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Geochemical Consequences of Widespread Clay Mineral Formation in Mars' Ancient Crust

Bethany L. Ehlmann · Gilles Berger · Nicolas Mangold · Joseph R. Michalski · David C. Catling · Steven W. Ruff · Eric Chassefière · Paul B. Niles · Vincent Chevrier · Francois Poulet

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Abstract Clays form on Earth by near-surface weathering, precipitation in water bodies within basins, hydrothermal alteration (volcanic- or impact-induced), diagenesis, metamorphism, and magmatic precipitation. Diverse clay minerals have been detected from orbital

B.L. Ehlmann (✉)
Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA
e-mail: ehlmann@caltech.edu

B.L. Ehlmann
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA

G. Berger
IRAP, CNRS-Université Toulouse, 31400 Toulouse, France

N. Mangold
Laboratoire Planétologie et Géodynamique de Nantes, CNRS/Université de Nantes, Nantes, France

J.R. Michalski
Planetary Science Institute, Tucson, AZ 85719, USA

J.R. Michalski
Mineralogy, Natural History Museum, London, UK

D.C. Catling
Department of Earth and Space Sciences/Astrobiology Program, University of Washington, Seattle, WA 98195, USA

S.W. Ruff
School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, USA

E. Chassefière
Laboratoire IDES, UMR 8148, Université Paris-Sud, CNRS, 91405 Orsay, France

P.B. Niles
Astromaterials Research and Exploration Science, NASA Johnson Space Center, Houston, TX 77058, USA

investigation of terrains on Mars and are globally distributed, indicating geographically widespread aqueous alteration. Clay assemblages within deep stratigraphic units in the Martian crust include Fe/Mg smectites, chlorites and higher temperature hydrated silicates. Sedimentary clay mineral assemblages include Fe/Mg smectites, kaolinite, and sulfate, carbonate, and chloride salts. Stratigraphic sequences with multiple clay-bearing units have an upper unit with Al-clays and a lower unit with Fe/Mg-clays. The typical restriction of clay minerals to the oldest, Noachian terrains indicates a distinctive set of processes involving water-rock interaction that was prevalent early in Mars history and may have profoundly influenced the evolution of Martian geochemical systems. Current analyses of orbital data have led to the proposition of multiple clay-formation mechanisms, varying in space and time in their relative importance. These include near-surface weathering, formation in ice-dominated near-surface groundwaters, and formation by subsurface hydrothermal fluids. Near-surface, open system formation of clays would lead to fractionation of Mars' crustal reservoir into an altered crustal reservoir and a sedimentary reservoir, potentially involving changes in the composition of Mars' atmosphere. In contrast, formation of clays in the subsurface by either aqueous alteration or magmatic cooling would result in comparatively little geochemical fractionation or interaction of Mars' atmospheric, crustal, and magmatic reservoirs, with the exception of long-term sequestration of water. Formation of clays within ice would have geochemical consequences intermediate between these endmembers. We outline the future analyses of orbital data, *in situ* measurements acquired within clay-bearing terrains, and analyses of Mars samples that are needed to more fully elucidate the mechanisms of martian clay formation and to determine the consequences for the geochemical evolution of the planet.

Keywords Mars · Clay minerals · Phyllosilicates · Weathering · Alteration · Geochemistry · Mineralogy · Noachian

1 Introduction

The first telescopic observations of Mars, indicated widespread ferric oxides and demonstrated that the surface has been altered from its primary mineralogic composition (Singer et al. 1979; Bell et al. 1990), while the Viking landers provided some circumstantial evidence for salts and a component of clay minerals in the soil (Clark 1978; Banin et al. 1992). More recently, the detection of crystalline hydrous minerals demonstrates that interaction with liquid water has left a mineralogic record from the first billion years of Mars history in the form of widespread clay-bearing terrains and large-scale sulfate deposits (Poulet et al. 2005; Gendrin et al. 2005; Bibring et al. 2006). In particular, clay minerals have been identified in units dating from Mars' Noachian period, indicating a global process or set of processes altering the mostly basaltic bedrock at this time (Poulet et al. 2005; Bibring et al. 2006; Mustard et al. 2008).

As detailed below, most information on clay mineral formation conditions on Mars derives from constraints from orbital datasets with additional constraints derived from study

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V. Chevrier
W.M. Keck Laboratory for Space and Planetary Simulation, Arkansas Center for Space and Planetary Science, University of Arkansas, Fayetteville, AR 72701, USA

F. Poulet
Institut d'Astrophysique Spatiale, Université Paris-Sud, Orsay 91405, France

of the martian meteorites and from landing sites visited to date. Our objective herein is to understand the consequences of various geochemical scenarios for clay formation on Mars. Processes leading to clay formation on Earth are important mechanisms in terrestrial geochemical cycles. Ocean and river water chemistry is partly controlled by continental silicate weathering to form clays and clay-forming reactions of seawater with the basaltic seafloor (Spencer and Hardie 1990). Clay formation by weathering also serves as an important feedback on atmospheric chemistry, climate, and sequestration of volatiles in the crust (Kump et al. 2000). To understand the broader geochemical consequences of clay formation on Mars, we focus on two sets of questions. First, what style of alteration/formation process(es) drove clay formation? Second, to what degree did/could clay formation result in geochemical fractionation? What were the implications of clay formation for subsequent evolution of martian geochemical reservoirs? Were new reservoirs created, e.g. sediments/salts? Was the crustal or atmospheric reservoir altered, e.g. by sequestration of water or other volatile species?

We first review the various possible mechanisms of clay formation with reference to the literature from terrestrial studies. We then review observations to date from remote sensing of clay-bearing terrains on Mars, including their mineralogy and stratigraphy, which provide constraints on alteration scenarios and their timing. Next, we examine the likelihood and geochemical consequences of potential scenarios for clay formation on Mars, in light of the data from Mars, lessons from terrestrial analogues, geochemical modeling, and experimental data. Our primary goal is to understand the implications of different scenarios for the evolution and/or formation of martian geochemical reservoirs. Finally, we discuss what further data are needed to distinguish between models for clay formation, including measurements obtainable from future landed, orbital, and sample return missions.

2 Clay Formation on Earth

Clay minerals or phyllosilicates are comprised of sheets of tetrahedrally-coordinated silica and octahedrally-coordinated metal cations in regular, repeating layers (e.g. Meunier 2005). The term "clay" can refer either to the smallest particle size fraction in sediments (<4 μm) or phyllosilicate mineralogy. Herein, we use the term "clay" in the latter sense. Clays are hydrated or hydroxylated and sometimes have swelling properties associated with exposure to water. We discuss clay minerals and associated phases (other hydrated silicates, salts, and mineraloids) formed during aqueous alteration.

On Earth, clay minerals form by near-surface weathering, in hydrothermal systems located mostly at sea floor spreading centers and less commonly in continental settings, by diagenesis and metamorphism, or more rarely by direct precipitation in lake basins or from magmatic fluids within cooling lavas. Clay minerals are then eroded, transported, buried, and metamorphosed in processes driven by climate and tectonics (for review see Merriman 2005; Meunier 2005). There are seven major mechanisms by which clay minerals are formed or transformed, described below. Table 1 details expected deposit characteristics for each mechanism with particular attention to traits that may be discernible from orbit, based on examples from terrestrial sites with basaltic precursor materials. The clay formation mechanism—i.e., the composition and quantity of reacting fluids, the chemistry of the precursor rock, temperature of the reaction, distance of transport of fluids, and the degree to which atmospheric volatiles participate in the reaction—determines the composition and petrology of the clays. The formation mechanism and extent of alteration together dictate the geochemical consequences of clay formation, depicted schematically for global geochemical reservoirs for each of the mechanisms detailed below (Fig. 1).

Table 1 Mineralogy and facies of hydrated silicates produced by seven formation mechanisms from a basaltic precursor (references in text)

Setting	Clay mineralogy	Facies and abundance (% vol.)	Setting	Accompanying minerals
Near-surface pedogenic	Fe/Al smectites, kaolinite	Bulk soil component (up to 95 %)	Horizons of leaching and deposition, with alteration lessening with depth	Fe/Al oxides, carbonates, silica, allophone
Near-surface basin	Fe/Mg/Al smectites, kaolinite, illite, chlorite	Layered deposits with sedimentary textures; clay minerals (up to 95 %) mostly detrital, *in situ* formation at very high Si, Al activities	Deposits within a river, lake, or ocean, later exposed by erosion	Other minerals eroded from rocks in basin; evaporites, e.g. chlorides, carbonates, hematite, silica, sulfates (if acidic), potassium feldspar and zeolites (if alkaline)
Hydrothermal (volcanic)	Fe/Mg/Al smectites, kaolinite	Bulk component (variable)	Zoned alteration surrounding fumaroles, vents, and cones	Sulfates (alunite, jarosite), ferric oxides, amorphous silica, allophane, anatase
Hydrothermal (impact)	Saponite, nontronite, celadonite, kaolinite	Fracture fill within breccia, alteration rinds on mineral grains (5–10 % total area)	Beneath the crater floor and rim in fractures and pore spaces of breccia; not exposed unless by erosion	Amorphous silica and altered impact glasses, carbonate, sulfates, sulfides, potassium feldspar quartz, zeolites, native metals
Diagenesis	Illite (from K, Al-rich precursors); Chlorite (from Mg-rich precursors), mixed-layer clays	Bulk rock; veins and pore space (variable)	Bulk rock/sediment altered; sometimes preferential alteration in pore space and veins	silica, original clay minerals
Metamorphism	Fe/Mg smectites, chlorite, zeolites, prehnite, pumpellyite, serpentine, epidote, actinolite	Bulk rock (variable)	100s m to km beneath the surface; not exposed unless by deep erosion or impact excavation	Amorphous silica, zeolite, sulfite, iron oxides, garnet, original rock forming minerals
Magmatic	Fe/Mg smectite, celadonite	Within pores, veins of bulk rock (<15 %)	Formed during final degassing of lavas with substantial volatile content	Silica, primary minerals

2.1 Near-Surface Pedogenesis

Soil formation on Earth involves the soil microbes processing detrital organic matter in addition to mechanical breakdown and abiotic leaching processes. On Mars, "pedogenesis" presumably involves only the latter two processes. The amount and type of alteration observed in terrestrial soil formation varies widely depending on time, starting materials, and degree of leaching. On Earth, pedogenic smectites form in relatively dry conditions from waters with dissolved constituents concentrated by evaporation; kaolinite forms in dilute waters; and gibbsite is an end product of weathering under warm

