Identification of Shocked Feldspar Glass
Preserved in DSDP Site 231 at 5.07 Ma

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I. Abstract

Tephra from volcanic eruptions are an important means to date the geological record in and around volcanically active regions. Volcanic activity has been well documented in the East African Rift valley since the Oligocene, with glassy shards from explosive eruptions reaching the marine sediments of the Gulf of Aden thousands of kilometers from source numerous times in the last 4 million years. We searched for the presence of tephra in marine sediments of DSDP Site 231 from 4.9 to 5.2 Ma, and while there should have been at least a small amount of the so-called ‘cryptotephra’ in the core, we determined that no tephra are visible neither to the naked eye nor in microscopic analyses of these sediments. Furthermore, sieving and density separations to concentrate large fragments and silicaceous minerals also indicated the absence of the cryptotephra found in younger sediments. However, we have identified a small amount of ‘diaplectic glass’, feldspars that have undergone a solid-state or liquid-state transformation to glass due to high shock pressures. This diaplectic glass may be difficult to differentiate from volcanic glass due to similar isotropy and morphology, but the two can be potentially distinguished via morphology. In this case, electron microprobe analysis was the means used to identify that the grains were not volcanic glass. These findings will be cataloged at LACCORE to inform future cryptotephra studies.
II. Introduction

Characterizing the environment early Hominids evolved in is an important task in explaining the evolutionary changes we have observed. To assist in accomplishing this, I have attempted to analyze the frequency and intensity of volcanism in the region during the time period of 4.9 – 5.2 Ma in order to characterize the long-term environment and living conditions of the Ethiopian Rift System. Due to the location of the core sample used – DSDP Site 231 Section 28 (Figure 1), any tephra found would have traveled much farther than the tephra at most terrestrial sites. The presence of tephra at both a terrestrial site and an offshore site would indicate the relatively large strength of an eruption, if the eruptions can be correlated (Feakins et al., 2007). Thus, any pulses of volcanism contained in DSDP Site 231 must have covered a large geographical extent, and affected the hominids of the region directly or indirectly.

It has been proven that offshore sediment cores can be used to identify cryptotephra horizons that are not visible to the naked eye (Feakins et al., 2007). By further analyzing the core of Site 231 and finding tephra, it would be possible to construct a more complete record of tephra events that may or may not have been recorded in terrestrial or other oceanic sites. With a finer resolution of volcanic events and greater geochemical correlation between sample sites, it may be possible to infer climate on a smaller chronological scale across a larger area, and with a greater correlated record of cryptotephra horizons in Site 231, it would be possible to constrain the age of different sections of the core more tightly, providing a better age estimation for uncorrelated cryptotephra events.
III. Methods

III.1 Initial Slide Preparation

The first step of sample preparation was completed prior to my arrival at USC by Sarah Feakins when she was searching for cryptotephra in the interval of 1-4 Ma (Feakins et al, 2007). The samples were scraped from the DSDP core at Site 231 from Section 28 in 10 cm intervals from 244.5 meters below sea floor (mbsf) to 253.4 mbsf, resulting in a total number of 90 samples representing 9 meters of sediment. The samples are labeled according to the DSDP system: Leg-Site-Core-Section-Top Depth-Bottom Depth. The age range of the samples was given by fitting a linear trend to the known ages at other points in the core (Figure 2) and extrapolating the age of the first and last sample depths, giving an age range of 4.9 – 5.2 Ma.

The sample preparation process followed the processes described in Feakins et al, 2007, with modifications to accommodate for density separation. The samples were wet sieved through a 32 µm sieve using DI water. The samples were then placed in filter paper and dried in a combusting oven at a temperature of 50 degrees Centigrade. Once dry, small amounts of each sample were placed on slides in order to make a quantitative count of possible cryptotephra against the background sediment.

III.2 Sample Refinement

Later, the sediment samples were refined in order to remove the excess sediment. To remove carbonates, 10 molar Hydrochloric Acid was added until each sample ceased reacting to it, then the samples were rinsed with DI water and decanted three times in order to neutralize the acid. Once the carbonates were removed, the removal process was repeated using a 30% Hydrogen Peroxide solution to remove organic material from the samples, with the addition of leaving the samples to acidify overnight. Some
samples had much more organic matter and carbonates than others, and these steps combined reduced the amount of sediment in each sample by a vast amount.

