

Integrated hydrothermal evolution of a Botucatu paleodune and a blanketing lava flow from the Serra Geral Group, Uruguaiana

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Abstract

The integrated hydrothermal evolution of the large Santa Otília Paleodune from the Botucatu paleoerg and the cover Catalán Flow from the Serra Geral Group is here evaluated in Uruguaiana, southern Paraná Basin. Methods included satellite images, field surveying, petrography, and U-Pb geochronology of detrital and volcanic zircon. The tops of the compound linear-barchan paleodunes are exposed in the topographic highs. Rhombi and bowls at the top of the silicified sandstone units are significant, as is the poor preservation of eolian layering. The fish-bone-shaped dune tops are surrounded by the lavas. The oxidized top of the flow (upper Tier 2) overlies the reduced base (Tier 1), which consists of exposed, massive rocks in creek beds that are light gray-colored and contain small (10 cm) agate geodes and numerous silicified sandstone dikes. The youngest dated zircon grains from the sandstone are 225–300 Ma old (one 175 Ma age), and the main older age peaks are 450–600 Ma (predominant), 900–975 Ma, 1800–1900 Ma, and 2500 Ma; few Archean 2.5 Ga ages. The strongly altered volcanic zircon preserved in the reddened Catalán Flow yields a concordia-intercept age of 137.3 ± 7.6 Ma. Complex processes are thus constrained in the evolution of the Botucatu Formation and the first Serra Geral lava flow.

KEYWORDS: Botucatu paleodune; Serra Geral Group lava; hydrothermalism; paleo-hot spring field; zircon provenance.

INTRODUCTION

The geological evolution of major structures is significant for the understanding of ancient geological processes in large basins. Individual processes have been constrained in many sedimentary-volcanic basins. These processes include sand deposition in a major erg (Amarante et al., 2019), the formation of an eolian sandstone-hosted aquifer (Araújo et al., 1999), and the effusion of lavas from a large igneous province (Bellieni et al., 1984). However, the complex interaction of these processes in the same basin may be overlooked and requires a detailed description of structural, igneous, sedimentary, and hydrothermal features.

In that sense, a large erg (1.2 million km²) was formed in the hyperarid Botucatu desert during the Late Jurassic-Early Cretaceous (150–135 Ma; e.g., Amarante et al., 2019) in central-southern Gondwana. Eolian processes in this study area

have been investigated by Bertolini et al. (2020), Hartmann and Cerva-Alves (2021), and Scherer (2000). The Paraná Volcanic Province (specifically the Serra Geral Group) was established in the hyperarid Serra Geral desert. Humid climate prevailed locally during volcanism in the northeastern extreme of the basin (Buck et al., 2022; Manes et al., 2021). Nevertheless, dry climate controlled the sedimentation of the Upper Cretaceous Bauru Group in the northern part of the basin (Dias et al., 2021); the group occurs locally in the studied region. Volcanism was characterized by Bellieni et al. (1984), Gomes et al. (2018), Hartmann et al. (2010), Leinz (1949), Peate et al. (1992), and Rossetti et al. (2021), among many studies. The porous eolian sand became saturated in rainwater after being blanketed by the first lava flow (Hartmann et al., 2010), forming the large (1.2 million km²) Guarani Paleoaquifer. The first few lavas covered the active dunes (e.g., Scherer, 2000), but evaluation of the full interaction of the three main structures—sand sea, volcanic group, and paleoaquifer—has started recently (Hartmann & Cerva-Alves, 2021; Hartmann et al., 2021, 2022a, 2022b, 2023, 2024a, 2024b). Nevertheless, the large area and great diversity of geological processes require additional efforts for a full understanding of this unique geological configuration in the continents.

We selected the large (5 × 12 km) Santa Otília Paleodune (a compound sand mound) in the southern portion of the paleoerg to study the evolution and interaction of the erg-turned aquifer and the first lava flow represented by the Catalán quartz andesite. Observation of satellite images was followed

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by field survey, sample study by optical microscopy, scanning electron microscopy (SEM), and U-Pb zircon dating from a sandstone sample and from a lava sample. Lava cooling caused narrow thermal effects (2–10 cm-thick cornubianites) on the loose sand grains, but the recrystallization of the sand by action of the heated aquifer was intense. High Eh and low pH of the ascending water caused oxidation of the lava flow and formed the upper Tier 2. Modification of water chemistry to low-Eh and slightly lower pH led to a reduction of the lower half of the flow into Tier 1. Agate geodes formed in Tier 1, and hot springs formed at the surface of the dunes. Sandstones and volcanic rocks were fractured into rhombi during non-magmatic hydrothermalism, followed by transcurrent and normal faulting during the Gondwana break-up.

GEOLOGICAL SETTING

The studied paleodune occurs in the Fronteira Oeste Rift (Hartmann & Cerva-Alves, 2021), located in the southern portion of the Paraná Basin in Brazil (Zalán et al., 1990), close to the border with Argentina and Uruguay (Figs. 1a and 1b). Normal faulting extends into Argentina, Uruguay, and Paraguay (Mira et al., 2013; Torra, 2005; Veroslavsky et al., 2021). The geological units surfacing in the region belong mostly to the Botucatu Formation (Silva et al., 2004) and the Serra Geral Group (Wildner et al., 2007) and in a few places

to the underlying Guarú Formation (e.g., Silva et al., 2004). Intrusive and effusive sand bodies are small in area but numerous and are included in the Novo Hamburgo Complex (Duarte et al., 2020), which was coeval with the volcanic group. The division of the Serra Geral Group into formations was made by Rossetti et al. (2018) for a region situated 1,000 km from the study area.

The Guarú Formation is constituted by alternating eolian and fluvial beds totaling 60 m in the region. A flat-lying unconformity separates the formation from the overlying Botucatu Formation of eolian beds, which are 100 m thick. This large (1.2 million km²) desert lacked wet interdunes (e.g., Amarante et al., 2019) and is made up in the region mostly by compound linear and barchan dunes (Cosgrove et al., 2021), in addition to sand sheets (e.g., Hartmann & Cerva-Alves, 2021). The Botucatu Formation sandstones from the region (Bertolini et al., 2020) have a quartz-dominated framework and mean $Qz_{89}F_8L_3$ mineralogical composition (Q = quartz; F = feldspar; L = lithic fragments). Intense silicification is displayed by the sandstones in a large part of the occurrences in the Fronteira Oeste Rift (Hartmann et al., 2022c).

The active sand sea was flooded by tholeiitic volcanic rocks from the Serra Geral Group (ca. 134.5 Ma; e.g., Gomes & Vasconcellos, 2021; Hartmann et al., 2019; Scherer, 2000). Six lava flows were recognized by Hartmann et al. (2010, 2024a), Martins et al. (2011), although Bergmann et al. (2020)

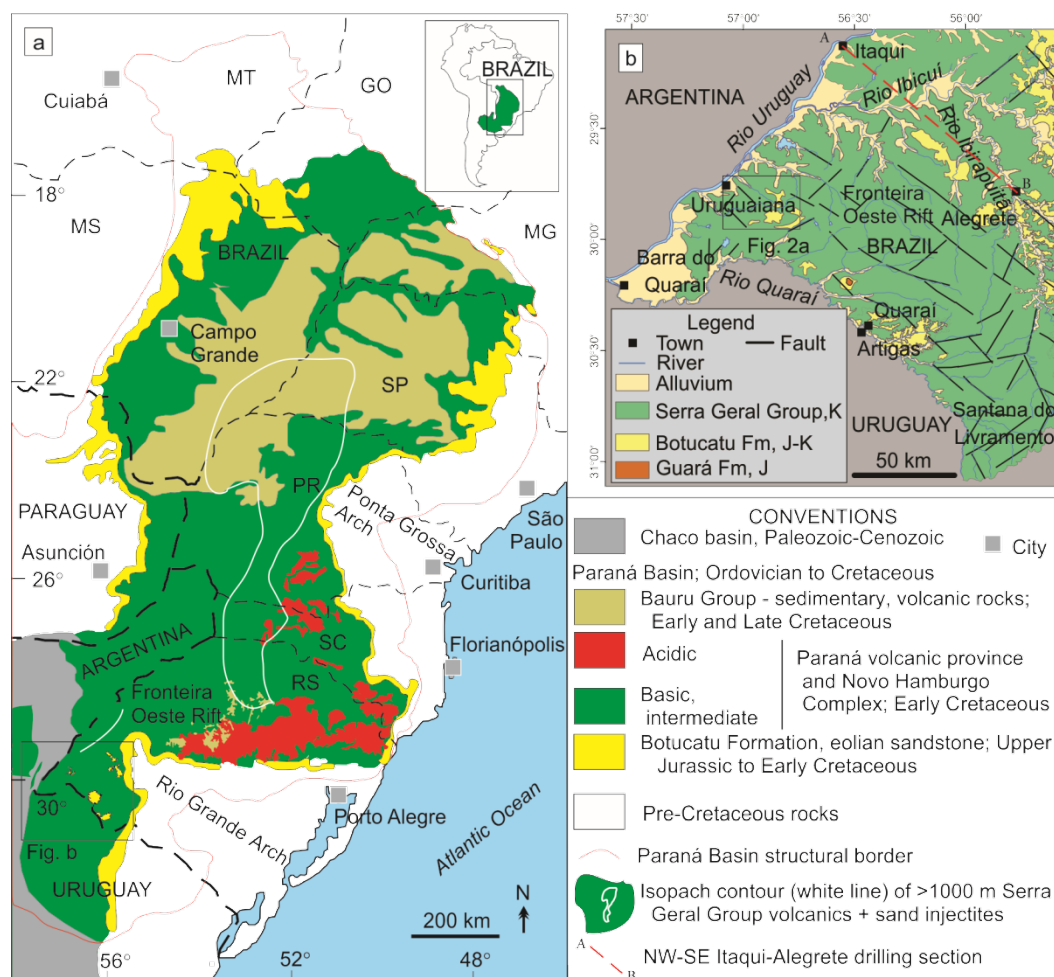


Figure 1. (a) Geological map of the Serra Geral Group and underlying Botucatu Formation; external limit of Paraná Basin indicated; map from Hartmann and Cerva-Alves (2021). Location of (b) shown. (b) Geological map of the Fronteira Oeste Rift (simplified from Silva et al., 2004).

identified 12 flows in a larger area. Support for the stratigraphy came from studies and drilling logs by SIAGAS-CPRM (2022). The interdunes were flooded by basalt lava (Mata Olho Flow) and further covered by three successive, extensive lava flows. These are a quartz andesite (Catalán Flow) and two basaltic andesites (Cordillera and Muralha Flows). In higher elevations, the hills are topped by a basaltic andesite (Coxilha Flow). Because the rift has been subjected to erosion since the Early Cretaceous, the eventual presence of additional flows at the top of the local stratigraphy was estimated (1,000 m thick) from the apatite fission track studied in the eastern portion of the rift (e.g., Bicca et al., 2020).

