**LOOKING FOR A SOURCE OF WATER IN MARTIAN BASALTIC BRECCIA NWA 7034.** N. Muttik[1], C.B. Agee[1], F.M. McCubbin[1], W.A. McCuttcheon, P.P. Provencio, L.P. Keller[2], A.R. Santos[1], C.K. Shearer[1], [1]Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131 (e-mail: nmuttik@unm.edu), [2]Laboratory for Space Science, Mail Code KR, ARES, NASA Johnson Space Center, Houston, TX 77058.

**Introduction:** The recently described martian meteorite NWA 7034 has high water content compared to other SNC meteorites [1-2]. Deuterium to hydrogen isotope ratio measurements indicates that there are two distinct $\delta D$ components in NWA 7034, a low temperature (150-500°C) light component around −100‰ and a high temperature (300-1000°C) heavy component around +300‰ [1].

NWA 7034 [1] contains iron-rich phases that are likely secondary aqueous alteration products. They are commonly found as spheroidal objects of various sizes that are often rich in Fe-Ti oxides and possibly iron hydroxides. Iron oxides and oxyhydroxides are very common in weathered rocks and soils on Earth and Mars and they are important components of terrestrial and Martian dust [3]. In NWA 7034 iron-rich phases are found throughout the fine-grained basaltic groundmass of the meteorite. The total amount of martian $H_2O$ in NWA 7034 is reported to be 6000 ppm [1], and in this study we attempt to determine the phase distribution of this $H_2O$ by texturally describing and characterizing hydrous phases in NWA 7034, using Fourier transform infrared spectrometry (FTIR) and transmission electron microscopy (TEM).

**Material and Methods:** NWA 7034 was examined by FTIR spectroscopy at UNM. FTIR spectra of mineral phases and matrix areas were collected in reflectance mode using a Nicolet Nexus 670 Fourier Transform IT spectrometer. Additional TEM analysis of the hydrous phases from a powdered sample and FIB cuts were performed at UNM and JSC.

**Results:** FTIR measurements of the Fe-oxohydroxide minerals from the groundmass (Fig.1) documented a broad spectral band centered near 3400 $cm^{-1}$ due to stretching vibration of $H_2O/OH$ that in some extent have been bound to iron (e.g. additional Fe–OH bending modes have been detected at ~890 and ~975 $cm^{-1}$). Weak $H_2O$ bending vibration has also been detected around ~1640 $cm^{-1}$. A spectral band due to Fe–O bonds has been observed near 650 $cm^{-1}$ and additional strong band at ~1150 $cm^{-1}$ due to Fe–O–Si stretching. Observed spectral features suggest the best match to ferrihydrite [4] and in some extent to maghemite [5], however in some iron minerals additional spectral bands near 1400 and 1500 $cm^{-1}$ have been identified. These bands have been described as characteristic spectral features for ferrihydrite [4]. Although carbonates also exhibit spectral features near 1400 $cm^{-1}$, no other bands characteristic of carbonates have been observed.
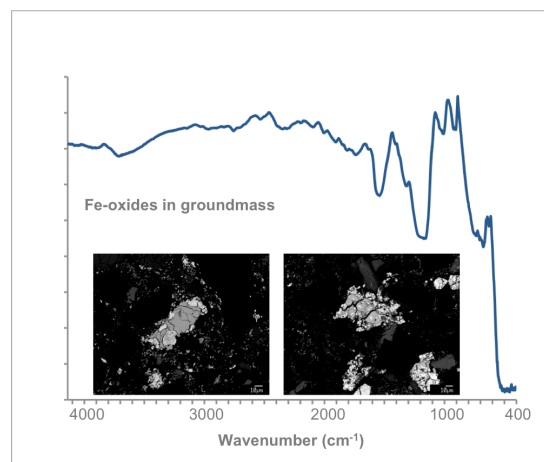


*Fig.1. Representative FTIR spectra and BSE images of measured Fe-rich phases (scale bar 10μm).*

