CrossMark

A Noachian source region for the "Black Beauty" meteorite, and a source lithology for Mars surface hydrated dust?

P. Beck [a,*], A. Pommerol [b], B. Zanda [c], L. Remusat [c], J.P. Lorand [d], C. Göpel [e], R. Hewins [c,f], S. Pont [c], E. Lewin [g], E. Quirico [a], B. Schmitt [a], G. Montes-Hernandez [g], A. Garenne [a], L. Bonal [a], O. Proux [h], J.L. Hazemann [i], V.F. Chevrier [j]

[a] *Univ. Grenoble Alpes, IPAG, F-38000 Grenoble, France*
[b] *Physikalisches Institut, Universität Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland*
[c] *Institut de Minéralogie, Physique des Matériaux et de Cosmochimie, CNRS UMR 7590, Museum National d'Histoire Naturelle, CP52, 57 rue Cuvier, 75005 Paris, France*
[d] *Laboratoire de Planétologie et Géodynamique de Nantes, CNRS UMR 6112, Université de Nantes, 2 rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France*
[e] *Institut de Physique du Globe, Sorbonne Paris Cité, University Paris Diderot, CNRS UMR 7154, F-75005 Paris, France*
[f] *Department of Earth and Planetary Sciences, Rutgers University, Piscataway, NJ 08854, USA*
[g] *UJF-Grenoble 1 / CNRS-INSU, Institut des Sciences de la Terre (IsTERRE), Grenoble, France*
[h] *Observatoire des Sciences de l'Univers de Grenoble (OSUG), CNRS UMS 832, 414 rue de la piscine, 38400 Saint Martin d'Hères, France*
[i] *Institut Néel, 25 av. des Martyrs, 38042, Grenoble, France*
[j] *Arkansas Center for Space and Planetary Science, University of Arkansas, Fayetteville, AR 72701, USA*

ARTICLE INFO

ABSTRACT

The Martian surface is covered by a fine-layer of oxidized dust responsible for its red color in the visible spectral range (Bibring et al., 2006; Morris et al., 2006). In the near infrared, the strongest spectral feature is located between 2.6 and 3.6 μm and is ubiquitously observed on the planet (Jouglet et al., 2007; Milliken et al., 2007). Although this absorption has been studied for many decades, its exact attribution and its geological and climatic implications remain debated. We present new lines of evidence from laboratory experiments, orbital and landed missions data, and characterization of the unique Martian meteorite NWA 7533, all converging toward the prominent role of hydroxylated ferric minerals. Martian breccias (so-called "Black Beauty" meteorite NWA7034 and its paired stones NWA7533 and NWA 7455) are unique pieces of the Martian surface that display abundant evidence of aqueous alteration that occurred on their parent planet (Agee et al., 2013). These dark stones are also unique in the fact that they arose from a near surface level in the Noachian southern hemisphere (Humayun et al., 2013). We used IR spectroscopy, Fe-XANES and petrography to identify the mineral hosts of hydrogen in NWA 7533 and compare them with observations of the Martian surface and results of laboratory experiments. The spectrum of NWA 7533 does not show mafic mineral absorptions, making its definite identification difficult through NIR remote sensing mapping. However, its spectra are virtually consistent with a large fraction of the Martian highlands. Abundant NWA 7034/7533 (and paired samples) lithologies might abound on Mars and might play a role in the dust production mechanism.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Mars is a dusty planet. Most Martian rocks are partially covered by a red "dust" component, precluding a global mineralogical cartography of its surface. While the redness of the Martian surface can be seen from the Earth with the naked eye, the exact mineral phase(s) and the geological processes responsible for its distinct color are still obscure. The presence of ferric iron in the soil is generally proposed (Bell et al., 2000; Morris et al., 2006), but in a moderate amount and/or as very fine grains to explain the relative weakness of the Fe^{3+}-related absorption around 0.9 μm (Sherman et al., 1982), which often occurs in Fe^{3+} bearing iron oxides. At longer wavelengths, Mars' surface also presents a strong absorption between 2.6 and about 3.6 μm with a maximum of absorption around 2.9 μm. This spectral feature, generally referred to as the 3-μm band, has been attributed to "water" since its earliest iden-

tification (Sinton 1967) but the exact form of this "water" is still debated. Different types of hydration have been mentioned in the literature, such as adsorbed water, structural water and structural hydroxyl. The discrimination between these various types of "water" has been discussed (Jouglet et al., 2007; Milliken et al., 2007; Poulet et al., 2010; Audouard et al., 2014). Behind these different possibilities exist very diverse scenarios for the processes that produce and alter the Martian dust. If the 3-µm feature is produced by adsorbed water, a "dry" process, such as a proposed H_2O_2-based scenario (Bibring et al., 2006), will be sufficient to explain the presence of Fe^{3+}. On the other hand, if a significant proportion of the dust contains bound water or hydroxyl, H_2O will be required at some step of the dust production mechanism, whether by erosion of hydrated units, or by chemical interaction between atmospheric H_2O and anhydrous minerals.

The Martian meteorite suite has provided unique insights into the geological evolution of the red planet (McSween, 2002). Of the ~100 members of this family, all but three are magmatic rocks corresponding to near-surface or shallow-subsurface flows. Three recently discovered samples are breccias: Northwest Africa (NWA) 7034 (Agee et al., 2013), paired with NWA 7533 (Humayun et al., 2013) and NWA 7475 (Wittmann et al., 2015). These stones are exceptional among the Martian meteorite family as they are lithified regolith samples. There is now compelling evidence that NWA 7533 is a regolith breccia made of a wide range of mafic and felsic clasts set in a fine-grained matrix and various impact melt rocks (Hewins et al., 2013a, 2013b). Some zircon clasts returned ages (4.4 Ga) of the earliest Martian crust (Humayun et al., 2013). The mineralogy and chemical properties of this rock appear to be representative of the old Martian terrains that cover the southern hemisphere, as well as the visible, near-infrared and mid-infrared spectral properties (Cannon et al., 2015). This meteorite is also unique because it contains a significant amount of "water", about 0.6 wt%, that originates from the red planet according to its oxygen isotope composition (Agee et al., 2013). The exact mineral host of "water" and the origin of this hydration has been investigated by Transmission Electron Microscopy (TEM) (Muttik et al., 2014) suggesting that OH-bearing iron oxides and phyllosilicate could account for some of the water budget.

We gained insights into the mineral hosts of water by means of infrared spectroscopy, which is one of the few methods that can directly probe protons. This method is also widely used to infer the surface mineralogy of Solar System objects from orbit. The infrared (IR) characteristics of NWA 7533 were determined by using transmission spectroscopy of a doubly polished slice, as well as by reflectance spectroscopy on a powder produced from the meteorite, which is directly analogous to remote sensing visible and near-infrared observations. In order to better interpret the infrared data, we also complemented our investigations by using a set of analytical techniques that probe the mineralogy and geochemistry of the sample. Fe-XANES (X-ray Absorption Near-Edge Spectroscopy) was used to determine the redox state of the iron in the sample whereas SEM-EDS (Scanning Electron Microscope Energy Dispersive Spectrometer) was employed to better identify the mineral phases and derive their chemistry.

