THE O ISOTOPE COMPOSITION OF MARTIAN METEORITES USING SHRIMP SI: EVIDENCE OF MULTIPLE RESERVOIRS IN SILICATE MINERALS OF THE REGOLITH BRECCIA NORTHWEST AFRICA 8114. L. Loiselle[1], P. Holden[1], J. N. Ávila[1], P. Lanc[1], J. C. Bridges[2], J. L. MacArthur[2] and T. R. Ireland[1], [1]Research School of Earth Sciences, The Australian National University, Acton, ACT 2601 Australia; liane.loiselle@anu.edu.au. [2] Space Research Centre, Dept. of Physics and Astronomy, University of Leicester, LE1 7RH, UK.

Introduction: Northwest Africa (NWA) 7034 (and pairs, including NWA 8114 studied here) represents a new class of martian meteorite that is distinct from the shergottite-nakhlite-chassignite (SNC) meteorites [1]. As the first observed sedimentary rock from Mars, the geochemical analysis of this meteorite is a noteworthy development in our understanding of martian planetary geology. Petrographic and geochemical evidence demonstrates that NWA 7034 is a polymict regolith breccia making it the first regolith breccia sample from a planetary body with an atmosphere [1-5]. Its discovery increases the diversity of our martian geologic sample suite as it is composed of clasts representing multiple igneous lithologies not represented by the SNCs [4,5].

The martian regolith breccias exhibit a similar, unique, and variable bulk rock $\Delta^{17}O$ isotope composition (e.g., NWA 7034 ranges from +0.47‰ to +0.65‰ [1]) which is significantly higher than the SNC silicate fractionation array occurring at ~+0.3‰ (as defined by [6]). Growing evidence [1,3,7-8] suggests that the O isotope systematics recorded in the martian regolith samples appears to be more complex than the SNCs, and possibly indicating heterogeneities within the samples.

Current models explaining the processes that may have caused the O isotope heterogeneities observed in the martian meteorites (e.g., atmosphere-lithosphere interactions, input of exotic planetary material) would benefit from obtaining more $\Delta^{17}O$ isotopic data from these samples. However, the complex mineralogy of the breccias can make it difficult to obtain sufficient material for repeated $\Delta^{17}O$ isotopic measurements of mineral separates using conventional techniques (e.g., [3,7]). An alternative is *in situ* secondary ion mass spectroscopy (SIMS; e.g., [8]), where isotopic measurements can be correlated to micro-scale variations in the mineralogical and/or chemical composition of a sample at the grain level. Providing a geologic context for the isotopic measurements may be important for complex samples like planetary breccias, but the analytical precision of *in situ* $\Delta^{17}O$ isotopic measurements has delayed the widespread application of the technique to the martian meteorite suite. Over the years *in situ* analytical precision has improved steadily due to the development of new instruments and refinements in the SIMS technique. For example, with careful sample preparation, tuning of the instrument and standardization we have improved the analytical capability of our SHIRMP SI instrument so that we can routinely resolve the 0.3‰ $\Delta^{17}O$ offset that is required to study martian meteorites (e.g., [9]).

Here we apply our SHRIMP SI method [9,10] to conduct high-resolution *in situ* $\Delta^{17}O$ isotopic measurements of the mineralogically complex martian regolith breccia NWA 8114. To ascertain the degree of heterogeneity within the sample we characterize the isotopic compositions of individual mineral populations (i.e., pyroxene, plagioclase, K-feldspar, apatite and the matrix).

Methods: A thin section of NWA 8114 (an NWA 7034 pair; [11]) was obtained from University of Leicester. FEI Quanta QEMSCAN analysis was used to generate a mineral phase assemblage map of the meteorite section (Figure 1) that guided the isotopic analysis.

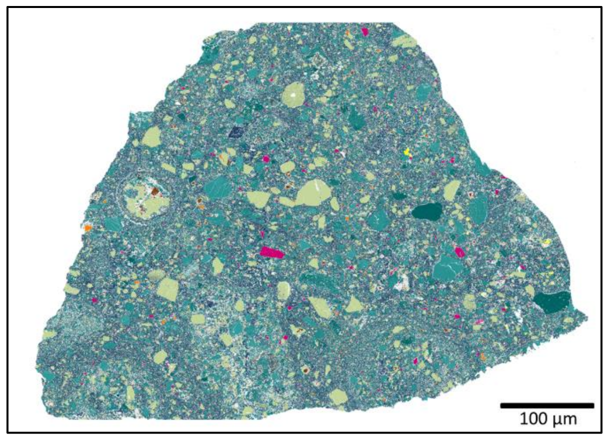

Figure 1. Mineral phase map of NWA 8114. The breccia contains a range of crystalline clasts within a fine-grained matrix. Mineral populations analyzed in this study include: pyroxene (green■), plagioclase (cyan■) alkali feldspar (dark cyan■), apatite (magenta■) and matrix (navy blue■).

Triple oxygen isotopic compositions ($\Delta^{17}O$) were measured using the Sensitive High-mass Resolution Ion Microprobe – Stable Isotope (SHRIMP SI) housed at the Research School of Earth Science at The Australian National University (ANU) in multiple-collection mode [e.g. 10]. A primary Cs ion beam was focused to a ca. 30 µm area spot to sputter samples. An electron column equipped with a low energy electron gun was used to accelerate electrons to the target for charge neutralization. Negative secondary ions were accelerated to real ground from the -10 kV sample potential and focused by the quadrupole triplet lenses before passing through the source slit and entering the secondary mass analyzer. Mass resolution during the analytical session was sufficient to resolve the potential isobaric interference of $^{16}OH^{-}$ from $^{17}O^{-}$. Secondary ion beam intensities were measured by Faraday cup current mode. Measured isotope ratios are corrected for EISIE (electron induced secondary ion emission) contributions, instrumental mass fractionation, counting statistics, and uncertainty in the compositions of the primary reference material (San Carlos olivine; SCO). Isotopic analysis of the various mineral phases within the NWA 8114 sample (e.g., pyroxene, feldspar, etc.) were bracketed by measurements of the primary reference material (i.e., SCO). A reference mount including olivine grains from the SNC meteorites ALHA77005 and Chassigny were also analyzed during the analytical session to monitor the martian fractionation line (MFL). SEM analysis was conducted after the *in situ* isotopic measurements to verify pit placement, ensuring that pits, cracks and epoxy resin were avoided during the isotopic analysis.

