pattern) of the hypogene conduit system.  
670 Rocks in unit A have low-medium porosity (ranging from 2% to 15%, mean value of 6%) and  
671 permeability values range from  $10^{-3}$  to  $10^2$  mD (maximum 129.1 mD). The silicified unit B1 presents  
672 medium porosity (from 5% to 16%, with a mean of 11%) and variable permeability with values  
673 ranging from  $10^{-2}$  to  $10^3$  mD (maximum 231.7 mD in bedding-parallel plugs). The heterolithic and

674 tempestite facies of units B2 and B3 have the highest porosity values, ranging from 6% to 29%, with  
 675 mean values respectively of 11% and 20%. On the other hand, the permeability of rock plugs is low,  
 676 with values ranging from  $10^{-3}$  to  $10^1$  mD. In unit C, values of porosity are significantly different  
 677 between the rocks in the upper speleogenetic storey (mean value of 6%) and those from the  
 678 passages comprised between the entrance and the intercalations of unit B2. The latter have the  
 679 lowest porosity of the entire dataset (1-2%). In a similar way, the permeability of rock plugs has low  
 680 values around  $10^{-3}$  mD in the upper interval of unit C, and variable values ranging from  $10^{-3}$  to  $10^1$   
 681 mD in the karstified upper storey.

682 EPM permeabilities for each speleogenetic unit in the CCS, calculated for discharge parallel to the  
 683 main fracture sets ( $K_P$ ) or normal to the main fracture sets ( $K_N$ ), are summarized in Table 3. These  
 684 values reflect the anisotropy in permeability for the different speleogenetic units in the CCS.

685

686 Figure 13. Boxplots show the variation of petrophysical properties, fracture normal spacing, and  
 687 fracture permeability of individual sets along the lithostratigraphic profile in the CCS gallery-conduit  
 688 system.

689

690 Table 3. Equivalent Porous Media (EPM) permeability calculated for the different CCS speleogenetic  
 691 units considering an elementary cubic cell of 1 m width.

Speleogenetic units	Sedimentary units	$K_P$ (mD)	$K_N$ (mD)
Doline entrance	C	0.019	0.003
Upper storey	C-B2	1.30	0.74
Middle storey (siliciclastic seal)	B3	34.22	3.09
Middle storey (heterolithic seal)	B2	10.93	0.96
Middle storey (high-K silicified dolostones)	B1	1176.38	36.67
Lower storey	A	737.60	11.55

692



693 Figure 14. Log-log diagrams showing the relationship between rock plug porosity and permeability  
694 grouped according to sedimentary units. The trendlines correspond to the best fit, power-law  
695 distribution for each dataset and for the whole population (black trendline,  $R^2$  value of 0.72).

696

## 697 **5 Discussion**

698 This study provides evidence for hypogene flow and karst dissolution in a silicified carbonate-  
699 siliciclastic sequence. Our observations allow us to propose a conceptual evolutionary model for  
700 the CCS, identifying different fluid flow pathways and hypogene speleogenetic mechanisms that  
701 drastically modified the original porosity-permeability of the layered sedimentary sequence.  
702 Furthermore, the CCS represents a conceptual analog of many deep carbonate reservoirs where  
703 silicification and hydrothermal alteration are common processes making the characterization of the  
704 reservoir properties a challenging task (De Luca et al., 2017; Montanari et al., 2017; Lima et al.,  
705 2020). In particular, the pre-salt carbonate reservoirs of Campos Basin (Lima et al., 2020) and  
706 Kwanza Basin (Poros et al., 2017) show silicification and dissolution features similar to those  
707 documented in the CCS.

708 In the next sections, we discuss the role of structural-stratigraphic variability in the definition of high  
709 vs. low permeability zones, hypogene fluid migration, and dissolution. Our observations are  
710 integrated into conceptual models illustrating the spatial-temporal evolution of the sequence and  
711 its implications for karst reservoirs.