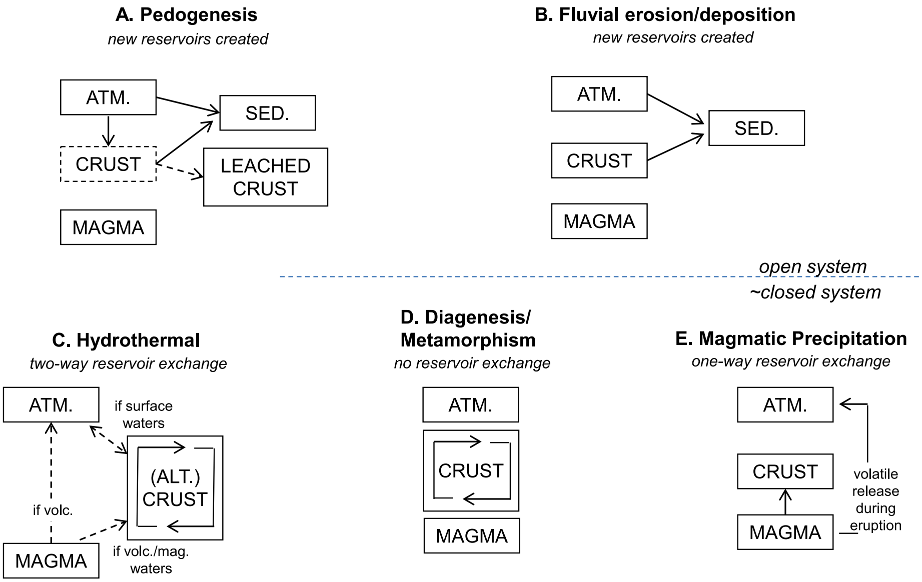


Fig. 1 Schematic of geochemical reservoirs during terrestrial clay formation by scenario. (**a**) Near-surface leaching during pedogenesis fractionates the crustal reservoir, leading to formation of a new sedimentary reservoir. The atmospheric and crustal reservoirs are modified. (**b**) Clay deposition in basins transports materials from the crustal reservoir to basins. A new sedimentary reservoir is formed with input from the crustal and atmospheric reservoirs. The atmospheric reservoir may be modified due to the quantity of volatiles sequestered in salts and hydrated minerals, but in a transport-only scenario, the crustal reservoir is not chemically modified. (**c**) Hydrothermal alteration may occur under open- or closed-system conditions, potentially altering the crust by input from atmospheric or magmatic reservoirs. (**d**) Diagenesis and metamorphism occur in closed system by recirculation of fluids in the crust. (**e**) Clay formation from magmatic precipitation adds to the crustal reservoir, some volatiles are sequestered in clay minerals and others escape to the atmosphere

conditions of very high water/rock ratio. Terrestrial examples of clay-bearing deposits formed by pedogenesis include kaolinite and Al, Fe oxide-rich laterites in tropical soils; smectite-zeolite altered volcanic ashes in the Cascades and New Zealand, and palagonitized recent lava flows in Hawaii (e.g., Singer 1966; Siefferman and Millot 1969; Chamley 1989; Ambers 2001; Ahn et al. 1988; Morris et al. 2000; Schiffman et al. 2000; Schiffman et al. 2002).

For a given protolith, the amount of rainfall and chemistry of the water (pH, Eh, dissolved ions) dictate composition of alteration products. For example, tephra deposits in the altered Keanakoko'i Ash Member at Kilauea volcano in Hawaii (Schiffman et al. 2002; Schiffman et al. 2000) have developed a rind of smectites and other clay minerals. Under acid conditions of pH < 6 owing to rainout of sulfur aerosols, opaline crusts form on outcrop faces of desilicated tephra, whereas under neutral to alkaline conditions of pH 6.5–7.8, the weathering product is dominantly smectites in areas with mean rainfall <50 cm/year and kaolinite, allophane and/or imogolite in areas with rainfall >250 cm year (Schiffman et al. 2000).

Vertical stratification of heavily leached horizons, depositional horizons, and minimally altered bedrock is expected and diagnostic of near-surface pedogenesis. Such strata in escarpments could be detectable by orbiting instruments. Pedogenesis occurs in an open system environment, usually at high water/rock ratio. The composition of the bedrock is changed as alkali and alkaline cations are dissolved and transported in fluids. Even ultramafic bedrock with a very low proportion of Al can transform into aluminum clay (kaolinite)-rich soils by strong alteration, as observed in Murrin, Australia (Gaudin et al. 2011). Salts including carbonates, chlorides, and sulfates precipitate by reaction of atmospheric volatiles dissolved in the water with dissolved cations.

2.2 Deposition and Formation in Basins

On Earth, alteration products frequently undergo erosion and are deposited in large sedimentary basins in a setting distinct from a non-transported, pedogenic one. Shales, which are a sedimentary end-product of continental weathering and gradation, typically contain 60–70 % clays with lesser amounts of feldspar and quartz. Most clays in these systems are detrital and undergo mineralogical transformation with depth and time (diagenesis), mainly leading the conversion of the detrital clays into illite or less frequently chlorite (see Sect. 2.5). The detrital fraction may also be accompanied by salt precipitation in an evaporitic basin. The dominant salt depends on the fluid chemistry and can be carbonate, sulfate, or chloride. If Al and Si activities are sufficiently high, clays can precipitate. Saline-alkaline waters can lead to zeolite precipitation and formation of chlorite and Mg-smectite from illites (Remy and Ferrell 1989; Hay and Tyser 2001; Bristow and Milliken 2011). Acid lake systems produce sulfates, halite, and hematite but are not generally conducive to formation and preservation of clay minerals. However, clays such as kaolinite, smectite and palygorskite-sepiolite are observed in some acid lakes (Benison et al. 2007; Baldridge et al. 2009; Story et al. 2010). Interbedding of clays and sulfates in some lakes, such as Lake Gilmore in Western Australia might be explained by authigenic sulfates and detrital clay minerals. If fluvial systems were operating on a large scale on early Mars, layered sedimentary strata with salts might be expected to be associated with some clay deposits in large basins.

Another source of sedimentary clay minerals in the deep ocean or inland water bodies originates from altered airborne volcanic ash. Large swaths of the Pacific Ocean floor are covered in aluminous smectites or mixed-layer smectites/illites that derive from volcanic ash (Lisitzin and Rodlfa 1972). Such clays can be distinguished because the devitrification process (i.e., the change from the glassy state) takes time and so the clay minerals are often mixed with ashy shards of volcanic glass. Montmorillonite-bearing altered tuffs forming Wyoming bentonite also form from deposition of ash into standing bodies of water. On Earth, some of the most clay-rich rocks are bentonites, which are derived from pyroclastic materials that are nearly completely altered (90 % clays or more), typically due to deposition into standing water (Chamley 1989).

2.3 Hydrothermal (Volcanic)

Clays that form by hydrothermal, acid-sulfate alteration in volcanic zones are accompanied by ferric oxides and sulfates (Morris et al. 2000; Bishop et al. 2007). Mineral distribution in terrestrial hydrothermal systems commonly exhibits quasi-concentric zoning because temperature and pH vary at spatial scales of tens of square meters around volcanic vents (Swayze et al. 1992, 2002; Guinness et al. 2007). In the basaltic tephras of Mauna Kea, Hawaii, well-crystalline hematite near the center of cinder cones grades to palagonitic material away from the cone. Montmorillonite is the most abundant clay mineral and tends to surround saponite and isolated occurrences of kaolinite and jarosite near cones (Swayze et al. 2002; Guinness et al. 2007). If volcanic hydrothermal systems were active on Mars, zoning and clays accompanied by sulfates and iron oxides would be diagnostic.

Sulfur-poor hydrothermal systems also occur in which intruded magma supplies subsurface heat, but sulfurous gases are not in contact with the water system. In these systems, Fe/Mg smectites and chlorite are the dominant alteration minerals in the bulk rock and celadonite, silica, and zeolites fill rock pore spaces; a smectite-zeolite zone often overlies a chlorite zone (e.g. Wiesenberger and Selbekk 2008; Franzson et al. 2008). Fluids interacting with mafic to ultramafic rock at depth can also generate veins of Fe/Mg clays, as in Uley Mine, South Australia, where nontronite, an iron magnesium smectite clay, infills fractures within amphibolite and gneiss (Keeling et al. 2000). Another type of hydrothermal alteration on Earth occurs under the ocean within the basaltic seafloor. Under these conditions, typical alteration assemblages include serpentines at high temperatures and ultramafic compositions, smectites and chlorite at intermediate temperatures, and nontronite at low temperatures (Alt 1999).

The content of clay in hydrothermal systems is highly variable, ranging from negligible to nearly complete alteration of primary phases to clay minerals. Many intensely hydrothermally altered deposits exhibit striking textural disruption and are penetrated by clays, but the clay minerals may constitute only a small fraction (<5 %) of the rock. Even basalts that have been 100 % converted to secondary minerals by crustal brines may contain only $\sim$25 % clays (Michalski et al. 2007).

2.4 Hydrothermal (Impact)

As in volcanic systems, the occurrence and mineralogy of impact-induced hydrothermal systems depend on water availability, the composition of the target rocks, and the temperature and composition of circulating fluids. Shock transforms some crystalline minerals to other phases (e.g. plagioclase to maskelynite), and heat released by impact generates glasses and, for sufficiently large craters, a coherent impact melt sheet within the crater. In terrestrial craters, a diverse suite of alteration minerals is observed, including clay minerals, carbonates, sulfates, sulfides, zeolites, quartz (amorphous and crystalline), potassium feldspar, iron oxides, and native metals (e.g. Allen et al. 1982b; Ames et al. 2004; Hagerty and Newsom 2003; Larsen et al. 2009). However, a survey of alteration minerals associated with terrestrial impact craters suggests that clays are not widely formed directly by the impact process, and where they occur, they are not abundant phases. For example, studies of altered products of the Manicouagan structure found abundances <15 % smectite in pyroxenes and glasses altered to hematite (Morris et al. 1995). The most common occurrences of alteration minerals formed by impact processes are those that occur in hydrothermally-fed crater lake deposits, where water has flooded the impact structure (Naumov 2005). Hydrothermal activity is restricted to the subsurface beneath craters in the lower parts of the rim, floor, and crater central peak, and if sufficient water is supplied, a hydrothermally circulating crater lake can form (Rathbun and Squyres 2002; Abramov and Kring 2005). Thus, typically, subsequent exhumation of buried alteration minerals would typically be required for detection from Mars orbit of non-lacustrine, impact-formed clays. Heat and shock from impact can also destroy pre-existing clays, from reversible loss of water at low temperatures, to irreversible changes in the crystal structure if temperatures experienced are greater than 600 °C (Milliken and Mustard 2005; Gavin and Chevrier 2010; Che et al. 2011).

2.5 Diagenesis

Water/rock interactions at depth and elevated temperature can generate and modify clay mineral deposits. The early diagenesis of sediments is promoted by bacterial activity leading to sulfate reduction, methane production, and carbonate precipitation. In the zone of intermediate burial (2 to 4 km depth), chemical compaction by pressure-solution of quartz or carbonate grains decreases porosity. The production of CO_2 and aliphatic acids (acids of non-aromatic hydrocarbons) by late organic diagenesis promotes the dissolution of feldspars and the transformation of detrital clays into illite or chlorite (Surdam et al. 1989). Even in the absence of organic material, buried smectites may transform to other phases such as illite and chlorite, during thermal- and pressure-related maturation (Ahn et al. 1988; Ambers 2001; Srodon 1999; Meunier 2005). The degree of transformation depends on time and temperature when sufficient water is available to promote transformations (e.g. Whitney 1990). Provided that sufficient K^+ is available in fluids, dioctahedral smectites such as montmorillonite convert to mixed layer illite/smectite clays, then to end-member illite with more advanced diagenesis at higher temperatures (e.g. Hower et al. 1976; Yau et al. 1988; Lanson et al. 2002; Fleet and Howie 2006). Provided that sufficient Mg^{2+} is available, trioctahedral smectites such as saponite transform to corrensite (a 1:1 mixed-layer chlorite/smectite) then to chlorite with increasing grade (Merriman and Peacor 1999 and refs. therein). This is a common process on Earth as tectonic activity creates deep sedimentary basins. Clays can also form diagenetically as cements in sandstone (Schneiderhöhn 1965). Clays occur along with other cements (typically silica or calcite) in sandstones, and in this context, constitute 15–30 % of the rock.

