AQUEOUS ALTERATION IN MARTIAN METEORITES: COMPARING MINERAL RELATIONS IN IGNEOUS-ROCK WEATHERING OF MARTIAN METEORITES AND IN THE SEDIMENTARY CYCLE OF MARS

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ABSTRACT: Many of the minerals observed or inferred to occur in the sediments and sedimentary rocks of Mars, from a variety of Mars-mission spacecraft data, also occur in Martian meteorites. Even Martian meteorites recovered after some exposure to terrestrial weathering can preserve preterrestrial evaporite minerals and useful information about aqueous alteration on Mars, but the textures and textural contexts of such minerals must be examined carefully to distinguish preterrestrial evaporite minerals from occurrences of similar minerals redistributed or formed by terrestrial processes. Textural analysis using terrestrial microscopy provides strong and compelling evidence for preterrestrial aqueous alteration products in a number of Martian meteorites. Occurrences of corroded primary rock-forming minerals and alteration products in meteorites from Mars cover a range of ages of mineral–water interaction, from ca. 3.9 Ga (approximately mid-Noachian), through one or more episodes after ca. 1.3 Ga (approximately mid–late Amazonian), through the last half billion years (late Amazonian alteration in young shergottites), to quite recent. These occurrences record broadly similar aqueous corrosion processes and formation of soluble weathering products over a broad range of times in the paleoenvironmental history of the surface of Mars.

Many of the same minerals (smectite-group clay minerals, Ca-sulfates, Mg-sulfates, and the K-Fe–sulfate jarosite) have been identified both in the Martian meteorites and from remote sensing of the Martian surface. This suggests that both kinds of samples—Martian meteorites and Mars’ surface rocks, regolith, and soils—were altered under broadly similar conditions. Temporarily and locally occurring but likely stagnant aqueous solutions reacted quickly with basaltic/mafic/ultramafic minerals at low water–rock ratios. Solutes released by primary mineral weathering precipitated locally on Mars as cation-rich clays and evaporite minerals, rather than being leached away, as on Earth.

The main secondary host minerals for Fe differ between Martian meteorites and Mars’ surface materials. In Martian meteorites, sideritic–ankeritic carbonate is the predominant secondary host mineral for Fe, whereas in Mars’ surface materials, ferric oxides and ferric sulfates are the predominant secondary host minerals for Fe. Differences in the initial compositions of the altering solutions are implied, with carbonate/bicarbonate dominating in the solutions that altered Martian meteorites, and sulfate dominating the solutions that altered most Mars’ surface materials. During impact on and ejection from Mars, Martian meteorites may have been exhumed from depths sufficient to have isolated them from large quantities of Mars’ surface solutions. Pre-ejection weathering of the basaltic rocks occurred in grain-boundary fracture microenvironments at high pH values in aqueous solutions buffered by reactions with basaltic minerals.

INTRODUCTION

On Earth, coarse clastic detritus is dominated by primary rock-forming minerals and rock fragments that persisted against the weathering to which the source rocks were subjected; fine clastic particles are products of weathering of primary minerals in source rocks; and chemical sediments formed by precipitation of dissolved products of weathering. Most introductory treatments of weathering on Earth begin with the weathering of Earth’s dominant continental igneous rock type, granite (e.g., Grotzinger and Jordan 2010). Martian meteorites are mafic and ultramafic rocks from the predominantly basaltic planet Mars, and they are presently the only samples available for study in terrestrial laboratories. The purpose of this paper is to examine the weathering of primary rock-forming minerals and the formation of secondary minerals on Mars from the perspective of mineral and textural evidence in Martian meteorites.

Mineral–water interactions during weathering at the interface between a solid rocky planet and its fluid envelope (hydrosphere and/or atmosphere) modify primary minerals, produce new minerals as alteration products, and modify the solute loads of the solutions. The relationships among these phenomena can be summarized in the following generic mineral weathering reaction:

$$\text{Primary mineral} + \text{water} + \text{solutes} \rightarrow \text{secondary mineral(s)} + \text{modified solutes}$$  (1)

A usually mobile solvent (water) brings mobile solutes (e.g., environmental acidity) to the surface of primary minerals in a soil, regolith, or rock undergoing weathering. If the solution is sufficiently undersaturated with respect to the primary mineral, the primary mineral and the solution react. The primary mineral may be completely destroyed if geochemical reaction kinetics are fast, but partially weathered primary mineral grains survive for a variety of reasons. Factors favoring persistence of primary minerals in weathered residues include:

- slow reaction kinetics caused by intrinsically sluggish reactions due to strong bonding in the reactant mineral (Velbel 1999) or attributes of the reactant solution, such as low degree of undersaturation of solution with respect to the primary mineral (Velbel 1989a, White and Brantley 2003);
- restricted abundance of reactive solution (Nahon 1991, Taylor and Eggleton 2001); or
- physical removal of grains from the soil or regolith by erosion before weathering completely destroys them (Granthon and Velbel 1988; Johnsson et al. 1988; Johnsson and Stallard 1989; Johnsson 1990, 1992; Velbel 2007; Velbel et al. 2007).

Secondary minerals are weathering products (e.g., clay minerals and oxides/oxhydroxides of major trivalent cations, Al$^{3+}$, Fe$^{3+}$) that form in the soil or weathered regolith. Other secondary minerals (carbonates, sulfates) can form from dissolved products if leaching is restricted, for example, due to the paucity of percolating water. The anions (e.g.,
carbonate, sulfate, chloride) are often the anions of dissociated and consumed environmental acidity (e.g., carbonic acid, sulfuric acid, hydrochloric acid, respectively) that drove hydrolysis reactions. If abundant mobile solvent is present, dissolved products may be removed as solutes and transported elsewhere.

Reaction Eq. 1 also has applications to the sedimentary cycle as a whole. Residual primary minerals, which are unreacted either because of slow geochemical reaction kinetics (persistence) or because of environmental factors (e.g., limited water or reactive solutes), often occur in soils and regoliths as coarse (sand-size) grains. When eroded, transported, and deposited, these become sands, and with burial diagenesis, sands become sandstones, the volumetrically dominant terrestrial coarse clastic sedimentary rock (Garrels and Mackenzie 1971, Railsback 1993; conglomerates make up only a small volume fraction of Earth’s clastic sedimentary rocks). Secondary minerals include clay minerals and oxides/ohydroxides of major trivalent cations (Al$$^{3+}$$, Fe$$^{2+}$$) that commonly form during the weathering of weatherable (nonpersistent) Al- and Fe-bearing silicate minerals. Clay minerals are generally fine-grained (clay-size). When eroded, transported, and deposited, these become muds, and with burial diagenesis, muds become mudstones and shales, the volumetrically dominant terrestrial clastic sedimentary rocks (Garrels and Mackenzie 1971, Railsback 1993; shales make up the largest volume fraction of all Earth’s sedimentary rocks).

Soluble ions can form other secondary minerals (carbonates, sulfates) at the weathering site if leaching is restricted by, for example, a paucity of mobile water. However, on Earth, with an active and long-lived hydrologic cycle operating over much of the planet’s surface much of the time, soluble ions are more typically leached from a weathering profile, moving with the abundant mobile solvent (water). Eventually, many dissolved products of weathering become the constituents of chemical sediments, recombined either by abiogenic processes (e.g., evaporation) to form evaporite minerals and rocks or by biologically mediated processes (e.g., biochemical production of shells, skeletons, etc.) to form carbonate minerals, sediments, and sedimentary rocks (limestones, dolostones). Carbonates and other chemical sedimentary rocks make up a smallest fraction of the total volume of Earth’s sedimentary rock (Garrels and Mackenzie 1971, Railsback 1993). Thus, several of the various reactants and products in reaction Eq. 1 correspond to categories of sediments and sedimentary rocks.

The reaction for the congruent dissolution of olivine in the presence of natural acidity illustrates many attributes embodied in reaction Eq. 1 and elaborated upon in the preceding discussion.

$$\text{Mg}_2\text{SiO}_4 + 4\text{H}^+ \rightarrow 2\text{Mg}^{2+} + \text{H}_4\text{SiO}_4^{(aq)}$$

(2)

In this example, a primary mineral, olivine (represented for simplicity by end-member forsteritic olivine), reacts with reactant solutes (an acid, represented by H$$^{+}$$), producing a modified solute load in the resulting aqueous solution. If the acid (e.g., carbonic or sulfuric acid) is known and specified, the undissociated acid appears in place of the H$$^+$$ on the reactant side of reaction Eq. 2, and the anion group resulting from the dissociation of the acid (HCO$$^-_3$$, CO$$^-_3$$, or SO$$^-_4$$) appears on the product side. Solubility considerations then influence whether some of the dissolved products precipitate as products (e.g., silica, Mg-hydroxide, Mg-carbonate, Mg-sulfate, hydrous Mg-silicate), and where. Depending on the concentration of solutes in the solution, and the mobility of the solution itself, some or all of the secondary minerals (solid products) may form near the olivine-dissolution site; alternatively, some or all solutes may be leached away to precipitate as chemical sediments elsewhere. Reactions involving more realistic olivine compositions (e.g., some fayalite in solid solution, releasing Fe), and reactions involving incongruent dissolution of rock-forming silicates (e.g., plagioclase feldspar plus acid reacting to produce kaolinite plus solutes) become slightly more complicated, but they can be interpreted in the same framework provided by reaction Eq. 1.

