HYDRATION OF THE DARK METEORITE AND THE RED PLANET. P. Beck[1] , A. Pommerol[2], L. Remusat[3], B. Zanda[3], JP Lorand[4], C. Gopel[5], R. H. Hewins[3,6], S. Pont[3], E. Lewin[7], E. Quirico[1], B. Schmitt[1], G. Montes-Hernandez[7], A. Garenne[1], L. Bonal[1], O. Proux[8], JL Hazemann[9], V.C.F. Chevrier[10], [1]UJF-Grenoble 1 / CNRS-INSU, Institut de Planétologie et d'Astrophysique de Grenoble (IPAG) UMR 5274, Grenoble, F-38041, France, beckp@obs.ujf-grenoble.fr. [2]Physikalisches Institut, Universität Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland. [3]Laboratoire de Minéralogie et de Cosmochimie du Museum, CNRS and Museum d'Histoire Naturelle, 75005 Paris. [4]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. [5]Institut de Physique du Globe, Sorbonne Paris Cité, University Paris Diderot, CNRS UMR 7154, F-75005 Paris, France. [6]Department of Earth and Planetary Sciences, Rutgers University, Puscataway, NJ 08854, USA. [7]UJF-Grenoble 1 / CNRS-INSU, Institut des Sciences de la Terre (IsTERRE), Grenoble, France. . [8] Observatoire des Sciences de l'Univers de Grenoble (OSUG) CNRS UMS 832, 414 rue de la piscine 38400 Saint Martin d'Hères, France. [9]Institut Néel, 25 av. des Martyrs, 38042, Grenoble, France. [10]Keck Laboratory for Space an Planetary Simulation, Arkansas Center for Space and Planetary Science, University of Arkansas, Fayetteville, AR, USA.

Introduction: Martian breccias (so-called "Black Beauty" meteorite NWA7034 and its paired stones NWA7533 and NWA 7455) are unique pieces of the Martian surface, which display abundant evidence of aqueous alteration that occurred on their parent planet according to the oxygen isotope composition of water [1]. These dark stones are also unique in the fact that they arose from a near surface level in the Noachian southern hemisphere [2-4]. Here, we used IR spectroscopy, Fe-XANES and petrography to identify the mineral hosts of water in NWA 7533 and compare them with observations of the Martian surface.

Methods: A double polished thin slice of NWA 7533 was prepared at MNHN. The section was prepared using cyanoacrylate glue, which was subsequently removed with acetone. There was no detectable IR signature of residual glue in the prepared section. The transmission spectra of the double polished thin section were measured with a Brucker Hyperion FTIR spectrometer in the 500-4000 cm^{-1} range with a 4 cm^{-1} resolution. The spectra were obtained in an environmental cell [5], equipped with a primary vacuum and a heating resistance (T=70°C) and purged to pimary vacuum to ensure the lack of contamination by adsorbed water.

Diffuse bidiretionnal reflectance spectra of NWA 7533 were measured using the spectro-photo-goniometer available at IPAG [6](Brissaud et al., 2004). About 300 mg of NWA 7533 powder were manually deposited on a sample holder. The setup is located in a cold room (-10°C), and the air is dried using a cold trap in order to minimize signatures from atmospheric water. The spectra were normalized to spectralon™ and infragold™, and obtained under standard geometric conditions (incidence=0°, emergence=30°). This setup enables us to measure reflectance level accurately (+/- 0.5 %) in the 0.7-4.6 µm range.

About 20 mg of powder were mixed with 100 mg of boron nitride and pressed in order to obtain a compact pellet of 6 mm of diameter. This pellet was analyzed for Fe- K-edge XANES on MB30b (CRG-FAME) beamline at the European Synchrotron Radiation Facility. The spectrum of the pellet (Fig. 1) was measured in transmission mode with a typical energy resolution of 0.3 eV using Si(220) monochromator crystal. Energy calibration was achieved setting the first inflection point of an Fe metal foil K edge spectrum at 7112eV. The data were then reduced following the procedure of [7] 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 (Fig. 2).

IR transmission spectra: The two IR transmission spectra measured on a doubly polished section of NWA 7533 reveal the presence of an absorption feature between 2.6 and 3.6 µm, with a maximum at 2.8-2.9 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-bound hydroxyl groups (Mg-OH), within Mg-rich phyllosilicate [8] or in brucite ($Mg(OH)_2$) always shows a maximum of absorption around 2.7 µm ruling out such phases as a potential host of water. 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 [8]. 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 resemble the band shape most, as observed by [9].

Reflectance spectra: The reflectance spectra of NWA 7533 reveal that the shape and position of the 3-µm band are similar to those of the Martian surface measured from orbit. On Mars, this feature occurs ubiquitously on the surface and is systematically intense (with a band depth typically above 35 %) [10-11]. 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 [12], or under very specific climatic conditions [13]). As a consequence, the ubiquitous 3-µm band of Mars and NWA 7533 likely originates from an –OH bearing phase.

