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GEOSCIENCES

Evolution of the redox-altered, two-tiered Muralha Flow in the Fronteira Oeste Rift, southern Paraná Volcanic Province

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Abstract: The thorough redox alteration of a lava flow is an undescribed feature in intraplate basaltic provinces. The Early Cretaceous (134.5 Ma) Paraná Province displays that alteration in the major Muralha Flow. This oxidized and reduced flow from the southern part of the province was studied with satellite images, field surveying, petrography, and published whole rock geochemistry. The 100 x 100 km flow from the Cuesta de Haedo presents two hydrothermal tiers – lower Tier 1 is gray to white, upper Tier 2 is red. Iron oxyhydroxides characterize Tier 2. Tier 1 contains clay minerals, zeolites, pyrite and calcite, and agate (possibly amethyst) geodes. In a first event, the upper Tier 2 was oxidized by hot water from the underlying Guarani Paleoaquifer. The high water/rock ratio decreased due to porosity clogging by precipitation of secondary minerals, and the fluid became reducing. Lowering of Eh and pH was caused by reaction of water with reducing particles (calcite, organic molecules) present in the paleoerg sandstones and with fresh rock surfaces. A lower Tier 1 was then formed during slow, hot water percolation. Reduction was interrupted below 30 °C (calcite formation). Large scale, similar alteration occurred in all studied oceanic ridges and only rarely in continental environments.

Key words: Redox reactions, two tiers, Muralha Flow, Serra Geral Group, amethyst geode, agate geode.

INTRODUCTION

The interaction of the first lava flows from a large igneous province with an active sand sea produces unique structures. The displacement of lava over the loose sand causes limited mechanical effects, and the thermal impact is confined to a few centimeters of hornfels and a few meters of more diffuse alteration. However, the inversion of the direction of heat flux is a source of remarkable changes in the structure and composition of the ambient-temperature lava. Heat flux from the lava downward into the sand can be reversed to flow from the heated erg-turned-aquifer upward into the lava.

The Paraná Volcanic Province (Fig. 1a) is a major LIP on the continents and displays the relationship with the underlying Botucatu paleoerg over a large area (1.0 mi. km^2). In the southern part of the province, the mechanical and chemical responses of the paleoerg-turned-Guarani Paleoaquifer, after the sealing by the first lavas, were evaluated by Hartmann & Cerva-Alves (2021), Hartmann et al. (2021, 2023, 2024). The lavas dip at a low angle (10° to WNW) for 200 km forming the Cuesta de Haedo.

The 134.5 Ma tholeiitic volcanic group (Hartmann et al. 2019, Gomes & Vasconcellos 2021) formed before the rifting that resulted in the opening of the Atlantic Ocean at 120-115 Ma (Stica et al. 2014). In the region, the cooling of

