

TERRESTRIAL PERSPECTIVE ON AUTHIGENIC CLAY MINERAL PRODUCTION IN ANCIENT MARTIAN LAKES

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Abstract—The discovery of phyllosilicates in terrains of Noachian age (>3.5 Ga) on Mars implies a period in the planet's history that was characterized by wetter, warmer conditions that may have been more hospitable for life than the cold and dry conditions prevalent today. More specific information about the original locations and mechanisms of clay mineral formation on Mars is not as well constrained, however, in part because the origin of particular clay minerals is often non-unique. For example, Fe and Mg smectite-bearing deposits on Mars may have formed in various environments, including the weathering profiles of basic volcanic rocks, impact-induced hydrothermal sites, or in bodies of standing water. The identification of lacustrine deposits on Mars is of great interest due to their potential for the preservation of organic material, but identifying any given suite of sedimentary rocks as such is difficult when limited to mineralogy and morphology derived from orbital data. Here, the processes and conditions leading to clay mineral formation in lakes and evaporative marine basins on Earth are reviewed, with a focus on the spatial and stratigraphic distribution of clays in these settings. The goal is to provide criteria to determine if certain Martian clay deposits are consistent with such an origin, which in turn will aid in the identification of possible ancient habitable environments on Mars.

Key Words—Authigenic Clay Minerals, Lacustrine Clay Minerals, Martian Phyllosilicates, Mineral Facies, Neof ormation, Transformation.

INTRODUCTION

Occurrences of clay minerals on Mars are widespread in the spatial domain but are often interpreted to be temporally restricted to the Noachian era (>3.5 Ga) – a proposed consequence of warmer and wetter conditions during this period (Poulet *et al.*, 2005; Mustard *et al.*, 2008; Wray *et al.*, 2009; Carter *et al.*, 2010). Although some of these clay mineral deposits probably represent alteration products of primary (basaltic) crustal material, strata indicative of aqueous sedimentation are also known to contain phyllosilicates (*e.g.* Mustard *et al.*, 2008; Ehlmann *et al.*, 2008a; Murchie *et al.*, 2009; Milliken and Bish, 2010). The latter includes ancient deltas and other distributary systems interpreted as supplying basins with water and sediment (Figures 1, 2; Ehlmann *et al.*, 2008a; Grant *et al.*, 2008; Milliken and Bish, 2010). In contrast, some locations on Mars lack clear geomorphic evidence for fluvial/lacustrine processes but exhibit mineralogical patterns suggestive of aqueous deposition or precipitation, including interbedded clay and sulfate-bearing strata in closed basins (*e.g.* Milliken *et al.*, 2010; Wray *et al.*, 2011). Due to their high potential for the concentration and preservation of organic compounds, deposits rich in clay

minerals and other fine-grained sediments, such as lacustrine deposits, are prime targets in the search for organic remnants of life on Mars (*e.g.* Ehlmann *et al.*, 2008a; Summons *et al.*, 2011). In this context, it is important to develop criteria for using orbital data to help distinguish such depositional environments from clay-bearing strata that may have formed by other mechanisms such as hydrothermal activity, eolian processes (loess), or alteration of volcanic ash.

Previous work on identifying ancient lakes on Mars focused largely on morphological evidence for bodies of standing water, including the identification of closed basins with inlets, open basins characterized by inlets and outlets that occur at higher elevations, the presence of fan/deltaic features, and thin, laterally continuous parallel bedding, to name a few (*e.g.* Grin and Cabrol, 1997; Cabrol and Grin, 1999; Grant and Parker, 2002; Malin and Edgett, 2003; Fassett and Head, 2008; Grant *et al.*, 2008; Ehlmann *et al.*, 2008a; Figures 1, 2). This approach has limitations because many Martian clay deposits occur as stratified units with parallel bedding that extends for kilometers or longer but which lack unambiguous sedimentary or morphological features, leaving their mode of deposition uncertain. Mineralogical criteria that may support lacustrine interpretations are rarely discussed, despite the fact that certain types of clay minerals frequently form in terrestrial lakes under certain conditions, including varieties commonly reported to exist on Mars. For example, when Mg-rich smectites are found as major

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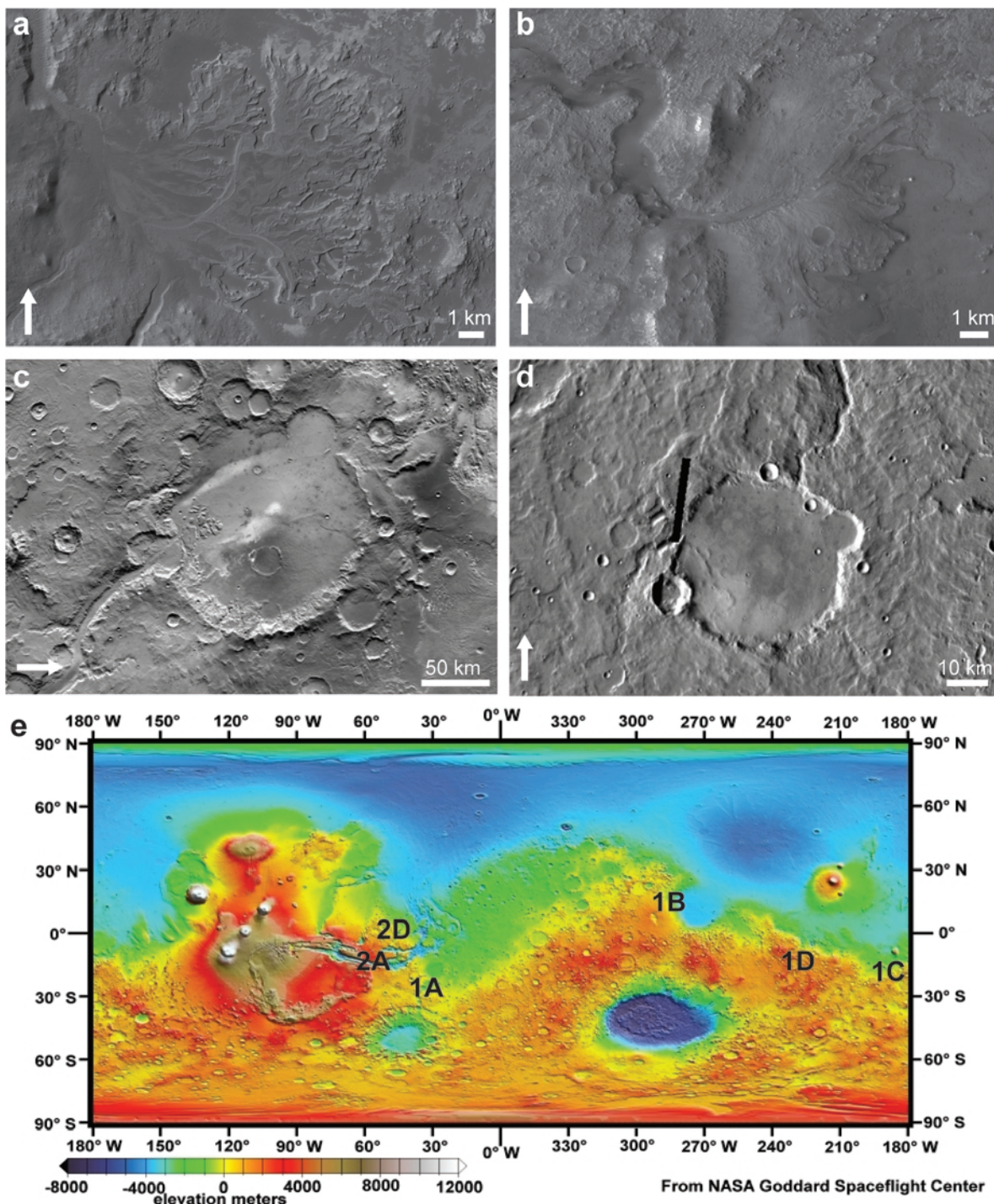


Figure 1. Examples of possible ancient lacustrine environments on Mars. Some putative crater lakes exhibit clear evidence of sedimentary strata bearing clay minerals, such as: (a) the deltaic deposits in the closed-basin Eberswalde Crater (Milliken and Bish, 2010); and (b) deposits in the open-basin Jezero Crater (Fassett and Head, 2008; Ehlmann *et al.*, 2008a). Other craters exhibit geomorphic evidence (*e.g.* inlets and outlets) for standing bodies of water but currently lack clear sedimentological and/or mineralogical evidence for lacustrine deposits, such as (c) Gusev Crater (Cabrol *et al.*, 1996) and (d) a crater located at -9.5°S , 135°E (Cabrol and Grin, 1999; Fassett and Head, 2008). Arrows point North. (e) Topographic map of Mars based on Mars Orbiter Laser Altimeter (MOLA) data (produced by the MOLA team) showing the locations of sites in Figures 1 and 2.

components of lake deposits on Earth, their presence often indicates *in situ* formation under alkaline or saline conditions. This is because the majority of clay minerals produced on the continents, in soils, in weathering profiles, and through the alteration of volcanic material are Al-rich phyllosilicates such as montmorillonite and kaolinite. Both are a result of the immobility of Al^{3+} under moderate pH conditions and the granodioritic composition of the continental crust. The apparent paucity of concentrated sedimentary deposits of Mg-rich smectite on Earth means the probability that such occurrences are reworked and redeposited (*i.e.* detrital), and that their depositional environments are misinterpreted is relatively low.

