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Journal of Geophysical Research: Planets

RESEARCH ARTICLE

10.1002/2015JE004805

Key Points:

- The wide spatial distribution of bassanite suggests its Martian origin
- Solid solutions of (K, Na)-jarosite exist in veins and in mesostasis
- The sulfide mineral rasvumite is firstly identified in Martian meteorite

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Citation:

Ling, Z., and A. Wang (2015), Spatial distributions of secondary minerals in the Martian meteorite MIL 03346,168 determined by Raman spectroscopic imaging, *J. Geophys. Res. Planets*, *120*, 1141–1159, doi:10.1002/2015JE004805.

Received 11 FEB 2015 Accepted 13 MAY 2015 Accepted article online 15 MAY 2015 Published online 9 JUN 2015

Spatial distributions of secondary minerals in the Martian meteorite MIL 03346,168 determined by Raman spectroscopic imaging

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Abstract Miller Range (MIL) 03346 is a nakhlite meteorite that has been extensively studied due to its unique complex secondary mineral phases and their potential implications for the hydrologic history of Mars. We conducted a set of Raman spectroscopic and Raman imaging studies of MIL 03346,168, focusing on the secondary mineral phases and their spatial distributions, with a goal to better understand the possible processes by which they were generated on Mars. This study revealed three types of calcium sulfates, a solid solution of (K, Na)-jarosite and two groups of hydrated species with low crystallinity (HSLC) in the veins and/or mesostasis areas of the meteorite. The most abundant Ca-sulfate is bassanite that suggests two possible paths for its direct precipitation from a Ca-S-H₂O brine, either having low water activity or with incomplete development (producing bassanite with gypsum microcrystals) on Mars. The second most abundant Ca-sulfate is soluble γ -CaSO₄ which raises a new question on the origins of this phase in the Martian meteorite, since γ -CaSO₄ readily hydrates in the laboratory but is apparently stable in Atacama Desert. The close spatial relationship of (K, Na)-jarosite solid solutions with rasvumite (KFe₂S₃), magnetite, HSLC, and fine-grained low-crystallinity alkali feldspar in mesostasis suggests a potential in situ formation of mesostasis jarosite from these Fe-K,Na-S-O-H₂O species.

1. Introduction

Shergottites, nakhlites, and chassignites (SNC) are meteorites from Mars which record the diagenetic and alteration processes on the red planet. Nakhlites, as the second most abundant group (11 separate meteorites) [*Hallis et al.*, 2014] of SNC, have been intensively studied for their primary igneous and secondary alteration processes relevant to Mars [e.g., *Treiman*, 2005; *Day et al.*, 2006; *Imae and Ikeda*, 2007; *Changela and Bridges*, 2010]. Miller Range (MIL) 03346 is a nakhlite meteorite found in Miller Range, Antarctica, in 2003. It is reported to experience a fast cooling process, supported by the texture evidence of the glassy intercumulus with few albitic feldspar laths [*Day et al.*, 2006; *Hallis*, 2013]. The major elemental composition of MIL 03346 is somewhat depleted in Mg and Fe but more enriched in Na, K, and Al than Nakhla, and the composition may be affected by the existence of alteration phases [*Anand et al.*, 2005; *Imae and Ikeda*, 2007; *Stopar et al.*, 2013]. MIL 03346 is one of the two nakhlites that contains jarosite [*Herd*, 2006], indicating aqueous alteration might have happened during its stay on Mars [*McCubbin et al.*, 2009; *Hallis and Taylor*, 2011].

However, the origin of the secondary minerals found in MIL 03346 remains an open question. The existence of sulfates in MIL 03346 from Mars has been validated through recent orbital remote sensing and surface exploration missions [e.g., *Klingelhöfer et al.*, 2004; *Bibring et al.*, 2006; *Vaniman et al.*, 2014]. Jarosite in MIL 03346 is suggested to be Martian in origin based on its nonterrestrial D/H ratios and its microtextural property [*Vicenzi et al.*, 2007]. *McCubbin et al.* [2009] reported that the jarosite found in the melt inclusion of MIL 03346 is hydrothermally precipitated from the reaction of Martian liquid phase with sulfide minerals. On the other hand, based on the textural and mineralogical studies of MIL 03346 and its three pairs, *Hallis and Taylor* [2011] suggested that the majority of sulfate veins along the exposed edges of the meteorites are terrestrial alterations. Their hydrogen isotope study of the secondary alteration phases in MIL 03346 indicated that the δD values were within the terrestrial range [*Hallis et al.*, 2012]. However, *Hallis* [2013] did not exclude the possibility of Martian origin of interior jarosite in MIL 090136 by comparative

©2015. American Geophysical Union. All Rights Reserved. study with terrestrial Antarctic samples, and further study suggested that the alteration conditions on Mars might be similar to those in Antarctica [*Hallis et al.*, 2014].

Martian meteorites are the only samples that we have available for full scale investigation using a wide range of analytical methods in laboratories. For future planetary missions especially for Mars surface exploration, Raman spectroscopy has a great advantage due to its power in fast molecular (organic and inorganic) phase identification in mixtures, characterization of mineral chemistry, and the minimum-to-no sample preparation requirement [e.g., Rull et al., 2011; Sharma et al., 2003; Wang et al., 1995, 2003]. The applications of Raman spectroscopy in planetary sciences and its potential in planetary explorations have been developed since 1995, for igneous mineralogy and petrology that target the Moon, Mars, and Venus [Freeman et al., 2008; Haskin et al., 1997; Kuebler et al., 2006; Ling et al., 2011; Wang et al., 1994, 1995, 1999a, 1999b, 2001, 2004a, 2004b; Wang, 2009]; and for secondary mineralogy and alteration processes that target Mars, asteroids, and other primary planetary bodies [Chio et al., 2004, 2010; Chou et al., 2013; Gough et al., 2011, 2014; Nuding et al., 2014; McSween and Treiman, 1998; Kong et al., 2011a, 2011b; Kong and Wang, 2010; Ling and Wang, 2010; Wang et al., 2002; Wang and Valentine, 2002; Wang et al., 2006, 2009, 2011, 2012; Y. W. Wang et al., 2012; Wang et al., 2015; Wang and Ling, 2011; Wang and Zhou, 2014; Wei et al., 2015; Liu and Wang, 2015; Wang et al., submitted to Journal of Raman Spectroscopy]. Recently, three Raman units have been selected as scientific payloads for 2018 ExoMars and 2020 Mars rover, with the mission goals of fine-scale definitive mineralogy and biosignature detection.

We report here a detailed study of a thin section of MIL 03346,168 using Raman spectroscopic imaging. Our goal is to get not only the detailed information on mineral identifications and mineral chemistry of this meteorite but more importantly the spatial relationships among all mineral phases. The spatial correlations of secondary minerals may hint at the origin of secondary minerals as well as the aqueous processes and the environments that this rock has experienced either on Mars or on Earth. This study also presents an example on the types and the depth of information that could be obtained from a set of stand-alone in situ Raman spectroscopic measurements during a surface exploration on Mars, if the right instrument configuration and operational scenario would be adopted.