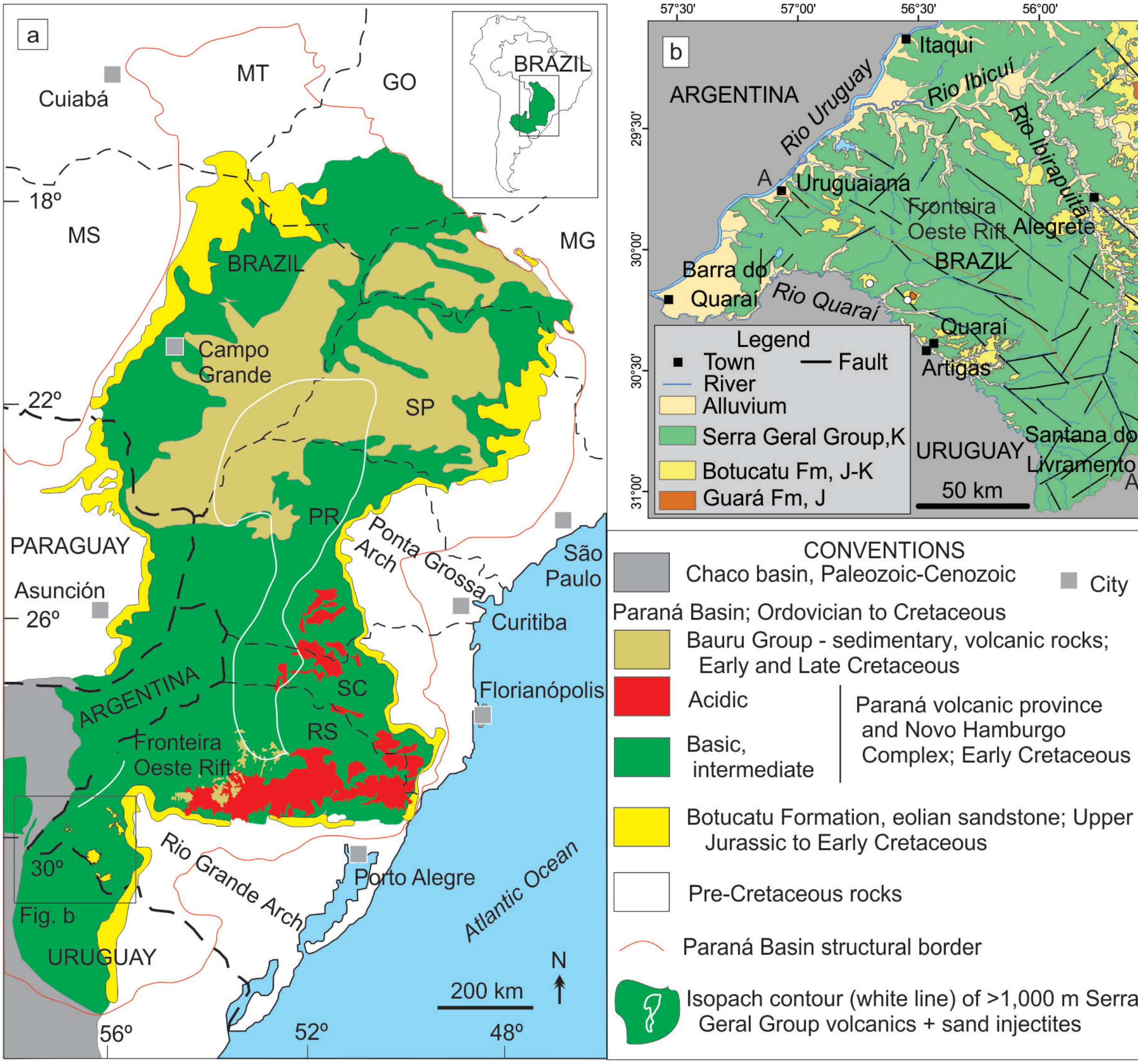

Figure 1. (a) Geological map of the Serra Geral Group (e.g. Hartmann et al. 2024); (b) Geological map of the Fronteira Oeste Rift (Silva et al. 2004), showing the dominance of the volcanic rocks and minor exposures of Botucatu Formation sandstones.

each lava flow was accompanied by a limited downward heat flux into the sand. Heat from mantle melting and sill cooling increased the geothermal gradient in the overlying crust, including the Paraná Basin.

The hyperdry erg sand likely contained a large volume of water below a deep water table, as observed in less-arid, active sand seas, where oases are common. The volcanic-sealed paleoerg quickly filled with rainwater above the previous water table and heated to 100-250°C. The ascent of hot water inverted the direction of heat flux upward into the ambient-temperature lavas, causing major alteration in the volcanic rocks. No technique is available to measure the time span between the successive processes, but the duration was likely several hundred years. The cooling of a 30m- thick lava takes less than 500 years, which is presumably the time taken for the 'heat wave' emanating from the heated mantle (higher geothermal gradient) to reach the rocks near the surface. The effusion of a new lava above the Muralha Flow probably occurred after 1,000 years or more. This estimate is based on the duration of magmatism to form the Serra Geral Group (1-2 Ma) and the number of flows in the group (n = 100-300, more than half eroded away). The sequence of events occurring in the construction of the Fronteira Oeste Rift by aeolian sedimentation and volcanism was determined. Nevertheless, the timing and duration of each event can only be estimated from geological relationships.

We selected the Muralha Flow in the Fronteira Oeste Rift of Brazil in Rio Grande do Sul to study the alteration and the resulting amethyst and agate geode mineralization generated by the flux of hot water into the third lava flow that extensively covered the paleoerg – the Muralha Flow. We integrated the studies of Hartmann et al. (2010) and Bergmann et al. (2020) with field work, petrography and revision of whole-rock chemical analyses. The flow was altered into two tiers by the upward flux of hot water from the Guarani Paleoaquifer, forming an oxidized portion that spanned the full thickness of the volcanic unit and a reduced layer in the lower half of the flow. The lower tier has the potential of hosting amethyst and agate geode deposits, similar to the underlying Catalán and Cordillera Flows (Hartmann et al. 2024). Small agate mines were described in the lower portion of the flow by Bergmann et al. (2020).

Geological setting

The Fronteira Oeste Rift is part of the Paraná Basin (e.g., Zalán et al. 1991, Santos et al. 2010), exposing at the surface in a few places the Guará Formation of alternating fluvial and aeolian beds (Fig. 1b). The large Botucatu erg covered the region and the basin, forming 100 m-thick bedforms in the region. The aeolian formations were described by Scherer (2000) and Scherer et al. (2023); field guides to the paleodunes are available (Hartmann et al. 2022a, Leitzke et al. 2023). Intense silicification of the paleodunes and overlying lavas was described by Hartmann et al. (2021, 2022b,c, 2023). The Early Cretaceous Serra Geral Group (*sensu* Wildner et al. 2007) of volcanic rocks is near the top of the basin, only covered by the Late Cretaceous Bauru Group of sedimentary and volcanic rocks in the northern part of the basin and locally in the studied region (Tupanciretã Formation). Transcurrent and normal faults cut the volcanic group.

The Muralha Flow is one of the basal volcanic units (Fig. 2) that covered the Botucatu paleoerg in the Early Cretaceous, Fronteira Oeste Rift, southern Paraná Volcanic Province

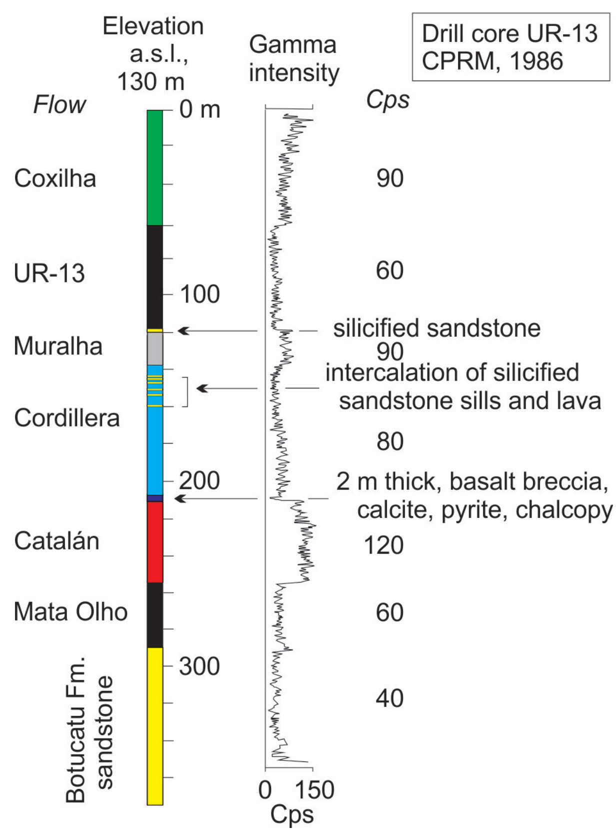

Figure 2. Log of drill core UR13 displaying six lava flows from the Alegrete Formation, representative of the lava stratigraphy in the studied region. Drilling and logging by the GSB (CPRM) in the 1980´s, previously described by Hartmann et al. (2010).

