

# Subsurface water and clay mineral formation during the early history of Mars

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Clay minerals, recently discovered to be widespread in Mars's Noachian terrains, indicate long-duration interaction between water and rock over 3.7 billion years ago. Analysis of how they formed should indicate what environmental conditions prevailed on early Mars. If clays formed near the surface by weathering, as is common on Earth, their presence would indicate past surface conditions warmer and wetter than at present. However, available data instead indicate substantial Martian clay formation by hydrothermal groundwater circulation and a Noachian rock record dominated by evidence of subsurface waters. Cold, arid conditions with only transient surface water may have characterized Mars's surface for over 4 billion years, since the early-Noachian period, and the longest-duration aqueous, potentially habitable environments may have been in the subsurface.

Chemical interactions between water and rock transform nominally anhydrous materials formed by volcanic and igneous processes into hydrous phases, including clay minerals<sup>1</sup> (phyllosilicates), which incorporate OH or H<sub>2</sub>O in their structures (Table 1). On Earth, clay minerals form from near-surface weathering to produce soils, in hydrothermal systems located mostly at sea-floor spreading centres, or more rarely by direct precipitation in lake basins<sup>2</sup>. Clays are then eroded, transported, buried and metamorphosed in processes driven by climate and tectonics<sup>3</sup>. The chemical changes accompanying clay formation influence global geochemical cycles<sup>4</sup>, and the types and distributions of clay minerals and their stratigraphic contexts record and permit reconstruction of environmental histories on global and regional scales<sup>3,4</sup>.

The length of this terrestrial record is truncated, however. Plate tectonics has destroyed or obscured most of the record of Earth's first billion years, a critical period encompassing formation of the crust, heavy impact bombardment and the emergence of microbial life. In contrast, half of Mars's surface dates from its Noachian and Hesperian periods<sup>5</sup> (4.1–3.7 billion years (Gyr) ago and 3.7–3.1 Gyr ago, respectively). The early Martian record is disrupted but preserved, and the composition and stratigraphy of units with alteration minerals record changes in water availability, climate and the nature of Mars's earliest aqueous, potentially habitable environments.

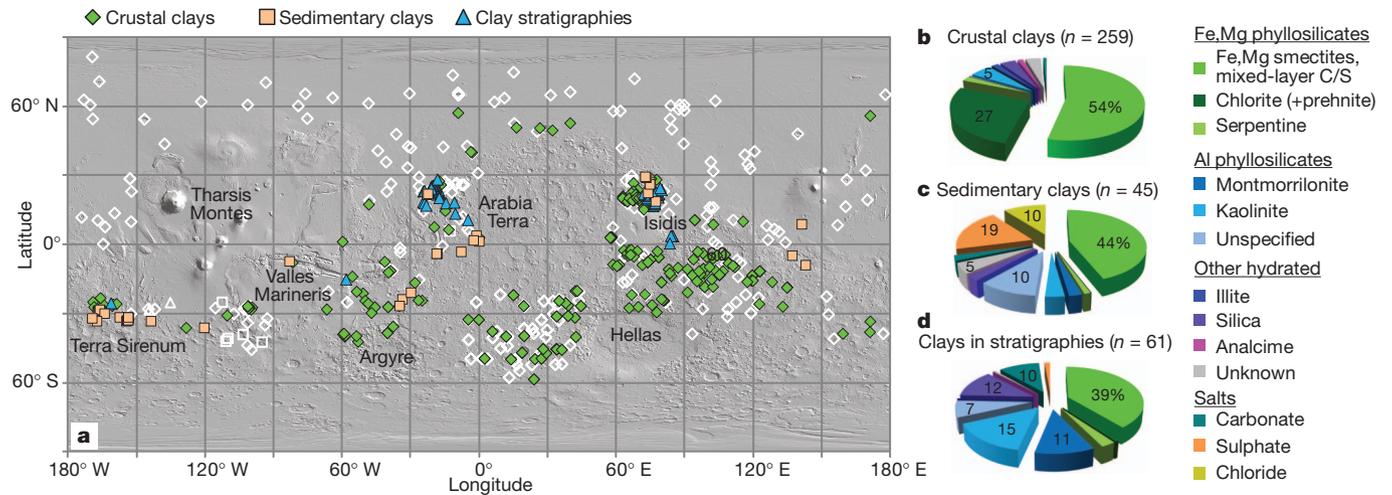
Globally widespread bedrock exposures of clay minerals (Fig. 1) indicate that long-term interaction with liquid water altered large portions of Mars's basaltic crust early in its history<sup>6–8</sup>. Clay minerals are exposed in ancient, heavily cratered Noachian terrains and contrast markedly with younger terrains, which are dominated instead by crystalline igneous materials<sup>9</sup> with weakly altered and possibly coated surfaces<sup>10</sup> as well as by spatially restricted sulphate-bearing layered deposits<sup>7,11</sup>. The apparent restriction of clays to Mars's oldest Noachian terrains and of sulphates largely to younger Hesperian terrains has been proposed to indicate a transition from an early, comparatively water-rich era with near-neutral-pH weathering to a more arid era with saline and acidic surface and near-surface waters<sup>7,12</sup>. Data from *in situ* rover measurements, orbital hyperspectral imaging, geochemical models and hydrological models have converged to support formation of late-Noachian to Hesperian sulphate-bearing deposits by precipitation of

salts from evaporating, sometimes acidic, groundwater discharge<sup>13</sup>. However, earlier Noachian environmental conditions resulting in clay formation are less well understood. In particular, it is not known whether clay formation occurred mainly at the surface or in the subsurface<sup>7</sup>.