2. Methods

2.1. Transmission infrared spectroscopy

A doubly polished thin section of NWA 7533 was prepared at MNHN (Museum National d'Histoire Naturelle), using cyanoacrylate, which was subsequently removed with acetone. There was no detectable infrared signature of residual cyanoacrylate in the prepared section. The transmission spectra of the double polished thin section were recorded with a Brucker Hyperion FTIR micro-spectrometer in the 500–4000 cm^{-1} range with a 4 cm^{-1} resolution. The size of the measurement spot was typically of 100 µm × 100 µm. The thin section was measured using an environmental cell equipped with a primary vacuum and a heating resistance ($T = 70\,^\circ$C) and evacuated to primary vacuum to ensure no contamination by adsorbed water. Because of the thickness of the section (50 µm) it was not possible to attribute specific IR signatures to specific crystallographic phases. Indeed, typical size of matrix grains is of the order of 1-µm and thus much smaller that the section thickness. The 3-µm band is present across the sample, suggesting that the host of –OH is a component present diffusively in the sample. The band is not saturated.

2.2. VNIR reflectance spectroscopy

Diffuse reflectance spectra of NWA 7533 were measured using the spectro-photogoniometer available at the Institut de Planétologie et d'Astrophysique de Grenoble (IPAG) (Brissaud et al., 2004). About 300 mg of residue after dry sawing were manually deposited on a sample holder. The original sample was fresh, and we do not expect to have much contamination from possible weathering material from the outer part of the meteorite. Still this cannot be strictly excluded. Grain size was roughly estimated to be <50 µm with a binocular microscope. The setup is located in a cold room ($-10\,^\circ$C), and the air is dried using a cold trap in order to minimize signatures from atmospheric water. The spectra were normalized to Spectralon^{TM} and Infragold^{TM}, and obtained under standard geometric conditions (incidence = 0°, emergence = 30°). Four different spectra were averaged. This setup enables us to accurately measure reflectance level (±0.5%) in the 0.7–4.6 µm range.

2.3. Fe-XANES at the K_α-edge

20 mg of NWA 7533 powder were mixed with 100 mg of boron nitride and pressed in order to obtain a compact pellet of 5 mm of diameter. This pellet, as well as model compound pellets, were analyzed for Fe–K-edge XANES at CRG-FAME beamline at the European Synchrotron Radiation Facility. Spectra were measured in transmission mode with a typical energy resolution of 0.3 eV. Energy calibration was achieved by setting the first inflection point of a Fe metal foil K-edge spectrum at 7112 eV. The data were then reduced following the Wilke et al. (2001) procedure in order to extract the Fe^{3+}/F_{tot} ratio from the intensity and the energy position of the centroid of the pre-edge feature.

2.4. SEM-EDS

Five polished sections of NWA7533 were investigated by scanning electron microscopy using the Direction des Collections SEM-EDS facility at LMCM, MNHN (Paris). In order to locate the Fe-rich minerals, the sulphides and the Ti-rich oxides, we recorded high resolution maps of backscattered electrons and energy dispersive X-ray spectrometry (EDS) over the whole surface of the sections. They were obtained at a 20 kV accelerating voltage using automated image stitching. The chemistry of the previous phases and their mineralogical context were studied by EDS analyses performed at 15 kV using a silicon drift detector with a 133 eV spectral resolution and a Phiroz standardless program.

3. Results

3.1. The reflectance spectra of NWA 7533

In order to compare the optical properties of NWA 7533 with those of Mars, the reflectance spectra of powdered NWA
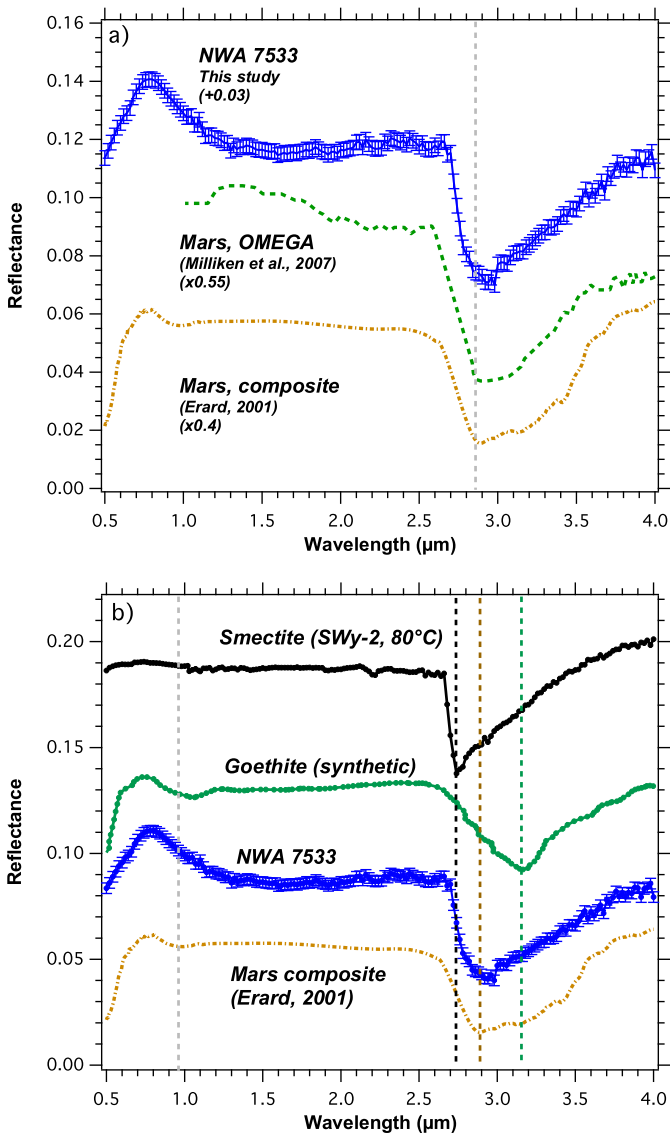
Fig. 1. a) Reflectance spectra obtained for NWA 7533 compared with spacecraft measurements of the Martian surface (Erard, 2001; Milliken et al., 2007). b) These spectra are compared to reflectance spectra obtained for a H_2O free smectite and a well-crystallized goethite. The position of the 3-μm band of NWA 7533 (and Mars) is inconsistent with a Mg–OH absorption since its maximum of absorption is at lower wavelength (2.75 μm). Goethite, a well crystallized oxy-hydroxide, also fails to explain this feature since its maximum of absorption occurs at 3.15 μm. A poorly crystalline Fe–OH bearing mineral is rather favored (see Fig. 2). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

7533 were measured under dry conditions with a spectro-gonio-radiometer. The reflectance spectrum of NWA 7533 is characterized by a generally low reflectance (0.09 in the continuum at 2-μm), typically darker than most Martian meteorites (Fig. 1a). It shows a subtle red slope in the visible and a blue slope that extends from 0.8 to 1.5 μm. Such a blue slope can be attributed to the presence of magnetite or maghemite, that have been observed in NWA 7034 (Gattacceca et al., 2014) and in the present study of NWA 7533, and that usually show such a diagnostic blue slope in the NIR (see for instance Cloutis et al., 2011).