of Brazil and Uruguay. The rifting of the crust in the region during Atlantic Ocean opening also caused a shoulder effect and the formation of the Cuesta de Haedo (Chebataroff 1951, Müller Filho 1970, Suertegaray 1998, Verdum et al. 2012). The cuesta front slope is aligned N-S between the town of Santana do Livramento (BRA) and the hill Montes de Haedo (UY). The backslope has a dip of 10° to the WNW – 360 m a.s.l. in the eastern limit (Santana do Livramento town) and 60 m a.s.l. by Rio Uruguay (Uruguaiana town). The width of the cuesta is 350 km from Rio Ibicuí in the north (BRA) to Rio Negro in the south (UY).

A first basalt lava flowed into the interdunes (Mata Olho Flow; Hartmann et al 2010) of limited distribution. Wide stretches of active dunes, draas and sand sheets were first buried by a quartz andesite (Catalán Flow; Hartmann et al. 2010, 2024) and then by a basaltic andesite (Cordillera Flow; Hartmann et al. 2010). These two flows underlie the studied basaltic andesite (Muralha Flow) in the rift. One basaltic andesite (Coxilha Flow; Hartmann et al. 2010) occurs above the Muralha Flow in a few hills. A basalt (UR-13 Flow) underlies the Coxilha Flow in places, as registered in drill cores (Hartmann et al. 2010).

All flows in the rift are tholeiitic with pahoehoe structure, displaying an upper amygdaloidal crust, a massive core and a lower amygdaloidal crust. The core of the Catalán Flow is mostly massive; vertical cooling joints are recorded only in a few places. In contrast, the Cordillera Flow has the magmatic core partitioned into two layers; the upper, thicker (20-30 m) layer is massive with vertical cooling joints and the lower layer is massive without the joints. Both the Catalán and Cordillera Flows have a lower Tier 1 that was reduced and mineralized with amethyst and agate geodes. The two flows have a reddened upper Tier 2 that was oxidized and is barren of geodes. The presence of two tiers and mineralizations is unknown from the Muralha Flow. An upper massive layer with vertical cooling joints is displayed by the studied flow; a lower layer is massive without cooling joints. Both the Cordillera and Muralha Flows yield crushed stone for highway construction.

Flow thicknesses vary from 20 m to 40 m; the Muralha Flow reaches 60 m in some places. The upper crust was eroded in the hills, an observation that applies to all flows in the cuesta. The crust is only preserved in the immediate vicinity of the contact with the upper, cover flow. The physiography of the flows in the pampa consists of grassy hills, which end in 25-35°-inclined ramps. The Muralha Flow is observed in the field as overlying the Cordillera Flow. In satellite images, the studied flow has a green core of grasslands bordered by a wide rim with white to light gray tones.

MATERIALS AND METHODS

We used satellite image observation (GoogleEarth, which is based on Landsat8 images) to identify occurrences and describe the internal structure of the studied flow, including the measurement of approximate thickness. We also used the constellation Dove Cube Sat 3U PSB.SD of spectral images. Field observations were focused on several occurrences of the flow, including collection of rock samples. Two typical examples are shown in Figures 3a, b and Figures 4a-4j, with geographic coordinates of the hill. We studied thin sections under a petrographic microscope. Whole-rock geochemistry from the ACME Laboratories (Hartmann et al. 2010) and GEOSOL (Bergmann et al. 2020) laboratories were used for confirmation of flow identification and the evaluation of genetic processes. Supplementary Material Table SI displays selected examples of chemical analyses of rock

