WATER AND THE FORMATION OF THE NORTHWEST AFRICA 8114 MARTIAN REGOLITH. J. L. MacArthur[1], J. C. Bridges[1], L. J. Hicks[1], R. Burgess[2], and K. H. Joy[2]. [1]Space Research Centre, Dept. of Physics & Astronomy, University of Leicester, LE1 7RH, UK, jm650@le.ac.uk. [2]SEAES, University of Manchester, UK.

Introduction: Northwest Africa 8114 (a pair of Northwest Africa 7034) is a polymict, martian basaltic regolith breccia with varied clasts in a fine grained matrix [1-3]. It is the most hydrated martian meteorite discovered [4] and the oxygen isotope and D/H isotope ratio analyses support the martian origin of water [4]. As this meteorite is a breccia, further study is required to determine which phases contain the water. The majority of the water is suggested to be hosted by hydrous Fe oxides, with a minor contribution from apatite [5,6]. The ferric phases maghemite and goethite have been detected [7], making this potentially the most oxidized known martian meteorite [4,7].

The meteorite was likely formed as a result of an impact event [8] which may have led to hydrothermal systems causing further alteration to it [7,9]. Previous study has characterized sections of NWA 8114 and shown partial breakdown and mantling by fine-grained material of pyroxene clasts to be associated with oxidation [10]. This investigation uses XRD, FTIR and Ar-Ar dating to better understand the origin of this impact regolith and the role of water in its evolution.

Methods: Three polished sections from the main mass of NWA 8114, held at the University of Leicester were examined with a Hitachi S-3600N SEM with INCA 350 EDX system for initial elemental analyses. This was followed by analyses with a JEOL 8600S EPMA with an accelerating voltage of 15 kV and a beam current of 30 nA.

The FIB sections for TEM analysis were taken from different specifically chosen clasts of NWA 8114 using an FEI Quanta 3D Dual Beam FIB/SEM. A JEOL JEM-2100 LaB6 TEM with a Princeton Gamma Technology Avalon EDX system was used to obtain TEM and STEM images and EDX data.

Beamlines at the *Diamond Light Source* synchrotron, Oxfordshire, UK were used: I-18 for X-ray absorption near edge structure (XANES) analyses [10] and X-ray diffraction (XRD), and B-22 for Fourier Transform Infrared (FTIR) spectroscopy. Transmission spectra of a double polished thin section and reflectance spectra of the 3 single polished sections were recorded with a Brucker Vertex 80 V FTIR interferometer in the 500-4000 cm^{-1} range with a 4 cm^{-1} resolution. The measurement spot was 10 µm x 10 µm. A reference water-bearing silicate glass standard was also measured [11].

Fe-K XANES, XRD and FTIR were carried out at sample points on a representative variety of clasts, as well as XANES 5 µm resolution and FTIR 8 cm^{-1} resolution maps.

Four clasts were separated from the bulk meteorite, analysed by SEM-EDX and fragments of them subsequently analysed with an Argus VI mass spectrometer, at SEAES, for Ar isotopes and halogens [12].

Results: *FIB-TEM:* Some of the pigeonite clasts, with bulk compositions $Wo_{12-18}En_{31-34}Fe_{47-56}$, and low-Ca pyroxene clasts $Wo_2En_{65-68}Fs_{29-33}$, when examined by TEM, are seen to have broken down to a submicron, granular mixture of iron oxide ~10-20% and an amorphous Al-silicate ~20%, with relict and recrystallised pigeonite or low-Ca pyroxene (<2.5% Wo) the remainder (Fig. 1). Unaltered cpx-dominated clasts have negligible ferric iron contents - determined by Fe-K XANES - but altered pigeonite and low-Ca pyroxene have Fe^{3+}/Fe_{tot} ≤25% [12].

