An Anomalous Breccia in the Mesoproterozoic (~1.1 Ga) Atar Group, Mauritania: Endogenic vs. Exogenic Genesis

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This thesis titled
An Anomalous Breccia in the Mesoproterozoic (~1.1 Ga) Atar Group,
Mauritania: Endogenic vs. Exogenic Genesis

by

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ABSTRACT

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An Anomalous Breccia in the Mesoproterozoic (~1.1 Ga) Atar Group, Mauritania: Endogenic vs. Exogenic Genesis (101 pp.)

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The Tawaz Breccia (TB) is an anomalous breccia within the Mesoproterozoic (~1.1 Ga) Atar Group on the West African Craton (WAC). This unit is unusual because its sedimentary features record a high energy event in an otherwise calm shallow marine depositional environment. In order to determine a depositional type 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 the TB. This analysis has shown that breccias generated by either an impact or non-impact tsunami correlate best with the TB. Geochemical analyses on a suite of samples collected during reconnaissance field work were used to discriminate between these two tsunami types. Os and Re concentrations and the ratios of $^{187}$Os/$^{188}$Os and $^{187}$Re/$^{188}$Os demonstrate that TB values correlate with impact mixtures and terrestrial materials. Therefore, although the TB was likely formed by a tsunami, preliminary analyses can not completely eliminate the possibility that the tsunami was triggered by an impact event (of possible iron composition).

Approved: _____________________________________________________________

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CHAPTER 1: INTRODUCTION

The West African Craton (WAC) is a large (~ 4.4 million km$^2$) and ancient portion of the African continent consisting of the Archaean to Proterozoic-aged Man and Reguibat Shields, the Anti-Atlas Mountains, and the Taoudenni Basin (Figure 1). WAC was assembled into its present configuration during the Eburnean orogeny at 2.0 Ga [Ennih and Liegeois, 2008], when the Paleoproterozoic-aged Eburnean terrane collided with an Archaean terrane along a NW-SE margin [Schofield and Gillespie, 2007], and has since remained tectonically stable. After assembly during the Mesoproterozoic, a period of minimal tectonic activity 1.7 – 1.0 Ga [Ennih and Liegeois, 2008] allowed this large area to become a craton through growth or accumulation of cooling asthenosphere at the base of the craton [Black and Liegeois, 1993]. After cratonization, a period of extensive subaerial erosion resulted in a nearly flat surface or peneplane. Between 1.1 and 1.0 Ga, subsidence (3-4 m/Ma) of the northern part of the Taoudeni Basin was controlled by the earlier Eburnean formation of the Tiris ferruginous gneisses within the surrounding (less dense) granites, gneisses and migmatites. This mass differential led to the formation of the Tiris-Richat-Tagant trough (Figures 1 and 2) [Bronner et al., 1980].

Subsidence along with eustatic changes resulted in a periodic epicontinental sea and the commencement of marine deposition. Within this basin, there are five supergroups (or 4 Megasequences [Deynoux et al., 2006] not counting the thin Mesozoic cover), which are divided by discontinuities related to extra-cratonal tectonic events [Bertrand-Sarfati et al., 1991]. Supergroup 1 (Figures 1 and 2) consists of
Figure 1. The West African Craton, modified from [Ennih and Liegeois, 2008] and [Bronner et al., 1980] after [Fabre, 2005] and [Liegeois et al., 2005]. Mesoproterozoic aged Supergroup 1 from [Teal et al., 2005].

Figure 2. Cross-section through north-central Mauritania (to basement), featuring the Tiris-Richat-Tagant trough. Modified from [Bronner et al., 1980].
carbonates, shales, and siltstones [Bronner et al., 1980] and contains the unit of interest for this study. This Mesoproterozoic supergroup varies (E-W) from 800 to ~3500 m in thickness across the trough [Moussine-Pouchkine and Bertrand-Sarfati, 1997; Deynoux et al., 2006], and is sub-divided into three groups (in ascending order and separated by unconformities): Char, Atar, and Assabet el Hassiane (Figure 3).

The focus of this study is the Atar Group, a ~1.1 Ga [Teal et al., 2005; Bartley, unpublished data], 550 m thick (near Atar) [Bertrand-Sarfati et al., 1991] package of sedimentary rock that has been correlated across 1500 km of Mauritania, Algeria, and Mali (Figure 1). The Atar Group (Figure 3) is composed of alternating carbonates and siliciclastics (shales and siltstones), both indicative of a shallow marine setting. Seventy-five percent of these carbonates are composed of columnar stromatolites such as Conophyton and Jacutophyton. The interstitial space of the Conophyton in the Atar Group was found to be free of transported sediment, indicating an environment located below wave base [Bertrand-Sarfati and Moussine-Pouchkine, 1988]. It is thought that these stromatolites grew in an epeiric sea (on the WAC), as evidenced by a very shallow bottom gradient and basin wide stromatolites. The more extensive columnar stromatolites (mainly Conophyton) can be biostratigraphically linked since they show basin-wide simultaneous evolutionary development of filmy microstructures (that do not show up again). Further up section another basin-wide development - tussocky microstructures (a mounded and radially fibrous fabric) - can be found, again showing that this area periodically existed as one continuous cratonic shallow sea [Bertrand-Sarfati and Moussine-Pouchkine, 1988]. This extensive columnar stromatolite regime alternates with
a facies mosaic system of marine shales and mixed carbonates of uncertain and likely irregular water depth (likely due to stromatolite topography) thought to relate to storm-
influenced shallow marine conditions and not a tidal system. A tidal system is not favored because common sedimentary features attributed to tidal environments (herringbone cross stratification, mud cracks, flat laminated stromatolites, channels, or evaporites) are rare or absent [Bertrand-Sarfati and Moussine-Pouchkine, 1988]. Within the Atar Group, the Tawaz Formation (Figure 3) contains a 2-6 m thick unit informally known as the Tawaz Breccia (TB), that is as extensive as the Atar Group (1500 km), and whose lithologic and textural characteristics are unrelated to the preceding and anteceding beds [Bertrand-Sarfati et al., 1997] and indicative of a high-energy depositional environment.

An ascending transect (Figures 4-8) [Kah, 2008] through the TB transitions from a faulted and laminated base (Figure 4), to ball and pillow structures (Figure 5) to fluidized beds (Figure 6), followed by interbedded breccia and molar-tooth structures (Figure 7 and 8). These breccias are composed of light (white to grey) clasts of allochthonous molar-tooth (MT) structures (Figure 7), thought to originate as rapidly lithified cracks in the substrate [Pratt, 2001; Shields, 2002; Crawford et al., 2006]. Also present are dark (bluish) clasts composed of MT microspar [Kah, 2008]. Clasts in the TB range from granule (2mm) to boulder size (meters in maximum diameter). No clasts larger than boulders (defined by Blair and McPherson [1999] as having a maximum diameter larger than 4.1m), are known in the TB [Kah, 2008]. Below and above this unit, the stromatolitic carbonates are indicative of a low energy depositional environment within the photic zone (relatively shallow water, 10-100m deep [Kah, 2010]). The presence of breccias along with features indicative of rapid erosion (scour surfaces) and
rapid deposition (suspended clasts, rip up clasts, ball and pillow structures) indicates an unusually high energy event (or events) was responsible for deposition of the TB. This unit has been variously referred to as a breccia, megabreccia, “blue bed” (due to its blue appearance at distance in the field), and a molar-tooth dominated carbonate. This nomenclature variability reflects the considerable lateral facies changes of this unit.

Figure 4.Faulted and laminated base of TB.
Figure 5. Ball and pillow structures.

Figure 6. Fluidized beds.
Figure 7. Interbedded breccia and molar-tooth structures.

Figure 8. Interbedded breccia and molar-tooth structures.
Earlier studies considered the TB to be a seismic deposit associated with the Pan-African Orogenic Belt in Algeria that was active in the Neoproterozoic [Moussine-Pouchkine, and Bertrand-Sarfati, 1997] However, later studies determined the TB to be Mesoproterozoic in age [Teal et al., 2005; Bartley, unpublished data], a stable time period, and therefore not associated with the Pan-African Hoggar Uplift [Kah et al., 2007]. Furthermore, the cyclic and extensive nature of the deposits does not correlate well with a seismic regime [Kah et al., 2007]. Therefore, a depositional mechanism for the TB remains to be determined. What depositional mechanism could create a deposit as laterally extensive as the TB? What type of breccia is associated with the features described in the TB?