In most parts of the rift, the main flows (Catalán, Cordillera, and Muralha) display two tiers each. Tier 2 at the top is reddish and was oxidized in the Early Cretaceous during the percolation of hot water from the Guarani Paleoquifer (Hartmann et al., 2024a, 2024b). The lower part of the oxidized flow was altered by hot water from the same aquifer, which had turned reducing and acidic (Hartmann et al., 2024a, 2024b), due to lower velocity of water percolation (lower fluid/rock ratio). The two lower flows (Catalán and Cordillera Flows) host world-class amethyst geode deposits in Artigas (UY) and many small agate geode deposits on the Brazilian side of the border. Large-scale production of agate geodes is made from the Catalán Flow in Artigas.

Ruptile, normal (100–300 m downthrow), and small transcurrent fault zones criss-cross the rift (Hartmann et al., 2010). These structures seem related to the distensive forces from crustal thinning and opening of the South Atlantic Ocean. The Pelotas Basin along the oceanic coast is a result of the tectonic process. The sedimentary and volcanic rocks in the region formed therefore in pre-rift conditions (Stica et al., 2014).

Strong distensive forces that led to ocean opening also formed the Cuesta de Haedo (Chebataroff, 1951; Verdum et al., 2012), which is a geomorphological structure that embraces the Fronteira Oeste Rift. The cuesta dips 10° to the west from 360 m elevation near the town of Santana do Livramento and 60 m elevation in Uruguiana; the backslope is 200 km wide. The top of the cuesta is protected from erosion by the presence of spaced occurrences of silicified Botucatu Formation sandstones and the dominant presence of the two extensive lava flows—Catalán and Cordillera Flow, in addition to the Muralha Flow. The lava flows were also silicified.

ANALYTICAL METHODS

The area was selected from the literature and field campaigns, including satellite image observations and previous studies. Subsequently, samples ($n = 20$) were collected for laboratory analyses. Methods included satellite image observation, field gamma spectrometry, mineralogy, petrography, SEM, and U-Pb zircon geochronology of igneous and detrital zircon via laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

A field guide to the Fronteira Oeste Rift was published by Hartmann et al. (2022a). The mapping of paleodune contacts and volcanic rocks, as well as the recognition and integration of

structural features, were performed during field work. A portable gamma spectrometer was used for gamma emission readings in the field, a Super Spec RS 125 from Exploration Radiation Detection Systems. The counts per second (cps) of the outcrop allowed the identification of the sandstones and lava flows, even under thin soil cover. Petrographic and SEM analyses were carried out at Universidade Federal do Rio Grande do Sul.

Zircon crystals were separated from the rock samples (sandstone and quartz andesite) by first crushing and milling in a disk mill. The material was then concentrated using a #80 mesh sieve. Denser fractions were additionally separated using a pan and dried between 50 and 70°C. The magnetic fraction was separated using a neodymium magnet and a Frantz magnetic separator for segregation in diamagnetic and paramagnetic portions. The concentrated detrital (ca. 300) and volcanic (ca. 20) zircon grains were handpicked and mounted in epoxy resin and then polished using alumina powder. Semi-quantitative analyses were carried out via energy-dispersive spectroscopy using a SEM JEOL 6610 to confirm that the crystals were all zircon. All these steps were performed at the Institute of Geosciences of the Federal University of Rio Grande do Sul.

U-Pb analyses were acquired using a Thermo Fisher Scientific Neptune multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) coupled with a Photon-Machines 193 nm ArF laser ablation (LA) system, housed at the Isotope Geochemistry Laboratory of the Universidade Federal de Ouro Preto (UFOP). A detailed description of the LA-MC-ICP-MS method employed for the acquisition of U-Pb zircon ages at UFOP is given by Lana et al. (2017). Background measurement during 20 s was followed by zircon ablation during 20 s and 30 μm spot size. The laser frequency was set to 10 Hz with a fluence of 3.7–3.9 J/cm². The LA-ICP-MS data were reduced online using the software Saturn (Silva et al., 2022). Calibration was performed using the GJ-1, BB, and Plesovice standard reference materials (Jackson et al., 2004; Santos et al., 2017; Sláma et al., 2008), which were measured between every ten zircon spots on the sample. The GJ-1 standard yielded an average age of 603.3 ± 1.7 Ma (2σ , mean square weighted deviation [MSWD] = 1.4), while the BB and Plesovice secondary standards yielded average ages of 561.6 ± 1.6 Ma (2σ , MSWD = 0.81) and 337.5 ± 1.0 Ma (2σ , MSWD = 1.06). Isoplot (Ludwig, 2003) was also used for plotting the data and calculating the ages, and the errors are given in 2 sigma. A minimum threshold of 90% concordance was established, and provenance ages were calculated based on the $^{206}\text{Pb}/^{238}\text{U}$ ratio given that most grains fall within the Proterozoic and Phanerozoic eons.

RESULTS

Results are presented for satellite imaging, field geology, petrography, SEM, and U-Pb age determinations of zircon from a sandstone and from a quartz andesite. Every rock outcrop had the cps intensity measured with the gamma spectrometer. In satellite images, the studied region displays subdued topography, elevations varying from 90 to 155 m asl in

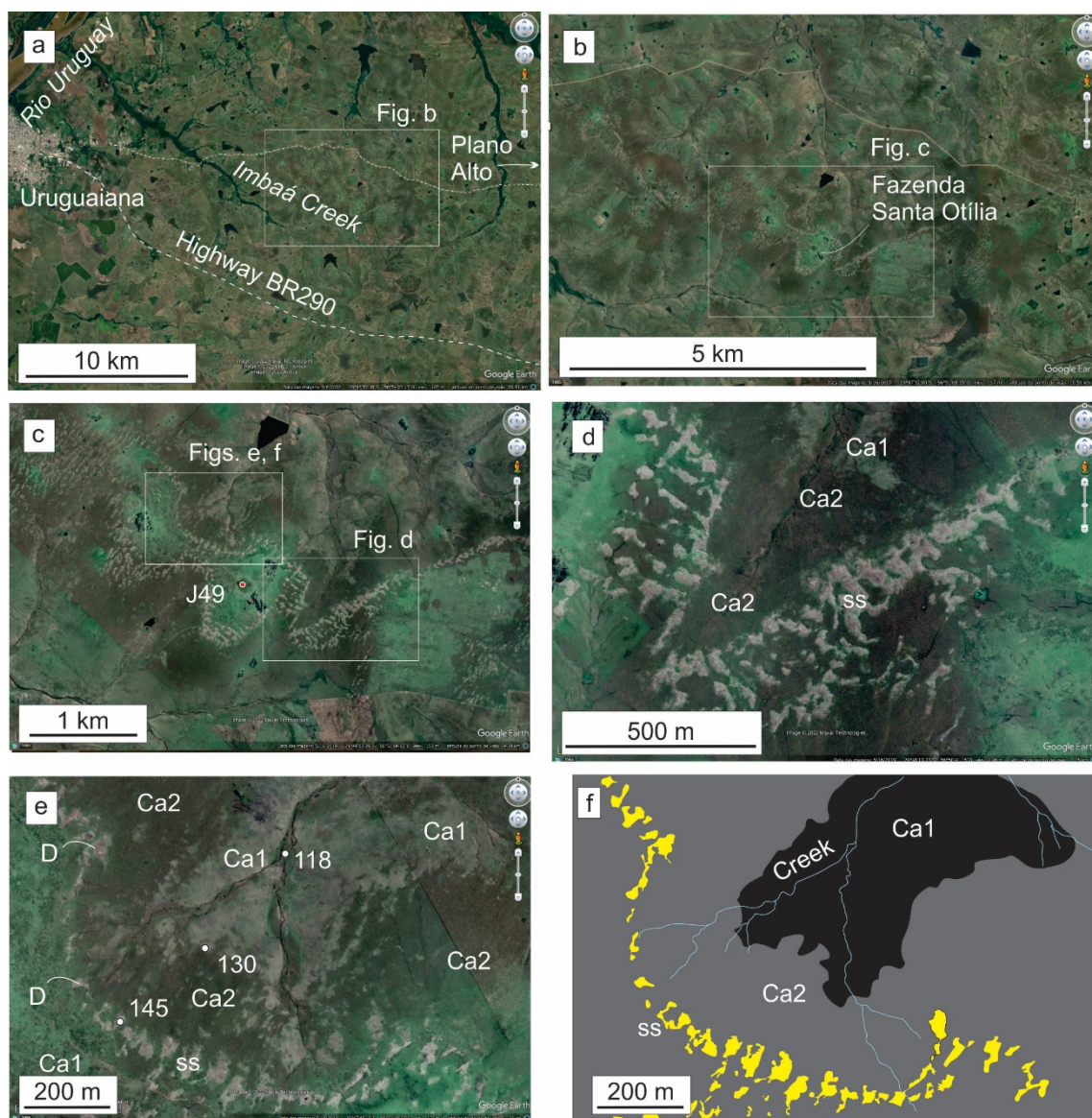
a traverse from west to east. The layer-cake geological structure of the units in the wider region (Hartmann et al., 2010) is less apparent in the studied region because of the presence of one flow (Catalán).