This issue has a substantial bearing on understanding Mars's early evolution. At present, the average atmospheric pressure on Mars is 7 mbar, the average temperature is 218 K, and ice typically sublimates to the water-undersaturated atmosphere without passing through the liquid phase<sup>14</sup>. However, valley networks, deltas and outflow channels provide geomorphic evidence of Noachian and Hesperian surface waters<sup>15,16</sup>. These observations have led to the promulgation of atmospheric models involving carbon dioxide pressures 100–1,000 times higher than at present, or a distinctly different trace gas composition, to produce the higher pressures and temperatures needed to sustain surface liquid water and possibly precipitation<sup>17,18</sup>. It has proven problematic for models to produce sufficient greenhouse warming and, moreover, to explain what happened to the proposed thick early atmosphere. Loss to space and trapping in carbonate rocks, ice or clathrates have been proposed, although current estimates are that these loss fluxes are insufficient and that trapping reservoirs hold only a few tens of millibars or less of carbon dioxide<sup>19</sup>. Consequently, alternative models of a continually cold, arid early Mars, with ice, brines, low atmospheric pressure and groundwater-driven hydrological systems have also been proposed<sup>20,21</sup>.

Here we review diverse data sets on the composition of Mars obtained over the past decade, focusing on observational constraints on the processes leading to clay mineral formation. Within a conceptual framework for chemical changes and mineral assemblages expected under different alteration scenarios, we examine mineral associations in clay-bearing terrains and review the relative ages and stratigraphic relationships of clay-bearing deposits. Collectively, these data sets show that much aqueous alteration on ancient Mars occurred in the subsurface, with clay production, at low volume ratios of water to rock, by interaction with heated ground waters. Frozen, arid conditions may have been hallmarks of the surface environment since the early-Noachian period, and in this model the proposed warmer and wetter early Mars was largely beneath the surface.

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**Figure 1 | Clay mineral distribution and diversity on Mars.** **a**, CRISM-targeted images surveyed for the presence of clay minerals, grouped by geological setting and superimposed on a shaded relief map. Open symbols mark sites where no clays were found. **b, c, d**, Percentage frequency of detection of alteration phase(s), grouped by geological setting; *n* is the total number of

**Controls on clay mineralogy**

Waters interacting with rocks alter thermodynamically unstable primary materials such as glasses, olivine, pyroxenes and feldspars, and produce new stable minerals such as clays, salts and oxides (Table 1). Mafic and ultramafic iron and magnesium-rich compositions are typical of Martian rocks of all ages<sup>9</sup>. Given similar starting compositions over most of Mars’s surface, thermodynamic variables (for example temperature and pressure), kinetic parameters for mineral formation and destruction, and water chemistry (for example pH, oxidation state and ion activities) control which alteration minerals are produced. Two environmental parameters determining water chemistry are key: the degree to which alteration occurs in systems chemically ‘open’ or ‘closed’ to other reservoirs, for example the atmosphere; and the amount of water available to react with the rock, expressed as the water-to-rock ratio (W/R). These parameters control the mobility of elements during alteration, and distinctive mineral assemblages are produced, depending on the alteration environment (Fig. 2).

In closed systems in the subsurface, waters are isolated from the atmosphere and approach chemical equilibrium with precursor-rock chemistry. Temperature and pressure control the resulting alteration mineral assemblages<sup>22–25</sup>. The water-to-rock ratio is typically low (W/R < 1), and redox, pH and ion activities are determined on the local scale

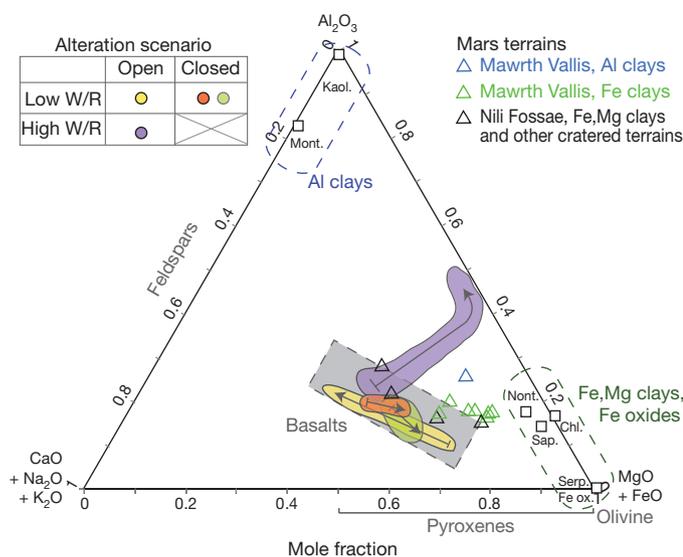
within the rock pore spaces<sup>22,26</sup>. Reactions with mafic and ultramafic lithologies control solution chemistry, buffering fluids to be anoxic and alkaline. Transport of soluble ions is limited, so alteration is largely isochemical; that is, although bulk mineralogy changes, elemental abundances remain approximately constant. This is observed for some basalt-hosted sea-floor hydrothermal systems<sup>27</sup> and terrestrial hydrothermal systems within Icelandic basalts<sup>26,28</sup> (Fig. 2). Because elemental abundances of altered rock differ little from the parent rock, mineralogy is key to deciphering the record of aqueous processes. Products of alteration of the bulk rock in systems with negligible sulphur include iron oxides and iron(II)/magnesium smectites, chlorite and serpentine at somewhat higher temperatures, and amphiboles at still higher temperatures<sup>22–24,26</sup> (>400 °C). Hydrous silicates such as silica, zeolite and prehnite silica precipitate in fractures and pore spaces<sup>22,23,26</sup>.

