Hydrothermal alteration at the basalt-hosted Vista Alegre impact structure, Brazil

Jitse ALSEMGEEST 1, Fraukje M. BROUWER 1, Luis F. AUQUE 2, Natalia HAUSER 3, and Wolf Uwe REIMOLD 3

1 Geology and Geochemistry Cluster, Faculty of Science, Vrije Universiteit, De Boelelaan 1085, Amsterdam 1081HV, The Netherlands
2 Department of Geosciences, University of Zaragoza, Calle Pedro Curbuna 12, Zaragoza 50009, Spain
3 Laboratory of Geochronology and Isotope Geochemistry, Geosciences Institute, University of Brasília, Brasília, DF CEP, 70910-900, Brazil

*Corresponding author. E-mail: jalsemgeest@vu.nl

(Received 13 July 2021; revision accepted 15 October 2021)

Abstract—Hydrothermal systems provide a possible habitat for early life and are key targets in the quest for life outside Earth. In impact craters on Mars, hydrous minerals can represent products of impact-generated hydrothermal systems (IGHS) or minerals already present in the crust and exposed during impact-caused excavation. Because of its basaltic target rock, similar in composition to Martian crust, the Vista Alegre impact structure in Brazil is one of the very few analog structures that may reveal the origin of these minerals, if evidence of hydrothermal alteration is established. This work presents the results of a systematic search for evidence of hydrothermal alteration at the Vista Alegre impact structure. Four types of alteration were identified, all within a 2.5–3.0 km radius from the crater center: a zircon-bearing melt veinlet, two sets of hydrothermal veins consisting predominantly of calcite and chabazite, and local alteration comprising saponite. Thermodynamic modeling suggests subsequent heating and cooling for each of the hydrothermal vein sets. Combined thermodynamic and spectrometric evidence indicates that development of a vigorous IGHS is unlikely. If similar processes occur on Mars, hydrous minerals are more likely preimpact phases exposed by excavation, rather than being formed through an IGHS.

INTRODUCTION

Hydrothermal systems on planetary surfaces have long been suggested as possible habitats for early life (e.g., Chatterjee, 2016; Cockell, 2006; Van Kranendonk, 2006). They, therefore, have been considered as starting points for the search for life outside Earth. Focusing on our nearest planetary neighbor, Mars, as the planet is covered with impact structures (Barlow, 2009; Neukum et al., 2010; Tanaka et al., 2014) and several hydrous minerals have been found within these structures (Carter et al., 2013), impact-generated hydrothermal systems (IGHS) there have been of special interest. If IGHS are active over a longer period of time after impact, they may well have formed a viable habitat to sustain life on Mars (e.g., Cockell, 2006; Fritz et al., 2014; Golding & Glikson, 2011; Schopf, 2004). However, hydrous minerals could also have been formed by regular geo-processes in the crust and subsequently excavated by impact (e.g., Ehlmann et al., 2011; Osinski et al., 2013; Pierazzo et al., 2005). To differentiate between products of IGHS and excavation of the products of prior hydrothermalism, it is essential to understand the development of hydrothermal systems within impact structures.

Sampling limitations on Mars still largely inhibit direct investigation/understanding of Martian impact structures, as even the recent Perseverance rover is limited to samples of 60 × 13 mm, which can only be taken close to the landing site, and sample return is yet to be achieved (NASA, 2021). Thus, because of availability of sampling material and access to hands-on analytical techniques, investigation of an analog on Earth might provide an important insight into processes.
likely active on Mars (e.g., Harris et al., 2015; Hooijschuur et al., 2015; Pullan, 2008). Considering that the crust of Mars is mainly basaltic in composition (McSween et al., 2009; Salvatore et al., 2010; Zuber, 2001), and hydrothermal minerals in an analog environment should have precipitated in a chemically similar target, a suitable analog impact structure should have been formed in a dominantly basaltic target terrain (Alsemgeest & Auqué, 2021). Out of the roughly 200 known impact structures on Earth (e.g., Gottwald et al., 2020), only four such targets have been identified on Earth: Lonar Lake in India, Logancha in Russia, and Vargéao Dome and Vista Alegre in Brazil (Cróstia et al., 2010, 2019; Cróstia, Jourdan, et al., 2012; Cróstia, Kazzuo-Vieira, et al., 2012; Feldman et al., 1983; Fredriksson et al., 1973; Masaitis, 1999). Of these, Vargéao Dome and Vista Alegre are well exposed and accessible (Cróstia et al., 2010, 2019; Yokoyama et al., 2015), and the possibility of the presence of an IGHS has already been suggested for Vargéao Dome (Alsemgeest & Auqué, 2021; Epstein et al., 2021; Yokoyama et al., 2015). However, no hydrothermal alteration has been reported from Vista Alegre to date, raising the issue whether IGHS in basaltic target terrain are a widespread phenomenon or rather depend on local conditions.

This study focuses on research about hydrothermal alteration in the Vista Alegre impact structure. A systematic search for evidence for hydrothermal alteration was conducted throughout the structure, and selected samples were analyzed using optical and scanning electron microscopy, and Raman spectrometry, as well as thermodynamic modeling, to provide a framework for hydrothermal evolution of the structure. The results are then used to draw conclusions on the origin of this hydrothermal alteration at Vista Alegre, and what the implications of this may be for the interpretation of similar systems on Mars.

**Vista Alegre Impact Structure**

The Vista Alegre impact structure (25°57'S, 52°41'W) is located in the southern part of the Paraná Basin, in southern Brazil (Fig. 1) (Cróstia et al., 2010, 2019; Gottwald et al., 2020). The structure was formed between 111 and 134 Ma (Cróstia et al., 2019) through impact of a stony meteorite projectile with a diameter of about 1000 m (Cróstia, Jourdan, et al., 2012; Thiede & Vasconcelos, 2010; Vasconcelos et al., 2019). The target comprised 700–800 m of tholeiitic flood basalts of the Serra Geral Formation (Cróstia et al., 2010, 2019) that rest on fluvio-eolian sandstones of the Pirambóia and Botucatu formations of unknown age (still controversial, possibly up to about 250 Ma, Christofoletti et al. [2021] and references therein). Constraints on the age of the impact are based on four 40Ar-39Ar measurements interpreted to provide a minimum age for impact melt, as well as the age of the Serra Geral Formation (Cróstia, Jourdan, et al., 2012; Cróstia et al., 2019). The Guarani aquifer of southern Brazil runs underneath the structure, within the Pirambóia and Botucatu formations (Manzano & Guimaraens, 2012; Sracek & Hirata, 2002; Wendland et al., 2006).

The structure has a diameter of about 9.5 km, and includes a central depression as well as sharp escarpments at about 4–5 km from the center. Since impact, the structure has undergone up to about 320 m of erosion, as estimated by Vasconcelos et al. (2019) based on geophysical information and numerical modeling results.

From the center toward the outer parts of the crater, quartzites, impact breccias, fractured basalts, and unfractured basalts are exposed (Fig. 1). The quartzites in the central part of the crater, in combination with concentric Bouguer anomalies, indicate that the underlying Pirambóia/Botucatu formation has been uplifted to the surface, although the exact outline, structure, amount of uplift, and amount of quartzites and sandstones within Vista Alegre are still unclear (Cróstia et al., 2019; Ferreira et al., 2013). Erosion of the central uplift has also been suggested (Ferreira, 2017), although numerical modeling suggests that the current morphology, and the uplifted strata in the center of the structure, could be mostly related to crater formation (Vasconcelos et al., 2019). Planar deformation features, shatter cones, and evidence of melting on shatter cones in basalt have all been observed. To date, no evidence for hydrothermal alteration has been reported (Cróstia et al., 2010, 2011, 2019; Pittarello et al., 2010, 2015).

**METHODS**

**Sampling**

A systematic search for rocks that show hydrothermal alteration was conducted in the Vista Alegre area, at every outcrop encountered within 7–8 km from the center of the structure (Fig. 1). The Vista Alegre area consists largely of farmland, and sampling is severely limited by the availability of outcrops. Outcrops occur mostly along roads and rivers (Cróstia et al., 2010, 2019). A total of 33 outcrops were found (Fig. 1), 13 of which are within the impact-breccia area (up to about 2.5 km from crater center), 12 within the fractured-basalt area (2.5–4.5 km from crater center), and another 8 in the unaffected-basalt area (>4.5 km
from crater center). Outcrop sizes are extremely limited and material is highly weathered in the innermost 3 km around the crater center. Between 3 and 5 km from the center, more outcrops are available, especially in the SW and NE quadrants, and a suite of samples was collected from a 1 km long section in the NE quadrant. Further away, outcrops are limited again.