Mineral–water interactions modify primary minerals, produce new minerals as alteration products, and modify the solute loads of the solutions. Reactants (minerals and mobile species) react by processes governed by interactions among structure, composition, surface properties, and solute composition (the latter itself influenced by the history of the solution, including its origin, and other reactions in which the solution participated prior to arriving at the current reaction site). Product minerals form, and the solution composition is altered. Except for situations in which the solutions still coexist with reactant and product minerals, properties of the solutions (e.g., the abundances of various solutes; the duration of their contact with the minerals) must be inferred from the mineral assemblages left behind. In many Earth and planetary materials, the solutions left the system long ago, and only the solids survive; it is from the surviving solids that we infer the former processes through a process-product framework (Naish 1991, Berner and Berner 1996, Delvigne 1998, Lasaga 1998, Taylor and Eggleton 2001).

This paper is about minerals and reactions. Abundant literature exists on identifying and interpreting the paleoenvironmental significance of preserved primary minerals and secondary minerals observed on Mars from orbital and surface missions (e.g., clay minerals and other phyllosilicates; sulfates; carbonates) and their implications for understanding past aqueous solution–mediated reactions. The Martian meteorites are the only available samples of Mars, so the smectite-group clays, carbonates, sulfates, and halite they contain are the only samples of Martian secondary minerals available for study on Earth. Although many Martian meteorites have an overprint of terrestrial aqueous alteration, this can be avoided with careful petrographic work and can under some circumstances be informative in its own right. Gooding (1992) reviewed aqueous alteration phenomena and products observed in Martian meteorites, but many more Martian meteorites have been recovered and recognized since then, and much research has been published in the ensuing decades. This paper examines alteration phenomena of Martian origin in meteorites from Mars, and explores implications for Martian mineral–water interactions.

**METEORITES: A PRIMER**

Meteorites and other rock samples from solar-system bodies preserve in their chemical compositions, minerals, and textures direct evidence of the processes by which our solar system’s planets and small bodies originated, were modified, and evolved to their present state. Returned samples of solar-system materials are of the highest scientific value because they are known to come from bodies for which other kinds of information are available to complement studies of the samples in terrestrial laboratories. However, only a few solar-system bodies other than Earth have been sampled by human or robotic missions. Lunar rocks returned by Apollo and Luna missions (Mason and Melson 1970, Taylor 1975, Papike et al. 1998, Warren 2005), comet dust returned from comet 81P/Wild 2 by the National Aeronautics and Space Administration’s (NASA) Stardust mission (Brownlee et al. 2006, Zolensky et al. 2006), and mineral grains from the regolith of asteroid 25143 Itokawa recently returned by the Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency (JAXA) Hayabusa mission (Yano et al. 2006) sample only a few specific solar-system bodies (the Moon, one comet, and one asteroid).

Most meteorites are naturally delivered asteroidal and possibly cometary samples; the remainder are samples from larger, differentiated solar-system bodies. Other than samples returned from the Moon, comet 81P/Wild 2, and asteroid 25143 Itokawa, and interplanetary dust particles recovered in Earth’s upper atmosphere and generally not
demonstrably associated with specific comets (Rietmeijer 1998, Bradley 2005), meteorites are our only direct samples of a large variety of materials formed and modified on numerous parent bodies during the earliest stages of solar-system evolution. Studies of meteorites also contribute to the knowledge base for interpreting asteroidal and cometary composition and history (including aqueous alteration) by both direct (sample return; e.g., NASA Stardust; ISAS/JAXA Hayabusa) and remote (fly-by) asteroidal and/or cometary missions (e.g., NASA Deep Impact; NASA Stardust NeXT; European Space Agency Rosetta).

A summary of the entire series of processes involving ejection of a meteoroid from its parent body, interplanetary transit, dramatic passage through Earth’s atmosphere, and arrival at Earth’s surface as a meteorite is beyond the scope of this paper. Interested readers are referred to McSween (1999), Bevan and de Laeter (2002), and Hutchison (2004) for up-to-date introductions to these phenomena. For brief descriptions of two case studies describing a broad and representative range of phenomena associated with the recent fall and recovery of two stony meteorites, see Osborn et al. (1997) and Velbel et al. (2002). Several specific aspects are discussed as needed elsewhere in this paper.

Meteorites are named for major geographic features near their recovery site. Where natural processes result in the accumulation of large numbers of meteorites, the recovery site name is followed by a number identifying each individual object within the accumulated population. For the abundant meteorites recovered in Antarctica, the recovery location name is abbreviated to one letter for meteorites recovered by Japanese research teams, and three letters for research teams from the United States of America. For example, the full name of the oldest known Martian meteorite, Allan Hills (Antarctica) 84001 (Fig. 1), is condensed to ALH 84001.

At the broadest level of compositional classification, meteorites include objects that consist mainly of metal (irons), predominantly of silicate minerals (stones or stony meteorites), and subequal abundances of metal and silicates (stony irons) (Dodd 1981, Wasson 1985, McSween 1999, Hutchison 2004). Stony meteorites are subdivided into those with textural evidence of familiar (to geologists) igneous differentiation processing on their parent bodies, and those containing textural evidence of cooling and solidification of individual grains from vapor and dust followed by assembly of the solids into rocks and parent bodies that did not differentiate to produce magmas and igneous rocks (Dodd 1981, Wasson 1985, McSween 1999, Hutchison 2004). The defining features of the latter group are “chondrules,” which are generally spherical, millimeter- to submillimeter-sized, silicate-dominated solids that are solidified droplets formed by flash heating, melting, and rapid cooling of precursor solids in the early solar nebula (Lofgren and Russell 1986; Lofgren 1989, 1996; Lofgren and Lanier 1990, McSween 1999; Hutchison 2004). Stony meteorites containing chondrules, and closely related meteorites in which evidence of chondrules may have been destroyed during the meteorite’s history, are called “chondrites.” Stony meteorites with igneous textures lacking chondrules are called “achondrites.” There are many more specific taxonomic classes of both chondrites and achondrites (Dodd 1981, Wasson 1985, McSween 1999, Hutchison 2004).

Most achondrites have igneous crystallization ages almost as old as old as the age of the solar system and likely formed on small (asteroid-size) parent bodies shortly after the accumulation of solids into planetesimals in the early solar system (Dodd 1981, Wasson 1985, McSween 1999, Hutchison 2004). However, one clan of compositionally and isotopically related achondrites consists of mafic–ultramafic igneous rocks with crystallization ages of ca. 1.3 Ga or younger. This group and more recently identified relatives are the subject of this paper. Before introducing this clan, some more general recovery-related phenomena are discussed.