By contrast, in open systems nearer the surface, fluids are in communication with an atmospheric reservoir, and atmospheric chemistry exerts strong control on pH, redox and ionic activities of the fluids. At high water-to-rock ratios (W/R > 1) in an open system, transport of elements by leaching changes the bulk elemental composition<sup>22,25,29–32</sup>. Oxidation and hydrolysis of iron(II) drive waters in contact with Mars’s atmosphere to acidic pH<sup>33</sup>. For oxic fluids interacting with basalt at moderate pH, silica, chlorine, sodium and potassium are highly soluble

**Table 1 | Alteration minerals reported on Mars as of July 2011**

Class	Group, mineral or phase	Formula
Phyllosilicates (clay minerals)	Fe,Mg smectites (for example nontronite and saponite)	(Ca, Na) <sub>0.3–0.5</sub> (Fe,Mg,Al) <sub>2–3</sub> (Al,Si) <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>
	Aluminium smectite (for example montmorillonite)	(Na,Ca) <sub>0.33</sub> (Al,Mg) <sub>2</sub> (Si <sub>4</sub> O <sub>10</sub> )(OH) <sub>2</sub>
	Kaolin group minerals (for example kaolinite and halloysite)	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>
	Chlorite	(Mg,Fe <sup>2+</sup> ) <sub>5</sub> Al(Si <sub>3</sub> Al)O <sub>10</sub> (OH) <sub>8</sub>
	Serpentine	(Mg,Fe) <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>
	High-charge Al,K phyllosilicate (for example illite/muscovite)	(K,H <sub>3</sub> O)(Al,Mg,Fe) <sub>2</sub> Al <sub>x</sub> Si <sub>4–x</sub> O <sub>10</sub> (OH) <sub>2</sub>
	Prehnite	Ca <sub>2</sub> Al(AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub>
Other hydrated silicates	Analcime	NaAlSi <sub>2</sub> O <sub>6</sub> ·H <sub>2</sub> O
	Opaline silica	SiO <sub>2</sub> ·H <sub>2</sub> O
	Carbonates	(Mg,Fe,Ca)CO <sub>3</sub>
Sulphates	Magnesium, calcium and iron carbonates	(Fe,Mg)SO <sub>4</sub> ·nH <sub>2</sub> O
	Fe,Mg mono- and polyhydrated sulphates	CaSO <sub>4</sub> ·2H <sub>2</sub> O
	Gypsum	KAl <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
	Alunite	KFe(III) <sub>3</sub> (OH) <sub>6</sub> (SO <sub>4</sub> ) <sub>2</sub>
	Jarosite	Fe(II)SO <sub>4</sub> (OH)
	For example NaCl and MgCl <sub>2</sub>	(Mg,Ca)(ClO <sub>4</sub> ) <sub>2</sub>
Chlorides	Chlorides	Fe <sub>2</sub> O <sub>3</sub>
	Perchlorates	FeO(OH)
	Iron oxides	Goethite

Near-infrared vibrational absorptions related to OH, water and CO<sub>2</sub> and electronic transitions related to iron permit the remote identification and mapping of numerous phases. All mineral phases are observed from orbit with imaging spectroscopy, except for chlorides and perchlorates, which have been reported by other orbiting and surface missions. The estimated abundance threshold for detection is ~10%.



**Figure 2 | Chemical and mineralogical changes observed during aqueous alteration of basalt.** Rocks of similar composition altered under different conditions show distinctive chemical changes characteristic of the alteration environment. Key parameters are the water-to-rock ratio (W/R) and whether the system is chemically open or closed to the atmosphere. Compositions of altered terrestrial basalts are plotted (after ref. 31) on a ternary diagram with major cations at the apices. The coloured regions encompass individual bulk-rock data points from the references (not shown), and arrows indicate the alteration trajectory. High-W/R, open-system weathering (purple<sup>29</sup>) leads to substantial chemical fractionation. Alkali and magnesium cations are removed, and primary minerals in rocks are replaced with aluminium clays and iron oxides. Cations liberated and transported during clay-forming reactions may subsequently form salts<sup>32</sup>. By contrast, low-W/R alteration results in little chemical fractionation and transport, although sample mineralogy changes. In open, low-W/R systems (yellow<sup>31</sup>), directionality of change is governed by olivine dissolution, and coatings of salts and amorphous products are generated by thin-film reactions before water evaporation. In closed, low-W/R systems (orange<sup>27</sup> and green<sup>28</sup>), primary minerals are replaced with Fe,Mg clay minerals and oxides and products such as silica and zeolites may precipitate in pore spaces<sup>26</sup>. Open triangles represent the chemical composition of clay-bearing units on Mars, calculated from estimates of dust-free modal mineralogy<sup>74</sup>. With the exception of aluminium-clay-bearing units in Mawrth Vallis, these lie on the mixing line between basalt and Fe,Mg clays expected for low-W/R, closed-system-type alteration. Chl., chlorite; Kaol, kaolinite; Mont., montmorillonite; Nont., nontronite; Sap., saponite; Serp., serpentine.

and, hence, mobile. Magnesium, calcium and sometimes silica are relatively mobile, whereas aluminium, iron(III) and titanium are conserved, that is, immobile<sup>29,30</sup>. Consequently, as weathering proceeds, the bulk chemistry of the residual rock becomes more aluminium rich, and leaching alters mafic lithologies to aluminium clay (for example kaolinite and montmorillonite) and iron oxide assemblages<sup>22,29</sup> (Fig. 2). From the transported weathering fluids, salts (chlorides, carbonates or sulphates) precipitate. Carbon dioxide or sulphurous gases present in the atmosphere help maintain fluid acidity and also dictate the composition of the salts<sup>12</sup>. Oxic surface conditions and/or oxidized sulphurous species generating acidity inhibit Fe,Mg smectite formation, promoting formation of jarosite, silica, iron oxides, amorphous products<sup>12,34,35</sup> and, if more water is available, kaolinite<sup>36</sup>. If less water is available (W/R < 1), the most soluble primary phase, olivine, dissolves first, moderately depleting the residual phase in magnesium and iron<sup>31</sup>, but little additional fractionation or alteration of the parent rock occurs. Transport to segregate fluids cannot occur in spite of the open nature of the system, and amorphous products and salts form as coatings and rinds from weathering by thin films of water<sup>31</sup>.

Armed with this conceptual framework for prediction of mineral assemblages under different environmental conditions, the composition of clay-bearing units on Mars can be compared with the above scenarios and used to determine the conditions under which alteration occurred.