2. Raman Spectroscopic and Raman Imaging Measurements

A thin section of MIL 03346,168 (Figure 1a) was used for this Raman imaging study. The sample surface area was estimated to be 142.7 mm², and an inVia[®] Raman System (Renishaw Company) was used for the imaging. In this study, a 532 nm Nd:YAG laser is focused on the sample using long working distance 50X (NA = 0.5) and 100X (NA = 0.75) objectives, which generate an ~1 μ m diameter laser spot at the sample. This Raman spectrometer has a spectral resolution better than 1 cm⁻¹. A neon emission lamp was used to calibrate the absolute wavelength of the spectrometer, while the ~520.5 cm⁻¹ line of crystalline Si was used to establish the Raman shift scale. These calibrations provide a Raman peak position accuracy and precision of ±0.2 cm⁻¹.

The first set of Raman measurements is the direct Raman point-check of the mineral grains in MIL 03346,168. The second set of Raman measurements is Raman imaging measurements using the StreamlineTM mode [methodology details in *Wang et al.*, 2015]. In making the Raman imaging measurements, we subdivided the meteorite into six regions (A to F as shown in Figure 1a). The origin position (0, 0) of each image is the same, which is controlled by an automatic *XYZ* stage with a precision of ~250 nm. The acquired Raman images for the regions of interest are produced by Direct Classical Least Squares of the WiRE 3.4TM software using the mineral end-member spectra obtained during Raman point-check measurements. In both sets of Raman measurements of this meteorite, there were very low to no fluorescence interferences in background of the recorded Raman spectra.

3. Mineral Identification and Mineral Chemistry

3.1. Percentage of Intercumulus in MIL 03346,168

MIL 03346 is a nakhlite mainly composed of clinopyroxenites with large augite grains and very few olivine phenocrysts (as shown in Figure 1a). The dark fine-grained intercumulus contains anhedral grains of fayalite overgrown with laihunite, orthopyroxene, skeletal Ti-Fe oxides, sulfides, and alteration phases. The mesostasis surrounding the large grains is composed of vitrophyric, feldspathic phases. The mineral



Figure 1. (a) The optical reflectance image of the thin section MIL 03346,168. The image is pixel referenced with origin at (0, 0), by which the location of each Raman spectra can be retrieved repeatedly. It is divided into A to F regions for ease of location of all Raman point-check and Raman imaging measurements. The pixel locations of the upper left and lower right for each region are indicated in the plot. (b) The classification of optical reflectance image of MIL 03366,168 for the estimation of intercumulus proportion in MIL 03346,168. The image is divided into two classes (color coded) by using the ENVI image analysis with a DN threshold value of 150.

percentages suggested by *Day et al.* [2006] are ~79% clinopyroxene, ~1% olivine, and ~20% vitrophyric intercumulus material. We estimated the percentage of intercumulus (veins and mesostasis) using the optical reflectance digital number (DN) value (Figure 1b). This method provides us an estimate of the intercumulus of ~25.4% in MIL 03346,168 that agrees well with previous studies [*Day et al.*, 2006; *Imae and Ikeda*, 2007]. It suggests MIL 03346 may have experienced a fast cooling history.

3.2. Primary Minerals

The main focus of this study is on the secondary minerals. The characterization of primary minerals, however, forms the basis of this investigation and will be presented first.

3.2.1. Pyroxene

Pyroxene as a major rock-forming mineral is the most common mineral with euhedral or subeuhedral morphology in MIL 03346,168. Most pyroxene grains are clinopyroxene rich indicated by their typical Raman peaks, located at ~1010 and 660 cm^{-1} , and triple or double peaks from 300 to 400 cm^{-1} . The different occupancies of cations (e.g., Mg, Fe, and Ca) in the distorted M1 or M2 sites of pyroxene lead to systematic variations of Raman peaks for those fundamental vibrations of SiO₄ tetrahedra. Based on the previous Raman studies [*Wang et al.*, 2001], the molar ratios of Mg/(Mg + Fe + Ca) and Ca/(Mg + Fe + Ca) of quadrilateral pyroxenes can be derived from their Raman peak positions.

As shown in Figures 2a and 2b, the pyroxene grains in MIL 3346,168 have two forms: phenocrysts and ~10 μ m-sized grain in mesostasis. From the grain rim (pos 1 of Figure 2a) to the grain center (pos 4), phenocrystic pyroxene shows a Raman peak position shift to a higher wave number (Figure 3a), which indicates a chemical zoning from a Fe-rich edge to Fe-poor center. All pyroxene grains in mesostasis are Fe rich (Figures 2b and 3a). We derived the molar ratio of Mg/(Mg + Fe) (the Mg#) of pyroxene grains, by conducting Raman peak curve fitting of peak 2 and peak 3 (marked in Figure 3a) using the mixed Gaussian and Lorentzian peak shape to obtain their precise peak positions with the WiRE 3.4TM software. We then plotted these Mg# values versus the frequency of occurrence in 64 pyroxene grains in MIL 3346,168, generating the compositional distribution of these pyroxene grains (Figure 3b). The apparent bimodal histogram suggests two separate events corresponding to the crystallization of phenocrystic augite in the cumulus and the formation of fine-grained Fe-rich pyroxene in the intercumulus. The cumulus euhedral pyroxene has very similar Raman peak position shift corresponding to Mg# ~0.5–0.6 in



Figure 2. The optical reflectance images of primary minerals and their spatial relationship with other mineral phases in MIL 03346,168. (a) A phenocrystic pyroxene (PX) in the cumulus and four positions of Raman point-check. Veins filled with bassanite (Bas), a laihunite (Laih) grain in mesostasis, and a Ti-magnetite (Mgt) grain are shown. (b) In mesostasis, fine grains of Fe-rich pyroxene (Fe-PX, lowest albedo) coexist with magnetite (highest albedo) and laihunite (median albedo); their phase ID were made by Raman point-check. (c) A phenocrystic olivine in cumulus and four positions of Raman point-check (pos 1 has a Raman spectrum of laihunite). Two skeletal magnetite grains in nearby mesostasis are shown. (d) A fayalite (FAY) grain (low albedo) in mesostasis, which is rimed by laihunite (Laih, higher albedo). A vein cutting through this grain is filled by ferrihydrite (Ferr) and magnetite (Mgt). (e) The newly found Martian mineral, a rasvumite (KFe₂S₃) grain (at cross center) with a higher albedo than skeletal T-magnetite (Mgt) in mesostasis. (f) In mesostasis, tiny grains of laihunite (median albedo), magnetite (higher albedo), and ferrihydrite (lowest albedo) are arranged in two linear features.

center (Wo35En38Fs30) and Fe-rich rim, in accord with previous studies [*Treiman*, 2005; or Wo40En36–38Fs24–22 by *Imae and Ikeda*, 2007; Wo38–42En35–40Fs22–28 by *Day et al.*, 2006]. These Fe-rich rims, which are also enriched in REEs compared with the cores, indicate diffusive cation exchange during a fractionation crystallization of the late-stage magma [*McSween and Treiman*, 1998; *Day et al.*, 2006; *Udry et al.*, 2012]. On the other hand, the fine pyroxene grains in the mesostasis have a relatively large range of Mg# (0.1–0.4), which suggests fast cooling of the residual magma.