The logic used on Earth cannot be used to conclude that ancient Mg/Fe-smectite-bearing strata on Mars probably formed in saline water bodies, however. External sources of Mg/Fe-smectites (*e.g.* saponite and nontronite) such as weathering profiles of basic/ultra-basic rocks and hydrothermal alteration related to impact events were probably abundant on an early, wetter Mars (Osinski, 2005; Schwenger and Kring, 2009). Furthermore, the importance of eolian, volcanic, and impact processes in the formation and redistribution of sediment on Mars for the past several billion years means that the clay-sized material, including clay minerals, found in a particular basin are more difficult to track back to their original location of formation. Because clay minerals are non-unique in terms of origin and are subject to sediment transport processes, attempting to distinguish specific depositional environments on Mars based on the composition and type of clay mineral alone is unlikely to be successful.

More promisingly, terrestrial studies demonstrate that the types and chemistry of clay minerals forming in saline and alkaline lakes (referred to here as ‘authigenic’ clays) are arranged in spatial and stratigraphic patterns, which are potentially diagnostic of their lacustrine origin. The authigenic mineralogy of terrestrial saline lacustrine and marine evaporative environments as observed in modern and ancient terrestrial deposits are reviewed here, with an emphasis on types of authigenic clay minerals and their spatial distribution. The goal is to provide researchers with mineralogical criteria that can be integrated with stratigraphic and morphological evidence to determine if certain Martian clay deposits may have a lacustrine origin, and whether or not any of the observed clay minerals may have formed *in situ*. Such criteria should be particularly useful for evaluating Martian clay-bearing strata whose original depositional context has been obscured or destroyed by erosion over the past several billion years. In addition, if certain clay minerals on Mars can be shown to have formed *in situ*, then they can be used as indicators of local environmental conditions and aqueous chemistry at the time of their formation. The advantage of this approach is that, although the crustal compositions of Earth and Mars are

different, the physical processes that ultimately control sedimentation and the hydrology of basins and, therefore, patterns in mineralogy, are arguably similar on both planets.

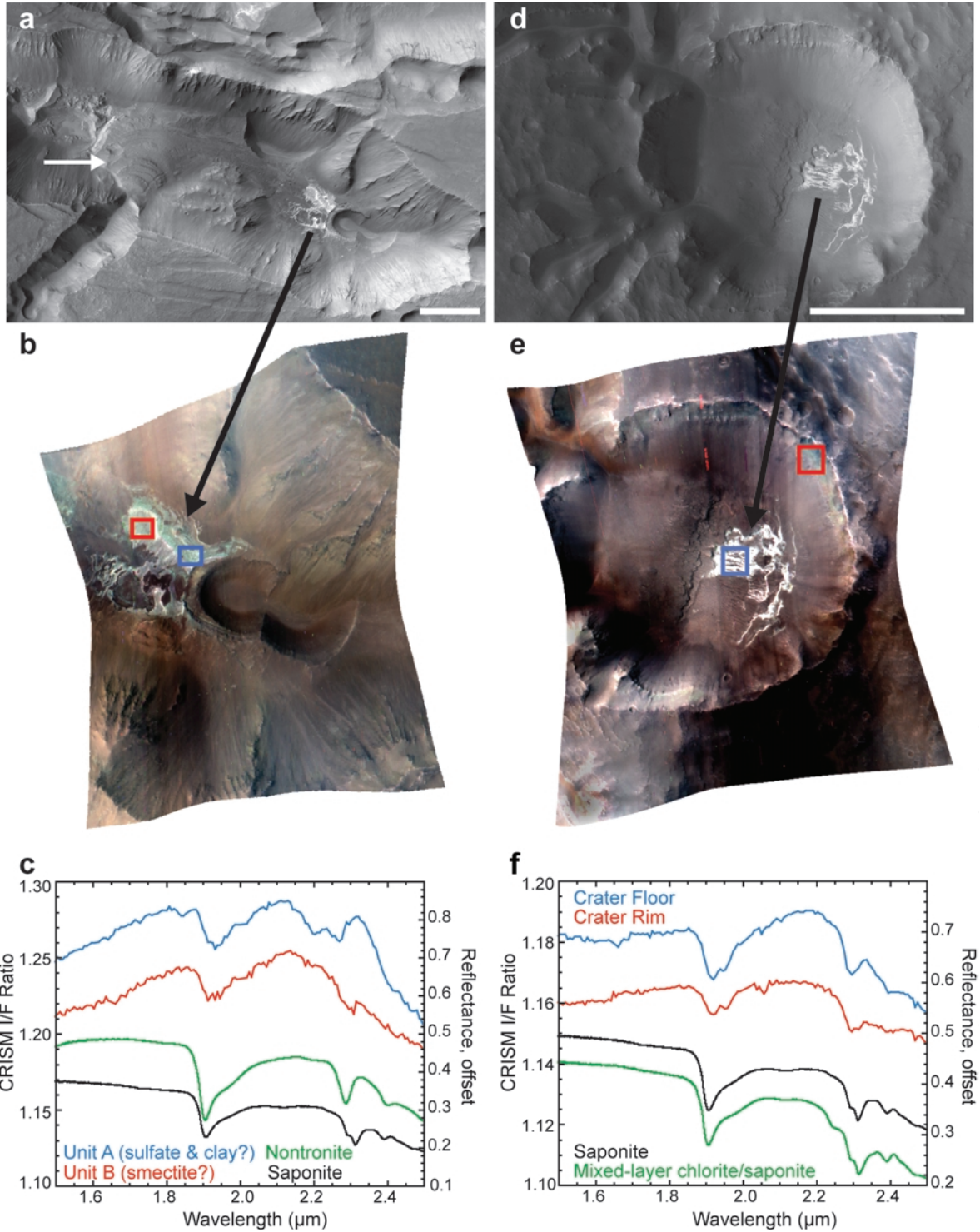
In terrestrial studies, detailed investigations of clay chemistry, crystallography, isotopic composition, and texture are crucial in informing the origin of clay minerals and their mechanism of formation. The techniques used in these studies, including electron microscopy and mass spectrometry of clay separates, are beyond current analytical capabilities for Mars missions, but they are discussed here because they highlight the complexity of the problem, and such techniques may be worth considering when planning future Mars missions.

ORBITAL DETECTION OF CLAY MINERALS ON MARS

Near infrared (NIR) reflectance spectroscopy is the main technique used for the orbital identification of phyllosilicates on the surface of Mars. Reflectance spectra are derived by dividing the amount of solar radiation reflected from the surface by the known solar flux at Mars distance. The first unambiguous orbital detections of clay minerals on Mars were made by the *Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité* (OMEGA) instrument onboard the Mars Express spacecraft (Poulet *et al.*, 2005; Bibring *et al.*, 2005). More recently, the greater spatial resolution of the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) instrument on NASA's Mars Reconnaissance Orbiter spacecraft has resulted in the detailed mapping of these deposits and the detection of additional types of clay minerals (Mustard *et al.*, 2008). To date, almost all major groups of clay minerals familiar from Earth have been detected on Mars, including kaolin, serpentine, illite/muscovite, smectite, and chlorite (Poulet *et al.*, 2005; Mustard *et al.*, 2008; Ehlmann *et al.*, 2009; Ehlmann *et al.*, 2010). The relative abundances of the various groups, however, differ on the two planets. Unlike Earth, where Al-rich phyllosilicates dominate, Fe/Mg-rich varieties are the dominant clay minerals detected on Mars (Poulet *et al.*, 2005; Mustard *et al.*, 2008; Murchie *et al.*, 2009), probably a result of a predominance of basaltic material in the Martian crust. Similar clay assemblages have been found in crust of Noachian age (>3.5 Ga) exposed on both sides of the Martian topographic dichotomy boundary (Figure 1e) that separates the rugged highlands in the south from the relatively flat lowlands of the north. However, most of the northern lowlands of Mars consist of post-Noachian terrains, and the majority of clay mineral deposits are found in the ancient (Noachian) southern terrains (Mustard *et al.*, 2008; Carter *et al.*, 2010). This apparent temporal-spatial segregation has led to the hypothesis that most Martian clays were formed during the earliest part of the planet's history, in the Noachian era (Bibring *et al.*, 2006).

The names used for the identification of clay minerals detected by imaging spectrometers like OMEGA and CRISM tend to be less specific than those used in terrestrial studies. Although NIR reflectance data can be used to distinguish between smectites, chlorites, micas,

serpentines, and possibly some mixed-layered clays (e.g. chlorite/smectite; Milliken *et al.*, 2011), some ambiguity exists in distinguishing between minerals within the different clay groups using NIR reflectance spectroscopy. This is because NIR spectra record vibrational



modes of H₂O and metal-hydroxyl bonds in clay minerals. The technique is somewhat less sensitive to the arrangements of those bonds in the crystal structure when compared with other techniques such as X-ray diffraction (XRD), the workhorse of the mineralogist working on terrestrial clay minerals. Clay-mineral detections on Mars are often reported as the name of the clay group qualified with the most abundant metal in the octahedral sites of the mineral structure (e.g. Fe/Mg-smectite or Al-smectite), as a means of further differentiating the types of clay minerals. Assigning to Martian clay minerals the more specific names that are used in terrestrial studies, or even differentiating unambiguously between di- and trioctahedral clay minerals, can be challenging with NIR data alone because the schemes of naming clays were developed based on crystallographic structure, element distribution, layer charge, and the bulk chemistry of these minerals. The payload for NASA's 2011 Mars Science Laboratory (MSL) rover, however, includes the CheMin instrument, which will analyze samples using XRD and X-ray fluorescence (XRF), giving crystallographic and chemical information about any phyllosilicates found (Sarrazin *et al.*, 2005). Moreover, because distinguishing between different types of clay minerals using these criteria has proven critical in providing paleo-environmental information on terrestrial lakes and restricted basins, and because it provides insight into why certain minerals form under certain conditions, this study follows the naming schemes of terrestrial studies on which the criteria are based.