## Clay distribution and diversity

The OMEGA and CRISM visible/near-infrared orbital imaging spectrometers, on board the Mars Express and Mars Reconnaissance Orbiter spacecraft, respectively, have revealed thousands of outcrops bearing clay minerals distributed throughout the southern highlands<sup>8</sup> and exposed by large craters that penetrated overlying lavas of the northern lowlands<sup>37</sup>. The distribution of clays on Mars (Fig. 1) is controlled principally by exposure. Hesperian or later lavas and mantling materials typically overlie globally widespread buried clays, except where tectonism, erosion or cratering exposes underlying units. In a meta-analysis of results from examination of 639 CRISM high-resolution images<sup>11,37–54</sup>, we catalogued the types and distribution of clay minerals and co-occurring alteration phases. Occurrences were classified into one of three geological settings: ‘crustal’, describing ancient terrains resulting from igneous processes and degraded by impact cratering (‘deep phyllosilicates’ in the terminology of ref. 11); ‘sedimentary’, describing fan-shaped or layered deposits within basins with a setting clearly pointing to transport of the materials (‘phyllosilicates in intracrater fans’, ‘plains sediments’, and ‘intracrater clay sulphate deposits’<sup>11</sup>); and ‘in stratigraphies’, describing multiple units where clays and other alteration minerals are found in contact with each other in a defined stratigraphy but where either a crustal or sedimentary origin cannot be assigned to all of the units (‘layered phyllosilicates’ or ‘carbonate deposits’<sup>11</sup>) (Fig. 1).

Across all geological settings, Fe,Mg smectites are the most commonly occurring clay mineral. Compositions range from nontronite (iron end-member) to saponite (magnesium end-member)<sup>8</sup>, and may in some cases include physical mixtures of chlorite and smectite or mixed-layer chlorite–smectite clays, which are mineralogically and structurally distinct but spectrally difficult to distinguish<sup>48</sup>. Notably, the other alteration minerals accompanying Fe,Mg smectites vary markedly depending on geological setting (Fig. 1b–d).

## Crustal clays

Fe,Mg smectite and/or chlorite are nearly always present in crustal clay units (detected in 78% and 39% of exposures, respectively). Chlorite is sometimes accompanied by the spectrally similar but mineralogically distinct phase prehnite, which forms at temperatures between 200 and 400 °C (refs 37, 39, 41). Distinctive associations of minerals vary from crater to crater, and can include silica, analcime, serpentine and illite/muscovite accompanying smectites and chlorite<sup>37,41–43</sup>. These minerals and the assemblages in which they are found indicate a range of formation temperatures from ambient to a maximum of 400 °C<sup>37,41,55</sup>. A few heavily eroded terrains near the Argyre basin<sup>39</sup>, Terra Sirenum<sup>54,56</sup>, the Claritas Fossae<sup>42</sup> and the Nili Fossae<sup>8,41,57</sup> host clays within geographically extensive Noachian units exposed at the surface, but most crustal clays are detected in the walls, ejecta or central peaks of impact craters<sup>8</sup>.

It is not known whether crustal clays associated with craters are generated as a result of impacts or are pre-existing compositions excavated from depth. Laboratory studies so far have shown that instantaneous shock does not form clays<sup>58</sup>. However, modelling<sup>59,60</sup> and terrestrial studies<sup>61</sup> demonstrate that heat from an impact can initiate hydrothermal systems. For the sizes of craters with which clays are associated (diameters of ~20–200 km in this study), hydrothermal systems may last thousands of years at depth<sup>59,60</sup>. These might produce clays near the hot central peak, beneath an impact melt sheet or in the lower crater walls<sup>62</sup>. For the Martian craters studied so far, the alteration minerals associated with ejecta and the upper walls, where hydrothermal circulation is not predicted, are the same as those associated with the central peak regions<sup>6,8,37,51,63</sup>. Although morphologies consistent with post-impact hydrothermal activity have been proposed<sup>64</sup>, collectively, observations are consistent with the greater relative importance of the excavation of pre-existing clay-bearing rocks. Materials emplaced ballistically as crater ejecta or constituting the central peaks originate from depths of up to about one-tenth the crater diameter<sup>65</sup>, or up to ~5–10 km for the craters in this study.

## Sedimentary clays

Clays and salts have been detected in several of Mars's many putative palaeolakes and fluvial basins. In marked contrast with clays in crustal settings, the hydrated silicates prehnite, analcime, illite/muscovite and chlorite (except possibly as mixed with smectite) have not been detected. Instead, mineral associations vary according to the fluvial system. Open-basin sediments in the Jezero system host Fe,Mg smectite clays and magnesium carbonate<sup>41</sup>. Holden<sup>48</sup>, Eberswalde<sup>48</sup> and other craters<sup>66</sup> contain predominantly Fe,Mg smectite clays. Broad, intercrater depressions in the southern hemisphere with poor drainage connectivity have distinctive units with chloride salt units overlying Fe,Mg clays<sup>11,44,67</sup>. Putative lacustrine sediments within the closed basins of Gale, Columbus and Cross craters contain sulphate salts, accompanied by aluminium clays and/or nontronite<sup>47,54</sup>. From the available data it is not possible to determine definitively whether the clay minerals are allochthonous (transported) or autochthonous (formed *in situ*). Nevertheless, basins fed by valleys typically host minerals closely comparable to those in nearby highland watersheds, consistent with detrital origin<sup>41,48</sup>. By contrast, salts found in closed basins are not identifiable in the surrounding terrains, and thus instead indicate *in situ* precipitation.