Figure 3. (a) Raman spectra of a Fe-rich pyroxene grain in mesostasis and of a phenocrystic pyroxene from center to rim. (b) Compositional distribution of 64 pyroxene grains in MIL 03346,168 measured in this study. The Mg# values were derived from the positions of Raman peak 2 and peak 3 (marked in Figure 3a) based on a previous calibration study [*Wang et al.*, 2001].

3.2.2. Olivine

MIL 03346 is reported to have the smallest abundance of olivine and largest abundance of mesostasis among all known nakhlite [*Imae and Ikeda*, 2007]. Since olivine is the easiest of the primary silicates to be altered by acidic brines on Mars, a study of olivine grains (cumulus and in mesostasis) and their spatial correlation with secondary minerals is of high priority. The Raman spectral features of olivine show doublet peaks near the 810–850 cm⁻¹ region, which is the most obvious feature for distinguishing olivine from other minerals. The enrichment of Fe in olivine would lead to the Raman doublet shifting to lower wave number [*Chopelas*, 1991]. Based on a previous calibration study [*Kuebler et al.*, 2006], the Fo value [molar ratio of Mg/(Mg + Fe)] of an olivine can be derived based on the precise positions of the characteristic Raman peaks. The phenocrystic olivine grains (Figure 2c) are chemically zoned with Fe-enriched rim and Mg-rich center (Figure 4a). The small olivine grains in mesostasis are often found to coexist with laihunite— $Fe^{2+}Fe_2^{3+}(SiO_4)_2$ (Figure 2d). Typical Raman spectra of relatively Mg-rich olivine and Fe-rich olivine acquired from MIL 03346,168 are presented in Figure 4a.



Figure 4. Raman spectra of a phenocrystic olivine grain from rim to center (spectrum of pos 1 is a mixture of Fe-rich olivine and laihunite); the bottom spectrum is from a pure laihunite grain in mesostasis. (b) Composition distribution of 49 olivine grains in MIL 03346,168. The Fo values [molar ratio Mg/(Mg + Fe)] were derived from the positions of Raman peak 1 and peak 2 (marked in Figure 4a) based on a previous calibration study [*Kuebler et al.*, 2006].

A ferric olivine, laihunite $Fe^{2+}Fe_2^{3+}$ (SiO₄)₂, has three major Raman peaks near 893, 568, and 312 cm⁻¹ (bottom spectrum in Figure 4a). Laihunite is a strongly oxidized, vacancy-bearing fayalite. Experiments show that it can be formed by oxidizing fayalite with or without aqueous fluid at 400–800°C [*Kondoh et al.*, 1985], 100°C, and 300°C [*Banfield et al.*, 1990; *lishi et al.*, 1997], and can be decomposed into magnetite and amorphous silicate [*Noguchi et al.*, 2009]. In the mesostasis of MIL 03346,168, we found fayalite grains coexisting with laihunite, as evidenced by the appearance of Raman peaks from both phases in a single Raman measurement (fifth and sixth spectra in Figure 4a). We also found cores of fayalite rimed by laihunite (Figure 2d). Their close association suggests a common genetic origin—possibly a later oxidation process during the crystallization of fayalite grains.

The range of Fo values and compositional distribution based on Raman peak positions (peak 1 and peak 2 marked in Figure 4a) of 49 olivine grains in MIL 3346,168 are shown in Figure 4b. The cores of phenocrystic olivine usually have Fo > 0.4, while the mesostasis olivine grains usually have Fo < 0.3. These values are consistent with Fo value of 0.43 to 0.04 found by *Day et al.* [2006] on the basis of EMPA. However, different from the compositional distribution of pyroxene (Figure 3b), Figure 4b suggests that most olivine grains in MIL 3346,168 are Fe rich and exist in the mesostasis.

3.3. Other Primary Minerals in Mesostasis

The primary mineral phases in mesostasis are important for the understanding of the later cooling history of MIL 03346,168 and the formation of some secondary minerals. Thus, most of our Raman point-check measurements were made there. The mesostasis of MIL 03346,168 is populated with many tiny grains (Figures 2b, 2d, 2e, 2f, 5c, and 5f) being amorphous or of low crystallinity as revealed by their Raman spectra. These textural features suggest a fast cooling of the residual magma that formed mesostasis [*Day et al.*, 2006; *Udry et al.*, 2012]. Typical Raman spectra of main minerals (except Fe-rich pyroxene, fayalite, and laihunite) from mesostasis are shown in Figure 6.

We found that the matrix of mesostasis was composed of fine-grained feldspar. A few crystalline feldspar grains have the major Raman peak vary from 510 to $513 \,\mathrm{cm}^{-1}$ (first spectrum of Figure 6a). Most Raman spectra of feldspar grains, however, have weak band intensities with wide band widths with variable center peak positions (average position near $512 \,\mathrm{cm}^{-1}$). End-member K- and Na-feldspar, microcline and albite, have the major Raman peak at 509 and $514 \,\mathrm{cm}^{-1}$, respectively [*Freeman et al.*, 2008]. The Raman spectral features of most mesostasis feldspar indicate that they are solid solutions of (K, Na)-feldspar (no Ca-feldspar) and have low crystallinity. Furthermore, the derived compositional distribution of K- and Na-feldspar in this meteorite (not shown) suggests that they are closer to K-rich feldspar. Both compositional and structural characters of these feldspar grains suggest a quench cooling process of residual magma that formed mesostasis in this meteorite, because the precipitation of K- and Na-feldspar would be formed when crystallizing below 900°C.

Minor amount of cristobalite grains were found in the mesostasis of MIL 03346,168, as evidenced by two sharp peaks at 231 and 418 cm^{-1} (second spectrum of Figure 6a). Cristobalite is a high-temperature polymorph (stable above 1470°C) of silica but persists metastably at lower temperatures. Its existence plus the nonexistence of other low-T SiO₂ phases, such as quartz in mesostasis, also suggests a fast cooling of residual magma that formed the mesostasis.