In order to answer these questions a survey of possible breccia formation methods was undertaken and then characteristics of known breccia types were compared with the TB (Chapter 2). Two correlation analyses were then used to determine which of the breccia forming mechanisms was the most likely to have led to the formation of the TB. In Chapter 3, geochemical analysis of samples from the TB are characterized using X-ray diffraction (XRD) followed by Re and Os analyses to better understand the composition of the rocks composing the TB, and to test for the possible presence of impactor components.
CHAPTER 2: COMPARATIVE STATISTICAL ASSESSMENT OF POSSIBLE DEPOSITIONAL MECHANISMS FOR THE TAWAZ BRECCIA

It is challenging to ascertain a specific breccia forming mechanism for the TB because there are many geologic processes that can form breccias. By systematically comparing the characteristics of common breccia types to the TB, breccia mechanisms that are more likely to have formed the TB can be identified.

Methods

An extensive literature review of one hundred and eight references was used to describe breccia types based on commonly-used characteristics. Of these references, all but eleven were journal articles, nine were text books (useful for general data) and two were personal communications with a collaborator regarding the TB. This was combined with personal observations of a few specific breccia types observed during field work in California (Inyo County, Dublin Hills, volcanic breccia), Tennessee (karst breccia in the Flynn Creek impact structure), Nevada (Alamo Impact breccia), and Wyoming (Yellowstone volcanic breccia). These personal observations were included as additional sources. Characteristics between each breccia type and the TB were compared based on these sources.

In order to identify the geologic process responsible for deposition of the TB, a spreadsheet was constructed to compare characteristics of different breccia types to the same characteristics in the TB (Table 1). Two correlation analyses were then applied to this table in order to determine which known breccia forming mechanism (of 14) correlated the best with the TB. The first correlation analysis compared the characteristics
Breccia types across the top, characteristics on the vertical axis. Green cells indicate that the respective breccia type commonly (correlation value of 1) has the respective characteristic. Yellow cells indicate that the respective breccia type sometimes (correlation value of 0.5) has the respective characteristic, and red cells indicate that the respective breccia type rarely/never (correlation value of 0) has the respective characteristic. Numbers in cells represent references; see separate reference list (Appendix A: Breccia Spreadsheet References).

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Breccia types across the top, characteristics on the vertical axis. Green cells indicate that the respective breccia type commonly (correlation value of 1) has the respective characteristic. Yellow cells indicate that the respective breccia type sometimes (correlation value of 0.5) has the respective characteristic, and red cells indicate that the respective breccia type rarely/never (correlation value of 0) has the respective characteristic. Numbers in cells represent references; see separate reference list (Appendix A: Breccia Spreadsheet References).
of each known breccia type to the TB to determine which breccia type was most comparable to the TB, thus serving as a proxy for associating a particular breccia depositional mechanism with the TB. The second correlation analysis initially compared the characteristics of each breccia type to every other known breccia type (excluding the TB) in order to determine which characteristics are most useful for distinguishing between breccias. Statistical correlation was then used to compare breccia types to the TB using the most discriminating characteristics.

Fourteen of the most common breccia types (glacial, tsunami, storm, turbidite, debris flow/alluvial fan, rock fall/talus slope, fault, pyroclastic flow, auto-brecciation, karst collapse, evaporite collapse, lithic ejecta, suevite ejecta, and impact tsunami) were selected for comparison. These were examined because they represent the range of common ways that breccia is formed at the Earth’s surface. A few special cases of breccia formation were not considered because they were found to be too localized or not long lasting enough to have formed the TB (extant since 1.1 Ga). An example of a breccia type that was not considered is hyaloclastic breccia; it forms in association with pillow lava and the resulting glassy clasts are very small and devitrify quickly into palagonite \cite{Winter, 2001}. This breccia mechanism could not have formed the large clasts that are found in the TB. Furthermore, the glass that volcanic eruptions form is short-lived and would have devitrified over the long period of time that the TB has existed.

Specific characteristics (62 in total) were used to describe each of these breccias, based on those commonly used in sedimentology literature; the first, clast size, is indicative of peak depositional energy. Grain sizes were delineated using an extension of
the Udden-Wentworth grain-size scale proposed by Blair and McPherson [1999]. Clast variability (mono- or polymict) is a combination of many factors (source, energy, range). Clast sorting (well, moderate, poor, unsorted) is determined by the energy of the system. Clast rounding (rounded, subrounded, subangular, angular) usually shows how far the sediments were transported or how easily they are weathered. Support (clast or matrix) depends on the clast/matrix ratio; in a clast-supported breccia the clasts rest on one another and would occupy the same volume if the matrix was not present. In a matrix-supported breccia, the clasts are held up by a framework of matrix. Clast lithology (igneous (intrusive or extrusive), metamorphic (contact, shock, dynamic, or regional), sedimentary (chemical or detrital)) indicates clast source and sometimes can narrow down formational mechanisms. Clast source (allo- parauthi- or authigenic) is reflective of transport distance and energy of deposition. Clast grading (vertical, lateral, or multi-sequence) varies depending on the energy gradient. Vertical grading implies that energy was decreasing (or increasing if reverse) throughout deposition, lateral grading is a result of energy decreasing in a horizontal direction such as shoreward. Multi-sequence grading occurs when the energy source increases and decreases multiple times (e.g. storm surges). Clast alignment (parallel or perpendicular to movement, bi- or unidirectional imbrication, random) indicates if there was entrainment and if it was in one direction, or cyclic (multiple directions). Thickness per event (<1m, 1-10m, or >10m) and lateral extent (<100km, 100-1000km, >1000km) are also related to the amount of sediment moved and the system energy. Depositional environment (subaqueous, transitional, subaerial) and morphology of deposit (cross-sectional and plan view) can be distinctive of particular
types of breccia, for example karst and evaporite collapse breccias are often sinkhole shaped in cross-section, and fault breccia commonly has a linear expression.

The spreadsheet (Table 1) used for comparing the characteristics between different breccia types was constructed after an extensive literature search. Each cell in the spreadsheet contains reference information (represented by numbers) for characteristics pertaining to each breccia type and indicates whether or not a particular breccia has that characteristic. If literature references indicated that a particular breccia type was likely to display a specific characteristic, then that cell was assigned the color green to visually represent a positive occurrence. If literature references indicated that a particular breccia type sometimes displayed a specific characteristic, then that cell was colored yellow. If literature searches indicated that a breccia type did not display a particular characteristic, the associated cell was color-coded red. This color-coding allowed for simplicity of visual identification for subsequent correlation analyses.

Correlation Analyses

Two correlation analyses of the spreadsheet (Table 1) were performed to determine which of the breccia types correlates best with the sedimentological characteristics of the TB. Correlation analysis #1 compared all characteristics of each breccia type to the TB. As an added step, non-distinguishing characteristics were removed from comparison and the remaining characteristics were compared to the TB. Correlation analysis #2 compared each breccia type to each other breccia type (initially excluding the TB) in order to determine which characteristics are the most suitable for distinguishing between breccia types in general. Then the least distinguishing
characteristics are progressively removed (through the use of bins on a histogram) and the remaining (more distinguishing) characteristics compared to the TB after each removal.

For both correlation analyses #1 and #2 (Figure 9), once the characteristics to be compared to the TB were chosen, (or in the case of analysis #1 part 1, all characteristics), each spreadsheet cell for each breccia type (column) was assigned a number (by assigned color comparison) indicative of the significance of the correlation (positive, partial, or negative) between the breccia type and the TB. For example, if a specific breccia-forming method commonly had a particular characteristic (assigned green) and the TB also had this characteristic (green), the spreadsheet cell for the known breccia type would be assigned a value of one (commonly + commonly = 1) however if one of the two only sometimes (assigned yellow) had a characteristic only a 0.5 would be assigned since the correlation is not as strong (commonly + sometimes = 0.5). Next, since absence of evidence (assigned red) does not imply evidence of absence, negative correlations were assigned a zero; if two breccia types lack a particular feature, that does not imply that they are the same, or correlate better with each other, (rarely or never + anything = 0).