The samples were then placed into 15 ml centrifuge tubes and density separated using Lithium Polytungstate (LPT) at the densities of 2.0 g/cm³ and 2.4 g/cm³. First, the lightest grains, labeled ‘floats’ were centrifugally separated and decanted using the 2.0 g/cm³ LPT solution, and the heavier fraction, labeled ‘heavies’ was separated out using the 2.4 g/cm³ solution, leaving the fraction between 2.0 – 2.4 g/cm³ suspended in the 2.4 g/cm³ LPT, which was then decanted onto filter paper optimistically labeled ‘tephra’. This fraction suspended in the 2.4 g/cm³ LPT was assumed to contain trace cryptotephra and a small amount of sediment. Small portions of this separate from each sample were placed onto smear slides in the same manner as the bulk samples, and were examined to confirm or deny the presence of glass – possible cryptotephra – in the 10 cm interval of sediment. These counts were to be only semi-quantitative, and it is more likely that they would speak to only the frequency of volcanism, and not the intensity due to the increased proportion of tephra to background sediment because much of the background sediment was separated and removed. The light and the heavy fractions were cleaned of LPT by drip-rinsing through filter paper and centrifugal rinsing, respectively. These fractions were kept for potential further analysis to ensure the possible cryptotephra did indeed go into the ‘tephra’ separate.

III.3 Identification

Identification was performed on a polarizing petrographic microscope, mainly at magnifications of x10 to x20. The slides were placed on an X-Y mechanical stage for ease of movement, and glass was identified chiefly by shape and isotropy. In the initially attempted quantitative counts, possible cryptotephra were counted in 1 cm² of slide that
was as evenly populated as possible in order to determine the relative level of volcanism. In the later counts, possible cryptotephra were counted over a whole slide onto which the 2.0 – 2.4 g/cm³ fraction of a specific sample had been placed. Based on the relative amount of glass, each slide was rated from 0 to 5 in increments of .5, 0 being no visible cryptotephra, and 5 being populated chiefly by glass. The samples were placed in a central location on the slide to facilitate an easy search. Once this was completed, two samples with counts high enough to be deemed possible events were sent to the lab of Nelia Dunbar at New Mexico Tech for geochemical determination via Electron Microprobe.

IV. Results

Reviewing the counts of all 90 samples resulted in the identification of 7 slides with notable amounts of cryptotephra. These 7 slides consolidated into 2 events which consist of more than one consecutive slide each with a notable amount of glass identified on it. Slides with a previously described rating of 2 or less were discounted, having assumed these to represent background levels of volcanism of the area. Out the 2 events catalogued, one sample each was sent out for geochemical analysis.

Using an Electron Microprobe to determine major element oxide percentages, Nelia Dunbar established that all grains tested were a variety of feldspar. Based upon a Harker Diagram of SiO₂ vs. CaO, Na₂O, and K₂O (Figure 3), 52% of grains analyzed were Albite, with a prevailing Alkali oxide of Na₂O, and 48% were Orthoclase, with a prevailing Alkali oxide of K₂O. The results of this major element oxide analysis are confirmed using a feldspar ternary diagram (Figure 4), which shows all tested grains to be <An₁₅₉ and in two main groups of >Ab₉₀ and >Or₉₀. Both Albite and Orthoclase are fairly common and stable minerals at the surface of the earth, and would be expected in
some quantity in both near-shore and off-shore environments. From this, it is then assumed that all grains counted while searching for cryptotephra were in fact various kinds of feldspar, altered to appear optically similar to cryptotephra in smear slide (Figure 5).

V. Discussion

V.1 Shocked Feldspar Glass

Pictures of feldspar grains taken from the Lacustrine Core (LACCORE) database at the University of Minnesota (Figure 6) show characteristic feldspar grains in smear slide. Note the polysynthetic twinning observed in the crystals of Microcline, a variety of feldspar. This twinning is a key feature of all feldspars under cross-polarized light, and is used to identify them both in thin sections and smear slides (LacCore). The fact that this is not seen in the isotropic feldspar grains found in Core 231 (Figure 5) raises the question of what process caused this isotropy in the feldspar grains.

One method of altering feldspar grains to either polarize all twinning planes toward the same direction, or to completely destroy anisotropy of the crystals, is to induce a great shock event, such as a meteorite impact (Stöffler 1966, 1972). This feature comes from not just the high overall stress of the shock event, but from the high rate of strain of meteorite impacts (Stöffler 1966). When feldspars are shock metamorphosed at a pressure between 35 and 45 gPa, they become a ‘solid-state glass’ phase commonly called ‘diaplectic glass’. Above 45 gPa, at impact pressures typically also associated with higher temperatures, the glass that is formed is a ‘liquid-state glass’, which can consist of fused minerals or simply a single mineral transformed into a glass via a higher temperature route, possibly by going from solid to liquid and back (Stoffler 1972). Due to the complete isotropy of the grains and the presence of only one distinct
composition per grain, it is proposed that the glass found in Core 231 between 4.9 – 5.2 Ma is a high pressure ‘solid-state diaplectic glass’, above the transition pressure of minerals solid-state glass, up to 45 gPa (Stöffler 1972).

