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Long lasting habitable periods in Gale crater constrained by glauconitic clays

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Abstract

In situ investigations by the Mars Science Laboratory, *Curiosity* rover, have confirmed the presence of an ancient lake 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 XRD data obtained with the Chemistry and Mineralogy instrument (CheMin), on board the *Curiosity* rover, to characterize the degree of disorder of clay minerals in the Murray formation (MF) 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, signature of an aqueous regime with slow evaporation at low temperatures. More in general, the identification of lacustrine glauconitic clays on Mars provides

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Author contributions

E.L.-A. and L.G.-D. conceived the original idea, analyzed, and interpreted the data. C.G.-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.G.-L., A.G.F., J.L.B., and E.B.R. contributed preliminary discussions defining the direction of the project. A.G.F., J.L.B., and E.B.R. 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.

Competing interests

The authors declare no competing interests.

a key parameter in the characterization of aqueous Martian paleoenvironments that may once have harbored 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, aging for decades to millennia and providing information on the geochemical evolution concomitant to 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 in a wide range of physicochemical conditions: (1) at high temperature¹, from melt crystallization or by aqueous precipitation in hydrothermal systems; (2) during metamorphism by the solid-state reorganization of precursor silicates; and (3) at low temperature², 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 recently³. Among low-temperature clay minerals, glauconite –a partially disordered K^+ , Fe^{3+}/Fe^{2+} illite⁴– is particularly interesting because it requires specific conditions for its formation and subsequent transformation toward well-crystallized illite. Unlike the expandable ferric smectites, such as nontronite, which have been identified on Mars through orbital and in-situ measurements^{5–7}, glauconites have 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 formation⁸ in Gale crater, identified by the CheMin X-ray diffractometer on the Mars Science Laboratory *Curiosity* rover. Previous studies⁹ suggested that the structural and chemical transition from expandable Fe-smectite to illitized glauconite is a solvent-mediated process, which occurs simultaneously with the incorporation of K^+ into the interlayer region and induces particular variations in the stacking of glauconite sheets^{4,10}. 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^{11,12}, e.g. ~3–15 °C. On Earth, favorable environments for glauconitization are associated with marine continental shelves^{13,14} but have also been reported at the bottom waters of saline lakes¹⁵. Lakes have been proposed previously to have existed in the past in craters on Mars due to the morphology of the crater walls, valley networks, and sediments¹⁶ and relationships between the sediment layering and phyllosilicate mineralogy¹⁷. The sedimentology of the MF indicates the presence of an intracrater lake system that may have persisted intermittently in Gale crater for up to 10 million years¹⁸.

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 eolian sediments from Gale Crater. The XRD data have revealed the presence of clay minerals in most drilled rock samples, indicative of past aqueous conditions^{8,19,20}. In

most samples, the clay minerals show basal d -spacing of ~ 10 Å (e.g., Marimba (MB), Quela (QL), Sebina (SB)), whereas the Cumberland sample contains clay minerals with basal d -spacings of ~ 13.5 Å and ~ 10 Å. It is unclear if the 10 Å value for most phyllosilicates corresponds to collapsed smectites, due to dehydration, or if these samples contain partially illitized clay minerals with non-expandable interlayer regions, due to the incorporation of K^+ in the ditrigonal cavities. The latter 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 phases form in different sedimentary environments. Fe-smectites are commonly associated with wet/dry cycling²¹ and can be formed through low-temperature (e.g., 20–50 °C) crystallization processes induced by a sudden change in the physicochemical parameters (i.e., pH, solution composition, redox state²). Alternatively, their formation may also occur at high temperature (e.g., 75–100 °C) in hydrothermal systems¹, but at formation at temperatures over 100 °C, smectites are typically accompanied by high temperature phyllosilicates such as chlorites or serpentines²¹. The term “glauconitic clay” refers to the mixed-layer mineral sequence according to the definition proposed by the AIPEA Nomenclature Committee^{22,23}, evolving towards a more ordered state as a result of the process known as “maturation”. Their presence reveals specific paleoenvironmental conditions: where steady-state conditions prevailed for a long time, including a quiescent sediment-water interface with circumneutral pH, low temperatures (~ 3 –15 °C)^{11,12}, under nearly anoxic conditions, and where a slow and continuous supply of potassium and iron promotes the structural aging of the clay minerals²⁴. Spectroscopic analyses of mixed-layer smectite-glauconite samples from ocean environments revealed distinct spectral features for identification of glauconite-bearing clay minerals that were used to differentiate and map these on Mars using orbital spectral data²⁵.