TYPES OF AUTHIGENIC CLAY MINERALS FORMING IN TERRESTRIAL LAKES

A wide variety of authigenic clay minerals forms in terrestrial lakes, a product of: (1) the interplay between the diverse conditions characterizing these settings; (2) the array of physicochemical factors that determine the kind of clay mineral favored; and (3) a range of formation mechanisms. The main types of authigenic clays that form in terrestrial lakes and evaporative marine basins are summarized below. They have been split into Mg-rich and Fe-rich groups – a chemical

division that is useful for later discussions of formation conditions and mechanisms. For details of the chemistry and crystallography, readers are directed to clay mineral texts (e.g. Weaver, 1989; Moore and Reynolds, 1997; Meunier, 2005).

Mg-rich clay minerals

Many of the authigenic clay minerals forming in terrestrial lacustrine basins under alkaline and/or saline conditions are enriched in Mg (Calvo *et al.*, 1999; Jones and Deocampo, 2003). This occurs because evaporative concentration of lake waters in hydrologically closed basins where bicarbonate (HCO₃⁻) concentrations are greater than Ca²⁺ concentrations results in precipitation of calcium carbonate (CaCO₃), resulting in high pH and Mg-rich waters that tend to promote the formation of Mg-rich clay minerals (Gac *et al.*, 1977; Jones, 1986; Jones and Deocampo, 2003; Larsen, 2008). Commonly observed Mg-rich clay minerals include (1) several members of the smectite group, including saponite, stevensite, and hectorite; (2) Mg-chlorite; (3) fibrous clays such as palygorskite and sepiolite; (4) talc; and (5) various interstratified clay minerals such as kerolite-stevensite and corrensite (regularly interstratified chlorite-smectite) (Dyner, 1976; Jones and Galán, 1988; Chamley, 1989; Weaver, 1989; Turner and Fishman, 1991; Calvo *et al.*, 1999; Hay and Kyser, 2001; Hover and Ashley, 2003; Meunier 2005).

Fe-rich clays

The most abundant Fe-rich authigenic clay minerals that form in lacustrine settings are illites. The two main types found in hydrologically closed lakes are Fe-illite and illites with compositions and cation distributions similar to celadonitic-type micas (Kossovskaya and Drits, 1970; Hover and Ashley, 2003; Meunier, 2005; Deocampo *et al.*, 2009). Notably, illites contain significant amounts of Mg²⁺ and could have been included with the previous 'Mg-rich' group of this paper (e.g. see compositional analysis of authigenic illites by Hay and Kyser, 2001; Hover and Ashley, 2003). However, the factors promoting the formation of authigenic illite are different from those that produce the Mg-rich clays mentioned above, so they have been kept in the same

Figure 2 (*facing page*). Examples of closed basins on Mars exhibiting evidence for sediment deposition and hydrated minerals: (a) Context Camera (CTX) mosaic of Coprates Catena showing light-toned deposits, incised valley, and fan deposit (arrow); (b) CRISM false-color image (FRT00011DF2) showing locations of (c) spectral ratios indicative of possible smectites and sulfate salts; the latter are similar to those reported by Roach *et al.* (2010). The CRISM absorption near ~2.3 μm (red spectrum) is similar to features observed in lab spectra of Fe/Mg-smectites (green and black spectra). (d) CTX image of a possible crater lake near Shalbatana Vallis showing multiple inlet channels. (e) CRISM false-color image (FRT00008EBF) showing locations of (f) spectral ratios indicative of clay minerals (smectite) on the crater floor (blue spectrum) and possible mixed-layer chlorite-smectite in the crater wall (red spectrum); differences in symmetry of the 2.3 μm absorption are similar to those observed in lab spectra (black and green spectra) of smectite and chlorite-smectite. Clay minerals on the crater floor may have been transported from the crater wall, as shown by the channels that cut through those deposits. Alternatively, they may be authigenic, thus explaining the apparent difference in the spectral signatures. Scale bars in the lower right corners of (a) and (d) are 5 km. The CRISM spectra are ratios, where spectra from the area of interest have been divided by those from a spectrally 'bland' (e.g. dusty) area to enhance the absorption features.

group for simplicity in the discussion of formation conditions below.

Nontronite, an Fe-rich dioctahedral smectite, has also been reported to form in recent sediments of Lake Chad (Pedro *et al.*, 1978). Terrestrial occurrences of nontronite may be of particular interest because this ferric smectite has also been reported in stratified deposits on Mars (Figure 2; Poulet *et al.*, 2005; Ehlmann *et al.*, 2009; Milliken *et al.*, 2010).

Detrital clay minerals

Detrital clay minerals are an important, indeed often dominant, component of most lacustrine sediments, but the compositions of these minerals are controlled primarily by regional geology and weathering conditions in the catchment and thus may not be diagnostic of their ultimate depositional environment. One of the biggest challenges facing mineralogists studying Mars is to differentiate between authigenic and detrital minerals, an objective this manuscript aims to make easier through improved understanding of typical spatial and stratigraphic patterns of authigenic mineral assemblages in lacustrine environments.

CLAY-MINERAL FORMATION

In the discussion below, a variety of clay-mineral formation mechanisms important in lakes and restricted marine basins are encompassed under the term 'authigenesis,' although this term is not exclusive to clay minerals formed in these settings. A description of the mechanisms involved in authigenic clay-mineral formation in lakes is useful because it provides insights into why certain conditions favor the formation of certain types of clay minerals. The description also provides the basis for interpreting the spatial and temporal patterns in clay-mineral distribution in lacustrine deposits observed in the terrestrial sedimentary record. The different types of authigenic mechanisms also leave varied textural, geochemical, and crystallographic signatures that may provide clues about clay mineral genesis and locus of formation.

The authigenesis of lacustrine clay minerals is usually split into two categories: (1) the transformation of detrital precursor clay minerals that have been transported into the basin; and (2) direct mineral precipitation, termed neof ormation, from pore fluids or basin waters (Moore and Reynolds, 1997).

Transformation

Clay transformation involves the modification of an existing clay mineral with retention of some aspect(s) of the original texture, polytypic stacking of layers, crystallographic orientation, or composition (Moore and Reynolds, 1997). Transformation occurs in several ways. In one process, detrital clays may act as templates for the growth of new phyllosilicate material and early

hypotheses proposed that detrital, Al-rich, dioctahedral smectites (*e.g.* montmorillonite) acted as templates for the interstratification of new Mg-silicate layers (Jones and Weir, 1983; Jones, 1986). Since then, however, nano-scale observations and compositional measurements have provided evidence that new Mg-phyllosilicate material (typically stevensite) forms topotactic overgrowths on pre-existing clay particles rather than being truly interstratified (Banfield *et al.*, 1991b). Other studies have confirmed that this process occurred in several different basins in the past (Cuevas *et al.*, 2003; Hover and Ashley, 2003; Mayayo *et al.*, 2000) and that it is actively occurring in sediments of the Great Salt Lake, Utah (Jones and Spencer, 1999). Given the abundance of clay-mineral deposits on Mars with inferred saponitic (Mg-rich) compositions, worth noting is that the bulk compositions of these types of transformation products are often saponitic because they are intimate mixtures of neof ormed Mg-phyllosilicate overgrowths and the precursor Al-phyllosilicate.

Transmission electron microscope (TEM) studies also reveal that further transformations involve the preferential dissolution of Al-rich dioctahedral smectite components under the highest pH conditions (10 or more), leaving authigenic smectites with compositions closer to pure stevensite. In some cases the dissolution of smectite is accompanied by direct precipitation of celadonitic illite (Hover and Ashley, 2003).

Formation of palygorskite is often assumed to involve a dissolution-precipitation reaction of a detrital precursor, retaining some chemical components and signatures of the original clay and, therefore, counted as a transformation process (Jones and Galán, 1988 and references therein). Microscopic textural evidence such as "glomerules associated with cotton-wool like remains of montmorillonite and abundant fibrous laths of palygorskite" and other SEM images of palygorskite fibers forming from smectite (Jones and Galán, 1988, and references therein) support this assertion. The relatively high Al content and REE concentrations observed in palygorskites are thought to be inherited from detrital precursor materials (Torres-Ruiz *et al.*, 1994; Jamoussi *et al.*, 2003).

A recent study by Deocampo *et al.* (2009) provided evidence of transformation *via* an inferred solid-state mechanism. Based on XRD, infrared (IR) spectroscopy, and clay-mineral chemistry, Deocampo *et al.* (2009) reported an Mg-rich 2:1 clay mineral phase with intermediate octahedral occupancy. In addition, high-resolution TEM images (figure 6, Deocampo *et al.*, 2009) show abrupt lateral transitions of interlayers from a collapsed to an expanded state (*i.e.* from illitic to smectitic), indicating that transformation was localized. The preferred explanation by Deocampo *et al.* (2009) was that octahedral Al migrated to the tetrahedral sheet and was replaced by Mg, while the clay crystal structure remained intact. In addition to causing enrichments in

Mg, this transformation produced increased layer-charge that led to illitization. Despite the highly localized and heterogeneous nature of this transformation, thermodynamic constraints and diffusion rates at Earth-surface temperatures require the involvement of fluid (Ahn and Peacor, 1986), even if only in the hydrous interlayer (see descriptions of interlayer-by-interlayer transformation model by Altaner and Ylagan, 1997), so this process is probably not a solid-state transformation *sensu stricto*. Thus, even if authigenic minerals have a high degree of structural inheritance they are probably products of nano-scale dissolution-precipitation reactions (Velde and Meunier, 2008).