2.6 Subsurface Metamorphism

There are poorly-defined boundaries between low-grade metamorphism, hydrothermal activity, and diagenesis with different authors adopting different conventions through time (see Arkai et al. 2003 for a review). In metamorphism, as in diagenesis, small amounts of water interacting with rock lead to the transformation of minerals to phases stable at higher temperatures and pressures. Amphibole minerals (e.g. actinolite), kyanite, and sillimanite occur in high pressure and temperature metamorphism, caused by tectonic activity, e.g. subduction of oceanic plates and thrusting to create mountain ridges (Spear 1995). This type of tectonism has not been observed on Mars. At lower temperatures and pressures ($T <\sim 400\,^{\circ}\mathrm{C}$ and pressures typically <4 kbar but extending to 8 kbar), sub-greenschist metamorphism occurs and is defined by the thermodynamic stability of prehnite and pumpellyite (Schiffman and Day 1999). The lowest metamorphic temperature and pressure conditions are represented by the zeolite facies, where laumontite and analcime form at lower temperatures in the presence of CO_2-poor or non-CO_2 bearing alkaline fluids (e.g. Hay 1986). These originally subsurface deposits would have to be exposed by erosion or uplift to be detectable from orbit.

2.7 Magmatic

When mafic-ultramafic lavas erupt, they may have volatile contents of a few percent. As these lavas cool, incompatible H_2O becomes concentrated and Fe–Mg clays precipitate directly from the residual liquid that is concentrated in voids remaining in the crystallizing, solidifying lava (Meunier et al. 2010). Nontronite-celadonite and chlorite-saponite have been observed covering solid surfaces, glasses, and grains of pyroxene and apatite in the rock mesostasis. Tens to hundreds of micrometer-wide clay-rich patches exist in lavas at abundances of $\sim$10 % (Meunier et al. 2010).

3 Clay Distribution and Diversity on Mars

Consideration of the seven settings above illustrates that component mineral assemblage, alteration mineral abundance, and stratigraphic setting are constraints that are at least partially ascertainable from orbit and that allow distinguishing among clay mineral formation mechanisms (Table 1) each of which has different consequences for geochemical fractionator (Fig. 1). Below, we consider the nature of martian clay-bearing deposits, reviewing constraints from orbital, landed, and meteorite datasets.

3.1 Clay Detection and Global Distribution

Clay minerals are detectable and mappable in remote sensing data because of distinctive absorptions that occur at infrared wavelengths of light due to vibrations of molecules within the mineral structure. These include fundamental H_2O stretching and bending modes (near 3.0 µm and 6.0 µm) and combinations and overtones of these (near 1.4 µm and 1.9 µm). Metal-OH stretching (near 2.8 µm), bending (16–25 µm), overtone (near 1.4 µm) and combination absorptions (2.2–2.5 µm) are particularly useful in identifying the precise clay mineral because the position and shape of the absorption features depend on the composition of the cations and the configuration of the cation site (e.g. Michalski et al. 2005; Bishop et al. 2008a). For example, in smectite clays, the near-infrared overtones and combination tones occur at 1.41 µm and 2.21 µm for Al-rich montmorillonites, at 1.43 µm and 2.28 µm for Fe-rich nontronites, and at 1.38 µm and 2.32 µm for Mg-rich saponites (Bishop et al. 2008a; Ehlmann et al. 2009).

A global survey for clay minerals at 1 pixel per degree was first undertaken using thermal infrared (TIR) spectra from the Thermal Emission Spectrometer (TES) onboard Mars Global Surveyor, but no definitive identification was made at this scale (Bandfield 2002). Clay minerals were first detected unambiguously in dark deposits and outcrops within Noachian terrains in several locations throughout the southern highlands using visible/near-infrared (VNIR) spectral data from the OMEGA (Observatoire pour la Mineralogie, l'Eau, les Glaces et l'Activité) instrument onboard Mars Express (Poulet et al. 2005, 2007). Subsequent global mapping with OMEGA and the VNIR imaging spectrometer CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) on the Mars Reconnaissance Orbiter (Murchie et al. 2007, 2009) has demonstrated that areas around the Nili Fossae and Mawrth Vallis host the largest ($>$100,000 km^2) regionally extensive clay-bearing outcrops (Loizeau et al. 2007; Mangold et al. 2007; Mustard et al., 2007; Bishop et al. 2008b; Ehlmann et al. 2009; McKeown et al. 2009; Noe Dobrea et al. 2010), while thousands of isolated occurrences of clay minerals in outcrops of smaller size are found throughout the southern highlands (Mustard et al. 2008; Loizeau et al. 2012) as well as associated with large craters of the northern lowlands (Carter et al. 2010) (Fig. 2). The majority of clays detected are associated with impact craters, in central peaks, walls or ejecta. Some large tectonic scarps and heavily eroded terrains expose clay minerals exhumed from depths of hundreds to thousands of meters (Murchie et al. 2009; Mustard et al. 2009; Buczkowski et al. 2010; Ehlmann et al. 2011a). Some sedimentary deposits also host clays (Ehlmann et al. 2008b; Murchie et al. 2009; Milliken and Bish 2010; Dehouck et al. 2010; Ansan et al. 2011; Milliken et al. 2010; Wray et al. 2011). While clays are globally distributed among Noachian terrains (Fig. 2), the major Hesperian volcanic plains within Syrtis Major and the northern plains show no unambiguous spectral evidence for the presence of clay minerals, nor do younger terrains. Instead, sulfates are found within some Hesperian- and Amazonian-aged units around Valles Marineris (Gendrin et al. 2005; Milliken et al. 2008;

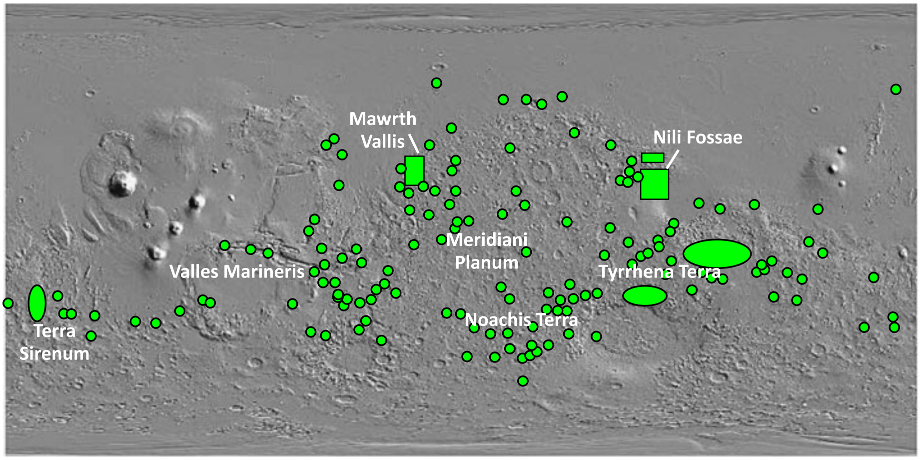


Fig. 2 Schematic distribution of clay mineral detections on Mars

Murchie et al. 2009; Mangold et al. 2010). Sediments in the northern lowlands and Hesperian and Amazonian lava plains show evidence for formation of coatings or rinds of amorphous weathering products (Mustard et al. 2005; Michalski et al. 2006; Skok et al. 2010; Salvatore et al. 2010; Horgan and Bell 2012).

3.2 Estimates of Clay Abundance for Multiple Terrains

Constraining the abundances of clay minerals in clay-bearing rocks on Mars is important for distinguishing between rocks that may be only slightly altered by traces of water versus sedimentary rocks analogous to shales or bentonites (see Sect. 2.2) that may be thoroughly altered and physically processed. Quantitative information is critical for evaluating how geochemical reservoirs are partitioned between clay-bearing rocks and the protoliths from which they were derived. As discussed in Sect. 2, clay abundance is not necessarily an indication of degree of alteration. But, understanding the abundances can help to bracket the types of rocks that contain clays on Mars and their formation mechanisms. The determination of abundances from orbital data is strongly influenced by textural context of the clays within the rocks (as a component of the clastic budget, as cement, as grain coatings, veins and veinlets, etc). Consequently, an alternative indicator of alteration from infrared data can be the presence or absence of primary phases.

Although clay minerals have been identified unambiguously across the planet, their abundance is less clear. For example, at Mawrth Vallis, modeling of VNIR spectra using a nonlinear radiative transfer approach gives estimates of 20–65 % clay for the bulk composition of the iron-magnesium clay bearing unit, the highest for any of the exposures examined to date on Mars (Poulet et al. 2008a). However, clay mineral abundance at Mawrth Vallis does not rise above the approximate detection limit of 15 % by volume based on thermal infrared spectra (TIR), modeled linearly to provide abundance estimates of component phases (Michalski and Fergason 2009). Elsewhere in the southern highlands, including Nili Fossae, Tyrrhena Terra, and Terra Sirenum, clay mineral abundance estimates from VNIR spectra are lower than at Mawrth, between 5–35 % (Poulet et al. 2008a). TIR data are consistent with this, suggesting clay mineral fractions by area of ∼30 % or less (e.g., Michalski and Fergason 2009; McDowell and Hamilton 2009; Michalski et al., 2010). Various explanations have been advanced to explain the occasional disparities between TIR and

VNIR results (e.g., Michalski and Fergason 2009; McDowell and Hamilton 2009), but at present the issue remains unresolved. Even so, TIR observations point to clear differences between alteration seen in the Mawrth Vallis region, where spectra are dominated by poorly crystalline alteration phases with little evidence for primary phases, and alteration in the Nili Fossae region, where spectra contain evidence for both clays and primary phases together. Hydrogen abundance in the upper half-meter of the martian surface, acquired by the gamma ray and neutron spectrometers onboard Mars Odyssey at hundreds of kilometer spatial scale, generally shows no correlation with IR-detected exposures of hydrated minerals in mid- and equatorial-latitudes (Feldman et al. 2004; Jouglet et al. 2007; Milliken et al. 2007; Boynton et al. 2008).

3.3 Clay Mineral Diversity and Mineral Assemblages

Over the last decade, the number of alteration minerals identified on Mars and mappable from orbit has expanded significantly, now including hydrated silicates, salts, and oxides/hydroxides (Table 2). In particular, hydrated silicate minerals, i.e. clay minerals and associated phases, have been found to exhibit significant diversity, varying regionally and by geologic setting (Mustard et al. 2008). This diversity in clay minerals and accompanying phases may indicate a diversity of processes and thermodynamic, kinetic, and geochemical parameters responsible for their formation.

Iron-magnesium smectites are the most common clay minerals on Mars, found in over 75 % of locations in which any hydrated silicate is detected (Table 3; Poulet et al. 2005; Mustard et al. 2008; Ehlmann et al. 2011a). Mixed-layer clays, such as chlorite/smectite, are similar spectrally and may also be part of these deposits (Milliken and Bish 2010). Chlorite is the second most commonly detected clay mineral phase. Rarer phases include prehnite, serpentine, illite or muscovite, hydrated silica, and analcime, comprising mineral assemblages that indicate alteration at elevated temperatures. As discussed below, these and chlorite are almost exclusively associated with craters (Ehlmann et al. 2011b).