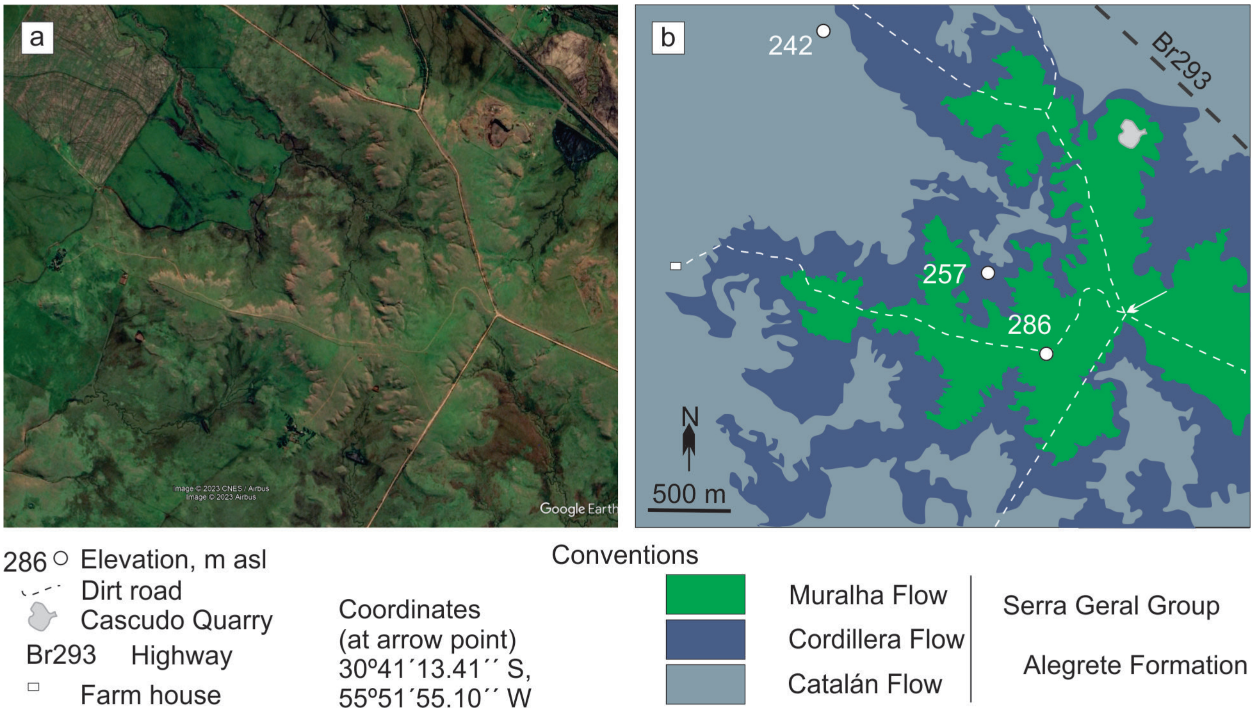

Figure 3. Selected occurrence of the three main lava flows from the Fronteira Oeste Rift, displaying the Muralha Flow on top of the Cordillera and Catalán Flows. (a) Satellite image; (b) Geological map of same area displayed in (a). Similar stratigraphy extends for tens of kilometers to the north.

samples from the studied flow at ACME (Duarte 2011). We emphasized the characterization of two tiers in the flow with a view to the possible presence of amethyst and agate geode deposits.

Three samples were analyzed by X-ray diffraction (XRD) to identify the minerals, particularly the white, powder material. The samples were collected at the outcrop shown in Figures 4a, 4b, 4c. The samples are LED46 (sand injectite in the Muralha Flow; 30°19’36.7’’ S, 56°05’58.6’’ W), LED99 (30°19’38.5’’ S, 56°05’58.1’’ W) and LED101 (30°30’04.5’’ S, 55°50’15.4’’ W) (both white portions of the outcrop). XRD analyses were done in an X-ray diffractometer Siemens (BRUKER AXS), MODEL D-5000 (θ-θ) equipped with a fixed anodic Cu tube (λ = 1.54), operating at 40 kV and 30 mA in the primary beam, and a curved grafite monochromator in the secondary beam. The equipment is installed at the Centro de Pesquisa em Petrologia e Geoquímica, Instituto de Geociências, Universidade Federal do Rio Grande do Sul, Brazil. The powder sample was analyzed in the 2θ angular interval of 2 to 72° in steps of 0.02°/1s using divergence and anti-spreading windows of 1° and 0.2 mm in the detector.

RESULTS

Several characteristics lead to the identification of the Muralha Flow in the rolling pampas – satellite images, field description and chemical analyses. We selected two examples to illustrate the geological relationships of the flow (Fig. 3a, b, Fig. 4a-j). In the images, the top of the vertically-jointed flow appears as homogeneous green grasslands surrounded by a wide (100-200 m), white rim. The homogeneity of the green core and the large width of the white rim distinguish the flow from the underlying Cordillera Flow, which has more irregular cores and narrower white rims. The rim is wider (up to 300 m) in hills

