Long-lasting habitable periods in Gale crater constrained by glauconitic clays

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In situ investigations by the Mars Science Laboratory Curiosity rover have confirmed the presence of an ancient lake that existed in Gale crater for up to 10 million years. The lake was filled with sediments that eventually converted to a compacted sandstone. However, it remains unclear whether the infilling of the lake was the result of background sedimentation processes or represents punctual flooding events in a largely isolated lake. Here, we used the X-ray diffraction data obtained with the Chemistry and Mineralogy instrument onboard the Curiosity rover to characterize the degree of disorder of clay minerals in the Murray formation at Gale crater. Our analysis shows that they are structurally and compositionally related to glauconitic clays, which are a sensitive proxy of quiescent conditions in liquid bodies for extended periods of time. Such results provide evidence of long periods of extremely low sedimentation in an ancient brackish lake on Mars, the signature of an aqueous regime with slow evaporation at low temperatures. More in general, the identification of lacustrine glauconitic clays on Mars provides a key parameter in the characterization of aqueous Martian palaeoenvironments that may once have harboured life.

Evaluating the structural properties of clay minerals on Mars provides relevant insights about aqueous processes and chemical conditions prevailing at the time of formation of these minerals. Disordered clay minerals are particularly interesting, as they behave like an open system, ageing for decades to millennia and providing information on the geochemical evolution concomitant with their structural reorganization. Therefore, characterizing clay mineral structure may help to understand the climatic evolution of Mars, including potential periods of habitability.

Phyllosilicate formation occurs under a wide range of physico-chemical conditions: at high temperature, from melt crystallization or by aqueous precipitation in hydrothermal systems; during metamorphism by the solid-state reorganization of precursor silicates; and at low temperature, by the formation of authigenic clay minerals via hydrolysis of silicate minerals, following a process that usually involves the initial formation of an amorphous precursor whose atomic rearrangement gives rise to a suite of different types of clay minerals. Kaolinites and smectites are typical examples of low-temperature clay minerals derived from chemically weathered rocks. The implications for climate on Mars of such low-temperature clay minerals were described recently. Among low-temperature clay minerals, glauconite, a partially disordered K+ and Fe3+/Fe2+ illite, is particularly interesting because it requires specific conditions for its formation and subsequent transformation towards well-crystallized illite. Unlike the expandable ferric smectites, such as nontronite, which have been identified on Mars through orbital and in situ measurements, glauconites typically show a non-expandable basal spacing around 10 Å or even lower. These values are consistent with the basal spacing observed in phyllosilicates in the Murray formation in Gale crater, identified by the Chemistry and Mineralogy (CheMin) instrument X-ray diffractometer on the Mars Science Laboratory Curiosity rover. Previous studies suggested that the structural and chemical transition from expandable Fe-smectite to illitized glauconite is a solvent-mediated process that occurs simultaneously with the incorporation of K+ into the interlayer region and induces particular variations in the stacking of glauconite sheets. This process requires long-term stable aqueous conditions and restricts glauconitization to areas where low sedimentation rates prevail for long periods of time and at low temperatures, for example ~3–15 °C. On Earth, favourable environments for glauconitization are associated with marine continental shelves but have also been reported at the bottom waters of saline lakes. Previously, lakes have been proposed to have existed in the past in craters on Mars owing to the morphology of the crater walls, valley networks and sediments and owing to the relationships between the sediment layering and phyllosilicate mineralogy. The sedimentology of the Murray formation indicates the presence of an intracrater lake system that may have persisted intermittently in Gale crater for up to 10 million years.

Since Curiosity landed in August 2012, the CheMin X-ray diffractometer has provided both structural and compositional information on the mineralogy of ancient sedimentary rocks and modern aeolian sediments from Gale crater. The X-ray diffraction (XRD) data have revealed the presence of clay minerals in most drilled rock samples, which is indicative of past aqueous conditions. In most samples, the clay minerals show basal d-spacing of ~10 Å (for example, at the Mariimba, Quela and Sebina locations), whereas the Cumberland sample contains clay minerals with basal d-spacings of ~13.5 Å and ~10 Å. It is unclear whether the 10 Å value for most phyllosilicates corresponds to smectites that collapsed owing to dehydration, or whether these samples contain partially illitized clay minerals with non-expandable interlayer regions owing to the incorporation of K+ in the ditrigonal cavities. The later would be the case if glauconitic clays were present.