It is difficult to distinguish among various hydrous Fe-oxide phases based on FTIR spectral features alone, so we also conducted TEM measurements of selected Fe-oxide (hydroxide) phases from the groundmass, Fe-oxide rich spherules, and the powdered Fe-rich fragments of NWA 7034. Preliminary TEM analysis resulted in the detection of abundant magnetite and maghemite type Fe-oxides. The presence of ferrihydrite in powdered sample fragments and in FIB cut sections were determined based on several selected area electron diffraction SAED patterns that displayed d values (for the diffuse rings) within errors of determination from those reported for ferrihydrite [6]. However, in addition to the nanocrystalline ferrihydrite (5-10 nm) in the FIB section of Fe-rich spherule (Fig.2), several micrographs displayed regions that were rich in magnetite, maghemite, hematite and ilmenite, making it hard to distinguish the presence of ferrihydrite in these regions due to overlapping d values of different Fe-oxides. TEM analysis from the FIB cut of Fe-oxide grain from the groundmass shows the troilite grain surrounded by concentric bands of nanocrystalline maghemite (Fig.3). No observations of goethite were made either by FTIR measurements, Raman analysis, or by TEM analysis, indicating that most likely the main Fe-oxohydroxide phase in NWA 7034 is ferrihydrite.

**Discussion:** Ferrihydrite forms in the presents of water on Earth [5] and may have formed on early Mars in association with aqueous/hydrothermal activity [4]. Hydrothermal activity has also been implicated in the formation of other iron hydroxides in Martian meteorites [7]. Greater abundances of nanophase ferric oxides

near volcanic features on Mars may indicate that ferrihydrite was formed initially in these regions as in the case of the Icelandic ferrihydrites [4]. Ferrihydrite formation in such an environment may have contributed to the ferric oxide-rich surface material on Mars. However, ferrihydrite is generally unstable in solutions and is subject to further evolution into crystalline phases [10]. Hematite and goethite are the most thermodynamically stable end products of ferrihydrite oxidation and abundance of hematite has been detected in the martian surface material [11, 12], however, in NWA 7034 the excess abundances of hematite or goethite have not been detected. Additional to hematite and goethite formation, ferrihydrite can transform under lower temperatures and in the presence of a reductant to magnetite and/or maghemite [10, 13, 14]. Bulk rock analysis have shown that magnetite and maghemite is making up ~70% and ~30%, respectively, of the detected iron oxides in martian breccia NWA 7034. Maghemite component in the meteorite may also account for the magnetic properties of NWA 7034 [15, 16]. These findings are also consistent with the TEM analysis of fine-grained groundmass [17], showing that main Fe-rich phase in matrix is magnetite with nanocrystalline maghemite. Various authors have reported that maghemite contains ca. 2% water (as protons on the vacant octahedral sites) [5] and it occurs in soils as weathering product of magnetite.
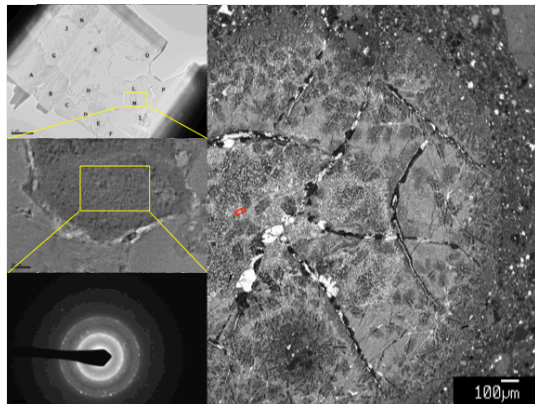


Fig.2. BSE image of Fe-oxide rich spherule. (a) TEM image of extracted region, scale bar 1μm (b) ferrihydrite rich region in FIB section, scale bar 50 nm (c) measures SAED pattern showing additional to ferrihydrite some peaks of magnetite/maghemite.