The basal stratigraphic unit (Botucatu Formation) occurs both along the tops of the hills at the highest elevations and beneath the quartz andesite in lower elevations. The base of the Catalán Flow is poorly exposed in the studied area; exposures in creek beds at the lowest elevations (90 m) correspond to that basal part. The exposures of the upper part (core) of the flow start 2–5 m lower than the silicified-sandstone-supported hill tops and continue downhill to reach the Imbaá Creek bed and other creeks. The upper amygdaloidal crust was eroded.

The studied, exposed paleodune top constitutes a string of fishbone-shaped sand mounds aligned WNW (Figs. 2a–2f).

Local and regional occurrence of composite paleodunes is extensive in all directions outside the study area, covered extensively by remnants of the Catalán and Cordillera (basaltic andesite) Flows.

The studied set of dunes is here called Santa Otilia Paleodune from the name of the Santa Otilia Ranch (Hartmann & Cerva-Alves, 2021). Linear and barchan dune types predominate (Figs. 2c–2f). Intense fluidization (and accompanying dune collapse) and silicification occurred most of the sedimentary layering of the eolian sandstones. Layering was only locally preserved. Bare exposures of silicified sandstone are at the highest elevation of the hills and stand 2–5 m above the surrounding grasslands. A large number of paleothermal bowls occur at the rounded tops of the silicified sandstone (Fig. 3).



Ca1: lower, reduced Catalán Flow; Ca2: upper, oxidized Catalán Flow; ss: paleodune top; creeks in blue lines.

Figure 2. Satellite images of the studied region. (a) Location of the studied region. Highway to Porto Alegre (state capital) and dirt road to Plano Alto village indicated. (b) Studied region, referenced to Santa Otilia Ranch. (c) Closer view around Santa Otilia Ranch. Location of rock sample J49 indicated; chemical analysis (Catalán Flow, oxidized) published by Hartmann and Cerva-Alves (2021). (d) Selected example of light gray, fishbone-structured paleodune tops (ss) exposed at the highest position in the hills, surrounded by the brown Catalán Flow (Ca), which is underlain by the Mata Olho Flow along the creek. Greenish-gray portion of the Catalán Flow is the silicified upper amygdaloidal crust; (e) selected exposure of the three main geological units of the studied region; elevations asl indicated (e.g., 118); and (f) simplified geological map.

The volcanic rock is poorly exposed in the upper portion, mostly as sparse, small (0.1–0.5 m), weathered blocks. The rock and the soil are brown-colored (enriched in Fe-oxyhydroxides) both in satellite images and in the field, but the rock appears light gray from a distance whenever the exposure is covered by lichen. Rock sample J49 was analyzed for its chemical composition by Hartmann and Cerva-Alves (2021); location in Fig. 2c. That sample is a quartz andesite from the upper, oxidized portion of the Catalán Flow. The reduced lower portion is poorly exposed along creek beds and margins, forming discontinuous stretches 50–100 m long (Fig. 4a). Many silicified sandstone dikes (0.1–2.0 cm thick) occur intrusive in the reduced portion of the volcanic rock (Fig. 4b). Quartz-chalcedony (inset in Fig. 4a) geodes (1–30 cm large) are common in the reduced lower portion of the flow. The overlying Cordillera Flow, occurring to the south of the Imbaá Creek, seems to be downthrown by a fault positioned along the creek. This flow displays rhombohedral fracturing (Fig. 5). The Catalán Flow near the contact with the sandstones consists of hypocrySTALLINE rocks with very fine to fine grains, featuring subhedral plagioclase microphenocrysts. These rocks may exhibit glomeroporphyritic texture with clinopyroxene microphenocrysts. Ophitic and subophytic textures are locally present. The matrix is composed of plagioclase, clinopyroxene, and opaque minerals. The plagioclase crystals within the matrix exhibit clay formation, resulting in a yellowish-brown color and a cloudy

aspect. Dispersed in the matrix, the opaque crystals are cubic to rectangular, and some are anhedral.

The numerous 0.1–10.0 m-sized blocks of silicified sandstone present criss-crossing fractures. The number of fractures identified (Figs. 6a, 6b, and 7) is six, distributed along three different directions. This structure results in three-dimensional rhombi. The fractures show no evidence of faulting, such as displacement along crossing fractures, polished surfaces, or slickensides. “Fracture” is used because distinction between joints and faults cannot be made (Dávalos-Elizondo & Laó-Dávila, 2022).

Two lithofacies were defined from the petrography of the sandstones. One lithofacies exhibits a massive, chaotic, or sub-parallel grain orientation. The framework consists of polycrystalline and monocrystalline quartz, potassium feldspar, and rare plagioclase. Hydrothermal processes affected the sandstones in three steps (Fig. 8). H1 caused precipitation of hematite around detrital grains. H2 was caused by the collapse of the dune and the expulsion of water and fluidized sand. H3 corresponded to the precipitation of quartz and chalcedony around detrital grains wherever pores remained after the collapse. This dominantly intergranular porosity is estimated at 15 vol.%.

The other lithofacies consist of sandstones exhibiting parallel and irregular bedding, with alternating packing and cementation between layers, resulting in variations in porosity. That bedding

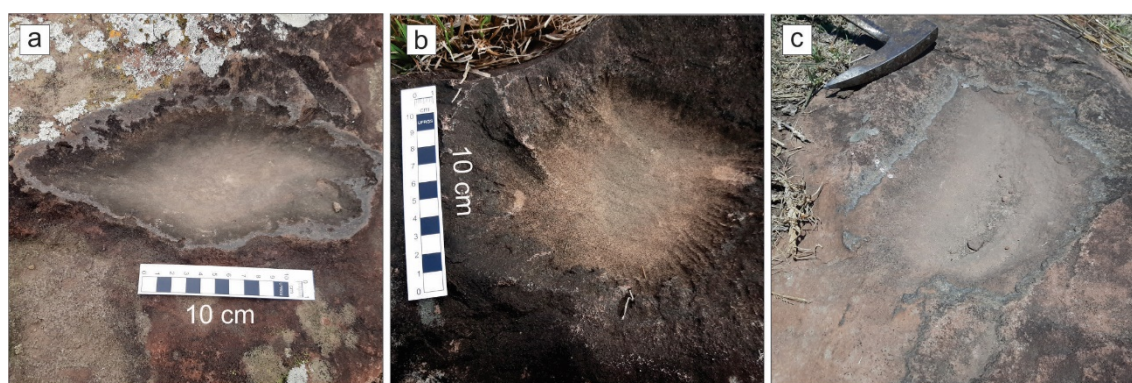


Figure 3. Paleo-hot spring bowls on top of the Santa Otilia Paleodune.

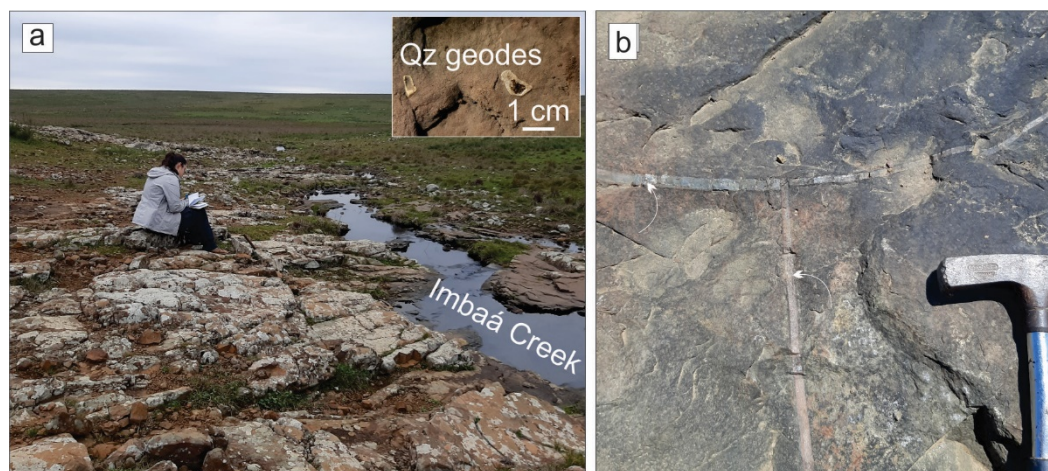


Figure 4. Field photos of the lower, reduced Catalán Flow at 1 km to the south of Fazenda Santa Otilia farmhouse. (a) Extensive, continuous exposure in creek bed and margins; grasslands in the hill are underlain by the upper Catalán Flow, partly Cordillera Flow on the hill past the creek (normal fault along creek); the rock presents rhombohedral fractures; the inset shows small geodes in the volcanic rock; (b) silicified sandstone dikes in the basalt.

originated in the accumulation of grains under water after compaction of the dune. The framework is composed of medium- to well-sorted grains, dominantly monocrystalline quartz and subordinate polycrystalline quartz, potassium feldspar, and



Figure 5. Field exposure of the upper, oxidized portion of Catalán Flow near Santa Otilia Ranch.

plagioclase. Thin (micrometric) iron oxide films are present at grain edges. Authigenic kaolinite formed a layer around the grains. Intergranular porosity predominates over intragranular porosity, which is secondary and results from the dissolution of feldspar.

The histogram of ages (Table 1) of 188 detrital zircon grains—which fall within the established threshold of 90–100% concordance—show a significant variation in the source area of these sediments (Fig. 9). The detrital zircon $^{206}\text{Pb}/^{238}\text{U}$ ages from the studied sample have five main populations. The predominant peak is 450–600 Ma (Upper Ordovician–Ediacaran). Four other populations are individualized with smaller peaks. These peaks are at the Upper Triassic–Upper Carboniferous (225–300 Ma), Tonian (900–975 Ma), Orosirian (1.8–1.9 Ga), and Paleoproterozoic–Archean (2.5 Ga).