Optical Microscopy, Scanning Electron Microscopy, and Raman Spectroscopy

Optical microscopy was performed on standard, 30 μm thick, polished thin sections. Selected samples were analyzed with a JEOL JCM-6000 benchtop scanning electron microscope at the Microanalysis Laboratory at Vrije Universiteit Amsterdam, using 15 kV accelerating voltage, high probe current, standard filament current, and high vacuum (exact probe current, filament current, and pressure in the column were not provided by the manufacturer). Two types of data were collected: BSE (backscattered electron) images and EDS (energy-dispersive spectroscopy) analyses, the latter providing a semiquantitative analysis of major elements. Element analysis uses an internal calibration without reference material, with an approximate standard deviation of 1–2% of the measured element mass (exact
Thermodynamic Modeling

Reaction path thermodynamic modeling was performed using the phreeqc.r package (Charlton & Parkhurst, 2011) that uses the aqueous geochemical calculation software PHREEQC (Parkhurst & Appelo, 2013) in the R programming language. This type of modeling simulates dissolution and precipitation of minerals, and is dependent on the selected conditions, such as dissolution type and amounts of dissolved material, minerals allowed to precipitate, thermodynamic data, initial water composition, temperature, and pressure. As noted by Alsemgeest and Auquê (2021), Lucia and Kühn (2013), and Thoenen (2007), small variations in all of these conditions can strongly influence the modeling results. Therefore, a program was developed in R to allow randomization of all conditions (program code available in the supporting information, limitations discussed in the Model Limitations section). By running a large number of models (about 125,000 per simulation), and tracking the theoretical conditions at which minerals, actually observed in the samples, can precipitate, it is possible to provide stability limits in terms of pressure, temperature, initial water composition, and water composition at the time of precipitation for each mineral. The following constraints were used:

Initial water compositions were based on extrapolation of water compositions of the Guarani Aquifer present beneath the impact structure (da Silva, 1983; Manzano & Guimaraens, 2012). A total of 100,000 randomized compositions were generated using the methods described in Alsemgeest and Auquê (2021) and a randomly selected composition was used in each single model. For the dissolution type, a randomized average basalt composition was used to incorporate the variability in basalts found throughout the Vista Alegre area and based on EDS analyses (see the Thermodynamic Modeling section). The temperature was limited to between 0 and 300 °C, based on earlier modeling for a similar structure (Vargeão—Yokoyama et al., 2015). The pressure was limited between 70 and 110 bar, based on an estimated erosion of roughly 250 m at the center of the structure to 320 m at the rim (Vasconcelos et al., 2019) of basalt at 2.9–3.0 kg m⁻³. Thermodynamic data were taken from five suitable databases. The LLNL and SIT databases are distributed with PHREEQC (Delany & Lundeen, 1991; Giffaut et al., 2014; Parkhurst & Appelo, 2013), whereas Thermosol is freely available online (Blanc et al., 2012; BRGM, n.d.). The Soltherm and YMP databases (Palandri, 2015; Reed, 1998; Reed & Palandri, 2006; Wolery & Jarek, 2003; Wolery et al., 2007) are available for PHREEQC, after conversion by Alsemgeest et al. (2021). Mineral identification was based on petrographic evidence, EDS analyses, and Raman spectra. Minerals were selected from the mentioned databases, using a minimized difference $D$ between measured compositions and compositions of minerals present in the database:

$$D = \sqrt{\frac{\sum (X_{\text{measured}} - X_{\text{database}})^2}{n_X}}$$  \hspace{1cm} (1)

where $X$ represents atomic percentage of an element in a mineral composition and $n_X$ is the number of elements present in the mineral composition. A randomized selection of minerals with a low compositional difference was used in each model run, with the exact selection based on availability of minerals in each database.

Thermodynamic models were run in two iterations. The first iteration included a randomized selection of all 100,000 initial water compositions and a large number of minerals. The selection was refined in the second iteration to exclude water compositions that could not be involved in the production of minerals present in the samples. Minerals that were only produced with these excluded water compositions were also excluded in the second stage. Results of the second iteration are discussed here.

RESULTS

Alteration in the Vista Alegre Area

Sampling around the Vista Alegre area largely confirms that reported earlier about the target rock (Cróstoa et al., 2004, 2011, 2019). This comprises tholeitic flood basalts of the Serra Geral Formation (Cróstoa et al., 2010). These basalts contain amygdales infilled with quartz, which are also found in other locations where the Serra Geral Formation occurs (Torres Trough, Paraná Igneous Province, Besser et al.,...
Gray polymict impact breccias with angular fragments of mostly basalt and a matrix with a powdery texture, corresponding to the more detailed description by Cróst et al. (2010), occur in the central area of the structure (e.g., sites 69 and 91, Fig. 1), whereas fractured basalt characterizes the outer parts of the structure. A small outcrop of quartzite was also confirmed, which is thought to be part of the Botucatu/Pirambóia Formation (site 72, Fig. 1). In this study, no evidence was found of hydrothermal alteration of the quartzite outcropping on a very small scale at site 72. However, possible evidence of hydrothermal alteration may have been removed by continuous ploughing of the field in which the outcrop was found (Cróst, personal communication).

Notably, signs of alteration such as veins (white, mm-sized in hand samples), veinlets (only visible in thin section), and local (patchy) alteration (only visible in thin section) were only found at three locations in the area (sites 79, 80, and 92, Figs. 1 and 2a–e), exclusively in basalt between 2.5 and 3.0 km from the center of the structure (possible reasons discussed in the Cause of Hydrothermal Alteration section). Due to limited availability and poor quality of outcrop, it was not possible to obtain orientations of the veins, hindering comparison with local and regional fault trends. The polymict impact breccia also hosts several clasts of calcite, stilbite, and fragments of basalt with analcime and calcite (samples from sites 69 and 91, Fig. 2f).

**Optical and Scanning Electron Microscopy**

Four types of alteration were identified in thin sections of fractured basalts (Figs. 2a–e). (1) A melt veinlet composed of zircon and μm-sized crystals of mainly zeolite, clay, Fe-Ti-oxides, and pyroxene; (2) and (3) hydrothermal alteration consisting predominantly of calcite and zeolite; and (4) local alteration consisting mostly of saponite. The original basalt has a similar, fine-grained texture in all samples and corresponds in mineralogy to that described by Cróst et al. (2010).

**Possible Melt Veinlet**

In a sample retrieved from a weathered outcrop of fractured basalt at site 92 (Fig. 1), a veinlet consists of minerals that are randomly distributed throughout the veinlet with crystal sizes mostly smaller than 10 μm (Fig. 2a). The minerals include a Na-Fe-pyroxene or amphibole, two potential zeolites or clay minerals, and Fe-Ti-oxides with Fe:Ti ratios of 5:1 and 8:1, respectively (Table 1). Furthermore, EDS peaks at 6.77 and 2.01 keV indicate increased amounts of F and P, which in combination with Ca suggest the presence of fluorite and apatite. The presence of zircon is indicated by EDS peaks at 2.04 keV (Zr) and 1.739 keV (Si), although crystals were too small (smaller than 20 μm) to determine this with certainty. Zircon was only encountered in this veinlet. The occurrence of zircon, suggesting formation temperatures above 580 °C (Watson & Harrison, 2005), and pyroxene/amphibole leads us to the interpretation that this veinlet could have been filled with melt and does not reflect hydrothermal alteration (as further discussed in the Paragenetic Sequence and Thermal Evolution section). It was not possible to further identify minerals by EDS or Raman spectroscopy due to their small crystal size, and no evidence was found to relate this veinlet to the impact.

**Hydrothermal Alteration Type 1**

In the same sample from site 92 in which the melt veinlet was found (fractured basalt, Fig. 1), another set of veins is found, which intersect the melt veinlet at one point in the thin section (Figs. 2a and 2b, see the Possible Melt Veinlet section). Throughout the sample, the veins of this set have similar orientation and mineralogy. As this particular sample was retrieved from a shallow outcrop in a field and was concealed by a considerably weathered layer, it was not possible to determine the vein orientation in relation to the crater. The center of the veins consists predominantly of calcite, whereas the outer parts consist mainly of quartz. Within the calcite, small crystals of CuSO4 (likely the hydrated sulfate chalcantite, CuSO4·5H2O) occur, as well as two potential zeolites (Table 2). Between the calcite and quartz, a Na-Fe-pyroxene or amphibole was detected that is similar to the one in the melt veinlet, as well as a potential clay mineral and, based on the composition (see Table 2 for details), a further unidentified nesosilicate. The nesosilicate and pyroxene/amphibole are always in close proximity to each other. Possible interpretations of the mineral types are indicated in Table 2; implications for the relationship to hydrothermal alteration are discussed in the Hydrothermal Alteration Type 1 section in the Discussion. Within the quartz-rich zone, another potential zeolite occurs, as well as several Fe- and Ti-oxides and apatite, indicated by elevated levels of Ca and P. All minerals, except for quartz and calcite, have crystal sizes smaller than 20 μm and are therefore unidentifiable by Raman spectroscopy as individual crystals are not optically distinguishable.