In order to evaluate whether the basal d -spacing of 10 Å in Murray formation (MF) clay minerals corresponds to dehydrated smectite or a partially ordered glauconite, we have analyzed the type of structural disorder in the clay mineral-bearing samples from the MF site. We hypothesize that the presence of glauconitic clays provides evidence for long periods (on the order of thousands of years) of depositional quiescence in seas or lakes on Mars. Our study is based on the fact that smectites exhibit a random disorder between layers –the so-called turbostratic disorder–, whereas glauconitic clays show mixed layers corresponding either to 1M or 1M d polytypes involving particular sequences of stacking faults and rotations⁹. Since 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 (QPA).

CheMin X-ray diffraction patterns

We analyzed the XRD patterns from drill samples in the locations MB, QL, and SB due to their high clay mineral content. Previous studies of these samples⁸ 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 (e.g., ferric illite, 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^{4,11,26}, but these treatments are currently unavailable on Mars. The diurnal temperature changes in the CheMin instrument dehydrate gypsum²⁷ 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 behavior 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. Preferential fixation of K^+ is assumed to occur due the low hydration energy and the larger ionic radius of dehydrated K^+ compared with those of Na^+ and Ca^{2+} . 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 Fe^{2+} in the octahedral layer. Natural nontronites on Earth typically contain primarily Fe^{3+} ²⁸. The high content of Fe^{2+} and Mg^{2+} in the octahedral sheet of glauconites increases 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 method²⁹ to extract the intensities of the clay phases from the bulk material XRD pattern. The results of this analysis are shown in figure 1, note the presence of the (001) basal reflection at $\sim 10 \text{ \AA}$ 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 analyze 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 cavities⁹ 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, G-S³⁰, is based on the “Fundamental Particles” approach³¹, where two or more 2:1 layers with non-hydrated cations in the interlayer region are rotated 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 modeling the interaction of all of these effects together. Here we have applied the FAULTS³² code to perform these calculations (Fig. 3). Our results on the ordering mechanism of the $10 \text{ \AA}$ clays of the samples analyzed are consistent with the structural model for glauconites described by Drits³³. In this model, the stacking disorder is described by the probability of occurrence of layers rotated by multiples of $n \cdot 60^\circ$ or $n \cdot 120^\circ$, generating prismatic or octahedral coordination for K^+ , respectively. Rotations of $n \cdot 120^\circ$ and $n \cdot 60^\circ$ have different effects on diffraction patterns. In the first case, the $k = 3n$ reflections at coincident planes across such rotations render $k = 3n$ unchanged, and $k \neq 3n$ reflections are broadened or missing. In the case of $n \cdot 60^\circ$, there are no coincident planes in the interface

across rotations, and therefore $n\cdot 60^\circ$ rotations are usually accompanied by changes in the angular range $2\theta = 34^\circ$ to 39° .