Small amounts of apatite grains were found in the mesostasis of MIL 03346,168. Most of these apatite grains have a Raman peak occur near 962–963 cm⁻¹ (third spectrum of Figure 6a), except one with a Raman peak at 960 cm⁻¹. Considering that these apatite were formed from the residual magma that is volatile rich, they can be fluroapatite $[Ca_5(PO_4)_2F]$, or chlorapatite $[Ca_5(PO_4)_2CI]$, or rarely hydroxylapatite $[Ca_5(PO_4)_2OH]$. The v_1 Raman vibrational mode of the above end-member apatites occurred at 965, 959, and 962 cm⁻¹, respectively [*Levitt et al.*, 1970; *Kravitz et al.*, 1968; *Blakeslee and Condrate*, 1971]. The Raman peak position range of mesostasis apatite grains in MIL 03346,168 suggests that a solid solution of (F, Cl) $Ca_5(PO_4)_2$ is a candidate for the apatites in this meteorite.

Large amounts of titanomagnetite grains are found distributed randomly in the mesostasis. Raman peaks of pure magnetite [Fe₃O₄] are located at 667, 539, and 305 cm⁻¹ [*Wang et al.*, 2004a]. Increasing Ti content can cause the peak to shift to a higher wave number from 667 cm⁻¹ of magnetite to 679 cm⁻¹ of ulvospinel Fe₂TiO₄ [*Wang et al.*, 2004a]. Magnetite and ulvospinel form solid solutions at $T > 600^{\circ}$ C. The titanomagnetite

10.1002/2015JE004805



Figure 5. (a) Ca-sulfates in a vein gradually changed from gypsum (pos 1) to bassanite (pos 4). (b) γ -CaSO₄ is found to be stable in this meteorite, a grain (at cross center) on the wall of vein that is filled with bassanite. (c and d) End-members of K-jarosite, Na-jarosite, and their solid solutions (K-rich jarosite and Na-rich jarosite) are found in mesostasis and in veins. (e) The hydrated species with low crystallinity (HSLC, appears as "iddingsite" here) in the fracture of an olivine grain. (f) A group 1 HSLC (ferrihydrite, lower albedo) grain is surrounded by several laihunite grains (higher albedo).

grains in mesostatis of MIL 03346,168 have the major Raman peak position varying from 670 to 661 cm⁻¹ (fourth spectrum in Figure 6a), presumably caused by the increase of Ti content and the reduction of crystallinity (which can also shift Raman peaks to lower wave numbers).

A few grains of hematite were found in mesostasis, with typical spectral peaks located at 217, 280, and 391 cm^{-1} (fifth spectrum in Figure 6a). The downshifted peak positions from standard hematite (227, 292, and 411 cm^{-1}) [*Wang et al.*, 2004a] can also be caused by the increase of Ti content.

Ti-rich magnetite is the most abundant Fe-bearing phase in the mesostasis, suggesting Ti-enrichment in the residual melt of MIL 03346. Laihunite appears to be the second most abundant mineral. Many titanomagnetite grains have a skeletal texture (Figures 2c and 2e). Some small grains of Ti-magnetite and



Figure 6. (a) Typical Raman spectra of some primary minerals found in mesostasis of MIL 03346,168. (b) The newly discovered mineral rasvumite (KFe_2S_3) is found in MIL 03346,168 by its Raman spectrum that matches with spectrum r060491 in the RRUFF database. The third and fourth spectra are two typical Raman spectra of the hydrated phases with low crystallinity (HSLC). The first is tentatively assigned to ferrihydrite with low crystallinity, and the second is assigned to mixtures of poorly crystalline ferrihydrite, altered laihunite with a hydrous component, and low-crystallinity, hydrous phyllosilicate(s).

laihunite show as straight lines in mesostasis (Figure 2f). Both textural features support the quenching cooling of residual magma to form mesostasis [*Hallis and Taylor*, 2011].

3.4. A Newly Identified Mineral in Mesostasis, Rasvumite—KFe₂S₃

This mineral is found as a single phase grain in mesostasis and in veins of MIL 03346,168. It has a high reflectivity and irregular grain shape, and it often coexists with Ti-magnetite (Figure 2e) and both K-rich and Na-rich jarosites. Its Raman spectrum has three sharp bands at 471, 220, and 152 cm⁻¹ (top two spectra of Figure 6b). The identification of rasvumite was made by matching with the standard Raman spectrum shown in the RRUFF database (first spectrum of Figure 6b, R060491). When Rasvumite coexists with jarosite, detecting its three Raman bands of rasvumite was sometimes difficult, because of overlapping with nearby jarosite peaks. On the other hand, the close proximity of rasvumite to jarosite in mesostasis of this meteorite, especially with K-rich jarosite, may suggest a common origin for their compositional similarity. This mineral has not been reported in previous studies of MIL 03346 or of other nakhlites. The discovery of rasvumite provides new information of iron sulfide minerals on Mars. However, as an interesting K-bearing and mixed valence sulfide mineral, the origin and alteration processes of rasvumite on Mars remain unknown and may need further laboratory experimental work.

3.5. Secondary Minerals

3.5.1. Ca-sulfates

Ca-sulfates were found in MIL 03346 [Hallis and Taylor, 2011]. Previous Raman study indicated the presence of gypsum, CaSO₄•2H₂O, and bassanite, CaSO₄•1/2H₂O, in this sample [Kuebler, 2013]. In this Raman imaging study, we find that bassanite is the major Ca-sulfate that fills the veins throughout the MIL 03346,168 thin section. At various locations, bassanite was accompanied by soluble γ -CaSO₄ (not the insoluble anhydrite β -CaSO₄) and by gypsum. Ca-sulfates with different degrees of hydration have characteristic sharp and strong v_1 bands in their Raman spectra (Figure 7a) located at 1008, 1015, 1017, and 1025 cm⁻¹ for gypsum, bassanite, β -CaSO₄, and γ -CaSO₄ respectively [*Chio et al.*, 2004].

Figure 5a shows a vein filled with Ca-sulfates in region C of MIL 03346,168, as evidenced by a gradual change from a single Raman peak at 1008 cm^{-1} (pos 1 of Figure 7a), to double peak (pos 2 and 3), and finally a single



Figure 7. Raman spectra of three Ca-sulfates found in MIL 03346,168. (a) The positions of the fundamental vibration v_1 mode near 1000 cm⁻¹ of gypsum and bassanite indicate the variations in their proportions in a vein (from pos 1 to pos 4, Figure 5a). The fifth spectrum in Figure 7a, soluble γ -CaSO₄, has distinct Raman spectral features, which were often found to coexist with bassanite or K-jarosite in veins of this meteorite. (b) Raman peaks of these Ca-sulfates in H₂O/OH spectral range.

peak at 1015 cm⁻¹ (pos 4), indicating the change in hydration from mainly gypsum to mixtures of gypsum and bassanite, and finally just bassanite in different sections of the same vein (Figure 5a). The water peak around 3500 cm⁻¹ (Figure 7b) can also be used to identify the mineral phase. Gypsum has double peaks at 3402 and 3493 cm⁻¹, and bassanite has a weak peak at 3556 cm⁻¹ [*Chio et al.*, 2004]. The γ -CaSO₄ has a characteristic Raman spectrum (bottom spectrum in Figures 7a and 7b) [*Chio et al.*, 2004] and was found in the vein system of MIL 03346,168, either by itself (at the center of the cross in Figure 5b) or coexisting with gypsum, bassanite, and sometimes jarosite (evidenced by a multi-phase Raman spectra).