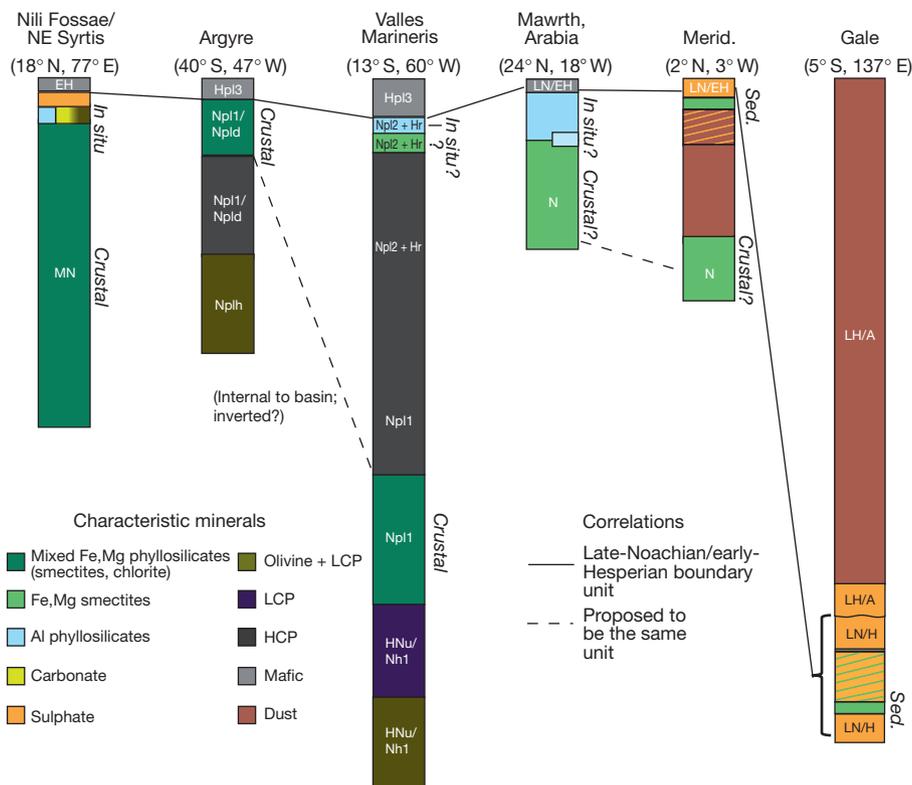
## Clays in stratigraphies

A few geographically extensive stratigraphic sections preserve contacts between different clay-bearing rock compositions. By contrast with sedimentary clays found in low-lying depositional basins or their eroded remnants, clays in stratigraphy occur in high-standing topography, and the contacts between clay units typically follow a pre-existing

topographic surface. The nature of this contact suggests formation by either *in situ* alteration, that is, leaching, of pre-existing surface materials, or draping by later air-fall deposits. Hence, these clays in stratigraphy cannot be defined as distinctly crustal or sedimentary. A characteristic feature is the presence of aluminium clays overlying Fe,Mg clays (Figs 1d and 3). In fact, except for a few detections in materials disrupted by cratering<sup>42</sup> and in sedimentary basins<sup>54,66</sup>, almost all aluminium clays detected so far on Mars are found in upper, late-Noachian clay-bearing strata above Fe,Mg clays. In Mawrth Vallis and greater Arabia Terra, kaolinite, montmorillonite and silica overlie a nontronite-bearing unit<sup>6,50,68–70</sup>. Around the Nili Fossae, a thin kaolinite-bearing unit overlies both crustal and sedimentary Fe,Mg smectite clay units. In the eastern portion of this region, magnesium carbonate and serpentine associated with an olivine-rich unit occupy a stratigraphic position similar to that of kaolinite<sup>41,42,57</sup>. Aluminium clays overlying Fe,Mg clays are also exposed high in the walls of Valles Marineris<sup>11</sup> (Fig. 3) and in other scattered exposures across the southern highlands<sup>56</sup>.

## Establishing timing

For six regions of Mars<sup>11,39,46,47,49,50,53,68–70</sup>, the compositional stratigraphy of clay-bearing units has been defined relative to regional geological units for which surface age has been determined from crater counts, making it possible to correlate stratigraphic sections from different parts of the planet (Fig. 3). The deepest portions of the stratigraphies include discrete units containing Fe,Mg smectites, chlorites or their mixtures and are a few hundred metres to kilometres in thickness. Their morphology ranges from discontinuous, quasi-horizontal layers, found at



**Figure 3 | Compositional stratigraphy of clay-bearing units.** Published regional stratigraphies from different locations on the planet—Nili Fossae/northeastern Syrtis<sup>41,49,57</sup>, Argyre<sup>39</sup>, Valles Marineris<sup>11</sup>, Mawrth Vallis and Arabia Terra<sup>46,50,68–70</sup>, Terra Meridiani<sup>53</sup>, and sedimentary clays at Gale crater<sup>47</sup> (latitudes and longitudes as shown)—have been compiled and correlated. Columns, except those for Valles Marineris and Gale, are drawn on the same vertical scale. Section thickness ranges from ~250 m, at Mawrth Vallis, to 8 km, at Valles Marineris. Characteristic minerals or compositions that characterize each unit in near-infrared spectral data are shown. Hatching indicates the interbedding of two minerals in the same large-scale unit, and colour gradation indicates that the corresponding minerals occupy the same unit, grading from

one to the other at various points. Upper units have been dated to the Noachian/Hesperian boundary and can be correlated globally. Correlations between lower stratigraphic units can sometimes be inferred on a regional basis<sup>39,50</sup>. Unit labels correspond to inferred age (EH, early Hesperian; LN, late Noachian; MN, middle Noachian; A, Amazonian) or assigned global geological map units (for example Np1) identified in the section by the authors of the original published stratigraphy, where the first letter indicates the age of the rock unit. The geological setting of clay formation is given in italics, and, where consensus does not exist in the literature, a question mark is appended. *In situ* means in-place formation of the stratigraphic unit by *in situ* alteration; sed., sedimentary. HCP, high-calcium pyroxene; LCP, low-calcium pyroxene.