Whether the 10 Å clay minerals found in Gale crater are Fe/Mg-smectites or glauconitic clays is important because each of these...
processes induced by a sudden change in the physico-chemical through low-temperature (for example, 20–50 °C) crystallization
Intensity axes are in arbitrary units (a.u.) normalized to 100.

from the database, and are shown for comparison.

correspond to glauconite from the Galician continental shelf and nontronite
formation. The two XRD powder patterns at the lower part of the figure
correspond to the Marimba, Quela and Sebina locations in the Murray
bulk diffraction pattern with the Le Bail method.

Fe-smectites phases forms in different sedimentary environments. Fe-smectites
are commonly associated with wet/dry cycling\(^1\) and can be formed
through low-temperature (for example, 20–50 °C) crystallization processes induced by a sudden change in the physico-chemical

parameters (that is, pH, solution composition or redox state\(^3\)). Alternatively, their formation may also occur at high temperature
(for example, 75–100 °C) in hydrothermal systems\(^1\), but at formation
at temperatures over 100 °C, smectites are typically accompanied by high-temperature phyllosilicates such as chlorites or
serpentines\(^2\). The term ‘glauconitic clay’ refers to the mixed-layer
smectite-glauconite samples from ocean environments revealed distinct spectral features for identification of
glaucconite-bearing clay minerals that were used to differentiate and
map these on Mars using orbital spectral data\(^5\).

To evaluate whether the basal \(d\)-spacing of 10 Å in Murray formation
clay minerals corresponds to dehydrated smectite or a partially
ordered glauconite, we analysed the type of structural disorder
the so-called turbostratic disorder, whereas glauconitic clays show
mixed layers corresponding either to 1M or 1Md polytypes (where
‘M’ refers to monoclinal and ‘d’ refers to disordered) involving

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Fig. 1 | Intensities corresponding to clay minerals after extraction from the bulk diffraction pattern with the Le Bail method. The three upper diagrams correspond to the Marimba, Quela and Sebina locations in the Murray formation. The two XRD powder patterns at the lower part of the figure correspond to glauconite from the Galician continental shelf and nontronite from the American Mineralogist database, and are shown for comparison. Intensity axes are in arbitrary units (a.u.) normalized to 100.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Fig. 2 | Stacking faults in clay minerals. (a) The clay disorder may involve displacement from layer to layer, rotation according to \(c\) axis or a combination of both. (b) Summary of the different types of expected stacking as a result of the combination of two parameters associated with a layer (\(L\), non-rotated layer; \(R\), rotated layer): the relative abundance of each type of layer (\(W_L\) or \(W_R\)) and the probability that two layers of the same type are arranged consecutively (\(P_{LL}\) or \(P_{RR}\)). The diagonal line in the vertical plane indicates the conditions of smectite formation where the stacking occurs randomly (turbostratic disorder). Above this line, the two layers tend to segregate. The dotted line in the same plane represents the maximum possible degree of order (MPDO) for each pair of values, (\(W_L\), \(P_{LL}\)) or (\(W_R\), \(P_{RR}\)). The left side of the panel indicates that the probability of rotated layers is higher than the probability of purely translated layers (\(P_{RR} > P_{LL}\)); then the initial smectite may evolve to glauconite (S-G). The opposite side (\(P_{LL} > P_{RR}\)) leads to formation of illite (S-I).}
\end{figure}
particular sequences of stacking faults and rotations. As our primary sources of information are diffraction patterns of whole mineral assemblages, to extract the intensities of clay minerals from the raw patterns it was necessary to perform a quantitative phase analysis.

**CheMin X-ray diffraction patterns**

We analysed the XRD patterns from drill samples from the Marimba, Quela and Sebina locations owing to their high clay mineral content (Extended Data Fig. 1). Previous studies of these samples have shown the presence of (2:1) clay minerals with a basal spacing of ~10 Å, consistent with a collapsed, disordered iron smectite to a more-ordered mica-like mineral (for example, ferric illite or glauconite). In principle, because the basal spacing of smectite minerals is known to shrink under high-vacuum conditions, XRD analyses of oriented clay minerals performed using ethylene glycol are necessary to unambiguously distinguish smectite from other non-expandable clay minerals such as celadonite or glauconite, but these treatments are currently unavailable on Mars. The diurnal temperature changes in the CheMin instrument dehydrate gypsum and may dehydrate expandable clay minerals, but techniques to do the opposite are not available in CheMin; therefore, discrimination between collapsed smectite and ferric illite solely based on the behaviour of the (001) reflection is not possible in this case.

