GEOCHEMICAL ANALYSES OF THE TAWAZ BRECCIA, AN ANOMALOUS MESOPROTEROZOIC BRECCIA IN WEST AFRICA. K. A. Milam[1] D J. Aden[2], and L. C. Kah[3], [1]Department of Geological Sciences, Ohio University, 316 Clippinger Laboratories, Athens, Ohio, 45701 (milamk@ohio.edu), [2]Ohio Division of Geological Survey, 2045 Morse Road, Building C-1, Columbus, Ohio 43229-6693 (da109304@ohio.edu), [3]Department of Earth and Planetary Sciences, University of Tennessee, Knoxville, TN, 37996-1410 (lckah@utk.edu).

Introduction: The Tawaz Breccia (TB) is an anomalous breccia within the Mesoproterozoic (~1.1 Ga[1,2]) Atar Group on the West African Craton (WAC) in present day Algeria and Mauritania. The Atar Group is composed of alternating shales and siltstones indicative of a shallow marine setting. Sedimentary features suggests that the Atar Group was deposited at or below wave base.

The TB is an unusual carbonate breccia because its sedimentary features record a high energy event in an otherwise calm shallow marine depositional environment. In order to identify a depostional mechanism for this unit, breccia types produced by common geologic processes (described through an extensive literature search) were evaluated for their statistical correlation with initial field observations of theTB [3,4]. Preliminary analyses have shown that breccias generated by either an impact or non-impact tsunami correlate best with the TB [4].

In an effort to determine if the TB interval was associated with a Mesoproterozoic impact event, 17 samples (2 from the underlying and overlying units + 15 from the TB) from reconnaissance field trip to Mauritania were examined to identify unequivocal macroscale indicators of impact, such as shatter cones or potential meteorite fragments. None were identified. Identification of microscale evidence of shock metamorphism (e.g. shocked quartz, coesite) was precluded by the large amount of acid dissolution required for our limited, carbonate-dominated samples. Therefore, geochemical analyses were needed to identify potential meteoritic components and to discriminate between mechanisms that may have generated the tsunami respsonsible for the TB.

Methods: Portions of each 17 samples collected from the Atar Group [5] were crushed using clean laboratory techniques as described in [4]. Fine clay-sized powders were produced using an agate mortar and pestle [4].

XRD Analyses. XRD analyses were used to characterize all 17 samples to identify primary minerals present in the TB and to search for minerals indicative of a meteoritic component from primary meteorite types (e.g. achondrites and chondrites – olivine and pyroxene; iron and stony-iron meteorites – kamacite, taenite, troilite). XRD analyses also allowed us to characterize the mineralogy of each sample in order to select representative or anomalous samples for additional isotopic analysis.

Rhenium-Osmium and Osmium Isotopic Analyses: Four samples were selected for Re-Os isotopic analyses to compare the concentrations and ratios in the TB to those in known meteorites. Two of the four TB samples were selected as background samples because they were collected from above or below the TB, thereby providing a baseline for Re-Os during the Mesoproterozoic. These locations are the least likely to have been influenced by a possible impactor and were analyzed in order to determine what background Os and Re concentrations and isotopic ratios were during the Mesoproterozic. The remaining two samples were selected from horizons within the breccia that were most likely to have elevated Os and Re concentr tions and low (meteoritic) isotopic ratios. Since depositional energy dissipates with time, slow settling of sediments (after the high energy event) allows for concentration of impactor components (if they are present) near the top of a fining upward sequence in marine sediments [6].

Samples were spiked by the addition of a specific amount of enriched isotope (^{190}Os and ^{185}Re) using a process called isotope dilution analysis [7-8]. When the spike is added to the sample, it alters the isotopic ratios of the sample. Given the initial isotopic abundance of the sample and spike, how much spike was added to a known amount of sample, spike concentration, and the new isotopic ratio, the concentration of the element of interest in the sample can be calculated with high precision [8]. Next, the samples were digested for at least 2 days in reverse aqua regia (HCl:HNO3 = 1:3) in Carius tubes (sealed thick walled Pyrex tubes) at 230 °C. Separation/purification of Os was then performed by solvent extraction [9-12] and Os was analyzed by negative thermal ionization mass spectr metry (N-TIMS) [see 12 for additional details]. N-TIMS involves vaporizing the purified sample (Re and Os done separately) by heating in a vacuum and analyzing it with a 30cm radius of curvature, 68º sector mass spectrometer at the University of Maryland. Re was measured using an electrometer and a Faraday cup, and Os was measured using a Faraday cup and a 17-stage electron multiplier [13].