Although less common than the iron-magnesium clay minerals, aluminum clays have also been detected on Mars. As discussed further below, a few regions exhibit a distinctive stratigraphy of Al clays above Fe/Mg clays. The Al-clays in these settings include a kaolin family mineral, as well as less commonly an Al smectite such as montmorillonite or beidellite (Poulet et al. 2005; Loizeau et al. 2007, 2010; Bishop et al. 2008b; Wray et al. 2008; Ehlmann et al. 2009; McKeown et al. 2009; Bishop et al. 2011). Al-clays also occasionally occur associated with impact craters and within sedimentary basins (Table 2; Wray et al. 2009a).

To the limit of spectral detection capabilities, salts such as carbonates, chlorides, and sulfates are not usually found in the same geologic units as clay minerals (Milliken et al., 2009), an exception being clays and carbonates found within the Leighton crater central peak in southwestern Syrtis Major (Michalski and Niles 2010). However, chlorides, sulfates, and carbonates are found in association with clays in sedimentary deposits (see Sect. 3.5).

3.4 Clays and Craters

The ancient Noachian crust of Mars has been heavily churned by meteorite impacts, and it is mostly within these terrains that clay minerals are found. Most exposures of clay minerals on Mars are in association with craters of diameters <200 km. Craters serve as basins for collecting sediments; we discuss these in Sect. 3.5. Craters can also serve as probes of the subsurface by excavating buried materials from depth and exposing them

Table 2 Alteration minerals discovered from Mars orbit and on the ground

Group/mineral/phase	References[b]
Fe/Mg smectites (e.g., nontronite, saponite)	Poulet et al. 2005; Mustard et al. 2008; Bishop et al. 2008b; Ehlmann et al. 2009; McKeown et al. 2009
Al-smectite (e.g. montmorillonite)	Poulet et al. 2005; Mustard et al. 2008
Kaolin group minerals (e.g. kaolinite, halloysite)	Gondet et al. 2006; Mustard et al. 2008; Bishop et al. 2008b; Ehlmann et al. 2009
Chlorite	Poulet et al. 2005; Mustard et al. 2008; Ehlmann et al. 2009
Serpentine	Ehlmann et al. 2010
High charge Al, K phyllosilicate (e.g. muscovite or illite)	Mustard et al. 2008; Ehlmann et al. 2009
Prehnite	Clark et al. 2008; Ehlmann et al. 2009
Analcime	Ehlmann et al. 2009
Opaline silica	Squyres et al. 2008; Milliken et al. 2008; Ehlmann et al. 2009
Magnesium (iron) carbonate	Bandfield et al. 2003; Ehlmann et al. 2008a; Morris et al. 2010
Calcium carbonate	Boynton et al. 2009; Michalski and Niles 2010[a]
Fe/Mg mono- and poly-hydrated sulfates	Gendrin et al. 2005; Bishop et al. 2009; Murchie et al. 2009
Gypsum	Langevin et al. 2005
Alunite	Swayze et al. 2008
Jarosite	Klingelhofer et al. 2004; Milliken et al. 2008; Farrand et al. 2009
Hydroxylated ferric sulfate (not a named mineral)	Bishop et al. 2009; Lichtenberg et al. 2010
chlorides	Osterloo et al. 2008
perchlorates	Hecht et al. 2009
Goethite	Morris et al. 2006; Farrand et al. 2009
Coarse-grained hematite	Christensen et al. 2000; Klingelhofer et al. 2004; Bibring et al. 2007
Nanocrystalline hematite	Morris et al. 1989; Bell et al. 1990

[a] Orbital near-infrared data are also consistent with an Fe-rich carbonate

[b] Numerous papers been published on these and the references are to the first papers reporting and justifying the detections with particular instruments

at the surface in ejecta, crater rims, and central uplifts (Fig. 3). The cratering process can also serve as an agent for modifying surface composition. Shock and heat transform the properties of impacted materials, generating new minerals or shocked or melted modified phases. Laboratory studies to date have shown that instantaneous shock does not form clays (Allen et al. 1982a), but shocked, glassy materials may be more susceptible to later weathering to form clays. Numerical modeling (Rathbun and Squyres 2002; Abramov and Kring 2005) and studies of terrestrial craters (Newsom 1980) demonstrate that heat from impact can initiate hydrothermal systems at depth, given sufficient supply of water (see Sect. 2.4).

Table 3 For 365 sites with hydrated silicates, percentage of sites with each alteration mineral by geologic setting. Alteration minerals were found in 259 crustal sites (craters, ancient degraded terrain), 45 sedimentary sites (transported, basin-filling materials), and 61 in stratigraphic sections (preserved, coherent stratigraphies with multiple clay-bearing units). Sites tallied are the same as those in Ehlmann et al. (2011a)

	Alteration phase	Crustal (% sites)	Sedimentary (% sites)	In stratigraphy (% sites)
Fe/Mg clays	Fe/Mg smectite	77.6	84.4	95.1
	Chlorite/prehnite	39.0	0	1.6
	Serpentine	3.1	0	6.6
Al clays	Montmorillonite	3.9	4.4	26.2
	Kaolinite	7.7	6.7	36.1
	Al-clays (unspecified)	0	20.0	18.0
Other hydrated silicate	Illite	2.3	0	0
	Silica	5.4	4.4	29.5
	Analcime	1.9	0	0
	Other hydrated (unspecified)	5.4	8.9	1.6
Salts	Carbonate	1.2	4.4	24.6
	Sulfate	0	35.6	3.3
	Chloride	0	20.0	0

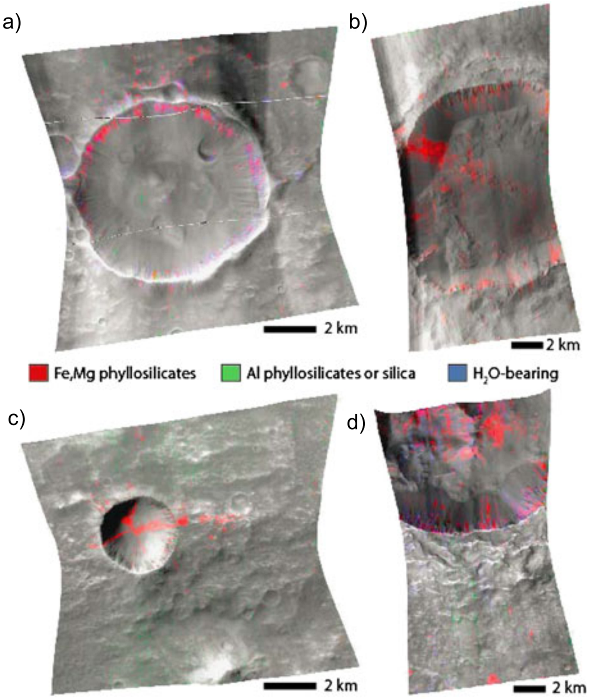


Fig. 3 Clays in craters within Tyrrhena Terra. Crater walls, ejecta, and central peaks have signatures of clay minerals. Parameters (Pelkey et al. 2007) for mapping Fe, Mg clays (D2300), Al clays and silica (BD2200), and hydrated minerals (BD1900) are mapped on infrared albedo for CRISM images (**a**) FRT00013FA4, (**b**) HRL0000D721, (**c**) FRT0000A33C, and (**d**) HRL00013BA7

Thus, clay minerals associated with impact craters could have been formed by either excavation of buried, pre-existing clays within the crust or via local impact-induced hydrothermal circulation. This question has persisted since the first detections of hydrated minerals in crater ejecta (Mangold et al. 2007). In general, observations are consistent with excavation being the primary process responsible for the association of clays with craters (Mangold et al. 2007; Mustard et al. 2008; Fairen et al. 2010; Carter et al. 2010; Ehlmann et al. 2011b). The same kinds of alteration minerals are associated with units in the ejecta and the upper walls, where numerical modeling predicts hydrothermal circulation would be absent or limited, as with the central peak regions, where numerical modeling predicts hydrothermal fluid flow would be most vigorous (Fig. 3; Poulet et al. 2005; Mustard et al. 2008; Ehlmann et al. 2009; Carter et al. 2010; Michalski and Niles 2010, Loizeau et al. 2012). If instead impact-induced hydrothermal activity had generated the clays associated with craters, minerals zoned by temperature and fluid availability would exist mainly within the crater interior (Schwenzer and Kring 2009).

Fe, Mg smectite and/or chlorite are nearly always present in crustal clay units associated with craters (Poulet et al. 2005; Mustard et al. 2008). Distinctive associations of minerals vary from crater to crater, and can include prehnite, hydrated silica, analcime, serpentine, and illite or muscovite, which accompany the smectites and chlorite and indicate excavation of minerals formed at higher temperatures, up to 400 °C (Ehlmann et al. 2009, 2011b). With the exception of silica, these distinctive phases have only been detected in association with craters (Ehlmann et al. 2011a). The materials, associated with craters <200 km in diameter, would originate from maximum depths of ~ 5–10 km (Melosh 1989), although multiple impacts, including large basin-forming impacts, may have exposed still deeper materials by repeated churning.

Apart from excavation, craters inside Hesperian plains locally display alteration that could be related to local hydrothermal activity. For example, Toro crater, an impact structure in northern Syrtis Major, displays hydrated minerals including clays and silica in association with possible vents related to hydrothermal circulation (Marzo et al. 2010), although simple impact excavation has also been proposed to explain the distribution of clay minerals in this crater (Ehlmann et al. 2009). Another unnamed 45-km crater that impacted Late Hesperian lava flows displays Fe, Mg smectites on the crater floor and in the lower section of an alluvial fan, possibly indicating aqueous alteration at depth derived from atmospheric snow melted by impact heat (Mangold et al. 2012a). Several craters >40 km in Tyrrhena Terra also have complex assemblages of minerals that could reveal local hydrothermal alteration (Loizeau et al. 2012). Distinguishing hydrothermal alteration from excavation is difficult given the fact that similar minerals can derive from both processes, but careful observations of their setting may lead to additional examples of potential impact-related alteration in the future.

3.5 Clays and Sedimentary/Fluvial Activity

Initial studies found that fluvial valleys and clays were not co-located (Bibring et al. 2006). However, both are found in Noachian-aged terrains almost exclusively, raising the question of whether their formation was coeval. In Nili Fossae, the water–rock interactions that formed clays occurred mostly before the time of the Isidis impact (Mustard et al. 2007; Mangold et al. 2007). Fluvial landforms post-dating Isidis basin in this region are poorly developed, and their formation generated little or no alteration (Mangold et al. 2007; Mangold 2008). In Mawrth Vallis, valley networks incise into clay-bearing terrains without obvious genetic relationships (Fig. 4; Loizeau et al. 2007, 2010; Mangold 2008). Despite the fact that both valley networks and clays are predominantly in Noachian terrains, there is little evidence that valley networks and these alteration products formed at the same time or are characteristic of the same environmental conditions (Fassett and Head 2011).