Correlation Analysis #1

Analysis #1 is divided into two parts. In the first part, all 62 characteristics of the 14 breccia types are directly compared to the TB as a means of determining which breccia mechanism may have been responsible for deposition/emplacement of the TB.
Figure 9. Flowchart for correlation analysis #1 and #2.
The cell corresponding to a particular characteristic of each breccia type (column) was compared to the TB and a correlation value was calculated (1, 0.5 or 0 as described above). Correlation values were summed per breccia type (column) and divided by the total number of characteristics (62). This gave an approximation of how well each breccia type correlated with the TB using all characteristics (Appendix B: Breccia Spreadsheets, first one). In the second part, characteristics that occur in every breccia type (ignoring the TB), or only correlate negatively, are removed because they did not distinguish breccia types (characteristics that never occur in any breccia type would also be eliminated by this step, but they were not initially included on the spreadsheet). New correlation values were calculated (in the same way as part one) but only for the remaining (most distinguishing) characteristics. Then, in order to determine an average percent correlation of each breccia type with the Tawaz Breccia, the correlation values for each column (breccia type) were individually summed and then divided by the number of remaining (48 of 62 original) characteristics (Appendix B: Breccia Spreadsheets, second one).

Correlation Analysis #2

In order to provide an independent assessment of which breccia characteristics are the most discriminating among the breccia types (initially excluding comparison to the TB) a second correlation analysis between breccia types was performed. With this analysis, each characteristic for all 14 breccia types was compared to the same characteristic for each other breccia type (excluding the TB). This resulted in 91 comparisons with each pair of spreadsheet cells compared and assigned a 1, 0.5 or 0 (by using the colors assigned from the referenced sources) and a series of new spreadsheets.
(Appendix B: last 7 breccia spreadsheets). The logical statement used to calculate correlation values between each pair of cells compared is: IF cell X = cell Y THEN assigned value = zero because cells are the same (non-distinguishing), ELSE take the absolute value of cell X – cell Y to find the difference in correlation value as a positive number. For example; [1 compared to 1=0], [1 compared to 0.5=0.5], [0.5 compared to 0.5=0], and [0 compared to 1=1]. Then cell values for each row resulting from this comparison, were summed and divided by the total number of comparisons (91). The resulting row average falls between zero (characteristic never correlates between any pair) to one (characteristic correlates between every pair), the values between these two extremes show how often a characteristic correlated between breccia types. Next, characteristics (rows) that had averages of zero were excluded because they were not useful for distinguishing between breccias. The remaining 56 distinct characteristics were compared to characteristics of the TB using correlations assigned by color, and each spreadsheet cell for each breccia type was given a new correlation value of 1, 0.5, or 0 after comparison with the TB. Correlation values in each column (each corresponding to a specific breccia type) were then individually summed and divided by the number of utilized (56 of the 62 original) characteristics, which resulted in an average percent correlation of each breccia type/mechanism with the unknown (TB).

Since a breccia characteristic is not as distinguishing if it is almost always present (closer to 1) or usually not present (closer to 0) in all breccia types, a method was devised to progressively eliminate these less distinct characteristics using a frequency distribution histogram (Figure 10). Correlation values were divided into bins and plotted on a
histogram (Figure 10) that shows more distinguishing characteristics toward the center and less distinguishing characteristics toward the edges of the histogram. Fourteen bins were used because the range of correlation value sums is from 0 to 14. If all 14 breccia types correlate they have a row (characteristic) sum of 14. For this analysis the bin size was set at 1, with 14 chances to correlate or not. This histogram was used to retain the most discriminating characteristics, by eliminating the least distinguishing (one high and one low bin at a time). Each of the 14 bins represents the number of correlations for the respective characteristic, if a characteristic is commonly found in all breccia types (all green) then it falls into the fourteenth bin (14 of 14 or 100%). If a characteristic is found
in 6 (all green) of 14 breccia types it falls into the sixth bin (6 of 14 or 43%). Elimination of the bins in this way selectively removes the specific characteristics that correlate the least with other breccia types and focuses on the ones most discriminating for breccias in general. This process was repeated six times (Appendix B: last 7 breccia spreadsheets), each time by eliminating the next highest and lowest bins (and thus their respective characteristics) then summing each column (corresponding to a breccia type) and dividing by the number of remaining characteristics, resulting in a new percent correlation, based on more distinct characteristics (Table 2). The outcome is a percent agreement between each known mechanism and the Tawaz Breccia based on the most distinct physical characteristics of breccia. This elimination is based on the idea that the most distinguishing characteristics among all breccia types are not those that are always present (since they don’t distinguish anything), nor those that are rarely or never present (since they seldom distinguish a specific breccia type), but the features that lie between these extremes and eliminate some breccia types but still identify others. Therefore, analysis #2 identifies characteristics that are the best for distinguishing between breccia types (while analysis #1 compares all characteristics to the TB, and then compares again after removing those known to not be distinguishing). In addition, analysis #2 is a check to see if analysis #1 is valid by comparing the results of two independent methods of analysis.

Results

The results of correlation analysis #1 (Table 2) for all ranges of characteristic included (or excluded) show that the breccia type that correlates best with the Tawaz
Table 2. Results of analysis #1 and #2

<table>
<thead>
<tr>
<th>Correlation analysis #1 (values express % correlation with the TB)</th>
<th>non-impact breccias</th>
<th>impact breccias</th>
<th>statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>glacial</td>
<td>tsunami</td>
<td>storm</td>
<td>turbidite</td>
</tr>
<tr>
<td>all characteristics</td>
<td>65</td>
<td>71</td>
<td>60</td>
</tr>
<tr>
<td>non distinct excluded</td>
<td>50</td>
<td>54</td>
<td>35</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Correlation analysis #2 (values express % correlation with the TB)</th>
<th>non-impact breccias</th>
<th>impact breccias</th>
<th>statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>glacial</td>
<td>tsunami</td>
<td>storm</td>
<td>turbidite</td>
</tr>
<tr>
<td>non distinct excluded</td>
<td>43</td>
<td>46</td>
<td>30</td>
</tr>
<tr>
<td>minus 1 high and low bins</td>
<td>42</td>
<td>47</td>
<td>28</td>
</tr>
<tr>
<td>minus 2 high and low bins</td>
<td>40</td>
<td>44</td>
<td>28</td>
</tr>
<tr>
<td>minus 3 high and low bins</td>
<td>34</td>
<td>41</td>
<td>22</td>
</tr>
<tr>
<td>minus 4 high and low bins</td>
<td>39</td>
<td>34</td>
<td>18</td>
</tr>
<tr>
<td>minus 5 high and low bins</td>
<td>39</td>
<td>39</td>
<td>14</td>
</tr>
<tr>
<td>minus 6 high and low bins</td>
<td>57</td>
<td>57</td>
<td>29</td>
</tr>
</tbody>
</table>

Presented as percent correlation.
Breccia, when all characteristics are used, is normal tsunami (71% correlation) closely followed by impact tsunami (69% correlation) and then glacial and evaporite collapse (both 65% correlation). If non-distinguishing characteristics are removed, impact tsunami is highest (57% correlation) followed by non-impact tsunami (54% correlation) glacial (50% correlation) and turbidites (43% correlation).

The results of analysis #2 provide a similar set of percent correlations; of which impact tsunami is the highest (in all seven eliminations of non-distinguishing characteristics), closely followed by non-impact generated tsunami breccia types in the first four sets of eliminations. After the first four sets of eliminations of non-distinguishing characteristics, 70% of characteristics (and 4 bins from each side of the histogram; 8 of 14 total bins) have been removed and few (19 of 62) distinguishing characteristics remain. At this point, other breccia types begin to correlate as well as non-impact tsunami (though impact tsunami remains the highest). Here impact tsunami is 45% correlated and karst collapse and glacial types are 39% correlated followed by lithic impact ejecta at 37%. At 5 bins eliminated, impact tsunami is 43% correlated, while glacial, non-impact tsunami, and lithic ejecta are 39% correlated, with four others 32% correlated. Finally, with 6 bins eliminated (only 7 characteristics remaining) impact tsunami is 64% correlated with the TB, and again glacial, non-impact tsunami, and lithic ejecta are 57% correlated. In all cases but one (for analysis #1 when all categories were retained, and non-impact tsunami was 2% higher), the percent correlation between impact tsunami and the TB is highest.
Error Analysis

Resolution Error

Since the literature does not often report details to within specific percents (x breccia characteristic occurs y% of the time), it is possible that resolution is being lost in this study by limiting the number of correlation values to three. In order to address potential error arising from insufficient numerical resolution (of the detail of breccia characteristics) a spreadsheet was constructed and assigned hypothetical values of higher resolution than the literature. For this study (Table 1) correlation values were limited to 1, 0.5, and 0 (commonly, sometime, and rarely to never). However, for this hypothetical spreadsheet, random correlation values (using the Excel random number generator function) were assigned from 0 to 1 in steps of 0.1 (i.e. 0.0: the characteristic never occurs for the breccia type, 0.1: the characteristic occurs 10% of the time, 0.6: the characteristic occurs 60% of the time for the given breccia type, etc., Table 3).