Specific structural features in the G-S sample have also been described³⁴ for glauconitic clays forming in a shallow-water basin, with a sufficiently high content of Mg^{2+} and reducing conditions. The formation of mixed-layer sequences of glauconite is, in this case, constituted by a $1M$ polytype with alternating rotations at $n\cdot 120^\circ$, in agreement with the results obtained in our refinements (see Supplementary Table 5). Furthermore, the dehydroxylation of glauconite takes place between 570°C and 650°C ³⁵, which matches the data obtained by the Evolved Gas Analysis (EGA) onboard *Curiosity* applied to the MB sample⁸, where 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 Fe^{3+} is transiently available in solution¹³. Interestingly, the sedimentary sequence in Gale crater shows evidence of stratigraphic redox changes, and oxidizing conditions may have formed from photooxidation within the ancient lake waters³⁶. There is a positive correlation between K^+ content and glauconite layers relative to smectite layers in G-S. 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 geochemical conditions prevailing for long time periods (10^3 to 10^6 yrs.)^{14,37} in several natural environments, always related to authigenic processes occurring at the sediment-water interface. Glauconitic clay formation has been typically associated with zones of low deposition rate, not requiring a specific water depth²⁴. Glauconitization has been found to occur in saline lakes^{15,38} where cations are concentrated through evaporation, and precipitation occurs exclusively through inorganic processes (i.e., Precambrian glauconites)¹², 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. Additionally, the geochemical parameters required for their formation (i.e., 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 (see Methods: Geochemical modeling section). First, 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 pressure values rather than by high temperatures. It occurred in a cold environment, and it was associated with the rate of sublimation (see details in previous studies^{39–41}). And second, the existence of a chemical diffusion gradient of K^+ between the aqueous environment and the glauconitic clays, enhancing the stability of the structure. The presence of this primary K-bearing source providing a continuous supply of K^+ to the aqueous environment is a key factor in the formation of these phases. In the MF outcrops, the main

source of K^+ would have been the dissolution of alkali feldspar⁴². The chemical availability of K^+ could provide exchanges between the aqueous environment and the glauconitic clays in the top centimeters or decimeters of the lake bed⁴³. Interestingly, all analyzed samples have a positive abundance of K_2O , 0.72 wt. % for SB, 0.63 wt. % for QL, and 0.79 wt. % for MB, as measured by the Alpha Particle X-Ray Spectrometer (APXS). As the samples contain both primary and secondary minerals, an exclusive assignment of K_2O to primary minerals by Cross, Iddings, Pirsson and Washington (CIPW) normative analysis is not strictly possible. Furthermore, the calculated percentage of clays from the XRD patterns strongly depends on the amount of K_2O incorporated into the structure; thus, the possibility that samples containing 10 Å clays act as K^+ -sinks cannot be ruled out (see Supplementary Discussion).

The process of slow incorporation of K^+ into the clay structure is consistent with the results of K-Ar dating⁴⁴ made in the Mojave-2 sample. These results give an age of 2.12 ± 0.36 Ga –corresponding to the Amazonian period– for secondary minerals, and an age of 4.07 ± 0.63 Ga for the primary minerals –late Noachian-early Hesperian– which is in agreement with crater density measurements⁴⁴. 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 glauconites¹³. A possible explanation is the slow incorporation of K^+ 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 disordered³³, as is the case of the CheMin diffraction patterns in Gale crater. Furthermore, the *Curiosity* rover cannot use conventional lab techniques to determine the expandability of the interlaminal layer, and it is necessary to analyze the complete structure factor to evaluate clay mineralogy. The stacking fault analysis applied to the phyllosilicates present in the XRD patterns of MB, QL, and SB is compatible with the presence of glauconitic clays in the lower flanks of Aeolis Mons. Authigenic crystallization occurring in a mass of standing water at cold temperature would have permitted the slow incorporation of K^+ into the structure during the time required for glauconitic “maturation” (10^3 to 10^6 yrs.). Consequently, the presence of glauconitic clays records periods of low sediment supply in a longterm sedimentary environment at low-temperature (~ 3 - 15 °C)^{11,12} 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 boundary¹⁸ and it formed ~ 3.8 to 3.6 billion years ago⁴⁵. 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 consistency⁴⁶ 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-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 X-ray diffraction instrument incorporated in the Chemistry and Mineralogy suite (CheMin) onboard the Mars Science Laboratory rover. Detailed information concerning the experimental set up employed by the CheMin instrument is available in the technical references^{47,48}.

Data processing

The XRD data of the samples analyzed were obtained from the Planetary Data System (PDS) 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 (see Supplementary Note).