**Hydrothermal Alteration Type 2**

The second hydrothermal alteration type is the most common type observed in samples (locations 79,
80, and 92, all fractured basalts, Fig. 1). Hydrothermal alteration type 2 was not found in the same samples with either the melt veinlet or with hydrothermal alteration type 1, and these samples showed a lower degree of weathering and a typical dark-gray color. Type 2 consists of chabazite veins, with occurrences of several other zeolites, calcite, and phyllosilicates (Figs. 2c–e; Table 3). The other zeolites are Ca-stilbite, thomsonite, and possibly analcime, levyne or phillipsite, and heulandite. The Raman study identified the latter three phases only in one sample from site 92, although the signal for analcime was unclear and might also allow for the interpretation of heulandite (Fig. 3).

In polymict impact breccias (site 69 and 91, Fig. 1) several fragments were also found that could correspond to type 2, consisting of either calcite (entire fragment, site 91), stilbite (entire fragment, site 91), or basalt with calcite and analcime (one fragment with mixed composition, site 69). In the last fragment, a better signal for analcime was obtained than within the actual vein set, so that it has
remained unclear whether this mineral is part of the paragenetic sequence of type 2 alteration, or not. Chabazite has variable composition, and the analyses can be classified into two groups depending on Mg content (Table 3). This mineral is found mainly in the central parts of veins, where it seems to have formed in a fluid-filled space, after growth of calcite and stilbite, both of which form euhedral crystals (Figs. 2c

Table 1. Compositions of selected minerals in the melt veinlet and localized alteration; data in wt% oxides.

| Type | Melt veinlet | Localized alteration |
|------|--------------|----------------------|
|      | Pyroxene/amp | Phyllosilicate/zeolite| Phyllosilicate (inner part of the vein) | Phyllosilicate (outer part of the vein) |
|      | amphibole    | zeolite               | inner part of the vein                     | outer part of the vein                     |
| SiO₂ | 50.4         | 60.1                  | 66.0                                        | 56.9 ± 1.5                                  |
| TiO₂ | 3.1          | n.d.                  | n.d.                                        | n.d.                                        |
| Al₂O₃| n.d.         | 24.8                  | 17.2                                        | 5.2 ± 0.5                                   |
| MgO  | 5.6          | n.d.                  | n.d.                                        | 8.9 ± 1.2                                   |
| CaO  | 6.3          | 4.8                   | n.d.                                        | n.d.                                        |
| Na₂O | 9.9          | 8.3                   | 2.8                                         | n.d.                                        |
| K₂O  | n.d.         | 0.8                   | 11.0                                        | 8.6 ± 0.3                                   |
| FeO  | 24.6         | 1.4                   | 3.0                                         | 20.4 ± 1.9                                  |

Possible minerals:
- Aegirine
- Riebeckite
- Mesolite
- Smectite
- Erionite
- Clinoptilolite
- Phillipsite
- Heulandite
- Montmorillonite
- Celadonite

n.d. = not detected. Composition measured using semi-quantitative EDS, data from which were normalized to totals of 100 wt%; these results are only used for mineral identification.

*aNumber of measurements/locations used to obtain an average composition as displayed in the table. Error margins reflect variability between different measurements, reflecting compositional variability for single mineral types.

*bPossible minerals reflect all minerals in the databases that satisfy the conditions explained in the Thermodynamic Modeling section.

Table 2. Composition of selected minerals in hydrothermal vein set 1 in normalized wt% oxides.

| Type | Neso-silicate | Pyroxene/amphibole | Zeolite 1 | Zeolite 2 | Phyllosilicate |
|------|--------------|--------------------|----------|----------|---------------|
|      | Between quartz and calcite | Between quartz and calcite | Within calcite | Within calcite | Between quartz and calcite |
|      | 1            | 2                  | 1        | 1        | 1             |
| SiO₂ | 21.8         | 54.4 ± 0.1         | 69.2     | 67.7     | 45.5          |
| TiO₂ | n.d.         | 2.3 ± 0.4          | n.d.     | n.d.     | n.d.          |
| Al₂O₃| 4.6          | n.d.               | 18.6     | 16.9     | 11.4          |
| MgO  | 6.6          | 2.8 ± 0.2          | n.d.     | n.d.     | 16.4          |
| CaO  | 56.0         | 4.6 ± 0.2          | 9.6      | 4.0      | n.d.          |
| Na₂O | n.d.         | 12.0 ± 0.1         | 2.6      | 2.6      | 0.9           |
| K₂O  | n.d.         | n.d.               | n.d.     | n.d.     | 22.4          |
| FeO  | 11.0         | 23.9 ± 0.9         | n.d.     | n.d.     | 22.4          |

Possible minerals:
- Bellite
- Aegirine
- Hillebrandite
- Fe-Glaucophane
- Larinite
- Riebeckite
- Merwinitite

Possible minerals:
- Chabazite
- Erionite
- Smectite
- Clinoptilolite
- Clio-optilolite
- Erionite
- Phillipsite
- Heulandite
- Phillipsite
- Stellerite
- Stilbite
- Wairakite

n.d. = not detected. Composition measured using semi-quantitative EDS, data from which were normalized to totals of 100 wt%; these results are only used for mineral identification.

*aNumber of measurements/locations used to obtain an average composition as displayed in the table. Error margins reflect variability between different measurements, reflecting compositional variability for single mineral types.

*bPossible minerals reflect all minerals in the databases that satisfy the conditions explained in the Thermodynamic Modeling section.
Table 3. Composition of selected minerals in hydrothermal alteration type 2 in normalized wt% oxides.

| Type          | Zeolites                   | Phyllosilicates |
|---------------|----------------------------|-----------------|
| 
|                | Chabazite                  | Stilbite Thomsonite Heulandite |
| 
| n°b           | 3                          | 8               | 16  | 3         | 3  | 3  | 1 | 2 | 3 | 4 | 5 |
| SiO₂          | 63.9 ± 6.5                 | 61.3 ± 1.6      | 68.1 ± 1.8 | 50.0 ± 1.7 | 65.3 ± 3.2 | 61.3 | 48.4 | 53.1 ± 0.8 | 56.2 | 50.8 ± 5.1 |
| TiO₂          | n.d.                       | n.d.            | n.d.       | n.d.       | n.d.        | n.d. | n.d. | n.d. | n.d. | 5.9 ± 8.3  |
| Al₂O₃         | 21.3 ± 1.2                 | 22.2 ± 0.8      | 20.3 ± 0.6 | 32.5 ± 1.8 | 19.6 ± 1.4  | 10.8 | 10.3 | 8.2 ± 0.3 | 6.1  | 13.2 ± 2.3 |
| MgO           | 0.7 ± 0.1                  | n.d.            | n.d.       | n.d.       | n.d.        | 21.2 | 20.8 | 15.4 ± 0.6 | 10.7 | 5.9 ± 1.4  |
| CaO           | 9.5 ± 2.2                  | 11.5 ± 1.5      | 10.0 ± 0.7 | 13.1 ± 0.5 | 11.3 ± 1.0  | 4.5  | 2.9  | 1.8 ± 0.1 | n.d. | 12.0 ± 2.4 |
| Na₂O          | n.d.                       | n.d.            | 0.6 ± 0.3  | 4.4 ± 0.4  | n.d.        | n.d. | n.d. | n.d. | n.d. | 1.0 ± 1.4  |
| K₂O           | 4.7 ± 2.7                  | 4.9 ± 1.4       | 0.9 ± 0.2  | n.d.       | 3.8 ± 0.5   | 2.3  | 1.1  | 4.7 ± 0.2 | 7.9  | 1.4 ± 0.8  |
| FeO           | n.d.                       | n.d.            | n.d.       | n.d.       | n.d.        | n.d. | n.d. | n.d. | n.d. | 16.6 ± 1.6 |
| Possible minerals b | CaMg-Chabazite       | Ca-Chabazite    | Ca-Stilbite | Thomsonite | Heulandite |
|                |                             | Montmorillonite        | Celadonite   | Saponite   | Smectite |
|                |                             | Saponite            | Edinite      | Smectite   | Vermiculite |
|                |                             | Glauconite           | Montmorillonite | Saponite | Smectite |
|                |                             | Nontronite           | Vermiculite  | Saponite   |
|                |                             | Saponite             | Smectite     | Vermiculite |
|                |                             | Phlogopite           | Smectite     |
|                |                             | Sepiolite            | Vermiculite  |
|                |                             | Talc                 | Smectite     |
|                |                             |                      | Vermiculite  |
|                |                             |                      | Talc         |
| n.d. = not detected. Composition measured using semi-quantitative EDS, data from which were normalized to totals of 100 wt%; these results are only used for mineral identification. |
| aNumber of measurements/locations used to obtain an average composition as displayed in the table. Error margins reflect variability between different measurements, reflecting compositional variability for single mineral types. |
| bPossible minerals reflect all minerals in the databases that satisfy the conditions explained in the Thermodynamic Modeling section. |
and 2d). The other zeolites show no systematic textural relationships. Five different compositional types of phyllosilicates (Table 3) mark the border between type 2 veins and their basaltic host rock.