3.5.2. Jarosite

In MIL 03346,168, we found jarosite in two regions: (a) in the mesostasis as less than 10 μ m-sized grains or in short veins, and (b) filling in larger veins. Raman spectra acquired from these locations suggest the existence of end-member K-jarosite, Na-jarosite, and their solid solutions.

The typical Raman spectra of end-member K-jarosite and Na-jarosite are presented in Figure 8a, where the spectra have been separated into two spectral regions. The major differences between synthesized end-member K-jarosite and Na-jarosite reported in the past [*Chio et al.*, 2010; *Lu and Wang*, 2012] are their v_1 peaks at 1006 and 1010 cm⁻¹, the v_3 peak at 1102 and 1108 cm⁻¹, and the v_2 peak at 430 and 444 cm⁻¹, respectively. In addition, the OH peaks occur at 3414–3417 cm⁻¹ for K-jarosite and at 3395–3388 cm⁻¹ for Na-jarosite. We recently synthesized a series of end-member K-jarosite, Na-jarosite, and six of their solid solutions, measured the Raman peak positions of each sample, and established a calibration procedure to derive a molar ratio of K/(K + Na) in jarosite in terms of their typical Raman peaks (v_1 , v_2 , and v_3) [*Ling et al.*, 2015]. Because the peak position differences between end-member Na-jarosite and K-jarosite are rather small ($\Delta v_1 = 5$ cm⁻¹, $\Delta v_3 = 10$ cm⁻¹), the uncertainties in derived molar ratio of K/(K + Na) are quite large. This study is still underway.



Figure 8. (a) Raman spectra showing the fundamental vibration modes and OH stretching modes of the jarosite in the meteorite MIL 03346,168. Note the major differences between K-rich or Na-rich jarosite are the Raman peak positions of peak 1 (~1010 cm⁻¹) and peak 2 (~1110 cm⁻¹). (b) Composition ranges of K- and Na-jarosite solid solutions reflected by the two Raman peak positions (peak 1 and peak 2, marked in Figure 8a). End-members of K-jarosite, Na-jarosite, and H₃O-jarosite are also marked in the plot [*Ling et al.* [2015]. (c) Compositional distributions of 206 jarosite grains measured in MIL 03346,168. The histogram suggests that most of them are solid solutions of (K, Na)-jarosite.

We plotted in Figure 8b the v_1 and v_3 peaks of 206 jarosite grains measured in MIL 03346,168 compared with the peak positions of synthesized end-member Na-, K-, and H₃O-jarosite. Using this calibration procedure, we calculated a rough estimation on molar ratio of K/(K + Na) for MIL 03346,168. These data allow us to divide the observed spectra into two groups, the K-rich jarosite and Na-rich jarosite, indicated by a dashed line in Figure 8b. We further generated a histogram (Figure 8c) to show the compositional distribution of 206 measured jarosite grains. On the basis of Figure 8c, we concluded that most measured jarosite grains are solid solutions of (K, Na)-jarosite, with very few grains falling into the category of end-member Na-jarosite or K-jarosite. We have not found H₃O-jarosite [*Lu and Wang*, 2012], NH₄-jarosite [*Chio et al.*, 2010], and solid solutions in jarosite-alunite series [*McCollom et al.*, 2014] in MIL 03346,168.

3.5.3. Hydrated Species With Low Crystallinity (HSLC)

In the vein system and the mesostasis of MIL 03346,168, our Raman point measurements frequently encountered a complex set of mineral phases. They have mid-to-low optical reflectance, have no-regular grain shape, and often coexist with laihunite, Ti-magnetite, and jarosites. They all have low S/N Raman spectra, variable broad Raman bands, and central peak positions at $100-1200 \text{ cm}^{-1}$ and in $3000-4000 \text{ cm}^{-1}$. Based on these features, they can be classified as hydrated species with low crystallinity

(HSLC). Furthermore, these phases (based on hundreds of Raman spectra) can be separated into two groups. The third and fourth spectra in Figure 6b show the differences between these two groups.

The central grain surrounded by laihunite grains (with higher reflectivity) in Figure 5f is one of the common occurrences for group 1 HSLC. It sometimes coexists with magnetite and jarosite in mesostasis and in the veins cut through with olivine grains (Figure 5e). The most common feature in their Raman spectra (third spectrum Figure 6b) is a suddenly increased background (stair-like) near 750–800 cm $^{-1}$, and then a high plateau from 700 to 100 cm^{-1} appears sometimes overlapped with weak and broad peaks centered near 700, 500, and 350 cm^{-1} . This phase has a very broad H₂O/OH Raman band centered near $3550-3580 \text{ cm}^{-1}$ (spectra not shown), which is very different from the OH/H₂O bands of jarosites and Ca-sulfates. These features bear certain similarities to those of ferrihydrite, 5Fe₂O₃•9H₂O [Das and Hendry, 2011; Hanesch, 2009; Mazzetti and Thistlethwaite, 2002], and maghematite γ-Fe₂O₃ [De Faria et al., 1997], but not to FeOOH minerals (e.g., goethite and lepidocrocite) [Das and Hendry, 2011]. We tentatively assign group 1 of HSLC to ferrihydrite, on the basis of observable H_2O/OH peak and the absence of 1320 and 1560 cm⁻¹ bands of maghematite. Additional reasons for this assignment are (1) the extreme heat sensitive nature of these phases that is consistent with reports in the literature [Mazzetti and Thistlethwaite, 2002] and (2) the finding of ferrihydrite in Lafayette [Changela and Bridges, 2010] and the presence of at least partially hydrous Fe oxides in MIL 03346 [Hallis and Taylor, 2011]. Ferrihydrite was reported to have nanocrystalline structure [Michel et al., 2007], and all reported that ferrihydrite Raman spectra show broad bandwidth [Das and Hendry, 2011; Hanesch, 2009; Mazzetti and Thistlethwaite, 2002]. We believe that the greatly reduced Raman peak intensities from group 1 HSLC phase of MIL 03346,168 demonstrate their extremely low crystallinity arising from the lack of long-range 3-D structural ordering. The crystallinity of each minerals of the 1 HSLC phase is dependent on their location in MIL 03346,168, the primary phases from which they formed, and on environmental conditions they formed.