Prior to performing the Quantitative Phase Analysis (QPA), we extracted the XRD intensities of clay minerals from the bulk patterns following a two-fold procedure: each phase in the diffraction pattern, except clay minerals, was fitted to a structural model –space group, cell parameters and fractional coordinates– with the Rietveld method⁴⁹. Simultaneously, we treated the phyllosilicate phase contained in the pattern using the Le-Bail method²⁹. 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 formula⁵⁰ to obtain the best fit. We focused on the 2θ range from 7° to 52° (Extended Data Fig. 4) to discard the Kapton® peak from the diffraction window. The QPA of the crystalline phases in the patterns was performed by the Rietveld method using the Fullprof code^{51,52} (Supplementary Table 2). In most previous studies with *Curiosity* rover data, the quantitative analysis was based on the Reference Intensity Ratio (RIR). This methodology uses standards 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 were already observed in the CheMin technical-instrumental study⁴⁸, 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 hkl , especially (-112) and (112) , and the distances between (001) and (020) further reveal the amount of K in the sample⁵³. We observed similar distances between (001) and (020) in SB and MB and smaller distances in QL, indicative of higher K concentration values (Supplementary Table 3). Furthermore, when rotations are combined with layer stacking, the intensities tend to convolve indicating a more complex structure. Generally, $n \cdot 120^\circ$ rotations ($n = 0, 1$, or 2) affect the intensities of the (hkl) reflections with $k \neq 3n$, while $n \cdot 60^\circ$ rotation ($n = 1, 3$, or 5) modifies the peaks that meet the condition $k=3n$ (Extended Data Fig. 5). Furthermore, the layer stacking can follow specific paths with a particular ordering sequence (Reichweite) or be completely at random as the turbostratic disorder of smectites.

To study the presence of stacking faults and rotational disorder in clay minerals, we used the FAULTS program³² applied to the intensities profile obtained by the Le Bail method. The FAULTS code³², based on the DIFFaX⁵⁴ program, includes a fitting algorithm based on the Crystallographic Fortran Modules Library (CrysFML). In order to interpret the crystal structure as a sequence of sheets, which can be related to each other by stacking operations and according to a certain probability, the program uses a recursive algorithm. This algorithm explores the patterns looking for random stacking sequences capable to fit the experimental data. These sequences are based on the probability that each type of sheet overlaps another. Before generating the 2:1 stacking sequences, the atomic coordinates of the monoclinic space group $C12/m1$ were transformed into an orthogonal cell within the triclinic space group, $P1$. We used the fractional coordinates in $P1$ from Sakharov et al. (1990)⁵⁵ as the starting values in the refinements. Constrained refinement of occupation factors was allowed to account for isomorphic substitutions in both positions, octahedral and tetrahedral. The interlayer cation was fixed at the position $(0, 0, 0)$. The recalculated sheet structure is shown in Supplementary Table 4. We obtained the six possible rotations on the c -axis, in the ab plane, of the previous sheet ($n = 6$; each 60° , by restriction of three-dimensional periodicity). In order to rotate the sheet, we applied the following rotation matrix:

$$\begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix}$$

where x_1, y_1, z_1 are the atomic coordinates for each atom of the sheet without rotation, 0° or 360° , meanwhile 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 $60^\circ, 120^\circ, 180^\circ, 240^\circ$ or 300° over the x_1, y_1, z_1 sheet. Finally, we needed to specify the structure of each sheet independently, including its atomic coordinates, occupations and its translation vector concerning the position of its ideal crystal.

The pseudo-hexagonal arrangement of the base of the tetrahedral $(\text{SiO}_4)^{4-}$ generates the possibility of different stacking sequences of these sheets, which leads to the formation of different polymorphs. To try to deduce them, we used as adjustable parameters: (1) the number of cells along x, y and z , (2) the occupation and fractional coordinates of

the following elements: Fe, K, Mg, Si and Al, (3) the probability of existence of each rotation (0° , 60° , 120° , 180° , 240° and 300°), and (4) the probability of sheets with cis- and trans-vacancy. The refinement was carried out using the Levenberg Marquardt⁵⁶ algorithm. We included in the calculations a 2θ range from 16° to 36° . The Goodness of fit was estimated from the χ^2 , which is commonly reported in Rietveld refinements.