Results: XRD analyses demonstrated that the TB is comprised primarily of calcite and lesser amounts of dolomite and quartz. Samples with less detrital quartz were deemed more suitable for Re-Os analysis since they may indicate deeper and therefore calmer water. Since a majority of oceanic silica is sourced from the continental crust [14], shallower and less calm waters close to the shore tend to have more quartz. However, quartz can also be diagenetically formed in the marine environment [15] so the presence of quartz does not necessarily eliminate the possibility of a deep calm environment.

Concentrations of Os in the four TB samples analyzed range from ~0.004 to 0.008 ppb, much lower than normal chondritic values (~600 ppb) [10]), stony-irons (2212 ppb [16,17]), iron meteorites (17826 ppb [18]), and achondrites (2.6 ppb [19]). Furthermore, the Os concentrations of the TB are even lower than typical continental crust and oceanic crust Os values on Earth (<0.05 ppb Os [20-21]) and average marine sedimentary rocks (0.831 ppb [22-24]. However Os concentrations are within known ranges of ocean island basalts, oceanic crust, and fluvial sediments.

Discussion: Low Os and Re concentrations demonstrate that, if an impactor component is present, then it is very minimal and has been diluted by mixing with crustal rocks. Furthermore, these concentrations are too low to allow impactor contributions to be distinguished from terrestrial sources of Re and Os. Re concentrations and $^{187}Re/^{188}Os$ ratios of the TB correspond to impact mixtures, as well as the ranges of ocean island basalts, fluvial sediments and others. Because of this overlap, the specific source of Re (or $^{187}Re/^{188}Os$) cannot be determined. For $^{187}Os/^{188}Os$, the ratio of the TB does intersect iron and stony-iron meteorites, but this signal also corresponds to ocean island basalts, oceanic crust, continental crust, mantle, marine sediment and fluvial sediment ranges, so again meteoritic contributions cannot be unequivocally confirmed.

In the marine environment, the majority of Os is contributed by fluvial sources (70%; of which 5% is from ocean island basalts and the rest from continents), meteoritic material (14%), leeching of ultramafic rocks in the oceans (16%), and a negligible amount from aeolian (wind born) dust [25]. Little is known about sources of marine Re (especially in carbonates). Since fluvial sediments contain minor Re and Os contributed from continental sources [*Esser and Turekian,* 1993], it is possible that the Re and Os present in the TB is a mixture of components; contributed by continental fluvial sources into the epicontinental Taoudenni Basin. However, the possibility of an impact mixture cannot be excluded because an impact mixture could also produce the low Re and Os concentrations and isotopic ratios determined for the TB. If the TB is an impact mixture, then the $^{187}Os/^{188}Os$ ratio corresponds to stony-iron and iron meteorites, while the $^{187}Re/^{188}Os$ ratio corresponds to a chondritic impactor similar to that from the K-T boundary [26-27]). Furthermore, the Re concentrations correlate with the chondritic K-T boundary concentrations and the Ivory Coast Tektites (an iron or chondritic impactor [28]).

Os concentrations of the TB do not correlate with meteorites or impact mixtures, but this low range may be a result of dilution of impact materials. It is also possible that the modern micrometeorite flux (background flux to the Earth) is higher [29] than it was in the Mesoproterozoic, which could explain why the TB samples have low values relative to modern values. Since the $^{187}Os/^{188}Os$ ratio suggests stony-iron or iron while the Re concentrations suggests chondritic or iron, perhaps the correlation of iron meteorites in both suggests that if the TB is an impact mixture then the Re and Os could be sourced from an iron meteorite.

References: [1] Teal et al. (2005) [2] Bartley, J. K. unpublished data, [3] Aden et al., (2010) *GSA Abs. with Programs NC Meeting, Branson MO,* [4] Aden, D. J. (2010) M. S. Thesis, Dept. of Geol. Sci., Ohio Univ., [5] Kah, L. C. et al. (2008), [6] Bourgeois et al. (1988), [7] Walker R. (2010), [8] EPA, 2007, [9] Shirey and Walker (1995), [10] Gelinas et al. (2004) [11] Lee et al. (2006) [12] Walker et al. (2002), [13] Walker et al. (1994), [14] Tréguer et al. (1995), [15] Sharma (1968) [16] Chen et al. (2002), [17] Shen et al. (1998), [18] Shen et al. (1996), [19] Mason (1979), [20] Morgan and Lovering (1967), [21] Walker et al., (2002), [22] Rooney et al., 2010, [23] Cohen et al., 1999, [24] Dalai and Ravizza, 2006, [25] Levasseur et al., 1999, [26] Kyte, 1998, [27] Trinquier et al., 2006, [28] Koeberl and Shirey, 1997, [29] Goswami and Lal, 1977

Acknowledgements: The authors would like to thank Richard Walker of the University of Maryland his facilities and assistance with this project.