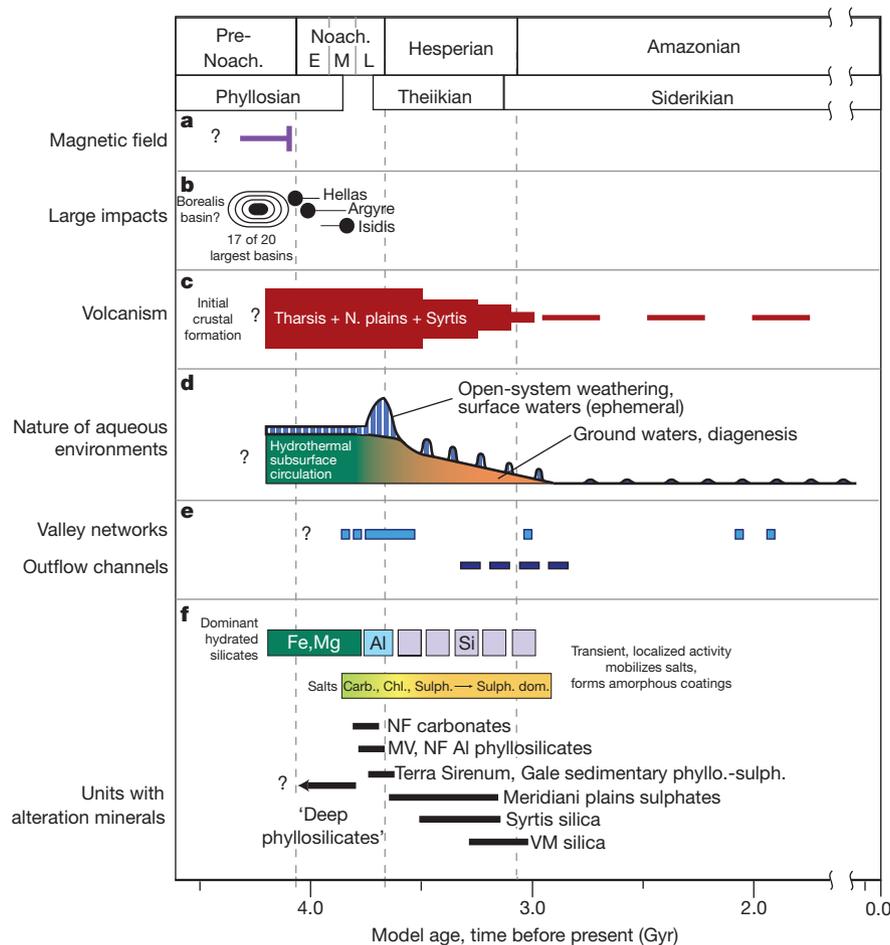
Mawrth Vallis<sup>69</sup>, to brecciated deposits with heterogeneous 10<sup>0</sup>–10<sup>3</sup>-m-scale blocks bearing Fe,Mg smectite or low-calcium pyroxene in crust disrupted by Isidis basin formation<sup>57</sup>. Volumetrically large units with spectral signatures of olivine and low- and high-calcium pyroxene but no signs of hydrous minerals are also found in the deepest sections exposed around the Argyre basin and in Valles Marineris<sup>11,39</sup>. As was previously found using OMEGA data<sup>7</sup>, stratigraphic relations in CRISM data show that nearly all sulphates occur in units younger than the Fe,Mg clays. CRISM data also resolve a similar relationship for multiple clays in stratigraphic section: relatively thin (<50-m) aluminium-clay-bearing units lie above Fe,Mg smectites and chlorites. They are constrained in timing by crater count dating of overlying unaltered late-Noachian/early-Hesperian mafic rocks above and Noachian units beneath. No Fe,Mg clays stratigraphically above aluminium clays or with interbedding of aluminium and Fe,Mg clay units has been found.

We next consider how sedimentary clays fit into the temporal-stratigraphic framework. The lower strata of the Gale crater mound are sedimentary and were probably emplaced during the late Noachian<sup>47</sup> (Fig. 3). Crater count data show that clay- and sulphate-bearing sediments were emplaced in Cross and Columbus craters in the late Noachian/early Hesperian<sup>54</sup>. Similarly, most occurrences of smectite chloride deposits correspond to this time period<sup>44,67</sup>. The ages of these sedimentary clay deposits agree well with ages assigned previously to geomorphic features indicative of surface waters. Most valley networks were last active at the late-Noachian/early-Hesperian boundary<sup>16</sup>, when

fluvial processes intensified relative to the early-to-middle-Noachian period<sup>71,72</sup>. Thus, stratigraphy and crater counts together show that the timing of sedimentary clay deposition, surface fluvial activity and the period of aluminium clay formation are coincident within present age-discrimination capabilities and post-date formation of many of the thicker, deep Fe,Mg clay units (Fig. 4).

### Early Martian environments

Considered in the context of scenarios for aqueous alteration, evidence from the Martian rock record (Fig. 2) indicates that most clay minerals—specifically, those comprising Fe,Mg clay mineral units deep in the crust—formed in the subsurface in closed systems at temperatures ranging from ambient to low-grade hydrothermal (<400 °C). This formation mechanism is indicated by five lines of evidence: (i) observed mineral assemblages of Fe,Mg smectites and chlorite, which form under anoxic, alkaline, high-pH conditions<sup>22,24,34,35</sup>; (ii) the presence of the accompanying phases prehnite, analcime, serpentine and illite/muscovite, which form at higher temperatures, ranging up to 400 °C (refs 22, 23, 37, 39, 41, 55); (iii) the pervasive presence of clay minerals in large volumes of Mars’s deepest exposed crustal materials in spite of (iv) thermal infrared and elemental data consistent with the dominance of primary minerals by weight fraction<sup>9,44,73,74</sup> (Fig. 2); and (v) the morphology of Noachian fluvial valleys indicating hyperarid surface conditions except during the late Noachian<sup>71,72</sup>, when episodic floods incised numerous highland valley networks<sup>75</sup>.