The best fit for all samples corresponds to a sequence of stacked sheets rotated 120° from each other for about one third of the sheets (Supplementary Table 5). Although the resulting sequence was the same for the three samples evaluated, the fits differ among the stacking vectors. Furthermore, we observed slight variations in the unit-cell parameters and the composition of the crystals (Supplementary Table 6). The latter is due to the atomic site occupancies in the crystalline structure, which are mainly associated with isomorphic substitutions in the octahedral sheet, involving Al^{3+} , Fe^{3+} , Fe^{2+} , and Mg^{2+} .

Nomenclature aspects regarding glauconitic phases

Nomenclature committees including the *Association Internationale pour l'Etude des Argiles*, AIPEA²² and the International Mineralogical Association, IMA⁵⁷, advise that the mineral name is used in reference to chemical and structural features, regardless of the specific source.

The AIPEA recommends²² 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 minerals⁴.

In this line of thought, we used the term “glauconitic clays” to refer to these mixed-layer iron-mineral sequences, evolving towards a more ordered state as a result of the process known as “maturation”.

Geochemical Modeling of glauconitic clay precipitation by evaporation in Gale

We have performed geochemical models 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. In order to do that, we have equilibrated with water the average mineralogy (primary minerals, see Supplementary Table 2) of different samples of the MF. We used a water/rock ratio of 10 (in mass terms), and an initial pH of 7, with slightly reducing conditions (Supplementary Table 7). Since the dissolution of silicates depends on pH and temperature, the equilibrium concentration of this dissolution will also be dependent on these parameters. Geochemical modeling was performed by using the Phreeqc 3.6 code⁵⁸. 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 have performed the calculations at temperatures of 293K and 273K, with a $p\text{CO}_2$ of 0.5 atm and 0.3 atm, respectively. In both cases (Extended Data Fig. 6), the salinity of these initial solutions is relatively low, always within the low range of brackish water.

This is a consequence of the low solubility of basalt-bearing minerals. In order to generate supersaturation to allow the precipitation of secondary phases, the solution was evaporated at low temperatures simulating a cold early Mars or the loss of atmosphere on early Mars^{39–41}. This resulted in an increase in the salinity which, depending on the initial concentration, will either remains within the limits of brackish (Extended Data Fig. 6.c) during the main part of the evaporative process or may evolve to more saline conditions, like seawater (Extended Data Fig. 6.a) or brines at the later stages of evaporation. In this context of the continuous increase of supersaturation, we have evaluated the precipitation of nontronite and glauconite.

In both models, nontronite precipitates first, but when the concentration reaches a salinity level of ~20 mS/cm, glauconite also starts to precipitate. From this moment on, nontronite becomes unstable (Extended Data Fig. 6.a, 6.c) and dissolves.

It is noteworthy that a given potassium threshold must be overcome for glauconite precipitation (Extended Data Fig. 6.b, 6.d), which is not necessary for the formation of nontronite. The increase of K^+ in solution results from the K-Feldspar dissolution and continues until the glauconite formation that incorporates it into the structure.

In summary, the models allow us to describe the generation of a solution based on the mineralogy of the Gale crater, showing a chemical composition compatible with the glauconite stoichiometry. The model output allows us to estimate the state of supersaturation of glauconite driven by evaporation. Then, the compositional trend can be deduced. Initially, during the increase of salinity by evaporation, as nontronite does not consume K^+ , this cation increases in solution. As glauconite starts to grow, K^+ decreases because it is incorporated into glauconite. Iron is first incorporated into nontronite. Since glauconite and nontronite follow an opposite trend of dissolution-precipitation, the iron from nontronite is recycled. Consequently, the amount of iron in solution remains constant, increasing only at the end of the process and providing the source for the further formation of oxyhydroxides. The solvent-mediated transformation, nontronite-glauconite, captured by the model, reproduces the main features observed in the HRTEM image of Extended Data Fig. 7.

Finally, an important outcome of our model is that it is consistent, in general terms, with the geological setting for glauconite formation in Gale, shown in Extended Data Fig. 8 based in the Goldschmidt sequence.