Of interest is the presence of a 3-μm feature in the reflectance spectra of NWA 7533. This feature has a band depth of about 0.5 at its maximum of absorption that occurs around 2.9 μm similar to observations of the Martian surface (Fig. 1b). To confirm the presence of such an absorption feature, transmission IR measure-
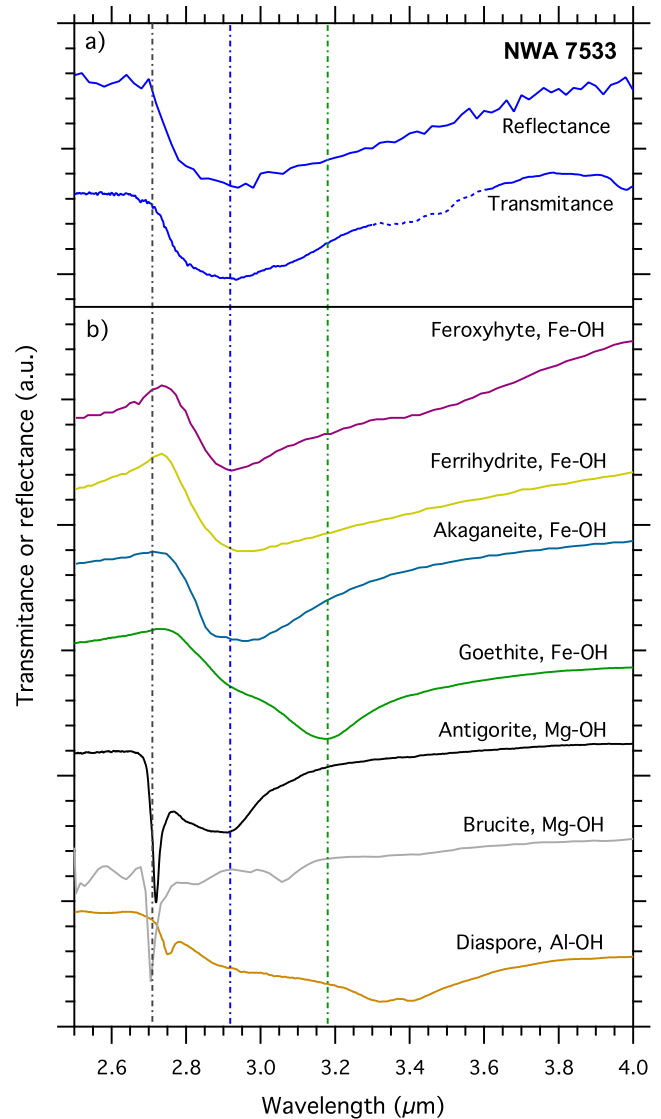

Fig. 2. a) The 3-μm band of NWA 7533 measured in reflectance (in blue, top spectrum) and in transmission through a double-polished thin section (in blue bottom spectrum). b) Spectra of various –OH bearing phases. The spectra of feroxyhyte, akaganeite and ferrihydrite are digitized from Lair et al. (2006). The spectrum of goethite is from a synthetic sample and the spectra of antigorite, brucite and diaspore are from samples provided by the MNHN. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ments were performed on a doubly polished thin section of NWA 7533.

3.2. Transmission spectra

The two transmission spectra measured on the doubly polished section of NWA 7533 (Fig. 2) reveal the presence of an absorption feature between 2.6 and 3.6 μm, with an absorbance maximum at 2.9 μm. This 3-μm band is due to the presence of –OH groups in the sample, confirming that NWA 7533 is significantly hydrated or hydroxylated. Because the oxygen isotope signature of water released from NWA 7533 testifies to an extraterrestrial origin, this hydration phase is interpreted as an authentic Martian alteration product. Some insights into this alteration phase can be gained from the shape and position of the absorption band. The vibration of Mg-bonded hydroxyl groups (Mg–OH), within Mg-rich phyllosilicate (Calvin and King, 1997) or in brucite ($Mg(OH)_2$) always shows
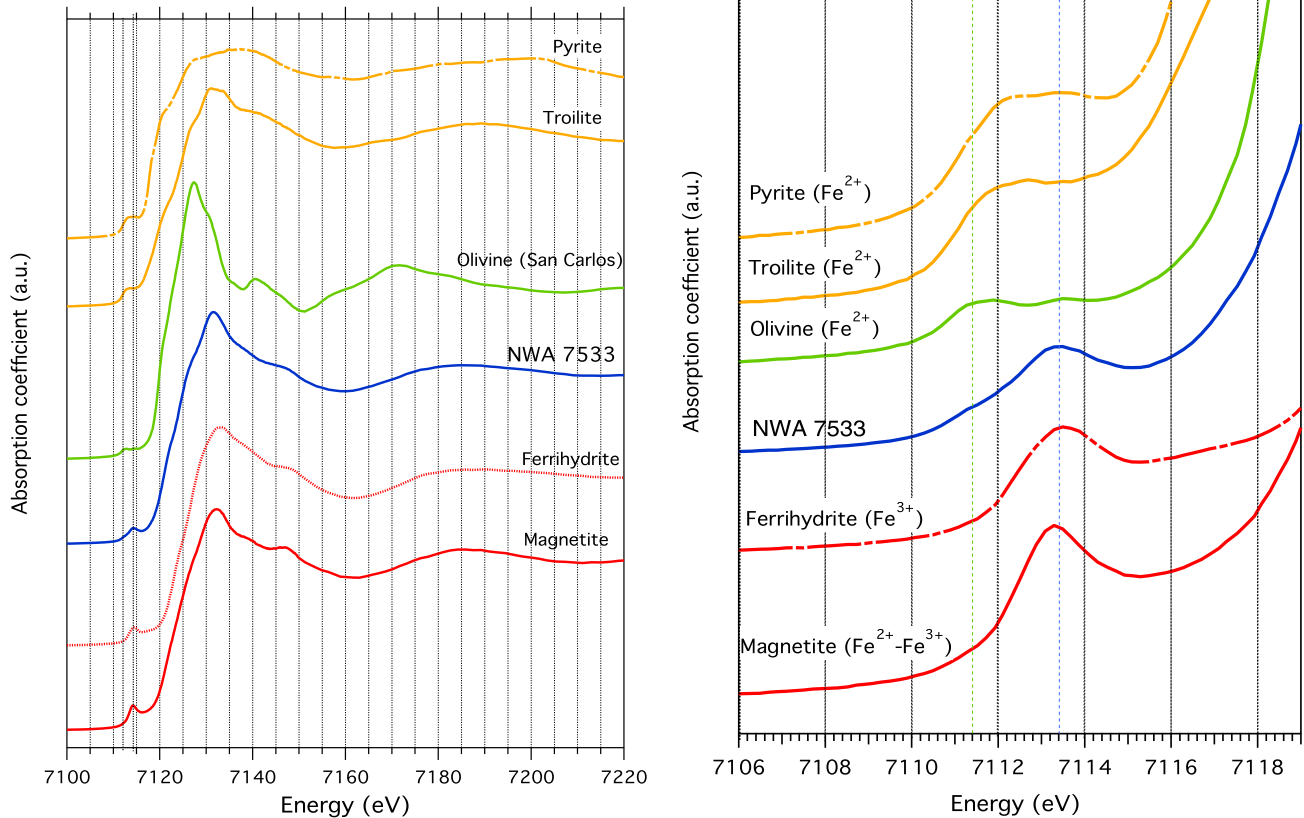
Fig. 3. Fe-XANES spectra of standards and NWA 7533. The left panel shows the whole spectra while the right panel emphasizes the pre-edge region. Spectra were offset for clarity. Standards shown are from Beck et al. (2012).