Then, assuming that these random values were the true resolution of breccia characteristics in the field, each column of correlation values was summed and then divided by 10 (100% correlation) and multiplied by 100 to give the average percent correlation for each breccia type with the TB, using this random data set at 10% data resolution. Next, these random values were binned into the original lower resolution (Table 4) (0=<.25, .25<0.5<.75, and 1=>.75) to see what potential resolution is lost by only using three (available) instead of ten (hypothetical) divisions.

Comparing the differences in percent correlation between Table 3 and Table 4, results in a mean error of 6.1% (1σ standard deviation of 4.4%, max 14.3%). This shows
that if the details of every breccia and characteristic considered could be specified to within 10% of their occurrence frequency (i.e. glacial breccia has boulder sized clasts 90% of the time), but were binned into categories of commonly, sometimes, and rarely to never, then correlation values could be off by 6% on average. Errors this high mean that some of the correlation values presented in Table 2 are indistinguishable within the margin of error. For example, for correlation analysis #1 (all characteristics included) 12 of the 14 breccia types are indistinguishable; only rock fall and auto-breccia have correlations values low enough to be distinguishable from other breccia types.

Table 3. Spreadsheet with random values between 0 and 1

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.157</td>
<td>0.980</td>
<td>0.733</td>
<td>0.765</td>
<td>0.785</td>
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<td>0.876</td>
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<td>2</td>
<td>0.933</td>
<td>0.747</td>
<td>0.187</td>
<td>0.938</td>
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<tr>
<td>3</td>
<td>0.733</td>
<td>0.450</td>
<td>0.874</td>
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<tr>
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<td>0.173</td>
<td>0.468</td>
<td>0.778</td>
<td>0.135</td>
<td>0.775</td>
<td>0.109</td>
<td>0.615</td>
<td>0.128</td>
<td>0.988</td>
</tr>
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<td>0.850</td>
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</tr>
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<td>0.424</td>
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<td>0.713</td>
<td>0.111</td>
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<td>0.964</td>
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</tr>
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</table>

Rounded past the first decimal place, breccia types A-J, characteristics 1-10.

Table 4. Spreadsheet with values from Table 3

<table>
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<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
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</thead>
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</tr>
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</tr>
<tr>
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<td>4.5</td>
<td>4.5</td>
<td>5.0</td>
<td>6.5</td>
</tr>
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<td>80.0</td>
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<td>40.0</td>
<td>45.0</td>
<td>45.0</td>
<td>50.0</td>
<td>65.0</td>
</tr>
</tbody>
</table>

Rounded to 0, 0.5 or 1, breccia types A-J, characteristics 1-10.
For correlation analysis #1 (when non-distinguishing characteristics are excluded), the most correlative tsunami and impact tsunami breccia types are distinguishable from other breccia types except for glacial breccias. For correlation analysis #2 (when non-distinct characteristics are excluded) the most correlative tsunami and impact tsunami are indistinguishable from glacial, turbidite, debris flow, and pyroclastic flow. Similarly for correlation analysis #2 (when more non-distinguishing characteristics are excluded – one high and one low bin) tsunami and impact tsunami are distinguishable from everything except for glacial and turbidite breccia types. The other elimination steps of correlation analysis #2 (Table 2) are similar.

If the correlation values used for Table 1 have lost resolution (from a hypothetical precision of 0.0, 0.1, 0.2, 0.3, etc.) by being grouped into the less precise categories of 0, 0.5 and 1, then this analysis shows that not all breccia types are distinguishable. Unfortunately, this hypothetical error analysis could only be achieved if each breccia outcrop was reexamined to determine the percent likelihood of each characteristic occurring within each breccia type.

Potential Error from the Number of References

Since the breccia spreadsheet is based on literature review, having as many references as possible is important for covering a wide range of breccia types and examples. Due to time constraints, the maximum number of references in each comparison (spreadsheet cell) was set at 5 (a sixth would not be used unless it was more detailed and could replace one of the five) and the minimum at 1. During my literature search, I attempted to fill each cell with a total of 5 references. For the entire spreadsheet
5 references were used in 10% of cells, 4 references in 15%, and 3 and 2 for 33% of the cells (868 cells total). In cases where only 1 reference was used (10% of cells); specific details of the characteristics of a breccia are not well studied and/or reported in the literature. In order to determine error for cells with only one reference, a test was run on each of the 9 statistical analyses presented in Table 2. For these, the value of an arbitrary cell was changed from a positive to a negative correlation to test what the percent error in the correlation value for that breccia type would be if one cell was incorrect, which is more likely if a cell only has one reference (Table 5). Next, 2 and then 3 cells were changed from positive to negative to observe the percent correlation change if 2 or 3 cells were incorrect. Table 5 shows the potential (plus or minus) percent correlation errors if one, two, or three cells (characteristics) for any of the breccia types are wrong. As the number of characteristics used is decreased the potential percent error (in correlation) remains much the same until there are only a few characteristics left (i.e. the last three columns of Table 5). For all 9 correlation analyses presented on Table 2, if one cell is inaccurate then the percent error (± the values in Table 5) of impact tsunami overlaps with non-impact tsunami, and the two correlations are indistinguishable. If more than

<table>
<thead>
<tr>
<th># of char. used</th>
<th>62</th>
<th>48</th>
<th>50</th>
<th>36</th>
<th>29</th>
<th>19</th>
<th>14</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>correl. analysis</td>
<td>#1 part 1</td>
<td>#1 part 2</td>
<td>#2 all bins</td>
<td>#2 elim. 1</td>
<td>#2 elim. 2</td>
<td>#2 elim. 3</td>
<td>#2 elim. 4</td>
<td>#2 elim. 5</td>
</tr>
<tr>
<td>1 wrong cell</td>
<td>1.61%</td>
<td>2.08%</td>
<td>1.79%</td>
<td>2.00%</td>
<td>3.00%</td>
<td>3.45%</td>
<td>5.26%</td>
<td>7.14%</td>
</tr>
<tr>
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<td>3.23%</td>
<td>4.17%</td>
<td>3.57%</td>
<td>4.00%</td>
<td>6.00%</td>
<td>6.90%</td>
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<td>14.29%</td>
</tr>
<tr>
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<td>6.25%</td>
<td>5.36%</td>
<td>6.00%</td>
<td>8.00%</td>
<td>10.31%</td>
<td>15.79%</td>
<td>21.43%</td>
</tr>
</tbody>
</table>

For analyses #1 and #2 if 1, 2, or 3 cells are incorrect.
one cell is inaccurate then other breccia types begin to overlap as well. The potential error for the later correlation analysis (analyses #2 elimination 4 and beyond) is very large. Since there are so few characteristics remaining even a single incorrect cell generates a significant percent error. Thus, use of as many references as possible minimized the error in these correlation analyses.

In addition, the average number of references per correlation type was calculated and found to be comparable; 2.9 references per green cell, 2.5 per red, and 2.3 per yellow cell. This shows that the different correlation significances (colors) were given equal weight through the literature research and that no correlation category had significantly more references than another.

*Number of Characteristics Used*

In order to determine if 62 characteristics (and not a smaller number) were the most useful for distinguishing breccia types, an additional error analysis was performed. For each of the 14 breccia types, a random selection of 10, 20, 30, 40, and 50 characteristics (generated by Excel, one random set was used for all cases) were removed and a new correlation analysis performed with the remaining characteristics for each breccia type versus the TB. Figure 11 shows that changes in percent correlation with a decreasing number of characteristics used is minimal (averages between 1% and 3%), but that below 22 (to 12) characteristics, percent correlation falls (more significantly) an average of 7%. This suggests that the number of characteristics used in this study were sufficient to minimize error.
Discussion

In addition to correlation analyses, which show that impact tsunami or non-impact tsunami are the most likely generative mechanisms for the TB, several breccia formational types can also be qualitatively eliminated if their most distinct characteristics are absent from the TB. Others can be labeled as unlikely if the type/mechanism is not known to have been active during the time of formation of the TB, or on the WAC.