The identification of diaplectic glass raises the question of where this glass originated. The sharp edges with characteristically glassy conchoidal fracture on the grains and complete lack of rounding indicate that these diaplectic glasses were distally transported through the atmosphere to the site of their deposition in the Gulf of Aden. During the time interval of the sample range, there are 2 possible known impact events in the region close enough to have distal transport be a likely method of transport, if the glass found is indeed diaplectic glass. The crater locations are in Kazakhstan and Tajikistan (Figure 7), with the names Bigach and Kara-kul respectively.

Bigach Crater, in eastern Kazakhstan, north of Tajikistan, is both slightly farther away and significantly smaller than Kara-kul, with an age of 5 ± 3 Ma and a diameter of 8 km (Napier 2006). Its size and location make it much less likely to have ejected enough diaplectic glass high enough into the atmosphere to be distally transported to Site 231 in the Gulf of Aden, as compared to the Bosumtwi crater in western Africa and the aerial extent of its shocked glass spherules (Figure 8). Bosumtwi crater is approximately 10.5 km in diameter, so it is assumed that a crater 2 km smaller than Bosumtwi, and one that is downwind of Site 231, would not have the power to put shocked glass, either broken or spherical, at Site 231.

Kara-kul Crater, in the east of Tajikistan, is 52 km in diameter, and has a highly disputed age due to the lack of radiometric dating (Kelley 2007). The upper limit is 25 Ma (Yabushita 2002), however, the more generally accepted age limit of the event is 5 Ma, which has also been interpreted as 2.5 ± 2.5 Ma (Napier 2006, Kelly 2007). I here take the age of the event to be ≤5 Ma, an age within the 2.5 ± 2.5 Ma that Napier 2006
and Kelly 2007 use, which would place the event in the time frame of Core 231 sedimentation between 244.8 mbsf – 244.9 mbsf. The larger size of Kara-kul places its ejecta within range of Core 231 (Figure 8). Given both the spatial and temporal proximity of the Karakul event, there is a possibility that the diaplectic glass in DSDP Site 231 comes from the Karakul event.

There are a variety of possible impactors and impact scenarios that would result in a crater of Karakul’s diameter. Using the web program described and implemented in Collins et al., 2005, I quantitatively tested various scenarios to confirm the possibility of the presence of ejecta at Site 231. At a distance of approximately 4,000 km from the source crater, the ejecta expected from two scenarios of a Karakul event are the same: a rocky meteorite with a diameter of 4 km and a speed of 20 km s⁻¹, and a rocky meteorite with a diameter of 4.5 km and a speed of 17 km s⁻¹ create a crater with diameters of approximately 51.3 km and 52.5 km, respectively, and would be expected to throw ejecta as far as approximately 10,000 km. The 3,906 km to DSDP Site 231 is well within the range of an event the size of which could possibly create Karakul Crater. An scenario representing the event that created Bigach Crater, with a rocky impactor of a diameter of 600 m, a velocity of 20 km s⁻¹, and an impact angle of 45 degrees, would place little to no solid ejecta at DSDP Site 231, concurrent with previous conclusions. (Collins et al., 2005)

The presence of diaplectic glass in DSDP Site 231 suggests the possibility that ejecta from Karakul reached at least an aerial extent of approximately 4,000 km. The prevailing wind direction is North North-East (Figure 9), which makes the presence of shocked feldspar more significant, as the ejecta would have had to overcome prevailing winds, which would typically greatly constrict its aerial extent. This implies that the fine ejecta, if they are indeed from the Karakul event, would have had enough velocity
to overcome the prevailing winds, and likely would have had enough velocity to travel much further, possibly up to the 10,000 km range set by the equations of Collins et al., 2005.

V.2 Possible Error

During the process of sample preparation and analysis, many possible sources of error have been identified that could possibly lead to the destruction or loss of cryptotephra. During the sieving process, it is possible that tephra smaller than 32 µm were discarded, or tephra larger than 32 µm could have been crushed and subsequently discarded. The only evidence of this is the absence of cryptotephra in the samples after sieving, and as the presence of cryptotephra could not be confirmed before sieving and the absence of cryptotephra may be explained in other ways, the possibility of this having occurred is minimal.