a maximum of absorption around 2.7 μm ruling out such phases as a potential host of water here. Absorptions at higher wavelength are found, however, for Fe-bonded hydroxyl (Fe–OH) whether in Fe-rich phyllosilicates or iron hydroxides and iron (oxy)-hydroxides (Fig. 2) (Calvin and King, 1997; Lair et al., 2006). The vibration of iron-bonded –OH groups has typically a maximum of absorption located around 2.85–2.95 μm, with the exception of goethite for which the H-bond network moves the absorption to an even higher wavelength (3.18 μm) (Fig. 2). Because Fe-rich phyllosilicates were not observed in the meteorite, despite thorough SEM investigation on 5 polished sections, the 3-μm feature can be attributed to an iron (oxy)-hydroxide, and ferrihydrite appears to have the most similar band shape (Fig. 2).

3.3. The redox state of iron

The bulk redox state of iron in NWA 7533 was determined by means of synchrotron Fe-XANES spectroscopy at beamline BM 30 (FAME) at ESRF. The XANES spectra clearly show evidence for some amount of Fe^{3+} from the position of the absorption jump (Fig. 3) and the overall spectral shape that appear similar to our Fe^{3+} standards (ferrihydrite and magnetite). Examination of the pre-edge region confirms this observation, i.e. that a significant fraction of Fe in NWA 7533 is present as Fe^{3+}. In order to quantify this redox state of iron, we used Wilke et al. (2001) method that uses the combination of the pre-edge centroid energy and intensity (Fig. 4). From this method it is calculated that about 50% of the Fe atoms in the meteorite are ferric iron (Fe^{3+}), making NWA 7533 the most oxidized Martian meteorite so far. This value is close to the average redox state of iron in Gusev soil dust end-member (Fe^{3+}/Fe^T ~40%) (Morris et al., 2006).

4. Discussion

4.1. The peculiar spectra of NWA 7533

NWA 7533 is dominated by crystal and lithic clasts, and pyroxene makes a significant fraction of the modal mineralogy. Still, diagnostic pyroxene related absorptions are clearly absent in the reflectance spectrum of NWA 7533. This is unlike any other reflectance spectrum measured for shergottites and nakhlites where the 1-μm and 2-μm bands are deep (McFadden and Cline, 2005). The sole exception is the dunite NWA 2737 (Beck et al., 2006) where the spectrum is dark and featureless, which is interpreted to be the result of a shock-induced mineralogical transformation (Pieters et al., 2008; Van de Moortele et al., 2007). In the case of NWA 7533, the presence of abundant opaque phases is likely responsible for the decrease of optical path length in the sample and the disappearance of the pyroxene absorption feature. These results are in agreement with hyperspectral imaging on NWA 7034 obtained on an unpolished chip (Cannon et al., 2015).

The absence of absorption feature in the reflectance spectra of NWA 7533 makes it challenging to firmly identify its source region on Mars with reflectance spectroscopy. However, global mineralogical mapping of the Martian surface shows that a significant fraction of the planet, the southern highlands, have a low albedo and are mostly devoid of spectral features (Poulet et al., 2007). This is particularly the case of the Noachian terrains, which are heavily cratered and whose surface are expected to be brecciated in nature. The petrology of NWA 7533 indicated that it is a regolith breccia, made of lithic clasts derived from the earliest Martian crust (i.e. Noachian) (Humayun et al., 2013). The petrology and geochemistry of NWA 7533 seem to draw a link between Noachian
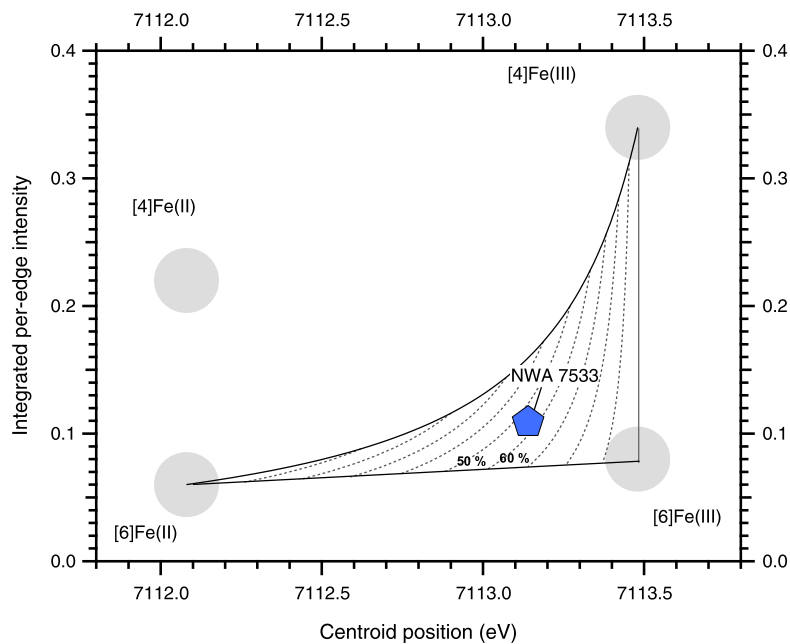
Fig. 4. Integrated pre-edge intensity of the XANES spectrum of NWA 7533 as a function of the centroid position, following Wilke et al. (2001).

terrains and NWA 7533, and the reflectance spectra measured here seem to strengthen this connection.

4.2. The 3-μm band: Mars vs NWA 7533

On Mars, this feature occurs ubiquitously on the surface and is systematically intense (with a band depth typically above 35%) (Jouglet et al., 2007; Milliken et al., 2007). Of importance is the general absence of a significant 1.9-μm feature in the reflectance spectra of Mars, except very locally where hydrous minerals, essentially phyllosilicates and sulphates are detected (Gendrin et al., 2005), or under very specific climatic conditions (Poulet et al., 2010). The reflectance spectra of NWA 7533 share this characteristic with the Martian surface. Because the 3-μm band is a composite of fundamental stretching (near 2.8–2.9 μm) and bending overtones (near 3.1 μm), it can be found both in H_2O and –OH bearing materials. The 1.9-μm band is a combination of bending and stretching ($n_1 + n_2$ and $n_3 + n_2$) modes of H_2O and thus requires water molecules to be present. It will not occur in the case of phases bearing only hydroxyl groups (X–OH where X = Fe, Ca, Mg, Al, . . .). Adsorption experiments on various Martian analogues revealed that adding a significant amount of adsorbed water (>1 wt%) increases the strengths of both the 1.9- and 3-μm band depth (Pommerol et al., 2009) (Fig. 5). In the case of –OH bearing materials devoid of H_2O, only the 3-μm band is present. This is most likely the case for the Martian dust, since the 3-μm band of Mars surface is deep but the 1.9 μm feature is generally absent (Fig. 5). In addition, the adsorption isotherms measured on the same Martian soil analogues suggest that given the low humidity of Mars atmosphere during daytime (when reflectance spectra are measured from orbit) (Smith, 2002), very little adsorbed water is expected (Pommerol et al., 2009) with only minor contribution to the 3-μm band. The lack of observed variation of the 3-μm band on Mars with surface humidity was also taken as an argument that adsorbed water only marginally contributes to the Martian 3-μm band (Audouard et al., 2014). As a consequence, the ubiquitous 3-μm band of Mars likely originates from an –OH bearing phase present all over its surface, and an –OH bearing phase is also likely responsible for the 3-μm band of NWA 7533.