Fe-XANES measurements: The electronic and structural states of iron in NWA 7533 was determined by mean of XANES spectroscopy. These measurements permit us to determine the bulk redox state of iron in NWA 7533, and show that about 50 % of Fe atoms in the meteorite are ferric iron (Fe^{3+}), making NWA 7533 the most oxidized Martian meteorite so far (Fig. 1 and 2). This value is close to the average redox state of iron in Gusev soil dust end-member (Fe^{3+}/Fe^{T} ~ 40 %; [14]). Using a bulk Fe abundance of 10 wt % [1], and assuming that each Fe^{3+} atom is balanced by an OH^-, a bulk equivalent content of about 0.8 wt % H_2O is estimated for NWA 7533, in agreement with the bulk content measured by [1] (0.6 wt %). This is again suggesting that iron hydroxides or oxy-hydroxides are likely mineral hosts of "water" in NWA 7533. Still, some other Fe^{3+} phases are present in NWA 7533 (Maghemite, 3 vol. % according to [1], Ti-magnetite, ilmenite and pyroxene), which, although nominally anhydrous, might also contribute to the hydrogen budget. In situ measurements of the Martian soil have shown a significant level of hydration at least locally [15-16].

Conclusions: We confirm that NWA 7533 presents some hydration in the form of an –OH bearing phase and that about half of the Fe is present as Fe^{3+}, making NWA 7533 the most oxidized Martian meteorite (confirming magnetic analysis of its paired meteorite NWA 7034 [17]). The similarity of the 3-µm band between NWA 7533 and the Martian surface, together with the high oxidation state of this regolith breccia suggest that geological units similar to NWA 7533 might be at the core of the dust production mechanism on Mars.

[1] Agee C. B. et al. (2013) *Science* 339, 780. [2] Humayun M. et al. (2013), *Nature* 503, 513. [3] Hewins R.H. et al. (2013), *Meteoritics & Planet. Sci., 76,* 5252. [4] Hewins R. H. et al. (2013) LPSC 44th abstract #2385. [5] Beck P. et al. (2010) *GCA* 74, 4881. [6] Brissaud O. et al. (2004) *Applied Optics* 43, 1926. [7] Wilke M. et al. (2001) *Am. Min.* 86, 714. [8] Calvin W. M. and King T. V. V. *(1997) Meteoritics & Planet. Sci.* 32, 693. [9] Muttik N. et al. (2013), *Meteoritics & Planet. Sci., 76,* 5216. [10] Jouglet D. et al. (2007) JGR 112.[11] Milliken R. E. and Mustard J. F. (2007) *Icarus,* 189, 550. [12] Gendrin A. et al. (2005) *Science*, 307, 1587. [13] Poulet F. et al. (2010) *Icarus* 205, 712. [14] Morris R. V. et al. (2006) *JGR*, 111. [15] Meslin et al. (2013) *Science* 341, 1238671 [16] Archer P. D. et al. (3014) *JGR* in press. [17] Rochette P. et al. (2013) LPSC 44th abstract #1343.

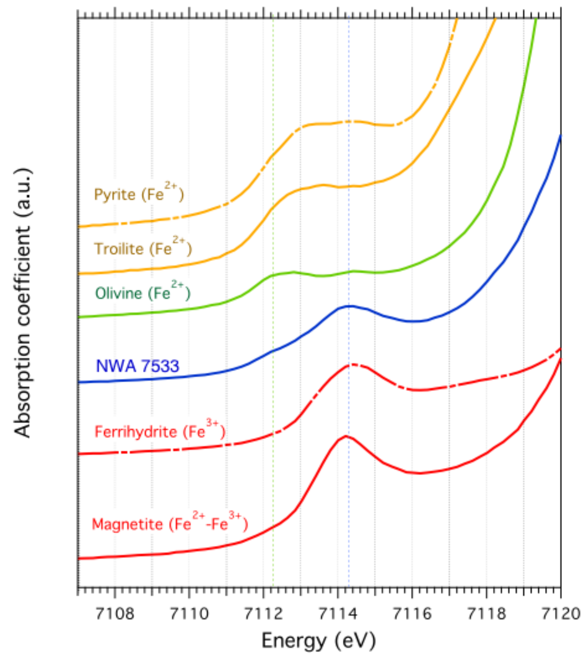

Fig. 1 : Fe K-edge pre-edge XANES spectra of NWA 7533 and various terrestrial standard (Fe in Oh site).

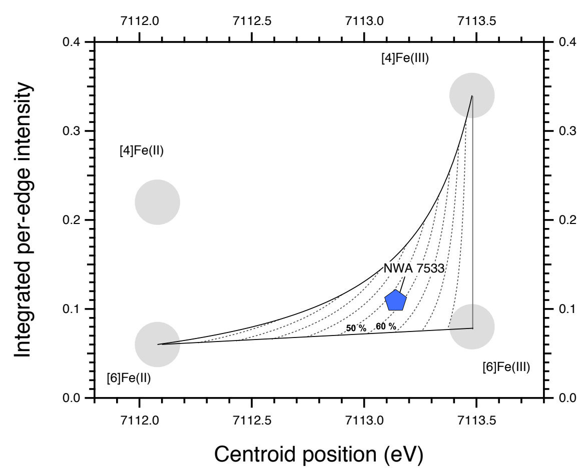

Fig. 2 : The pre-edge feature of NWA 7533 plotted in the Wilke et al. (2001) diagram.