**Meteorites from Mars, and How Scientists Know Martian Meteorites Are from Mars**

Most of the >50 meteorites now attributed to Mars belong to one of three compositional classes. The longest-known members of these three classes, Shergott (fell 1865; Grady 2000), Nakhl (fell 1911; Grady 2000), and Chassigny (fell 1815; Grady 2000), each gave their name to a group of similar meteorites. The most abundant are the “sherogottites,” which are basalts and harzburgites with radiometric ages indicating crystallization in the ca. 150–475 Ma range (McSween 1994, 2002, 2008; Meyer 2005). There are subclasses of shergottites (McSween and Treiman 1998; Hutchison 2004; Meyer 2005; McSween 2002, 2008); basaltic shergottites, Iherzolitic shergottites, and olivine–phyric shergottites. Intermediate in abundance, there are “nakhites” (eight examples presently known), which are clinopyroxenites with radiometric crystallization ages ca. 1.3 Ga (Treiman 2005). The smallest class (presently known from two examples) is the “chassignites,” which are dunites with radiometric crystallization ages ca. 1.3 Ga (McSween 1994, 2002; Meyer 2005). The ensemble of these three classes became known as the SNCs (pronounced “snicks”). Oxygen isotopes suggest that the SNCs are related to each other and are not related to the Earth–Moon system or any other meteorite group (Clayton et al. 1976; Wasson and Wetherill 1979; Wood and Ashwal 1981; Clayton and Mayeda 1983, their Fig. 1; Wasson 1985; McSween 1999, his Fig. 4.4; Meyer 2005, his Fig. 1-3). The unique orthopyroxenite ALH 84001 (Fig. 1) has oxygen-isotopic affinities with the nakhlites (Clayton 1993, Mittlefehldt 1994) and a crystallization age of ca. 4.1 Ga (Lapen et al. 2010). Being a different rock type than any of the SNCs, ALH 84001 has expanded the definition of “Martian meteorite” beyond the SNCs proper (Mittlefehldt 1994). However, all pre–ALH 84001 literature equates “SNCs” with “Martian meteorites,” where previous inferences were drawn from SNCs alone.
Viking Mariner orbiters on impact-crater populations indicated that (including SNC spacecraft (Mutch et al. 1976), and MICHAEL A. VELBEL has on 14 June 2019 by guest Downloaded from https://pubs.geoscienceworld.org/books/chapter-pdf/4266951/9781565763135_ch03.pdf reseros in the solar system (Bogard and Johnson 1983, Becker and different from those of Earth’s atmosphere or other known gas glasses were essentially identical to the Martian atmosphere (elemental shock glass in EETA79001. The gases implanted in those shock related on the basis of the evidence described previously, was by extension other shergottites and all the SNCs to which they are 1980s, the case for Mars as the parent body of SNCs was strong (Wasson and Wetherill 1979, Wood and Ashwal 1981). This meteorite was the first SNC meteorite analyzed for inert and noble gases that matched those of Mars’ atmosphere (Bogard and Johnson 1983) and was found to contain low-temperature aqueous alteration products, including clay mineraloids, carbonates, and gypsum, many of which are preserved in textures indicating their preterrestrial origin on Mars (Gooding 1986a, Gooding et al. 1988). See text for further details. NASA Johnson Space Center image S80–37480. before recovery and recognition of ALH 84001, then-known Martian meteorites will be referred to here as “SNCs.” Even before a specific parent body was identified, it was recognized that magma genesis on the “SNC” parent body persisted longer than on the parent bodies of any other then-known meteorite group (McSween et al. 1979, Wood and Ashwal 1981), and longer than on the Moon (McSween and Treiman 1998, McSween 1999, Hutchison 2004). This in turn suggested that the “SNC” parent body retained internal heat longer, and was thus larger, than any asteroid (McSween et al. 1979, Wood and Ashwal 1981) or the Moon. Mars volcanoes, the largest volcanoes in the solar system (Carr et al. 1977, Carr 2006), were first observed in data from the Mariner spacecraft (Mutch et al. 1976), and data from the Viking orbiters on impact-crater populations indicated that the volcanic landforms were relatively young Martian geomorphic features (Carr et al. 1977, McSween 1999, Carr 2006). By the early 1980s, the case for Mars as the parent body of SNCs was strong (Wasson and Wetherill 1979, Wood and Ashwal 1981), if still circumstantial. The case for a Martian origin of shergottite EET 79001 (Fig. 2), and by extension other shergottites and all the SNCs to which they are related on the basis of the evidence described previously, was strengthened in the early 1980s. Several research groups simultaneously and independently measured abundances of inert gases and noble gas isotopes implanted in preterrestrial veins and pockets of shock glass in EETA79001. The gases implanted in those shock glasses were essentially identical to the Martian atmosphere (elemental and isotopic abundances) as analyzed by the Viking landers, and different from those of Earth’s atmosphere or other known gas reservoirs in the solar system (Bogard and Johnson 1983, Becker and Pepin 1984, Wiens et al. 1986, Treiman et al. 2000). Similar gases were soon found in several other SNC meteorites, confirming their consanguinity and their connection to Mars (Carr et al. 1985, Marti et al. 1995, Garrison and Bogard 1998, Grady et al. 1998, Mathew et al. 1998, Terribilini et al. 1998, Treiman et al. 2000). By the mid-1980s, a Martian origin of SNC meteorites was becoming widely accepted (McSween 1984, 1985), and a decade later, the Martian origin of what had finally become known as “Martian meteorites” (including SNCs and the related ALH 84001; Mittlefehldt 1994) was firmly established (Treiman 1996, Treiman et al. 2000). Absolute crystallization ages of Martian meteorites, all of which are igneous rocks, are known from geochronology using common radioactive-decay series (e.g., U-Pb, Rb-Sr, K-Ar, Ar-Ar). Relating igneous crystallization to other aspects of Martian geologic history requires relating absolute crystallization ages of Martian meteorites to the Martian geologic timescale. Relative ages of the landscapes and surface features on Mars are based on morphostratigraphy. The three Martian relative-age intervals are, from oldest to youngest, Noachian, Hesperian, and Amazonian. In the absence of radiometrically datable samples from known localities, absolute-age calibration of surface ages inferred from size-frequency distributions of impact craters on Martian surface units (Hartmann 2005, Soderblom and Bell 2008) is not yet possible, and errors for the absolute ages of boundaries, especially younger boundaries, are large (Nyquist et al. 2009). At present, the best estimate for the age of the Noachian–Hesperian boundary is ca. 3.7–3.5 Ga, and the best age for the Hesperian–Amazonian boundary is ca. 3.2–2.0 Ga (Hartmann 2005, Soderblom and Bell 2008). Igneous crystallization ages (see previous) of all SNCs all fall within the Amazonian; only one Martian meteorite, ALH 84001, samples ancient Noachian material (McSween 2002). The question, “Specifically where on Mars does any specific Martian meteorite come from?” has not yet been answered for any Martian meteorite (McSween 2002, 2008). While specific Martian meteorites cannot be matched to specific source craters on Mars, meteorites with similar ejection ages can be identified using cosmic-ray–induced radionuclides. During transit from their parent body to Earth, all meteoroids accumulate cosmic-ray–induced radionuclides (Herzog 2005, Eugster et al. 2006, McSween 2008). From measurements of such nuclides, it is possible to infer a cosmic-ray exposure (CRE) age, the time at which such radionucleide accumulation began, which can in turn be interpreted as the time when the meteoroid was ejected from its parent body. For Martian meteorites, it appears that, despite the large number of individuals in many groups, most members of each group have a small number of ejection ages. For example, ejection ages of Chassigny and all of the longer-known, most thoroughly studied nakhlites have been determined to be similar (Fritz et al. 2005, Herzog 2005, Eugster et al. 2006, McSween 2008; ejection ages have not yet been determined for the most recently recovered nakhlites). This is interpreted to indicate that all 10 NC meteorites (eight known nakhlites, two known chassignites) not only have essentially identical igneous crystallization ages (ca. 1.3 Ga; McSween 1994, 2008; Treiman 2005), but they were also all ejected together with one another, at a different time than the ejection of other Martian meteorites (Fritz et al. 2005, Herzog 2005, Eugster et al. 2006, McSween 2008). It is unlikely that 10 different clinopyroxenites and dunites with identical crystallization ages were all ejected from different places on Mars with identical geologic histories, and all at the same time. It is much more likely that one impact ejected these 10 meteorites from a single geologic locale. This insight has led Martian meteorite petrologists to interpret the seven longest-known nakhlites as different samples of the same thick flow (Friedman Lentz et al. 1999) or shallow sill; systematic variations between nakhlites in compositional zoning or homogeneity of olivines and pyroxenes, and in the degree of crystallization and devitrification of interstitial igneous glass, are interpreted in terms of different nakhlites sampling different...
distances from the cooling surfaces of the flow or sill (Mikouchi et al. 2003, 2005, 2006; McKay et al. 2007). Nakhlites with interstitial glass and compositionally zoned olivine and pyroxene are interpreted to have cooled quickly, near the upper and possibly lower margins of the magma body, while nakhlites with devitrified interstitial glass and compositionally homogeneous olivines and pyroxenes cooled slowly in the interior of the magma body (Mikouchi et al. 2003, 2005, 2006; Treiman 2005; McKay et al. 2007). The inferred solidification products of this magma body are referred to as the “nakhlite stack” (Friedman Lentz et al. 1999; Mikouchi et al. 2003, 2005, 2006; McKay et al. 2007). Thus, the eight known nakhlites and two known chassignites may all represent samples of different parts of the same rock unit on Mars, all ejected at the same time during the same impact.

Similarly, all lherzolitic shergottites seem to have the same CRE age (Herzog 2005, Eugster et al. 2006, McSween 2008). In contrast, the CRE ages of basaltic shergottites cluster into four groups (up to six meteorites per cluster), suggesting four different ejection events (Herzog 2005, Eugster et al. 2006, McSween 2008).

The overall sense of current understanding suggests that the >50 presently known Martian meteorites may have been ejected by a total of some seven (some worker suggest as few as five, some as many as eight) impact events on Mars (Herzog 2005, Fritz et al. 2005, Eugster et al. 2006, McSween 2008) and thus sample the geology of a comparably small number of geologically distinct but locally lithologically homogeneous source areas on Mars. The localities of the half-dozen or so impact craters from which the currently known Martian meteorites were ejected have not been identified. However, the Martian meteorite source localities they represent are comparable in number to the six surface locations on Mars examined to date by Mars landers (Viking 1 and 2, and Phoenix) and rovers (Mars Pathfinder rover Sojourner and Mars Exploration Rovers [MER] Spirit and Opportunity) (McSween 2008) and thus provide detailed information from a number of (not specifically known) locations on the surface of Mars other than those visited by robotic missions.

**Meteorite Recovery and Associated Effects**

Among the many phenomena of meteorite arrival at Earth (McSween 1999, Bevan and de Laeter 2002, Hutchison 2004), one, the formation of fusion crust, bears on the interpretation of hydrous minerals and thus warrants discussion here. When the orbit of a meteoroid intersects Earth’s orbit and both objects are at the same point in space at the same time, the meteoroid enters Earth’s atmosphere at high relative velocity (kilometers per second). At these velocities, heating caused by friction between the fast-moving meteoroid and Earth’s atmosphere melts and ablates the outer surface of the meteoroid, without significant heating of the meteoroid’s interior (except immediately beneath the ablated surface—a few millimeters in stony meteorites; up to a centimeter in irons). Understanding of this natural phenomenon inspired the design of the heat shields on the space capsules of the previous century, which allowed the heat of spacecraft re-entry to be dissipated without thermal harm to the **Mercury, Gemini, and Apollo** astronauts.