712

### 713 **5.1 High permeability vs. seal (buffering) units, fluid flow pathways, and hypogene dissolution**

714 Permeability pathways and karst formation in fractured and layered carbonates mostly depend on  
715 the interaction between stratigraphy, fracture patterns, diagenetic features, and the  
716 hydrogeological-speleogenetic setting (Audra and Palmer, 2015; Klimchouk, 2019; Balsamo et al.,

717 2020). The recognition of the main hydrological behavior of the sedimentary units composing a  
718 layered sequence is fundamental to correctly interpret its hydrological (speleogenetic) evolution in  
719 space and time (Klimchouk, 2007; Klimchouk et al., 2009).

720 The analyses of fracture patterns, petrophysical properties, and speleogenetic features in the  
721 different sedimentary units of the CCS allowed to recognize high permeability and “seal” (buffering)  
722 units (Tab.3; Fig.13). These hydrogeological-speleogenetic units strongly influenced fluid flow  
723 directions and resultant karst geometries. Due to the limited scale of observation and the lack of  
724 regional data, we define these “seal” units as low permeability buffer zones. Such zones vary in  
725 lateral thickness and might be breached by non-stratabound fractures (Fig.11). These vertically  
726 extended fractures act as conduits in specific discharge areas of the regional groundwater system  
727 (Klimchouk et al., 2016).

728 Based on the field analyses, microtextural observations and analytical results presented in the  
729 previous sections, we propose a timeline for the main diagenetic, structural and speleogenetic  
730 phases that affected the CCS sequence. The spatial-temporal evolution is illustrated in the  
731 conceptual model of Figure 15. In the following sections, we refer to three main diagenetic evolution  
732 stages as defined by Choquette and Pray (1970) and Morad et al. (2000): eodiagenesis,  
733 corresponding to the early processes taking place at shallow depth near the surface (commonly up  
734 to a few hundred meters below the surface); mesodiagenesis, corresponding to the burial interval  
735 below the influence of near-surface processes until the onset of low-grade metamorphism; and  
736 telodiagenesis, corresponding to the processes that take place during uplift and exhumation of  
737 previously buried rocks.

738

739 *5.1.1 Stages 1 and 2 – early diagenetic silicification and burial*

740 Silicification in the CCS affected selected carbonate layers; in some of these layers (unit B1) SiO<sub>2</sub>  
741 content can reach up to 80-85 wt% (Fig.4). The main episode of diffuse silicification is represented  
742 by the formation of chert nodules. Micro-crystalline quartz (Qtz-A) replaces the carbonate grains  
743 and cement and forms nodular aggregates (Figs.6, 9, 10).

744 The precursor carbonate units in the CCS are entirely composed of dolostones. Almost no calcite  
745 has been found, although several fabric characteristics and microtextures (like ooids) are still  
746 preserved in thin sections indicating original calcite deposition. Since it is not the focus of this work,  
747 we will not discuss the dolomitization process. However, we hypothesize that the dolomitization  
748 should have occurred during eodiagenesis before the formation of chert nodules and after the  
749 diagenetic cementation of the original carbonate sediments.

750 From meso- to microscopic observations, the chert nodules in the carbonates predate pressure  
751 solution caused by burial (Fig.8B and 9C), which developed at a depth generally < 800-900 m (Van  
752 Golf-Racht, 1982; Rolland et al., 2014; Araújo et al., 2021). Furthermore, burial-related stylolites are  
753 common features consistent with eodiagenetic to early-mesodiagenetic settings (Caracciolo et al.,  
754 2014; Souza et al., 2021). We suggest, therefore, that the diffuse dolomite replacement and the  
755 formation of the chert nodules was likely restricted to shallow burial conditions and early diagenetic  
756 settings (< 1 km: Fig.15). The sources of Si-rich fluids which could have triggered this diffuse  
757 silicification, common also in other carbonates of the Salitre *Fm*, are still unknown. The hypothesis  
758 of hydrothermal solutions rising through the underlying Chapada Diamantina quartzites along  
759 basement-rooted structures has been suggested by some authors (Bertotti et al., 2020; Cazarin et  
760 al., 2021).