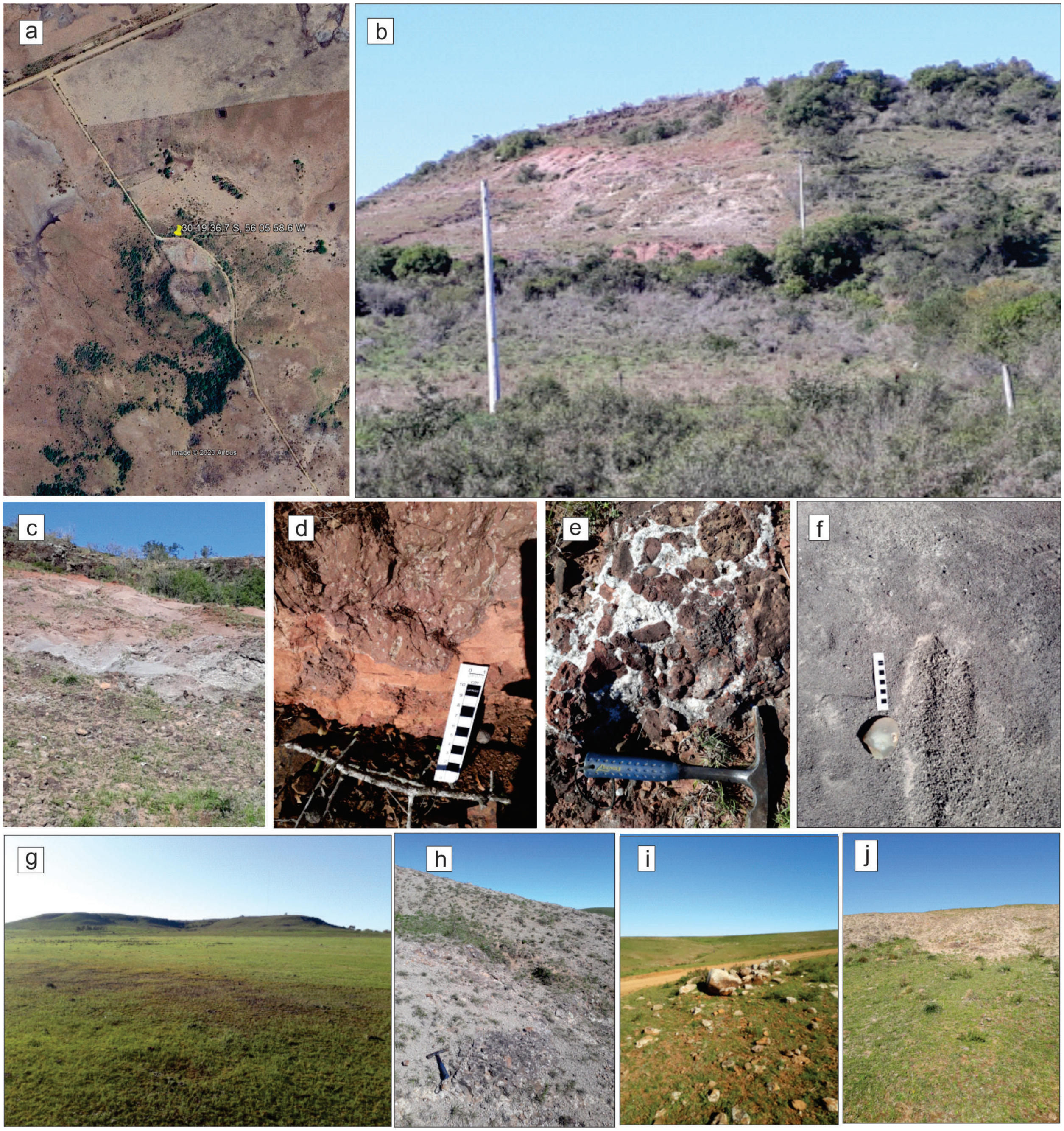

Figure 4. (a) GoogleEarth image, displaying Tier 2 at the top of the hill, Tier 1 at the bottom (white) of the Muralha Flow; Cordillera and Catalán Flows are underneath. (b), (c), (d), (e), (f) are field photos of Muralha Flow from (a). (g), (h), (i), (j) are field photos from other locations in the region, displaying geological relationships of the Muralha Flow. (b) Field photo showing the white, reduced, massive layer of the Muralha Flow covered by 2 m of the red, oxidized, vertical-jointed flow. (c) detail of Tier 1, same outcrop. (c) detail of Tier 1. (d) hydrothermal breccia of angular fragments of volcanic rock in a matrix of silicified sand. (e) breccia of angular fragments of volcanic rock in a matrix of calcite. (f) small quartz-chalcedony geode incrusted in basaltic andesite. (g) Table hill of Muralha Flow overlying the Cordillera Flow. (h) Tier 1 of the Muralha Flow distant 10 km from hill shown in (a). (i) Outcrop of the Muralha Flow at the top of a hill, displaying the red Tier 2. (j) White Tier 1 of the Muralha Flow; Tier 2 was eroded from this hill.

where the upper layer of the studied flow was more extensively eroded, exposing the lower layer. In many hills, the absence of the upper crust is an indication of higher resistance to erosion by Tier 1.

In the studied region, the Muralha Flow occurs mostly at the top of hills, locally covered by the Coxilha Flow. The thickness of the studied flow is also distinctive, because it is the thickest among the three most extensive flows in the Fronteira Oeste Rift – Catalán (30 m), Cordillera (30-40 m), and Muralha (40-60 m) Flows. The thickness of the several flows varies along the extent of the flows, as measured in drill cores (e.g., Hartmann et al. 2010; their Figure 7).

In the field, the flow is distinctive for two main features – prominent vertical columns and the division into a basal Tier 1 and an upper Tier 2 (Fig. 4a-j, Fig. 5). The lower crust is thick (10 m). Exposures of the lower crust occur in several places where hills have a remnant core at the top. Tier 1 is 30 m thick and is stratigraphically below Tier 2. The lower tier is remarkable for displaying white color both in satellite images and in the field due to pervasive alteration to clay minerals – smectite and minor kaolinite – and a zeolite (chabazite). This lower tier also displays small (10-20 cm) agate geodes in a flat-lying layer positioned 10 m below the top of the tier. As observed in several occurrences by Duarte (2011), a massive volcanic rock layer occurs below the vertically-jointed core; in this layer, agate and small amethyst geodes are common in the rift.

Large (5-10 cm) calcite crystals form the matrix of hydrothermal breccias that contain angular, 10-20 cm-large basaltic andesite fragments. These breccias occur close (10 m) to the contact with the vertical jointed layer. Tier 1 is mostly clay and is strongly altered, with fine rubbly blocks at the inclined surface; 1-5 m thick layers of better-preserved rock are present. The two-layered lava flow can be visually identified in the field from a distance. Tier 2 occurs above the white tier and is vertically jointed; the rocks have a red color on fresh surfaces and in the soil due to the presence of iron oxyhydroxides, including hematite. Altered Tier 1 rocks have