Also worth noting is that precursor materials need not be clay minerals. Siliceous diatom frustules can be transformed into phyllosilicates with stevensitic and saponitic compositions in saline lakes, the waters of which are saturated with respect to amorphous silica and have a pH >8.5 (Badaut and Risacher, 1983). As another example, nontronite peloids forming in recent deltaic deposits in Lake Chad were originally Fe oxide (Pedro, 1978). This may be particularly relevant for ancient Mars, and more details are discussed below.

Neof ormation

Clay minerals forming by direct precipitation tend to be Al-poor phases such as sepiolite, stevensite, and interstratified stevensite-kerolite (Meunier, 2005). Demonstrating that direct precipitation has occurred can sometimes be straightforward, as in the case of shiny, brown stevensitic ooids forming the “coffee ground” beds reported by Tettenhorst and Moore (1978) in lacustrine sediments of Eocene age of the Green River Formation, western USA. Formation *via* direct precipitation is supported by the purity of the clays (with the exception of quartz grains that commonly form cores), spherical morphology, and concentric internal structure. An accretionary precipitation process that is commonly observed in carbonate ooids is implied, and a modern analog has been described from the sediments of Lake Yoa in northeastern Chad, where stevensitic ooids precipitate with aragonite (Darragi and Tardy, 1987).

In the absence of macroscopic textures, microscopic textures have been used as indicators of direct precipitation. Neof ormed trioctahedral smectites may exhibit an unusual fibrous habit (Khoury *et al.*, 1982) or lath-shaped morphology (Pozo and Casas, 1999). Sepiolite has been reported precipitating inside secondary porosity such as burrows, desiccation cracks, veins, and fractures (Khoury *et al.*, 1982; Pozo and Casas, 1999; Calvo *et al.*, 1999). In addition, some neof ormed smectites (stevensitic) and celadonic clay minerals have a pseudohexagonal shape when viewed parallel to the *c* axis (Singer and Stoffers, 1980; Hover and Ashley, 2003).

As mentioned above, the concentrations of REEs and certain trace transition elements (TRTE) in clay minerals

have been useful in diagnosing the mechanism of formation. These elements tend to be conserved in detrital materials, and thus higher concentrations are retained in clay minerals formed by transformation. In contrast, clay minerals formed by direct precipitation tend to have lower REE and TRTE concentrations that reflect values typically found in lake waters and pore fluids (Torres-Ruiz *et al.*, 1994; Jamoussi *et al.*, 2003; Furquim *et al.*, 2008).

Influence of physicochemical conditions

Discussion of mechanisms of clay authigenesis reveals that the availability of reactive detrital material influences the types of authigenic clays that are formed. The chemistry of the fluids to which reactive materials are exposed is also crucial, with important physicochemical factors including pH, salinity, redox conditions, and the activity of Si, Mg, and K (Jones, 1986; Jones and Galán, 1988; Calvo *et al.*, 1999; Meunier, 2005; Deocampo, 2005). The current understanding of the influence these factors have on the types of authigenic clays that form is based in part on thermodynamic calculations (*e.g.* Badaut and Risacher, 1983; Jones, 1986; Birsoy, 2002; Klopogge *et al.*, 1999; Deocampo, 2005; Furquim *et al.*, 2008) as well as laboratory synthesis of clay minerals (*e.g.* Siffert, 1962; Harder, 1972, 1976; Decarreau, 1980). Theoretical and experimental studies typically do not take into account which reactants are available in natural settings or the strong influence of reaction kinetics, and results must ultimately be reconciled with observations from modern and ancient sedimentary basins to obtain a full understanding of physicochemical controls.

Evaporative concentration has a major influence on the evolution of brine chemistry in closed lakes and evaporative marine basins. The following discussion of the types of authigenic clays that form in these systems (and the summary shown in Figure 3) is presented in order of increasing salinity. The chemistry of solutions evolves along different pathways during concentration, depending on the starting fluid composition. For example, the dominant anion in solution determines how pH will change as salinity increases. Evaporative concentration of a solution with an initial composition in which $[\text{HCO}_3^-] > [\text{Ca}^{2+}]$ will cause pH to increase and produce a carbonate-rich brine. In contrast, if sulfate and/or chloride are the main anions then brines will tend to maintain circum-neutral pH levels even in the most saline solutions. Because pH influences the types of authigenic clay minerals that form in these environments, the following discussion (and Figure 3) makes a distinction between chloride/sulfate-dominated and carbonate-dominated brines.

More detailed descriptions on the topic of brine evolution, including the concept of chemical divides, can be found in Drever (1997) and Jones and Deocampo (2003). Tosca *et al.* (2005) used chemical divides to

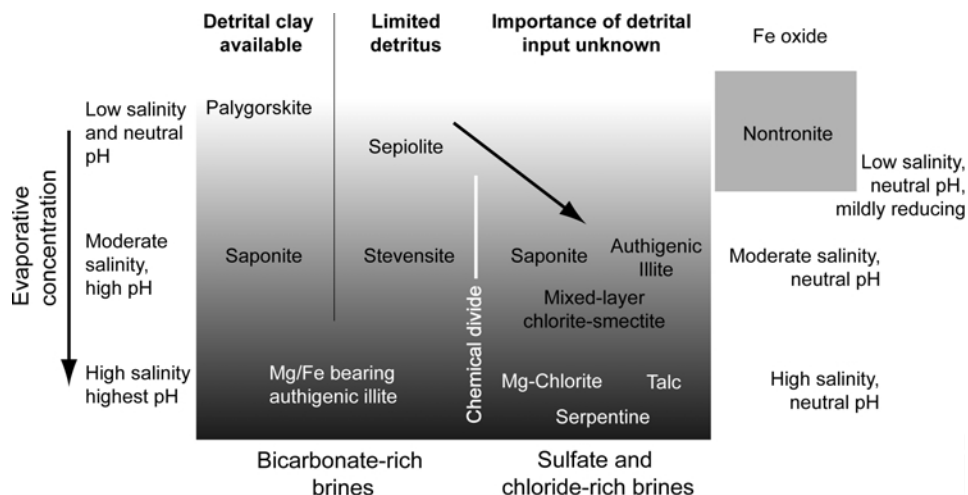


Figure 3. Summary of the different types of authigenic clay minerals favored under different chemical conditions. The influence of the availability of reactive detrital clay minerals on the types of clay minerals that form is shown where known. Clay minerals forming in the most dilute solutions are shown at the top of the diagram and those forming from more concentrated fluids are at the bottom of the figure. As solutions are concentrated, the changes in pH depend on the dominant anion in the fluid (*i.e.* where the initial fluid composition falls in terms of the chemical divide). Bicarbonate-rich fluids will become more alkaline as they are concentrated, whereas saline chloride/sulfate-rich fluids will remain at circum-neutral pH. Palygorskite and sepiolite form in brackish waters with compositions from both sides of the chemical divide, hence the diagonal arrow shown in the diagram. The mineral assemblage on the left side of the chemical divide (bicarbonate-rich fluids in alkaline lakes) is based on the work of Jones and Galán (1988). The neutral saline assemblage (right side of the chemical divide) is a summary of Weaver (1989). Nontronite, which forms in recent sediments of Lake Chad (Pedro, 1978), is uncommon in terrestrial lakes and requires inputs of Fe oxide, a situation that may be more common on Mars.

understand the evolution of Martian brines that would give rise to mineral assemblages observed in Martian meteorites and detected by orbital and *in situ* instruments, including sulfate-bearing sandstones examined by the *Opportunity* rover at Meridiani Planum. Such concepts are important for understanding the full mineral assemblages that might form from a given fluid, a critical step in being able to identify possible lacustrine deposits in the Martian rock record.

Controls on the formation of Mg-rich clays

Brackish waters with moderate pH and high silica activity tend to favor the formation of the fibrous clay minerals palygorskite and sepiolite, as opposed to trioctahedral Mg-smectites with phyllosilicate structures (Weaver and Beck, 1977; Weaver, 1989; Bellanca *et al.*, 1992; Webster and Jones, 1994; Calvo *et al.*, 1999). The formation of fibrous clay minerals is thought to be favored under brackish conditions because of their water-accommodating structure (Jones and Galán, 1988). In saline lake systems, palygorskite formation is confined to marginal areas at the boundary of lacustrine and alluvial deposits where pedogenic processes dominate and the detritus to water ratio is high, such as in calcretes and mudflats where solutions remain dilute (Jones and Galán, 1988; Webster and Jones, 1994; Calvo *et al.*, 1999). In addition, abundant palygorskite formed during the Miocene in shallow, brackish, peri-marine waters that covered large parts of the southeastern

United States. These clay mineral deposits are associated with chert and phosphates (Weaver and Beck, 1977; Weaver, 1989).

Experimental studies and thermodynamic calculations indicate that sepiolite should be favored at higher pH levels and lower Al activities than palygorskite and, thus, in settings starved of reactive detrital minerals (Siffert, 1962; Birsoy, 2002; Meunier, 2005). Sepiolite has mainly been reported from marginal lacustrine areas in ponds and marshes close to springs (Khoury, 1982), between the toes of alluvial fans (Calvo *et al.*, 1999), in small lakes during periods when waters were dominantly brackish (Webster and Jones, 1994), as well as in older calcareous soils where Al is immobilized (Calvo *et al.*, 1999).

