Summary: The past decade of mineralogy and geochemistry investigations from orbit and in situ have opened a new perspective for assessing the history of liquid water on Mars and the nature of aqueous environments during its first billion years. Orbital data indicate the widespread occurrence and diversity of Noachian and Hesperian aqueous environments, ranging from sedimentary hematite-bearing units reported in 2000 [1], to time-ordered phyllosilicate and sulfate deposits discovered in 2005 [2], to >20 water-formed minerals in a dozen distinct aqueous environments, varying in space and time, known presently [3-5]. Rovers and landers have refined our understanding of local-scale mineralogy and aqueous alteration, including variations in soil composition across landing sites and variations from acid to alkaline geochemical environments over only 10s of meters of strata [6-14].

Water-related minerals, a global view: Hydrated silicate minerals are found in most locations where Noachian-aged crust is exposed, pointing to globally widespread neutral to alkaline aqueous alteration on early Mars (Fig. 1). As originally reported by [2], there is little correlation between fluvial features and hydrated silicates. In contrast to the widespread distribution of phyllosilicates, salts (sulfates, carbonates, and chlorides) show regionally restricted distributions.

Clay Mineralogy: Fe/Mg phyllosilicates, with Fe/Mg smectites and/or mixed layer smectite/chlorites comprise >50% of secondary mineral deposits. Chlorite is the second most common phyllosilicate, sometimes accompanied by prehnite, which indicates hydrothermal activity [15]. At Endeavour crater, Terra Meridiani, Fe/Mg phyllosilicates have been detected from orbit and associated with a dark veined- and nodule-rich Matijevic unit [7]. Light-toned veins cross-cutting this unit include Al-phyllosilicate- and silica-bearing materials as well as younger sulfate-rich veins likely related to the impact. At Gale crater, Mg,Fe-smectite clays have been identified in association with very fine-grained sedimentary rocks in Yellowknife bay, cross-cut by diagenetic ridges and Ca-sulfate veins [12, 22, 23]. Al clay minerals have been suggested for rocks at Gusev crater [9].

To date, clay mineral bearing units examined from orbit and on the ground more commonly exhibit evidence for formation in geochemically closed systems with relatively low W:R ratios for the bulk of the deposits [7, 15, 22] (Fig. 2). Interestingly, carbonate is not found as part of any of the assemblages, though it is an expected by-product during weathering from fluids in contact with a CO₂-rich atmosphere. Collectively, these data indicate the importance of closed system and perhaps subsurface processes. Extensive open system weathering is not indicated.

Nevertheless, select regions including Nili Fossae, Mawrth Vallis, portions of Valles Marineris, and sedimentary deposits in Terra Sirenum include large deposits of Al-phyllosilicates, a typical product of near-surface, open-system weathering. This indicates select regions with either greater water availability and/or enhanced acidity to promote leaching. The Al-clay...
deposits are typically stratigraphically above Fe/Mg-clays, and beneath Hesperian-aged units, pointing to late Noachian/early Hesperian formation ([15]; for an exception, [24]).

**Salts:** Sulfates are found in select locations around Valles Marineris, Aram Chaos, Terra Meridiani, Mawrth Vallis, Northeast Syrtis, and Terra Sirenum in locations where groundwater upwelling is predicted [3]. Chloride salts are found in the southern highlands but not in the north [17]. Carbonates are restricted in distribution, found associated with olivine-bearing rocks around the Nili Fossae and northeastern Syrtis Major [18] as well as in a few impact craters [19]. At rover scale, sulfate- and hematite-bearing sediments formed by episodic diagenesis have been characterized at Meridiani [6], Ca-sulfate has been found in veins at Gale, and sulfates have also been found in soils and altered igneous rocks at Gusev. Carbonates are associated with olivine-lithologies at Gusev [10].

**Implications for Early Climate:** Collectively, the data indicate that liquid water was globally widespread on early Mars and important in producing secondary mineral assemblages that are superimposed on a mostly basaltic starting composition [e.g. 5]. However, evidence for sustained interactions at high water-rock ratios and in chemically open systems appears less common, restricted to local to regional occurrences and particular time periods. Observed deposits can be generated with localized and/or episodic waters; a continuously warm, wet Mars is not required. Longer-lived, groundwater-derived systems, promoting hydrothermalism, diagenesis and isochemical secondary alteration, may have produced the Fe/Mg phyllosilicates. Mineral assemblages observable from orbit and at two locations on the surface (Meridiani, Gale) are consistent with clay formation in low W:R, low fO2 and low pCO2 conditions. Mars during its first billion years was certainly wetter than at present but may have always been relatively cold and dry at the surface. Punctuated periods of episodic enhanced near-surface liquid water availability (caused by obliquity changes, volcanism, or impacts) were important in shaping the mineralogy and geomorphology during select periods, but subsurface, closed chemical systems appear to have dominated Mars’ earliest aqueous environments [15].

**Five key questions:** (1) Most Fe/Mg phyllosilicates are associated with scarp{s and crater walls, ejecta, and central peaks. Are the host rocks altered lavas, ashes, or sediments? The nature of these rocks hosting “typical”, globally widespread crustal clays has substantial bearing on the relative prevalence of early sedimentary (fluvial?) vs. igneous processes. (2) The mechanism of Fe/Mg phyllosilicate formation is uncertain: did they form via deuteric precipitation as lavas cooled [27], afterwards by volcanic- or impact-driven hydrothermal systems, later as diagenetic cements, or from surface-driven weathering? (3) Does the existence of clay minerals in Noachian units mean they formed almost exclusively in the Noachian or indicate the influence of later water-infiltration? (4) Water chemistries must have varied in space and time to produce the spatially discretized salt deposits observed; what is the control: precursor rock chemistry or atmospheric chemistry? (5) Why so little carbonate? Did subsurface fluids out of contact with the atmosphere form most of the alteration minerals? Or was acidity responsible for inhibiting or destroying carbonate deposits? Study of small-scale compositional gradients, petrologic textures, minor components in mineral assemblages, and age dating are required to address these key unknowns related to aqueous alteration and climate during Mars’ first billion years.


**Figure 2.** Ternary diagram showing the composition of clay-bearing terrains on Mars. Orbital abundances of select terrains from [25], Meridiani clay-bearing rocks from [7], Gale clay-bearing rocks from [22].