Results: Measurements of the mineral populations present in NWA 8114 (i.e., pyroxene, plagioclase, K-feldspar, apatite and matrix) show that the meteorite has a heterogenous O isotopic composition (Figure 2). The $\Delta^{17}O$ value of the NWA 8114 pyroxenes (green circles) are indistinguishable from the MFL established by the SNC silicates (red circles) and agree with a nonmagnetic fraction of NWA 7034 (conventional measurement) as reported by [7]. By contrast, the remainder of the NWA 8114 analyses exhibit larger $\Delta^{17}O$ values than the pyroxenes, plotting above the MFL. The plagioclase feldspar values (blue circles) agree with the whole rock bulk NWA 8114 $\Delta^{17}O$ value (black square); while the K-feldspar is even more enriched in ^{17}O (yellow circle), plotting above the reported bulk composition. The apatite $\Delta^{17}O$ value is indistinguishable from both the MFL and the whole rock bulk $\Delta^{17}O$ values for NWA 8114 due to its large error bar. The error associated with apatite is larger than the other mineral groups as there are fewer replicates (n = 6) than the other materials analyzed (n ~ 20). The matrix measurement has the highest $\Delta^{17}O$ values observed in the NWA 8114 section during the analytical session.

Discussion: We demonstrate that our improved analytical capability using SHRIMP SI can resolve the 0.3‰ offset of martian meteorites (from the TFL). We replicate the SNC silicate fractionation line (i.e., MFL [6]) and document evidence of additional multiple O isotopic reservoirs in the martian regolith breccia samples. Our results indicate that there are three distinct (i.e., errors do not overlap) O isotopic reservoirs in the NWA 8114 silicate minerals (i.e., pyroxene, plagioclase and K-feldspar; Figure 2).

We demonstrate that SHRIMP SI measurements can be successfully used as an alternative and/or complementary method when understanding the $\Delta^{17}O$ isotopic compositions of complex, planetary samples where there is a limited amount of (analytical) sample or a high number of replicate analyses is required.

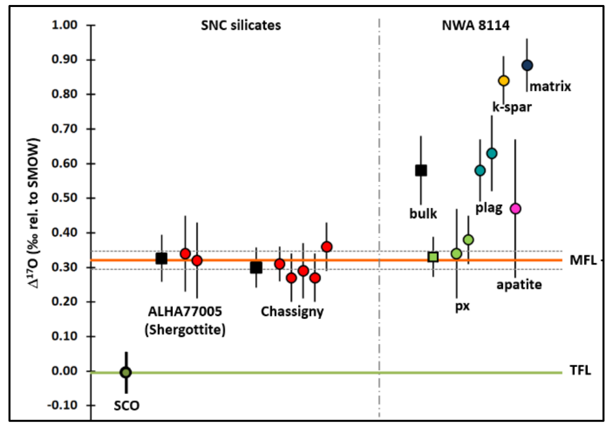

Figure 2: $\Delta^{17}O$ isotopic compositions of martian meteorites analyzed using SHRIMP SI, demonstrating the internal heterogeneity of the O isotopic composition of minerals in NWA 8114. Also shown are the terrestrial fractionation line (TFL; green line), the martian fractionation line (MFL; red line with error ellipses; [6]). The NWA 8114 mineral populations (left side) include pyroxene (px; green circle), plagioclase (plag; cyan circles), potassium feldspar (k-spar; yellow circle), apatite (magenta circle) and matrix (dark blue circle). Two conventional $\Delta^{17}O$ isotopic compositions are included: the bulk rock oxygen isotopic composition for NWA 8114 (black square; MB 102) and the nonmagnetic fraction of NWA 7034 (green square; [7]). The right side of the plot shows the in situ isotopic compositions (red circles) obtained for the SNCs (i.e., ALHA77005 (shergottite) and Chassigny) along with conventional values (black squares) as reported by [6]. Circles are in situ SHRIMP SI (SIMS) measurements, and squares are reported (conventional) $\Delta^{17}O$ values [6,7].

References: [1]Agee C.B. et al.(2013) *Science, 339*, 780–785. [2]Humayun M. et al.(2013) *Nature, 503*, 513–516. [3]Wittmann A. et al.(2015) *MAPS, 50*, 326–352. [4]Santos A.R. et al.(2015) *GCA*, *157*, 56 – 85. [5]Hewins R.H. et al.(2017)MAPS, *52*, 89–124. [6]Franchi I.A. et al.(1999) *MAPS, 34*, 657-661. [7]Ziegler K. et al. (2013) *LPSC XLIV*, #2639 [8]Nemchin A.A. et al. (2014) *Nature Geosci., 7*, 638-642. [9]Loiselle L et al. (2017) 80th*MetSoc (LPI Cont.No.1987), #6176*. [10]Bridges J.C. and Ireland T.R. (2015) *LPSC XLVI*, #1674. [11]MacArthur J.L et al. (2019) *GCA*, *246*, 267-298.