The typical Raman spectrum of the group 2 HSLC phase is shown as fourth spectrum of Figure 6b. It retains the stair-like feature near 750–800 cm⁻¹ but with additional broad Raman bands centered near 300, 590, 969 cm⁻¹ and a shoulder near ~685 cm⁻¹. Furthermore, this phase has a broad and weak Raman shoulder near 3450 cm⁻¹ in addition to the major broad Raman peak centered near 3550–3580 cm⁻¹ (spectra not shown). This spectral pattern also has bands assigned to group 1 HSLC, and the spectral pattern bears some similarity to crystalline laihunite whose major, narrower bands occur near 310, 570, and 900 cm⁻¹. Furthermore, the band shoulder of 685 cm⁻¹ of group 2 HSLC matches with the stretching vibration modes of Si-O_b-Si (O_b = bridging oxygen) in the phyllosilicate structure [*Gillet et al.*, 2002; *Hallis and Taylor*, 2011; *Hallis*, 2013]. Combining all features, we can tentatively assign group 2 HSLC to be the mixtures of low-crystallinity ferrihydrite, altered, low-crystallinity laihunite with a hydrous component, and hydrous phyllosilicate(s) with low crystallinity.

4. Raman Imaging of MIL 03346,168—The Spatial Correlations of Molecular Species

In this section, we will present the Raman images from a few selected areas of the thin section, which reveal additional information on the abundances, distributions, and the spatial correlations among specific mineral assemblages, for the purpose of deriving the origins of these minerals. Figure 9 shows four Raman images from selected areas in MIL 03346,168 using the StreamlineTM procedure of Renishaw inVia Raman imager.

In most veins in MIL 03346,168, bassanite and jarosite (with small amount of ferrihydrite) are the two typical phases filling the veins, but we occasionally found a mixture of bassanite, jarosite, and "ferrihydrite" filling a vein. Figure 9a1 is a gray scale image of a vein cut through an augite grain. Figure 9a2 is the Raman image of the phases in the vein. It shows that jarosite and "ferrihydrite" occur near the wall of the vein, while bassanite occurs near the center of the vein.

A mesostasis area next to an augite grain is shown in Figures 9b1 and 9b2. Two veins along the edges of this mesostasis area intersect with each other and then connect with a larger vein that cuts through the augite grain. The Raman image (Figure 9b2) reveals that fine-grained, low-crystallinity alkali feldspar and Ti-magnetite are the major phases in mesostasis matrix. The vein system is filled mainly by (K, Na)-jarosite, gypsum (coexisting with jarosite in one of the veins adjacent to the mesostasis), and bassanite (in a larger

10.1002/2015JE004805



Figure 9. (a1-d1) Optical and (a2-d2) Raman images of four selected areas from MIL 03346,168. Details are described in text.

vein that cuts through augite). The spatial distributions and the large amounts of jarosite and Ca-sulfates in this area support the origin of these two sulfates to occur throughout the vein system.

A mesostasis area that contains a skeletal Ti-magnetite (high albedo) and a laihunite grain (mid-albedo) is shown in Figures 9c1 and 9c2. The Raman image (Figure 9c2) reveals the close proximity of a jarosite grain to a laihunite grain. The jarosite grain is rimed by Ti-magnetite and a tiny grain of rasvumite. Additional tiny grains of jarosite and rasvumite also exist near skeletal Ti-magnetite grains. The close proximities of



Figure 10. Spatial distributions of secondary hydrated minerals in MIL 03346,168. (a) Ca-sulfates in veins; (b) K-rich jarosite and Na-rich jarosite in veins or mesostasis.

these four Fe-bearing phases suggest that these small jarosite grains were formed in situ from locally available Fe and S. A rather large rasvumite grain occurs (upper-left corner of Figure 9c2) in the matrix of alkali feldspar, neighbored by a few tiny grains of Ti-magnetite. This occurrence supports the conclusion that rasvumite is a primary phase in the mesostasis of this meteorite.

A mesostasis area next to a CPX grain and containing a high albedo fractured grain is shown in Figures 9d1 and 9d2. The fractured high albedo grain does not have a Raman signal and is thus presumed to be a Fe/Ni metal. The Raman image (Figure 9d2) reveals a large amount of jarosite filling the fractures of this grain. Ti-magnetite and rasvumite grains were found coexisting with jarosite within the fractures, but these minerals were also in the matrix of mesostasis. A major difference from previous Raman image (Figure 9c2) is the coexistence of ferrihydrite with jarosite in this area mainly in the area between CPX grain and metal grain but also presented in a few tiny spots in mesostasis matrix.

5. Overall Distribution of Secondary Minerals

With the Raman spectral measurements of all secondary minerals and their particular correlations found in MIL 03346,168, we now consider their distributions throughout the thin section of the meteorite (Figure 10a for Ca-sulfates and Figure 10b for jarosites).

All Ca-sulfates were found in the veins of this thin section. As shown in Figure 10a, bassanite $CaSO_{4}$ •1/2H₂O is the most abundant Ca-sulfate and has the widest spatial distribution in the vein system of this meteorite. γ -CaSO₄ (the soluble anhydrite) is the second most abundant Ca-sulfate and occurs either as single phase or coexisting with bassanite and jarosite in regions E, F, C, and B of the thin section. Gypsum CaSO₄•2H₂O has the lowest abundance and occurs in the veins and along the edge in regions C and B (within one in the middle of region C). The abundant Ca-sulfates with such a high degree of hydration in this meteorite are extraordinary and bear very important implications for the origin of Martian salts.

Jarosites are widely distributed in the mesostasis and in the veins of this meteorite (Figure 10b). Note that the compositional distribution of (K, Na)-jarosites in this meteorite is continuous (Figures 8b and 8c). The names "K-rich" and "Na-rich" jarosites used in this manuscript are only for the purpose of grouping. These minerals are separated by a dotted line in Figure 8b. The most abundant jarosite grains belong to (K, Na) solid solutions, with very few grains falling into the end-members of K- or Na-jarosite. Based on Figure 10b, K-rich jarosites appear to be more concentrated in regions E, C, and B, and occur less frequently in regions F and D. Na-rich jarosites appear to be more concentrated in regions F and D, and less frequently in

regions E, C, and B. There are no obvious difference among the occurrences of either K-rich or Na-rich jarosites in veins or in mesostasis. The F region is special in that the Na-rich jarosite is more ubiquitous than K-jarosite and bassanite, which may suggest different episodes of aqueous history in this meteorite.