The permanent loss of smectite expandability requires the fixation of K⁺ at the ditrigonal cavity, a process that is concomitantly followed by a reordering of the tetrahedral and octahedral layers (Extended Data Figs. 2 and 3). Preferential fixation of K⁺ followed by a reordering of the tetrahedral and octahedral layers (ref. 28). The high contents of Fe²⁺ but these treatments are currently unavailable on Mars. The diurnal temperature changes in the CheMin instrument dehydrate gypsum and may dehydrate expandable clay minerals, but techniques to do the opposite are not available in CheMin; therefore, discrimination between collapsed smectite and ferric illite solely based on the behaviour of the (001) reflection is not possible in this case.

The permanent loss of smectite expandability requires the fixation of K⁺ at the ditrigonal cavity, a process that is concomitantly followed by a reordering of the tetrahedral and octahedral layers (Extended Data Figs. 2 and 3). Preferential fixation of K⁺ is assumed to occur owing to the low hydration energy and the larger ionic radius of dehydrated K⁺ compared with those of Na⁺ and Ca²⁺. The ionic radius of dehydrated K⁺ is a good fit to the size of the ditrigonal cavities in glauconite, allowing the interlayer to collapse. In turn, the K⁺ fixation depends on the content of Fe³⁺ in the octahedral layer. Natural nontronites on Earth typically contain primarily Fe³⁺ (ref. 23). The high contents of Fe³⁺ and Mg²⁺ in the octahedral sheet of glauconites increase the net negative charge of the sheet layer, which is balanced by the progressive uptake of K⁺.

**Identifying distinct clay minerals in Gale crater**

In our analysis, we applied the Le Bail method to extract the intensities of the clay phases from the bulk material XRD pattern (Extended Data Fig. 4). The results of this analysis (Fig. 1) show the presence of the (001) basal reflection at ~10 Å in all of the data. Observable variations in other reflections are attributable to the interaction between the chemical occupancy and the layer sequence, affecting both d-spacing and intensities. We used these variations to analyse the disorder along the c crystallographic direction, which can be associated with stacking faults and rotations. The latter is of great importance because glauconitic clays have a rotational disorder based on turns of 60° or 120°, which allows accommodation of the K⁺ in the ditrigonal cavities in the course of their maturation process. Figure 2 shows, schematically, the different types of stacking along the c axis of the structure, including rotation, displacement or a combination of both. The different alternating layers tend to indicate segregation or structural order, which is mainly controlled by the probability of two overlapping layers being equally oriented. This stacking sequence observed for glauconite-smectite is based on the 'fundamental particles' approach in which two or more 2:1 layers with non-hydrated cations in the interlayer region are rotated.

**Fig. 3 | Experimental and calculated patterns of the glauconitic clays.**

**a-c** Patterns for Sebina (a), Quela (b) and Marimba (c) resulting from the fits by the FAULTS code for the 16°–36° 2θ range (d-spacing from 6.43 Å to 2.9 Å). The three graphs show the observed intensity, I (obs.), marked with stars; the calculated intensity, I (cal.), with solid black line; and the difference between both intensities, I (obs.) – I (cal.), with solid golden line. The intensities are in arbitrary units. Bragg’s positions are marked as bars, and the (hkl) correspond to Miller’s indices of glauconite lattice planes. The goodness of fit, χ², is marked at the bottom of the plots.
Precipitation associated with microenvironments. The legend in the left panel shows the reconstructed topographic profile of the basin during the late Noachian to early Hesperian. The current topography is marked by the dashed thin golden line. The water level is not to scale. a. In the first stage, a moderate level of supersaturation can be expected from the dissolution of basalt-bearing minerals or hydrothermal clay minerals. This stage will induce the precipitation (authigenesis) of more insoluble phases, that is, low-temperature smectites, by heterogeneous nucleation over mineral fragments at the bottom water interface. b. Glauconite-smectite was formed through structural reorganization of this precursor by a slow dissolution-recrystallization process driven by the introduction of K⁺ in the structure, inducing the rotation of tetraoctahedral layers and the variation in the chemical composition, in particular the Fe²⁺/Fe³⁺ ratio in octahedral sheets. The low sedimentation rate favoured an ionic exchange between water and clay minerals, being slower and more selective, especially during its early stages of formation. c. In the last stage, the increase in evaporation promoted the precipitation of soluble salts and acidification. In addition, the reduction in depth of the water column owing to evaporation progressively decreased the porosity, initiating the diagenetic processes controlled by vertical diffusion instead of the diagenetic precipitation associated with microenvironments. The legend in the left panel shows the K₀ increase and the time-lapse interval associated with the maturation process of the glauconites represented in panels a–c.