Often, the meteorite that is eventually recovered represents only a small fraction of the pre-atmospheric mass, the remainder of the meteoroid’s pre-atmospheric mass having been lost by ablation and related processes and/or because of loss of fragments that survive fall but are not recovered. For example, cosmogenic-nuclide systematics indicate that the 469 g Coleman (Michigan) ordinary chondrite was the only recovered fragment of a meteoroid with a preatmospheric mass in the 10–100 kg range (Osborn et al. 1997), implying a recovery fraction of ~0.5–5%. Before arrival at Earth’s surface, meteoroids smaller than ~1 m diameter decelerate through the velocity below which too little frictional heat is produced to melt rock or metal (skydivers at terminal fall velocity do not burn up). On meteorites, the last remnant of the material melted at high velocity solidifies when the meteoroid deCELERates, and it remains on the meteoroid’s surface, forming a thin (almost always < 1 mm thick on stony meteorites) usually black glassy “fusion crust” (McSween 1999, Bevan and de Laeter 2002, Hutchison 2004). Figures 1–4 show fusion crust at several different scales. The fusion crust is a relative age datum for distinguishing preterrestrial (including parent-body) from terrestrial (postarrival) phenomena (e.g., Gooding 1986a).

When interpreting aqueous alteration phenomena in meteorites, it is necessary to distinguish between preterrestrial (parent body) and terrestrial alteration. Chemical and mineralogical properties of meteorites, including indicators of preterrestrial aqueous alteration, may be affected by their journey from their parent body to the laboratory especially if it involved a long hiatus at Earth’s surface prior to recovery. In freshly fallen meteorites (“falls”) recovered promptly after their witnessed arrival, aqueous alteration minerals crosscut by or

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**Fig. 3.**—Backscattered-electron (BSE) image of a polished thin section of Antarctic nakhlite find MIL 03346. In BSE imagery, contrast is determined by atomic number (Z). Large areas of uniform medium gray are clinopyroxene (cpx). Darker-gray material with high-Z-contrast speckles is slightly devitrified mesostasis (volcanic glass; m). The black area across the top is outside the sample. Between the primary meteorite phases and the sample exterior, there is the vesicular fusion crust (fc; see text for discussion). At right (below arrow), a vein crosses the fusion crust and penetrates into the meteorite’s interior. Preliminary EDS analyses of vein material indicate Ca-S, K-Al-S, and K-Al-Si associations consistent with a Ca-sulfate (probably gypsum), an alunite–jarosite group K-sulfate, and K-rich Si-bearing alteration product. Since this vein crosses the fusion crust, the precipitation of the various vein phases postdates the arrival of this meteorite at Earth’s surface, and the vein materials were redistributed and/or formed by terrestrial weathering. Similar phases elsewhere in this meteorite must be examined for textural indications of preterrestrial origin; occurrences with textures indicative of preterrestrial origin are included in inventories of Mars’ minerals in Martian meteorites. Occurrences that lack such textures may have formed by terrestrial weathering as did the vein material shown here; alteration minerals formed by terrestrial weathering should not be included in inventories of Mars’ minerals in Martian meteorites.
metamorphosed immediately beneath the fusion crust are preterrestrial and record aqueous alteration on their parent body (Reid and Bunch 1975, Gooding et al. 1991). Most Martian meteorites available for scientific study (e.g., Figs. 1–4) are “finds,” recovered after unwitnessed arrival and some exposure to the terrestrial surface environment, often over millennial or longer timescales. In finds, effects of terrestrial aqueous weathering and contamination (Figs. 3, 4) are superimposed upon the aqueous alteration mineral assemblages of preterrestrial origin. Such phenomena are broadly understood for stony meteorites in general (Gooding 1986a, 1986b; Jull et al. 1988; Velbel 1988; Velbel and Gooding 1990; Velbel et al. 1991; Losiak and Velbel 2011), achondritic meteorites (Gooding 1986a), and Martian meteorites in particular (Gooding and Muenow 1986, Gooding et al. 1988, Schandt 2005, Treiman 2005).

AQUEOUS ALTERATION IN MARTIAN METEORITES

Minerals and mineral groups understood to occur in Martian meteorites and surface materials on Mars are summarized in McSween (2008) and Ming et al. (2008). Pyroxene and olivine are the most abundant minerals in Martian meteorites and constitute, by volume, >70% of the shergottites, >85% of the nakhlites, and >90% of the chassignites and ALH 84001 (Meyer 2005). This section summarizes terrestrial-analog case studies, reviews existing concepts from terrestrial analogs, and then follows with existing applications to Mars samples (meteorites) and mission images. Many Martian meteorites contain small quantities of aqueous alteration minerals (Reid and Bunch 1975; Gooding, 1986a, 1986b; Gooding and Muenow 1986; Gooding et al. 1988, 1991; Treiman et al. 1993; Wentworth and
Olivine is a major constituent of Martian meteorites; the

after (a) smooth or (b) conchoidal, jagged-edge–forming mechanical
after jagged-edge–forming chemical corrosion (etching) of olivine,

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simultaneously with shaping of the olivine surface at an isovolu-

metric replacement front that originated at a fracture around or across
the primary mineral grain and replaced the primary mineral from the
fracture into the remnant primary mineral, a texture known as peripheral or centripetal replacement (Velbel 1984, 1993; Delvigne 1998). The replacement front may be either smooth as in terrestrial serpentinization of olivine (Fig. 5b; see also Velbel, 2009, and references therein) or serrated by corrosion along fractures or dislocations, forming interfaces identical in geometry to etch pits known to form by terrestrial weathering of terrestrial olivine (Velbel, 2009). Olivine–iddingsite interfaces in altered terrestrial volcanic rocks imaged at TEM scales by Banfield et al. (1990) have jagged sawtooth features that are identical in orientation and geometry to arrays of etch pits formed by corrosion rather than replacement of olivine during weathering (Velbel, 2009). In the case of peripheral/centripetal replacement, the paragenetic sequence of secondary minerals would be the opposite of that inferred assuming mineral precipitation in a preexisting fracture—in the replacement case, the oldest, first-formed product mineral would be in the center of the “vein,” and successively later generations of replacement product would form the outer margins, as the interface between the replaced and replacing minerals progressed away from the initial fracture and toward the interior of the primary mineral remnant.

Some carbonates in nakhlites are associated with olivine surfaces showing etch pits typical in form for weathered olivine (Fig. 6), suggesting that the olivine was actively corroded prior to or during carbonate precipitation. Distinguishing whether veins form by precipitation into a fracture or by replacement originating from a fracture is important to correctly interpreting the sequence of environmental changes recorded by the different vein minerals and their textures. It is not clear whether all reported interfaces between olivine and iddingsite and/or carbonate in nakhlites formed by the same process; it is possible that different assemblages and/or occurrences formed by different specific processes among those hypothesized here. Much detailed work on the assemblages and textures of olivine’s alteration products in nakhlites is required.

Iddingsite is dated at ca. 670 Ma in the nakhlite Lafayette (Swindle et al. 2000), but from whole-rock geochronology of the three longest-known and best-studied nakhlites, it appears more likely that aqueous alteration occurred in multiple episodes since the igneous crystallization of the nakhlites rather than occurring as a single discrete datable aqueous alteration event (Swindle and Olson 2004). Regardless of the

Weathering of Primary Rock-Forming Minerals in Martian Meteorites

Olivine: Olivine is a major constituent of Martian meteorites; the chassignites are nearly pure olivine, the lherzolitic shergottites contain up to 60% olivine, and the nakhlites contain >10% olivine (Meyer 2005, Treiman 2005). Serrated or sawtooth interfaces separating olivine from iddingsite veins are widely reported (Treiman et al. 1993, Bridges and Grady 2000, Bridges et al. 2001, Treiman 2005, Leshin and Vicenzi 2006), but less visually attractive smooth interfaces also occur in nakhlites (Fig. 5a), which resemble the smooth featureless interfaces commonly observed in terrestrial serpentinization (Fig. 5b; see also Velbel, 2009, and references therein). Several paragenetic sequences are possible; iddingsites and associated minerals may have formed

- after (a) smooth or (b) conchoidal, jagged-edge–forming mechanical fracturing of olivine, as vein fillings, where the first-precipitated product precipitated directly upon the olivine surface and later precipitates were superposed upon earlier ones, as proposed by Changela and Bridges (2010),
- after jagged-edge–forming chemical corrosion (etching) of olivine, as documented in terrestrially weathered olivines by Velbel (2009), followed by precipitation of vein-filling minerals in the sequence suggested by Changela and Bridges (2010), or
- simultaneously with shaping of the olivine surface at an isovolumetric replacement front that originated at a fracture around or across the primary mineral grain and replaced the primary mineral from the

process; it is possible that different assemblages and/or occurrences formed by different specific processes among those hypothesized here. Much detailed work on the assemblages and textures of olivine’s alteration products in nakhlites is required.