Higher salinity, higher pH (*i.e.* bicarbonate-dominated solutions), and lower silica activities tend to favor phyllosilicate formation (*e.g.* saponite, stevensite, interstratified stevensite-kerolite, and hectorite). These minerals are commonly found in marginal to open-water lacustrine deposits of alkaline systems, in carbonate-rich sediments that sometimes contain traces or pseudomorphs after gypsum (Dyini, 1976; Calvo *et al.*, 1999; Larsen, 2008). The specific type of trioctahedral smectite formed depends on the authigenic mechanism, which is influenced by the amount of detrital clay minerals in the sediment and the chemical conditions. As discussed previously, transformation of detrital precursors tends to produce clay minerals with saponitic

compositions (although evidence for the direct precipitation of saponite has also been documented, see Mees, 2001; Furquim *et al.*, 2008). Hectorite contains octahedral Li, and whether stevensite or hectorite forms is ultimately determined by the chemistry of inflowing waters and, therefore, the geology of the lake catchment. Given the dearth of more evolved, silicic lithologies in the Martian crust, to find Li enrichment in Martian clay minerals would be rather surprising. In interstratified smectite-kerolite bearing deposits, which contain varying proportions of stevensite and kerolite, oxygen isotope compositions of the clays indicate that increased numbers of stevensite layers are associated with more saline conditions (Hay *et al.*, 1995).

At high pH (>8.5) the formation of trioctahedral Mg-smectite does not require fluids to have high Mg activity (Badaut and Richet, 1983). Badaut and Richet (1983) found trioctahedral smectites forming in numerous saline lakes in Bolivia where Mg concentrations ranged from 34 to 1900 mg/L. In contrast, high Mg activity becomes more important for Mg-smectite formation at lower pH values (*i.e.* in chloride/sulfate-dominated systems). For example, in the only reported instance of saponite forming in a modern marginal marine evaporative environment (at pH ~8), in Salina Ometepc, Baja California, saponite forms because of a ten-fold concentration of Mg in solution through evaporation of seawater and precipitation of gypsum (Hover *et al.*, 1999; Martini *et al.*, 2002). This depositional setting is unusual because little carbonate is precipitated, and so Mg is incorporated into clay minerals instead. These observations are in agreement with the experimental findings of Harder (1972), who showed the lower threshold of Mg activity in solution required to allow smectite formation decreases with increasing pH.

Saponite, corrensite, chlorite, chloritic interstratified clay minerals, and talc are found in a number of ancient evaporitic sequences where brines were largely derived from seawater (chloride-dominated) and did not become alkaline during evaporative concentration. The authigenic clay minerals in these deposits tend to be associated with evaporite minerals, whereas muddier interbeds, possibly representing the influx of fresh water, contain mostly detrital clay minerals (Weaver, 1989). This may indicate that elevated salinity is required for Mg-clay authigenesis at moderate pH or that rates of deposition were too high in siliciclastic-rich intervals for clay authigenesis to take place (Calvo *et al.*, 1999). The influence of salinity on the products of clay-mineral authigenesis is implied, however, by a systematic increase in the degree of chloritization of interstratified chlorite-smectite through a typical evaporite cycle in the Paradox Formation in Utah (Weaver, 1989).

Terrestrial saline environments with chloride/sulfate-rich waters may be particularly relevant analogs for Mars given the orbital detections of chloride (Osterloo *et al.*, 2008) and abundant sulfate salts in local topographic

basins (*e.g.* Gendrin *et al.*, 2005; Wray *et al.*, 2009; Milliken *et al.*, 2010; Roach *et al.*, 2010). The current knowledge of clay authigenesis in these types of systems is largely based on studies of terrestrial Paleozoic deposits, however, and determining which of the clay minerals represent original authigenic assemblages and which may have been subject to alteration during burial diagenesis is difficult (Weaver, 1989). Unfortunately, more recent studies of clay minerals in evaporite sequences are lacking. Detailed studies of the clay mineralogy of younger terrestrial evaporite successions may, therefore, be a fertile area of research for scientists looking for Martian analogs.

Controls on the formation of Fe-bearing clays

Nontronite rarely forms in terrestrial lacustrine settings. An exception is nontronite reported from the deltaic deposits of the River Chari in the SE corner of Lake Chad. The nontronite occurs as 5–15 cm thick beds of peloids in deltaic deposits and is found exclusively in recent sediments. Nontronite is thought to form through the reaction of Fe oxide grains (goethite) with silica in lake waters at neutral pH, at the redox interface. The recent influx of large amounts of Fe oxide into the delta is posited as a response to vegetal and soil degradation in the catchment. This occurrence appears to be anthropogenically induced and nontronite does not commonly occur in terrestrial lakes. The situation may have been different on Mars because Fe oxides are abundant (*e.g.* Singer, 1982; Morris *et al.*, 1989; Bell *et al.*, 1993; Christensen *et al.*, 2000, 2001; Bibring *et al.*, 2005, 2007; LeDeit *et al.*, 2008). Iron oxides transported to standing bodies of water could, thus, act as nucleation sites for nontronite formation if conditions were locally reducing. Interestingly, nontronite forming in Lake Chad is Al poor (<1 wt.% Al₂O₃ in the most mature samples) when compared with nontronites forming *via* the alteration of ocean basalts and in weathering profiles (Weaver, 1989). This may be a potential means of distinguishing lacustrine nontronite on Mars.

Reports of authigenic illite in terrestrial lacustrine environments are less frequent than Mg-smectites and fibrous clay minerals. This might be because illite is a common product of weathering and diagenesis; therefore, authigenic illites are easily misidentified as a component of recycled detrital sediments. Interestingly, the opposite could be the case on Mars because illite deposits (and other Al-rich clay minerals) are rather uncommon (*e.g.* Mustard *et al.*, 2008; Ehlmann *et al.*, 2009; Murchie *et al.*, 2009).

Most terrestrial authigenic illite forms in one of two lacustrine settings: (1) basin depocenters, where waters and porefluids have the highest salinities and pH; (2) playa settings or mudflats with strong evaporative concentration (Turner and Fishman, 1991; Hay *et al.*, 2001; Hover and Ashley, 2003; Larsen, 2008).

The high concentration of Fe in many authigenic illites suggests that the presence of this mineral may be used to infer reducing conditions. This is only true in some cases, however, because authigenic illite can form by two mechanisms. The first involves increase in the layer charge of a smectitic precursor by replacement of trivalent octahedral cations (Al or Fe(III)) with Mg, along with substitution of some Al into the tetrahedral sheet. The products of this reaction are celadonic illites, as observed at the center of several paleolakes forming under the highest pH and salinity conditions (Hay and Kyser, 2001; Hover and Ashley, 2003; Deocampo, 2004, 2005; Larsen, 2008; Deocampo *et al.*, 2009). This illite may still contain significant Fe, but most of the Fe seems to be inherited from precursor minerals. For example, Singer and Stoffers (1980) showed that the progressive illitization of smectitic clays during lake evaporation involved increased Mg and K content of the clay minerals and conservation of Fe at ~8 wt.% oxide. Furthermore, this transition is inferred to have occurred under oxidizing conditions based on the red color of the mud and the apparent immobility of Fe³⁺.

Fe-illites, on the other hand, derive layer charge from the tetrahedral sheets (Kossovskaya and Drits, 1970). The formation of Fe-illite may be analogous to the process of glauconization more commonly observed in marine sediments on continental shelves where depositional rates are low (Meunier and El Albani, 2007). Although Fe in Fe-illite is predominantly in the oxidized state (Fe(III)) (Keller, 1956; Parry and Reeves, 1966), authigenesis involving migration and fixation of Fe and K in the mineral has been proposed. Mobilization of Fe from ferro-magnesium detritus requires reducing conditions, such as in microenvironments centered around organic debris or at a redox interface in sediments (Meunier and El Albani, 2007). True glauconite, which tends to have a marine origin, and Fe-illites that form primarily in continental settings, are compositionally different (Kossovskaya and Drits, 1970). Why Fe-bearing micaceous minerals forming in different environments evolve toward different compositional end members is unclear, but note that Fe-illites thought to have formed *in situ* are reported from Cambrian and Precambrian marine sedimentary rocks (Berg-Madsen, 1983; Deb and Fukuoka, 1998).

Authigenic illite in lacustrine settings is commonly found with authigenic K-feldspar, analcime (a sodium zeolite), and in some cases opal (Singer and Stoffers, 1980; Hay *et al.*, 1991; Turner and Fishman, 1991; Hay and Kyser, 2001; Larsen, 2008). Interestingly, both illite and analcime have recently been identified on Mars (Ehlmann *et al.*, 2009). Opal, which has also been identified on Mars (Milliken *et al.*, 2008; Squyres *et al.*, 2008), may form because of the increased solubility of silica at elevated pH.

In terrestrial deposits, the co-occurrence of K-feldspar and illite has been used to support the idea

that high K activities in solution is important in promoting illitization (*e.g.* Singer and Stoffers, 1980, but see Deocampo *et al.*, 2009, for another point of view). The formation of analcime from precursor zeolites in Na-rich brines releases K⁺, providing a possible reason why these minerals are found together (Singer and Stoffers, 1980). In an alternative formation mechanism proposed for playa settings, Al³⁺ and Si⁴⁺ are supplied by the preferential dissolution of smectite at elevated pH and high Na concentration, which can result in the precipitation of analcime (Remy and Ferrell, 1989). Laboratory experiments have demonstrated the importance of high pH and repeated wetting and drying in promoting low-temperature illitization of smectites (Eberl *et al.*, 1993), factors that could be particularly important for illitization in lacustrine settings. Finally, note that Fe-illite has also been reported in marine evaporite sequences but appears to be absent from intervals corresponding to the highest inferred salinity values (Weaver, 1989 and references therein).