4.3. What mineral host for water in NWA 7533?

Thin sections of NWA 7533 were prepared and studied with optical and electron microscopy (scanning electron microscope, SEM) in order to identify the alteration phases and their petrographic context. Possible hosts that were identified for NWA 7533 hydrogen include abundant fine-grained iron oxides, some alteration products of ilmenite (leucoxene) and apatite. Also some Fe-hydroxides that develop at the expense of pyrite were observed, but textural considerations suggest a terrestrial origin for the pyrite alteration product (Lorand et al., 2014). Recent TEM investigations have revealed that potential H-bearing phase in NWA 7034 include OH-rich maghemite, amorphous iron oxides and phyllosilicates (Muttik et al., 2014). The exact contribution of each of these alteration products to the H_2O budget of NWA 7533 is not known. While some alteration products may have formed on Earth, given its oxygen isotopic composition, the bulk of NWA 7533 water is of Martian origin (Agee et al., 2013).

4.4. Surface hydration, the rover views

The origin and age of the Martian soils are debated. After landing at six different locations on Mars, little variations have been measured in bulk soil composition over the surface of the red planet (Meslin et al., 2013). Major element measurements by APXS and GRS have revealed that the soils are globally basaltic, with little chemical leaching of elements compared to the source rock (Newsom et al., 2007; Yen et al., 2005) although some mineralogical fractionation might occur (Bandfield et al., 2011; McGlynn et al., 2011). Still, an oxidative process is recorded by the presence of ferric iron bearing phases that typically represent 20–25 at.% of the budget of Fe in Martian soils and that can reach a value as high as 90 at.% in some localities according to Mossbauer studies (Morris et al., 2006, 2008). This ferric iron is dominantly hosted by a poorly crystalline or short-range order phase usually referred to as nanophase ferric oxide (np-Ox; Morris et al., 2006). The np-Ox can be a combination of hematite, goethite, lepidocrocite, schwermannnite, akaganeite, hisingerite or finally ferrihydrite (Morris et al., 2008). This ferric component is also present in the fine atmospheric dust collected by the Mars Exploration Rovers (Goetz et al., 2005) and detailed analyses of soil
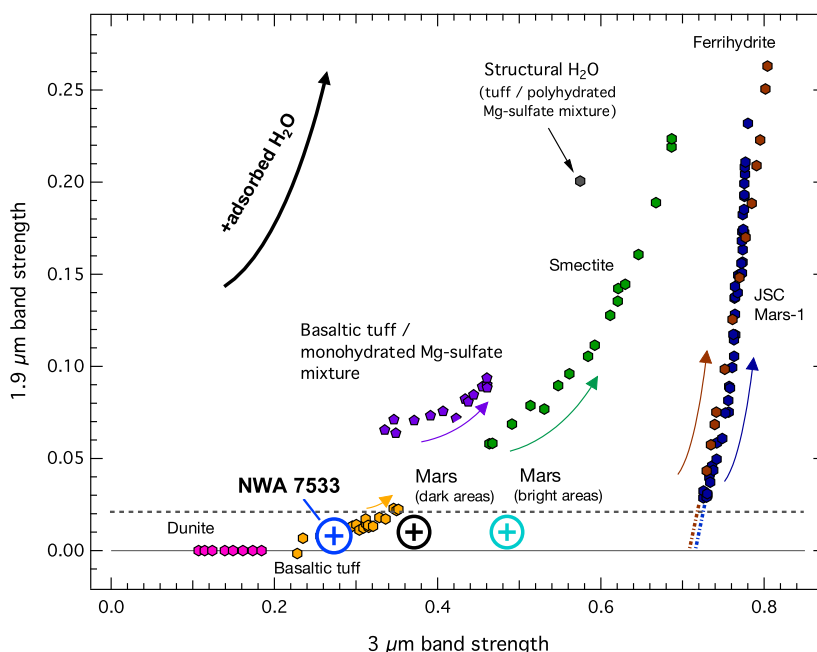
Fig. 5. Integrated band depth at 1.9- and 3-µm for the Martian surfaces and adsorption experiments. The 1.9-µm band is due to a combination of bending and stretching modes of H_2O. On the contrary the 3-µm is a composite band that can occur when either X–OH (with X a transition metal) or H_2O are present. When H_2O is added (adsorption experiments) both bands are increasing (Pommerol et al., 2009). When structural water is present, the two bands are also strong. In the case of purely hydroxylated materials, only the 3-µm band occurs and the one at 1.9 µm is absent. This is the case of the Martian surface in general as well as NWA 7533. Values for Mars surface derived from data obtained by the OMEGA instrument on two different areas are also plotted for comparison. The values have been calculated from averaged OMEGA spectra, extracted from Olympus Mons (Orbit #501_4) and Vastistas Borealis (Orbit #979_3) areas at spring–summer time. The OMEGA detection threshold of 0.02 for the 1.9-µm band is indicated by the horizontal dashed line. The absence of the absorption band at 1.9 µm over most of the Martian surface would be clearly inconsistent with the intensity of the 3-µm band if this latter absorption band were due to H_2O, as it is the case for smectite or hydrated Mg-sulphate.

samples by the Curiosity rover suggest that this component is the likely host of significant OH/H_2O (Leshin et al., 2013; Archer et al., 2014). Evolved gas analyses of soil samples by SAM have shown an average 2 ± 1 wt% H_2O released, mostly at temperatures below 450 °C and with a peak release at 250 °C (Leshin et al., 2013; Archer et al., 2014). Combined with CheMIN X-ray diffraction results, showing the presence of an abundant X-ray amorphous component in the soil, it was concluded that mineral phases similar to the np-Ox are the favorite candidates for hosting most of the soil OH/H_2O (Archer et al., 2014).

Taking a bulk Fe abundance of 10 wt% (Agee et al., 2013), a Fe^{3+}/Fe_{Tot} of 50%, and assuming that each Fe^{3+} atom is balanced by an OH^- cation, a bulk equivalent content of about 0.8 wt% H_2O is estimated for NWA 7533. This simple calculation is in fair agreement with the bulk content measured by Agee et al. (0.6 wt%). Although quite indirect, this could be taken as an additional indication that iron hydroxides or oxy-hydroxides are the main mineral hosts of "water" in NWA 7533. Still, some other Fe^{3+} phases are present in NWA 7533 (maghemite, 3 vol.%) (Agee et al., 2013), Ti-magnetite, ilmenite and possibly pyroxene, which, although nominally anhydrous, might also contribute to the hydrogen budget.