**Figure 4 | Timeline of major processes in Mars history.** a–c, Major geological processes influencing water availability, including the presence of a magnetic field<sup>95</sup> (a), impact cratering<sup>96,97</sup> (b) and volcanism<sup>86,98</sup> (c). d, Schematic depicting the changing nature of environments hosting liquid water, as implied by the geological evidence discussed herein. e, f, Evidence of liquid water: timing of valley network and outflow channel activity<sup>15,16</sup> ages of key minerals

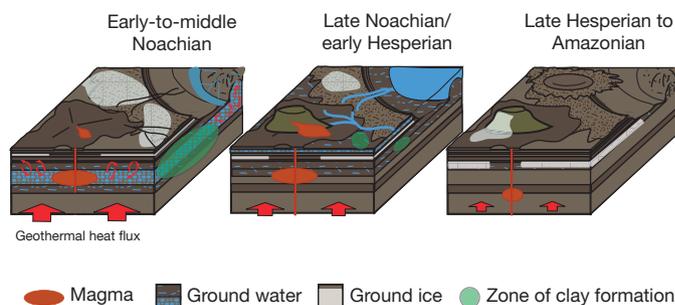
formed by aqueous alteration (e) and important regional units with alteration minerals (f). Relative timing is determined using relative crater densities and stratigraphic relationships. Absolute ages of period boundaries<sup>5</sup> have uncertainties of several hundred million years, inherent to extrapolation from cratering statistics<sup>99</sup>. NF, Nili Fossae; MV, Mawrth Vallis; VM, Valles Marineris; Carb., carbonates; Chl., chlorites; Sulph., sulphates.

The physiochemical conditions for globally widespread Fe,Mg clay formation imply the existence of widespread low-grade metamorphism/diagenesis<sup>23</sup>, hydrothermal systems<sup>25,26</sup> or direct precipitation during cooling of volatile-rich basaltic lavas<sup>76</sup>. For the final mechanism, substantial volatile content in lavas could be obtained by assimilation of ice or liquid water during magma ascent. For the first two mechanisms, subsurface liquid waters, specifically large-scale groundwater aquifers, are required. A long-standing model is that of a Martian cryosphere and melting of subsurface ice at depth<sup>77</sup>. Several mechanisms existed on ancient Mars to melt ice and promote hydrothermal circulation of ground water: large impacts<sup>61</sup>, especially during early, heavy impact bombardment<sup>78</sup>; widespread extrusive and intrusive volcanism<sup>79,80</sup>; and a geothermal gradient<sup>81</sup> greater than that at present.

Implications of widespread Noachian subsurface aqueous activity in thick sections of crust include enhanced rates of crustal cooling<sup>81</sup>, possibly significant sequestration of volatiles (for example water and carbon dioxide) in crustal alteration minerals<sup>25</sup>, and, most importantly, relaxation of the requirements for atmospheric partial pressures adequate to maintain continually warm surface conditions that support long-term liquid water and clay formation by near-surface weathering. Proposed hydrological models driven primarily by ground water rather than precipitation<sup>20,82</sup> are more consistent with the composition of most Noachian units, which do not show evidence for globally widespread open-system weathering. In the subsurface, and largely out of contact with the atmosphere, low-W/R formation of clays took place, occasionally at increased temperatures. Late-Noachian open-basin lakes<sup>16,71</sup>, valleys<sup>71,72,75</sup> and out-flow channels<sup>15</sup> demonstrate at least the episodic presence of liquid water on the Martian surface. Although fluvial degradation was widespread, it implies only local reworking<sup>75</sup>. For most of the Noachian period, surface water derived from snow or ice melt may have quickly entered the subsurface through basaltic rocks made highly permeable on the macroscopic scale by impact- and cooling-induced fractures. This particular model for an early Mars with a warm, wet subsurface and an icy, arid surface simultaneously resolves two paradoxes: the scarcity of salts coeval with clay deposits, in which salts serve as the sink for cations liberated during weathering<sup>32</sup>, and juvenile-clay mineralogy, that is, the persistence of smectite clays, even at great depths rather than their total diagenetic conversion to illite or chlorite phases<sup>83</sup>.

On ancient Mars, typical surface conditions may have been dominated by water-ice/water-vapour interactions, much as in the present day, but punctuated by episodic melting to supply liquid water. In the thick Noachian crustal units, there is indeed evidence for sustained diagenesis, the burial-induced transformation of smectite clay minerals, or hydrothermal activity throughout the Noachian, extending into the Hesperian (Fig. 5). Chlorite (which forms directly from hydrothermal fluids or from an Fe(II),Mg smectite precursor) and, more rarely, illite/muscovite (which forms directly from hydrothermal fluids or from an aluminium-rich precursor, given a sufficient supply of potassium) are both found in crustal clays<sup>23,41</sup>. Abundant salts would not be expected in subsurface, low-W/R alteration because ions are not removed by transport. The fluids are isolated from atmospherically derived volatiles (for example  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$ ), and saturation with respect to secondary aluminosilicates and oxides/hydroxides is favoured over the formation of abundant carbonates, sulphates and chlorides.

In late-Noachian/early-Hesperian boundary units, there is evidence for a period of open-system-style alteration by surface water that may have been intense regionally. Water carved valley networks, eroded and transported highland clays, and redeposited these in sedimentary basins (Fig. 5). The incised, better-integrated, late-Noachian valley networks require higher run-off rates and lower sediment transport, conditions that are reproducible by flow of water over duricrust or partly frozen ground<sup>72,75</sup>. Clays in stratigraphy may have formed by leaching of surface material to form aluminium clays; after evaporation of water, sulphates and chloride salts precipitated. The salts are found in basins within the southern highlands and—where cation composition can be inferred—seem to be mostly magnesium rich<sup>11,54,84</sup> as expected given relative cation mobilities<sup>29,30</sup>.