761 Mechanical compaction during progressive burial until the transition to early-mesodiagenesis  
762 caused open-mode regularly spaced fractures represented by the NE-SW and NW-SE striking sets

763 (Fig.11A; Tab.2). Fracture localization in layers with high concentration of stiff chert nodules (unit  
764 B1) forms highly-connected joint networks (Fig.12A and 12B).

765

#### 766 *5.1.2 Stage 3 – rising flow and deep-seated silica dissolution*

767 Chert nodules in the CCS show a porous texture (Fig.7C and 10A) and single quartz grains  
768 characterized by solutional pits, “V”-shaped notches, and dissolution related vugs (Fig.10C and 10D;  
769 Higgs, 1979; Burley and Kantorowicz, 1986; Shanmugam and Higgins, 1988; Sauro et al., 2014;  
770 Itamiya et al., 2019). Dissolution features at different scales (Fig. 7 and 10), blocky mega-quartz and  
771 chalcedony filling solutional pores and fractures, and quartz-rich brecciated micro-textures suggest  
772 a complex history of fluid-rock interaction and mineralization during mesodiagenesis.

773 The widespread evidence of silica dissolution observed at the micro-scale in the CCS is particularly  
774 relevant for its implications regarding deep carbonate reservoirs. It is commonly known that quartz  
775 solubility exponentially increases with temperature (Siever, 1962; Rimstidt, 1997; Dove, 1999;  
776 Gunnarsson and Arnorsson, 2000; Marin-Carbonne et al., 2014; Sauro et al., 2014; Cui et al., 2017).  
777 Furthermore, silica solubility is nearly constant at  $\text{pH} < 8$ , and significantly increases at greater values  
778 (Mitsiuk, 1974; Andreychouk et al., 2009; Mecchia et al., 2019). Also,  $\text{Ba}^{2+}$  transported in solution  
779 (suggested by the presence of barite mineralizations in the CCS) could have determined a significant  
780 positive effect on quartz solubility, as reported by previous works (Dove and Nix, 1997; Sauro et al.,  
781 2014; Mecchia et al., 2019).

782 We propose that an early phase of hypogene dissolution occurred in deep-seated conditions, where  
783 silica-dominant dissolution was driven by warm (likely  $> 100\text{-}150^\circ\text{C}$ ) and alkaline fluids able to reach  
784 the silicified layers. The result was the formation of micro-scale karst (vuggy) porosity and  
785 solutionally-enlarged fractures in the cherts (Fig.15). Mineral phases such as Fe-Cr spinels, Fe-Ti  
786 oxides, barite, anhydrite, sulfides, rutile, and phosphates (mainly apatite) found as solid inclusions

787 associated with quartz mineralizations (Fig.9 and 10; Tab.1) strongly support a hydrothermal origin  
788 for this deep-seated hypogene phase.

789 Mechanical compaction during progressive burial and multiple tectonic events at the time of the  
790 *Brasiliano* Orogeny caused the formation of many different permeable structures (Figure 11). Driven  
791 by pressure gradient and/or fluid buoyancy, the permeable structures focused upward flow, as  
792 suggested by the presence of the solutionally-enlarged feeders in the lower storey of the cave.

793 Our structural data indicate two main contractional events that postdate burial. The E-W striking  
794 open-mode fracture set is consistent with the first contractional phase (~ E-W direction of maximum  
795 shortening) recorded also in other areas of the Una-Utinga basin (D'Angelo et al., 2019; Pontes et  
796 al., 2021). The second contractional event is related to the formation of the N-S to NNE-SSW open-  
797 mode fracture sets formed parallel to a roughly NNE-SSW direction of maximum shortening.  
798 Progressive deformation during this contractional phase produced the clustering of NNE-SSW  
799 joints/veins with the formation of through-going FZ in unit A. Based on our structural analysis, we  
800 propose that the same NNE-SSW contractional phase also controlled the reactivation of the pre-  
801 existent NW-SE joints/veins sets, causing the formation of clustered FZ eventually reactivated in  
802 shear (Myers and Aydin, 2004) with oblique-slip kinematics (Fig.11E). These vertical structures acted  
803 as the main permeability pathways for rising fluid flow (Fig.5B). Bedding-parallel NNE-SSW-oriented  
804 shortening also caused the formation of ESE-WNW small-scale reverse faults observed in the middle  
805 storey (Fig.11A).