6. Implications for Mars

6.1. Ca-sulfates

The stability and dehydration of hydrous Ca-sulfates have been extensively studied in the past [e.g., *Chio et al.*, 2004; *Vaniman and Chipera*, 2006; *Robertson and Bish*, 2013]. It has been commonly known that gypsum is the most stable phase at low temperatures ($T < 97^{\circ}$ C) and anhydrite β -CaSO₄ at high temperatures ($T > 97^{\circ}$ C), bassanite is metastable at all temperatures, and γ -CaSO₄ is unstable in the terrestrial laboratory under ambient conditions [*Chio et al.*, 2004; *A. Wang et al.*, 2012; *Y. W. Wang et al.*, 2012; *Robertson and Bish*, 2013; *Wei et al.*, 2014]. The observation of abundant and widespread bassanite in this meteorite and of the persistence (after many years' storage and handling in laboratory) of the unstable structural form (γ -CaSO₄) is inconsistent with terrestrial field and experimental observations. In contrast, an orbital remote sensing data analysis has found bassanite on the outflow channel in the Mawrth Vallis region of Mars [*Wray et al.*, 2010]; the CheMin instrument on Curiosity rover at Gale Crater has identified bassanite coexisting with anhydrite in Sheepbed mudstone, and anhydrite alone in Rocknest surface soil, while no gypsum was found in any of these Martian materials [*Vaniman et al.*, 2014].

On the basis of past experimental studies, we could hypothesize three possible formation paths for the abundant and widespread bassanite in the vein system of this meteorite. Path A is by dehydration of gypsum. Among Ca-, Mg-, Fe^{2+} , Fe^{3+} , and Al-sulfates, Ca-sulfate (gypsum) has been demonstrated to have the slowest dehydration rate under Mars relevant conditions [*Wang and Zhou*, 2014]. As indicated by *Robertson and Bish* [2013], through gypsum dehydration experiments, even in the most desiccated environment like the Martian equatorial region (with the warmest *T*), gypsum dehydration would take over ~500 years; thus, the gypsum dehydration is unlikely to occur on Mars.

The second possible path (B) for formation of bassanite is by direct precipitation from a Ca-S-H₂O brine. First, the solubility of CaSO₄ in H₂O is the lowest among all sulfates (0.205 g/100 g H₂O at 25°C) [*Lide*, 2001]. This means that in order to fill a vein with bassanite (density = 2.69-2.76 g/cm³), the quantity of a original brine should have a volume to be nearly 1350 times of the volume of the vein. The only possible condition to precipitate bassanite directly is in an environment with extremely low water activity. This condition could be satisfied on Mars by (1) an extremely low atmospheric partial water pressure (P_{H2O}) and/or (2) an extremely high ionic strength in the brine. The case for (1) would be possible if the bassanite precipitation occurred in only a few drops of brine; i.e., the precipitation was heavily affected by the surrounding atmosphere. This environment is inconsistent with the observation of abundant bassanite in the widespread vein system of this meteorite. The case for (2) would occur if in some veins in this meteorite, jarosites (and ferrihydrite) and bassanite are found to coexist, thereby satisfying the high ionic strength criterion (Figure 9a2). However, in MIL 3346,168, most veins filled with Ca-sulfates do not coexist with jarosite and/or ferrihydrite. The only possible exception for case (2) would be some high concentration of chlorides (NaCl, KCl, etc.) widely present in the vein system of this meteorite, but chlorides would not be detected because monoatomic ions do not generate Raman signals.

A third possible path (C) for the formation of bassanite, which bears a certain relationship with the second path (B), is that nano-to-microcrystals of bassanite precipitated from a dilute brine (without high ionic strength) as the precursor to gypsum, but the precipitation is stopped before converting to gypsum. Two recent studies [*Van Driessche et al.*, 2012; *A. Wang et al.*, 2012; *Y. W. Wang et al.*, 2012] revealed that nanocrystal particles of bassanite (in the form of rods with 10–15 nm length) [*Van Driessche et al.*, 2012] and potentially an amorphous Ca-sulfate [*A. Wang et al.*, 2012; *Y. W. Wang et al.*, 2012] were formed at the beginning of precipitation. These bassanite nanorods can grow up to 100 nm in length (as step one) and then self-assembled into aggregates to more than 1 μ m in length (as step two). As the final step, these aggregates transform from bassanite to gypsum. Apparently, the width of most veins in MIL 03346,168 is ~10 μ m. We therefore hypothesize that within such a confined space, the full development of the above three steps for forming gypsum microcrystals from brine may have not reached completion; i.e., it is stopped between steps two and three. A structure form like that would generate a Raman spectrum with

the major peak of bassanite at 1015 cm^{-1} and a peak shoulder at 1008 cm^{-1} due to gypsum. These are exactly the Raman spectral features that we observed in most of the vein filling materials in MIL 03346,168.

Based on these observations, we tentatively assign the formation mechanism of bassanite in this meteorite as follows. We can probably exclude path A based on *Robertson and Bish* [2013]. The brine with high ionic strength in path B would work for a few veins filled with bassanite coexisting with jarosite and/or ferrihydrite, while path C would work for most of the veins in MIL 03346,168 that are filled by bassanite without coexisting with jarosite and other salts. For both paths B and C, however, large amounts of brine (~1350 volume ratio) would be required to generate the observed abundance of Ca-sulfates. Brine of such large quantity could not be produced by ice melting in Antarctica during impact and seasonal changes. Thus, our observations support the Martian origin of Ca-sulfates in the vein system of this meteorite. The possibility of some bassanite fully rehydrating to gypsum in the veins near the surface of this meteorite induced by Antarctica melting ice, however, would remain. A few gypsum occurrences near the edge of region C of the analyzed thin section might be the evidence of this process.

The observation of γ -CaSO₄ as the second most abundant Ca-sulfates that exists widely in the vein system (Figure 10a, regions A–F) of this meteorite is inconsistent with the laboratory experiments. γ -CaSO₄ was observed and identified by XRD [*Robertson and Bish*, 2013] and by Raman spectroscopy as the dehydration product of gypsum at 105°C [*Wei et al.*, 2014] and of bassanite at 61–65°C [*Chio et al.*, 2004]. In addition, γ -CaSO₄ was observed to be extremely unstable in terrestrial laboratory ambient conditions. It converts in less than 5 min at 20°C and 10% RH to bassanite [*Wei et al.*, 2014]. However, it does agree with some of the terrestrial field observation such as the recent paper of in situ Raman study of playa soils at Atacama Desert where there are reported many occurrences of γ -CaSO₄ [*Wei et al.*, 2015]. Our observations of stable existence of γ -CaSO₄ in a Martian meteorite and the similar existence in a highly arid region on Earth raise a new question on the thermodynamic and kinetic properties of this phase, thus requiring further experimental work to address that beyond the scope of this study.

6.2. Jarosites

Jarosite is the first sulfate mineral definitively identified on Mars by Mars Exploration Rover Opportunity [*Klingelhöfer et al.*, 2004], within the outcrop at Meridiani Planum. The large continuous compositional variation of (K, Na)-jarosite found in MIL 03346,168 requires a large K/Na variation in the surrounding fluid at relatively high temperature (~140°C). Conversely, at a lower temperature, limited K/Na differences in the acid brine will lead to the crystallization of K- or Na-jarosite end-members which were rarely seen in our data as discussed in section 3.5.2.