or translated parallel to each other by well-defined angles or translation vectors. The coupling of these parameters made the final structure factor unpredictable unless we considered all of the intensities in the diffraction pattern by modelling the interaction of all of these effects together. Here, we applied the FAULTS code32 (October 2018 version) to perform these calculations (Fig. 3). Our results on the ordering mechanism of the 10 Å clays of the samples analysed are consistent with the structural model for glauconites described by Drits31. In this model, the stacking disorder is described by the probability of occurrence of layers rotated by n×60° or n×120°, where n is the multiple, generating prismatic or octahedral coordination for K⁺, respectively. Rotations of n×120° and n×60° have different effects on diffraction patterns (Extended Data Fig. 5). In the first case, the k = 3n reflections at coincident planes across such rotations render k = 3n unchanged, and k ≠ 3n reflections are broadened or missing. In the case of n×60°, there are no coincident planes in the interface across rotations, and therefore n×60° rotations are usually accompanied by changes in the angular range 2θ = 34° to 39°.

Specific structural features in the glauconite-smectite sample have also been described33 for glauconitic clays forming in a shallow-water basin with a sufficiently high content of Mg²⁺ and reducing conditions. The formation of mixed-layer sequences of glauconite is, in this case, constituted by a 1Md polytype with alternating rotations at n×120°, in agreement with the results obtained in our refinements (Supplementary Table 5). Furthermore, the dehydroxylation of glauconite takes place between 570 °C and 650 °C (ref. 35), which matches the data obtained by the evolved gas analysis onboard Curiosity applied to the Marimba sample3, in which dehydroxylation was observed at 610 °C.

**Authigenic glauconitic clays in a stable lake on early Mars**

Glauconitic clays are formed only where the sediments reside for lengthy periods at the interface between oxidizing and reducing environments and where Fe³⁺ is transiently available in solution1. Interestingly, the sedimentary sequence in Gale crater shows evidence of stratigraphic redox changes (Extended Data Fig. 6), and oxidizing conditions may have formed from photo-oxidation within the ancient lake waters1. There is a positive correlation between K⁺ content and glauconite layers relative to smectite layers in glauconite-smectite. The level of maturity is a reflection of the residence time on the bottom water interface in sediment-starved conditions, serving as a key parameter to determine past aqueous conditions. On Earth, glauconitic clays are considered indicative of specific geochronal conditions prevailing for long time periods (10⁴ to 10⁵ years) in several natural environments, and are always related to authigenic processes occurring at the sediment–water interface (Extended Data Fig. 7). Glauconitic clay formation has been typically associated with zones of low deposition rate, not requiring a specific water depth11. Glauconitization has been found to occur in saline lakes17,18 where cations are concentrated through evaporation and where precipitation occurs exclusively through inorganic processes (that is, Precambrian glauconites)15, suggesting that the same inorganic process may have worked on Mars. The existence of glauconitic clays indicates the presence of liquid water remaining long-term under steady-state conditions. In addition, the geochemical parameters required for their formation (that is, neutral pH and low temperature) would have also created supportive habitable conditions for potential organisms.

The process of glauconitization in lacustrine environments (Fig. 4) requires two conditions (Methods, section on geochemical modelling and Extended Data Fig. 8). The first condition is the generation of an initial level of supersaturation necessary to induce the precipitation of a disordered precursor phase. This moderate level of supersaturation has to be produced by the dissolution of basalt-bearing minerals or hydrothermal clay minerals, together with evaporation, bearing in mind that the mechanisms of water evaporation in a lacustrine context on early Mars was mainly driven by low pressures rather than by high temperatures. It occurred in a cold environment and was associated with the rate of sublimation
(see details in previous studies\textsuperscript{16–19}). The second condition is the existence of a chemical diffusion gradient of K\textsuperscript{+} between the aqueous environment and the glauconitic clays, which enhanced the stability of the structure. The presence of this primary K-bearing source that provided a continuous supply of K\textsuperscript{+} to the aqueous environment is a key factor in the formation of these phases. In the Murray formation outcrops, the main source of K\textsuperscript{+} would have been the dissolution of alkali feldspar\textsuperscript{21}. The chemical availability of K\textsuperscript{+} could provide exchanges between the aqueous environment and the glauconitic clays in the top centimetres or decimetres of the lake bed\textsuperscript{22}. Interestingly, all analysed samples have a positive abundance of K\textsubscript{2}O, 0.72 wt\% for Sebina, 0.63 wt\% for Quela and 0.79 wt\% for Marimba, as measured by the alpha particle X-ray spectrometer (APXS). As the samples contain both primary and secondary minerals, an exclusive assignment of K\textsubscript{2}O to primary minerals by CIPW (Cross, Iddings, Pirrson and Washington) normative analysis is not strictly possible. Furthermore, the calculated percentage of clays from the XRD patterns strongly depends on the amount of K\textsubscript{2}O incorporated into the structure; thus, the possibility that samples containing 10 Å clays act as K\textsuperscript{+} sinks cannot be ruled out (Supplementary Discussion).