4.5. NWA 7533, a dust-rich lithology or the source-lithology of dust?

Northwest Africa 7533 is the rock most resembling the Martian soil in composition. This breccia was assembled during the Noachian era, and radiometric ages were subsequently reset by younger impacts, the latest being around 1.7 Ga (Humayun et al., 2013) or 1.35 Ga (Bellucci et al., 2015). As discussed earlier, there is some strong evidence connecting NWA 7533 to the southern highlands and in particular the Noachian terrains. If similar in petrology to NWA 7533, the heavily cratered southern highlands might provide a new pathway to Martian dust production. The mechanical erosion of this geological unit could be at the core of the

soil-forming mechanism and provide a source of oxidized and hydroxylated dust covering the Martian surface. Mechanical sorting of the finest fraction, enriched in oxidized phase as observed in NWA 7533, could produce the bright red dust that will be subsequently transported and deposited across the surface. Such a mechanical sorting and enrichment in the finest fraction might explain the difference in 3-µm band depth between NWA 7533 and Mars's surface dust (as well as the difference in slope in the visible). In this putative scenario, the formation of the hydrated and oxidized Martian dust does not require either the recent action or water (liquid or vapor) or a powerful oxidant (like H_2O_2), but would rather be inherited from its old, "habitable", Noachian era.

5. Conclusion

In this article we have searched for potential hosts of water in NWA 7533 by mean of infrared spectroscopy (transmission and absorption). From these results we were able to draw the following conclusions:

– The infrared spectra of NWA 7533 show a 3-µm band, which is indicative of hydration. This was found in the reflectance of bulk powder and in transmission. Because the hydration of the paired sample NWA 7034 is indigenous to Mars, the 3-µm feature found for NWA 7533 is related to a Martian process.

– The reflectance spectrum of NWA 7533 does not show any 1.9-µm absorption feature, nor do observations of the Martian surface. When considered in the context of adsorption experiments obtained previously (Pommerol et al., 2009), this is a strong indicator that the hydration found for NWA 7533 is related to an –OH bearing phase rather than H_2O (structural or adsorbed). Similarly, the lack of the 1.9-µm feature on most of the Martian surface supports the fact that regolith/atmosphere adsorption phenomena are marginal on most of the planet.

– The shape of the 3-µm band with a maximum of absorption at 2.85 µm points toward a Fe–OH origin. This is in agreement with

the fact that iron oxy-hydroxides have been described in the sample (Muttik et al., 2014) and could account for some of this feature. The shape of the feature observed for NWA 7533 resembles that of the Martian surface.

– The reflectance spectra of this breccia, do not show any of the typical 1- or 2-µm features related to mafic silicates. Although pyroxenes are abundant, they could not be detected from the reflectance spectra only. The only feature we observe is a shallow absorption band at 0.8–0.9 µm that we interpret by the presence of iron-oxide (magnetite or maghemite). This suggests that most of the geological areas on Mars that do not show any silicate feature, in particular in the southern highlands, could correspond to lithologies similar to NWA 7533.

– The reflectance spectra of NWA 7533 present the two spectral features that are ubiquitous on Mars, a red slope and a 3-µm band. These two features are likely due to a hydroxylated component present in the fine red dust, in agreement with in-situ results. The correspondence with the reflectance spectra of NWA 7533 suggests that this lithology could have incorporated a regolith component similar to the Martian dust. Conversely, it is possible that if abundant in the Martian highlands, such a lithology could be involved in the dust production mechanism by mechanical erosion.

Acknowledgements

References

Agee, C.B., Wilson, N.V., McCubbin, F.M., Ziegler, K., Polyak, V.J., Sharp, Z.D., Asmerom, Y., Nunn, M.H., Shaheen, R., Thiemens, M.H., Steele, A., Fogel, M.L., Bowden, R., Glamoclija, M., Zhang, Z., Elardo, S.M., 2013. Unique meteorite from Early Amazonian Mars: water-rich basaltic Breccia Northwest Africa 7034. Science 339, 780–785.

Archer, P.D., Franz, H.B., Sutter, B., Arevalo, R.D., Coll, P., Eigenbrode, J.L., Glavin, D.P., Jones, J.J., Leshin, L.A., Mahaffy, P.R., McAdam, A.C., McKay, C.P., Ming, D.W., Morris, R.V., Navarro-Gonzalez, R., Niles, P.B., Pavlov, A., Squyres, S.W., Stern, J.C., Steele, A., Wray, J.J., 2014. Abundances and implications of volatile-bearing species from evolved gas analysis of the Rocknest aeolian deposit, Gale Crater, Mars. J. Geophys. Res., Planets 119, 237–254. http://dx.doi.org/10.1002/2013JE004493.

Audouard, J., Poulet, F., Vincendon, M., Milliken, R.E., Jouglet, D., Bibring, J.-P., Gondet, B., Langevin, Y., 2014. Water in the Martian regolith from OMEGA/Mars express. J. Geophys. Res., Planets 119, 1969–1989. http://dx.doi.org/10.1002/2014JE004649.

Bandfield, J.L., Rogers, A.D., Edwards, C.S., 2011. The role of aqueous alteration in the formation of martian soils. Icarus 211, 157–171. http://dx.doi.org/10.1016/j.icarus.2010.08.028.

Beck, P., Barrat, J.A., Gillet, P., Wadhwa, M., Franchi, I.A., Greenwood, R.C., Bohn, M., Cotten, J., van de Moortele, B., Reynard, B., 2006. Petrography and geochemistry of the chassignite Northwest Africa 2737 (NWA 2737). Geochim. Cosmochim. Acta 70, 2127–2139. http://dx.doi.org/10.1016/j.gca.2006.01.016.

Beck, P., De Andrade, V., Orthous-Daunay, F.-R., Veronesi, G., Cotte, M., Quirico, E., Schmitt, B., 2012. The redox state of iron in the matrix of CI, CM and metamorphosed CM chondrites by XANES spectroscopy. Geochim. Cosmochim. Acta 99, 305–316. http://dx.doi.org/10.1016/j.gca.2012.04.041.

Bell, J.F., McSween, H.Y., Crisp, J.A., Morris, R.V., Murchie, S.L., Bridges, N.T., Johnson, J.R., Britt, D.T., Golombek, M.P., Moore, H.J., Ghosh, A., Bishop, J.L., Anderson, R.C., Bruckner, J., Economou, T., Greenwood, J.P., Gunnlaugsson, H.P., Hargraves, R.M., Hviid, S., Knudsen, J.M., Madsen, M.B., Reid, R., Rieder, R., Soderblom, L., 2000. Mineralogic and compositional properties of Martian soil and dust: results from Mars Pathfinder. J. Geophys. Res. 105, 1721–1756.

Bellucci, J.J., Nemchin, A.A., Whitehouse, M.J., Humayun, M., Hewins, R., Zanda, B., 2015. Pb-isotopic evidence for an early, enriched crust on Mars. Earth Planet. Sci. Lett. 410, 34–41.