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Pyroxene: Pyroxene is a major constituent of Martian meteorites, including nakhlites (clinopyroxenites, dominated by clinopyroxene \([\text{cpx}]\); Meyer 2005, Treiman 2005), many shergottites (basalts; Meyer 2005), and the orthopyroxenite (dominated by orthopyroxene \([\text{opx}]\)); Allan Hills (ALH) 84001 (Meyer 2005). Martian meteorites contain multiple examples of textures consistent with low-temperature aqueous corrosion of pyroxene, at a range of times in the paleoenvironmental history of the surface of Mars.

“Straight-pointed alteration” features, identical in size and geometry to denticles on naturally weathered terrestrial pyroxene (e.g., Berner et al. 1980, Berner and Schott 1982, Delvigne 1998, Velbel 2007, Velbel and Barker 2008, Velbel and Losiak 2010) and related chain-silicate minerals (e.g., amphiboles; Velbel 1989b, 2007; Velbel et al. 2009), have been reported from transmitted-light images of pyroxene associated with iddingsite formed by preterrestrial aqueous alteration (Treiman 2005) in petrographic thin sections of the Martian clinopyroxenite meteorite Nakhla (Fisk et al. 2006). Smaller-scale versions of denticles occur on pyroxene in the naklite MIL 03346 (Antarctic find), immediately beneath fusion crust, where they may have been formed by terrestrial weathering (Fig. 7).

Thomas-Keprta et al. (2009) reported a variety of possible aqueous alteration textures in ALH 84001, including a number associated with this meteorite’s carbonate rosettes (Fig. 8a). Among them, there is a disk-shaped carbonate patch on pyroxene (e.g., Thomas-Keprta et al. 2009, their Fig. 1C). Fracturing during SEM sample preparation exposed both the top of disk and a section through it. The close-up view (their Fig. 1F) shows (1) the nonporous nature of the carbonate patch; (2) possible twinning striae, suggesting recrystallization of the carbonate into a single crystal occupying the disk-shaped space along the fracture; and (3) possible fine-scale corrosion textures on the pyroxene surface exposed from areas formerly beneath the carbonate. The fine-scale corrosion textures on pyroxene beneath carbonate in ALH 84001 (Fig. 8b) strongly resemble microdenticles on terrestrially weathered terrestrial chain-silicate minerals (Fig. 8c) (Velbel 2011). A lower-magnification view shows that the fine-scale corrosion texture is confined to an area beneath the former extent of the carbonate patch, whereas the pyroxene away from the formerly covered area lacks the corrosion Texture. This suggests a long and complex history of the carbonate (not at all surprising in light of the abundant literature on carbonates in ALH 84001, stimulated by the initial report of McKay et al. 1996; see carbonates section later herein), including reaction with the pyroxene beneath. Such reaction might either have accompanied or followed precipitation of the carbonate and, as such, is different from instances in which mineral surfaces were inert substrates for evaporites.

Microdenticles (with lengths in the micrometer–submicron range rather than tens of microns; Velbel 2011; Fig. 8b, c) are a small-scale variant of the denticles (a.k.a. sawteeth, or hacksaw terminations, or cockscomb terminations) commonly formed during natural weathering of pyroxenes and amphiboles as described in a previous paragraph. Microdenticles share the shape and orientation of the larger more typical denticles, producing arrays of microdenticles that give the larger host denticle the appearance of a surface covered with imbricate pointed or rounded scales (Velbel 2011), as expressed in both the terrestrial analog example (Fig. 8c; Velbel 2011) and ALH 84001 (Thomas-Keprta et al. 2009; Fig. 8b). In the terrestrial case, microdenticles are superposed upon and modify the lateral surfaces of larger “classic” denticles formed by natural weathering of the parent chain silicate and are therefore either a concurrent modification of low-temperature denticulation or postdate it as a later episode of small-scale modification after production of the larger denticles by weathering (Velbel 2011). In either case, the microdenticles are weathering features formed under low-temperature surface conditions (Velbel 2011). In the case examined to date, microdenticles are associated with weathering solutions that have compositions suggesting possible
control by extreme undersaturation of solutions with respect to the primary chain silicate (Velbel 2011). The occurrence of microdenticles on pyroxene beneath carbonate in ALH 84001 (Thomas-Keprta et al. 2009; Fig. 8b) may indicate a locally extreme microenvironment for pyroxene corrosion associated only with the microenvironment of carbonate formation, relative to the conditions to which the remainder of the pyroxene surface was exposed.

Alteration Product Minerals in Martian Meteorites

Many Martian meteorites contain small quantities of aqueous alteration minerals (Gooding 1986a, 1986b; Gooding and Muenow 1986; Gooding et al. 1988, 1991; Treiman et al. 1993; Wentworth and Gooding 1993, 1994; Bridges and Grady 1999, 2000; Bridges et al. 2001; Meyer 2005; Treiman 2005; Wentworth et al. 2005; Fisk et al. 2006; McSween 2008). In finds, it is important to distinguish products of terrestrial aqueous alteration from products of preterrestrial aqueous alteration indigenous to the meteorite, present when it arrived at Earth, and therefore likely formed on Mars (e.g., Gooding and Muenow 1986, Gooding et al. 1988). In falls, it is widely assumed that any aqueous alteration products are indigenous to the meteorite and were formed on its parent body. Where such minerals are crosscut by or thermally modified near fusion crust, preterrestrial origin is proven (Reid and Bunch 1975, Gooding et al. 1991). However, some of the inventory of highly soluble minerals (e.g., halite) is known to occur in fractures and vugs in the fusion crust of Nakhla (fall) and therefore postdates Earth arrival of Nakhla (Gooding et al. 1991), and elemental redistribution and formation of halite are known to occur even during curatorial exposure of finds to laboratory atmosphere (Schwandt 2005). Consequently, careful textural study is required to distinguish preterrestrial ( Martian) aqueous alteration products from products of terrestrial weathering in Martian meteorites.

Aqueous alteration products are present in only small quantities in Martian meteorites, so their characterization is often only partial. Identification is commonly by a combination of morphological crystallography (by SEM) and qualitative abundances of some elements (by EDS or EPMA). Usually, the volume of product minerals available is insufficient for determination of crystal structure (e.g., by XRD) or a complete structural formula (including light elements, e.g., H in OH or structural H2O).

Minerals are defined by composition and structure. Much of what is identified as clay minerals in Martian meteorites is classified on the basis of composition (by EPMA or EDS). Some structural data from TEM SAED exist for the material called iddingsite in nakhlites (Gooding et al. 1991, Treiman et al. 1993, Gillet et al. 2002, Noguchi et al. 2009, Changela and Bridges 2010). However, in general, structural data requiring larger or more abundant sample material (e.g., XRD, SAED) are uncommon, and most occurrences of such materials would be more accurately described as clay mineraloids (following Gooding 1986a, 1986b). Changela and Bridges (2010) have shown that most iddingsite in nakhlites lacks crystal structure at TEM scale. Similarly, carbonate and sulfate minerals are usually identified by the major cations present using EPMA or EDS (e.g., Harvey and McSween 1996; Bridges and Grady 1999, 2000; Bridges et al. 2001; Thomas-Keprta et al. 2009). Only sometimes is compositional information supplemented by crystal morphology (from SEM) and XRD (e.g., Gooding 1986a; Gooding et al. 1988, 1991; Wentworth and Gooding 1994). It is generally possible to discern different solid-solution carbonates and end members from one another by composition, and to confidently identify a mineral by composition as, for example, a calcium carbonate. However, insufficient crystallo-
graphic data generally exist to identify a specific polymorph (e.g., calcite or aragonite), although the TEM-SAED characterization of siderite in Lafayette by Bridges et al. (2004) and Changela and Bridges (2010) is a welcome improvement. Similarly, Ca-sulfates, Mg-sulfates, and mixed-cation sulfates can be distinguished from one another on the basis of compositional evidence, but it is usually difficult to distinguish between different hydration states of sulfates of the same cations (e.g., gypsum from anhydrite; or the many known hydration states of Mg-sulfates). The recent TEM-SAED identification of gypsum as the specific Ca-sulfate in Nakhla by Changela and Bridges (2010) is an important step forward. Intergrowths of multiple phases at scales smaller than the EDS or EPMA probe spot size can give the same compositions as many solid solutions, so it is not always possible to distinguish among several possible mineralogical interpretations of the same analyses (Gooding et al. 1988). Interestingly, this is also true for mission data from the surface of Mars. Partial (major element) compositional data, some spectroscopic data for some specific ions, species, bonds, and sites (e.g., monohydrated sulfates can be distinguished spectroscopically from polyhydrated sulfates; Gendrin et al. 2005, Bibring and Langevin 2008), and rarely morphological information are available to arrive at plausible identifications of minerals likely to be present in any analyzed area. However, complete data sets consisting of both chemical analyses and crystallographic data that would definitively characterize mineral structure (e.g., XRD or SAED), the combination of which would thereby permit the writing of mineral structural formulae for individual phases, are lacking.