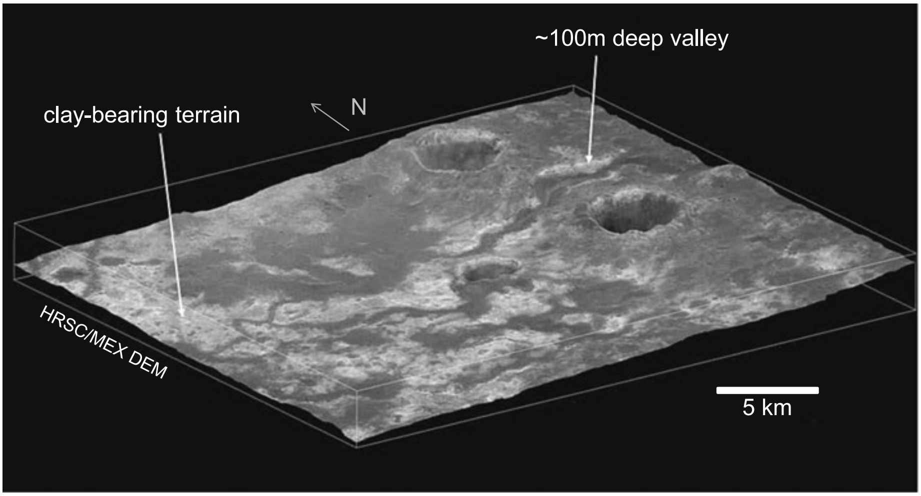


Fig. 4 Valley incising clay-bearing terrain (light-toned outcrops) in the Mawrth Vallis region. A 100-m deep fluvial valley post-dates the clay-bearing unit. The stronger erosion in the western part of the region has degraded the valley to small residual landforms and exhumed clay-bearing rocks. The three-dimensional topography was created by overlaying a single High-Resolution Stereo Camera (HRSC) image on a digital elevation model constructed using HRSC stereo images by V. Ansan (methods in Ansan et al. 2008)

Clays and salts have been detected in several of Mars' many putative paleolakes and fluvial basins. In marked contrast to clays in crustal settings, the hydrated silicates prehnite, analcime, illite/muscovite, and chlorite (except possibly as mixed with smectite) are not detected. Holden, Eberswalde, and other craters contain predominantly Fe, Mg clays (Milliken and Bish 2010). Ismenius Cavus, a depression in Mamers Vallis, displays >300 m thick layered deposits that host clear signatures of Fe, Mg-smectite clays (Dehouck et al. 2010). Some sedimentary basins host clays and salts. Open-basin sediments in the Jezero system, including in its deltas, host Fe, Mg-smectite clays and Mg-carbonate (Ehlmann et al. 2008a, 2009). Terby crater contains layered deposits interpreted as deltaic and composed of Fe, Mg smectites with local zeolites (or sulfates) present in the lowest sections (Ansan et al. 2011). Broad, intercrater depressions in the southern hemisphere with poor drainage connectivity have distinctive units with probable chloride salt units overlying Fe, Mg-clays (Murchie et al. 2009; Glotch et al. 2010; Osterloo et al. 2010). Putative lacustrine sediments within the closed basins of Gale, Columbus, and Cross craters contain sulfate salts, accompanied by Al-clays and/or nontronite (Swayze et al. 2008; Milliken et al. 2010; Wray et al. 2011). At Gale crater, nontronite is interbedded with sulfate and sulfate-iron oxide units at the bottom of a 5-km tall sedimentary mound and will be investigated by the Mars Science Laboratory mission (see Sect. 3.7). Layered deposits in two pits of Noctis Labyrinthus, on the western end of Valles Marineris, also display interlayered sulfates and clays (Weitz et al. 2011; Thollot et al. 2012).

Mineralogic data alone do not permit definitive determination of whether the clay minerals in basins formed *in situ* or were transported. Basins fed by valleys typically host hydrated silicates closely comparable to those in nearby highlands watersheds, consistent with detrital origin (Ehlmann et al. 2009; Milliken and Bish 2010). In contrast, salts found in closed basins are not identifiable in the surrounding terrains, pointing instead to *in situ* precipitation. The timing of deposition may have been coeval to the main fluvial phases on Mars (Late Noachian/Early Hesperian; Fassett and Head 2008) for the oldest lacustrine systems (e.g., Terby, Columbus, or Jezero). But much of the observed alteration may have occurred prior to valley network formation, and clay-bearing sediments in paleolakes could be mainly detrital. In addition, several examples (e.g., Ismenius Cavus, Holden and Eberswalde) show crater retention ages late in the Hesperian (Dehouck et al. 2010; Grant and Wilson 2011; Mangold et al. 2012b) supporting a detrital origin in a climate already too cold to generate *in situ* clay alteration, as shown by the scarcity of alteration in volcanic plains of similar Hesperian ages.

3.6 Key Stratigraphic Sections with Clays, Similarities and Differences

A few geographically extensive stratigraphic sections preserve contacts between different clay-bearing units. These include Mawrth Vallis, Nili Fossae, and Valles Marineris. A distinctive stratigraphy of Al clays above Fe/Mg clays is most typically observed. The Al-clays in these settings include a kaolin family mineral, as well as less commonly an Al smectite (Poulet et al. 2005; Loizeau et al. 2007, 2010; Bishop et al. 2008b; Wray et al. 2008; McKeown et al. 2009; Ehlmann et al. 2009). In Mawrth Vallis and greater Arabia Terra, kaolinite, montmorillonite, and/or silica overlie a nontronite-bearing unit (Loizeau et al. 2007, 2010; Bishop et al. 2008b; Wray et al. 2008; McKeown et al. 2009; Noe Dobrea et al. 2010; Michalski et al. 2010a, 2010b). The exposures are typically in high-standing topography, and the contacts between clay units sometimes follow a pre-existing topographic surface. The nature of these contacts suggests formation by either *in situ* alteration, i.e. leaching, of pre-existing surface materials, or draping by later airfall deposits.

The section of clay-bearing rocks at Mawrth Vallis contains unconformities within the Fe-rich section, indicating that the unit containing the clays was deposited over an extended period of time (Michalski and Noe Dobrea 2007). Around the Nili Fossae, a thin kaolinite-bearing unit overlies both impact-brecciated and sedimentary Fe, Mg-smectite clay units (Fig. 5; Ehlmann et al. 2009; Gaudin et al. 2011). In the eastern portion of this region, Mg-carbonate and serpentine associated with an olivine-rich unit occupy a stratigraphic position similar to that of kaolinite (Ehlmann et al. 2009; Mustard et al. 2009). Al-clays overlying Fe, Mg clays are also exposed high in the walls of Valles Marineris (Murchie et al. 2009; Le Deit et al. 2012) and in other scattered exposures across the southern highlands. In these locations, the clay-bearing units are capped by Hesperian-aged rock units. In other portions of Valles Marineris, near Noctis Labyrinthus, Al clays occur in the lowermost layers of the stratigraphy and are inferred to be a product of volcanically-derived acidic groundwaters later in Mars history (Thollot et al. 2012).

3.7 In Situ Examination of Clay Minerals: Present and Future

The Viking lander missions provided geochemical data (e.g. Toulmin et al. 1977), which indicate that the soils of Mars are mafic in composition but likely with an additional salt component, perhaps added via reaction with volcanic gases (Baird and Clark 1981; Banin et al. 1997). The mafic component could be primary, secondary, or both (e.g. including smectite clays); Viking data are equivocal concerning the mineralogy (Arvidson et al. 1989). Most knowledge of the mineralogy of Mars' rocks and soils is derived from remote telescopic and orbital observations (Table 2) and recent *in situ* measurements from the Mars Exploration Rovers (MERs). The MERs carried both a thermal emission spectrometer (Mini-TES) for mast-mounted remote mineralogic determination and an arm-mounted Mössbauer spectrometer for contact measurement of Fe mineralogy and an alpha particle X-ray spectrometer (APXS) for elemental chemistry. To date, clay minerals have not been identified definitively

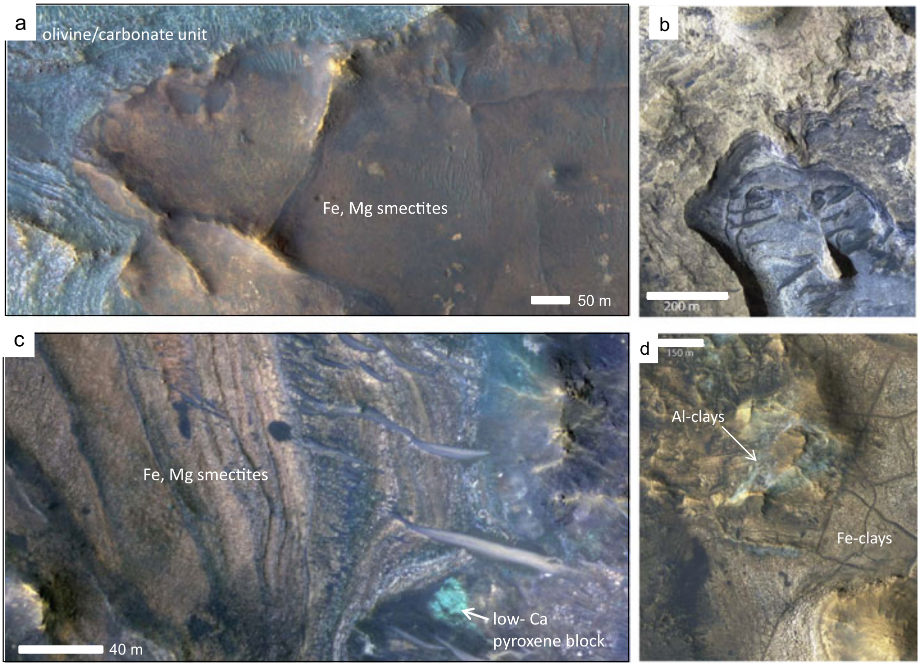


Fig. 5 HiRISE infrared color images of (**a**) crustal clays in Nili Fossae, stratigraphically beneath carbonate, crossed by ridges, and with breccia blocks within the deposit (PSP_002888_2025); (**b**) Mawrth Vallis clays exhibiting meters-scale layering (PSP_001929_2050); (**c**) layered clays within the Nili Fossae trough, overlying a brecciated smectite-pyroxene deposit (ESP_019476_2005); (**d**) layered clays in Mawrth Vallis with Al-rich clays in a butte above fractured, Fe-rich clays (ESP_011383_2030)

in situ at either the Gusev Crater or Meridiani Planum landing sites, despite clear evidence for other aqueously derived phases at both sites (e.g. sulphates, goethite, opaline silica, Mg/Fe carbonate), though have been reported in CRISM VNIR orbital data (Wray et al. 2009b; Carter and Poulet 2012). The Clovis class rocks in the Columbia Hills of Gusev Crater present chemical evidence for the presence of materials with a composition equivalent to that of aluminium clay minerals, specifically montmorillonite (Wang et al. 2006; Clark et al. 2007), although neither mineralogic instrument confirmed this identification. The rocks with montmorillonite-like chemical compositions exhibit TIR spectral character similar to basaltic glass (Ruff et al. 2006), which could either be a primary phase or a non-crystalline altered material. At Meridiani Planum, Mini-TES spectra of the sulfate-rich outcrops were modelled with 10 % smectite (Glotch et al. 2006), but this is not a definitive identification nor was it corroborated via the Mössbauer spectrometer. The 2007 Phoenix lander was not equipped to identify clay minerals. However, Phoenix identified denticles (sawtooth terminations) in atomic force microscopy of soil particles; such denticles are features of pyroxene aqueous alteration that are usually associated with clay mineral formation (Velbel and Losiak 2010).

As of the writing of this manuscript, the Opportunity rover has reached the rim of Endeavour crater, which orbital data indicate host Fe/Mg clays (Wray et al. 2009b), possibly detectable by the rover's Mössbauer spectrometer. The 2011 Mars Science Laboratory, with its ChemMin instrument, a combined XRD/XRF, will visit a location in Gale crater for which orbital identification of clay minerals has been made (Milliken et al. 2010). These rover investigations will allow for the first time the *in situ* investigation of the composition, petrographic texture, and abundance of martian clays.