The process of slow incorporation of K\textsuperscript{+} into the clay structure is consistent with the results of K–Ar dating\textsuperscript{43} made in the Mojave-2 sample. These results give an age of 2.12 ± 0.36 Gyr (corresponding to the Amazonian period) for secondary minerals, and an age of 4.07 ± 0.63 Gyr (late Noachian to early Hesperian) for the primary minerals, which is in agreement with crater density measurements\textsuperscript{44}. The important time gap observed between the age of formation of primary and secondary minerals may be connected to the potential for Ar loss during mineral growth. This trait has also been observed in K–Ar measurements performed on Earth’s glauconites\textsuperscript{1}. A possible explanation is the slow incorporation of K\textsuperscript{+} into the structure of glauconitic clays during the maturation process for periods of thousands to millions of years, coupled with the simultaneous Ar loss. As glauconitic clays behave like an open system, the continuous diffusion of Ar, especially at the first stages of maturation, gives systematically younger ages than those that can be expected if diffusion had taken place during an abrupt precipitation event.

Obtaining information about clay minerals in multicomponent diffraction patterns is technically challenging, especially when the clay minerals are partially disordered\textsuperscript{23}, as is the case of the CheMin diffraction patterns for Gale crater. Furthermore, the Curiosity rover cannot use conventional lab techniques to determine the expandability of the interlaminar layer, and it is necessary to analyse the complete structure factor to evaluate clay mineralogy. Results of the stacking fault analysis applied to the phyllosilicates present in the XRD patterns of Marimba, Quela and Sebina are compatible with the presence of glauconitic clays in the lower flanks of Aeolis Mons. Authigenic crystallization occurring in a mass of standing water at low temperature would have permitted the slow incorporation of K\textsuperscript{+} into the structure during the time required for glauconitic ‘maturation’ (10\textsuperscript{4} to 10\textsuperscript{5} years). Consequently, the presence of glauconitic clays records periods of low sediment supply in a long-term sedimentary environment at low temperature (−3–15°C)\textsuperscript{11,13}, inside the Gale crater lake.

Methods

Study area, samples and instrumentation. Gale crater is located in the southern highland crust, fluvially dissected, along the Martian topographic dichotomy boundary\textsuperscript{24}. It formed ~3.8 to 3.6 billion years ago\textsuperscript{25}. Inside this crater, the study area involves the lower slope of the central mound, Aeolis Mons, commonly known as Mount Sharp. Stratigraphically, this area corresponds to the base of the Mount Sharp Group, Murray formation. We selected three samples at the Marimba, Quela and Sebina locations (Supplementary Table 1). The three samples have a similar mechanical consistency\textsuperscript{5} corresponding to a compacted sedimentary rock (mudstone). More specifically, Marimba and Quela were drilled from finely laminated mudstone, whereas Sebina was drilled from a heterolithic mixture of mudstone and sandstone. Curiosity’s sample acquisition, processing and handling (SA/SPaH) system collected the three samples at a depth of ~5–6 cm in the bedrock. The data were acquired by the XRD instrument incorporated in the Curiosity onboard the Mars Science Laboratory rover. Detailed information concerning the experimental set up employed by the CheMin instrument is available in the technical references\textsuperscript{26–28}.

Data processing. The XRD data of the samples analysed were obtained from the Planetary Data System database (https://pds.nasa.gov/) (Extended Data Fig. 1). We used these data to quantitatively characterize the mineralogy present on Mars, as well as to determine the crystallographic parameters of the detected clay minerals associated with bulk patterns (Supplementary Note).