Figure 11. Calculated percent correlation by random characteristic removal.
The lack of apparent igneous clasts common to pyroclastic breccias [Curtis, 1954] or melt in the TB precludes emplacement by volcanic pyroclastic flows or auto-brecciation. Marine slumps are restricted to steeper gradient settings (such as a continental shelf break) than that in which the TB was deposited. Furthermore, slumps involve the movement of large coherent masses [Vestal and Lowrie, 1982] rather than mobilization of clasts to form a breccia such as the TB. Glacial mechanisms can also be excluded because the only known glacial deposit in the Mesoproterozoic is the recently identified Vazante Formation in Brazil (Geboy, 2006; Miller et al., 2009). Tectonic breccias can be distinguished by their requisite confinement along tectonically-active margins [Woodcock and Mort, 2008]. The Atar Group, however, represents cratonal deposition [Ennih and Liegeois, 2008] with no indication of active syndepositional orogenesis.

Evaporitic collapse breccias form by the dissolution of evaporites, rapidly leading to weakening and collapse of overlying rocks [Johnson, 2008]. Although there is evidence of localized evaporites in the Atar Group [Goodman and Kah, 2004], the timing of TB deposition is earlier than the development of thick, basin-wide evaporites, which did not arise until the Neoproterozoic [Kah, 2001]. Karst collapse breccias are also typically limited in lateral extent, based on the size of the failing cavity. A collapse 1500 km wide and a few meters thick (like the TB) is very unlikely and does not match the morphology or extent of even the largest karst landforms [Ford, 1988].

Another possible mechanism with wider lateral extent includes turbidites or sediment gravity flows which can transport large amounts of material hundreds of
kilometers. Unlike the TB, however, they are only preserved in deeper water environments below 250-300m [Walker, 1992; Walker and Plint, 1992], where they are seen to cut pre-existing beds. Storm deposits (formed with enough energy to move clasts) preserve unidirectional imbrication of clasts [Kortekaas and Dawson, 2007] unlike the Tawaz Breccia, in which clasts are bidirectional to multidirectional. However, storm deposits rarely contain the large rip-up clasts or boulders [Kortekaas and Dawson, 2007] as are commonly found in the Tawaz Breccia [Kah, 2008].

Deposition by tsunami can result in laterally-extensive deposits in shallow marine and onshore environments. However, tsunamis require a high-energy triggering event such as an earthquake, whose source would not likely be nearby in this cratonic region which was stable throughout the Mesoproterozoic. It has also been proposed that marine impact events could provide sufficient energy for tsunamis that could deposit allochthonous material ripped up from the seafloor [Oberbeck et al., 1993]. Well known examples include the breccias from the Alamo [Morrow et al., 2005], Chicxulub [Smit, 1999], and Lockne [Sturkell et al., 2000] marine impact events. Clasts deposited by ballistic sedimentation can also be a significant component of an impact event, emplaced by an expanding ejecta curtain in the shape of an inverted cone, with clast size fining away from the impact [Melosh, 1989]. Depending on the size of the trigger impact, large clasts can be ejected long distances, contributing to the clasts transported by the tsunami. Multi-sequence beds [Dypvik et al., 1996], high energy deposition, and the large lateral extent of deposits that can be generated by an impact tsunami match the characteristics of the TB, and therefore, the remainder of this thesis will specifically attempt to determine
whether or not the tsunami that deposited the Tawaz Breccia was induced by a marine impact event.

Summary

Most correlation analyses from this study support deposition of the TB by tsunami. Since tsunamis can be generated by non-impact and impact mechanisms, additional analysis is needed to determine whether or not the TB contains a meteoritic component indicative of an impact event.
CHAPTER 3: RHENIUM-OSMIUM ANALYSIS OF THE TAWAZ BRECCIA

Introduction

In order to determine if a stratigraphic horizon is associated with an impact event, unequivocal impact indicators; i.e. remnant impactor fragments, shatter cones, petrographic shock effects, and extraterrestrial geochemical markers must be identified [French, 1998]. No impactor fragments or shatter cones were located (limited samples) in the Tawaz Breccia (TB) and in order to locate shocked quartz, large amounts (tens of kilograms) of sample must be dissolved or thin sections made. Samples of the TB were too small for either acid dissolution or production of thin sections. Of these, geochemical markers are useful because they can indicate the presence of an impactor far from an impact site [Ryder, 1996], even when only preserved in very small concentrations.

Rhenium-osmium (Re-Os) isotopic analyses have been used to identify meteoritic contributions in crustal materials. Meteorites are enriched in Re and Os relative to crustal materials because they source from the mantle or core of disrupted parent bodies that are concentrated in Re and Os during differentiation [Warren et al., 1999] (stony-iron, iron, and achondrites), or are undifferentiated (Re and Os not ubiquitous in chondrites). Re-Os analyses have been used on impact-melt rocks and lithic clasts from within the outer crater ring of the Chicxulub multi-ring impact basin [Gelinas et al., 2004], as well as on the K-T boundary clay [Luck and Turekian, 1983; Lichte et al., 1986; Meisel et al., 1995; Muñoz-Espadas et al., 2003]. They have also been used on impact-melt rocks from the Chesapeake Bay impact crater [Lee et al., 2006]. Since the Re-Os system was able to
detect impactor contributions in these impact horizons and craters it is suitable for detecting a meteoritic component in the Tawaz Breccia.

Concentrations (in parts per billion, ppb) of Os and Re are useful for identifying a meteoritic component in crustal materials. If abundances of Re and Os in the TB are significantly higher than in average crust, they may be indicative of the collision of a large asteroid or comet at the Earth’s surface. Osmium, a platinum group element, is relatively depleted in crustal materials (<0.050 ppb [Morgan and Lovering, 1967; Walker et al., 2002]). This depletion occurred during core and mantle formation when metals, sulfides, and silicates separated due to elemental partitioning [Chou et al., 1983], and highly siderophile elements (HSE’s: including Re and Os) were largely differentiated from the (still-forming) crust and mantle of the Earth and concentrated in the core [Warren et al., 1999]. In order to be compatible, elements must have the correct charge and atomic radii to combine with a host mineral [Hiraga and Kohlstedt, 2009]). In a magmatic system, Re (charge +4, atomic radii 0.65Å) is incompatible with most minerals, such as olivine [Warren et al., 1999], and becomes enriched in the melt. Conversely, Os (charge +4, atomic radii 0.69Å) is compatible with newly-formed cumulates, such as olivine [Warren et al., 1999], that settle out of the melt. Little Re and Os is present in the continental crust (due to fractionation) compared to the mantle or core. However, the continental crust formed from upper mantle melt that was concentrated in Re (incompatible) relative to Os (compatible), resulting in high concentrations of Re relative to Os. In the mantle, less Re and Os have been lost to the core (relative to crust) so Re and Os are more enriched in the mantle than the crust.
Finally, due to this early differentiation, the core has the majority of highly siderophile elements (HSEs) (due to their affinity for iron, and density) and therefore has the highest concentrations of Re and Os [Warren et al., 1999].

Osmium (a HSE) is, however, concentrated in three of the four primary meteorite types: chondritic, iron, and stony-iron [Koeberl and Shirey, 1997; Koeberl et al., 2002], all of which have Fe-Ni phases. Chondrites are enriched in Os because they have not been differentiated (undifferentiated abundances), while iron and stony-iron are enriched because they source from the core or core mantle boundary (respectively) of a differentiated body (concentrated in compatible elements such as Os) that has been disrupted. For chondritic impactors, typical Os concentrations are about 600 ppb [Gelinas et al., 2004]. Chondritic sources are of particular importance because they make up more than 85% of all observed meteorite falls [Grady, 2000], thus a significant number of potential impactors are chondritic [Tagle and Berlin, 2008]. In contrast to chondrites, stony-iron meteorites have average Os concentrations of 2212 ppb [Chen et al., 2002; Shen et al., 1998] and iron meteorites 17826 ppb [Shen et al., 1996]. The fourth type, achondrites, on the other hand, represent differentiated crustal or mantle material from disrupted or impacted parent bodies and are thus relatively depleted (Os = 2.6 ppb) in HSE’s [Mason, 1979].