**Phyllosilicates:** Among Martian meteorites, only nakhlites contain noteworthy abundances of phyllosilicate minerals. TEM lattice-fringe images from the phyllosilicate component of siderite in Lafayette by Bridges et al. (2004) and Changela and Bridges (2010) is a welcome improvement. Similarly, Ca-sulfates, Mg-sulfates, and mixed-cation sulfates can be distinguished from one another on the basis of compositional evidence, but it is usually difficult to distinguish between different hydration states of sulfates of the same cations (e.g., gypsum from anhydrite; or the many known hydration states of Mg-sulfates). The recent TEM-SAED identification of gypsum as the specific Ca-sulfate in Nakhla by Changela and Bridges (2010) is an important step forward. Intergrowths of multiple phases at scales smaller than the EDS or EPMA probe spot size can give the same compositions as many solid solutions, so it is not always possible to distinguish among several possible mineralogical interpretations of the same analyses (Gooding et al. 1991), Lafayette (Treiman et al. 1993, Changela and Bridges 2010), NWA 817 (Gillet et al. 2002), and Yamato 000593 (Noguchi et al. 2009). A phyllosilicate with d(001) = 0.7 nm (consistent with serpentine-group minerals) has recently been reported to be part of the phyllosilicate assemblage in Yamato 000593 (Noguchi et al. 2009) and Lafayette (Changela and Bridges 2010). The occurrence of smectite-group phyllosilicates has also been inferred from Fourier transform infrared (FTIR) spectroscopy in the Yamato 000593 nakhlite (Imae et al. 2003) and from electron probe microanalysis in MIL 03346 (Imae and Ikeda 2007). Noncrystalline Fe-Mg-Al-Si material with smectite- and serpentine-like compositions occurs as a volumetrically dominant part of the “iddingsite” vein assemblage in all five of the nakhlites examined by Changela and Bridges (2010). The material called iddingsite in Martian meteorites resembles its terrestrial counterpart in being a mixture of the same constituent minerals (a smectite-hydroxide assemblage) and in being associated exclusively with olivine, but it differs in being volumetrically dominated by amorphous material without the systematic crystallographic relationships with the reactant olivine common among terrestrial iddingsites examined by optical petrography (Delvigne et al. 1979) and TEM (Eggleton 1984, 1986; Smith et al. 1987).
Iddingsite in the Lafayette nakhlite contains alkalis and Br in excess of amounts attributable to olivine, and the chemical compositions of Lafayette iddingsites are effectively modeled as local olivine + local siliceous mesostasis + water containing magnesium, sulfate, and chloride (Treiman et al. 1993, Treiman and Lindstrom 1997). Changela and Bridges (2010) interpreted measured compositional variations in the predominantly amorphous material of nakhlite iddingsite veins in terms of impact-induced hydrothermal flow upward through the vertical arrangement of nakhlites in their source igneous body suggested by the “nakhlite stack” hypothesis introduced previously (Friedman Lentz et al. 1999; Mikouchi et al. 2003, 2005, 2006; McKay et al. 2007).

While other more soluble minerals (carbonates, sulfates, halite) might form readily during natural (Velbel et al. 1991) or curatorial/ laboratory (Schwandt 2005) weathering of stony meteorites, including achondrite falls (Gooding et al. 1991, Schwandt 2005), the occurrence of demonstrably preterrestrial iddingsite in the fall Nakhla (Gooding et al. 1991, Wentworth et al. 2005) permits the interpretation of all similar occurrences in other nakhlites as also being preterrestrial. Preterrestrial aqueous alteration of olivine to iddingsite in the nakhlite Lafayette occurred ca. 670 Ma (Swindle et al. 2000). Phyllosilicates are unknown from either of the two chassignites that crystallized at the same time as the nakhlites.

Unspecified phyllosilicates have also been noted by SEM-EDS in the shergottite finds EETA 79001 (Gooding 1986a, 1986b; Gooding and Muenow 1986) and ALHA 77005 (Wentworth and Gooding 1993). These phyllosilicates are no older than the phyllosilicates in which they occur, but they cannot be unequivocally attributed to preterrestrial origin from finds alone.

Laihunite: Laihunite, a mineral with a structure similar to olivine but with oxidized Fe and vacancies, has been reported from Yamato 000593 (Noguchi et al. 2009). Laihunite forms during subsolidus oxidation of olivine (Banfield et al. 1999). Noguchi et al. (2009) inferred an alteration temperature of 400–800 °C.

Carbonates: Carbonate minerals occur in all classes of Martian meteorites, and in both falls and finds. Carbonates (Fig. 8) in ALH 84001 (Fig. 1) have a broad range of compositions, including calcite, dolomite–ankerite solid-solution, siderite–magnesite solid-solution, and intermediate compositions (Mittlefehldt 1994; Romanek et al. 1994; Harvey and McSween 1996; McKay et al. 1996; Valley et al. 1997; Scott et al. 1997, 1998; Treiman and Romanek 1998; Scott 1999; Barber and Scott 2003, 2006; Treiman 2003; Corrigan and Harvey 2004; Thomas-Keptra et al. 2009). Compositional diversity carbonate minerals often occur adjacent to one another in concentrically zoned disks or rosettes (Fig. 8) (Mittlefehldt 1994; Romanek et al. 1994; Harvey and McSween 1996; McKay et al. 1996; Kirschvink et al. 1997; Valley et al. 1997; Scott et al. 1998; Scott 1999; Brearley 2003; Treiman 2003; Barber and Scott 2003, 2006; Corrigan and Harvey 2004; described recently and in great geometric detail by Thomas-Keptra et al. 2009). Carbonates occurring as veins and fracture and void fillings are also noted (Harvey and McSween 1996; Barber and Scott 2003; Corrigan and Harvey 2004), but many are compositionally zoned like the disks (Scott et al. 1997, 1998; Scott 1999) and are probably just disks exposed as apparent slabs in cross section (Corrigan and Harvey 2004). ALH 84001 carbonates are associated with corroded opx, but this is only seen using high-magnification/high-resolution microscopic methods (FEG-SEM, TEM) employed by only a few published studies (McKay et al. 1996; Barber and Scott 2003, 2006; Thomas-Keptra et al. 2009). If the textures imaged at the opx–carbonate interface by high-magnification methods are typical of carbonate-disk–opx interfaces, this association may be quite widespread. The genesis of carbonates in ALH 84001 (especially the temperature of their formation) as inferred from mineral-composition/phase-equilibrium relationships, stable isotopes, and paleomagnetism, has been the subject of considerable debate and disagreement (Mittlefehldt 1994, Harvey and McSween 1996, McKay et al. 1996, Hutchins and Jakosky 1997, Kirschvink et al. 1997, Valley et al. 1997, Farquhar et al. 1998, McSween and Harvey 1998, Scott et al. 1998, Treiman and Romanek 1998, Warren 1998, Scott 1999, Golden et al. 2000, Brearley 2003, Treiman 2003, Corrigan and Harvey 2004, Romanek et al. 2004, Bell 2007, Steele et al. 2007, Niles et al. 2009, Thomas-Keptra et al. 2009), as has their possible subsequent shock-metamorphic modification (Ash et al. 1996; Scott et al. 1997; Treiman 1998, 2003; Brearley 2003; Barber and Scott 2003, 2006; Bell 2007; Steele et al. 2007). Carbonate (associated with corroded opx) in ALH 84001 formed ca. 3.6–4.0 Ga (Knott et al. 1995, Borg et al. 1999). Interested readers should acquaint themselves with the primary papers cited in this paragraph.

A Ca-bearing calcite-group mineral has been inferred to occur in Nakhla from morphological crystallography using SEM-EDS (Gooding et al. 1991). Subsequent EPMA analyses of carbonates in multiple nakhlites revealed a broad range of compositions, including near-end-member siderite (structure confirmed by ATEM-SAED; Bridges et al. 2004, Changela and Bridges 2010), Mg- and Mn-rich siderite, and compositions intermediate between the dolomite–ankerite and siderite–magnesite solid-solutions (Bridges and Grady 1999, 2000; Bridges et al. 2001, 2004; Changela and Bridges 2010). Unlike ALH 84001 carbonates, compositionally distinct carbonates in nakhlites are spatially discrete or related as bands or laminae rather than juxtaposed in concentrically zoned disks or rosettes, and Ca-rich carbonates (e.g., more Ca-rich than the dolomite–ankerite solid-solution series) have not been reported from nakhlites.

Carbonates are reported from both chassignites. Calcite, magnesite, and hydromagnesite were identified in the fall Chassigny by morphological crystallography in SEM, with EDS (Wentworth and Gooding 1994). Wentworth et al. (2005) reported additional occurrences of Ca-carbonate on exposed olivine grain-boundary fracture surfaces in Chassigny. Occurrences of carbonates in the fall Chassigny are consistent with a preterrestrial origin, but formation of hydromagnesite after the recovery of olivine-bearing chondritic stony meteorites has been documented (Velbel et al. 1991). In addition to occurrences of individual evaporite minerals, some disk-shaped masses occur with nonporous Ca-sulfate in the center, surrounded by microgranular or porous (dehydrated? devolatilized?) Ca-carbonate (Wentworth et al. 2005). Calcite and aragonite in NWA 2737 (chassignite find) were distinguished from one another by Raman spectroscopy, and some carbonates appear to have experienced shock metamorphism, indicating preterrestrial origin for at least those occurrences (Beck et al. 2006).