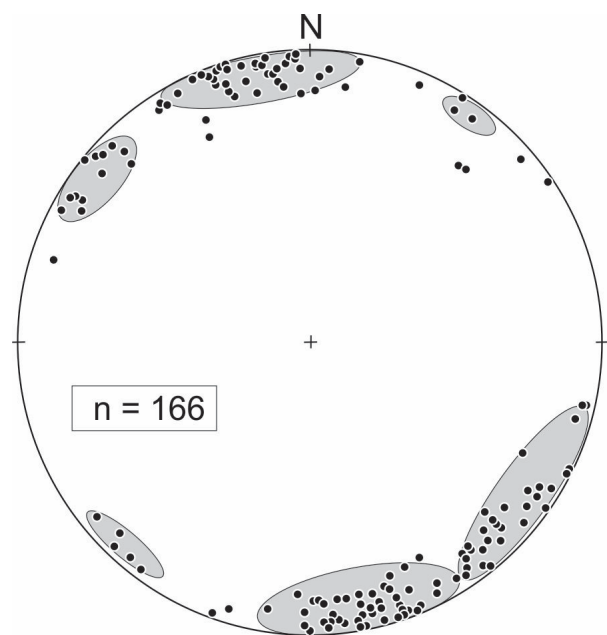


Figure 7. Pole projection on equal area, lower hemisphere stereogram, indicating the presence of six fracture surfaces in the compound Santa Otilia Paleodune and defining rhombi.



Figure 6. (a) and (b) Field photos of the Santa Otilia Paleodune sandstone, displaying rhomboheral fractures. Grasslands between paleodunes are underlain by the oxidized Catalán Flow. Rocky exposure of paleodune stands 5 m above the grass in the middle distance.

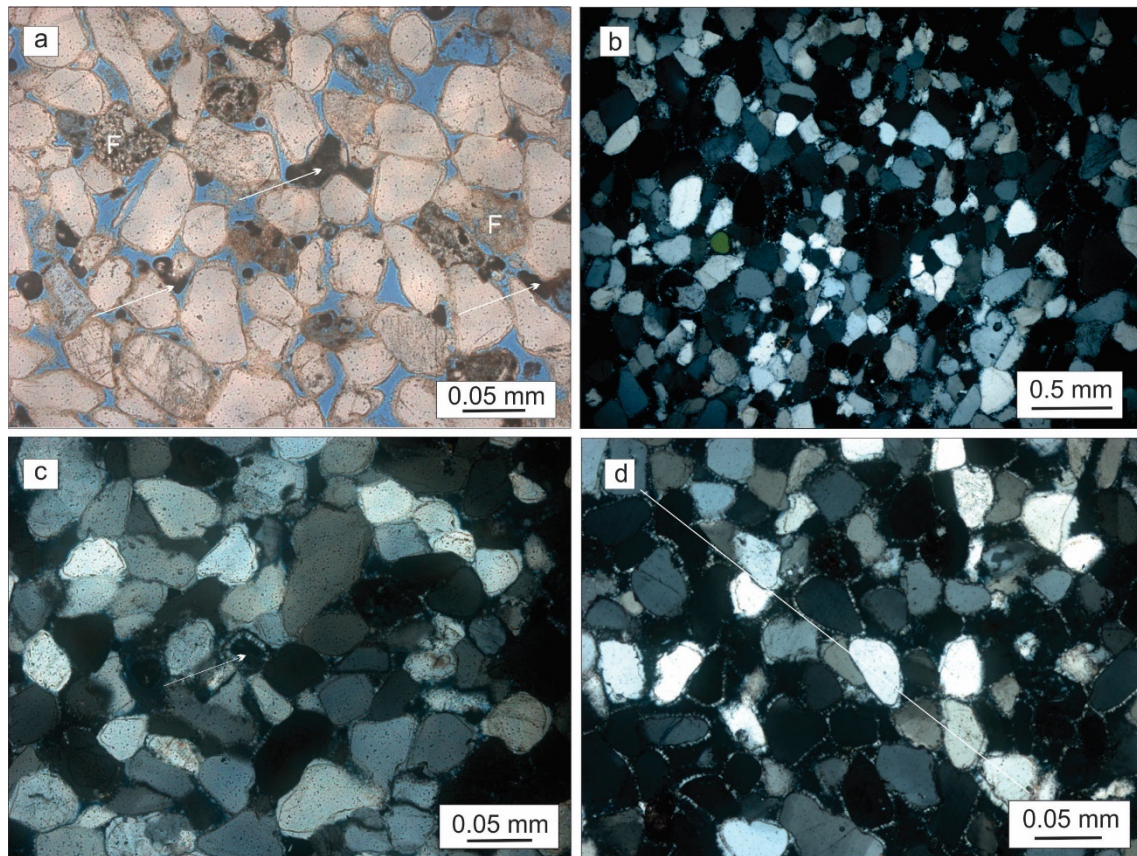


Figure 8. Photomicrographs of eolian sandstone from the Santa Otilia Paleodune. (a) Parallel nicols. Rounded to subangular sand grains, made up mostly of quartz and minor feldspar. Blue color indicates presence of voids (15 vol.%). Hematite (crystals in black indicated by white arrows) formed before compaction of dune sand—hydrothermal event H1. Compaction followed—H2, indicated by lateral contacts of detrital grains. Silicification during H3 is indicated by quartz overgrowths into pores remaining after compaction. (b) Crossed nicols. Rounded to subangular sand grains. (c) Crossed nicols. Quartz-dominated sandstone, post-compaction, displaying multiple lateral contacts of detrital grains. Quartz overgrowths abundant into remaining pores. Micro-geode rimmed by quartz, shown by the white arrow. (d) Crossed nicols. The white line is parallel to bedding originated by the settling of grains under water during compaction.

Table 1. U-Pb in zircon data by LA-MC-ICP-MS from the sandstone of the Santa Otilia Paleodune.

Sample SO10b	U (ppm)	Th (ppm)	U/ Th	Isotopic ratios				Ages (Ma)					Concordance (%)
				$^{207}\text{Pb}/^{235}\text{U}$	2σ (%)	$^{206}\text{Pb}/^{238}\text{U}$	2σ (%)	ρ	$^{206}\text{Pb}/^{238}\text{U}$	2σ (abs)	$^{207}\text{Pb}/^{235}\text{U}$	2σ (abs)	
213	98.19	19.45	0.20	0.65967	1.21	0.08154	1.10	0.91	505.32	5.35	514.41	5.37	98.23
214	175.34	72.88	0.42	5.31462	1.35	0.31949	1.31	0.97	1787.22	20.43	1,871.22	13.28	95.51
215	107.84	31.22	0.29	0.80541	1.43	0.09532	1.35	0.94	586.91	7.57	599.88	7.06	97.84
216	284.37	15.63	0.05	0.69350	1.31	0.08465	1.26	0.96	523.79	6.32	534.90	5.94	97.92
218	169.16	48.85	0.29	0.79550	1.38	0.09405	1.31	0.95	579.46	7.28	594.29	6.74	97.50
219	270.85	117.36	0.43	0.65511	1.51	0.07991	1.22	0.81	495.59	5.83	511.62	6.55	96.87
220	400.71	34.99	0.09	0.73134	1.36	0.08829	1.31	0.96	545.40	6.84	557.34	6.36	97.86
223	325.61	72.46	0.22	3.26244	1.31	0.24747	1.24	0.95	1,425.42	15.87	1,472.14	11.53	96.83
224	86.74	44.65	0.51	2.89456	1.40	0.22768	1.28	0.92	1,322.33	15.34	1,380.50	11.86	95.79
225	171.12	19.19	0.11	1.58372	4.22	0.14157	2.51	0.59	853.54	20.11	963.83	27.50	88.56
226	356.95	70.61	0.20	11.56945	6.35	0.47240	3.87	0.61	2,494.09	80.50	2,570.21	63.46	97.04
227	289.85	133.79	0.46	0.83392	16.55	0.08578	1.95	0.12	530.52	9.94	615.79	79.92	86.15
228	297.15	32.52	0.11	0.69814	1.62	0.08522	1.53	0.95	527.20	7.76	537.68	7.26	98.05
229	101.75	24.60	0.24	3.77230	2.51	0.23429	2.46	0.98	1,356.93	30.15	1,586.87	21.78	85.51
230	80.40	25.27	0.31	0.61781	1.51	0.07705	1.33	0.88	478.48	6.15	488.48	6.31	97.95
233	127.89	52.37	0.41	0.53174	2.02	0.06965	1.92	0.95	434.02	8.07	432.96	7.54	100.25
234	207.01	64.00	0.31	0.61704	1.24	0.07736	1.11	0.90	480.33	5.15	487.99	5.25	98.43
235	83.84	73.00	0.87	6.14458	1.30	0.34674	1.27	0.97	1,919.02	21.04	1,996.60	13.25	96.11
236	58.05	11.53	0.20	4.11127	1.24	0.27924	1.18	0.95	1,587.54	16.69	1,656.55	11.70	95.83
237	70.14	27.36	0.39	0.84308	1.46	0.09771	1.09	0.75	600.98	6.28	620.84	7.39	96.80

Continue...

Table 1. Continuation.