Re is a siderophile element that can be used to identify meteoritic contributions in a similar way to Os concentrations. Re is enriched in the crust relative to Os (see above) with average concentrations of 0.5 ppb [Esser and Turekian, 1993], but even more enriched in the Earth’s mantle (55 ppb [Walker et al., 1994]) and core (see analog iron
meteorite samples above) due to fractionation. Achondritic, stony-iron, and iron meteorites have average Re concentrations of 19.3 ppb [Mason, 1979], 167 [Chen et al., 2002; Shen et al., 1998], 1305 [Shen et al., 1996], respectively. These values represent material from the crust/mantle, core/mantle boundary, and core, respectively. Chondrites also have high Re values (70 ppb [Walker et al., 2002]) since they originate from undifferentiated bodies (no Re lost to the core).

Along with Re and Os concentrations, Re and Os isotopes are useful for identifying the presence of meteoritic components in crustal materials. This is because small meteoritic contributions (concentrated in Re or Os) can change the isotopic ratio of crustal materials. The Re-Os system is based on the β-decay of \(^{187}\text{Re}\) into \(^{187}\text{Os}\) (half-life of 42.3±1.3 Ga [Lindner, 1989]) and 6 other stable Os isotopes. Of these stable isotopes, the current concentration of \(^{188}\text{Os}\) (some studies use \(^{186}\text{Os}\), but \(^{188}\text{Os}\) is preferred because more is produced during the decay of \(^{187}\text{Re}\), and therefore \(^{188}\text{Os}\) is easier to measure) can be compared to current concentrations of \(^{187}\text{Re}\) and \(^{187}\text{Os}\) to determine the initial Os isotopic \(^{187}\text{Os}/^{188}\text{Os}\) ratio of a set of samples with the same age [Koeberl and Shirey, 1997]. Since crustal rocks have high Re values (relative to Os), the \(^{187}\text{Re}/^{188}\text{Os}\) ratio remains high because the decay of \(^{187}\text{Re}\) produces new Os isotopes slowly (half life 42 Ga). Thus continental crust has an average \(^{187}\text{Re}/^{188}\text{Os}\) ratio of 34.5 [Peucker-Ehrenbrink and Jahn, 2001]. Conversely, chondrites have higher concentrations of Os than Re (undifferentiated abundances) so their \(^{187}\text{Re}/^{188}\text{Os}\) ratios are lower (0.411) than continental crust [Walker et al., 2002]. \(^{187}\text{Re}/^{188}\text{Os}\) ratios are 0.32 for stony-irons [Chen et al., 2002; Shen et al., 1998] and 0.8 for iron meteorites [Shen et al., 1996], also lower
than continental crust since they source from the core (or core boundary) where Os concentrations are higher than Re (Os and Re are both very high in the core, but Os is more abundant due to pre-differentiation concentrations). Achondrites are representative of either crustal or mantle material (or combinations thereof) and should approximate that value, however the average achondrite value (0.343 [Mason, 1979]) is much lower, possibly due to incomplete or inefficient mixing during differentiation (Re and Os remain in the crust at higher values than expected) [Day et al., 2009].

Another way to determine if a crustal sample is enriched beyond normal values is to use the ratio of $^{187}\text{Os}$ to $^{188}\text{Os}$. For a crustal system, the initial concentration of Re is high relative to Os, so the ratio of $^{187}\text{Os}$ to $^{188}\text{Os}$ increases as $^{187}\text{Re}$ decays to Os isotopes. This results in continental crust with an average ratio of about 1 [Koeberl and Shirey, 1997]. However meteorites contain less Re than Os [Gelinas et al., 2004] (unlike continental crust which has more Re than Os due to partial melting of the mantle) so the $^{187}\text{Os}/^{188}\text{Os}$ ratio is not as strongly affected by the conversion of $^{187}\text{Re}$ into Os isotopes. This results in a meteoritic average (chondrites, achondrites, stony-iron, and iron) ratio of about 0.17 [Walker et al., 2002; Day et al., 2009; Chen et al., 2002; Shen et al., 1998; Shen et al., 1996]. Both the Earth’s mantle and meteorites can contribute to enrichment, but mantle rocks have relatively lower concentrations of Os (3.5 ppb [Chou et al., 1983]) than meteorites (resulting in higher $^{187}\text{Os}/^{188}\text{Os}$ ratios). On the other hand, higher concentrations of Os can be found in chondrites, stony-iron, and iron meteorites. Therefore, a much larger mantle contribution would be required to produce the same $^{187}\text{Os}/^{188}\text{Os}$ ratio as high as that from a meteoritic contribution. It should be noted that
even though impactor contributions are normally much less than 1 wt.% [Koeberl, 1998] this is enough to change the $^{187}\text{Os}/^{188}\text{Os}$ ratio.

Methods

Analyses were performed on 17 samples previously collected from the TB in Mauritania (West Africa) by Kah [2008] in the vicinity of Atar (Figure 1, Supergroup 1) (Figure 12). Initial XRD analyses were used for mineralogic characterization of the TB and to determine if any samples were atypical or unlikely to be suited for Re-Os analysis due to the presence of quartz (see XRD Analysis below). From the initial 17, four were selected for Re-Os analysis to determine if the TB contained an impact component.

Sample Preparation

Initial sample preparation for XRD and Re-Os analyses is the same, and exacting contamination prevention steps must be taken. Very small amounts of dust or sample fragments can cause contamination when geochemical detection limits are parts per billion (ppb) and parts per trillion (ppt). In order to prevent sample contamination, all metal objects (watches, jewelry) were removed and hands were washed thoroughly (a plastic bag was placed over the metal faucet handle to prevent contact). Each sample was photographed, described, weighed and catalogued. Each rock was scrubbed (with a different brush for samples with and without clasts (TB), or from different formations) and then placed in a sealed labeled plastic bag. The plastic sample preparation table was cleaned (with paper towels and dilute Lysol) three times between each handling of a single sample.

Next, samples were crushed with a rock hammer one at a time on a cement block.
<table>
<thead>
<tr>
<th>Sample #</th>
<th>Sample Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>no sample</td>
<td>stromatolitic carbonates (low energy)</td>
</tr>
<tr>
<td>1228B:</td>
<td>clast to matrix supported breccia</td>
</tr>
<tr>
<td>1224:</td>
<td>MT breccia</td>
</tr>
<tr>
<td>1221:</td>
<td>no clasts</td>
</tr>
<tr>
<td>1220:</td>
<td>agglomerated MT breccia clasts</td>
</tr>
<tr>
<td>1219:</td>
<td>matrix supported, fluid aligned breccia</td>
</tr>
<tr>
<td>1218B:</td>
<td>clast supported breccia</td>
</tr>
<tr>
<td>1218A:</td>
<td>MT breccia</td>
</tr>
<tr>
<td>1217:</td>
<td>no clasts</td>
</tr>
<tr>
<td>1215:</td>
<td>no clasts</td>
</tr>
<tr>
<td>1214:</td>
<td>matrix supported breccia</td>
</tr>
<tr>
<td>1213:</td>
<td>no clasts</td>
</tr>
<tr>
<td>1212:</td>
<td>matrix supported breccia</td>
</tr>
<tr>
<td>1211:</td>
<td>ball and pillow structures</td>
</tr>
</tbody>
</table>

Figure 12. Relative stratigraphic positions and descriptions of the 13 TB samples from ATJ location near Atar (not to scale). All samples are composed of micritic limestone, 1228B also contains quartz. Four other samples from the SERIZE location, AT98-34B, AT98-37A-3, AT98-37B-2, AT98-38A-1 were (spray painted orange so concrete contaminants can be removed – see below). Samples were positioned between five to ten layers of brown butcher paper (on each side) to minimize contact with the rock hammer and concrete during crushing. Rock specimens that penetrated the paper were removed and discarded. Approximately 10-20g of granule-
sized (or smaller) material was collected following crushing, and new paper was used for each new sample. Back in the lab, this finer material was then placed in a plastic tray. Any remaining orange paint, concrete, or other non sample contaminants (such as butcher paper) were removed using a wooden toothpick and plastic tweezers while viewing the specimen through a binocular reflected light microscope.