Bibring, J.-P., Langevin, Y., Mustard, J.F., Poulet, F., Arvidson, R., Gendrin, A., Gondet, B., Mangold, N., Pinet, P., Forget, F., Team, O., Berth, M., Gomez, C., Jouglet, D., Soufflot, A., Vincendon, M., Combes, M., Drossart, P., Encrenaz, T., Fouchet, T., Merchiorri, R., Belluci, G., Altieri, F., Formisano, V., Capaccioni, F., Cerroni, P.,

Coradini, A., Fonti, S., Korablev, O., Kottsov, V., Ignatiev, N., Moroz, V., Titov, D., Zasova, L., Loiseau, D., Pinet, P., Doute, S., Schmitt, B., Sotin, C., Hauber, E., Hoffmann, H., Jaumann, R., Keller, U., Arvidson, R., Duxbury, T., Neukum, G., 2006. Global mineralogical and aqueous mars history derived from OMEGA/Mars express data. Science 312, 400–404.

Brissaud, O., Schmitt, B., Bonnefoy, N., Douté, S., Rabou, P., Grundy, W., Fily, M., 2004. Spectrogonio radiometer for the study of the bidirectional reflectance and polarization functions of planetary surfaces. 1. Design and tests. Appl. Opt. 43, 1926–1937.

Calvin, W.M., King, T.V.V., 1997. Spectral characteristics of Fe-bearing phyllosilicates: comparison to Orgueil (CI1) Murchison and Murray (CM2). Meteorit. Planet. Sci. 32, 693–701.

Cannon, K.M., Mustard, J.F., Agee, C.B., 2015. Evidence for a widespread basaltic breccia component in the martian low-albedo regions from the reflectance spectrum of Northwest Africa 7034. Icarus 252, 150–153. http://dx.doi.org/10.1016/j.icarus.2015.01.016.

Cloutis, E.A., Hiroi, T., Gaffey, M.J., Alexander, C.M.O'D., Mann, P., 2011. Spectral reflectance properties of carbonaceous chondrites: 1. CI chondrites. Icarus 212, 180–209.

Erard, S., 2001. A spectro-photometric model of Mars in the near-infrared. Geophys. Res. Lett. 28, 1291–1294. http://dx.doi.org/10.1029/2000GL012347.

Gattacceca, J., Rochette, P., Scorzelli, R.B., Munayco, P., Agee, C., Quesnel, Y., Cournède, C., Geissman, J., 2014. Martian meteorites and Martian magnetic anomalies: a new perspective from NWA 7034. Geophys. Res. Lett. 41, 4859–4864.

Gendrin, A., Mangold, N., Bibring, J.P., Langevin, Y., Gondet, B., Poulet, F., Bonello, G., Quantin, C., Mustard, J., Arvidson, R., LeMouelic, S., 2005. Suffates in martian layered terrains: the OMEGA/Mars Express view. Science 307, 1587–1591. http://dx.doi.org/10.1126/science.1109087.

Goetz, W., Bertelsen, P., Binau, C.S., Gunnlaugsson, H.P., Hviid, S.F., Kinch, K.M., Madsen, D.E., Madsen, M.B., Olsen, M., Gellert, R., Klingelhofer, G., Ming, D.W., Morris, R.V., Rieder, R., Rodionov, D.S., de Souza, P.A., Schroder, C., Squyres, S.W., Wdowiak, T., Yen, A., 2005. Indication of drier periods on Mars from the chemistry and mineralogy of atmospheric dust. Nature 436, 62–65. http://dx.doi.org/10.1038/nature03807.

Hewins, R.H., Zanda, B., Humayun, M., Lorand, J.-P., Deldicque, D., Pont, S., Fieni, C., Nemchin, A., Grange, M., Kennedy, A., Göpel, C., Lewin, E., 2013a. Petrology of NWA 7533: formation by impacts on ancient martian crust. Meteorit. Planet. Sci. Suppl. 76, 5252.

Hewins, R.H., Zanda, B., Humayun, M., Pont, S., Fieni, C., Deldicque, D., 2013b. Northwest Africa 7533, an impact breccia from Mars. In: Lunar and Planetary Science Conference, p. 2385.

Humayun, M., Nemchin, A., Zanda, B., Hewins, R.H., Grange, M., Kennedy, A., Lorand, J.-P., Göpel, C., Fieni, C., Pont, S., Deldicque, D., 2013. Origin and age of the earliest Martian crust from meteorite NWA 7533. Nature 503, 513–516.

Jouglet, D., Poulet, F., Milliken, R.E., Mustard, J.F., Bibring, J.-P., Langevin, Y., Gondet, B., Gomez, C., 2007. Hydration state of the Martian surface as seen by Mars Express OMEGA: 1. Analysis of the 3 mum hydration feature. J. Geophys. Res., Planets 112.

Lair, V., Antony, H., Legrand, L., Chausse, A., 2006. Electrochemical reduction of ferric corrosion products and evaluation of galvanic coupling with iron. Corros. Sci. 48, 2050–2063. http://dx.doi.org/10.1016/j.corsci.2005.06.013.

Leshin, L.A., Mahaffy, P.R., Webster, C.R., Cabane, M., Coll, P., Conrad, P.G., Archer, P.D., Atreya, S.K., Brunner, A.E., Buch, A., Eigenbrode, J.L., Flesch, G.J., Franz, H.B., Freissinet, C., Glavin, D.P., McAdam, A.C., Miller, K.E., Ming, D.W., Morris, R.V., Navarro-Gonzalez, R., Niles, P.B., Owen, T., Pepin, R.O., Squyres, S., Steele, A., Stern, J.C., Summons, R.E., Sumner, D.Y., Sutter, B., Szopa, C., Teinturier, S., Trainer, M.G., Wray, J.J., Grotzinger, J.P., 2013. Volatile, isotope, and organic analysis of Martian fines with the Mars curiosity rover. Science 341. http://dx.doi.org/10.1126/science.1238937.

Lorand, J.-P., Hewins, R.H., Remusat, L., Zanda, B., Pont, S., Humayun, M., Nemchin, A., Grange, M., Kennedy, A., Göpel, C., 2014. Pyrite tracks late hydrothermal alteration in Martian regolith breccia NWA 7533. In: LPI Contrib., vol. 1800, p. 5123.

McFadden, L.A., Cline, T.P., 2005. Spectral reflectance of Martian meteorites: spectral signatures as a template for locating source region on Mars. Meteorit. Planet. Sci. 40, 151.

McGlynn, I.O., Fedo, C.M., McSween, H.Y., 2011. Origin of basaltic soils at Gusev crater, Mars, by aeolian modification of impact-generated sediment. J. Geophys. Res., Planets 116, E00F22. http://dx.doi.org/10.1029/2010JE003712.

McSween, H.Y., 2002. Leonard medal address: the rocks of Mars, from far and near. Meteorit. Planet. Sci. 37, 7–25.