In the process of removing carbonates and organics, it is possible that tephra in the samples were altered by the processes designed to destroy the excess sediment (Blockley et al., 2005). As such, I followed the softer methods of Feakins et al., 2007, not using the harsher acid and combustion treatments. The 10 M HCl acid bath was only sustained long enough to see that the reaction had visibly halted, typically 5-10 minutes, and was normally softened by the presence of water. To remove organics, the 30% Hydrogen Peroxide solution used was also not harsh enough to alter the chemical composition of tephra. It can therefore be concluded that the chemistry of the tephra was not altered to appear to be that of feldspar. There also remains the possibility that during the decanting process the tephra could have been decanted and discarded, if it was floating on the surface of the HCl or Peroxide solutions. Unless the cryptotephra was especially vesicular, this possibility remains unlikely.
Density separation of the samples presents multiple possibilities for error or contamination. When pouring the Lithium Polytungstate onto filter paper to catch the separated grains after the separation using a $< 2.0 \text{ g/cm}^3$ solution, it is possible that the cryptotephra were decanted onto the filter paper for the ‘floats’ section by too heavy-handed a decanting. This possibility remains unverified. There is also the possibility that cryptotephra were separated into the ‘heavies’ section, due to errors in the preparation of the $2.4 \text{ g/cm}^3$ Lithium Polytungstate. This source of error is also unconfirmed, but unlikely to have occurred, as a precision hydrometer was used to measure the density of the solution during creation.

In inferring the source of the shocked glass in DSDP Site 231, I limited myself to only known meteorite impacts that fit the date of the core samples – about 5 Ma, and that were in the same region as the samples. Due to the rate of erosion and lack of long-term preservation of impact craters, it is possible that the event from which the diaplectic glass in Site 231 originates is much nearer to the Gulf of Aden and is undiscovered, or is an unrecognized impact even from elsewhere in the world, both of which could have been eroded and erased from the terrestrial record, or are otherwise unrecorded. I have also made assumptions about the composition, velocity, and impact angle of the impactor. The average velocity of a rocky impactor is 12 to 20 km s$^{-1}$ and the most typical impact angle is 45$^\circ$ (Collins et al., 2005). To achieve a proper crater size, I assume a velocity nearer to 20 km s$^{-1}$, with a smaller meteorite diameter in order to form a crater of the size of Karakul. There could be errors my assumptions and/or in the assumption of Collins et al., 2005, that is, it is possible that large impact crater formation does not follow the same principles and equations that smaller, observed impacts follow. Thus, the scaling equation developed therein may be faulty. Due to the fact that this is the most reliable, simple, and easily accessible impact simulator, the error in the
assumptions and calculations of Collins et al, 2005 is negligible; however, the possibility of an unrecognized or unrecorded event, and/or an oversight in my search for events that fit the parameters remains large.

VI. Implications

The absence of tephra in this section of DSDP Site 231 is surprising, as cryptotephra have been found in this core and those have been correlated with other events of the Afar Rift Zone (Feakins et al., 2007), and there are known volcanic eruptions in the region at the time. The lack of tephra can be explained by a mixture of environmental factors, such as changes in wind direction and intensity, changes in ocean current direction and its intensity, and/or changes in the geographic location or composition of volcanism – if the volcanism occurred too far away, it is less likely to be recorded, and if the volcanism was more basaltic, tephra would not be transported as far due to the less eruptive nature of basaltic magma.

The preservation of possible diaplectic glass at DSDP Site 231 suggests the possibility of an impact event in the region at the time of deposition, somewhere around 5 Ma. There are two known impacts in the spatial and temporal region of DSDP Site 231 large enough and close enough to be a possible source of the diaplectic glass found therein: Bigach Crater and Karakul Crater. Of the two, only Karakul Crater is large enough and close enough to be a possible source of the diaplectic glass, but the glass could also originate from an unknown event. If the diaplectic glass is indeed from Karakul, it would strengthen the 5 Ma age of Karakul Crater as opposed to its older maximum of 25 Ma, and show that ejecta from the impact were able to travel 4000 km through the atmosphere, partially against prevailing winds, to be distally deposited. More distal ejecta will have to be found at other sites to place sure boundaries on the
range of ejecta from Karakul and to further strengthen its possible age. Geochronology upon the crater itself would also be useful in dating the event, and it would be extremely important to test for an iridium layer in sediments at the possible times of deposition.