The remaining sample was weighed and powdered to clay/silt with an agate mortar and pestle. A porcelain mortar and pestle is not suitable since clay can retain measurable amounts of trace elements. After each sample was powdered and weighed it was placed in a plastic vial and labeled. Amounts of sample ranged from 9-14g of crushed material. First the original sample vial was shaken for one minute and then stirred for one minute (using circular and vertical motions) to ensure heterogeneous mixing. The sample was then poured onto a clean piece of paper and divided into three aliquots with a target of 3g or more for each vial (one for XRD analyses, one for Re-Os analyses, and one placed in reserve at the Ohio University Planetary Geology Laboratory) weighed, and labeled. The reserve material was returned to the original vial and kept as a backup in case any samples were lost or contaminated.

**XRD Analyses**

XRD was used to characterize the 17 samples from Mauritania, to determine the nominal mineralogy of the TB. XRD was also used to search for minerals indicative of a meteoritic component: olivine and pyroxene, (chondrites or achondrites) as well as kamacite, taenite, troilite, and graphite, (iron or stony-iron) and to assist in selection of samples for Re-Os analysis.
XRD is a process where X-rays (produced when a stream of high speed electrons hit a metal target) are directed to collide with a sample. When X-rays diffract they obey Bragg’s Law, and behave as a reflection. Bragg’s law shows that diffraction occurs when; 

\[ n*\lambda = 2d_{hkl}*\sin\theta \]

Where \( n \) is the order of reflection, an integer usually set at 1, \( \lambda \) is wavelength, \( d \) is the distance between the atomic planes \( hkl \) in a crystal, and \( \theta \) is the incidence (or reflection) angle. Thus, when X-rays strike a powdered sample (which contains a virtually infinite number of randomly oriented micro crystals) many crystals satisfy the Bragg Law, and X-rays are diffracted. Counts of the amount of diffraction are plotted for each measured angle (2 theta or \( 2\theta = 2*\text{angle of reflection} \)) ranging from 20º to 80º (covering the important peaks for the minerals of interest) for these samples and are recorded by a diffractometer. Since different crystals have unique \( d \) spacing and the counts are a measure of how many atoms have that specific \( d \) spacing, these values can be compared to known reference sets. Peaks in XRD spectra were compared to those from a database of X-ray powder diffraction files, available through the International Center for Diffraction Data or ICDD. These values are usually given as 20 values (20 is divided by two for use in calculating \( d \) with the Bragg Law) [Perkins, 2002].

All seventeen samples (Figure 12) were analyzed using XRD. In addition, 3 repeat analyses were run on previously analyzed samples to ensure that the XRD machine was still properly calibrated and not changing over time. XRD analyses show that the Tawaz Breccia is comprised primarily of calcite and lesser amounts of dolomite and quartz. Samples with less detrital quartz are 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 [Tréguer et al., 1995], 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 [Sharma, 1968] so the presence of quartz does not eliminate the possibility of a deep calm environment. Sample number 1228B was excluded from Re-Os analyses because it contains quartz of unknown origin. Since the TB has multiple fining upward sequences of breccia, the tops of these sequences indicate periods of lower energy between breccia deposition events. These calmer periods are a more likely time to concentrate slowly settling impact components [Bourgeois et al., 1988].

Re-Os (and Os Isotope Analysis)

Four (of the total 17) samples were selected for Re-Os isotopic analyses. Two of these four were selected as background samples because they were collected from above or below the TB. 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 should be. ATJ-1211 was from the ball and pillow structures at the base of the TB, whereas ATJ-1224 was sampled from above the TB (Figure 12). The remaining two samples were selected from locations that were most likely to have elevated Os and Re concentrations 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 [Bourgeois et al., 1988].
Therefore, the final two samples (ATJ-1217 and ATJ-1219) were selected since they were sampled from the top of breccia sets within the TB (Figure 12).

Samples chosen for analysis were sent to Rich Walker at The University of Maryland. First, these samples were spiked by the addition of a specific amount of enriched isotope ($^{190}$Os and $^{185}$Re) for a process called isotope dilution analysis [Walker, 2010; EPA, 2007]. 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 [EPA, 2007]. Next, the samples were digested for at least 2 days in reverse aqua regia (HCl:HNO$_3$ = 1:3) in Carius tubes (sealed thick walled Pyrex tubes) at 230 °C. Separation/purification of Os was then performed by solvent extraction [Shirey and Walker, 1995; Gelinas et al., 2004; Lee et al., 2006; Walker et al., 2002] and Os was analyzed by negative thermal ionization mass spectrometry (N-TIMS) [see Walker et al., 2002 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, 68° sector mass spectrometer (The Bobcat 1, 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 [Walker et al., 1994].

Results

The results of XRD (Figure 13) show that the majority of the samples are calcite (one contains quartz) and appropriate for Re-Os analysis. No minerals were identified
that were indicative of a meteoritic component (e.g. olivine, pyroxene, kamacite, taenite, troilite, or graphite).

Concentrations of Os in the four TB samples analyzed range from ~0.004 to 0.008 ppb (Table 6 and Figure 14), much lower than normal chondritic values (~600 ppb [Gelinas et al., 2004]), stony-irons (2212 ppb [Chen et al., 2002; Shen et al. 1998]), iron meteorites (17826 ppb [Shen et al. 1996]), and achondrites (2.6 ppb [Mason, 1979]).

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 [Morgan and Lovering, 1967; Walker et al., 2002]) and average marine sedimentary rocks (0.831 ppb [Rooney et al., 2010; Cohen et al., 1999; Dalai and Ravizza, 2006]. However Os concentrations are within known ranges of ocean island basalts, oceanic crust, and fluvial sediments (Figure 14).

Table 6. Re-Os concentrations and isotopic ratios

<table>
<thead>
<tr>
<th>Samples</th>
<th>Os (ppb)</th>
<th>Re (ppb)</th>
<th>$^{187}$Re/$^{188}$Os</th>
<th>$^{187}$Os/$^{188}$Os</th>
<th>$^{187}$Os/$^{188}$Os$_{(1.1Ga)}$</th>
<th>$^{187}$Os/$^{188}$Os$_{(1.1Ga)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATJ-1211</td>
<td>0.0077</td>
<td>0.0132</td>
<td>9.3812</td>
<td>0.0188</td>
<td>-58.7126</td>
<td>0.0037</td>
</tr>
<tr>
<td>ATJ-1217</td>
<td>0.0056</td>
<td>0.0050</td>
<td>4.7564</td>
<td>0.0095</td>
<td>0.8552</td>
<td>0.0035</td>
</tr>
<tr>
<td>ATJ-1219</td>
<td>0.0041</td>
<td>0.0044</td>
<td>5.6948</td>
<td>0.0114</td>
<td>0.8962</td>
<td>0.0036</td>
</tr>
<tr>
<td>ATJ-1224</td>
<td>0.0037</td>
<td>0.0573</td>
<td>78.0565</td>
<td>0.8000</td>
<td>0.2687</td>
<td>0.0027</td>
</tr>
</tbody>
</table>

ATJ-1211 $^{187}$Os/$^{188}$Os ratio is erroneous, this ratio is not possible and indicates that Re was lost (or Os was added) sometime in the samples history.
Figure 13. XRD: All 17 Mauritania samples, ATJ-1211 at actual position, each offset by +400 count. Prominent peak (all samples) is calcite, minor dolomite peaks in 1220, 1228B, and 34B, and a quartz peak in 1228B. 38A, 37B, 37A, and 34B are from a different section than the other samples, and were not used for Re-Os analyses.
Re concentrations for the TB range from 0.004 to 0.057 ppb (Table 6), these values are within the range of impact mixtures, ocean island basalts, and fluvial sediments (Figure 14). Of these concentrations, only the Ivory Coast tektites have an average that falls within the range of the TB (0.0097 ppb [Koeberl and Shirey, 1997]), while the K-T boundary, ocean island basalts and fluvial sediments have averages that are higher; 0.243 [Frei and Frei, 2002], 0.399 [Becker, 2000], and 0.200 [Chesley et al, 2000; Singh et al., 2003] ppb, respectively (Figure 14).

^{187}Os/^{188}Os ratios of the TB samples range from 0.27 to 0.9 (Table 6), correlating with the average for stony-iron (0.30 [Chen et al., 2002; Shen et al. 1998]) and within known ranges for iron meteorites, ocean island basalts, mantle, oceanic crust, continental crust, marine sediments and fluvial sediments (Figure 14).
$^{187}\text{Re}/^{188}\text{Os}$ ratios for the TB range from 4.76 to 78.06 (Table 6), correlating with the averages for the K-T boundary, continental crust, and fluvial sediments; and within known ranges for ocean island basalts, oceanic crust and mantle (Figure 14).