Local Alteration

Local, patchy alteration is found at site 80 in the same basalt sample in which hydrothermal alteration type 2 occurs, and is developed around central spots that are now voids (Fig. 2e; Table 1). From the central zone outward, a brown and a dark green phyllosilicate occur, likely two different varieties of saponite. An Fe-Ti-oxide, possibly ulvöspinel, is also present within the phyllosilicate. However, it is unclear whether this mineral is part of the alteration sequence or not. Finally, an increased amount of Fe around pyroxene suggests increased amounts of Fe-oxides, although the exact type could not be determined.

Thermodynamic Modeling

Thermodynamic modeling was performed on the two hydrothermal alteration types described in the section Results (subsections Hydrothermal Alteration Type 1 and Hydrothermal Alteration Type 2). The other alteration types were not suitable for modeling, because the melt veinlet formed at higher temperature and was likely not related to hydrothermal alteration (see the Paragenetic Sequence and Thermal Evolution section) and both the melt veinlet and the local alteration lack clearly identifiable minerals. As described in the Methods section, two iterations were run, to allow constraints on the initial water composition to be incorporated into the models. Mineral selection methods are described in the Thermodynamic Modeling section. Mineral compositions are given in Tables 2 and 3, and are detailed in Tables S1 and S2 in the supporting information. The dissolution type was based on EDS results for unaltered basaltic material found throughout the Vista Alegre area (Table 4).

Hydrothermal Alteration Type 1

In the first iteration of the PHREEQC model for hydrothermal alteration type 1, the only minerals providing strong constraints on the initial water composition (see the Thermodynamic Modeling section) for the second iteration were calcite and quartz. These minerals were only produced at a total amount of dissolved solids, TDS, higher than 60 mg L$^{-1}$, which was observed for $\sim$40% of the initial water compositions. It was possible to further determine concentrations of individual elements within the initial water composition for the second iteration based on mineral stability limits of minerals listed in the Hydrothermal Alteration Type 1 section (Results). The resulting water composition used in the second iteration is given in Table 5.

The second modeling iteration provided constraints on temperature and chemical composition of the water during precipitation of each mineral (Figs. 4 and see Fig. 6a). Overall, there is a strong variability for all minerals in terms of stability for different stages of basalt dissolution, temperature, pH, pe, and water composition. Most minerals can form between $\sim$10 and 4000 μmol L$^{-1}$
Table 5. Constraints obtained on initial water composition, used for the second iteration of thermodynamic modeling of hydrothermal alteration type 1.

| Species | Concentration (mg L$^{-1}$) |
|---------|-----------------------------|
| Na$^+$  | >10                         |
| K$^+$   | >0.3                        |
| Ca$^{2+}$ | >1                        |
| Mg$^{2+}$ | >0.1                    |
| CO$_3^{2-}$ | >10                    |
| SO$_4^{2-}$ | >1                 |
| F$^-$   | >0.03                       |
| SiO$_2$ | >10                         |
| TDS     | >60                         |

TDS = total dissolved solids.

dissolved basalt (composition in Table 4), whereas the nesosilicate forms only at $\simeq 2500$–$8000 \mu$mol L$^{-1}$ (Fig. 4a). Notably, this mineral is also only stable under temperature of approximately 200–280 °C (Fig. 4b) and at very low SO$_4^{2-}$ concentrations (Fig. 6a), in contrast to the other minerals. Several other minerals provide temperature constraints; quartz is limited to $\simeq 30$–$100$ °C, and zeolites 1 and 2 are constrained to 70–140 °C and 30–110 °C, respectively (Fig. 4b). All minerals indicate a pH between 5.9 and 8.3 and a pe between $\sim$8 and $\sim$3 (Figs. 4c and 4d).

**Hydrothermal Alteration Type 2**

Quartz is not present in hydrothermal alteration type 2 and therefore only calcite provides constraints on the initial water composition for use in the second iteration. This indicates an initial TDS higher than 60 mg L$^{-1}$ as the only constraint on the initial water composition. Results for the second modeling iteration again show a large variability in terms of stability at different amounts of dissolved basalt, temperature, pH, pe, and water composition (Figs. 5 and 6b). The modeling results provide temperature constraints for heulandite, stilbite, phillipsite, and analcime between 10 and 70 °C and for chabazite between approximately 110 and 250 °C (Fig. 5b). Phyllosilicates 1 and 2 generally form at higher temperatures than phyllosilicates 3 and 4, which, in turn, form at higher temperatures than phyllosilicate 5. Calcite reflects slightly higher temperatures than the phyllosilicates, although the temperature range obtained for this (75–250 °C) is too large to draw strong conclusions.

All minerals are stable in a fluid pH range of roughly 6–9, with the clay minerals stable at higher pH than the zeolites (Fig. 5c). The pe indicates the opposite trend, with zeolites stable at a pe of roughly $\sim$6 to $\sim$2, whereas the phyllosilicates are stable at a pe between $\sim$9 and $\sim$5 (Fig. 5d). In contrast to other minerals, analcime only forms at higher amounts of dissolved basalt (Fig. 5a) and at very low Ca$^{2+}$ concentrations (Fig. 6b). Furthermore, phyllosilicate 5 behaves differently from the other phyllosilicates, and is stable at a relatively broader pH range (6.3–8.6), higher pe range ($\sim$6.5 to $\sim$3), and also at higher SO$_4^{2-}$ concentrations (Fig. 6b).

**DISCUSSION**

**Model Limitations**

The thermodynamic model for fluid–rock interaction provides reasonable constraints for the stability of the minerals observed in our samples from the Vista Alegre impact structure, but some limiting aspects need to be considered.

First, the models assume that all minerals identified in the hydrothermal alteration assemblages formed as a result of the interaction of water of only a single composition and with variable degrees of dissolution of a single dissolving phase, the basaltic target rock. Only one batch step is calculated by each model, meaning that the precipitation of minerals early in the sequence, possibly affecting the water composition later in the sequence, is not taken into account. Effectively, this means that the water composition is externally buffered. It is not known whether this assumption is valid, and to what degree the precipitation of minerals early in the sequence affects the water composition applied later in the sequence. However, a broad variability of the initial water composition is already considered through the large amount of randomization incorporated in the model. This means that even if prior mineral formation affects water composition, this new water composition is likely already within the range of all water compositions considered in the model.

Second, it should be taken into account that randomization itself may cause a bias. For both the initial composition and the dissolving phase, concentrations of elements have been randomized. This means that there may be a bias toward medium concentrations for individual elements in the water, from which minerals will precipitate, as well as for the TDS present in each produced solution.

An alternative processing method was investigated to solve this issue. Calculated concentrations were separated into logarithmically divided bins, tracking the number of times a bin is produced ($n_1$) and the number of times a certain mineral is produced in the bin ($n_2$). Using only $n_2$ gives the same results as shown throughout this article, but dividing $n_2$ by $n_1$ gives the likeliness of a bin (i.e., a certain concentration range) to lead to precipitation of the mineral. Therefore, the highest $n_2/n_1$ ratio should correspond to the bin with the most likely water composition. However, this also gives unrealistic predictions of the water composition, as minerals often preferentially precipitate at very low or high element...
concentrations (i.e., very high concentrations of Ca\(^{2+}\) to produce calcite, high concentrations of SiO\(_2\) to produce quartz, very low concentrations of K\(^+\) and Mg\(^{2+}\) to produce Fe-oxides, etc.). As these types of water compositions are highly unlikely to actually be produced, using this type of correction would result in an unrealistic prediction of chemical evolution, and this processing method was therefore not further applied.

Paragenetic Sequence and Thermal Evolution

The paragenetic sequence interpreted in this study is limited to the two hydrothermal alteration types described in the section Results (subsections Hydrothermal Alteration Type 1 and Hydrothermal Alteration Type 2). The possible melt veinlet is most likely not related to hydrothermal alteration because of the possible presence of pyroxene/amphibole (as discussed for hydrothermal alteration type 1 in the Cause of Hydrothermal Alteration section) and zircon; zircon is not usually formed, but rather altered and recrystallized, through hydrothermal alteration (Jiang et al., 2019), and suggests formation temperatures above 580 °C (Jiang et al., 2019; Watson & Harrison, 2005). Furthermore, Zr has been interpreted to be immobile during hydrothermal alteration within Serra Geral basalts (Pinto & Hartmann, 2011). As zircon is not found anywhere else in the basalt, and hydrothermal alterations.
formation of zircon is hindered by Zr being immobile, crystallization from a melt phase is more likely. However, as crystal sizes are very small (≤20 μm), there are no features that can further distinguish between primary and hydrothermally, or recrystallized, zircon, rendering it impossible to determine the cause of formation of the veinlet with absolute certainty.