Sample SO10b	U (ppm)	Th (ppm)	U/ Th	Isotopic ratios					Ages (Ma)				Concordance (%)
				²⁰⁷ Pb/ ²³⁵ U	2σ (%)	²⁰⁶ Pb/ ²³⁸ U	2σ (%)	ρ	²⁰⁶ Pb/ ²³⁸ U	2σ (abs)	²⁰⁷ Pb/ ²³⁵ U	2σ (abs)	
238	195.57	86.56	0.44	1.62311	2.04	0.15984	1.56	0.76	955.89	13.85	979.20	13.76	97.62
239	198.26	31.75	0.16	1.36432	1.40	0.13572	1.02	0.73	820.44	7.88	873.73	9.02	93.90
240	128.55	38.99	0.30	0.79622	2.97	0.09430	2.85	0.96	580.89	15.85	594.69	13.97	97.68
243	219.78	54.22	0.25	0.30645	2.15	0.04271	1.24	0.58	269.63	3.28	271.43	5.37	99.34
244	706.18	52.49	0.07	1.24469	4.14	0.12376	2.97	0.72	752.17	21.14	821.01	24.29	91.62
245	1023.02	50.34	0.05	0.73989	1.70	0.08956	1.65	0.97	552.93	8.77	562.34	7.88	98.33
246	147.27	18.36	0.12	1.87436	0.93	0.17308	0.80	0.86	1,029.07	7.64	1072.07	7.16	95.99
247	102.89	27.89	0.27	0.84233	1.34	0.09614	0.69	0.51	591.77	3.91	620.43	6.82	95.38
248	298.53	64.94	0.22	0.62900	1.32	0.07772	1.26	0.95	482.49	5.86	495.48	5.65	97.38
249	351.07	60.08	0.17	0.30890	1.80	0.04229	1.61	0.90	267.04	4.22	273.33	4.57	97.70
250	86.11	15.05	0.17	3.98439	0.70	0.27064	0.58	0.82	1,544.03	7.95	1631.02	7.20	94.67
253	226.13	28.31	0.13	1.51513	1.25	0.15178	1.20	0.96	910.92	10.21	936.51	8.50	97.27
254	179.96	36.28	0.20	0.71087	1.24	0.08671	1.18	0.95	536.05	6.05	545.26	5.74	98.31
255	101.06	17.10	0.17	1.03133	1.26	0.11523	1.21	0.96	703.05	8.08	719.59	7.17	97.70
256	109.80	26.98	0.25	4.10081	1.31	0.27754	1.27	0.97	1,578.97	17.79	1,654.46	12.26	95.44
257	98.58	25.29	0.26	5.49916	1.48	0.32373	1.05	0.71	1,807.92	16.61	1,900.47	14.56	95.13
258	190.69	0.03	0.00	0.61843	1.34	0.07696	1.26	0.94	477.98	5.82	488.86	5.66	97.77
258	819.56	46.72	0.06	0.69814	1.31	0.08527	1.26	0.96	527.53	6.41	537.68	5.98	98.11
260	496.91	39.10	0.08	0.68910	1.24	0.08339	1.09	0.88	516.32	5.40	532.26	5.62	97.00
263	213.35	25.88	0.12	0.78951	1.16	0.09414	1.07	0.92	579.97	5.94	590.89	5.73	98.15
264	149.41	32.48	0.22	0.53567	1.38	0.06862	1.28	0.92	427.81	5.29	435.57	5.31	98.22
265	682.88	31.39	0.05	0.75455	1.30	0.09048	1.25	0.96	558.39	6.70	570.86	6.23	97.82
266	491.47	95.39	0.19	0.86457	1.34	0.10066	1.27	0.95	618.26	7.47	632.61	6.88	97.73
267	172.46	48.31	0.28	0.62529	1.22	0.07806	1.14	0.93	484.52	5.32	493.16	5.22	98.25
269	109.46	61.76	0.56	0.68125	1.27	0.08335	1.15	0.91	516.09	5.73	527.53	5.71	97.83
270	211.36	48.40	0.23	0.56889	1.30	0.07270	1.23	0.95	452.41	5.39	457.30	5.22	98.93
273	127.54	49.60	0.39	0.28087	7.27	0.03755	3.22	0.44	237.64	7.52	251.34	16.54	94.55
274	391.09	80.11	0.20	1.56619	0.85	0.15576	0.73	0.86	933.18	6.34	956.92	6.16	97.52
275	136.04	14.75	0.11	0.74742	1.04	0.09156	0.91	0.88	564.78	4.94	566.73	5.02	99.66
276	152.00	37.09	0.24	6.30125	1.29	0.34992	1.08	0.84	1,934.20	18.02	2,018.63	13.18	95.82
277	208.26	69.49	0.33	0.80618	1.41	0.09465	1.35	0.95	582.99	7.51	600.31	6.96	97.11
278	246.75	89.34	0.36	0.80306	1.42	0.09448	1.37	0.96	581.96	7.61	598.55	6.97	97.23
279	360.11	112.84	0.31	0.76679	1.02	0.08938	0.81	0.80	551.89	4.31	577.92	5.03	95.50
280	361.51	94.92	0.26	1.07094	1.00	0.12066	0.95	0.95	734.36	6.59	739.20	5.92	99.34
283	577.91	16.58	0.03	0.71438	1.32	0.08682	1.29	0.97	536.68	6.63	547.34	6.11	98.05
284	96.33	17.52	0.18	0.70155	1.08	0.08602	0.85	0.78	531.95	4.32	539.71	5.03	98.56
286	42.98	28.32	0.66	2.48632	1.26	0.20886	1.18	0.94	1,222.72	13.21	1,268.06	10.35	96.42
287	207.08	51.61	0.25	2.20778	1.33	0.19601	1.29	0.97	1,153.83	13.68	1,183.51	10.40	97.49
288	107.96	13.36	0.12	0.66871	1.33	0.08241	1.22	0.91	510.50	5.97	519.93	5.91	98.19
289	420.90	13.84	0.03	1.42402	2.30	0.14498	2.05	0.89	872.76	16.77	899.05	14.65	97.08
290	481.87	18.14	0.04	1.28731	3.38	0.13325	3.25	0.96	806.36	24.67	840.10	20.27	95.98
293	103.95	17.07	0.16	1.30098	3.96	0.12247	1.98	0.50	744.74	13.91	846.16	23.76	88.01
294	19.14	12.35	0.65	0.61698	2.36	0.08107	1.68	0.71	502.51	8.13	487.95	9.64	102.98
295	15.03	9.39	0.62	0.61571	2.81	0.07947	1.96	0.70	492.95	9.31	487.16	11.37	101.19
296	206.05	10.14	0.05	0.84311	6.48	0.09854	6.05	0.93	605.85	35.08	620.86	31.09	97.58
297	175.54	44.48	0.25	0.57757	1.17	0.07378	1.11	0.95	458.88	4.92	462.90	4.76	99.13
298	160.70	44.43	0.28	0.57409	1.24	0.07286	1.18	0.95	453.39	5.15	460.66	5.03	98.42
299	314.00	55.73	0.18	0.75560	1.63	0.09158	1.56	0.96	564.86	8.43	571.47	7.66	98.84
300	545.06	157.26	0.29	0.74046	1.48	0.08993	1.39	0.94	555.13	7.38	562.68	6.92	98.66
313	1,107.20	73.18	0.07	0.39369	1.07	0.05363	1.00	0.94	336.74	3.27	337.06	3.37	99.91
325	285.13	35.55	0.12	0.80705	2.93	0.09534	2.23	0.76	587.02	12.50	600.80	13.92	97.71

Continue...

Table 1. Continuation.