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 $^{187}\text{Re}/^{188}\text{Os}$ ratios of the TB correspond to impact mixtures (Figure 14), as well as the ranges of ocean island basalts, fluvial sediments and others. Because of this overlap, the specific source of Re (or $^{187}\text{Re}/^{188}\text{Os}$) cannot be determined. For $^{187}\text{Os}/^{188}\text{Os}$, 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 [Levasseur et al., 1999]. 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 Tawaz Breccia 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 $^{187}\text{Os}/^{188}\text{Os}$ ratio corresponds to stony-iron and iron meteorites, while the $^{187}\text{Re}/^{188}\text{Os}$ ratio corresponds to the impact horizon at the K-T boundary, a collision which was produced by a chondritic impactor [Kyte, 1998; Trinquier et al., 2006]). Furthermore, the Re concentrations correlate with the chondritic K-T boundary concentrations and the Ivory Coast Tektites (an iron or chondritic impactor [Koeberl and Shirey, 1997]). 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 [Goswami and Lal, 1977] than it was in the Mesoproterozoic, which could explain why the TB samples have low values relative to modern values. Since the $^{187}\text{Os}/^{188}\text{Os}$ ratio suggests stony-iron or iron while the Re concentrations suggest 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.

Of the samples used (Figure 12), two (ATJ-1217 and ATJ-1219) were selected from the tops of fining-upward sequences in the Tawaz Breccia, which should be concentrated in impactor components by settling (through a water column) [Bourgeois et al., 1988]. Two others were analyzed, and predicted to have lower concentrations; one near the top (ATJ-1224) and another near the bottom (ATJ-1211) of the TB. However, Os was most concentrated in ATJ-1211 (the ball and pillow structures at the base of the TB),
while $^{187}\text{Os}/^{188}\text{Os}$ was the highest in ATJ-1219 (a fluid aligned breccia at the top of a fining-upward sequence). Conversely, Re and $^{187}\text{Re}/^{188}\text{Os}$ were the highest in ATJ-1224 (a breccia at the top of the TB). It is unclear why Re and Os concentrations and the $^{187}\text{Re}/^{188}\text{Os}$ ratios are not the highest near the tops of fining upward sequences, however the differences in concentrations are very small from sample to sample, and no clear impact horizon is apparent. Since this study only used four samples from field reconnaissance, future Re-Os analyses should be of samples from a more thoroughly-defined stratigraphic section of the TB. Cores have also been drilled in locations that should intersect the TB, analyses and sampling of fining-upward sequences in these cores could also be useful. These new samples combined with analyses of samples known to not be affected by the TB event (above and below) and samples of other marine carbonates from around the world (in order to determine the normal marine carbonate, meteoritic input) would allow for better measure of baseline Mesoproterozoic Re and Os concentrations and isotopes. Samples have been prepared from The Belt Supergroup (Helena Formation, 1.44-1.45 Ga) recently collected by the author, as well as samples from the Beck Springs Dolomite, (0.9-1.1 Ga), The Bylot Supergroup, Baffin Island (Victor Bay, and Athole Point Formations, 1.2 Ga) and samples from India (The Sarangarh also known as the Charmuria Limestone, late Mesoproterozoic). The combination of baseline, core, and more targeted TB samples could lead to possible confirmation of an impact horizon in the TB.
CONCLUSION

Correlation analyses #1 and #2, along with a qualitative analysis of breccia types (and their distinguishing characteristics) demonstrated that the TB was likely formed by a tsunami mechanism. In order to distinguish between impact tsunami and non-impact tsunami, Re-Os analyses were used to determine if impactor components were present. Preliminary analyses have determined that if impactor components are present, then they have been diluted below recognizable concentrations and ratios; but that impact mixtures (possibly from an iron meteorite component) cannot be eliminated as a possibility.
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APPENDIX A: BRECCIA SPREADSHEET REFERENCES


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Analysis #1, no exclusions, all 62 characteristics present.
Analysis #1, exclusion of characteristic (row) sums of 0, 14, and negative correlations, (48 characteristics remain).
Analysis #2, exclusion of characteristic (row) sums of 0, 14, and negative correlations, (56 characteristics remain).
Analysis #2, exclusion of characteristic (row) sums of 0, 14, negative correlations, and one high and one low bin, (50 characteristics remain).
Analysis #2, exclusion of characteristic (row) sums of 0, 14, negative correlations, and two high and two low bins, (36 characteristics remain).
Analysis #2, exclusion of characteristic (row) sums of 0, 14, negative correlations, and three high and three low bins, (29 characteristics remain).
Analysis #2, exclusion of characteristic (row) sums of 0, 14, negative correlations, and four high and four low bins, (19 characteristics remain).
Analysis #2, exclusion of characteristic (row) sums of 0, 14, negative correlations, and five high and five low bins, (14 characteristics remain).
Analysis #2, exclusion of characteristic (row) sums of 0, 14, negative correlations, and six high and six low bins, (7 characteristics remain).
APPENDIX C: TAWAZ BRECCIA SAMPLE DESCRIPTIONS AND PHOTOS

Note: all ATJ- samples collected from near Atar in 2003, all AT98- samples collected from SERIZE in 1998. All samples react to 5% HCl, appear sandblasted, and have saw marks. Samples weighed with a digital scale that has a limit of 80.4g. Analyses require more than 9.0g of sample. From thin-section work; samples are 99% clean fine-grained carbonate micrite or microspar, very little clay material, very few opaques (rare digenetic pyrite) [Kah, 2009]. From XRD; all samples dominated by calcite, minor dolomite peaks in 1220, 1228B, and 34B, and a quartz peak in 1228B.

ATJ-1211, micritic limestone, dominated by calcite, from ball and pillow structures near base of unit, way up unknown, 12.248g.
ATJ-1212, matrix supported breccia, dominated by calcite, tabular to rounded clasts, way up unknown, >80.4g.
ATJ-1213, micritic limestone, dominated by calcite, no clasts, way up known, 31.560g
ATJ-1214, matrix supported breccia, dominated by calcite, way up unknown, >80.4g.
ATJ-1215, micritic limestone, dominated by calcite, no clasts, white band, way up known, 72.050g.
ATJ-1217, micritic limestone, dominated by calcite, no clasts, top of fining up set (1212-1217), way up known, 27.327g.
ATJ-1218A, molar tooth breccia, dominated by calcite, way up known, >80.4g.
ATJ-1218B, clast supported breccia, dominated by calcite, way up unknown, 55.272g.
ATJ-1219, matrix supported, fluid aligned breccia, dominated by calcite, tabular angular clasts, way up known, 51.322g.
ATJ-1220, agglomerated molar tooth breccia clast, dominated by calcite, some dolomite, way up unknown, 35.413g.

ATJ-1221, micritic limestone, dominated by calcite, no clasts, conical columnar stromatolites [Stagner, 2003] way up known, 25.195g.
ATJ-1224, molar tooth breccia, dominated by calcite, way up unknown, 50.403g.
ATJ-1228B, clast to matrix supported breccia, dominated by calcite, some dolomite, matrix different color; tan to brown (all previous grey), according to XRD only sample with quartz, cross-beds directly above; may indicate a barrier isle or beach facies [Stagner, 2003], way up unknown, 56.470g.
AT98-34B, no photo, powdered by previous lab worker, no un-powdered sample remaining, dominated by calcite, contains some dolomite, 15.865g.

AT98-36A, molar tooth breccia, dominated by calcite, way up known, 3.389g (too small for analyses).

AT98-37A, molar tooth breccia, dominated by calcite, way up known, 5.830g (too small for analyses).
AT98-37A-3, molar tooth breccia, dominated by calcite, way up known, 22.853g.
AT98-37B-2, molar tooth breccia, dominated by calcite, way up known, 15.458g.

AT98-38A, possible clast edges (breccia), dominated by calcite, way up known, 4.158g (too small for analyses).
AT98-38A-1, molar tooth breccia with stylolitic like contacts, dominated by calcite, way up unknown, 20.300g.
AT98-40A, clast supported breccia, dominated by calcite, angular clasts, way up unknown, 4.702g (too small for analyses).