806 Similar deformation patterns were documented in the region by D'Angelo et al. (2019). These latter  
807 authors interpreted left-lateral N-S and right-lateral NW-SE strike-slip faults as reactivated deep-  
808 rooted structures related to a N-S- to NNE-SSW-oriented contractional phase. Main migration routes  
809 of rising hydrothermal fluids may be related to these buried strike-slip fault zones cross-cutting the

810 basement (D'Angelo et al., 2019; Bertotti et al., 2020). Similar fault orientations occur in the CCS  
811 (Fig.11A and 11E).

812  
813 *5.1.3 Stage 4 – main hypogene karst formation and silica reprecipitation*

814 During stage 4 (Fig.15) the rising hydrothermal fluids driven by pressure gradients and/or fluid  
815 buoyancy shaped the main hypogene karst in the CCS. The timing of the proposed hypogene large-  
816 scale karst porosity formation is still unknown. The occurrence of other hydrothermal events in the  
817 São Francisco Craton with similar mineral paragenesis (Kyle and Misi, 1997; Misi et al, 2005; Misi et  
818 al., 2012) and hypogene caves (Klimchouk et al., 2016) suggest a possible late Cambrian age.  
819 However, multiple phases of burial and denudation after the Early Cretaceous Pangea break-up  
820 occurred in the São Francisco Craton. The cumulative overburden above the present-day surface in  
821 the Chapada Diamantina quartzites (west of the study area) was estimated around 2-3 km (Japsen  
822 et al., 2012). This evidence suggests a complex and long burial-exhumation history for the  
823 carbonates of the Salitre *Fm*, during which hydrothermal fluids could have been able to drive  
824 dissolution generating large-scale karst porosity in hypogene settings.

825 The variability in petrophysical properties among the sedimentary units in the CCS (Fig.13)  
826 determined the formation of the different speleogenetic storeys (and their associated  
827 morphologies). The lower storey hosted channelized vertical permeability pathways that acted as  
828 feeders for vertical fluid flow. In this storey, permeability pathways are mainly expressed by  
829 through-going fracture zones with high hydraulic apertures and good connectivity, which provided  
830 high vertical permeability ( $K_p = 10^2$  mD, Tab.3). On the contrary, the middle storey is characterized  
831 by a sub-horizontal network of galleries developed mainly in the silicified unit (B1). The contrasting  
832 mechanical behavior of stiff chert nodules in the silicified layers with respect to surrounding  
833 dolostones, heteroliths, and marls, concentrated stress and caused fracture localization (Alvarez et