Sample SO10b	U (ppm)	Th (ppm)	U/ Th	Isotopic ratios					Ages (Ma)				Concordance (%)
				$^{207}\text{Pb}/^{235}\text{U}$	2σ (%)	$^{206}\text{Pb}/^{238}\text{U}$	2σ (%)	ρ	$^{206}\text{Pb}/^{238}\text{U}$	2σ (abs)	$^{207}\text{Pb}/^{235}\text{U}$	2σ (abs)	
326	29.24	4.60	0.16	2.03924	1.35	0.18736	1.22	0.91	1,107.06	12.40	1,128.71	10.23	98.08
327	111.49	20.35	0.18	1.60156	1.34	0.15227	1.13	0.84	913.65	9.59	970.82	9.29	94.11
328	94.64	28.23	0.30	0.65203	1.42	0.08052	1.29	0.91	499.23	6.19	509.73	6.16	97.94
329	169.32	84.79	0.50	0.65647	1.38	0.08093	1.31	0.96	501.68	6.35	512.45	6.01	97.90
330	297.64	41.37	0.14	0.26134	53.94	0.03698	53.10	0.98	234.11	123.26	235.75	120.44	99.31
333	122.71	21.43	0.17	1.95544	1.26	0.17947	1.22	0.97	1,064.08	11.98	1100.32	9.51	96.71
334	118.04	23.62	0.20	0.67817	1.34	0.08292	1.27	0.95	513.52	6.29	525.67	5.98	97.69
335	94.13	41.52	0.44	0.58120	1.26	0.07300	0.87	0.69	454.18	3.82	465.23	5.12	97.62
336	871.00	182.75	0.21	2.31130	1.55	0.20045	1.51	0.98	1,177.71	16.27	1215.76	12.13	96.87
337	628.98	32.71	0.05	0.60140	1.34	0.07569	1.31	0.98	470.32	5.95	478.12	5.57	98.37
338	324.90	35.33	0.11	0.61312	1.35	0.07679	1.31	0.97	476.95	6.02	485.52	5.65	98.23
339	311.94	32.24	0.10	0.61374	1.34	0.07668	1.29	0.96	476.26	5.92	485.92	5.63	98.01
340	60.94	24.97	0.41	6.36785	1.23	0.34836	1.19	0.97	1,926.78	19.93	2,027.85	12.70	95.02
343	57.10	24.04	0.42	5.42818	1.31	0.32304	1.27	0.97	1,804.56	20.09	1,889.31	13.02	95.51
344	110.35	71.93	0.65	0.79183	1.51	0.09125	1.35	0.90	562.94	7.29	592.21	7.33	95.06
345	151.28	29.70	0.20	0.69690	1.50	0.08590	1.40	0.94	531.26	7.16	536.94	6.75	98.94
346	112.71	28.98	0.26	0.30962	3.49	0.04143	1.50	0.43	261.70	3.86	273.89	8.66	95.55
347	123.07	34.96	0.28	0.28791	1.64	0.04114	1.24	0.75	259.87	3.15	256.92	3.96	101.15
348	41.39	8.94	0.22	1.49549	1.38	0.15300	1.26	0.92	917.77	10.82	928.55	9.25	98.84
349	50.09	23.76	0.47	1.06381	1.97	0.11416	1.82	0.93	696.86	12.05	735.70	11.01	94.72
350	207.58	28.95	0.14	0.67797	1.97	0.08385	1.63	0.83	519.05	8.13	525.54	8.59	98.76
353	52.61	21.98	0.42	5.87947	0.82	0.32770	0.75	0.91	1,827.22	11.97	1,958.21	8.94	93.31
354	63.00	22.78	0.36	6.15504	1.31	0.34188	1.27	0.97	1,895.72	20.84	1,998.09	13.30	94.88
355	142.90	67.09	0.47	0.52082	1.37	0.06695	1.12	0.82	417.73	4.53	425.70	5.17	98.13
356	175.74	92.56	0.53	5.00657	4.09	0.29708	4.04	0.99	1676.83	59.90	1,820.43	36.87	92.11
357	116.86	26.41	0.23	1.27828	4.41	0.12259	1.30	0.30	745.46	9.17	836.09	26.16	89.16
358	152.46	67.73	0.44	5.41458	1.20	0.35498	0.99	0.83	1,958.33	16.74	1,887.16	12.03	103.77
359	181.58	105.87	0.58	0.66558	1.37	0.08236	1.30	0.95	510.17	6.39	518.02	6.06	98.48
360	145.28	40.10	0.28	1.48343	1.25	0.14914	1.18	0.95	896.15	9.92	923.64	8.44	97.02
363	93.50	14.47	0.15	1.72146	5.30	0.16437	5.19	0.98	981.00	47.37	1,016.57	35.50	96.50
364	511.67	6.05	0.01	0.93332	1.33	0.10681	1.28	0.97	654.19	7.98	669.38	7.13	97.73
365	212.38	78.92	0.37	0.79284	1.18	0.09506	1.12	0.95	585.42	6.28	592.78	5.85	98.76
366	103.56	49.87	0.48	0.78118	4.65	0.09253	3.78	0.81	570.48	20.69	586.16	21.45	97.32
367	194.81	50.03	0.26	9.07239	1.61	0.38068	1.49	0.93	2,079.46	26.53	2,345.33	16.92	88.66
368	117.25	45.33	0.39	5.39069	1.30	0.32273	1.25	0.96	1,803.07	19.68	1,883.38	12.87	95.74
369	176.32	26.23	0.15	1.60756	1.50	0.15793	1.45	0.97	945.24	12.73	973.16	10.30	97.13
370	96.45	61.96	0.64	6.06028	1.02	0.34184	0.94	0.92	1895.52	15.43	1,984.55	10.76	95.51
373	125.98	18.44	0.15	0.75314	1.37	0.09106	1.31	0.96	561.78	7.05	570.04	6.50	98.55
374	81.64	31.78	0.39	1.22425	1.37	0.12864	1.22	0.89	780.11	9.00	811.72	8.44	96.11
375	215.88	30.86	0.14	6.08237	1.26	0.35053	1.18	0.94	1,937.14	19.69	1,987.72	12.81	97.46
376	111.92	88.81	0.79	6.12253	1.44	0.34652	1.39	0.97	1,917.98	23.16	1,993.46	14.41	96.21
377	220.82	81.65	0.37	0.27078	1.78	0.03770	1.49	0.84	238.54	3.50	243.32	4.08	98.04
378	322.47	14.97	0.05	1.70873	1.79	0.16224	1.66	0.93	969.23	14.98	1,011.81	12.42	95.79
379	300.07	62.14	0.21	1.55715	1.55	0.15432	1.49	0.96	925.11	12.83	953.34	10.50	97.04
380	95.99	30.35	0.32	18.27962	1.39	0.55799	1.33	0.96	2,858.32	30.81	3,004.57	16.21	95.13
383	169.21	36.80	0.22	4.80413	1.50	0.30419	1.43	0.95	1,712.04	21.56	1,785.62	14.34	95.88
384	187.74	44.12	0.24	10.68791	1.35	0.43829	1.32	0.98	2,342.97	26.02	2,496.37	14.93	93.86
385	151.57	96.75	0.64	11.96712	1.47	0.47283	1.44	0.98	2,495.95	29.92	2,601.83	16.24	95.93
386	197.89	118.95	0.60	11.87666	1.44	0.46816	1.41	0.98	2,475.50	29.08	2,594.73	15.89	95.41
387	351.85	166.37	0.47	1.24096	1.29	0.13183	1.26	0.97	798.30	9.44	819.32	8.03	97.43
388	684.75	40.71	0.06	0.77245	1.23	0.09247	1.20	0.97	570.14	6.52	581.17	5.99	98.10

Continue...

Table 1. Continuation.

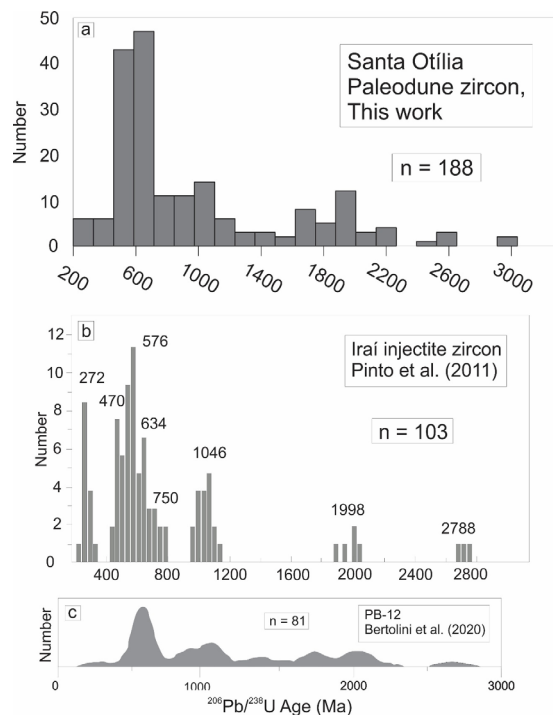
Sample SO10b	U (ppm)	Th (ppm)	U/ Th	Isotopic ratios					Ages (Ma)				Concordance (%)
				²⁰⁷ Pb/ ²³⁵ U	2σ (%)	²⁰⁶ Pb/ ²³⁸ U	2σ (%)	ρ	²⁰⁶ Pb/ ²³⁸ U	2σ (abs)	²⁰⁷ Pb/ ²³⁵ U	2σ (abs)	
389	73.45	21.06	0.29	0.62523	1.66	0.07634	0.97	0.58	474.26	4.43	493.12	6.94	96.17
390	92.92	28.01	0.30	1.32280	1.43	0.13748	1.36	0.95	830.39	10.63	855.74	9.09	97.04
393	292.16	45.25	0.15	0.80358	2.50	0.09368	2.08	0.83	577.29	11.50	598.84	11.92	96.40
394	295.08	17.94	0.06	0.79570	1.53	0.09458	1.50	0.98	582.54	8.35	594.40	7.47	98.00
395	250.96	66.29	0.26	0.66502	1.34	0.08141	1.29	0.96	504.51	6.26	517.68	5.92	97.46
396	142.26	29.00	0.20	0.72530	1.29	0.08222	1.14	0.88	509.33	5.60	553.79	6.04	91.97
397	470.08	58.65	0.12	5.77091	2.89	0.31428	1.86	0.64	1,761.72	28.73	1,942.06	27.06	90.71
398	45.03	6.95	0.15	2.17309	1.52	0.19230	1.43	0.94	1,133.81	14.89	1,172.47	11.68	96.70
399	452.32	14.32	0.03	0.61420	1.42	0.07701	1.39	0.97	478.22	6.40	486.20	5.96	98.36
400	136.11	25.12	0.18	19.43445	1.33	0.56851	1.29	0.97	2,901.69	30.20	3,063.64	15.69	94.71
413	1045.43	74.35	0.07	0.39173	1.45	0.05356	1.24	0.86	336.32	4.06	335.63	4.45	100.21
424	295.29	18.01	0.06	0.99666	1.52	0.11223	1.33	0.87	685.71	8.66	702.11	8.39	97.66
425	146.75	30.94	0.21	1.24103	1.77	0.13045	1.34	0.75	790.40	9.95	819.35	10.75	96.47
426	132.10	46.32	0.35	0.62695	1.45	0.07896	1.20	0.83	489.89	5.66	494.19	6.12	99.13
427	138.25	46.15	0.33	6.12003	1.91	0.34749	1.76	0.92	1,922.60	29.31	1,993.11	18.63	96.46
428	790.09	93.07	0.12	0.74395	1.24	0.08825	0.93	0.75	545.16	4.86	564.71	5.88	96.54
429	195.34	53.58	0.27	0.72335	3.45	0.08724	2.61	0.76	539.18	13.50	552.64	15.31	97.56
430	146.82	25.08	0.17	2.16196	1.98	0.18649	1.23	0.62	1,102.31	12.45	1,168.90	14.86	94.30
433	208.88	15.13	0.07	1.13016	1.36	0.12227	1.11	0.81	743.61	7.77	767.83	8.03	96.85
434	376.04	114.02	0.30	0.28183	1.61	0.03965	1.38	0.86	250.66	3.40	252.11	3.83	99.43
435	354.98	58.80	0.17	6.30170	2.93	0.35318	2.65	0.91	1,949.77	44.73	2,018.69	27.80	96.59
436	26.02	7.51	0.29	8.38105	1.84	0.39917	1.65	0.90	2,165.23	30.34	2,273.13	18.86	95.25
437	224.08	24.52	0.11	5.15268	4.50	0.29456	3.96	0.88	1,664.30	58.34	1,844.84	40.67	90.21
438	94.63	23.62	0.25	1.88451	1.45	0.17619	1.15	0.79	1,046.14	11.14	1,075.65	10.64	97.26
439	134.03	7.60	0.06	1.76788	25.32	0.16503	25.25	1.00	984.67	234.79	1,033.74	179.87	95.25
440	192.06	33.91	0.18	0.68491	1.75	0.08389	1.53	0.88	519.29	7.65	529.74	7.71	98.03
443	77.67	28.44	0.37	0.66601	1.66	0.08181	1.29	0.78	506.94	6.29	518.28	7.23	97.81
444	191.47	131.44	0.69	0.60230	1.66	0.07363	1.14	0.68	458.00	5.04	478.69	6.80	95.68
445	213.50	63.38	0.30	0.61269	1.58	0.07753	1.35	0.85	481.37	6.26	485.26	6.57	99.20
446	627.23	68.19	0.11	0.67936	1.53	0.08337	1.32	0.86	516.23	6.54	526.39	6.77	98.07
447	155.88	21.46	0.14	0.81315	1.39	0.09579	1.12	0.81	589.69	6.32	604.22	6.87	97.60
448	64.50	21.41	0.33	27.99402	1.35	0.64877	1.11	0.82	3,223.38	28.30	3,418.89	16.47	94.28
449	49.27	16.36	0.33	0.55325	2.97	0.08647	1.45	0.49	534.64	7.45	447.12	11.21	119.57
450	169.39	23.18	0.14	0.66109	1.58	0.08067	1.22	0.77	500.15	5.88	515.28	6.88	97.06
453	178.26	44.68	0.25	4.57540	1.79	0.29376	1.61	0.90	1,660.27	23.55	1,744.80	16.57	95.16
454	156.59	32.54	0.21	10.19460	2.44	0.40137	2.30	0.94	2,175.36	42.62	2,452.59	25.03	88.70
455	976.45	82.12	0.08	1.04744	1.57	0.11672	1.39	0.89	711.66	9.38	727.61	8.84	97.81
456	118.51	29.13	0.25	4.27122	1.46	0.28468	1.25	0.86	1,614.88	17.89	1,687.83	13.62	95.68
457	81.95	11.72	0.14	5.48599	1.41	0.32404	1.20	0.85	1,809.44	19.00	1,898.40	13.92	95.31
458	38.08	16.64	0.44	1.74650	1.42	0.16813	1.12	0.79	1,001.80	10.36	1,025.87	10.11	97.65
459	254.41	38.66	0.15	0.59948	1.43	0.07556	1.20	0.84	469.56	5.45	476.91	5.89	98.46
460	156.15	28.62	0.18	1.52536	1.38	0.15174	1.15	0.84	910.70	9.81	940.63	9.36	96.82
463	153.93	70.18	0.46	0.58232	1.50	0.07367	1.23	0.82	458.21	5.43	465.95	6.04	98.34
464	358.95	45.85	0.13	0.74937	1.57	0.09016	1.37	0.88	556.49	7.33	567.86	7.35	98.00
465	288.34	34.42	0.12	1.55147	1.77	0.15340	1.57	0.89	920.00	13.48	951.08	11.83	96.73
466	622.95	75.92	0.12	0.64442	1.48	0.08019	1.28	0.86	497.28	6.11	505.04	6.35	98.46
467	286.12	23.29	0.08	0.70191	3.54	0.08706	3.40	0.96	538.12	17.58	539.93	15.42	99.66
468	24.59	4.02	0.16	6.30364	1.36	0.34707	1.08	0.80	1,920.61	18.03	2,018.96	13.83	95.13
469	47.08	17.76	0.38	0.84429	1.78	0.09365	1.41	0.79	577.10	7.81	621.51	8.87	92.85
470	666.74	95.57	0.14	0.77522	96.21	0.09354	96.20	1.00	576.45	553.56	582.75	553.38	98.92
473	80.72	31.09	0.39	4.07491	1.45	0.27365	1.23	0.85	1,559.29	17.00	1,649.29	13.38	94.54