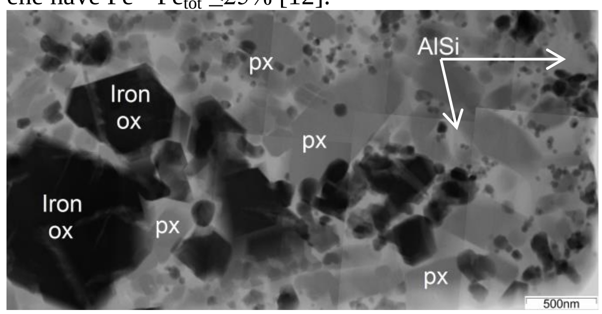

Figure 1: BF STEM image showing iron oxide (iron ox), pyroxene (px) and aluminium silicate (AlSi) in a sample of thermally altered pyroxene.

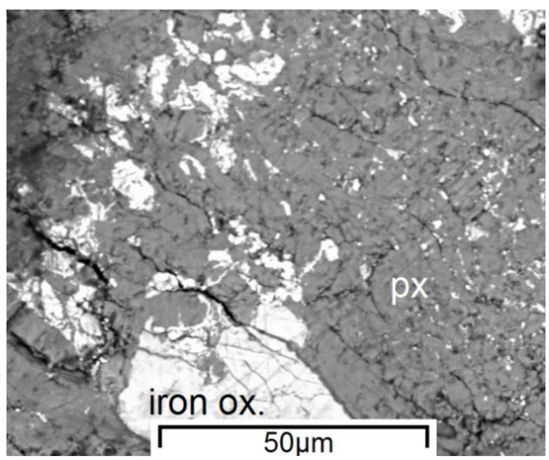

Figure 2: BSE image showing breakdown of pyroxene $En_{66}Wo_6Fs_{28}$ (grey, px) into iron oxide (white, iron ox.) in the double polished section.

FTIR: Transmission spectra from a double polished section of NWA 8114 were obtained and matched with SEM mineralogical data. Fig. 2**.** shows a pyroxene, $En_{66}Wo_6Fs_{28}$, which has partially broken down into iron oxide and Fig. 3 shows three FTIR spectra taken in that area.

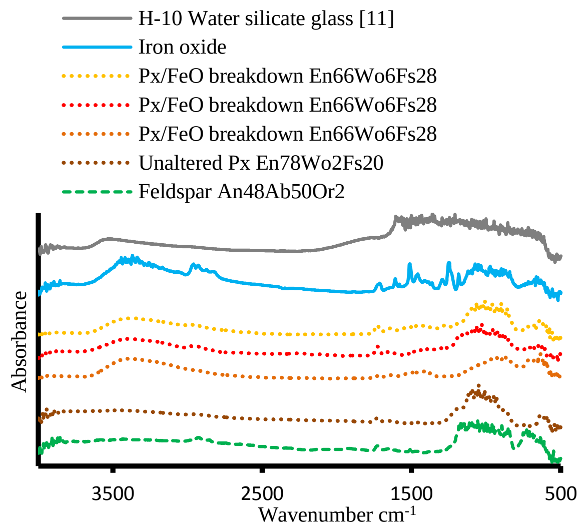

Figure 3: FTIR transmission absorbance spectra from different clasts of NWA 8114 and a water-bearing silicate glass standard [11]. The altered pyroxene contains microscopic grains of goethite.