834 al., 1976; Antonellini et al., 2020), producing networks of high permeability clustered joints (Fig.12).  
835 As a result of high fracture permeability and early dissolution of silica during stage 3,  $K_P$  in unit B1 is  
836 the highest observed in the whole CCS ( $K_P = 10^3$  mD, Tab.3), with values 2 to 3 orders of magnitude  
837 higher than those from units B2, B3, and C, and around 10 times the values observed in unit A. Unit  
838 B1 acted, therefore, as an inception horizon, defined as a lithostratigraphically-controlled element  
839 that favored hydraulic conductivity and the onset of dissolution (Lowe and Gunn, 1997).  
840 At the same time, the heterolithic and siliciclastic rocks of units B2 and B3, despite having high  
841 porosity (~10-20%), have a low EPM permeability ( $K_P = 10^1$  mD,  $K_N = 10^0$  mD; Fig.13, Tab.3). This  
842 evidence, combined with the morphological observations on conduit geometries and distribution,  
843 indicates that they acted as low permeability buffering units promoting sub-horizontal flow in the  
844 underlying layers (Klimchouk et al., 2016; Balsamo et al., 2020). Additionally, these units are mostly  
845 composed of heterogeneous siliciclastic grains (i.e., K-feldspar, muscovite, quartz, kaolinite,  
846 chlorite, clay minerals), which are less soluble. Karst formation eventually occurred in focused  
847 discharge areas along through-going FZ connecting the middle and upper storey (Fig. 13 and 15).  
848 Like unit B1, the occurrence of sub-horizontal solutional galleries in the upper storey is focused on  
849 the silicified ooidal grainstone and wackestone layers (Fig.8 and 13) sealed at the top by  
850 intercalations of low permeability heterolith layers.  
851 The very low porosity (~1-2%) and permeability of the dolomicrites in the upper sector of unit C ( $K_P$   
852 =  $10^{-2}$  mD,  $K_N = 10^{-3}$  mD; Tab.3) is 5 to 6 orders of magnitude lower than the middle and lower storey  
853 permeability. This suggests that unit C acted as an efficient buffer for vertical fluid migration and  
854 karst formation, although a certain degree of discharge is expected to guarantee rising flow at the  
855 regional scale (Klimchouk et al., 2016).  
856 The dissolution of carbonate and silicified layers to form the main conduit network required specific  
857 (and almost opposite) conditions, with the dolostone dissolution promoted by acidic and low

858 temperature conditions, and the silica dissolution promoted by alkaline and high temperature  
859 conditions (Andreychouk et al., 2009; Cui et al., 2017). These two “end-members” of the  
860 hydrothermal fluids (at different temperature and/or geochemistry) do not necessarily imply  
861 distinct temporal intervals. On the contrary, we propose that a recurrent system of multiple silica-  
862 vs. carbonate-dominant dissolution (and silica reprecipitation) phases happened during stage 4  
863 (Fig.15). Hot and alkaline conditions promoted the silica-dominant dissolution of the silicified layers,  
864 enlarging and connecting the vuggy pores in chert nodules (mostly concentrated in unit B1). Water  
865 cooling and/or gradual pH changes in the hydrothermal flow system led towards more acidic  
866 conditions and caused the switch from silica-dominant dissolution to carbonate-dominant  
867 dissolution. Conduit morphology in the lower storey (spongework pattern, vertically extended rising  
868 conduits and rift-like feeders with reactive fronts) and widespread vuggy porosity in the dolostones  
869 indicate the weathering and corrosion effects of the hydrothermal fluids on these carbonate units.  
870 The precipitation of Qtz-B/Qtz-C and the associated hydrothermal mineral suite of Ca-sulfates,  
871 barite, muscovite, K-feldspar, Fe-Ti oxides, Fe-Cr spinels, sulfides, and phosphates (Tab.1) occurred  
872 mainly in the lower sector of the cave below the heterolithic/siliciclastic units. The precipitation of  
873 these minerals caused partial occlusion of pore space in the vuggy and fracture porosity (Figs.7, 9,  
874 15). Similar hydrothermal mineral assemblages are common also in the Brazilian pre-salt reservoirs  
875 (Lima and De Ros, 2019; Lima et al., 2020) and associated with MVT-type ore deposits found in the  
876 São Francisco Craton (Kyle and Misi, 1997; Cazarin et al., 2019, 2021).

877

#### 878 *5.1.4 Stage 5 – late-stage speleogenesis*

879 The final stage of karst development (stage 5, Fig.15) involved sulfuric acid formation in supergene  
880 conditions derived from pyrite oxidation within a shallow oxygenated (aerated) environment (Auler  
881 and Smart, 2003). This is indicated by the occurrence of iron oxide and hydroxide pseudomorphs



882 replacing pyrite disseminated in the host rock, and secondary gypsum overgrowths and powders  
883 widely distributed in the cave system. The latter could be also the product of bat guano reactions.  
884 Condensation-corrosion processes likely enhanced the carbonate weathering in the cave system, as  
885 also suggested by the presence of condensation-corrosion features and dolostone weathering.  
886 Finally, collapse processes favored the widening of karst voids in the upper sector of the cave,  
887 ultimately causing the connection to the surface and the related transport of clastic sediments into  
888 the upper part of the CCS. All these late-stage processes overprinted the original dissolution  
889 morphologies of the karst system and amplified the dimensions of the passages observed today.