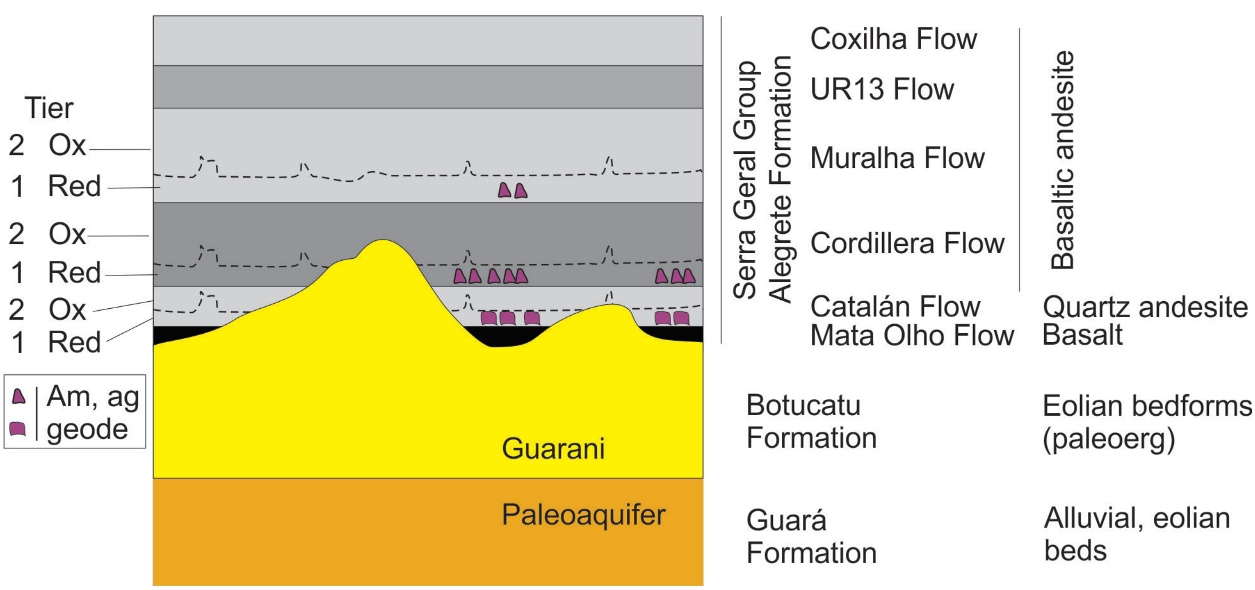

Figure 5. Schematic section of the six flows (flow number 1 not shown) present in the studied region. Displayed features include the stratigraphy, relative thickness of flows, the underlying Guarani Paleoaquifer, presence of two tiers in each flow, and the occurrence of agate and amethyst geodes in Tier 1.

locally a typical violet color. We followed the flow visually along dirt roads for tens of kilometers and made several traverses on the structure. In satellite images, the flow extends continuously for more than 30 km and erosional remnants for more than 100 km.

The Muralha Flow basaltic andesite is dark gray in the upper part and light gray to white in the lower part, aphanitic, microporphyritic. Under the microscope, a fine-grained matrix contains plagioclase, pyroxene and opaque minerals in intersertal texture. Hydrothermal minerals occur in the matrix in varying proportions, including smectite. Amygdales in the upper and lower crusts contain zeolites. Plagioclase phenocrysts are on average 0.8 mm large and 0.25 mm in the matrix. Short prismatic pyroxene crystals are strongly oxidized in Tier 2. Euhedral magnetite crystals are 0.1 mm large. Apatite is present throughout the rock as 0.03-0.10 mm-large crystals. Hydrothermal alteration is more intense in the light gray lower part of the flow, where a large volume (60-80%) of clay minerals (mostly smectite) formed.

Rocks from the Muralha Flow have a typical, unique chemical composition regarding several elements. Particularly, the TiO_2 vs P_2O_5 diagram is distinctive (Supplementary Material- Figure S1); the TiO_2 content is uniform near 1.5 wt.% and different from any other flow in the rift. The content of TiO_2 was lowered by higher LOI in the Mata Olho and Cordillera Flows, but remained constant in the Muralha Flow (Fig. S2a). The underlying Cordillera Flow has 1.1 wt.% TiO_2 and the overlying Coxilha Flow has 1.7 wt.% TiO_2. The UR13 Flow has 1.3 wt.% TiO_2. Adding to the typical aspect of the flow in satellite images and in the field, the chemical composition supports the classification of any unidentified exposure as belonging to the Muralha Flow.

We estimate the magmatic SiO_2 content of rocks from the Muralha Flow at 56.0 wt.% – basaltic andesite (e.g., Hartmann et al. 2010, Duarte 2011). This composition is shown by rocks from Tier 2 displaying LOI <1.5 wt.%. This LOI content marks the limit between strong geochemical modification of rocks by hydrothermal alteration as they evolved from Tier 2-composition to Tier 1 (Hartmann et al. 2024). Tier 1 had been presumably oxidized similarly to Tier 2 but was later reduced. Altered Tier 1 rocks from this flow have lower SiO_2 down to 54.0 wt.% (Duarte 2011). The magmatic content of K_2O is near 2.0 wt.% in Tier 2 but drops to 1.0 wt.% in Tier 1 due to hydrothermal alteration (Fig. S2b). As shown in Table SI, the increase in LOI above 1.5 wt.% results in lower SiO_2, K_2O, Na_2O, Rb, and higher Fe_2O_3, MgO, and CaO. Trace elements Sc, Co, Hf, Nb, Ta, and several REE remained constant after alteration, adding to the identification criteria of the flow.

XRD of sample LED99 determined the presence of plagioclase (24.7%), quartz (22.1%), mica/illite (14.3%), smectite (19.7%), and chabazite (19.3%). Sample LED99 showed plagioclase (38.6%), smectite (33.0%), chabazite (25.4%), and hematite (3.1%). Mineral content of sample LED101 was established at plagioclase (87.9%), smectite (7.4%), and kaolinite (4.7%).

DISCUSSION

The objective of characterizing processes related to the hydrothermal alteration of the Muralha Flow into two tiers and the related amethyst and agate geode formation was achieved with the use of integrated techniques and reached significant results. The flow has distinctive features in satellite images and in the field, also identified by the 1.5 wt.% TiO_2 content of the rocks, unique (and nearly constant) among Serra Geral Group rocks in the Fronteira Oeste Rift. Several elements were mobile during the reduction of the flow, but others remained constant and are indicative of the Muralha Flow.

The red color of rocks in Tier 2 (hematite) resulted from the oxidation of the pristine basaltic andesite. The large volume of continuously-renewed hot water available in the underlying Guarani Paleoaquifer ascended into the andesite and altered the rock thoroughly, particularly along fractures. Alteration reached the full thickness and the full extension of the flow. Only Tier 1 contains minerals indicative of a reducing and acidic environment – calcite, pyrite, amethyst, agate, smectite, and kaolinite, which formed after the oxidation of the entire flow. The lower half of the flow was reduced with the deposition of specific minerals.

The observation of agate geodes in Tier 1 (not present in Tier 2) is a strong indication that amethyst and agate geode deposits of economic value may be present in the core of the hills of the Muralha Flow. These cores are preserved from erosion because they were presumably more intensely silicified than the eroded, surrounding valleys. Thus, the cores host the amethyst geode deposits.

Mining for geodes is restricted in the Los Catalanes Gemological District (UY) to the Catalán and Cordillera Flows. The Muralha Flow occurs in that district but has not been explored for geode deposits yet. The two mined flows have Tier 1 and Tier 2, in which geodes are mined from Tier 1 (Hartmann et al. 2024). The similarity of structure and geological processes of redox alteration leads to the possibility of comparable occurrence of agate and giant amethyst geodes in the Muralha Flow.