STRATIGRAPHIC DISTRIBUTION OF LACUSTRINE CLAYS

The previous discussion demonstrates the potential utility of authigenic clay minerals as indicators of chemical conditions within a basin, assuming they can be identified confidently as forming *in situ*. As pointed out in the introduction, the basaltic composition of the Martian crust means that the types of clay minerals that typically form authigenically in saline/alkaline lakes and evaporative basins on Earth probably form by a variety of processes on Mars in a variety of environments. As a result, clay mineral composition alone cannot be used to identify Martian clay mineral deposits as authigenic. Complete characterization of the accompanying mineral assemblage would certainly help in this regard, but full alteration assemblages are often not observed in existing orbital data (Milliken *et al.*, 2009).

Fortunately, lakes are dynamic environments and often exhibit considerable spatial and temporal chemical variability. Under the right conditions this diversity is recorded in authigenic mineral assemblages, including clay minerals present in sediments, and can give rise to distinctive spatial and stratigraphic arrangements of mineral facies (an idealized schematic diagram of a closed alkaline basin is shown in Figure 4 as an example). The following section discusses the spatial and stratigraphic trends in clay mineralogy of a number of ancient terrestrial examples, with the aim of informing criteria for recognizing authigenic clay minerals in ancient lacustrine environments on Mars.

Lateral zonation of authigenic clay minerals

The hydrology of closed-lake basins, in which water is supplied at the periphery and lost by evaporation from the lake surface, often results in lateral gradients in

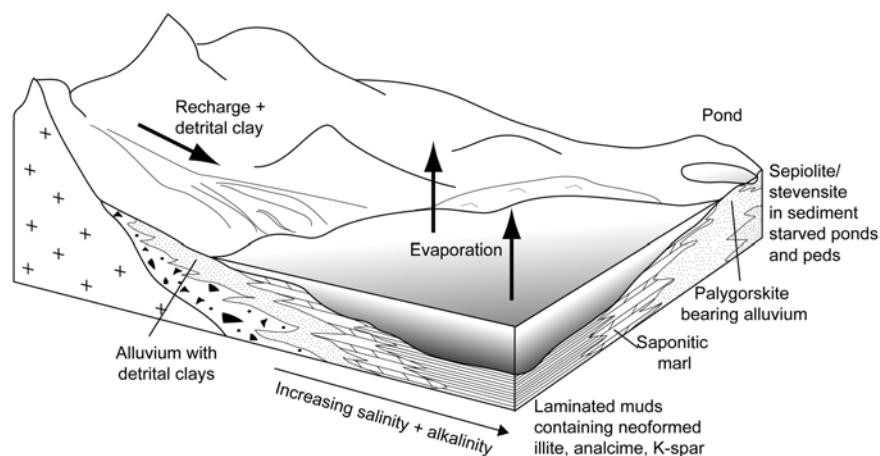


Figure 4. Schematic diagram showing the distribution of clay minerals (authigenic and detrital) in an idealized alkaline lake (adapted from similar diagrams in Calvo *et al.*, 1999; and Meunier, 2005).

aqueous chemistry. As water moves toward the center of a particular basin, its salinity, pH, and chemical composition evolve in response to evaporative concentration and mineral precipitation, with the most concentrated brines typically found at the depocenter (Surdam and Sheppard, 1978).

The lateral variability in chemical conditions and availability of detrital clay minerals leads to the formation of mineralogical facies and compositional gradients in the chemistry and species of authigenic clay minerals (Figure 4). The concentric zonation pattern commonly observed in carbonate and evaporite minerals is also observed in authigenic clay minerals in several basins. This distribution pattern was first described by Millot (1964), who proposed that clay minerals in the center of closed basins are enriched in Mg^{2+} and depleted in Al^{3+} relative to those at the lake margin. The compositional gradient corresponds to a change from a dominantly detrital to an authigenic mineral assemblage toward the basin center.

A comparison of clay mineral chemistry of recent (<25 ky old) sediments of the Great Salt Lake to the chemistry of detrital clay minerals from streams feeding the lake provides an example of a compositional gradient produced by clay-mineral authigenesis (Jones and Spencer, 1999). Although clay minerals from both sites are smectitic, compositional analyses show that those in the lake sediments are enriched in Mg^{2+} and Si^{4+} relative to the detrital clay minerals (Jones and Spencer, 1999). Multiple studies have found that the highest Mg^{2+} concentrations in authigenic clays in Pliocene Lake Olduvai are in deposits near the lake center (Hay and Kyser, 2001; Hover and Ashley, 2003; Deocampo, 2004; Deocampo *et al.*, 2009). This is in agreement with a corresponding enrichment in $\delta^{18}O$ of authigenic minerals from the basin depocenter, which also indicates that clay mineral authigenesis is tied to evaporative concentration of lake waters (Hay and Kyser, 2001).

Probably the oldest terrestrial example of the concentric arrangement of mineral facies is Jurassic Lake T'oo'dichi', a lake that covered a $500\text{ km} \times 300\text{ km}$ area just east of the four corners region (where Utah, Arizona, New Mexico, and Colorado meet) in the southwestern US. In this system the mineralogy of altered ash beds consists of concentric mineral zones: smectite – clinoptilolite – analcime \pm K-feldspar – albite, arranged from the margin to the center of basin, respectively. A corresponding systematic increase in the proportion of illite in interstratified I-S of ash beds toward the central and most saline part of the basin is also observed (Turner and Fishman, 1991). Authigenic chlorite is also present but is restricted to tuff beds in the central part of the lake.

Mineralogical zonation is also observed in the Eocene Green River Formation, another large, long-lived lacustrine system in the western US. Dyni (1976) studied the distribution of clay minerals in the Parachute Creek Member in northeastern Utah, a unit that was deposited when the lake was hydrologically closed. Hectorite is the dominant clay mineral in the marginal lacustrine marls and oil shales, making up to ~40 wt.% of the whole rock (Bristow, unpublished data), whereas temporally equivalent deposits in the center of the basin contain less clay, which is dominantly illitic. An authigenic origin for this illite is suspected, but more detailed studies are needed for confirmation. The monomineralic nature of the authigenic clay minerals in these lake deposits is in sharp contrast with the heterogeneous clay mineral mixtures in fluvial deposits at the edge of the basin, which contain mixtures of smectite, kaolinite, and illite.

Lateral changes in clay mineralogy are accompanied by changes in the types of carbonate, feldspar, zeolite, and evaporite minerals in the Parachute Creek Member (Dyni, 1976; Cole and Picard, 1978). This supports the hypothesis that clay minerals provide a valid record of variable environmental conditions. Similar mineralogi-

cal facies are observed in transects through Pliocene–Pleistocene Lake Tacopa beds in eastern California (Larsen, 2008).

Several evaporative continental basins that developed in Spain during the Tertiary also exhibit concentric mineral zones. Sepiolite and palygorskite are common clay mineral components in alkaline soils and ponds around the lake periphery, whereas stevensite, saponite, and interstratified kerolite-stevensite are the main clay minerals in mudflats and marginal lake sediments (see review by Calvo *et al.*, 1999). Short-term hydrological change, on the order of thousands of years, is commonly recognized in specific locations and expressed as vertical, meter-scale transitions in mineralogy. For example, green Mg-smectite-rich marls of Miocene age were deposited in the marginal lake environments of the Madrid basin and are overlain by and in transitional contact with pink, mottled, root-bioturbated mudstones containing interstratified kerolite-stevensite. These units are interpreted as shallowing upward cycles, with higher salinities and pH promoting the formation of interstratified kerolite-smectite as water depths decreased (Pozo and Casas, 1999).

This last example shows that concentric mineralogical facies are temporal snapshots and that over time the distribution, composition, and location of mineral facies will change with lake level. More examples of the stratigraphic arrangement of authigenic minerals and drivers are discussed below. Note that chemical gradients and, therefore, mineral zonation patterns in lakes are not always concentric (Calvo *et al.*, 1999). Freshwater inputs in Lake Chad, for example, come mainly from rivers that enter the lake from its southern end (Figure 5), and lake waters become concentrated *via* evaporation toward the north. As previously discussed, recent sediments in the southern deltaic deposits are rich in nontronite (Pedro, 1978). Central lake sediments, on the other hand, mainly contain Fe/Al smectites that are probably detrital, whereas sediments at the northern end contain stevensite that forms in response to evaporative concentration (Figure 5) (Chamley, 1989).

Cyclical changes in response to external forcing

Lakes are sensitive to a number of external factors which cause changes in hydrological balance and which may also be recorded in the mineralogy of their sediments. At timescales on the order of tens to hundreds of thousands of years, orbital-forcing causes changes in temperature, seasonality, precipitation, and evaporation rates in a lake's catchment (*e.g.* Morrill *et al.*, 2001, Cohen, 2003). These hydrological changes result in lake level changes that may impact lake chemistry and the circulation of basinal brines (Jones and Deocampo, 2003; Larsen, 2008). In Pleistocene-Holocene sediments from the Double Lakes Formation in West Texas, repeated changes in lake level and salinity produced meter-scale cyclical changes in the assemblage of

authigenic clay minerals (Webster and Jones, 1994). Palygorskite dominates horizons representing ephemeral lake stages when pedogenic processes were active. When the lake was filled, brackish conditions and a reduced flux of detritus favored sepiolite formation, whereas Mg smectite formed under more saline conditions when lake levels dropped (Webster and Jones, 1994).