3.8 Information from Meteorites

Some of the martian meteorites include alteration assemblages with clay minerals. A variety of Mg, Fe-rich alteration phases occur in the nakhlites, including iron oxides, smectites, and amorphous silicates (Gooding 1992). Fe-poor, Al-rich illite clay minerals may also be present in EETA79001 (Gooding 1992), a shergottite meteorite with a crystallization age typically accepted as 173 Myr (Nyquist et al. 2001), though ages at 4.0 Gy have also been proposed for shergottites (Bouvier et al. 2005). In the nakhlites, the secondary mineral assemblages are somewhat younger than the age of the rocks, which crystallized at 1.3 Ga (Swindle et al. 2000; Swindle and Olson 2004). These clay minerals are substantially younger than the widespread Noachian clays and occur in very small abundances; the veins of secondary minerals typically occupy 3–10 % by volume of olivine grains (Changela and Bridges 2011) and <1 % of the bulk rock. Nevertheless, detailed petrologic and compositional studies permit at least this type of later martian clay formation to be better understood.

The nakhlites are believed to come from a single source region that includes meteorites from different excavation depths (Mikouchi et al. 2006). In the nakhlite Lafayette, smectites and Ca-rich siderite ($(Fe, Ca)CO_3$) occur next to each other in veins. There is a spread in the composition of clay minerals, but the average is similar to saponite and nontronite, and the chemistry of secondary mineral assemblages shows trends with the depth of origin of each meteorite (Changela and Bridges 2011). The abundance of clay minerals and carbonates increases with depth and olivine alteration increases, while the abundance of sulfates decreases.

The chemical compositions of the secondary silicate phases in Nakhla and Lafayette suggest that the clay minerals and other secondary phases did not form via isochemical replacement of igneous minerals but rather from fluids that brought low-CO_2, Fe- and Mg-rich alkaline fluids in from elsewhere (Treiman and Lindstrom 1997; Changela and Bridges 2011). The alteration event recorded in nearly all of the nakhlites was also likely brief and occurred at temperatures $<60°$ based on the $\delta^{18}O$ values of associated carbonates and the modern atmosphere (Treiman and Lindstrom 1997; Saxton et al. 2000; Niles et al. 2010). Textural evidence is preserved from multiple nakhlites of a sequence of rapid cooling and changing water/rock ratios of 1–10 (Changela and Bridges 2011). (For further discussion of alteration in martian meteorites, particularly with regard to carbonate minerals, see Niles et al. (2012)).

4 Geochemical Consequences of Martian Clay Formation

The earliest rock record of Mars, particularly the Noachian, exhibits evidence for clay mineral forming conditions, distinct from later conditions characterized by a mineralogic record characterized by evidence for geochemical cycling of sulfur (see Gaillard et al. 2012). Clay mineral formation on Mars likely occurred by some or all of the same set of mechanisms operating on the Earth to form clays, discussed in Sect. 2. The geochemical consequences for reservoir modification and creation are likely to be similar to those depicted schematically in Fig. 1. However, some aspects of geochemical conditions on ancient Mars preclude direct comparison with the terrestrial rock record. First, the compositions of precursor protoliths and atmosphere differ on Mars. Additionally, the >3.5 Gyr age of the clay-bearing units means that Mars preserves a record of early geologic processes that operated when impact processes were relatively more intense, a period not well-preserved in Earth's rock record. Consequently, evaluating clay formation scenarios from a first principles approach, validated with modeling and laboratory experimentation, is essential. Additional complicating factors in interpreting the martian (and terrestrial) geologic records arise from the fact that clays may have been transported from their original formation environment. Furthermore, altered minerals can suffer post-depositional changes and clay mineral assemblages may reflect changes from later acid weathering (Altheide et al. 2010) or diagenesis (Tosca and Knoll 2009; Ehlmann et al. 2011a, 2011b).

Nevertheless, with improving constraints from orbital analyses as well as new data from *in situ* measurements on Mars, clay formation in multiple, diverse ancient environments has been identified. The critical question is which clay-formation mechanisms were more important and, consequently, how did martian clay formation influence the chemical composition of the crustal and atmospheric reservoirs? Some constraints exist from comparison of the martian clay record with results from laboratory and modeling efforts.

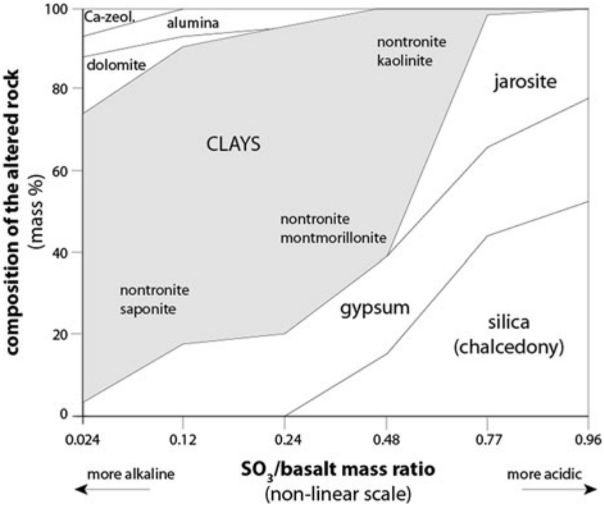
4.1 Constraints on Clay Formation Scenarios

4.1.1 Thermodynamic and Kinetic Considerations

For a chemical system to progress toward a more thermodynamically stable, minimum free-energy state, it must first surmount an energy barrier; the greater the Gibbs free energy of reaction, the greater the activation energy required. The Ostwald Rule derived from this constraint states that if a reaction has multiple pathways and can result in several products, it is the least stable product with free energy closest to the original state that crystallizes first instead of the most energetically stable phase. Hence, with multiple possible pathways, moderate mineralogical transformations with lower activation energies occur more rapidly than more radical changes, even though the more radical changes may be the thermodynamically favored lowest energy state. Because reaction rates are exponentially dependent on temperature, initial transformations are particularly important to understand for cold, martian environments. Carbonate, sulfate, and other salts with ionic bonds have relatively low kinetic barriers for dissolution and precipitation in comparison to minerals comprised of a covalently bonded lattice with Si, Al, and O. Therefore, amorphous aluminosilicate coatings and rinds, rather than clays, are also important alteration products throughout much of Mars history (e.g. Michalski et al. 2006), and the prediction of alteration sequences involving clay minerals requires taking kinetic considerations into account.

On Earth, clay minerals are produced principally during acid-activated pedogenic processes or abiotic temperature-activated alteration. Primary rock-forming minerals are a sink for protons produced by hydrolysis reactions, resulting in production of clay minerals and release of cations, first alkalis, then alkaline earths, and finally iron. On Earth, the proton source (acidity) commonly derives from CO_2, organic acids, or sulfuric acid formed by oxidation of pyrite (Meybeck 1987). On Mars, CO_2 is a potential source of acidity as are oxidation of iron sulfides (Burns and Fisher 1990; Dehouck et al. 2012), oxidation of iron (Baldridge et al. 2009; Hurowitz et al. 2010), and chlorine and sulfur species released by volcanism (Bullock and Moore 2007; Gaillard and Scaillet 2009). Whether or not clays form depends on four parameters: the mass of pristine rock relative to the mass of water (W/R), the amount and source of protons, time, and the supply of the reactants, e.g. from differential dissolution of heterogeneous mineral phases rather than dissolution of a homogeneous glass.

Fig. 6 Thermodynamic prediction for alteration of basalt (Adirondack composition), assuming W/R = 1, 0 °C, congruent dissolution of primary phases, and partial pressures for O_2 and CO_2 observed in the current Mars atmosphere. Figure is adapted from Berger et al. (2009). The parameter SO_3 corresponds to "dry" H_2SO_4, the source of acidity



These kinetic considerations were invoked by Tréguier et al. (2008) and Berger et al. (2009) when considering the nature and amount of secondary phases at Meridiani Planum, a site with sulfates, iron oxides, and primary minerals, detected *in situ* (e.g. Squyres et al. 2004), and clay minerals been detected from orbit in lower stratigraphic units in the region (Poulet et al. 2008b; Wray et al. 2009b). The effect of protons/acid is illustrated in Fig. 6, based on a thermodynamic model reported in Berger et al. (2009), showing the proportions of the secondary phases after the complete reaction of the pristine basalt with an acidic brine obtained by dissolution of SO_3 in water. The scenario has no time-limited kinetic effects and all reactant anions and cations are available. The leftmost part of the plot corresponds to low proton availability where only water is added to the rock, and the alteration assemblage is dominated by formation of clays and zeolite. The right part corresponds to high proton (acidic) conditions supplied by SO_3 dissolved in the fluid.

Thermodynamic calculations predict substantial clay mineral formation up to high concentrations of sulfur relative to basalt (nearly 1:1) (Fig. 6). However, the Fe/Mg clays most commonly observed on Mars are not thermodynamically stable at $pH < 4$ (Chevrier et al. 2007), and laboratory experiments show no formation at $pH < 7$ (Tosca et al. 2008). Modeling including kinetic considerations, i.e. dissolution of primary phases (reactant supply) and precipitation rates of salts (rapid) vs. clays (slow), demonstrates that clays are not a favored product of most short timescale reactions involving sulfur at low water/rock ratio, favoring instead the precipitation of salts (Berger et al. 2009). This results from an assumed high gas/rock ratio relative to water/rock (W/R) ratio, producing a concentrated sulfate brine favorable to the precipitation of sulfate salts.

In general, clay formation indicates long-term interaction of rocks with solution, sufficient for dissolution of primary silicates and crystallization of secondary silicates. The nature of clay minerals formed depends on the W/R and proton source. In basaltic hydrothermal systems, low water/rock ratio reactions lead to propylitic facies (chlorite, Fe/Mg smectites, epidote, prehnite) while higher W/R and/or acidity lead to argillic facies (kaolinite, Fe/Mg smectites, hematite, carbonate) (Berger and Velde 1992). Deep crustal clays excavated by cratering of clay-bearing terrains are more similar to propylitic facies (low W/R, little acidity) as discussed in Sect. 3.4 (Ehlmann et al. 2011a). When instead W/R is low but H^+/rock (acidity) is high, the concentration of the solute will reach the solubility of the secondary salts in which the anion (CO_3, SO_4, Cl) is the proton companion anion. In this scenario, an observed increase in the concentration of a particular anion in an altered rock relative to protolith geochemistry indicates the nature of the acid that drove the alteration, as with S at Meridiani Planum. Weathering at high W/R ratios and short residence time leads to leached horizons with Al clays and Fe oxides, fluid transport, and evaporative salts formed elsewhere. Fe oxides and Al clays, within the clay stratigraphic sections discussed in Sect. 3.6, are more similar to the argillic facies (higher W/R and/or more H^+/R).

4.1.2 Controls on Atmospheric Composition

Knowing how and where martian clays formed originally is vital to any understanding of whether they have implications for the early climate. Surface weathering would entail interaction of the atmospheric and crustal reservoirs (Fig. 1a). An equilibrium pCO_2 of ~5 mbar or greater during clay formation should result in the coexistence of carbonates and Fe/Mg-rich smectites (Chevrier et al. 2007). This coexistence has not been commonly observed, so it has been argued that if we assume that clay minerals formed at the martian surface, the atmosphere of ancient Mars was not CO_2-rich or other greenhouse gases were the dominant atmospheric components necessary to maintain near-surface liquid water (Chevrier et al. 2007). However, the prediction of carbonate precipitation from atmospheric CO_2 also includes other parameters. In the case of high run-off (low residence time of water within the martian regolith), near-neutral pH (slow dissolution kinetics), and/or presence of another acid gas (high carbonate solubility at low pH), carbonate precipitation is not expected (e.g. Fabre et al. 2011).