Comparable hydrothermal activity linked to basaltic intraplate volcanism was described for the Miocene Sahara, where larger structures formed by similar processes (Mazzini et al. 2019, Montanaro et al. 2022) (redox reactions not described). The percolation of water in thicker sections of intraplate basalts was evaluated by Burns et al. (2014), but we focus on the third flow rather than the full volcanic group.

To understand the redox reactions that formed the studied two tiers, we examine similar occurrences in other basalts that were in contact with large volumes of flowing hot water. We evaluate the processes in the Muralha Flow, following the descriptions of the Catalán Flow by Hartmann et al. (2024). The evaluation of the third flow is of utmost significance for the integrated evolution of a continental-scale freshwater aquifer and volcanic rocks from a major intraplate basaltic LIP. An essential assumption is the interaction of the underlying, heated, 160 m-thick Guarani Paleoaquifer with the overlying, cold volcanic rocks. The presence of thousands of paleohot springs at the top of the Botucatu paleodunes and of the first lava flows is evidence that supports the interpretation of heated aquifer interaction with all rocks in the overburden (Hartmann et al. 2022b, c, 2023). The freshwater aquifer is one of the largest (1.2 mi km^2) in the continents, even larger than the area of exposure of the Serra Geral Group (1.0 mi km^2). The Muralha Flow is the top flow in a 100 m-thickness of lavas in large extents of the region.

What geological conditions led the aquifer water to evolve from oxidizing to reducing? And why was only half of the thickness of the flow reduced in Tier 1, preserving the upper oxidized half as Tier 2?

Oxidation by water percolating upwards from the Guarani Paleoaquifer is expected, because the aquifer concentrates oxygenated, weakly acidic (pH = 6) rainwater. Upward percolation of the water is also expected from the heated aquifer because of water expansion and the added weight imposed by a third lava flow present in the overburden. Recently-cooled basalt has high porosity and permeability near 30% (e.g., Flóvenz & Saemundsson 1993).

The full sequence of three hydrothermal processes integrated one event of mantle melting that formed the studied lava flow and concomitantly increased the geothermal gradient in the region of the Paraná Basin. The gradient was more than 25 °C/km, higher than normal for sedimentary basins (Kolawole & Evenick 2023). Crustal thinning in rifts results in an increased geothermal gradient. Every lava flow was shortly followed by an event of heating of the aquifer and water ascent through the overlying sandstones and volcanic rocks. The ascent of hot water occurred in each (Hn) event in three pulses, named H1, H2, and H3 by Hartmann et al. (2010, 2023). The heated water (100-250°C) met a porous (30 vol.%), permeable rock during upward percolation, flowing at a high rate while oxidizing and filling the cavities with secondary minerals. During the ascent, iron from mafic minerals was oxidized from Fe^{+2} to Fe^{+3}, generating oxyhydroxides (hematite) and reddening the rock. Presumably, the flow was entirely oxidized from bottom to top. A Seal 1 was thus formed.

Oxidation was thorough in the upper part of the Catalán Flow – no cooling joints and focused along cooling joints in the upper part of the Cordillera and Muralha Flows. Reduction of the rock was more complete in the lower, massive (no cooling joints) core. Oxidation resulted in diminished porosity in the flow.

Water became pressurized in the aquifer and exploded upwards due to either overpressure or seal rupture caused by seismic activity and hydraulic fracturing. Flash vaporization occurred because of contact of the water at the vapor curve with atmospheric pressure. This hydrothermal event H2 carried fluidized sand from the dunes upwards, leaving dikes, sills, hydrothermal breccias and extrudites as evidence of the process. Continued flow of hot water resulted in a new Seal 2. This new sealing, associated with lowering of water temperature to less than 100 °C (formation of amethyst and agate), strongly decreased the velocity of water flux.

The resulting slow percolation of warm water through the aquifer and the basaltic andesite during H3 led to three mechanisms that turned the water reducing. (1) Water molecules had long contact with organic molecules present in the dune sand. (2) Water dissolved calcite from the large number of nanocrystals covering sand grains (King 1998). (3) Water dissolved H_2 from fresh surfaces of the volcanic rock. These three reducing processes acted together to make the Guarani Paleoaquifer reducing.

Slow upward percolation of the warm water reduced part of the dune sand and the lower half of the Muralha Flow. The reducing fluid precipitated agate (possibly amethyst) and calcite in the volcanic rocks and altered the rock to form voluminous smectite (some kaolinite) and chabazite. Calcite crystallized in Tier 1 at 30 °C in the Uruguayan mines (Duarte et al. 2009, 2011, Morteani et al. 2010). Because of the similarity of geology, a comparable temperature likely prevailed on the Brazilian part of the Cuesta de Haedo. Temperature lowering below 30 °C led to the interruption of the hydrothermal process. As a result, only the lower half of the previously-oxidized flow underwent the reducing process. The upper half of the flow remained oxidized, red.

The evolution of porosity and permeability of the volcanic rock resulted from hydrothermal alteration, both oxidation and reduction. We interpret the interruption of the reduction process in the middle of the flow as due to the temperature decrease of the aquifer below 30 °C. Specific studies of the surface that delimits the two tiers are necessary to further understand the process of reduction. The stop of the reducing fluids in the middle of the Muralha Flow could be due to properties of the corresponding rocks, requiring further examination.

A remarkable structure of lava flow was formed and preserved in this way. The entire flow was altered by hot water from the Guarani Paleoaquifer, which first oxidized the rocks and turned them red in Tier 2, and then reduced the oxidized flow into white rocks in Tier 1. The large scale of this process is restricted to the Paraná Volcanic Province among LIPS; a full 40-60 m-thick layer of basaltic andesite was oxidized either massively or along fractures and then had its lower half reduced to form agate and giant amethyst geodes.