Continue...

Table 1. Continuation.

Sample SO10b	U (ppm)	Th (ppm)	U/ Th	Isotopic ratios					Ages (Ma)				Concordance (%)
				²⁰⁷ Pb/ ²³⁵ U	2σ (%)	²⁰⁶ Pb/ ²³⁸ U	2σ (%)	ρ	²⁰⁶ Pb/ ²³⁸ U	2σ (abs)	²⁰⁷ Pb/ ²³⁵ U	2σ (abs)	
474	225.12	42.52	0.19	1.19967	1.52	0.13048	1.29	0.85	790.58	9.64	800.44	9.19	98.77
475	264.21	31.55	0.12	0.64097	1.62	0.07931	1.41	0.87	491.99	6.69	502.91	6.90	97.83
476	163.99	54.93	0.33	2.77425	1.34	0.22239	1.08	0.81	1,294.47	12.71	1,348.63	11.24	95.98
477	205.42	31.07	0.15	0.63617	1.96	0.07980	1.25	0.64	494.95	5.95	499.93	8.20	99.00
478	170.66	18.59	0.11	0.89650	1.81	0.10273	1.59	0.88	630.37	9.58	649.86	9.32	97.00
479	58.08	8.62	0.15	7.44732	2.22	0.38226	2.08	0.94	2,086.82	37.24	2,166.67	22.07	96.31
480	43.08	29.82	0.69	0.76596	1.88	0.09552	1.34	0.71	588.08	7.55	577.44	8.85	101.84
483	306.32	80.09	0.26	0.79806	1.43	0.09519	1.20	0.84	586.15	6.75	595.73	6.98	98.39
484	1,519.33	267.71	0.18	0.57097	1.66	0.07206	1.45	0.87	448.56	6.28	458.64	6.57	97.80
485	290.26	141.61	0.49	0.77806	1.36	0.09059	1.01	0.74	559.00	5.39	584.38	6.57	95.66
486	303.78	32.76	0.11	1.42757	4.41	0.14286	4.00	0.91	860.83	32.31	900.53	27.50	95.59
487	139.56	35.18	0.25	6.81668	2.65	0.33362	2.48	0.94	1,855.92	40.17	2,087.89	25.60	88.89
488	680.26	101.43	0.15	1.04469	1.36	0.11604	1.12	0.82	707.75	7.50	726.25	7.74	97.45
489	163.71	47.12	0.29	0.62459	1.35	0.07851	1.11	0.82	487.20	5.22	492.72	5.74	98.88
490	57.52	25.84	0.45	2.61744	1.40	0.21142	1.14	0.81	1236.36	12.80	1,305.55	11.49	94.70

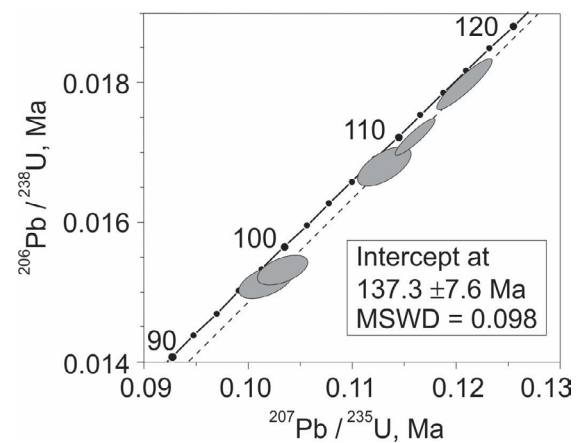
LA-MC-ICP-MS: laser ablation multi-collector inductively coupled plasma mass spectrometry.

**Figure 9.** Histograms of zircon U-Pb ages. (a) Ages of detrital zircon from the studied Santa Otilia sandstone, > 95% concordance. (b) Ages of detrital zircon from a sand injectite in the Serra Geral Group from Iraí (RS) (Pinto et al., 2011) (c) Data from detrital zircon from the Botucatu Formation (Bertolini et al., 2020). All three samples have similar zircon ages.

The U-Pb concordia age from the upper intercept based on the analyses of five euhedral igneous zircon crystals from the Catalán quartz andesite is 137.3 ± 7.6 Ma (Fig. 10 and Table 2). Mostly highly discordant ages (< 90% concordance) produced by Pb loss ($n = 15$) were discarded.

INTERPRETATION

We interpret the evidence as resulting from a wide range of geological processes active sequentially in the Early Cretaceous

**Figure 10.** (a) U-Pb zircon intercept age of Catalán Flow (quartz andesite). Isotopic ratios are strongly altered by oxidation. Data-point error ellipses are 2σ .

in the studied paleodune from the Botucatu Formation and the Catalán Flow from the Serra Geral Group. These results integrate the sandstones into the Inhanduí paleodune field occurring in the Fronteira Oeste Rift of southern Brazil.

Erosion since the Early Cretaceous uncovered the bare top of the composite paleodune, which has a typical fishbone design amid the grasslands covering the quartz andesite. The design is common to many paleodunes in the large, regional dune field.

Volcanic rocks in the studied region belong to the Catalán Flow, dominantly the upper red Tier 2. The gray, reduced Tier 1 is mostly hidden. Only the massive core of the lava is preserved in the studied area; the lower amygdaloidal crust is not exposed in the studied region because of the low-lying relief. No cooling joints were observed, similar to most exposures of the flow in the region (Hartmann et al., 2010). The volcanic rocks in the studied region are similar to the Catalán Flow studied in a wider region to the east (Hartmann et al., 2024a).

A significant structure of the flow is the presence of an oxidized, red Tier 2 at the top of the flow, and a reduced, gray Tier 1 at the base. Tier 2 covers the top of the hills side-by-side

with the top of the silicified paleodune. Extensive (50–100 m long), continuous, gray rock exposures are present in the Imbaá Creek and others. The numerous sandstone dikes (1.0–10.0 cm thick) were intensely silicified. Many small (1.0–20.0 cm large) agate geodes attest to the reduced, acidic environment of alteration of rocks along creeks. The lower solubility of SiO_2 resulted in widespread agate geode formation.

The two-tiered structure and mineralization of the Catalán Flow were extensively described by Hartmann et al. (2024a) in the eastern part of the rift. Similar processes seem operative in the Santa Otilia region, which is situated 100 km west of some of the exposures described by Hartmann et al. (2024a).

The rhombohedral structure identified in the sandstones was caused by forces related to vertical σ_1 . Six surfaces were formed, resulting in a rhombic structure (see Hartmann et al., 2022b). The volcanic rocks were also affected by similar deformation. Upward pressuring of hot water is considered the main mechanism that intensely broke the rocks (Hartmann & Cerva-Alves, 2021).