For both the possible melt veinlet and the local alteration, it is not possible to determine whether they are related to the impact or not, as minerals are not further identifiable (see the Possible Melt Veinlet and Local Alteration sections) and neither the apparent melt veinlet nor the local alteration were found as fragments in the polymict impact breccias, in contrast to hydrothermal alteration type 2 (discussed in the Cause of Hydrothermal Alteration section). However, the veinlet has a different texture from impact-related melt features (Pittarello et al., 2015): There is no dendritic growth or amorphous phase indicating rapid crystallization. Therefore, it is more likely that this possible melt veinlet is unrelated to the impact, and possibly was inherited from earlier processes, although there is not enough evidence to ascertain this.

The paragenetic sequence interpreted in this study is based on petrographic observations, mainly idiomorphism, and thermodynamic modeling results.

Fig. 5. Constraints from the second iteration of thermodynamic modeling of temperature, pH and pe for hydrothermal alteration type 2. Minerals are placed from top to bottom in order of the paragenetic sequence deduced in the Model Limitations section. \( \text{pe} = -\log a_e \), where \( a_e \) is the electron activity. Hul = heulandite; Stb = stilbite; Php = phillipsite; Anl = analcime; Cal = calcite; Cbz = chabazite; Phyl = phyllosilicate. Abbreviations after Whitney and Evans (2010). Numbers for phyllosilicates as in Table 3. (Color figure can be viewed at wileyonlinelibrary.com.)
Thin-section analysis was used to infer the order of precipitation of the minerals—minerals showing a euhedral crystal shape are interpreted to have formed earlier than surrounding minerals, which are interpreted to fill the leftover space (Fig. 7). The thermodynamic model provides three types of constraints. First, as the model simulates dissolution of basalt and sequential precipitation of secondary phases, minerals should precipitate in the order indicated by increasing amounts of dissolution of basalt. Second, inferred temperatures need to correspond to the simplest model possible, as fewer stages of cooling or heating present more likely scenarios. Third, element concentrations need to follow a logical order, without sudden, large, or irreversible changes in water composition. The interpretation for both hydrothermal alteration types is outlined below.

**Hydrothermal Alteration Type 1**

In hydrothermal alteration type 1 (see the corresponding section in the Results), zeolite 1 is present as subhedral crystals that are surrounded by calcite (Figs. 2b and 7a). As the calcite is stable at slightly higher temperatures than the zeolite (Fig. 4b), this suggests a heating sequence. Quartz surrounds the clay minerals, zeolite 2, and Fe- and Ti-oxides (Fig. 2b). As quartz is also the mineral forming at the lowest temperature, the simplest explanation of this sequence would be that out of these minerals, quartz forms last and fills up the voids left by the other minerals. This indicates a cooling sequence, meaning that the clay minerals and Fe-oxides precipitated first, followed by the Ti-oxides, the zeolite, and then quartz (Fig. 4b). As the phyllosilicate is stable at slightly higher temperatures than the oxides, it likely formed before the oxides. Considering that both the calcite-dominated part of the vein (heating sequence) and the quartz-dominated part of the vein (cooling sequence) are part of a coherent sequence of events, heating probably predated the final cooling of the entire vein resulting in the following likely paragenetic sequence (Fig. 7a):

\[
\text{zeolite 1} \rightarrow \text{calcite} \rightarrow \text{phyllosilicate, Fe – oxides} \rightarrow \text{Ti – oxides} \rightarrow \text{zeolite 2} \rightarrow \text{quartz}
\]

The resulting interpretation is that the vein likely first heated up from 50–140 °C (zeolite 1, Fig. 4b) to 130–240 °C (calcite), followed by slow cooling to 20–90 °C (quartz). However, because there is a large variability and there is some overlap between the stability limits for zeolite 1 and calcite, the occurrence of a heating cycle is somewhat uncertain.

The main mineral that does not correspond with this sequence is the nesosilicate (Table 2), the formation of which requires elevated temperatures of >200 °C and a high degree of dissolved basalt (Figs. 4a and 4b). Furthermore, this mineral requires an extremely low amount of SO\(_4^{2-}\) (Fig. 6a). Therefore, it is unlikely that the mineral forms part of the primary paragenetic sequence. Pyroxene/amphibole is harder to place as well, as it has a large stability range both in terms of dissolved basalt and temperature. If it is a pyroxene, it can theoretically be formed hydrothermally (Schwenzer &...
Kring, 2013) from temperatures of about 200 °C (Decarreau et al., 2004), but secondary deposition of this mineral in basalts has been interpreted either not to be the result of hydrothermal activity (Laverne, 1987) or to have a more Ca-rich composition than observed in pyroxene (Manning & Bird, 1986; Marks et al., 2010). Similarly, if this phase would be an amphibole, it is more likely to have formed under different conditions (metamorphic and pegmatitic environments; Ernst, 1962) or have a different composition from the one measured here (no Mg, Ca, or Ti; Azimov & Bushmin, 2007). Last, because this phase is found in conjunction with the nesosilicate, this secondary mineral may have formed around the time of nesosilicate formation, or alternatively may be related to the melt veinlet, as the pyroxene here is similar in composition (Tables 1 and 2) and found in the same sample.

Hydrothermal Alteration Type 2

In hydrothermal alteration type 2, calcite and stilbite occur as euhedral crystals (Figs. 2c, 2d, and 7b). This is seen especially well in the sample from site 79 (polymict impact breccia, Fig. 2d), where stilbite forms crystals with perfect habit and is surrounded by chabazite, and in the sample from site 80 (also a polymict impact breccia, Fig. 2c), in which calcite forms crystals at the edge of the vein that are also surrounded by chabazite. This indicates that chabazite formed after both calcite and stilbite. Other minerals show no clear petrographic indication of the crystallization sequence.

According to the thermodynamic model, chabazite is generally stable at higher temperatures than calcite, which is again stable at higher temperatures than stilbite (Fig. 5b). Both the heulandite and phillipsite stabilities fall within the predicted range for both the temperature and dissolution of basalt needed for stilbite, indicating that these phases likely formed around the same time. The clay minerals are all found in similar locations, at the edge of the vein (Figs. 2c and 2d), and do not occur as euhedral crystals. They also form at higher amounts of dissolved basalt (Fig. 5a), indicating late precipitation or alteration of earlier-formed phases. This suggests cooling after the precipitation of chabazite,
leading to the following possible precipitation sequence (Fig. 7b):

\[ \text{stilbite, heulandite, phillipsite} \rightarrow \text{calcite} \rightarrow \text{chabazite} \rightarrow \text{phyllosilicates.} \]

This indicates that this vein set experienced heating from about 10–60 °C to 120–250 °C, followed by cooling to around 20–100 °C.

Analcime is found in the same temperature range as heulandite, stilbite, and phillipsite, but requires more dissolved basalt (Figs. 5a and 5b). Furthermore, it requires a low amount of Ca\(^{2+}\) in the fluid in comparison with other minerals (Fig. 6b). Phyllosilicate 5, which requires a low temperature but a high amount of SO\(_4^{2-}\), does not follow the sequence suggested by other minerals (Figs. 5b and 6b). Therefore, it is possible that both analcime and phyllosilicate 5 are not part of this particular paragenetic sequence and reflect a different event.

**Cause of Hydrothermal Alteration**

The results obtained from the Vista Alegre impact structure comprise three different indications shedding light on the cause of hydrothermal alteration. First, analcime, stilbite, and calcite occur as fragments in impact breccias, indicating that these minerals were present prior to the impact and that they were exposed during the excavation. Analcime was not found as part of either of the hydrothermal alteration types, but stilbite occurs in type 2, and calcite occurs in both alteration types. Although this may be caused by distinct events, it may also indicate that at least hydrothermal alteration type 2, comprising both calcite and zeolite, could have been caused by the impact.

Second, all hydrothermally altered material was recovered within 2.5–3 km from the crater center, whereas the search range for altered material included everything within an 8–10 km radius from the crater center. Considering the (nearly) symmetrical elevation within the central parts of the crater (Vasconcelos et al., 2019), all hydrothermally altered material has likely been recovered from only one part of the depositional sequence. The uplifted part includes sandstones and quartzites as exposed at site 72, likely related to the Botucatu/Pirambôia formations (see the Vista Alegre Impact Structure section, Fig. 1), meaning that the part of the sequence in which the alteration occurs was relatively close to the sandstone stratum. A possible explanation for the fact that only material was recovered from within this range is that it only exists within this range, and represents alteration after deposition of the original lava flow, where the water source may have been in the sandstones. However, there is an insufficient number of outcrops to confirm this.

Alternatively, if the alteration is related to postimpact hydrothermal activity, the breccias occurring in the central parts of the crater may have acted as a fluid barrier. This means that hydrothermal alteration is limited to the contact zone between breccias and basalts, and that hydrothermally altered material exists close below the breccias but was not exposed.