Prior to performing the quantitative phase analysis, we extracted the XRD intensities of clay minerals from the bulk patterns following a twofold procedure. Extracting the diffusion pattern of the clay phase in the primary mineral pattern is essential for obtaining the structural model (space group, cell parameters and fractional coordinates) with the Rietveld method\textsuperscript{29}. Simultaneously, we treated the phyllosilicate phase contained in the pattern using the Le Bail method\textsuperscript{30}. In this procedure, only the space group (C2/m) and cell parameters were used as structural data. In the Le Bail method, the intensities are obtained starting with a dummy structure factor that is iteratively modified using the Rietveld extraction formula\textsuperscript{31} to obtain the best fit. We focused on the 20 range from 7° to 52° (Extended Data Fig. 4) to discard the Kapon peak from the diffraction window. The quantitative phase analysis of the crystalline phases in the patterns was performed by the Rietveld method using the FullProf code\textsuperscript{32} (April 2018 version) (Supplementary Table 2). In most previous studies with Curiosity rover data, the quantitative analysis was based on the reference intensity ratio. This methodology uses standard(s) of each mineral in the sample that are measured separately on a diffractometer with the same transmission geometry as CheMin. The addition of these patterns, each scaled differently, allows reproduction of the full diffraction pattern corresponding to a particular mineral assemblage. Although this procedure has the advantage that the instrumental profile is better constrained, it is challenging to apply when the samples are not fully ordered. These differences between both procedures have already been observed in a study of CheMin’s technical instruments\textsuperscript{33}, which demonstrated that the Rietveld method provided greater accuracy in the quantitative analysis.

Information from the structural disorder in clay minerals. The main intensity variations of the XRD patterns of glauconites can be associated with the stoichiometry. The (001) peak is dependent on the K occupancy, the (002) intensity has an inverse relationship with the iron content and the (003) reflection is related to the oxidation state of Fe in the octahedral sheets. The shape of the (004) reflection is strongly affected by the oxidation state of Fe in the octahedral sheets. The oxidation state of Fe in the octahedral sheets. The oxidation state of Fe in the octahedral sheets. The oxidation state of Fe in the octahedral sheets. The oxidation state of Fe in the octahedral sheets. The oxidation state of Fe in the octahedral sheets. The oxidation state of Fe in the octahedral sheets.

These sequences are based on the probability that each type of sheet overlaps for random stacking sequences that are capable of fitting the experimental data. The program uses a recursive algorithm to interpret the crystal structure as a stack of sheets, which can be related to each other by stacking operations and the complete structure factor to evaluate clay mineralogy. Results of the stacking fault analysis applied to the phyllosilicates present in the XRD patterns of Marimba, Quela and Sebina are compatible with the presence of glauconitic clays in the lower flanks of Aeolis Mons. Authigenic crystallization occurring in a mass of standing water at low temperature would have permitted the slow incorporation of K\textsuperscript{+} into the structure during the time required for glauconitic ‘maturation’ (10\textsuperscript{4} to 10\textsuperscript{5} years). Consequently, the presence of glauconitic clays records periods of low sediment supply in a long-term sedimentary environment at low temperature (−3–15°C)\textsuperscript{11,13}, inside the Gale crater lake.

\[
\begin{align*}
&z \cos \theta_1 - \sin \theta_1 y_1 \\
&y_2 = \sin \theta_2 z_2 - \cos \theta_2 x_2 \\
&y_3 = 0 \\
&z_3 = 1
\end{align*}
\]

where \(x_1, y_1, z_1\) are the atomic coordinates for each atom of the sheet without rotation, at \(0^\circ\) or \(360^\circ\), and \(x_2, y_2, z_2\) correspond to the atomic coordinates of the rotated sheet. These rotated sheets were obtained by applying a rotation of

\[
\begin{align*}
&z \cos \theta - \sin \theta y \\
&y = \sin \theta \cos \theta x \\
&z = 0 \\
&y = 1
\end{align*}
\]
Geochemical modelling was performed by using the PHREEQC 3.6 code. The dissolution of silicates depends on pH and temperature, the equilibrium is affected by the water/rock ratio of 10 (in mass terms), including those of the AIPEA and the International Mineralogical Association. Gale crater. These authors placed the clay layer in the intermediate area between greater resolution, the glauconite layer is preceded by the so-called ‘verdine’ facies (ferric 7 Å clays and smectite) together with iron oxides. This member is usually termed the ‘authigenic ferric clay member’. The glauconitic layer will be followed by 2:1 smectites (Fe, Al) and Mg-rich clays, and then saline deposits. Viewed with greater resolution, the glauconite layer is preceded by the so-called ‘verdine’ facies (ferric 7 Å clays and smectite) together with iron oxides. This member is usually termed the ‘authigenic ferric clay member’.

**Nomenclature aspects regarding glauconitic phases.** Nomenclature committees including those of the AIPEA and the International Mineralogical Association advise the mineral names to be used in reference to chemical and structural features, regardless of the specific source. The AIPEA recommends using ‘glauconite’ when there is a single phase that is not interstratified and ‘glauconitic’ when there are mixtures of iron-mica and expandable layers that may be described as randomly interstratified ‘glauconite-smectite’. More recently, the American Mineralogist journal published an article stating that glauconites should be broadly considered as mica-rich mica-smectite R3 interstratified minerals. Along this line of thought, we used the term ‘glauconitic clays’ to refer to these mixed-layer iron-mineral sequences that evolve towards a more ordered state as a result of the process known as ‘maturation’.