Plausible candidates for alternative greenhouse gases to provide ~80 K of warming necessary for a continually clement early Mars (Haberle 1998) have not been identified. For comparison, the modern, Holocene Earth has 33 K of greenhouse warming (e.g., Kasting and Catling 2003), primarily from small amounts of H_2O, CO_2, and CH_4. Sufficient quantities of methane on early Mars would require a flux larger than the current biogenic flux on Earth. Similarly, volcanic sulfurous gases, which have been suggested as a possibility for warming the early climate of Mars (Halevy et al. 2007; Johnson et al. 2009), may cool early Mars through the rapid formation of atmospheric aerosols that reflect sunlight to space, similar to the net cooling effect of volcanic sulfur on Earth and Venus (Tian et al. 2010). Existing evolution models of the CO_2 partial pressure similarly suggest that the CO_2 level in the atmosphere of Mars could have been low or moderate at the end of the Noachian, in the range from a few tens of millibars to 1 bar, insufficient for durably maintaining temperatures above freezing (Lammer et al. 2012).

Consequently, environmental conditions of clay formation may have been the result of repeated, transient periods of liquid water-rock interaction at the surface in a relatively cold climate with a sparse atmosphere, with only a slightly thicker atmosphere and warmer surface conditions than Mars today. In this case, most clays may have formed in a subsurface environment from groundwaters isolated from the atmosphere (Ehlmann et al. 2011a). An alternative interpretation of the data is that clay mineral assemblages formed under warm surface conditions may have been modified, i.e. surface-formed, clay-bearing assemblages may have been altered, for example, by removal of accompanying carbonates by acidic weathering and burial and impact churning of Al clay layers.

4.1.3 Geomorphology and Stratigraphy

The geomorphology and stratigraphy of particular martian clay deposits can be examined to help discriminate between the alternative hypotheses for clay formation (Table 1). The majority of clay minerals are exposed by craters and, consequently, the original physical characteristics of the deposit have been disrupted. Sedimentary deposits with clays indicate *in situ* evaporation of fluids leading to the deposition of salts, but as discussed in Sect. 3.5, likely reflect transport of clays from their original formation setting in most cases. A few stratigraphic sections preserve coherent bedding and relationships between geologic units with clay minerals of different composition. Fe/Mg smectite-bearing units range from horizontally layered to brecciated, indicating a range of processes from sedimentary, to extrusive volcanic, to impact disruption. The depth of these layers, both in thickness and in the stratigraphic column suggests that some portion of the alteration to Fe/Mg clays took place in the subsurface (Ehlmann et al. 2011a). In Mawrth Vallis, the uppermost Al-clays and silica bearing units follow the topography and overlie an Fe/Mg smectite-bearing unit (Bishop et al. 2008b; Wray et al. 2008; Loizeau et al. 2010), and similar stratigraphic sections are found in Valles Marineris and Nili Fossae. These Al clays may have formed by processes involving either weathering and pedogenesis or diagenesis by shallow aquifers (<200 m). Draping by volcanic ash, subsequently altered, is one possibility for formation, although whether groundwater or surface waters were the alteration agent cannot be definitely distinguished (McKeown et al. 2009). An alternative possibility may be greater degrees of near-surface leaching, possibly by acidic waters (Bishop et al. 2008b; Ehlmann et al. 2009; McKeown et al. 2009; Noe Dobrea et al. 2010).

4.1.4 Bulk Crust Chemical Composition and Clay Mineral Abundances

At a coarse spatial resolution of a few hundred kilometers, measurements of the upper 0.5 m of the surface by the gamma ray spectrometer onboard the Mars Odyssey orbiter do not show significant fractionation of K and Th, two elements expected to have different mobilities in open system weathering (Taylor et al. 2006, 2010). The observation of clay minerals at abundances <30 % in association with primary minerals pyroxene and plagioclase in most Mars terrains may indicate only partial alteration of the units. Only the Fe-smectite unit at Mawrth Vallis has higher abundances, reaching 65 % clay with little evidence for accompanying primary phases (Poulet et al. 2008a). However, only $\sim$10 of the thousands of exposures of clay minerals have thus far been examined for abundances. Hence, the significance of clay mineral abundance and geochemistry to inferring the geochemistry of alteration may have to await higher resolution geochemical studies and expanded calculations of modal mineralogy.

4.2 Geochemical Consequences

We consider the geochemical consequences of three endmember scenarios that have emerged to explain clay mineral formation on ancient Mars: near-surface (open) systems, ice-dominated systems, and rock-dominated subsurface (closed) systems.

4.2.1 Water in Near-Surface (Open) Systems

Surface or near-surface weathering to form clays has the potential to generate substantial reservoir fractionation, depending on the W/R and hydrological character of the system. If formed from a basaltic substrate, the Al clays found on Mars likely indicate high W/R leaching processes in an open system or from highly acidic waters. Any precipitation on ancient Mars would percolate through the crust, leading to chemical alteration (Fig. 7a). Evidence for such systems exists in Mawrth Vallis (Loizeau et al. 2007, 2010; Bishop et al. 2008b),

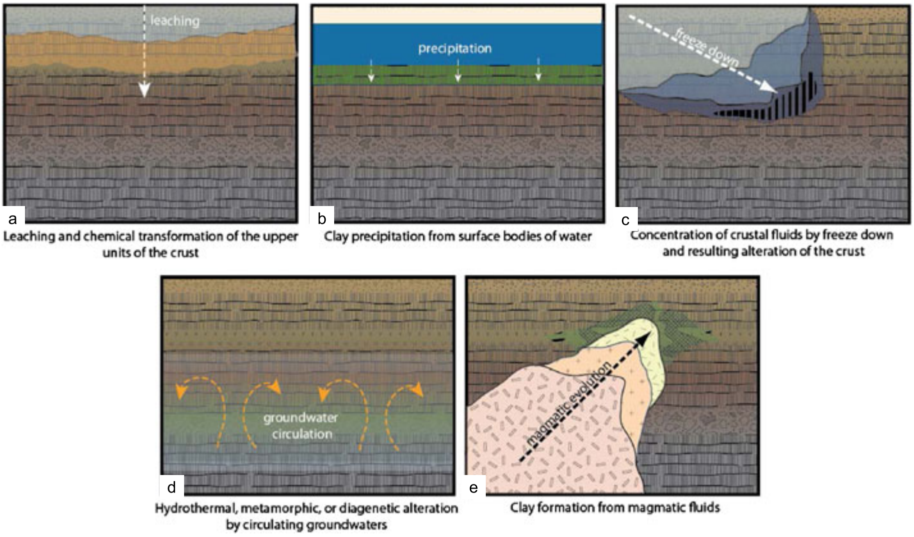


Fig. 7 Scenarios for Martian clay formation

near the Nili Fossae (Ehlmann et al. 2009); and in diverse terrains across the southern highlands (Wray et al. 2009a, 2009b).

As modeled by Milliken et al. (2009), leaching processes result in liberation of cations which then react with anions to form salts, of composition dictated by the composition of the atmosphere. These would include carbonates, sulfates, chlorides, and perchlorates. The result is creation of two reservoirs, a leached crust and a sedimentary reservoir, distinct in composition from the geochemistry of primary bedrock produced by volcanism (Fig. 1). The formation of large salt deposits in basins as water evaporates might be a potential reservoir for atmospheric gases, e.g. CO_2 in carbonates (Fig. 7b), although to date, carbonate-rich sedimentary bedrock units have not been identified (Ehlmann et al. 2008a).

Only a few regions display Al-clay mineralogic assemblages, either because of the lack of extensive global weathering or its poor preservation. Indeed, the difficulty in discriminating near-surface weathering from deeper alteration is a consequence of the subsequent >3.5 billion years of aeolian activity, volcanism, and impact gardening, which have eroded, blanketed and disturbed ancient surfaces. Nevertheless, in this scenario sedimentary units are predicted to have a different composition than altered crust; both would be different from primary crust, and the process of clay formation would have altered the atmospheric reservoir by co-precipitation of salts.

4.2.2 Ice-Dominated Systems

Some models of the evolution of the atmosphere and climate of Mars suggest that Mars lost most of its atmosphere soon after accretion and has not retained a dense enough atmosphere to support extensive, long-lived surface liquid water at any time in its history (Wordsworth et al. 2011; Lammer et al. 2012). In this scenario, an active hydrological cycle driven by warm greenhouse conditions would not supply and replenish the large amounts of water necessary to form the extensive deposits of clay minerals discussed above. Needed water might, however, be supplied by ice.

Obliquity variations change the distribution of ice stability across Mars, allowing for transport of ice and dust from the polar regions to the equator during periods of high obliquity (Jakosky and Carr 1985; Laskar et al. 2002; Head et al. 2003). The resulting deposits of ice and dust might have resembled the modern polar deposits in scale and morphology (Niles and Michalski 2009). In such deposits, cryo-concentration of volatile-bearing brines (e.g. S-rich and Cl-rich) could promote acid weathering of silicate dusts and sand grains inside the deposit (Fig. 7c; Burns 1993; Niles and Michalski 2009). In such a scenario, intra-ice acid weathering would lead to the release of cations and silica into solution leading to the precipitation of salts, the production of leached Si + Al-rich material (either an amorphous residue or crystalline Al-clays), and the possible production of mixed Fe oxide-smectite materials (Burns 1993).

Geochemical consequences of this scenario would include (1) removal of S and Cl volatile species from the atmosphere and sequestration in the crust, specifically within a sedimentary reservoir of different composition from the primary crust; and (2) possible water, Fe, and Mg addition to the primary crust by brines derived from cryo-concentration and acid weathering within the ice.

4.2.3 Rock-Dominated Subsurface Systems

Low-grade metamorphism, hydrothermal activity, and magmatic precipitation are means by which martian clays could form primarily in the subsurface within a crustal reservoir relatively closed with respect to the other reservoirs (Figs. 7d and 7e). Evidence to date indicates that some of the clays, especially the deep crustal units of the southern highlands, may have formed in these rock-dominated systems at temperatures slightly above surface-ambient (Ehlmann et al. 2011a, 2011b).

In metamorphism, the degree of chemical fractionation between parent material and alteration product is small and would result in little geochemical fractionation of Mars' crustal reservoir. If instead clays formed by magmatic precipitation, some volatiles would be released into the atmosphere during eruption of extrusive lavas, but lavas would largely retain their volatiles, precipitated into hydrous minerals during late-stage crystallization. This mechanism can produce new crust up to ∼10 % clay by volume (Meunier et al. 2010). Clay formation in hydrothermal systems can occur in chemically open or closed systems. Recirculation of crustal waters can generate clay minerals, as can hydrothermal systems driven by magmatic fluids. If hydrothermal systems are open to meteoric waters, formation of minerals can lead to sequestration of atmospheric volatiles, e.g. CO_2 in minerals precipitated in fractures and H_2O in hydrous silicates.