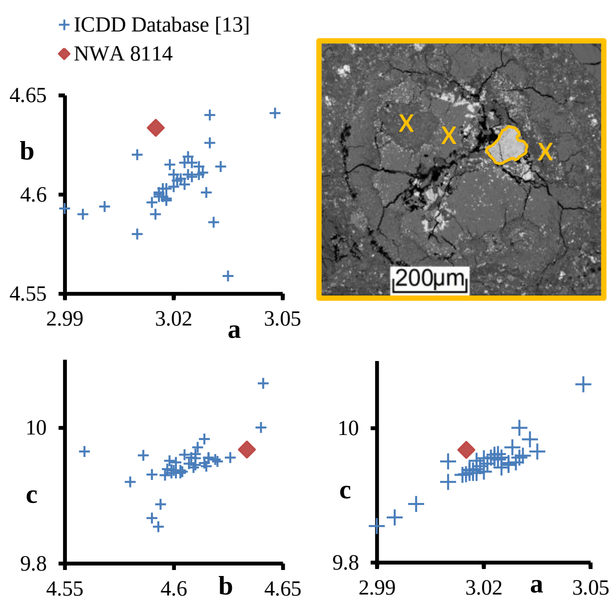

Figure 4: Unit cell dimensions a, b, c in angstroms plotted for goethite standards from the ICDD database [13] against calculated values from XRD data for NWA 8114 for the area highlighted in the BSE image. The five most intense d-spacings for NWA 8114 were: 2.704, 2.524, 1.840, 2.451, 4.188 vs the ICDD standard: 4.171, 2.443, 2.686, 1.715, 2.577 (all in angstroms). The yellow crosses indicate further XRD points similarly shown to be magnetite.

Fig. 3 shows a peak at 3565 cm^{-1} for the hydrated silicate glass standard containing 0.17 wt% H_2O [11]. The three pyroxene FTIR spectra, together with another taken from an iron oxide clast instead all show a peak at 3400 cm^{-1} in close agreement with [6] indicating the presence of –OH groups. The homogenous unaltered pyroxene clast and feldspar clast do not show a peak in this range. The small feature at 1730 cm^{-1} is indicative of pyroxene while peaks between 880-1120 cm^{-1} show the silicate bands. We don't see evidence in any NWA 8114 phases for dissolved H_2O.

XRD: Unit cell parameters were calculated after assigning *hkl* planes to the d-spacings calculated from the XRD data and compared to standards from the ICDD database (Figure 4), showing a good match with goethite FeO(OH). Similar analysis was carried out showing a good fit between the other grains marked on Fig. 4, and magnetite.

Ar-Ar Dating: Three alkali feldspar clasts and one augite clast show a range of disturbed ages. When calculated from measured ^{40}Ar-^{39}Ar ratios, the pyroxene clast showed a possible isochron between 1.1-1.2 Ga, whereas the feldspar clasts gave more varied values.

The Action of Water in the Formation of the NWA 8114 regolith: The pyroxenes which have recrystallised to form magnetite and amorphous silicate at a submicron scale, show the effect of high temperature and oxidation during the regolith formation. The oxidation may indicate the presence of H_2O. The additional presence shown by our XRD and FTIR analyses of goethite within much of the pyroxene clasts, shows that water was also present at a later, low temperature stage in the regolith's history. Given the D/H isotope ratio evidence [4], although some terrestrial contamination cannot yet be ruled out, this indicates alteration in the presence of water as the regolith was cooling on Mars. The ^{40}Ar-^{39}Ar potential age of 1.1-1.2 Ga may relate to the high temperature phase of regolith formation.

References: [1] Stephen N. R and Ross A. J. (2014) *LPSC XLIV*, Abstract #2924. [2] Humayun M. et al. (2013) *Nature 503*, 513-516. [3] Santos A. et al (2014) *GCA 157*, 56-85. [4] Agee C. B. et al. (2013) *Science 339*, 780-785. [5] Muttik N. et al. (2014) *GRL 41*, p. 2014GL062533. [6] Beck P. et al. (2015) *EPSL 427*, 104-111. [7] Gattacceca J. et al. (2014) *GRL 41*, 4859-4864. [8] Hewins R. H. et al. (2014) *LPSC XLIV*, Abstract #1416. [9] Humayun M. (2014) *Meteorit. Planet. Sci.* 49 Abstract #5413. [10] MacArthur J. et al (2015) *LPSC XLV* Abstract #2295. [11] Filiberto J. et al. (2008) *MAPS 43 Nr 7*,1137-1146. [12] Bridges J. C. et al (2015) *MAPS 50*, Abstract #5284. [13] ICDD PDF-4/Minerals 2014 database, http://www.icdd.com *Int. Centre for Diffraction Data*.