Meslin, P.-Y., Gasnault, O., Forni, O., Schroeder, S., Cousin, A., Berger, G., Clegg, S.M., Lasue, J., Maurice, S., Sautter, V., Le Mouelic, S., Wiens, R.C., Fabre, C., Goetz, W., Bish, D., Mangold, N., Ehlmann, B., Lanza, N., Harri, A.-M., Anderson, R., Rampe, E., McConnochie, T.H., Pinet, P., Blaney, D., Leveille, R., Archer, D., Barraclough, B., Bender, S., Blake, D., Blank, J.G., Bridges, N., Clark, B.C., DeFlores, L., Delapp, D., Dromart, G., Dyar, M.D., Fisk, M., Gondet, B., Grotzinger, J., Herkenhoff, K., Johnson, J., Lacour, J.-L., Langevin, Y., Leshin, L., Lewin, E., Madsen, M.B., Melikechi, N., Mezzacappa, A., Mischna, M.A., Moores, J.E., Newsom, H., Ollila, A., Perez, R.,

Renno, N., Sirven, J.-B., Tokar, R., de la Torre, M., d' Uston, L., Vaniman, D., Yingst, A., 2013. Soil diversity and hydration as observed by ChemCam at Gale crater, Mars. Science 341, 1238670. http://dx.doi.org/10.1126/science.1238670.

Milliken, R.E., Mustard, J.F., Poulet, F., Jouglet, D., Bibring, J.-P., Gondet, B., Langevin, Y., 2007. Hydration state of the Martian surface as seen by Mars Express OMEGA: 2. H_2O content of the surface. J. Geophys. Res., Planets 112.

Morris, R.V., Klingelhoefer, G., Schroeder, C., Fleischer, I., Ming, D.W., Yen, A.S., Gellert, R., Arvidson, R.E., Rodionov, D.S., Crumpler, L.S., Clark, B.C., Cohen, B.A., Mccoy, T.J., Mittlefehldt, D.W., Schmidt, M.E., de Souza, P.A., Squyres, S.W., 2008. Iron mineralogy and aqueous alteration from Husband Hill through Home Plate at Gusev Crater, Mars: results from the Mossbauer instrument on the Spirit Mars exploration rover. J. Geophys. Res., Planets 113, E12S42. http://dx.doi.org/10.1029/2008JE003201.

Morris, R.V., Klingelhofer, G., Schroder, C., Rodionov, D.S., Yen, A., Ming, D.W., de Souza, P.A., Fleischer, I., Wdowiak, T., Gellert, R., Bernhardt, B., Evlanov, E.N., Zubkov, B., Foh, J., Bonnes, U., Kankeleit, E., Gotlich, P., Renz, F., Squyres, S.W., Arvidson, R.E., 2006. Mossbauer mineralogy of rock, soil, and dust at Gusev crater, Mars: spirit's journey through weakly altered olivine basalt on the plains and pervasively altered basalt in the Columbia Hills. J. Geophys. Res., Planets 111.

Muttik, N., McCubbin, F.M., Keller, L.P., Santos, A.R., McCutcheon, W.A., Provencio, P.P., Rahman, Z., Shearer, C.K., Boyce, J.W., Agee, C.B., 2014. Inventory of H_2O in the ancient Martian regolith from Northwest Africa 7034: the important role of Fe oxides. Geophys. Res. Lett. 41, 8235–8244.

Newsom, H.E., Crumpler, L.S., Reedy, R.C., Petersen, M.T., Newsom, G.C., Evans, L.G., Taylor, G.J., Keller, J.M., Janes, D.M., Boynton, W.V., Kerry, K.E., Karunatillake, S., 2007. Geochemistry of Martian soil and bedrock in mantled and less mantled terrains with gamma ray data from Mars Odyssey. J. Geophys. Res., Planets 112, E03S12. http://dx.doi.org/10.1029/2006JE002680.

Pieters, C.M., Klima, R.L., Hiroi, T., Dyar, M.D., Lane, M.D., Treiman, A.H., Noble, S.K., Sunshine, J.M., Bishop, J.L., 2008. Martian dunite NWA 2737: integrated spectroscopic analyses of brown olivine. J. Geophys. Res., Planets 113, E06004. http://dx.doi.org/10.1029/2007JE002939.

Pommerol, A., Schmitt, B., Beck, P., Brissaud, O., 2009. Water sorption on martian regolith analogs: thermodynamics and near-infrared reflectance spectroscopy.

Icarus 204, 114–136. http://dx.doi.org/10.1016/j.icarus.2009.06.013.

Poulet, F., Arvidson, R.E., Bibring, J.-P., Gondet, B., Jouglet, D., Langevin, Y., Morris, R.V., 2010. Mineralogy of the Phoenix landing site from OMEGA observations and how that relates to in situ Phoenix measurements. Icarus 205, 712–715.

Poulet, F., Gomez, C., Bibring, J.-P., Langevin, Y., Gondet, B., Pinet, P., Belluci, G., Mustard, J., 2007. Martian surface mineralogy from Observatoire pour la Mineralogie, l'Eau, les Glaces et l'Activite on board the Mars Express spacecraft (OMEGA/MEx): global mineral maps. J. Geophys. Res., Planets 112, E08S02. http://dx.doi.org/10.1029/2006JE002840.

Sherman, D.M., Burns, R.G., Mee Burns, V., 1982. Spectral characteristics of the iron oxides with application to the Martian bright region mineralogy. J. Geophys. Res. 87, 10169–10180.

Sinton, W.M., 1967. On the composition of martian surface materials. Icarus 6, 222–228.

Smith, M.D., 2002. The annual cycle of water vapor on Mars as observed by the Thermal Emission Spectrometer. J. Geophys. Res., Planets 107, 5115. http://dx.doi.org/10.1029/2001JE001522.

Van de Moortele, B., Reynard, B., Rochette, P., Jackson, M., Beck, P., Gillet, P., McMillan, P.F., McCammon, C.A., 2007. Shock-induced metallic iron nanoparticles in olivine-rich Martian meteorites. Earth Planet. Sci. Lett. 262, 37–49. http://dx.doi.org/10.1016/j.epsl.2007.07.002.

Wilke, M., Farges, F., Petit, P.E., Brown, G.E., Martin, F., 2001. Oxidation state and coordination of Fe in minerals: an FeK-XANES spectroscopic study. Am. Mineral. 86, 714–730.

Wittmann, A., Korotev, R.L., Jolliff, B.L., Irving, A.J., Moser, D.E., Barker, I., Rumble, D., 2015. Petrography and composition of Martian regolith breccia meteorite Northwest Africa 7475. Meteorit. Planet. Sci. 50, 326–352.

Yen, A.S., Gellert, R., Schroder, C., Morris, R.V., Bell, J.F., Knudson, A.T., Clark, B.C., Ming, D.W., Crisp, J.A., Arvidson, R.E., Blaney, D., Bruckner, J., Christensen, P.R., DesMarais, D.J., de Souza, P.A., Economou, T.E., Ghosh, A., Hahn, B.C., Herkenhoff, K.E., Haskin, L.A., Hurowitz, J.A., Joliff, B.L., Johnson, J.R., Klingelhofer, G., Madsen, M.B., McLennan, S.M., McSween, H.Y., Richter, L., Rieder, R., Rodionov, D., Soderblom, L., Squyres, S.W., Tosca, N.J., Wang, A., Wyatt, M., Zipfel, J., 2005. An integrated view of the chemistry and mineralogy of martian soils. Nature 436, 49–54. http://dx.doi.org/10.1038/nature03637.