Third, when considering a meteorite impact as the most important heating mechanism, very rapid heating is expected, especially close to the center of the crater, where a possible impact melt body resides (Vasconcelos et al., 2019). It may be so that the heating phase in the outer parts of the crater is slower, as it may take time for heat to be conducted from the central parts of the crater outward. However, it is questionable whether this possible effect is sufficient to allow the time needed for precipitation of several euhedral hydrothermal minerals.

For hydrothermal alteration type 1 (Fig. 2b), hydrothermal alteration products recorded both a heating phase and a cooling phase (Fig. 4b), with some uncertainty remaining regarding heating, because the temperature ranges for zeolite 1 and calcite overlap considerably. This indicates that this alteration type has been formed by regular geo-processes, rather than by an impact event. However, indications are overall insufficient to exclude either excavation or formation by an IGHS. Furthermore, because of the limited sample material, it is impossible to put further constraints on the type of minerals and paragenetic sequence.

Thermodynamic modeling of hydrothermal alteration type 2 indicates a heating phase (Fig. 5b) with good crystallization of stilbite crystals (Fig. 2b), as well as precipitation of several other zeolite minerals. The precipitation of multiple minerals and the large difference in thermal stability indicate that fast heating is unlikely, and this type is not likely to be related to an IGHS. Instead, (1) the cooling–heating sequence, (2) the occurrence of minerals from this alteration type within fragments in the breccias, and (3) the fact that this alteration type may have affected only the basalts deposited in contact with the sandstones, make it likely that these minerals were exposed during the excavation rather than formed through an IGHS. The combined evidence for type 2 suggests excavation, rather than an IGHS. As type 2 is the most common type, this is an indication that in the Vista Alegre impact structure, IGHS-related activity is limited in comparison to excavation of preimpact altered target rocks.

Isotopic dating could help to link hydrothermal alteration type 1 to the impact, and could further confirm that hydrothermal alteration type 2 predates the impact. However, small sample size in combination with lack of suitable material prevents this for type 1. For type 2, Rb-Sr dating was attempted, but yielded insufficiently reliable data points to form an isochron.
due to limited material and resulting difficulties in separating vein material from the host rock.

On Earth, two other impact structures in dominantly basaltic target terrain are thought to have been affected by impact-generated hydrothermalism: Vargeão Dome (Brazil) and Lonar Lake (India) (Hagerty & Newsom, 2003; Yokoyama et al., 2015). Lonar Lake is very different from Vista Alegre, because of the smaller crater size of about 1.8 km and the fact that a crater lake formed, leading to a higher availability of liquid water (Hagerty & Newsom, 2003). Alteration products are also different, as they occur in the impact breccias rather than in the basaltic themselves and consist mostly of saponite and celadonite. Vargeão Dome is more similar to Vista Alegre, as alteration occurs in the basaltic, mostly within the inner collar, and involves minerals such as iron oxides, calcite, phyllosilicates, zeolites, and quartz (Epstein et al., 2021; Yokoyama et al., 2015). This mineral assemblage corresponds well with hydrothermal alteration type 1, and has been interpreted to result from impact-generated hydrothermalism (Yokoyama et al., 2015). However, the presence of chalcanthite and quartz, or the mineralization of calcite, quartz, zeolites, and clays (in order of importance) could also correspond to regional alteration in the Serra Geral basalts (Pacheco et al., 2018; Pinto & Hartmann, 2011; Pinto et al., 2011). Therefore, this type of alteration might be related to the impact, but the results for this alteration type are still insufficient to draw further and firm conclusions.

Implications for Mars

At the Vista Alegre impact structure, even with a possible aquifer underneath (Manzano & Guimaraens, 2012; Sracek & Hirata, 2002), only the sparsely occurring vein sets related to hydrothermal alteration type 1 are possibly impact-related. The other vein set does not present indications for an IGHS. This could be explained by either a large amount of erosion, destroying evidence of an IGHS, or the Vista Alegre impact structure having been formed in a relatively dry target. However, according to numeric modeling, erosion likely largely comprises the rim, where there is little impact-associated temperature change (Vasconcelos et al., 2019). It is unlikely that a hydrothermal system forms both in distances of 2.5–3.0 km from the crater center (identified alteration in this study) and at 5.0 km (the rim), but not in between. Therefore, erosion and destruction of hydrothermal alteration is unlikely and cannot explain the lack of alteration within the Vista Alegre impact structure, leaving the relatively dry target as an explanation. The dry target could also be indicated if the quartzite outcrop (Cróst et al., 2010) is representative of how the Pirambóia/Botucatu formations appear underneath the structure: as the permeability and porosity of quartzite are expected to be much lower than those of sandstone (INTERA, 1983; Manger, 1963). If the underlying formations consist largely of quartzite, access to water should have been limited. However, this remains speculation as the aquifer conditions beneath the structure are unknown, especially at the time of the impact.

This impact structure formed in a target comparable to that of impact structures on Mars and water on that planet has been a limited resource for the last 3.5 billion years (Bibring et al., 2006). Therefore, the results from Vista Alegre suggest that IGHS formation, at least for craters formed in the late Hesperian and Amazonian on Mars, is likely less common than impact-related excavation of hydrous minerals that formed prior to the impact (e.g., Carter et al., 2013; Mustard et al., 2008; Sun & Milliken, 2015) and which were probably formed over a long time in comparison to the time frame of an impact event. This is supported by remote sensing studies on Mars, which report that impact-generated hydrothermalism was probably rare on this planet during the Amazonian (Fairén et al., 2010; Turner et al., 2016). However, it cannot be excluded that IGHS existed in Martian impact craters, and it may well be that signals are simply too limited to be picked up through remote sensing. Furthermore, it is possible that any remains of life previously produced in hydrothermal systems in the crust (Fisk & Giovannoni, 1999; Jones et al., 2011; Michalski et al., 2013; Parnell et al., 2010) may be excavated and reactivated through an IGHS (Cabrol et al., 2001).

Furthermore, conditions on Mars may be different. For example, little information is available on the paleo-subsurface of the planet, and it is not known what aquifer conditions existed, whether (temporary) surface water could have been an alternative source of water after an impact, or in what amount differences in water chemistry, permeability, porosity, and rock type could produce differences in the formation of an IGHS. Therefore, although the results of this work are a first indication that most hydrous minerals, observed through remote sensing of craters on the Martian surface, have more likely been excavated than produced by an IGHS, local conditions should be taken into account for application of this work in the interpretation of data indicating hydrous minerals within craters on Mars.

CONCLUSION

At least four types of alteration occur at the Vista Alegre impact structure—a melt veinlet, two different
hydrothermal vein sets comprising dominantly zeolites and calcite, and one type of local alteration that comprises mainly saponite. There is no evidence to distinguish the origin, impact-related or otherwise, for the melt veinlet and the local alteration. Petrographic evidence combined with thermodynamic modeling suggests that the hydrothermal alteration types were formed through two separate events, each involving heating to about 200 °C followed by cooling to 20–100 °C. Stilbite and calcite fragments in impact breccias suggest that the event forming the zeolite-bearing vein set took place before the impact. For the calcite vein, no indications have been found to link it to the impact event, and the thermodynamic modeling instead suggests that this vein is related to regular geo-processes.

The results of this work suggest that if an IGHS was present at the Vista Alegre impact structure, it may have been very limited in comparison with preimpact hydrothermal alteration, evidence of which was exposed on the surface by the impact. If conditions are similar on Mars, hydrous minerals observed through remote sensing were likely exposed during excavation, rather than formed through an IGHS—in agreement with remote-sensing interpretations from Mars. This also indicates hydrothermal alteration in the crust that may have taken place over a long amount of time rather than within the time frame of a single impact event. However, differences in crustal composition and presence of aquifers should be taken into account.

Acknowledgments—This work is funded by the NWO Grant OCENW.KLEIN.206. The research by Hauser and Reimold was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior—Brasil (CAPES) through Finance Code 001. N. Hauser and W.U. Reimold are supported by Brazilian National Council for Scientific and Technological Development (CNPq) fellowship grants (309878/2019-5 and 305761/2019-6, respectively). All authors declare no conflict of interest. Also, we would like to thank the associate editor, John Spray, as well as Alvaro Penteado Crósta, for their comments and suggestions, which have greatly helped to improve the paper.

Data Availability Statement—The thermodynamic modeling code, written in R for use with the phreeqc.r package, is available in the supplementary material. The code is also openly available, together with all data related to this publication, at the DataVerseNL data repository (https://doi.org/10.34894/OL6MTF).

Editorial Handling—Dr. John Spray

REFERENCES

Alsemgeest, J., and Auqué, L. F. 2021. The Effect of Initial Water Composition on Thermodynamic Modelling of Hydrothermal Alteration in Basalt—A Case Study of the Vargeão Dome Impact Structure, edited by W. U. Reimold and C. Koeberl. Large Meteorite Impacts and Planetary Evolution VI. Geological Society of America Special Paper 550, 551–67. https://doi.org/10.1130/2021.2550(25).