Separately identifying diaplectic glass and cryptotephra is a problem to be faced when searching for trace amounts of cryptotephra in smear slides. The only easy way to separately identify the two is via morphology, which can prove difficult to do. It is possible for cryptotephra to have a vesicular morphology (Figure 10), or to have the remnants of a vesicular morphology, which can still be a distinguishing feature. However in smaller cryptotephra, the vesicular morphology is either not apparent or not present, causing the cryptotephra to have an appearance similar to other forms glass, diaplectic glass in this case, which does not form with vesicles due to the nature of the original crystals and the method of formation (Stöffler and Langenhorst, 1994). As isotropy and presence of conchoidal fracture are not sufficient to tell the two apart due to their similarity as glasses (Figure 11), great attention must be paid to the three-dimensional morphology of the grains to confirm or deny the vesicular nature of the glass. If the grains appear to have conchoidal fractures on the sides, top, and bottom of the grain, it is most likely not vesicular, and if there are perfectly circular edges, those are to be interpreted as the walls of a vesicle. While this in of itself is not entirely conclusive evidence of the identity of the grain, it may still be counted as evidence as to the volcanic origin of the grain.

VII. Conclusion

To better constrain the periodicity and intensity of volcanism in the Afar Rift Zone and further constrain the age and sedimentation rates of DSDP Site 231, I
attempted to construct a more complete record of cryptotephra layers in the sediment core from 4.9 – 5.2 Ma. To do so, I searched each sample in the section for cryptotephra layers that would indicate the level of volcanism in the region. After having identified two layers of glass in our samples, an Electron Microprobe was used to determine the chemistry of the glass, attempting to fingerprint the layer and correlate it to known eruptions.

The resulting identification of a feldspathic composition of approximately half Albite and half Orthoclase invalidated the hypothesis of cryptotephra in Core 231 from 5.06 to 5.2 Ma, but suggests that the feldspathic glass grains are diaplectic glass, indicating the possibility of a meteorite impact event at the time of deposition. Based on known impact events in the region with an age of 5 Ma, I have concluded that the most likely currently recorded origin event for the diaplectic glass in Core 231 is Karakul, a 52 km diameter crater in Tajikistan. However, considering the possibility of an origin from an unrecorded or undiscovered event, of which there are likely to be several (Kelly 2007), it is possible that the diaplectic glass in DSDP Core 231 records a yet unrecorded event.

VIII. Acknowledgements

I would like to thank Sarah Feakins for her constant support throughout my research, and USC’s SOAR program for their assistance in starting on my research. I would also like to thank Nelia Dunbar of New Mexico Tech for her geochemical analysis via Electron Microprobe, Miguel Rincon and Michael Cheetham for their advice and teachings in the laboratory, Alexa Sieracki for her help as an invaluable research partner, Scott Paterson, John Platt, Joshua West, and Steve Lund for the use of
their laboratory space and/or equipment, and Adam Ianno for his help during the density separation stage.
IX. Figures

Figure 1. A map of DSDP Leg 24 Site 231, off the coast of Somalia in the Gulf of Aden with late Miocene and early Pliocene Hominin fossil sites in the Afar Rift Zone.
Figure 2. Age model for DSDP Leg 24 Site 231. Y is depth in meters below sea floor.
Figure 3. Harker plot of SiO$_2$ vs. CaO, Na$_2$O, and K$_2$O. The high concentrations of K$_2$O in some samples and Na$_2$O in others indicate point to a mixture of Orthoclase and Albite compositions. Black dots represent Sample 24-231-1-20-30, Red 24-231-3-90-100.
Figure 4. Feldspar Ternary diagram from O’Connor 1965, developed for use on volcanic igneous rocks. Black dots represent Sample 24-231-1-20-30, Red 24-231-3-90-100.
Figure 5. Diaplectic Glass in slide 24-231-1-20-30, center of image. A: plane polarized light, B: cross polarized light, with small anisotropic grain on or near the glass fragment.
Figure 6. Microcline Feldspar grains with characteristic twinning in plane and cross polarized light.
Figure 7. Tajikistan, with Karakul lake shown in the enlargement.

Figure 8. Comparison of possible ejecta diameters of Bosumtwi, Karakul, and Bigach, based upon a linear extrapolation of size from Bosumtwi’s ejecta diameter.
Figure 9. Yearly average wind pattern over the Afar Rift Zone and the Gulf of Aden (Feakins et al., 2007).
Figure 10. Characteristic tephra grain taken from ash from the Mt. St. Helens eruption of 1980.
Figure 11. Comparison of A: diaplectic glass from DSDP Core 231 and B: cryptotephra from Mt. St. Helens.
X. References


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