The Jurassic lake cycle sequences in the Connecticut Valley of the northeastern US exhibit meter-scale variability in mineral assemblages caused by intermittent clay mineral authigenesis. A typical cycle consists of (1) a lower marginal lacustrine, gray mudstone, mainly containing detrital illite and chlorite; (2) black shale, representing elevated lake level, containing authigenic saponite and illite of unknown origin; and (3) upper gray mudstones containing interstratified chlorite-smectite and analcime that were deposited as lake level was dropping (as evident from ripple marks, mudcracks, and dinosaur footprints) (April, 1981a, 1981b).

The sediments of Owens Lake, east of the Sierra Nevada, California, demonstrate the importance of hydrologic closure for authigenic clay mineral formation. Over the past 800 ka the lake was an intermittently hydrologically open and closed system, with changes coinciding with glacial-interglacial cycles. The clay-size fraction of sediments deposited during periods when the lake was hydrologically closed (interglacial cycles) contains an authigenic, smectitic Mg silicate, whereas detrital illite is the predominant clay mineral in sediments deposited during glacial times when the

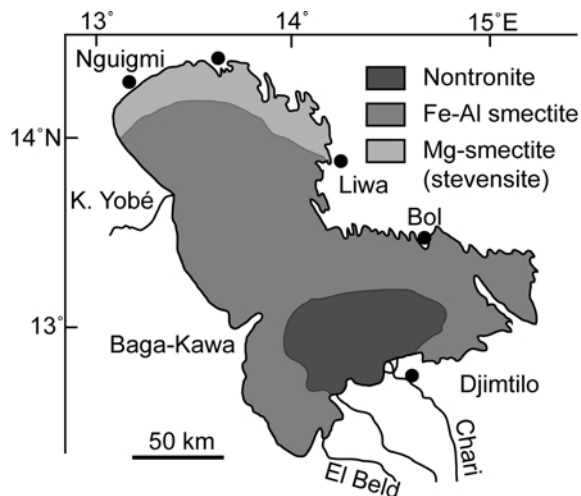


Figure 5. The spatial distribution of clay minerals in Lake Chad, after Chamley (1989). A concentration gradient forms as a result of the freshwater flux being concentrated at the south end of the lake. Nontronite forms in recent deltaic sediments as a result of inputs of Fe oxides from soil degradation in the river catchments. Much of the lake sediment contains Fe-Al smectite which is probably detrital. In contrast, more saline lake waters at the northern end of the lake favor clay authigenesis where the main product is stevensite.

climate was wetter and Owens Lake was flushed (Figure 6) (Bischoff *et al.*, 1997; Menkin, 1997). An increased carbonate content of sediments corresponds with the presence of smectites, supporting the idea that clay mineral authigenesis was favored by increased alkalinity that built up when the lake did not have an outlet (Figure 6) (Bischoff *et al.*, 1997).

Even where changes in the type(s) of clay minerals being formed are not obvious, changes in clay composition have been used as a proxy for lake salinity/alkalinity. Deocampo (2004) compared the octahedral cation index (OCI = $Mg/(Fe + Al)$) of a series of authigenic interstratified illite-smectites deposited over a period of ~18,000 y at the center of Pliocene paleolake Olduvai, East Africa, and found an inverse correlation between OCI and inferred lake level. High OCI values, and thus Mg concentration in octahedral sites of clay minerals, correspond to the most saline and alkaline conditions in this depositional system (Deocampo, 2004).

Step changes

In addition to orbitally induced changes, lake hydrology is subject to stepwise forcing related to tectonic control. Tectonic processes determine accommodation space and the elevation of basin spillways, and influence the flux of sediment and water to a basin (Carroll and Bohacs, 1999). These processes control the degree of hydrologic closure in a basin and, therefore, influence stratigraphic trends in the relative abundance of detrital *vs.* authigenic clay minerals. For example, the majority of clay minerals formed in the oldest deposits of the eastern part of the Oligocene to Miocene As Pontes Basin, Spain, were sepiolite and palygorskite

because the basin was hydrologically closed (Saez *et al.*, 2003). Subsequently, a tectonically induced increase in the size of the catchment led to open hydrologic conditions. At this stage, deep, organic-rich, lacustrine deposits consisted of a modified detrital clay-mineral assemblage of illite and kaolinite. Al smectites are present in surrounding alluvial deposits but are absent in the lake sediments. The transformation of smectite into kaolinite under the acidic conditions present in the organic-rich sediments has been proposed because the enrichment of kaolinite is more pronounced in peat accumulating in shallow, swampy parts of the basin at the same stage (Saez *et al.*, 2003).

As another example, the Ridge Basin of Miocene age is a well documented strike-slip basin in the central Transverse ranges of southern California the hydrology and mineralogy of which were strongly tied to tectonic processes. It contains a thick (14 km) package of lacustrine, fluvial, and alluvial sediments that were deposited over ~7 m.y. (Crowell, 2003). Paleolimnological conditions, including water depth and degree of hydrological closure, varied considerably over this period. For much of the time, lacustrine muds contained a mixture of clay minerals such as smectite, kaolinite, and illite, which appear to be detrital (Smith, 1982). In contrast, the 1 km thick Posey Canyon Shale, a unit deposited in a deep-water lacustrine setting and consisting of analcime-bearing, dolomitic mudstone, contains only illite (Smith, 1982). The presence of analcime, rare occurrences of gypsum and fossil evidence indicate alkaline, saline water chemistry. The reaction of smectite and kaolinite to form analcime under alkaline conditions is suggested (Smith, 1982; Link, 2003). These

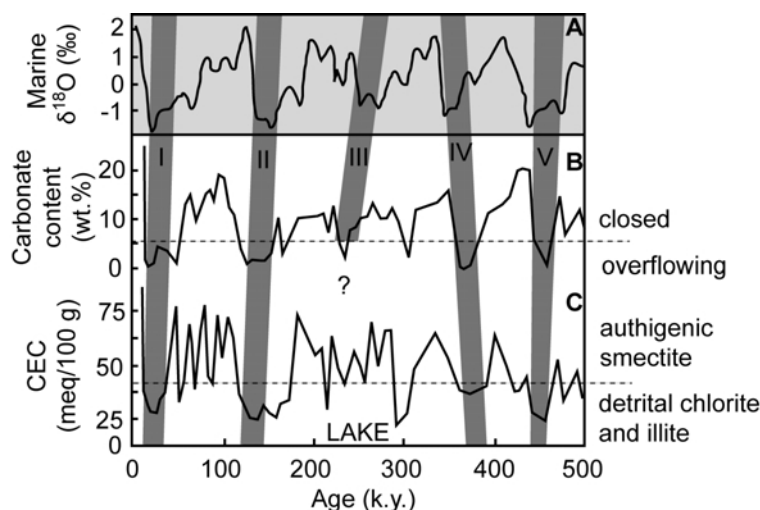


Figure 6. Comparison of the marine stable oxygen isotope record (panel A), showing global glacial-interglacial transitions (labels I–V are glacial intervals), with the carbonate content (panel B) and cation exchange capacity (CEC; panel C) of Owens Lake sediments, based on Bischoff *et al.* (1997). During glacial periods, Owens lake overflowed, the waters were fresh, the carbonate content of sediments was low, and clay minerals were mainly detrital chlorite and illite (which have low CECs). During interglacial periods a reduced flux of water to the lake caused it to become hydrologically closed and waters became saline and alkaline. The result was precipitation of carbonate and transformation of clay minerals into Mg smectites (with higher CECs).

results imply that illite is the last surviving remnant of the detrital clay mineral assemblage. The associated minerals and chemical conditions of the system raise the possibility that the illite could be authigenic, however. Although the exact origin of this illite remains open to interpretation, the Ridge Basin, nevertheless, provides evidence of tectonically controlled changes in hydrologic conditions that influence the stratigraphic distribution of clay mineral assemblages.

DISCUSSION

The previous sections clearly reveal that the formation of different types of lacustrine authigenic minerals, and specifically clay minerals are favored by different physicochemical conditions, and are influenced by the availability of reactive detritus, giving rise to distinctive spatial and stratigraphic arrangements of mineral facies. In the following discussion focus is moved to how this knowledge may be applied to identifying possible authigenic lacustrine clay mineral deposits on Mars.

Over the longest timescales, often represented by thicker sedimentary successions, a comparison of the clay mineralogy of units deposited during hydrologically closed and open intervals may reveal mineralogical differences produced by authigenesis. On Earth, the hydrology of ancient basins can be determined independently by a number of means, such as the presence of chemical sediments, stable isotope measurements made on those chemical sediments, and fossil evidence. The hydrology of Martian basins has been inferred largely from geomorphic evidence (*e.g.* Fassett and Head, 2005). Sedimentary intervals rich in sulfates, chlorides, or carbonates are also likely to be indicators of closed hydrologic conditions. A comparison of the clay mineralogy of neighboring basins with similar detrital inputs under the influence of different hydrologic conditions would provide a straightforward test for identifying the potential products of clay authigenesis.

Stratigraphic exposures on Mars for which sedimentary units can be followed from the periphery of the basin to the center, would make ideal targets in the search for the concentric distribution of clay minerals that result from lateral chemical gradients in closed basins. If possible, these types of surveys should also examine the mineralogy of distributaries feeding the basin, including fluvial, alluvial, and deltaic deposits, which are likely to contain unaltered clay detritus.