**Geochemical modelling of glauconitic clay precipitation by evaporation in Gale.** We performed geochemical modelling to obtain information about the water composition in the Gale crater lake and to evaluate whether it was consistent with the authigenic formation of glauconitic clay. To do that, we equilibrated with water representing the average mineralogy (primary minerals; see Supplementary Table 2) of different samples of the Murray formation. We used a water/rock ratio of 10 (in mass terms), an initial pH of 7 and slightly reducing conditions (Supplementary Table 7). As the dissolution of silicates depends on pH and temperature, the equilibrium concentration of this dissolution will also be dependent on these parameters. Geochemical modelling was performed by using the PHREEQC 3.6 code. The ANDRA database (www.thermochimie-tdb.com) was employed in the calculations. This database includes a great number of clay minerals and, in particular, glauconite and nontronite.

We performed the calculations at temperatures of 293 K and 273 K with a pCO₂ of 0.5 atm and 0.3 atm, respectively. In both cases (Extended Data Fig. 8), the salinity of these initial solutions is relatively low, always within the low range for brackish water. The consequence of the low solubility of basalt-bearing minerals is that nontronite precipitates first, but when the concentration decreases because it is incorporated into the glauconite. Iron is not expected for this process may be found under other circumstances. Among others, these include the absence of sedimentation for a long time interval, the presence of K and Fe³⁺/Fe²⁺, a certain salinity, circumneutral pH and the presence of an adequate substrate for nucleation. Within the context of a lake, the characteristic condensed sequence of marine glauconites is not expected. Furthermore, glauconites can be considered in terms of the evolutionary sequence of Goldschmidt (Extended Data Fig. 6). It is assumed that glauconite follows steps of first coarse-grained and then fine-grained detrital sediments deposited in a lacustrine basin and precedes the deposition of chemical products, either carbonates (on Earth) and/or saline deposits. Viewed with greater resolution, the glauconite layer is preceded by the so-called ‘verdine’ facies (ferric 7 Å clays and smectite) together with iron oxides. This member is usually termed the ‘authigenic ferric clay member’. The glauconitic layer will be followed by 2:1 smectites (Fe, Al) and Mg-rich clays, and then saline deposits. This is approximately the same type of sedimentary facies reported by Hurowitz et al. in Gale crater. These authors placed the clay layer in the intermediate area between detrital sediments at the base and evaporitic at the top. This would be the area leading to the formation of oxide–anoxic boundaries.

**Data availability**

Source data are provided with this paper. All data used in this study are freely available from the Planetary Data System database (https://pds.nasa.gov/). The data supporting the findings of this study are available within the paper, in the Supplementary Information file or from the corresponding author upon reasonable request.

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E.L.-A. and L.G.-D. conceived the original idea and analysed and interpreted the data. C.C.-L. and A.G.F. contributed to the interpretation of the results and gave technical support and conceptual advice. E.L.-A. and L.G.-D. drafted the manuscript and designed the figures. C.C.-L., A.G.F., I.L.B. and E.R.B. contributed preliminary discussions defining the direction of the project. A.G.F., J.L.B. and E.R.B. provided insights on current results of orbital and in situ measurements on Mars. All authors provided critical feedback and helped shape the research, analysis and manuscript.

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Extended Data Fig. 1 | Bulk XRD patterns of drill samples acquired by the CheMin instrument in the Murray formation (Sebina, Quela, and Marimba).