Summary of glauconitization pathways

In the Earth's sedimentological record, glauconite maturation requires prolonged residence time at the sediment-water interface. Since low sedimentation conditions are geochemically the most favorable ones for glauconite formation, their abundance in marine systems reflects transgressions⁵⁹. The maximum abundance is associated with the transition between the Transgressive Systems Tract (TST) and the Highstand Systems Tract (HST). The primary reason being that TST provides no-sedimentation conditions, which are favorable for the formation and further aging of glauconitic minerals. Classically, this has been the main argument to consider glauconites as “marine” minerals, always associated with continental

shelves. However, transgressions are not strictly necessary for glauconitization to take place since favorable factors 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 $\text{Fe}^{2+}/\text{Fe}^{3+}$, a certain salinity, circumneutral pH and the presence of an adequate substrate for nucleation. Within the context of a lake, the characteristic sedimentary condensed sequence of marine glauconites is not expected. Furthermore, glauconites can be considered in terms of the evolutionary sequence of Goldschmidt¹⁴ (Extended Data Fig. 8). It is assumed that glauconite follows a first step of coarse 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 more resolution, glauconite layer is preceded by the so-called “verdine” facies (ferric 7 Å clays and smectite)¹⁴ 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, and Al), Mg-rich clays and then saline deposits. This is approximately the same type of sedimentary facies reported by Hurowitz et al. (2017)³⁶ 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 oxy-anoxic boundaries.

Extended Data

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 (021) lattice planes of clay minerals.

Extended Data Fig. 2. XRD intensity profiles of “nascent” glauconite with 0 wt. % K_2O and “intermediate” glauconite with 4.5 wt. % K_2O

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. % K_2O 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). χ^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. χ^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 $n \cdot 120^\circ$ 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 $n \cdot 120^\circ$ 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 $n \cdot 60^\circ$ 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. Geochemical modeling of the process of dissolution-precipitation between nontronite and glauconite

The right panels show the trend of Fe_{tot} (Fe²⁺, Fe³⁺) 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.

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 1M 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. Redox stratification and location of glauconitic facies into the Gale Crater Lake according with the Goldschmidt sedimentation sequence.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Data availability

All data used in this study is freely available from the Planetary Data System (PDS) database (<https://pds.nasa.gov/>). Source data for figure 3 are provided with the paper. The data supporting the findings of this study are available within the paper, Supplementary Information file or from the corresponding author upon reasonable request.

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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 locations MB, QL, and SB in the Murray Formation. The two XRD powder patterns at the low part of the figure correspond to glauconite* and nontronite**, and they are shown for comparison. Intensity axes are in arbitrary units (a. u.) normalized to 100. (*) Glauconite is from the Galician continental shelf. (**) Nontronite pattern obtained from the American Mineralogist database.

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. The panel (b) summarizes 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_R or W_L) and the probability of 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 purely translated layers ($P_{RR} > P_{LL}$); then the initial smectite may evolve to glauconite (G-S). The opposite site ($P_{LL} > P_{RR}$) leads to formation of illite (S-I).

Fig. 3.

Experimental and calculated patterns of the glauconitic clays. a) SB, b) QL and c) MB resulting from the fits by the code FAULTS of the 16–36° 2 θ range (d -spacing from 6.43 to 2.9 Å). The three 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). The intensities are in arbitrary units. Bragg's positions are marked as bars, and the (hkl) correspond to Miller's indexes of glauconite lattice planes. The goodness of fit, χ^2 , is marked at the bottom of the plots.

Fig. 4.

Conceptual drawing of the possible sequence of precipitation of glauconitic clays in the MF, together with the main steps of the physico-chemical evolution of the water column (water level is not scaled). Note that the sketches show the reconstructed topographic profile of the basin during the late Noachian/early Hesperian. The current topography is marked by the dashed thin golden line. In the first stage a), 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, i.e., low-

temperature smectites, by heterogeneous nucleation over mineral fragments at the bottom water interface. b) G-S 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 TOT layers and the variation in the chemical composition, in particular the ratio Fe^{2+}/Fe^{3+} in octahedral sheets. The low sedimentation rate favored an ionic exchange between water and clay minerals, being slower and more selective, especially during its early stages of formation. Finally, in the last stage c), the increase of evaporation promoted the precipitation of soluble salts and acidification. Additionally, the shortening in depth of the water column, due 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 K_2O increase and the time-lapse interval associated with the maturation process of the glauconites represented in panels a-c.