On the basis of the spatial correlation of jarosite grains and other primary Fe-bearing phases (laihunite, Timagnetite, ferrihydrite, and rasvumite), we suggest that some jarosite grains in mesostasis are formed in situ, i.e., originating locally from the following reactions:

 $2(K, Na)Fe(SO_4)_2(OH)_6 \leftarrow KFe_2S_3(rasvumite) + O_2 + 2H^+ + SO_4^{2-} + 5H_2O;$

$$\begin{split} &3(K,\ Na)Fe(SO_4)_2(OH)_6 \leftarrow FeFe_2(SiO_4)_2(laihunite)\ +\ O_2\ +\ 12\ H^+\ +\ 6SO_4{}^{2-}\ +\ 3\ H_2O\ +\ 3(K,\ Na)\ AlSi_3O_8 \\ &or \leftarrow Fe_3O_4(magnetite)\ +\ 12H^+\ +\ 6SO_4{}^{2-}\ +\ 4H_2O\ +\ 3(K,\ Na)\ AlSi_3O_8 \end{split}$$

$$10(K, Na)Fe(SO_4)_2(OH)_6 \leftarrow 5Fe_2O_3.9H_2O(ferrihydrite) + 40H^+ + 20SO_4^{2-} + H_2O + 10(K, Na) AlSi_3O_8$$

The fine-grained and low-crystallinity nature of alkali feldspar in the matrix of mesostasis would make for easy chemical alteration and thus might be the (K, Na) source for the (K, Na)-jarosites. Ferric sulfate has an extremely high solubility in water (440 mg/100 g H₂O at 25°C, *Lide* [2001]), making it difficult for us to estimate the quantity of brine needed for the formation of jarosite in the mesostasis and vein system of this meteorite.

6.3. HSLC

The alteration processes and products of nakhlites have been intensively studied by previous authors [e.g., *Gillet et al.*, 2002; *Changela and Bridges*, 2010; *Hallis*, 2013; *Hallis et al.*, 2014]. *Changela and Bridges* [2010] suggested the presence of a hydrous amorphous silicate gel (named siderite-phyllosilicate-Fe oxide-hydrated) of variable composition but is chemically similar to phyllosilicate found in Lafayette, Governador Valadares, Nakhla, and Yamato 000593/000748. *Hallis et al.* [2014] found that the alteration veins of MIL

090032 (referred to as nanocrystalline phyllosilicate) are largely homogeneous consisting of Fe oxides and hydroxides with no siderite or coarse-grained phyllosilicate occurring in them. The group 2 HSLC observed by our Raman experiments should be equivalent to the nanocrystalline phyllosilicate as mentioned above. Our results are consistent with *Hallis et al.* [2014], where the alteration veins of MIL 03346,168 are rather homogenous with amorphous structure. During our Raman imaging of MIL 03346,168, we found the extensive distribution of HSLC, especially the group 1 "ferrihydrite", with a variety of occurrences. However, due to the low S/N Raman spectra of HSLC and their frequent coexistences with other phases, our current data cannot support a realistic explanation for the spatial distribution of these phases. Nevertheless, the strong spatial association of HSLC with magnetite, jarosite, and laihunite suggests some common origin for them.

The recent discoveries by CheMin measurements onboard Curiosity show significant X-ray amorphous components existing in the three analyzed samples (i.e., the scooped Rocknest soil, the drilled and collected John Klein, and the Cumberland outcrops) [*Bish et al.*, 2013; *Blake et al.*, 2013; *Vaniman et al.*, 2014]. However, the exact mineral phase compositions and origins of the amorphous components are still under investigation. One surprising finding during our measurements of MIL meteorites is the wide distribution of the amorphous phase HSLC, especially for ferrihydrite. Ferrihydrite can be grains or veins that appear in the cracks or mesostasis of MIL 03346,168. We suggest that the HSLC (especially ferrihydrite) may have experienced similar alteration processes like those of the amorphous phase found by the Curiosity rover. The distribution of hydrated low-crystalline-to-amorphous phases (e.g., ferrihydrite) on the Mars may be more widespread than previously thought and therefore would imply a very large reservoir for the Martian water budget.

7. Conclusion

Raman spectroscopic imaging study of MIL 03346,168 revealed the chemical zoning and narrow Fe-rich rim of phenocrystic pyroxene and olivine in cumulus, indicating an early crystallization episode and a continuous diffusive exchange with fractionation magma. The findings of fine-grained low-crystallinity (K, Na)-feldspar solid solutions, the existence of high-T SiO₂ phase (cristobalite), the solid solutions of magnetite and ulvospinel, and the textural characters of these grains all support a fast-quench-cooling process of the residual magma that formed the mesostasis. Many fayalite grains rimed by or coexisting with laihunite grains can be an indication of a later oxidation event.

Among the secondary minerals, the large abundance of bassanite and its wide spatial distribution suggest two possible paths for its direct precipitation from a very large amount of original brine, therefore supporting the Martian origin of Ca-sulfates. The persistence of γ -CaSO₄ posts a new question on its thermodynamic and kinetic properties that is worthy of further experimental study. Solid solutions of (K, Na)-jarosite exist in veins and in mesostasis. The close spatial relationship among mesostasis jarosites, rasvumite (a newly found Martian mineral), magnetite, laihunite, ferrihydrite, and fine-grained low-crystalline (K, Na)-feldspar suggests a potential in situ formation of mesostasis jarosite from these Fe-S-H₂O-(K, Na)bearing phases. Based on our current study, we have no definitive evidence to explain either Martian or terrestrial origins of the jarosite and HSLC phases in the vein system of this meteorite.

In addition, our study on the Raman spectra and phase identification for a greatly altered Martian nakhlite provides a valuable model for the in situ Raman investigation procedures. Our study suggests that with such a stand-alone Raman spectrometer, one can acquire precise mineral phase identifications and valuable geochemistry information, which will in turn provide essential information for interpreting the history of crystallization and alteration processes on Mars.

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Acknowledgments

This research was partly funded by the National Natural Science Foundation of China (41473065, 41490634, 41373068, and U1231103, for Z.C.L.). Supports from the Department of Earth & Planetary Sciences and the McDonnell Center for Space Sciences at Washington University in St. Louis for A.W. and Z.C.L. are greatly appreciated. We thank Bradley L. Jolliff, Randy L. Korotev, and Paul Carpenter for the helpful discussions. We are grateful to John Freeman for his helpful reviews and comments on this manuscript. The standard spectra of rasvumite (r060491) are available in the RRUFF database (http://rruff.info/). All the data necessary to generate the results of the manuscript are available on request from the corresponding author.

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