The large number of bowls identified in the paleodune is strong evidence of paleo-hot spring activity in the studied region. Hot water from the Botucatu paleoerg injected fluidized sand into the paleodune and the quartz andesite and intensely silicified sandstones and volcanic rocks.

Non-magmatic hydrothermalism in the region was similar to segments of the East African Rift where alteration was caused by deep percolation of surface water (Dávalos-Elizondo & Laó-Dávila, 2022). Large rift segments, e.g., Basin and Range, U.S.A., display dominant alteration caused by non-magmatic resources (Hinz et al., 2015). No magmatic sources were identified in the studied region, leading us to conclude that the fluid originated in the heated Guarani Paleoaquifer.

The provenance of zircon in the sand that formed the eolian dunes was similar (Fig. 9) to large extents of the Botucatu Formation in southern Brazil (Bertolini et al., 2020). The provenance signature is particularly similar (except for the 1600–1800 Ma ages) to the sand injectite (Fig. 9) studied by Pinto et al. (2011) in Iraí, situated 100 km to the NE of the Santa Otilia sample. The youngest zircon grains are 225–300 Ma old, and the main older age peaks are at 450–600 Ma (predominant), 900–975 Ma, 1.8–1.9 Ma, and 2.5 Ma. The youngest age obtained by those studies is 175 Ma with few Archean 2.5 Ga ages. The dominant ages from the extensive study by Bertolini et al. (2020) are Tonian-Stenian (900–1250 Ma) and Orosirian-Rhyacian (1800–2200 Ma). These ages from several studies are found

in zircon from Precambrian rocks, although the main provenance is interpreted by Bertolini et al. (2020) as recycling of detrital zircon from the Paraná Basin. A similar evaluation of basinal zircon reworking with minor basement contribution was made by Rodrigues et al. (2024). The absence of late Paleoproterozoic detrital grains in the study of Pinto et al. (2011) may be due to the varied paleowinds not originating in SW Amazon Craton (Sunsás Orogen).

Magmatic zircon grains from Tier 2 of the Catalán Flow still preserve a significant age of 137.3 ± 7.6 Ma, which is within the error of the magmatic age of the Serra Geral Group. The volcanism that formed the group is considered a short-lived (1–2 Ma) event close to 134.5 Ma (Gomes & Vasconcellos, 2021; Pinto et al., 2011). Zircon from the Catalán Flow was dated at 131.3 ± 1.4 Ma in a sample collected near Quaraí town, 150 km east of the studied region (Hartmann et al., 2019).

The evolution of the paleodune and cover lava flow is depicted (Fig. 11) as an initial sequence of eolian accumulation of sand in a hyperdry desert followed by lava flooding during continued dry atmospheric conditions. The Catalán Flow covered the active dune, causing little thermal effects. The filling of the porous sand with rainwater formed the Guarani Paleoaquifer in a short time ($< 1,000$ years). During the same time span, the aquifer was heated to 100–250°C and percolated at high velocity (H1 hydrothermal event) through the porous sand (50% porosity) and the porous quartz andesite (30% porosity), locally depositing Fe-oxyhydroxides in the pores. The temperature estimate is based on known, active geothermal fields; isotopic data from amethyst geodes in Artigas (Uruguay) resulted in an estimate of 50–120°C (Morteani et al., 2010). The porosity of uncompacted eolian sand is from Araújo et al. (1999), and the porosity of basalt is from Flóvenz and Saemundsson (1993).

Clogging of porosity of the quartz andesite by deposition of clay minerals and zeolites formed seal 1 above the aquifer. This resulted in event H2 of hot water + sand injection and effusion into and over the rocks. Dune collapse occurred during H2. Continued hot water percolation led to the formation of seal 2. The slow percolation of hot water caused the strong alteration (H3) of the volcanic rock and the formation of agate geodes (Duarte et al., 2009, 2011; Hartmann et al., 2012; Michelin et al., 2021). Zircon was strongly altered during hydrothermalism, but some of the crystals were sufficiently preserved from alteration to display the general magmatic U-Pb age despite Pb loss. Detrital zircon in the sandstone preserved the provenance ages.

Table 2. U-Pb in zircon data by LA-MC-ICP-MS from the andesite associated with the Santa Otilia Paleodune.

Sample SO13	U (ppm)	Th (ppm)	Th/U	Isotopic ratios					Ages (Ma)				Concordance (%)
				²⁰⁷ Pb/ ²³⁵ U	2σ (%)	²⁰⁶ Pb/ ²³⁸ U	2σ (%)	ρ	²⁰⁶ Pb/ ²³⁸ U	2σ (abs)	²⁰⁷ Pb/ ²³⁵ U	2σ (abs)	
167	806.91	231.49	0.29	0.12074	1.97	0.01797	1.91	0.97	114.81	2.18	115.74	2.26	99.19
168	792.94	308.71	0.39	0.11310	1.87	0.01680	1.40	0.75	107.39	1.49	108.79	2.03	98.70
174	1,201.60	278.98	0.23	0.10321	1.96	0.01532	1.03	0.52	97.99	1.00	99.73	1.95	98.25
175	905.30	222.52	0.25	0.10167	2.11	0.01514	1.27	0.60	96.85	1.22	98.32	2.07	98.51
177	774.54	205.78	0.27	0.11605	1.36	0.01724	1.25	0.92	110.17	1.37	111.48	1.54	98.82

LA-MC-ICP-MS: laser ablation multi-collector inductively coupled plasma mass spectrometry.

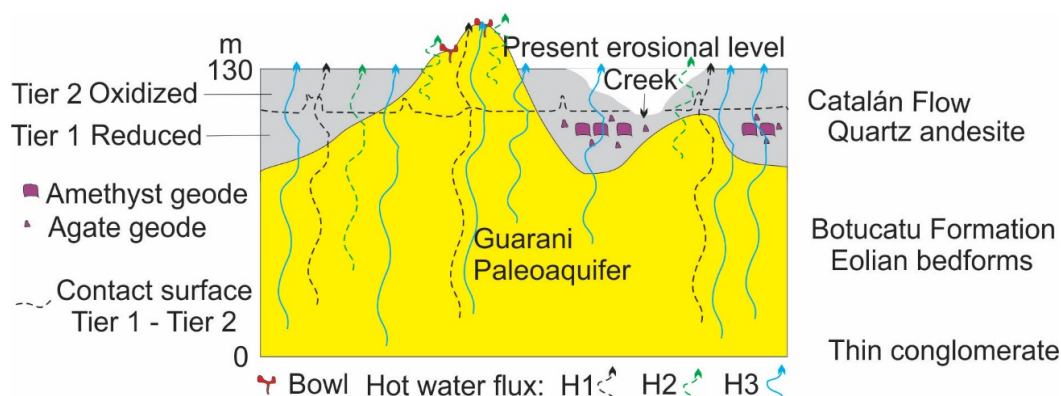


Figure 11. Evolutive model of the Santa Otilia Paleodune and blanketing Catalán Flow. Initial geological relationships consisted of eolian dune formation and its covering by the Catalán Flow. Intense hydrothermal events H1, H2, and H3 succeeded. Agate geodes and possibly amethyst geodes formed during H3 in the massive core of the flow.

The initial H1 alteration was oxidizing (black broken lines in Fig. 11), and we suggest an H3-reducing alteration (blue continuous lines). Sand injection during H2 is indicated by broken green lines. The resulting alteration of the flow displays a suggested lower Tier 1 (reduced, amethyst geode-bearing) and an upper Tier 2 (oxidized, barren). The presence of Tier 1 requires studies because the resulting rocks (agate-geode bearing) contain amethyst geodes in a deeper portion in other parts of the region and in Uruguay (Bergmann et al., 2020).

We have thus contributed to the understanding of a complex set of sedimentary, volcanic, tectonic, and hydrothermal processes in the southern Paraná Basin. The inception of intraplate volcanism covering an active erg resulted in the formation of the Guarani Paleoaquifer and the Serra Geral Group. Heating of the paleoaquifer by residual heat from volcanism caused intense hydrothermal interaction with the sandstones and the overlying volcanic rocks. Regional silicification ensued, including the formation of agate geodes (amethyst geodes in some places) and numerous bowls in paleothermal springs.

CONCLUSIONS

We evaluated the provenance of the large Santa Otilia Paleodune from the Botucatu paleoerg, the age of the cover Catalán Flow from the Serra Geral Group, and their hydrothermal alteration. Sand to form the dunes was sourced in the underlying Paraná Basin and from the Precambrian basement. Sand was sourced from rocks spreading in age between the Archean and 225–300 Ma, but the deposition of the sand is known to be Upper Jurassic-Lower Cretaceous from other studies. Zircon from the basalt is much altered, but the age of

five grains is 137.3 ± 7.6 Ma, compatible with previous studies in the volcanic group (ca. 134.5 Ma). A large paleo-hot spring field was established. Botucatu paleoerg dune tops were sealed during the percolation of hot water during hydrothermal event H1. Sandstones and basalt were oxidized during H1 and reduced during H3. Sealing was followed by rhombohedral fracturing of the sandstones and lavas during H2. The formation of a myriad of bowls at the top of the paleodunes during H3 was synchronous with the intense silicification of the Guarani Paleoaquifer. Agate geodes formed during H3 in the reduced basalt layer. Normal and transcurrent faulting occurred later during the rupturing of Gondwana. This evolutive description of the Santa Otilia Paleodune and the Catalán Flow adds to the knowledge of processes in this little-studied region of the Paraná Basin.

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L.A.H.: Conceptualization, field work, data compilation, data interpretation, article writing, drafting of figures. F.P.L.: Laboratory analyses, data compilation, revision of text and content. C.M.: Field geology, petrography, revision of text and content. M.J.: Field geology, petrography, sample preparation, revision of text and content. C.C.L.: U-Pb isotopic analyses of detrital and magmatic zircon, data handling, interpretation.

Competing interests: nothing to declare.

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