890

891 Figure 15. Conceptual spatial-temporal development model for the Calixto Cave system at the  
892 micro-scale (vuggy karst porosity formation) and macro-scale (solutional human-sized cave  
893 passages). See the Discussion section 5.1 in the main text for further explanations.

894

## 895 **5.2 Cave spatial-morphological organization and implications for karst reservoirs**

896 The 3D multistorey organization of the CCS is conceptually summarized in the sketch diagram of  
897 Figure 16. The strong heterogeneity observed in the cave pattern and morphology is related to the  
898 lithological differences (Fig.3A and 4) and the vertical distribution of fractures (Fig.12 and 13). At the  
899 same time, petrophysical properties at the scale of the rock plugs indicate significant differences  
900 among the sedimentary units, especially those affected by silicification (Fig.13). The variability in  
901 fracture spacing, individual fracture permeability, and petrophysical properties at the meso-scale  
902 (rock plugs) may be useful to recognize different hydrological units, fluid flow pathways and,  
903 therefore, speleogenetic storeys (Fig.13 and 16; Tab.3).

904 Estimated fracture permeability is calculated from present-day hydraulic apertures of the  
905 discontinuities but, at the time of speleogenesis, these apertures could have been significantly lower

906 due to stress-dependency laws and fracture closing induced by loading (Holt, 1990; Min et al., 2004).  
907 Such calculations are beyond the scope of this work. However, based on our geomorphological  
908 observations of the cave pattern, morphology, and former flow pathways, we propose that the  
909 spatial organization of the karst system is expression of the structural-stratigraphic variability in the  
910 sequence.

911

912 Figure 16. Schematic block diagram illustrating the spatial-morphological organization of the CCS  
913 and the main fluid flow pathways. In the lower right corner, the 3D model of the cave (see also Fig.3)  
914 is shown in a longitudinal section to visualize the vertical pattern of the multistorey system. Labels  
915 abbreviations: LS (lower storey), MS (middle storey), US (upper storey), DE (doline entrance).

916

917 In layered carbonate sequences of low primary porosity, through-going fractures (faults and fracture  
918 zones) are crucial for cross-formational fluid flow as they may determine the vertical connectivity  
919 of different sedimentary units. At the same time, the interplay between low-permeability buffering  
920 units and high-permeability units ( $K > 10^3$  mD) provided by high-aperture and closed-spaced  
921 (clustered) stratabound fractures may control horizontal permeability development and the  
922 formation of stratigraphically controlled voids. The combination of sub-seismic, meter-thick  
923 intercalations of low- ( $K < 1$  mD) and high-permeability ( $K > 10^3$  mD) units enhanced sub-horizontal  
924 karst formation in the CCS middle storey generating more than 1 km of large-scale, human-sized  
925 galleries (Fig.16). Additionally, through-going fracture zones form vertical permeability pathways  
926 that crosscut the seal/buffer units, allowing fluids to rise into the upper sectors of the sequence,  
927 and promoting the formation of multiple levels of sub-horizontal cave passages at different  
928 stratigraphic positions (Fig.16). The occurrence of similar multistorey karst patterns is not

929 uncommon, especially in the Salitre *Fm* (Klimchouk, 2007; Klimchouk et al., 2016; Cazarin et al.,  
930 2019).