The marked peaks as Kapton represent the signal emitted by the window of the sample holder. The figure also indicates the reflections corresponding to (001) and (02I) lattice planes of clay minerals.
Extended Data Fig. 2 | XRD intensity profiles of ‘nascent’ glauconite with 0 wt. % K₂O and ‘intermediate’ glauconite with 4.5 wt. % K₂O. The XRD patterns were calculated with the Rietveld method by using the same structural model (atomic coordinates, lattice parameters, and space group) and identical profile parameters (shape of intensities and scales). No multilayers are considered in the model. It is observable the difference in integrated intensities when the occupation factor of K⁺ is varied.
Extended Data Fig. 3 | Rietveld fits of MB sample using different compositional models for the refinement of the clay mineral phase. a, Using ‘nascent’ glauconite, without K and low iron content, similar to a ferric collapsed smectite, (b) using glauconite with a 4.5 wt. % K₂O and high iron content in the structure. The wt. % values resulting from the Rietveld fits are as follows: a) 28.2 wt. % of ‘nascent’ glauconite, and b) 17.6 wt. % of glauconite (wt. % values are referred to the sum of crystalline phases, excluding the background). \( \chi^2 \) of the refinements are marked at the bottom of the plots. The graphs show the observed intensity, I (obs.), marked with stars, the calculated intensity, I (cal.) (solid line), and the difference between both intensities, I (obs.) - I (cal.) (solid gray line). Bragg’s positions are marked as bars.
Extended Data Fig. 4 | Rietveld refinement of the XRD data of SB, QL, and MB. Le bail method was used to obtain the profile of the clay minerals. Bars (I) indicate the Bragg positions of the different mineral phases in the samples. From top to bottom: Glauconitic clay, andesine, hematite, anhydrite, bassanite, gypsum, sanidine, forsterite, diopside, jarosite, and tridymite. $\chi^2$ of the refinements are marked at the bottom of the plots. The graphs show the observed intensity, $I$ (obs.), marked with stars, the calculated intensity, $I$ (cal.) (solid black line), and the difference between both intensities, $I$ (obs.) - $I$ (cal.) (solid golden line).
Extended Data Fig. 5  | Comparison between XRD patterns of minerals affected for rotational disorder and the resulting in MB from the Le Bail method. (a), Top and bottom, XRD patterns (red) of rotationally disordered non-ferric illites showing the broadening effect of n·120° rotations over the set of reflections verifying the condition \( k = 3n \). The upper pattern corresponds to a cis-vacant structure (cv-1Md), as is marked by the diagnostic (111) peak. The bottom pattern corresponds to a trans-vacant disposition (tv-1Md), marked by the absence of (111) peak. In both cases, low iron content is reflected by the diagnostic presence of (002). The blue curve shows the intensity’s profile of MB resulting from the Le Bail method. Here, the absence of (002) corresponds to a clay mineral with high-iron content. The ratio \( (111) < (−112) \) is indicative of a tv/cv interstratification, a typical feature of interstratified G-S. The extensive broadening of the set of \( k = 3n \) reflections, not affecting the (001) peak is indicative of n·120° rotational disorder. All these features are diagnostic of a mixed layer G-S evolution. (b), Broadening of \( k = 3n \) reflections due to random stratification of layers or when rotational disorder of n 60° kind dominates. Upper curve (Blue) correspond to data from MB and the bottom curve (red) correspond to a 4.5 wt. % \( K_2O \) glauconite, without rotational disorder. The intensities are in arbitrary units.
Extended Data Fig. 6 | Redox stratification and location of glauconitic facies into the Gale Crater Lake according with the Goldschmidt sedimentation sequence. The sedimentary facies displayed to the left are similar to those reported by Hurowitz et al. in the Gale crater. These facies correspond to the Goldschmidt sequence, characterized by the presence of glauconite between coarse/fine-grained detrital sediments and carbonates (on Earth) and saline deposits.
Extended Data Fig. 7 | HRTEM lattice fringe image illustrating the glauconitization pathway. (a), Orientation relations between mature glauconite and ferric smectite. The central glauconite sheets consist of a defect-free regular sequence of 10 Å layers; whereas, the collapsed Fe-smectite show anastomosing d-spacings with abundance of edge dislocations. Both minerals are disposed in a subparallel way, with clear discontinuities between glauconite and smectite layers. The amorphization features of smectite around the border of grains (areas enclosed as circles) suggest a solvent-mediated growth of glauconite at expenses of smectite, in a process similar to Ostwald ripening. There are also appreciable dissolution features and d-spacings of 0.45 nm corresponding to (020) not perpendicular to (001) indicative of rotation between layers. (b), Partially dissolved glauconite after attack by 1 M HCl for 24 h showing the amorphization of the structural framework of tetrahedral and octahedral sheets, although the 10 Å basal repeat is still observable. c) SAED diagram of natural glauconitic mineral showing rotational disorder in the a*b* section. Glauconite samples were obtained from the sediment-water interface at a depth of 200 m from the Galician continental shelf (NW of Spain).
Extended Data Fig. 8 | Geochemical modeling of the process of dissolution-precipitation between nontronite and glauconite. The right panels show the trend of Fe_{tot} (Fe^{2+}, Fe^{3+}) and K⁺ along the process. The models were performed at 293 K (a) and b)) and at 273 K (c) and d)). Since the concentration of the solution depends on the initial temperature, the course of salinity is different through the same evaporative process.