Alsemgeest, J., Auqué, L. F., and Gimeno, M. J. 2021. Verification and Comparison of Two Thermodynamic Databases Through Conversion to PHREEQC and Multicomponent Geothermometrical Calculations. Geothermics 91: 11. https://doi.org/10.1016/j.geothermics.2020.102036.

Azimov, P. Y., and Bushmin, S. A. 2007. Solubility of Minerals of Metamorphic and Metasomatic Rocks in Hydrothermal Solutions of Varying Acidity: Thermodynamic Modelling at 400–800°C and 1–5 kbar. Geochemistry International 45: 1210–34. https://doi.org/10.1134/S0016702907120038.

Barlow, N. G. 2009. What We Know About Mars from Its Impact Craters. Geological Society of America Bulletin 122: 644–57. https://doi.org/10.1130/B30182.1.

Besser, M. L., Maria, E., Vasconcellos, G., José, A., and Nardy, R. 2018. Morphology and Stratigraphy of Serra Geral Silicic Lava Flows in the Northern Segment of the Torres Trough, Paraná Igneous Province. Brazilian Journal of Geology 48: 201–19. https://doi.org/10.1590/2317-4889201820180087.

Bibring, J.-P., Langevin, Y., Mustard, J. F., Poulet, F., Arvidson, R., Gendrin, A., Gondet, B. et al. 2006. Global Mineralogical and Aqueous Mars History Derived from OMEGA/Mars Express Data. Science 312: 400–4. https://doi.org/10.1126/science.1122659.

Blanc, P., Lassin, A., Plantone, P., Azaroual, M., Jacquemet, N., Fabbri, A., and Gaucher, E. C. 2012. ThermoDDEM: A Geochemical Database Focused on Low Temperature Water/Rock Interactions and Waste Materials. Applied Geochemistry 27: 2107–16. https://doi.org/10.1016/j.apgeochem.2012.06.002.

BRGM. n.d. ThermoDDEM. Retrieved January 23, 2020 from https://thermoddem.brgm.fr/.

Cabrol, N. A., Wynn-williams, D. D., and Crawford, D. A. 2001. Recent Aqueous Environments in Martian Impact Craters: An Astrobiological Perspective. Icarus 112: 98–112. https://doi.org/10.1006/icar.2001.6661.

Carter, J., Poulet, F., Bibring, J. P., Mangold, N., and Murchie, S. L. 2013. Hydrous Minerals on Mars as Seen by the CRISM and OMEGA Imaging Spectrometers: Updated Global View. Journal of Geophysical Research: Planets 118: 831–58. https://doi.org/10.1029/2012JE004145.

Charlton, S. R., and Parkhurst, D. L. 2011. Modules Based on the Geochemical Model PHREEQC for Use in Scripting and Programming Languages. Computers & Geosciences 37: 1653–63. https://doi.org/10.1016/j.cageo.2011.02.005.

Chatterjee, S. 2016. A Symbiotic View of the Origin of Life at Hydrothermal Impact Crater-Lakes. Physical Chemistry Chemical Physics: PCCP 18: 20033–46. https://doi.org/10.1039/C6CP0550K.

Christoforetti, B., Péixoto, B. C. P. M., Warren, L. V., Inglez, L., Fernandes, M. A., Alessandretti, L., Alexandre de Jesus Perinotto, J., Simões, M. G., and Assine, M. L.
Hydrothermal alteration at Vista Alegre

2173

Gases. Journal of Raman Spectroscopy 39: 1141–9. https://doi.org/10.1002/jrs.1950.

Harris, J. K., Cousins, C. R., Gunn, M., Grindrod, P. M., Barnes, D., Crawford, I. A., Cross, R. E., and Coates, A. J. 2015. Remote Detection of Past Habitability at Mars–Analogue Hydrothermal Alteration Terrains Using an ExoMars Panoramic Camera Emulator. Icarus 252: 284–300. https://doi.org/10.1016/j.icarus.2015.02.004.

Hooijschuur, J. H., Verkaaik, M. F. C., Davies, G. R., and Ariese, F. 2015. Raman Spectroscopy for Future Planetary Exploration: Photodegradation, Self-Absorption and Quantification of Carotenoids in Microorganisms and Mineral Matrices. Journal of Raman Spectroscopy 46: 856–62. https://doi.org/10.1002/jrs.4647.

INTERA Environmental Consultants Inc. 1983. Porosity, Permeability, and Their Relationship in Granite, Basalt, and Tuff. Houston: Batelle Project Management Division, Office of Nuclear Waste Isolation, U.S. Department of Energy.

Jiang, W., Li, H., Evans, N. J., and Wu, J. 2019. Zircon Records Multiple Magmatic-Hydrothermal Processes at the Giant Shizhuayuan W-Sn-Mo-Bi Poly metallic Deposit, South China. Ore Geology Reviews 115: 24. https://doi.org/10.1016/j.oregeorev.2019.103160.

Jones, E. G., Lineweaver, C. H., and Clarke, J. D. 2011. An Extensive Phase Space for the Potential Martian Biosphere. Astrobiology 11: 1017–33. https://doi.org/10.1089/ast.2011.0660.

Laverne, C. 1987. Unusual Occurrences of Aegirine-Augite, Fassaite and Melanite in Oceanic Basalts (DSDP Hole 504B). Lithos 20: 135–51. https://doi.org/10.1016/0024-4937(87)90003-X.

Lucia, M. D. and Kühn, M. 2013. Coupling R and PHREEQC: Efficient Programming of Geochemical Models. Energy Procedia 40: 464–71. https://doi.org/10.1016/j.egypro.2013.08.053.

Manger, G. E. 1963. Porosity and Bulk Density of Sedimentary Rocks: Contributions to Geochemistry. Geological Society Bulletin 114:E-60.

Manning, C. E., and Bird, D. K. 1986. Hydrothermal Clinopyroxenes of the Skaergaard Intrusion. Contributions to Mineralogy and Petrology 92: 437–47. https://doi.org/10.1007/BF00374426.

Manzano, M., and Guimaraens, M. 2012. Hidroquímica del Sistema Acuífero Guaraní e implicaciones para la gestión. Boletín Geológico y Min 123: 281–95.

Marks, N., Schiffman, P., Zierenberg, R. A., Franzson, H., and Fridleifsson, G. O. 2010. Hydrothermal Alteration in the Reykjanes Geothermal System: Insights from Iceland Deep Drilling Program Well RN-17. Journal of Volcanology and Geothermal Research 189: 172–90. https://doi.org/10.1016/j.jvolgeores.2009.10.018.

Masaitis, V. L. 1999. Impact Structures of Northeastern Eurasia: the territories of Russia and Adjacent Countries. Meteoritics & Planetary Science 34: 691–711. https://doi.org/10.1111/j.1954-5009.1999.tb03164.x.

McSween, H. Y., Taylor, G. J., and Wyatt, M. B. 2009. Elemental Composition of the Martian Crust. Science 324: 736–9. https://doi.org/10.1126/science.1165871.

Michalski, J. R., Cuadros, J., Niles, P. B., Parnell, J., Rogers, D., and Wright, S. P. 2013. Groundwater Activity on Mars and Implications for a Deep Biosphere. Nature Geoscience 6: 133–8. https://doi.org/10.1038/ngeo1706.

Mustard, J. F., Murchie, S. L., Pelkey, S. M., Ehlmann, B. L., Milliken, R. E., Grant, J. A., Bibring, J.-P. et al. 2008. Hydrated Silicate Minerals on Mars Observed by the Mars Reconnaissance Orbiter CRISM Instrument. Nature 454: 305–9. https://doi.org/10.1038/nature07097.

NASA. 2021. Mars Perseverance Press Kit. Retrieved September 15, 2021, from https://www.jpl.nasa.gov/news/press_kits/mars_2020/download/mars_2020_landing_press_kit.pdfiss.

Neukum, G., Basilevsky, A. T., Kneissl, T., Chapman, M. G., van Gasselt, S., Michael, G., Jaumann, R., Hoffmann, H., and Lanz, J. K. 2010. The Geologic Evolution of Mars: Episodicity of Resurfacing Events and Ages from Cratering Analysis of Image Data and Correlation with Radiometric Ages of Martian Meteorites. Earth and Planetary Science Letters 294: 204–22. https://doi.org/10.1016/j.epsl.2009.09.006.

Osinksi, G. R., Tornabene, L. L., Banerjee, N. R., Cockell, C. S., Flemming, R., Izawa, M. R. M., McCutcheon, J. et al. 2013. Impact-Generated Hydrothermal Systems on Earth and Mars. Icarus 224: 347–63. https://doi.org/10.1016/j.icarus.2012.08.030.

Pacheco, F. E. R. C., Caxito, F. D. A., Moraes, L. C. D., Marangoni, Y. R., Santos, R. P. Z. D., and Pedrosa–Soares, A. C. 2018. Basaltic Ring Structures of the Serra Geral Formation at the Southern Triângulo Mineiro, Água Vermelha Region, Brazil. Journal of Volcanology and Geothermal Research 355: 136–48. https://doi.org/10.1016/j.jvolgeores.2017.06.019.