931 Our results provide new insights for the understanding of deep-seated karst formation and  
932 dissolution/precipitation involving silicified carbonate units. The spatial and morphological  
933 organization of dissolution features documented in the CCS (both at macroscopic and microscopic  
934 scale; Fig.15 and 16) may be used as a conceptual analog or a proxy for many carbonate reservoirs  
935 where silicification and karst development are associated with specific sedimentary packages, like  
936 in the offshore pre-salt reservoirs of Brazil and Africa (Poros et al., 2017; Lima et al., 2020) or in the  
937 silicified reservoirs of the Tarim Basin (You et al., 2018). Karst cavities more than 2 m in diameter  
938 were observed at depths of 0.5-1.5 km in the Devonian and Carboniferous carbonate rocks of the  
939 Kizelovski basin and in the North Ural oil and gas basins (Andreychouk et al., 2009). Abundant  
940 cavities and macro-scale karst zones were intercepted by drillings at a depth down to 3-6 km in  
941 limestones, dolostones, and silicified carbonates of many basins worldwide (Zhao et al., 2018).  
942 Small-scale voids (vugs and fractures enlarged by dissolution) were also detected at depths larger  
943 than 5-10 km (Maximov et al., 1984; Andreychouk et al., 2009).

944 The observations presented in this paper may help to better understand the relations between  
945 silicification and hypogene dissolution in deep-seated settings, contributing to the prediction of  
946 karst patterns at different scales. Furthermore, the CCS provided an enlightening example of the  
947 complex speleogenetic history that could affect ancient basins, where deep-seated dissolution (and  
948 precipitation) may drastically modify porosity in quartz-rich rocks such as highly silicified carbonates,  
949 commonly considered less prone to karst formation.

950

## 951 **6 Conclusions**

952 Our analytical and field studies support a conceptual model on the relation among stratigraphy,  
953 silicification, fracture patterns, petrophysical properties, and hypogene karst formation in the CCS.

954 The main outcomes are summarized in the following points:

955 1) The mineralogy of the deposits and the geomorphological features of the cave suggest a  
956 deep-seated hypogene (hydrothermal) origin for the early karst phase. Early diagenetic  
957 silicification caused the replacement of dolomite grains and cement with microcrystalline  
958 quartz (up to 80-85 wt% of the bulk rock content). Below low permeability units, extensive  
959 mineral deposits are associated with blocky mega-quartz, chalcedony and a paragenesis of  
960 solid inclusions supporting the hydrothermal hypothesis.

961 2) The structural and stratigraphic variability in the CCS determined a strong anisotropy in  
962 fracture patterns, petrophysical properties, and fluid flow pathways. Fracturing  
963 concentrated in chert nodules causes a high intensity of open-mode fractures contributing  
964 to high permeability and dissolution localization. At the same time, through-going fracture  
965 zones and faults in the lower sector of the cave (characterized by low primary porosity and  
966 permeability) focused rising fluid flow along vertical permeability pathways (feeders and  
967 rising conduits).

968 3) Sedimentary units composed of heteroliths, marly dolostones, and fine-grained siliciclastic  
969 rocks represent a low-permeability seal/buffer unit that stopped/buffered vertical fluid flow.  
970 Through-going fracture zones breached these units, allowing vertical discharge and  
971 providing interconnectivity among the different sedimentary units.

972 4) The structural and stratigraphic variability in the CCS determined the formation of a complex  
973 3D multistorey karst system. Silica-dominant dissolution (likely at  $T \geq 100-150^{\circ}\text{C}$  and  $\text{pH} \geq 8-$   
974  $9$ ) promoted the formation of a stratigraphically-controlled inception horizon in the silicified  
975 and high-permeability dolostones of the middle storey. Multiple silica- vs. carbonate-

976 dominant dissolution phases driven by hydrothermal solutions produced large-scale karst  
977 porosity, as well as the precipitation of the quartz-rich mineral deposits filling pore space  
978 and fractures. During telodiagenesis, collapses, condensation-corrosion, and karstification in  
979 supergene and epigene settings further amplified the conduit dimensions until today.

980 5) The results presented in this study may contribute to expand our understanding of hypogene  
981 karst development in layered carbonate-siliciclastic units affected by silicification. The CCS  
982 example may be used to improve the conceptualization of predictive models on the spatial  
983 and morphological organization of buried hypogene conduit networks.

984

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1002

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