**Figure 5 | Evolution of aqueous environments during the first billion years of Mars history.** Locations of clay formation are indicated in green. Cold, arid and icy conditions characterized Mars during most of the Noachian, with clay formation mostly in a warmer, wetter subsurface environment. During the late Noachian/early Hesperian, volcanism was widespread and surface waters intermittently carved valleys, sustained lakes, transported sediments to basins and sustained near-surface weathering to form clays near the surface. Conditions from the late Hesperian to the present day have been cold and dry, resulting in the cessation of clay formation.

Seasonal changes coupled with orbital and obliquity parameters may have been sufficient to melt snow and ice and permit surface liquid waters episodically, especially if waters were briny<sup>21</sup> and atmospheric pressures were slightly higher than at present. Even the densest valley networks require only arid conditions; flows, once initiated, are stable against freezing for many hundreds of kilometres<sup>82</sup>. The key controls on aqueous environments early in Mars's history, permitting a geologically brief period with clement surface conditions at the late-Noachian/early-Hesperian boundary, seem to be heat supplied from volcanism, impacts, crustal cooling and, perhaps, effects of the first two on atmospheric composition (Fig. 4). Temporary release of volatiles by large impacts<sup>85</sup> or during volcanism<sup>86,87</sup> might have perturbed the climate to permit liquid surface water over a brief period. Indeed, episodic greenhouse conditions driven by volcanically degassed  $\text{H}_2\text{S}$  and  $\text{SO}_2$  (ref. 87) from Tharsis construction and Hesperian plains volcanism might explain the sulphur-rich salts within some closed-basin lakes dating from that period<sup>47,54</sup>.

As heat-supplying processes declined after Mars's first billion years, so too did the availability of liquid water. When clay formation on a global scale ceased by the Hesperian period, some Al and Fe,Mg smectite clay units were buried to depths of hundreds of metres or more, but little further diagenesis occurred, probably (as previously proposed<sup>83</sup>) because the availability of ground water decreased in most areas of the planet. By the late Hesperian period, there was neither sufficient surface water for open-system leaching to form clay and salt assemblages nor sufficient subsurface liquid water for hydrothermal circulation or diagenesis, even in the vicinity of the Tharsis volcanoes where evidence of the last sulphate and silica deposits are found<sup>11</sup>. Major Hesperian units including lavas of the Syrtis Major formation and northern plains are not altered, indicating either that clay formation had ceased by this time or that subsurface alteration occurred at depths  $>5$ – $10$  km, which are inaccessible to exposure by later cratering or tectonics.

### Continuing exploration

The Mars Exploration Rover Opportunity has, as of this writing, arrived at the walls and rim of Endeavour crater, where Fe,Mg clay minerals have been detected using orbital data<sup>88</sup>; and the Mars Science Laboratory rover Curiosity, scheduled for launch in late 2011, will investigate sedimentary clays within Gale crater<sup>47,89</sup>. The hypothesis that early environments with long-term liquid water were hosted in Mars's subsurface can be tested with data from future missions, most directly by *in situ* investigation of well-defined stratigraphies that include crustal clays. Predictions for our proposed environmental model include (1) direct detection of hydrothermal/metamorphic minerals or mixed-layer clays formed during diagenesis; (2) clay-bearing crustal units with elemental

abundances little changed from that of basalt, implying a low W/R ratio during alteration; (3) textures, similar to those observed in Mars meteorites<sup>90</sup>, with zonation of alteration phases (clays and salts) in veins and vesicles that indicate changing fluid compositions in intrarock flow; and (4) mildly hydrothermal mineral formation temperatures as determined from hydrogen, carbon and oxygen isotopic geothermometers. Additional, indirect evidence supporting an almost continually cold and dry Martian surface could come from measured isotopic ratios and calculation of loss rates of atmospheric gases made possible with future orbital data.

The stratigraphic record shows that most crustal clay units formed before the late Noachian and that all formed earlier than the Hesperian, but it is not known how old the oldest clay mineral occurrences are. Even though Mars's ancient record is better preserved than Earth's, it is still disrupted. Mars's earliest period is typically said to be the Noachian, but no surfaces datable by crater counting survive from before emplacement of the Hellas basin rim<sup>5</sup>. This does not mean that the record of the 'pre-Noachian' is completely lost. Rather, this record exists in the lowermost strata around large impact basins and in megabreccia blocks<sup>57</sup>. Materials comprising these deep units, some of which are crustal clays, have been heavily churned. Nevertheless, the scale of the sometimes layered strata preserved in these 10<sup>2</sup>–10<sup>3</sup>-m-scale blocks is comparable to the tens of metres of section explored during the Mars Exploration Rover traverses. Hints of Ca,Fe carbonates mixed with Fe,Mg clays in such blocks, excavated from depth<sup>45,91</sup>, could indicate earlier, near-surface alteration by waters in contact with an atmosphere. Alternatively, petrographic textures with veins of clays cross-cutting both breccia blocks and their matrix would indicate post-impact hydrothermal systems set up by early, large impacts. The pre-Noachian record of Mars is just beginning to be understood and will require careful examination of small-scale rock units and reconstruction of stratigraphic and temporal context.

Cumulatively, all data acquired so far support the idea that throughout the Noachian and the Hesperian, a persistent and volumetrically extensive aqueous environment existed in the Martian crust. Water activities and chemical gradients may have provided habitable conditions and energy for microbial life in these ancient Martian subsurface hydrothermal systems. Alternatively, intermittent surface waters provided by melting of ice and snow on an arid Martian surface may have sustained a habitable environment. The significant fraction of Earth's microbial biomass within its crust<sup>92</sup>, the thermophilic, chemoautotrophic nature of the last common ancestor of modern life<sup>93</sup> and the deep rooting within the phylogenetic tree of organisms from hydrothermal systems<sup>94</sup> point to the importance of subsurface water–rock reactions in the development of early terrestrial life. On Earth, rocks from the time of life's origins have been destroyed. On Mars, the oldest known aqueous environments in the crust, possibly the oldest habitats, remain preserved for exploration.

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