Calcite (confirmed by XRD), and unspecified Ca-carbonate and low-Ca-carbonate (identifying by SEM-EDS) have all been reported in the shergottite EETA 79001 (Fig. 2; Gooding 1986a, Gooding et al. 1988). Some Ca-carbonate in the shergottite EETA 79001 occurs in veins and pockets of shock melt formed during an impact on Mars (Gooding et al. 1988; the same shock melt that trapped Martian atmospheric gases; Bogard and Johnson 1983). This suggests that at least these Ca-carbonate grains were already present in the rock when it experienced impact and shock on Mars, and they are carbonate grains of Martian origin (Gooding et al. 1988). Evidence for the pre-ejection origin of some Ca-carbonates in EETA 79001 is strong (Gooding et al. 1988), although this may not extend to other carbonate occurrences in this meteorite; as a find, it may have been affected by terrestrial aqueous alteration during its Antarctic exposure prior to recovery.

In stony meteorites, carbonate minerals are known to form by terrestrial weathering of the meteorite before recovery. Witnessed falls can be similarly affected; samples collected many decades after the fall of the diogenite Tatahouine contain carbonates that are not present in samples collected immediately after the fall (Barrat et al. 1998, 1999;
Gillet et al. 2000; Benzerara et al. 2003, 2005a, 2005b, 2006). In one well-studied ordinary chondrite find from Antarctica (LEW 85320), carbonate minerals (the hydrous Mg-carbonates nesquehonite and hydromagnesite) formed both naturally before recovery and in the laboratory after recovery during sample processing and storage (e.g., Jull et al. 1988, Velbel et al. 1991). Consequently, given that 46 of the 50 presently known Martian meteorites are finds, considerable care must be taken to avoid overinterpreting occurrences of carbonates in Martian meteorite finds as indicators of carbonate-forming processes on Mars.

**Sulfates:** The nakhlites Nakhla (fall), Governador Valadares (find), NWA 998 (find), Yamato 000749 (find), and MIL 033346 (find; Figs. 3, 4), and the chassignite Chassigny (fall) all contain Ca-sulfates. Morphological crystallography indicates gypsum or bassanite in Nakhla (Gooding et al. 1991) and Chassigny (Wentworth and Gooding 1994). Gypsum and anhydrite are distinguished from one another by EPMA in Nakhla (fall) and Governador Valadares (find); analyses with totals near 100% are interpreted as anhydrite, whereas those with significantly lower totals are interpreted as gypsum (Bridges and Grady 1999, 2000). Gypsum in Yamato 000749 has been identified by Raman spectroscopy (Noguchi et al. 2009), and in Nakhla, it has been confirmed by TEM-SAED (Changela and Bridges 2010). In Nakhla, striated (corroded? dehydrated?) Ca-sulfate occurs on visibly unmodified silicate surfaces (Wentworth et al. 2005).

Multiple hydration states of Mg-sulfate are known to occur on Earth, and many of the known hydration states are stable or metastable under the range of Mars’ surface conditions (Vaniman et al. 2004, Vaniman and Chipera 2006, Peterson et al. 2007). Unspecified shrunken and cracked Mg-sulfate occurs immediately beneath fusion crust in Nakhla (Gooding et al. 1991, Wentworth et al. 2005). One interpretation is that the hydrous sulfate was metamorphosed (dehydrated?) by heating associated with fusion crust formation; this would indicate the sulfate was preterrestrial (Wentworth et al. 2005). However, it is less clear is the Mg-sulfates are intact away from fusion crust. Consequently, an alternate interpretation is that hydrous sulfates throughout Nakhla might have been dehydrated regardless of proximity to fusion crust; this would render the timing of sulfate formation ambiguous. However, there are published images of Ca-sulfates (reported to be anhydrite) in samples away from fusion crust, in the interior of Nakhla, that lack internal cracks or shrinkage textures (Bridges et al. 2001, Leshin and Vicenzi 2006). Further study of Nakhla is required to ascertain the state of Mg-sulfate away from the thermal influence of fusion crust.

Jarosite occurs as part of a jarosite–hematite assemblage in the Antarctic nakhlite find MIL 03346 (McCubbin et al. 2009). Identified by EPMA and Raman spectroscopy and situated in a pyroxene-hosted melt inclusion with no obvious indications of terrestrial weathering or contamination, this mineral assemblage in the melt inclusion leads to the interpretation that the jarosite formed from magma-associated hydrothermal fluids (McCubbin et al. 2009). Hydrothermal sulfate would not be closely related to the widespread primary sedimentary hydrothermal fluids (McCubbin et al. 2009). Consequently, given that 46 of the 50 presently known Martian meteorites are finds, considerable care must be taken to avoid overinterpreting occurrences of carbonates in Martian meteorite finds as indicators of carbonate-forming processes on Mars. However, even Martian meteorite finds (e.g., EETA 79001, MIL 03346) can preserve preterrestrial evaporite minerals in textures for which evidence of a preterrestrial (Martian) origin is compelling (Gooding et al. 1988, McCubbin et al. 2009), allowing retrieval of useful information about aqueous alteration on Mars. The textures and textural contexts of such minerals must be examined carefully to distinguish preterrestrial evaporite minerals from occurrences of similar minerals formed or redistributed by terrestrial processes.

**Halite:** Halite has been reported in several allocations of Nakhla (fall) (Gooding et al. 1991; Bridges and Grady 1999, 2000; Wentworth et al. 2005). Where secondary-electron imagery enables study of grain shape, rounded halite grains rest on a pyroxene surface in the meteorite’s interior (Wentworth et al. 2005). Rounding of halite (and other highly soluble minerals) is characteristic of (diffusion-limited) dissolution in undersaturated solutions (Velbel 2004). Dissolution experiments commonly proceed to complete destruction of the halite (Simon 1981, Alkattan et al. 1997), and although grain shapes and
Textures have been described at intermediate stages in such experiments (Walker and Kiefer 1985, Kerr 1995), it is not known how partially dissolved halite grains would look if their dissolution were interrupted (by, for example, a very small amount of water reaching saturation with respect to halite before complete dissolution of the halite grain).

It is possible that the halite in Nakhla was euhedral before sample preparation. Before the meteoritics community became aware of the possibility of halite occurring in meteorites, meteorites were cut and polished for thin sectioning using water, as have been most terrestrial rocks not expected to contain easily soluble minerals. Halite dissolves readily in dilute aqueous solutions (Simon 1981, Walker and Kiefer 1985, Kerr 1995, Alkattan et al. 1997; sand-size grains of halite dissolve completely in tap water or distilled water in tens of seconds at Earth-surface temperatures—Walker and Kiefer 1985, Velbel 2004). Some halite occurs in Nakhla (fall) fractures and vugs in the fusion crust and therefore postdates Earth arrival of Nakhla (Gooding et al. 1985). The restricted range of halite occurrence (only in Nakhla; Gooding et al. 1991) and during laboratory curation of finds cannot be safely inferred to indicate that halite was absent from ALH 84001 (McLennan and Grotzinger 2008, Ming et al. 2008). However, for many of the ancient altered-bedrock and ancient sedimentary assemblages observed from orbit, phyllosilicates do not coexist with the soluble salt–mineral phases that should have formed as a result of igneous mineral alteration and subsequent phyllosilicate mineral formation (Milliken et al. 2009). At least in isolated localities on the ancient Noachian surface of Mars, leaching and removal of soluble components may have been more prevalent, perhaps implying a more water-rich environment than has been inferred from landed-mission data sets and the alteration-mineral assemblages of Martian meteorites (Milliken et al. 2009).

The aqueous alteration record in Martian meteorites resembles that inferred from Mars' surface mineralogy (McSween et al. 2004, Bibring et al. 2006, Herkenhoff et al. 2006, Bibring and Langevin 2008, McLennan and Grotzinger 2008, Ming et al. 2008, Velbel and Losiak 2010) in that the parent minerals pyroxene and olivine are present, available for weathering, and detectably modified by alteration, and that phyllosilicates, carbonates, and sulfates formed during aqueous alteration without leaching of soluble products. The persistence of both primary silicates and many soluble products indicates that water was minor in abundance, limited in movement, and present for too short a time to consume primary minerals and/or leach away soluble products (McLennan and Grotzinger 2008; Ming et al. 2008).

The aqueous alteration record in Martian meteorites differs from that inferred from Mars' surface mineralogy (McSween et al. 2004, Bibring et al. 2006, Herkenhoff et al. 2006, Bibring and Langevin 2008, McLennan and Grotzinger 2008, Ming et al. 2008, Velbel and Losiak 2010) in that meteorites record phyllosilicate and sulfate formation long after the main phyllosilicate- and sulfate-forming intervals inferred from the distribution hydrous minerals among Mars' surface geomorphic units (early–mid-Noachian and latest Noachian to late Hesperian, respectively; Bibring et al. 2006, Bibring and Langevin 2008, Ming et al. 2008). Phyllosilicates and sulfates in 1.3-Ga-old nakhlites formed after the nakhlites crystallized, indicating aqueous alteration during the Amazonian, which appears from orbit to have been a period of oxide, rather than phyllosilicate or sulfate, formation (Bibring et al. 2006, Bibring and Langevin 2008). Meteorites may sample rock-dominated aqueous microenvironments within which alteration-mineral assemblages formed in near isolation from surface acidity (Newson 2005, Tosca and McLennan 2006, McLennan and Grotzinger 2008). Such relatively benign geochemical environments are potentially promising subsurface targets for future exploration of potentially habitable environments on Mars (Grotzinger 2009).