The concentric arrangement of clay minerals, however, is not a unique feature of closed sedimentary basins. Clay minerals produced by impact-induced hydrothermal alteration could form alteration halos around impact craters because of lateral changes in water/rock ratios and temperature gradients (Schwenzer and Kring, 2009). Alteration products related to impacts tend to occur in vugs, veins, and cracks tracking fluid pathways and do not necessarily follow bedding or

stratification (Hagarty and Newsom, 2003). Even in systems where hydrothermal fluids alter stratified sedimentary deposits, the passage of fluids and, therefore, the distribution of secondary minerals (including clay minerals) will not necessarily coincide with primary sedimentary bedding. In contrast, the products of clay mineral authigenesis are intimately related to the conditions in the basin at the time of sedimentation. Stratigraphic variations in clay mineralogy may coincide with sedimentary and other mineralogical indicators of changing water level, perhaps in a cyclical fashion if a regular external forcing mechanism is active. For instance, the lateral and vertical distribution of authigenic clay minerals may coincide with the abundance and type of evaporite minerals that are not normally associated with impact-related hydrothermal activity.

Martian authigenic clay assemblages

Two main uncertainties arise when trying to predict the types of authigenic clay minerals that may have formed in ancient Martian sedimentary basins. The first stems from the lack of information concerning the chemistry of waters occupying the basins. Based on the widespread occurrences of sedimentary sulfate deposits on Mars (and to a lesser extent chlorides), it seems likely that many contained sulfate-chloride-rich waters. Although the presence of Al- and Fe(III)-bearing sulfates (*e.g.* alunite and jarosite) in some locations implies acidic conditions (*e.g.* Klingelhöfer *et al.*, 2004; Tosca *et al.*, 2005; Morris *et al.*, 2006; Johnson *et al.*, 2007; Milliken *et al.*, 2008; Wray *et al.*, 2009), the global distribution and abundance of these minerals is poorly constrained. In addition, many sulfate deposits identified from orbit are consistent with Mg- and Ca-sulfates (Gendrin *et al.*, 2005), and these phases do not require highly acidic or alkaline conditions and suggest that many basins could have remained at circum-neutral pH even after concentration *via* evaporation. In this case salinity would be the primary control on the types of authigenic clay minerals forming, as is observed in some marine evaporative sequences on Earth. The stability of liquid water on the surface of ancient Mars would have required a thicker atmosphere, however, and if this atmosphere were dominated by CO₂, as it is today, then some basins may have contained carbonate-rich brines that could have evolved to a higher pH when concentrated. Despite this possibility, the occurrence of ancient carbonate deposits on Mars appears to be quite rare (Ehlmann *et al.*, 2008b; Morris *et al.*, 2010); thus, whether or not carbonate-rich brines played an important role on early Mars remains unanswered.

A second question concerns the susceptibility of nontronite to transformation reactions in alkaline/saline solutions. Fe-rich smectites such as nontronite may have been common detrital clay minerals on Mars because of the basaltic crustal composition, but no example of a terrestrial closed basin where true nontronite forms a

major component of the sedimentary detritus has been identified. The best indication may come from two alkaline terrestrial basins in which clay mineral authigenesis has been studied extensively: Lake Abert in Washington State, and Paleolake Olduvai in East Africa, both of which have voluminous volcanic rocks (mainly andesitic and trachytic compositions, respectively) in the catchments that weather to Fe-rich dioctahedral smectites (Jones and Weir, 1983; Banfield *et al.*, 1991a; Deocampo, 2009, and references therein). These Fe-rich smectites are subject to transformation reactions and form intermediate tri/dioctahedral and trioctahedral Mg-rich clay minerals in alkaline solutions, and so one predicts that Martian nontronites would be subject to similar reactions if exposed to alkaline solutions. The reactivity and products of any transformations of nontronite in circum-neutral, highly saline solutions are presently unknown.

The likely prevalence of detrital sources of saponite and nontronite on Mars also raises concerns that the diversity of authigenic clay minerals seen in the basin margin sediments of terrestrial closed systems might be obscured on that planet. In an idealized model of clay mineral zonation, based on terrestrial examples discussed in the earlier parts of this paper, detrital minerals dominate alluvial and fluvial deposits around a basin, fibrous clays form in soils, brackish water ponds, and mudflats in peripheral areas, and Mg-rich smectites dominate marginal lacustrine strata. Similar distribution patterns could form on Mars in response to lateral gradients in water chemistry because Mg-rich smectites and illites are destabilized when exposed to low-salinity and low-pH waters, and they can transform into Al-rich smectites or result in the precipitation of fibrous clays like sepiolite (Khoury *et al.*, 1982; Deocampo *et al.*, 2002). Thus, under certain conditions in ancient Martian lakes, detrital saponite and nontronite could have been unstable and may have been altered by authigenic processes in response to ambient conditions, just as Al-rich clays are altered in terrestrial closed basins.

Diagenetic processes

Any discussion of ancient clay minerals, particularly the multi-billion year old clay minerals on Mars, requires consideration of the affects of diagenetic alteration that may modify or obscure primary spatial and stratigraphic mineralogical patterns. The most widely documented diagenetic processes are the illitization and chloritization of smectites (dioctahedral and trioctahedral, respectively) which occur during burial and heating (Weaver 1989; Chamley, 1989; Meunier, 2005). These processes result in a decrease in the proportion of expandable, smectitic layers, and an increase in non-expandable chlorite or illite layers, with interstratified chlorite-smectites and illite-smectites as intermediate products. Hillier (1993) also documented a burial diagenetic reaction occurring at $\geq 120^\circ\text{C}$ between

dolomite and dioctahedral clay minerals which produced corrensite (a regularly interstratified chlorite-smectite) and chlorite.

The persistence of juvenile phases including smectite, opaline silica, and jarosite on Mars is posited as indicating the absence of diagenetic alteration in many Martian deposits and is attributed to the scarcity of water through much of the planet's history (Tosca and Knoll, 2009). However, recent detailed examination of laboratory and CRISM reflectance spectra indicate that subtle differences at near-infrared wavelengths may be used to identify interstratified chlorite-smectites, the potential products of diagenesis, and that these phases may be more common on Mars than previously thought (*e.g.* Milliken and Bish, 2010; Milliken *et al.*, 2011). As documented in this review, chloritization and illitization reactions can also occur at low temperatures under highly saline and highly alkaline conditions, respectively. Further study of the spatial and stratigraphic distribution of clay minerals, with particular attention to documenting interstratified clay minerals, is needed not only for the purpose of identifying authigenic minerals forming in sedimentary basins, but also to distinguish them from similar diagenetic products that could indicate parts of Mars experienced longer-lived aqueous activity than previously recognized.

Trace-element contents as environmental indicators

As discussed previously, REEs and transition elements have proven useful in diagnosing the formation mechanism (*i.e.* transformation *vs.* neof ormation) of clay minerals on Earth. Trace-element concentrations may also help constrain the environment of formation for Martian clays and, therefore, may be worth considering in plans for future ground-based missions. More specifically, high concentrations of certain trace elements have been used as indicators of a hydrothermal origin for nontronite and several types of 2:1 trioctahedral phyllosilicates, including saponite, stevensite, talc, and interstratified smectite-kerolite (Decarreau, 1985; Dekov *et al.*, 2007; Dekov *et al.*, 2008). Experiments by Decarreau (1985) showed that the divalent transition elements Cu, Zn, Co, Ni, and Mn are efficiently incorporated into the octahedral sheet of trioctahedral smectites from solution during crystallization. These results have been verified by chemical analyses of 2:1 trioctahedral clay minerals and nontronite in some oceanic hydrothermal settings, which show enrichments of these elements, particularly Cu and Zn (Meunier, 2005 and references therein; Dekov *et al.*, 2007, 2008). Elevated contents of Ba, Cr, V, and Sc are also noted in some systems (Setti *et al.*, 2004). These clay minerals formed while exposed to metalliferous brines circulating through hydrothermal systems.

However, not all clay minerals from hydrothermal settings exhibit these types of metal enrichments, a reflection of the variable chemical composition of

hydrothermal fluids. Furthermore, authigenic clay-mineral formation in some terrestrial evaporative basins, such as the Red Sea, involves a combination of precipitation from hydrothermal fluids and transformation through interaction with saline brines (Meunier, 2005, and references therein). Thus, trace-element chemistry of clay minerals can provide helpful information but it does not always provide an unambiguous indication of the formation mechanism. This kind of data must be examined in conjunction with other lines of evidence, including sedimentary and stratigraphic context.

CONCLUSIONS

Distinguishing between the multiple possible origins for clay minerals in terrestrial deposits is a complex and difficult task. The case is even more challenging for Martian clay minerals because of the lack of crustal differentiation and the limiting nature of remotely acquired data. Despite these drawbacks, the discussion presented here shows that the recognition of spatial and stratigraphic trends in types of clay minerals and other authigenic mineral phases such as zeolites, evaporites, feldspars, carbonates, and opaline silica provides a potential means of identifying authigenic clay minerals that formed in bodies of standing water on Mars. In turn, identification of such mineral assemblages and associated spatial/stratigraphic trends could help constrain the depositional environment of certain Martian sedimentary strata. The characteristic distribution patterns observed in authigenic clay minerals in terrestrial lake deposits result from the tendency of certain clay minerals to form preferentially under certain physico-chemical conditions (encompassing fluid chemistry and the availability of reactive mineral detritus), combined with the large spatial and temporal changes in chemical conditions characteristic of lakes with closed hydrology.

The main uncertainties in applying this approach to Martian deposits stem from the paucity of terrestrial studies of clay authigenesis in analogous environments, including recent saline systems with neutral chloride/sulfate-rich brines and systems where basic/ultrabasic rocks form the majority of the catchment. Though not perfect analogs, detailed studies of such systems would probably provide important insights into depositional processes and formation conditions of clay minerals in ancient Martian lakes.

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