This study of the Muralha Flow contributes significantly to the understanding of the evolution of the Guarani Paleoaquifer during the eruption of the Serra Geral Group. The freshwater is currently oxidizing, because the aquifer is replenished by rainwater. The Lower Cretaceous paleoaquifer was oxidizing but became reducing (H3) after each event of lava oxidation (H1) and sand injection and eruption (H2). We suggest that the main structure responsible for the redox reaction was the sealing of the flow after H2 (Seal 2), because the low volume of remaining pores slowed the percolation of hot water through the rocks. The low velocity allowed the reaction between the water molecules and the solid materials, thus lowering the Eh and the pH of the fluid.

Similar redox reactions have been described in the Serra Geral Group and in continental granitic rocks, in paleodunes from the Etendeka in Africa (covered by correlated basalts) and in oceanic basalts. The volcanic rocks of the Serra Geral Group underwent large-scale hydrothermal alteration (Gonçalves et al. 1990). A lava flow near Porto Alegre shows the sequence of oxidation followed by reduction during hydrothermal alteration (Schenato et al. 2003). In the Veia Alta Flow of Ametista do Sul, Gilg et al. (2014) attributed the origin of the amethyst to a reducing fluid from the Guarani Paleoaquifer. A gray alteration halo in the wall and the filling of an open fracture in columnar-jointed basalt from São Paulo state was described in sequential stages (Gonçalves et al. 1990). Near the rock wall, the mineral association is celadonite + saponite, while in the center of the open fracture opal and chalcedony are present. We interpret the fluid associated with the alteration as initially transitional oxidizing-reducing, evolving to reducing and more acidic.

The geode-mineralized flows of Uruguay were described as oxidized (reddened) by Morteani et al. (2010), which corresponds to Tier 2 in our interpretation. Hydrothermally altered, continental granitic rocks occur in the Thunder Bay area (McArthur et al. 1993). There, the percolation of an initially oxidizing, slightly acidic fluid was followed by a reducing, more acidic fluid. Amethyst was formed during the reducing event. In the Etendeka, paleodunes are either red or white, depending on the redox alteration caused by the percolation of hydrothermal water (Grove et al. 2017). Oxidation preceded reduction in the alteration of the dune sand.

Altered basalt from oceanic ridges shows a similar sequence of oxidation and reduction in different locations. Marescotti et al. (2000) described sequential oxidation in alkaline water followed by reduction in acidic water in the Juan de Fuca Ridge. In altered basalt from this ridge, Hunter & DP Leg168 Scientific Party (1998) identified a sequence of initial oxidative conditions (formation of iron oxyhydroxides and celadonite) evolving to non-oxidative conditions (saponite and pyrite). Alt (1995) documented a sequence of alteration from oxidative (celadonite is common) to reducing (pyrite, chalcopyrite) in the subseafloor processes of hydrothermal systems of the Mid-Ocean Ridge. A common initial alteration forms chlorite at higher temperature. Alt (1995) interpreted the sequence as corresponding to open hot water circulation during early alteration evolving to more restricted percolation in the basaltic rocks. We consider this evolution as corresponding to higher velocity of fluid migration through the volcanic rock at first, followed by lower velocity after extensive pore filling by secondary minerals. At the Galápagos rift zone, Ridley et al. (1994) identified a first higher temperature chlorite-forming event followed by extensive lower-temperature alteration. The stability of plagioclase during a large extent of the alteration processes was similar to Fronteira Oeste Rift volcanic rocks. In Yellowstone, sulfide-precipitating fluids are reducing (Hames et al. 2009).

Overall, redox evolution in hydrothermal alteration progresses from oxidative to reducing in both continental and oceanic environments. This sequence of fluid evolution has been observed in basaltic rocks and in continental granitic rocks. The evolution of Eh and pH in the fluid depended on the duration of contact between the water molecules and the reacting particles in the rock. For instance, desert sand grains have many nanoparticles of calcite adhered to their surfaces. Also, present sand seas are known to contain many organic molecules, which react with water. And the contact of water with fresh basalt releases H_2 to the fluid (Stevens & McKinley 2000). The integrated result in the Fronteira Oeste Rift was the modification of the hot Guarani Paleoaquifer water from the initial oxidative to the reducing composition. As a consequence, the Muralha Flow basaltic andesite was initially oxidized and then (lower half) reduced. Reducing, acidic fluid is a common agent of transport and deposition of many deposits in other provinces, making the Muralha Flow a key geological target for the prospecting of amethyst and agate geodes and for epithermal Au, Ag, and Cu deposits.

CONCLUSIONS

We report the presence and the investigation of the nature and evolution of a two-tiered structure in the Muralha Flow, the third lava that extensively covered the active Botucatu erg in the Early Cretaceous. The Guarani Paleoaquifer was heated to 100-250 °C due to the increased geothermal gradient caused by mantle-melting that generated the studied lava flow. Similar processes operated after every subsequent flow in the region. The interaction of hot water with both the host erg sandstone and the overlying lavas (including the Muralha Flow) was intense. The formation of many thousands of hot springs at the surface of the erg and of the ambient-temperature lava flows is a testimony of the thorough and long-lasting exposure of the rocks to hot water. Redox reactions turned the flow red during H1 by oxidation of Fe^{+2} to Fe^{+3} (iron oxyhydroxides). Sand injection and eruption occurred during the following hydrothermal event H2. During H3, the flow was reduced by hot water forming Tier 1. The presence of agate and giant amethyst geodes was only observed in Tier 1, which becomes a qualified prospective guide for new deposits in this world-class mineral province. The process was interrupted after the temperature dropped below 30 °C due to mantle cooling and the return to normal (25 °C) geothermal gradient.

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SUPPLEMENTARY MATERIAL

Table SI.
Figures S1, S2.

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