**H$_2$O inventory of NWA 7034:** As reported by [1] NWA 7034 has approximately 6000 ppm H$_2$O, and based on the O-isotopic composition of this H$_2$O it is almost entirely martian in origin. At this point, we will report an inventory of the phase distribution of this H$_2$O based on recent studies, including the present one. Up to 5% of NWA 7034 is maghemite, which can have up to 2 wt.% H$_2$O. Consequently, maghemite could account for 1000 ppm of the 6000 ppm bulk H$_2$O. The Cl-rich apatite has a stoichiometric missing component

that can be attributed to OH of 0.17 ± 0.06 structural formula units, which equates to 3000 ± 1000 ppm H$_2$O. The modal abundance of apatite in NWA 7034 was estimated to be up to 5%, so the maximum contribution of H$_2$O from apatite is approximately 150 ppm ± 50 ppm. The amount of ferrihydrite estimated to be in NWA 7034 from the present study is 1-2%, and given that ferrihydrite has about 5.4 wt.% H$_2$O, it can account for, at most, 1100 ppm H$_2$O of the 6000 ppm H$_2$O. The last phase that may contribute H$_2$O that we have identified are phyllosilicates [17]. Smectite, similar to Saponite was identified and could make up as much as 1% of NWA 7034. Saponite can hold up to 19 wt.% H$_2$O, so it could contribute as much as 1900 ppm H$_2$O to the NWA 7034 bulk H$_2$O content. In total, we can account for only 4150 ppm of the 6000 ppm H$_2$O detected in the bulk, and that is by using the higher end of the H$_2$O estimate for each of the hydrous phases, so additional work is needed to find the hosts of H$_2$O in NWA 7034.
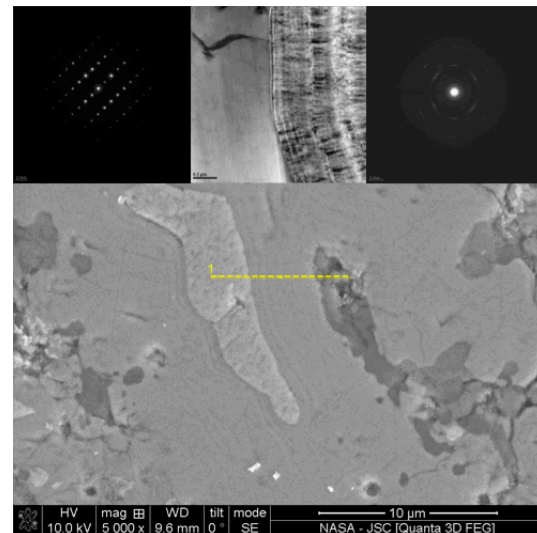


Fig.3 SEM back-scattered electron image of troilite grain surrounded with maghemite showing location of FIB section. (a) SAED of troilite grain, (b) Bright-field (BF) STEM image of extracted FIB section, scale bar 0.2μm (c) SAED of surrounding maghemite.

**References:** [1] Agee, C.B. et al. (2013) *Science* 339, 780-785. [2] Leshin, L.A. et al. (1996*) GSA*, 60, 2635-2650. [3] Pollack, J.B. et al (1979) *JGR*. 84, 2929–2945.[4] Bishop, J.L and E. Murad (2002) *Geological Society*, 202, 357-370. [5] Cornell R. M., and U. Schwertmann (1996) *The Iron Oxides* (VCH). [6] Michel, F.M. (2007) *Science* 316, 1726-1729. [7] McCubbin, F.M. et al. (2009) *GSA* 73, 4907-4917. [8] Fleischer, I. et al. (2011). . 46, 21-34. [9] Tosca et al. (2008) *JGR-Planets* 113 [10] Torrent et al (2007) *GRL*, 33, L02401. [11] Morris et al (2004) *Science*, 305, 833. [12] Bell at al (2004) *Science*, 305, 800. [13] Bishop, J.L. et al (2008) *GR* Abstracts, 10, EGU2008-A-11557. [14] Bishop, J.L. et al. (2000) *31$^{st}$ LPSC*, #1946. [15] Agee, C.B. et al (2013) *44$^{th}$ LPSC*, #2965. [16] Rochette, P. et al. (2013). 44$^{th}$ *LPSC, #1343*. [17] Muttik, N. et al (2014) *45$^{th}$ LPSC*, This volume.