Evaporation Sequences in Martian Meteorites

Abundant S and Cl have been observed in chemical analyses of Mars' surface materials since the Viking landers arrived at Mars in 1976, and they have been interpreted to indicate mediation of Mars'
surface chemistry by mobilization of sulfate and chloride by small amounts of water with sufficiently high solute loads to readily precipitate sulfate and chloride minerals (Clark et al. 1977, 1982, 2005; Clark and van Hart 1981; Banin et al. 1992; Gooding et al. 1992; Clark 1993; McLennan and Grotzinger 2008; Ming et al. 2008). Much remains to be resolved. The recent recognition at the Phoenix mission’s landing site of perchlorate compounds (Hecht et al. 2009) has motivated reexamination of oxidation–reduction phenomena in Viking lander data (Navarro-González et al. 2010), and will stimulate new understanding of chlorine dynamics and oxidation pathways in weathering reactions well beyond common terrestrial experience. The sulfate that eventually precipitates as sulfate minerals in Martian materials may have originated by localized volcanic hydrothermal or fumarolic processes, widespread dispersal of volcanogenic volatiles in acid fog, oxidation of primary igneous or sedimentary diagenetic sulfides, and/or redistribution of any such sulfur by hydrothermal alteration after impacts (see reviews by McLennan and Grotzinger [2008] and Ming et al. [2008]). Furthermore, multiple processes can produce brines; evaporation is most commonly considered (McLennan and Grotzinger 2008, Ming et al. 2008), but freezing or ablation of even initially dilute aqueous solutions produces brines as water (solvent) is removed, leaving the same quantity of solutes in a decreasing amount of solvent until the solution is supersaturated with respect to “evaporite” minerals (Herut et al. 1990, Marian et al. 1999, Starinksy and Katz 2003, McLennan and Grotzinger 2008, Morin et al. 2008, Niles and Michalski 2009, Frank et al. 2010). Nevertheless, ambiguity about sulfate and chloride sources and detailed concentration mechanisms notwithstanding, the ubiquity and importance of sulfate and chloride in Mars materials has long been and remain well established (Clark et al. 1977, 1982, 2005; Clark and van Hart 1981; Banin et al. 1992; Gooding et al. 1992; Clark 1993; McLennan and Grotzinger 2008; Ming et al. 2008). Consequently, meteoriticists were established (Clark et al. 1977, 1982, 2005; Clark and van Hart 1981; McLennan et al. 2005), on exposed surfaces of Mars’ surface materials have been directly accessible to volcanogenic sulfuric-acid dominated). This may be because Mars’ surface materials have been directly accessible to volcanogenic sulfuric acid, whereas Martian meteorites were exhumed (during impact and ejection) from subsurface depths (tens of meters up to ~200 m; Fritz et al. 2005) possibly sufficient to isolate those rocks from atmospheric sulfuric-acid acidity (Newsom 2005, Tosca and McLennan 2006). McLennan and Grotzinger 2008). This would allow acid-consuming reactions (e.g., reaction Eq. 2) with basaltic minerals (with reactions confined to igneous grain boundaries, and low water–rock ratios) to raise local pH sufficiently to allow shifts in carbonate equilibria and increases in bicarbonate abundances (Tosca and McLennan 2006).

Chassignites have the same (igneous) crystallization age as the nakhlites. Some previous evaporation models for nakhlite alteration minerals (Bridges and Grady 2000) and some evaporation sequences on the carbonate-dominant side of the chemical divide diagram of Tosca and McLennan (2006) are consistent with the crystallization sequence (sulfate first, then carbonate) implied by the sulfate–carbonate disks in Chassigny reported by Wentworth et al. (2005). However, observed carbonate minerals are more diverse and complicated than current models can address. Calcite occurs along with magnesite and hydromagnesite in the chassignite fall Chassigny (Wentworth and Gooding 1994), and along with aragonite (identified by Raman spectroscopy) in the recently recovered chassignite NWA 2737 (Beck et al. 2006, Treiman et al. 2007). Calcite occurs as apparently the only carbonate in the shergottite find EETA 79001 (identified as calcite by XRD; Gooding et al. 1988). Calcite occurs along with Mg-, Fe-, and Mn-carbonates in the unique orthopyroxenite find ALH 84001 (e.g., Harvey and McSween 1996, Corrigan and Harvey 2004). These occurrences of calcite, especially those in falls, are consistent with the overall bicarbonate-dominated branch of Tosca and McLennan (2006). If the carbonates in ALH 84001 and EETA 79001 are preterrestrial (the data, while not unequivocal, are strong for both meteorites), Martian meteorites of a broad range of crystallization
and alteration ages (not just nakhlites) all formed their carbonate and alkaline-earth sulfate minerals by evaporation from an initially bicarbonate-dominated solution, in contrast to sulfate-dominated Mars’ surface conditions (Tosca and McLennan 2006). However, the initial solute conditions and chemical divides required to produce calcite differ from those required to produce the sideritic–ankeritic carbonates of the nakhlites (Tosca and McLennan 2006). This may be important for nakhlites, in which siderite, magnesite, and a wide range of carbonates with partial Fe- and Mn-substitution all occur at various locations in different meteorites and samples, and it is particularly significant for ALH 84001, in which calcite, magnesite, and a wide range of carbonates with partial Fe- and Mn-substitution all coexist in rosettes. The causes of the solution-composition variations that produced carbonates from different chemical-divide sequences of Tosca and McLennan (2006) in different Martian meteorites from different groups (e.g., calcite in EETA 79001 as opposed to sideritic–ankeritic carbonates in nakhlites), different meteorites from the same group (nakhlites), and especially different parts of the same rosettes in the same meteorite (ALH 84001) require further investigation.

SUMMARY

Meteors of several igneous rock types have a variety of chemical and isotopic indicators of formation on Mars. Martian meteorites complement data from missions to Mars. Microscopic (petrographic) analysis of Martian meteorites in terrestrial laboratories reveals features much smaller in scale than almost all the smallest-scale imagery from Mars’ surface missions. Textural evidence from terrestrial microscopy also establishes paragenetic reaction and sequence relationships that cannot be distinguished in bulk mineral assemblages as detected by spectroscopic instruments from orbital or surface missions. Variations in hydration states among otherwise similar minerals can be better distinguished from samples in meteorites than from orbiter, lander, or rover spectroscopy, but even in Martian meteorites, hydration states of such minerals may have been modified from their Martian state during sample arrival at Earth, recovery, and curatorial processing. In addition, geochronologic analyses of Martian meteorite samples in terrestrial laboratories place absolute age-dating constraints on igneous crystallization and aqueous alteration processes on Mars that cannot yet be replicated by remote spacecraft instrumental methods.

The paucity of abundant and mobile solutions undersaturated with respect to primary minerals manifests itself as widespread persistence of olivine and pyroxene both in Martian meteorites and at the surface of Mars. Unlike Earth, where a vigorous hydrologic cycle results in widespread leaching of soluble products from weathering sites and eventual precipitation elsewhere as chemical sediments, the dissolved products of weathering reactions in Martian meteorites were not removed far from the reaction sites. Solutes released by primary mineral weathering in Martian meteorites precipitated locally in transmineral and grain-boundary fractures as cation-rich clays, carbonates, and evaporite minerals, rather than being leached away.

Primary mineral corrosion and secondary minerals occur in Martian meteorites of a range of ages, from ca. 3.9 Ga (approximately mid-Noachian; opx corrosion and associated carbonate formation in ALH 84001), through one or more episodes after ca. 1.3 Ga (approximately mid–late Amazonian; pyroxene corrosion and diverse alteration minerals in nakhlites), and possibly until quite recently (late Amazonian; preterrestrial carbonate and sulfate in the ca. 170 Ma shergottite EET 79001). These occurrences record aqueous alteration processes over a broad range of times in the paleoenvironmental history of Mars’ surface.

Both Martian meteorites and Mars’ surface materials exhibit corrosion features on the same primary minerals (pyroxene and olivine), and many of the same alteration-product minerals occur, including clay minerals and mineraloidals, carbonates, sulfates, and halite. However, aqueous alteration in Martian meteorites is not identical to the aqueous alteration inferred to have affected Mars’ surface materials. The main secondary host minerals for Fe differ; in Martian meteorites, sideritic–ankeritic carbonate is the main secondary host mineral for Fe, whereas in Mars’ surface materials, ferric oxides and ferric sulfates are the main secondary host minerals for Fe. This is most likely a consequence of differences in the initial compositions of the altering solutions, with carbonate/bicarbonate dominating in the solutions that altered Martian meteorites and sulfate dominating the solutions that altered most Mars’ surface materials. Martian meteorites may have been exhumed from depths on the order of tens of meters, depths that may have isolated Martian meteorites from large quantities of Mars’ surface solutions and created more basalt-mineral–buffered high pHs in the fracture microenvironments within which Martian meteorite aqueous alteration occurred. If so, Martian meteorites provide insight into the basic nature of low-temperature mineral–water interactions on Mars, and they direct attention to potentially promising subsurface targets for future exploration of potentially habitable environments on Mars (Grotzinger 2009).

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AQUEOUS ALTERATION IN MARTIAN METEORITES


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