Palandri, J. 2015. SOLThERM Thermodynamic Database for Geochemical Modeling. Retrieved November 23, 2021, from https://wwwosti.gov/servlets/purl/1805737.

Parkhurst, D. L., and Appelo, C. A. J. 2013. Description of Input and Examples for PHREEQC Version 3—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. U.S. Geological Survey Technical Methods, B 6: 497. https://doi.org/10.1016/0029-6554(94)90020-5.

Parnell, J., Boyce, A. J., and Blamey, N. J. F. 2010. Follow the Methane: The Search for a Deep Biosphere, and the Case for Sampling Serpentinites, on Mars. International Journal of Astrobiology 9: 193–200. https://doi.org/10.1017/S1473550410000200.

Pierazzo, E., Artemieva, N. A., and Ivanov, B. A. 2005. Starting Conditions for Hydrothermal Systems Underneath Martian Craters: Hydrocode Modeling. Large Meteorite Impacts III Geological Society of America Special Paper 384: 443–57. https://doi.org/10.1130/0-8137-2384-1.443.

Pinto, V. M., and Hartmann, L. A. 2011. Flow-By-Flow Chemical Stratigraphy and Evolution of Thirteen Serra Geral Group Basalt Flows from Vista Alegre, Southernmost Brazil. Anais da Academia Brasileira de Ciências 83: 425–40. https://doi.org/10.1590/S0001-37652011000200006.

Pinto, V. M., Hartmann, L. A., and Wildner, W. 2011. Epigenetic Hydrothermal Origin of Native Copper and Supergene Enrichment in the Vista Alegre District, Parana Basaltic Province, Southernmost Brazil. International Geology Review 53: 1163–79. https://doi.org/10.1080/00206810903465457.

Pittarello, L., Koeberl, C., and Crósta, A. P. 2010. Shock Features in Rocks from the Vista Alegre Impact Structure (Brazil). Abstracts with Programs—Geological Society of America 42: 172.

Pittarello, L., Nestola, F., Viti, C., Crósta, A. P., and Koeberl, C. 2015. Melting and Cataclastic Features in Shatter
Cones in Basalt from the Vista Alegre Impact Structure, Brazil. Meteoritics & Planetary Science 50: 1228–43. https://doi.org/10.1111/maps.12466.

Pullan, D. 2008. Analogue Studies for In Situ Surface Planetary Exploration. Leicester, UK: University of Leicester. https://doi.org/10.1002/rob.20289.

Reed, M. H. 1998. Calculation of Simultaneous Chemical Equilibria in Aqueous-Mineral-Gas Systems and its Application to Modeling Hydrothermal Processes, edited by J. P. Richards and P. B. Larson. Techniques in Hydrothermal Ore Deposits Geology. Society of Economic Geologists, 109–24. https://doi.org/10.5382/Rev.10.05.

Reed, M. H., and Palandri, J. 2006. SOLTHERM.H06, A Database of Equilibrium Constants for Minerals and Aqueous Species. Eugene: University of Oregon, Salvatore, M. R., Mustard, J. F., Wyatt, M. B., and Murchie, S. L. 2010. Definitive Evidence of Hesperian Basalt in Acidalia and Chryse Planitia. Journal of Geophysical Research 115: E07005. https://doi.org/10.1029/2009JE003519.

Schöst, J. W. 2004. Geochemical and Submicron-Scale Morphologic Analyses of Individual Precambrian Microorganisms. Geochemical Society Special Publications 9: 365–75. https://doi.org/10.1016/S1873-9881(04)80026-9.

Schwenzer, S. P., and Kring, D. A. 2013. Alteration Minerals in Impact-Generated Hydrothermal Systems—Exploring Host Rock Variability. Icarus 226: 487–96. https://doi.org/10.1016/j.icarus.2013.06.003.

Silva, M. R., Lecus, A., Gajdardziska-josifovska, M., Scho, M., and Virnoche, M. 2020. Graphene-Oxide Loading on Natural Zeolite Particles for Enhancement of Adsorption Properties. RSC Advances 10: 4589–97. https://doi.org/10.1039/c9ra00572b.

Sraćek, O. and Hirata, R. 2002. Geochemical and Stable Isotopic Evolution of the Guarani Aquifer System in the State of São Paulo, Brazil. Hydrogeology Journal 10: 643–55. https://doi.org/10.1007/s10040-002-0222-8.

Sun, V. Z., and Milliken, R. E. 2015. Ancient and Recent Clay Formation on Mars as Revealed from a Global Survey of Hydrous Minerals in Crater Central Peaks. Journal of Geophysical Research 107: 2293–332. https://doi.org/10.1029/2003JE002155.

Tanaka, K. L., Skinner, J. A., Dohm, J. M., Irwin, R. P., Kolb, E. J., Fortezzo, C. M., Platz, T., Michael, G. G., and Hare, T. M. 2014. Geologic Map of Mars, U.S. Geological Survey. Geologic Investigations Map 392. https://doi.org/10.3133/313302392.

Teramoto, E. H., Gonçalves, R. D., and Chang, H. K. 2020. Hydrochemistry of the Guarani Aquifer System Modulated by Mixing with Underlying and Overlying Hydrostratigraphic Units. Journal of Hydrology: Regional Studies 30: 100713. https://doi.org/10.1016/j.jhydrol.2020.100713.

Thiede, D. S. and Vasconcelos, P. M. 2010. Paraná Flood Basalts: Rapid Extrusion Hypothesis Confirmed by New "40Ar/39Ar Results. Geology 38: 747–50. https://doi.org/10.1130/g30919.1.

Thoenen, T. 2007. Monte Carlo Sensitivity Analysis of Modelled Opalinus Clay Porwaters from the Mont Terri Rock Laboratory. In Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, 343–4. Abstract #P/GM.24.

Turner, S. M. R., Bridges, J. C., Grebby, S., and Ehlmann, B. L. 2016. Hydrothermal Activity Recorded in Post Noachian-Aged Impact Craters on Mars. Journal of Geophysical Research: Planets 121: 608–25. https://doi.org/10.1002/2015JE004989.

Van Kranendonk, M. J. 2006. Volcanic Degassing, Hydrothermal Circulation and the Flourishing of Early Life on Earth: A Review of the Evidence from c. 3490–3240 Ma Rocks of the Pilbara Supergroup, Pilbara Craton, Western Australia. Earth-Science Reviews 74: 197–240. https://doi.org/10.1016/j.earscirev.2005.09.005.

Vasconcelos, M. A. R., Rocha, F. F., Crosta, A. P., Wünnemann, K., Guldemeister, N., Leite, E. P., Ferreira, J. C., and Reimold, W. U. 2019. Insights About the Formation of a Complex Impact Structure Formed in Basalt from Numerical Modeling: The Vista Alegre Structure, Southern Brazil. Meteoritics & Planetary Science 54: 2373–83. https://doi.org/10.1111/maps.13298.

Watson, E. B., and Harrison, T. M. 2005. Zircon Thermometer Reveals Minimum Melting Conditions on Earliest Earth. Science 308: 841–4. https://doi.org/10.1126/science.1110873.

Wendland, E., Rabelo, J., and Roehrig, J. 2006. Guarani Aquifer System—The Stratagical Water Source in South America. Köln: Institut für Tropentechnologie, 192–201.

Whitney, D. L. and Evans, B. W. 2010. Abbreviations for names of rock-forming minerals. American Mineralogist 95: 185–7. https://doi.org/10.2138/am.2010.3371.

Wolery, T. J. and Jarek, R. L. 2003. Software user’s manual EQ3/6, (Version 8.0). Albuquerque: Sandia National Laboratories.

Wolery, T. J., Jove-Colon, C. F., and Jareck, R. L. 2007. Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems, ANL-WIS-GS-000003 REV 01. Las Vegas, NV: Sandia National Laboratories.

Yokoyama, E., Nédélec, A., Baratoux, D., Trindade, R. I. F., Fabre, S., and Berger, G. 2015. Hydrothermal Alteration in Basalts from Vargão Impact Structure, South Brazil, and Implications for Recognition of Impact-Induced Hydrothermalism on Mars. Icarus 252: 347–65. https://doi.org/10.1016/j.icarus.2015.02.001.

Zuber, M. T. 2001. The Crust and Mantle of Mars. Nature 412: 220–7. https://doi.org/10.1038/35084163.

SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article.

Table S1. Overview of minerals used for thermodynamic models for hydrothermal alteration type 1. For each simulation and each mineral listed in the leftmost column, one mineral is randomly selected out of the database.

Table S2. Overview of minerals used for thermodynamic models for hydrothermal alteration type 2. For each simulation and each mineral listed in the leftmost column, one mineral variety is randomly selected out of the database columns.