In general, subsurface, rock-dominated systems are relatively closed, i.e. there is little interaction with other geochemical reservoirs. Subsurface alteration may result in some incorporation of atmospheric species into the uppermost crust, as may be the case for martian meteorites (discussed in Sect. 3.8), but to date, evidence for carbonates and sulfates incorporated in the same deep crustal units as the clays is uncommon (Michalski and Niles 2010). However, a significant effect of water interaction with the crust is that the water itself may be permanently sequestered in hydrous silicates, thus removing it from the atmospheric reservoir and continued cycling.

For example, the hydrothermal alteration of olivine in the serpentinization process is one effective means of sequestering water in the crust, as shown by recent modeling (Chassefière and Leblanc 2011). In the reaction, ferrous iron is oxidized by the water to ferric iron, which typically precipitates as magnetite, while hydrogen from water is reduced to H_2. If fluids vent to the surface, they can release high abundances of CH_4 and other hydrocarbons, provided that CO_2 is dissolved in the fluid and is reduced by H_2, which typically requires a catalyst. On Mars, the generation of H_2 by olivine during serpentinization can be expressed as (Oze and Sharma 2005),

$$(1)\quad \underset{\text{Olivine}}{Mg_{1.5}Fe_{0.5}SiO_4} + 1.17H_2O \rightarrow \underset{\text{Serpentine}}{0.5Mg_3Si_2O_5(OH)_4} + \underset{\text{Magnetite}}{0.17Fe_3O_4} + 0.17H_2$$

$$(2)\quad 4H_2 + CO_2 = CH_4 + 2H_2O,$$

assuming reaction of olivine with an Mg # of 0.75. For each released H_2 molecule, 6 H_2O molecules are stored in serpentine, and/or for each released CH_4 molecule, 24 H_2O molecules are stored in serpentine (Chassefière and Leblanc 2011). Over 85 % of the water participating in the serpentinization reaction is ultimately sequestered in the crust. The formation of serpentine and other hydrous silicates in the subsurface is thus a potential crustal sink for H_2O in other martian reservoirs and is a means of sequestering volatiles. High temperatures are not required for this process. Olivine dissolution at low temperatures, generating H_2 and CH_4, has been observed in the laboratory (Neubeck et al. 2011) and in terrestrial ophiolites (Etiope et al. 2011), both cases in which the necessary catalysts are available to promote the reaction.

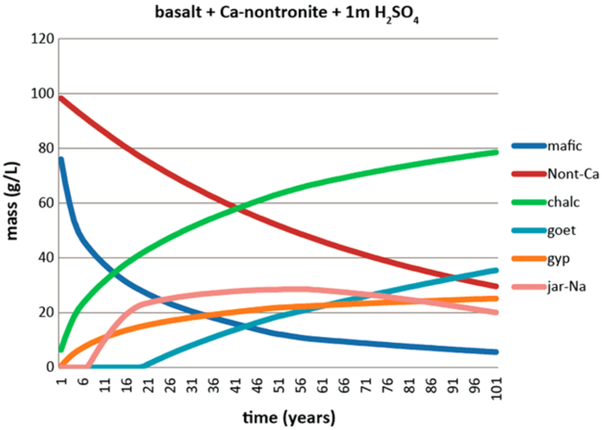
4.2.4 Subsequent Alteration once Formed

Regardless of the mechanism by which clays formed on Mars, following initial formation, subsequent alteration processes may affect clay-bearing deposits and the geochemical signatures of the original alteration process. There is widespread evidence for physical redistribution of clay minerals by transport in fluvial systems and by excavation during impact cratering (as discussed in Sects. 3.4 and 3.5). Impact cratering can also result in the heat- or shock-induced destruction of clay minerals near the point of impact (Weldon et al. 1982; Hviid et al. 1994; Gavin and Chevrier 2010; Che et al. 2011) or the generation of new and different species of clay minerals by impact-induced or later hydrothermal processes (Schwenzer and Kring 2009).

Chemical alteration may have affected clay-bearing materials following original clay formation, by mechanisms with varying degrees of impact on geochemical reservoirs. Exposure of Fe(II)/Mg smectites formed in an anoxic environment to oxidizing conditions at the present martian surface can lead to transformation to nontronite, an Fe(III) smectite (Burns 1992), although this mechanism would not lead to geochemical fractionation. Experiments with clay weathering in acidic fluids show that clay minerals are fairly resistant to strong acids like H_2SO_4, but do destabilize at low pH (<4) to form salt solutions, which can evaporate to precipitate sulfates, and often amorphous silica residual solid (Fig. 8). Depending on the amount of water, this can be either an open-system or closed system process. The resistance of clay minerals to acidic alteration depends on the nature of the phase. For example, kaolinite is the most resistant and Fe/Mg smectites the least resistant; consequently, acid weathering has been proposed to play a role in the generation of near-surface Al-rich clay units on Mars (Altheide et al. 2010). These scenarios for later clay alteration involve exchange of atmospheric and crustal reservoirs.

Under conditions of deep burial, diagenesis of smectite clays to more stable chlorite or illite phases is an expected transformation if sufficient water and Mg or K, respectively, are available to facilitate the reaction (Tosca and Knoll 2009). For clay diagenesis, the absence of K-rich feldspar—Gusev basalts contain less than 0.1 % K_2O, as reported in McSween et al. (2006)—precludes a significant illitization process, and the conversion of kaolinite to

Fig. 8 Low water/rock ratio acid alteration of clay-bearing units. A starting 54 % nontronite, 42 % mafic minerals, 4 % silica, simulating already altered crust. Nontronite is more resilient to later alteration than mafic minerals, but both are eventually replaced by silica, iron oxides, and sulfate salts



dickite, often considered as a spontaneous isochemical reaction, requires the dissolution of feldspars (Lanson et al. 1996). Thus, the more probable clay diagenesis is the chloritization of smectites. There is evidence for such transformations from the widespread presence of chlorite and occasional presence of illite in the southern highlands of Mars (Ehlmann et al. 2009, 2011a, 2011b) as well as the identification of probable mixed layer clays, chlorite/smectite, which is an intermediate product of the transformation (Milliken and Bish 2010). Such transformations occur within the crust in systems not exchanging with atmospheric and magmatic reservoirs.

5 Needed Future Measurements

A suite of possible formation scenarios, each with distinctive geochemical consequences, exists to explain Mars' globally widespread Noachian clays. To resolve the outstanding questions about clay formation environment and concomitant consequences for the evolution of martian geochemical reservoirs requires both detailed studies focused on clay-bearing units as well as broader ranging investigations aimed at understanding the evolution of the coupled Mars geologic-climatic system.

The continued acquisition of high-resolution image and spectroscopic datasets will allow detailed study of relationships between alteration mineral bearing units of different composition. These stratigraphic studies may lead to an understanding of whether clay-bearing units are primarily sedimentary or *in situ* altered volcanics. Further work is needed to develop best practices for modeling modal mineralogy of altered units remotely using the tens of meters scale visible/near-infrared data most conducive to the detection of clay to constrain their abundance. This will permit, not only identification of single minerals, but an understanding of full mineral assemblages most useful for geochemical modeling. Also useful in this regard would be higher resolution studies of the geochemical composition of clay-bearing units in the martian crust.

A combination of modeling and laboratory work is needed to understand the implications of various identified phases. For example, do the commonly detected Fe/Mg smectites require anoxic conditions to form? For how long can different clays persist in the presence of acidic waters at different temperatures? Have clays detected in central peaks of impact craters survived impact, or would they be destroyed by heat and pressure? Furthering these investigations will permit narrower constraints on formation environment.

More detailed *in situ* chemical, mineralogical, and textural data will soon be available for one site with clays, the landing site for the MSL rover mission, Gale crater. The CheMin instrument may identify the presence of smectites and other clay minerals by means of X-ray diffraction as well as provide *in situ* quantitative estimates of complete modal mineralogy, including measurement of accompanying primary phases or salts that might be undetectable with present orbiting instruments (Blake et al. 2012). Coupled with X-ray fluorescence measurements and elemental data from other instruments, the chemistry of the nontronite-bearing unit in Gale crater should be fully explored and evidence for post-formation diagenesis assessed. Trace elements and their mobility in different geochemical scenarios may supplement knowledge gained from major elements. Isotopic data from the gas chromatograph/mass spectrometer on the Sample Analysis at Mars (SAM) instrument suite may constrain alteration mineral formation temperatures or processes and will provide data on the possible presence/abundance of atmospheric CH_4 (Mahaffy et al. 2012). However, data of the last decade have revealed the great diversity of aqueous environments on early Mars, and no single mission can visit the many distinctive mineral/morphologic localities for clay-forming chemical environments on ancient Mars. For example, the question remains open as to whether the Al-over-Fe/Mg clay stratigraphy at several localities on Mars represents a top-down alteration mechanism, a fundamental shift in the depositional setting through time, or both. Definitive resolution of this question will likely require landing at a site with both types of minerals. Furthermore, understanding the nature of possible hydrothermal clays with chlorites and prehnite and their formation pre- or post-impact will likely require landed studies where examination of petrographic textures is possible.

Finally, datasets not focused on clay minerals are needed to constrain the evolution of Mars' atmosphere. Could it have hosted warm, wet surface conditions for an extended period of time or was the surface environment always relatively cold and dry? The 2013 MAVEN (Mars Atmosphere and Volatile EvolutioN) mission will provide isotopic estimates of atmospheric composition that will be useful in constraining loss rates and additional characterization of the atmosphere will be carried out by the mass spectrometer, SAM on MSL. Plausible scenarios can be envisaged where clay mineral assemblages do not tell us about the surface climate but indicate subsurface conditions. Generally, the available evidence and inferences from clay minerals in martian meteorites indicate that these formed in the subsurface rather than in thermodynamic equilibrium with ancient surficial conditions.

Nevertheless, if only a few outcrops of ancient clays were preserved from formation at warmer surface conditions, these outcrops would have a great importance for studies concerning life on Mars, similar to the role played by outcrops in the Barberton and Pilbara for terrestrial geobiology (Buick 2007). *In situ* geologic and geochemical observations at the surface are therefore critical for resolving the issue of the original provenance of clay minerals. The return of samples from Mars to Earth from clay-bearing terrains would provide an alternative means for comprehensive analysis of the origin of clay minerals, permitting use of a suite of laboratory techniques like micron-scale scanning electron microscopy, geochemical and isotopic analyses.

6 Conclusions

The dominant terrestrial clay formation mechanisms are near-surface weathering and hydrothermal processes in seafloor systems, although precipitation of clays in water bodies within basins, diagenesis, metamorphism, and magmatic precipitation also serve to form and modify clays. Like Earth, the geologic record from Noachian Mars also indicates multiple clay-forming processes operating in diverse chemical environments, varying in space and time. Clay formation in subsurface environments is indicated by some stratigraphic units whereas near-surface formation by precipitation-driven weathering or thin films of water derived from ice are favored in other locations. The latter two scenarios would fractionate the martian crustal reservoir into leached and sedimentary components, distinct in composition from primary crust, and would sequester volatiles. In contrast, subsurface formation might not substantially chemically fractionate major elements in the crustal reservoir but could effectively sequester water in the crust. Future modal mineralogy of clay bearing deposits derived from orbital data as well as mineralogic, geochemical, and petrological data acquired *in situ* can be used to discriminate clay formation mechanisms on the basis of their different geochemical consequences. However, no single clay-bearing unit is sufficient to obtain a global understanding of Noachian clay formation processes. Rather, investigations of multiple types of clay-bearing deposits are needed to develop a comprehensive model of the geochemical consequences of clay formation on Mars for its evolution over geologic time.

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