

Archaeobacterial lipids in drill core samples from the Bosumtwi impact structure, Ghana

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Abstract—Meteorite impacts are associated with locally profound effects for microorganisms living at the terrestrial surface and the subsurface of the impact zone. The Bosumtwi crater in Ghana (West Africa) is a relatively young (1.07 Myr) structure with a rim-to-rim diameter of about 10.5 km. In a preliminary study targeting the subsurface microbial life in the impact structure, seven samples of the impact breccia from the central uplift of the Bosumtwi crater were analyzed for the presence of typical archaeal membrane-lipids (GDGTs). These have been detected in four of the samples, at a maximum depth of 382 m below the lake surface, which is equivalent to 309 m below the surface sediment. The concentration of the GDGTs does not show a trend with depth, and their distribution is dominated by GDGT-0. Possible origins of these lipids could be related to the soils or rocks predating the impact event, the hydrothermal system generated after the impact, or due to more recent underground water transport.

INTRODUCTION

The Bosumtwi impact structure, in Ghana, West Africa, was the subject of the ICDP Bosumtwi Crater Drilling Project in 2004 (e.g., Koeberl et al. 2007). This relatively young crater (age of 1.07 Myr; Koeberl et al. 1997) was excavated in about 2.2 Ga metavolcanics and metasedimentary rocks and has a rim-to-rim diameter of about 10.5 km. The structure has a pronounced central uplift, presumably originating from the rebound of the target rocks (Scholz et al. 2002). It is almost completely filled with a lake that has a current maximum depth of 78 m. At present, underneath the lake there is a 150 to 310 m thick layer of post-impact lake sediments, with typical seismic velocity values of unconsolidated and water-saturated sediments (Scholz et al. 2007). The lake sediments, in turn, are underlain by about 200 m of various polymict and monomict impact breccias (see, e.g., Koeberl et al. 2007 for a summary). The velocities for the impact breccia are also relatively low, which suggests that the Bosumtwi impact structure is composed of highly fractured material (e.g., Scholz et al. 2007).

The interest in such impact events is not restricted to the geological structures originating as a consequence of the collisions, but they also have important geochemical and biological implications. For instance, moderate-sized impacts

and the subsequent hydrothermal systems generated can have profound effects on the organic matter abundance and composition, via processes including maturation, melting, and irradiation (Parnell and Lindgren 2006). Moreover, asteroid and comet impacts can have a profound effect on the availability and characteristics of habitats for the microorganisms living in the terrestrial surface and subsurface. Several estimates suggest that the biomass contained in microbial communities living at the terrestrial subsurface (terrestrial deep biosphere) is very large and that the total number of prokaryotes in this environment is close to the total number of microbial cells in the entire ocean (e.g., Gold 1992; Whitman et al. 1998; Karner et al. 2001). A common process associated to meteorite impacts is bulking, which increases the porosity of the shock rock lithologies and thus the surface area where lithophytic organisms can grow (e.g., Cockell et al. 2003, 2005). Furthermore, large impacts have the potential of locally sterilizing the soil, given high shock pressures and high temperatures that can persist in the impact-generated hydrothermal systems. This issue has recently been discussed for the Chesapeake Bay impact structure at the east coast of North America (Cockell et al. 2007; Glamoclija and Schieber 2007; Voytek et al. 2007). The Bosumtwi site, as it is a well-preserved and young impact structure, is an excellent site to explore the presence and structure of subsurface microbial life.

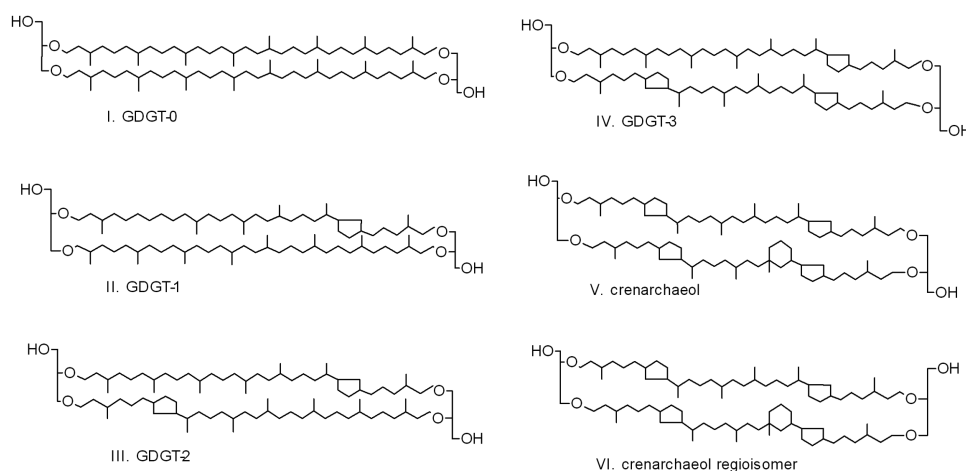


Fig. 1. Molecular structures of glycerol dialkyl glycerol tetraethers (GDGTs).

When searching for microbial life, the two prokaryotic domains of life, Archaea and Bacteria, are the usual targets of any molecular or geochemical survey. This preliminary study considers the presence of lipid biomarkers of prokaryotic life in the impact breccias. In particular, we focus on archaeal lipids, which are very refractory and thus are preserved and accumulated in sediments and soils (e.g., Schouten et al. 2000). Figure 1 shows the structures of the archaeal lipids investigated in this study, which are glycerol dialkyl glycerol tetraethers (GDGTs). The analysis of these biomarkers from Archaea in highly diverse environments, such as ocean water and surface sediments (e.g., Hoefs et al. 1997), deep-sea sediments (Fredricks and Hinrichs 2005), soils (e.g., Weijers et al. 2006), peats (e.g., Weijers et al. 2004), lakes (e.g., Powers et al. 2004), and hot springs (e.g., Pearson et al. 2004), has been used to corroborate that Archaea are ubiquitously distributed on Earth.

During the ICDP Bosumtwi Crater Drilling Project, several cores were retrieved from the geological structure. Here we report an exploratory survey of archaeobacterial biomarkers in the impactite rocks recovered from a core drilled in the Bosumtwi crater.

SAMPLES AND METHODS

Impact breccia samples were recovered from underneath the lacustrine sediments in core LB08 drilled near the central uplift of the Bosumtwi impact structure (cf. Koeberl et al. 2007), at 235.77, 240.04, 280.30, 283.50, 353.95, 382.17, and 417.60 meters below the lake surface (water column depth at this site was 73 m). The outer layer of the rock pieces was discarded in order to avoid contamination from handling. The samples were then finely ground by means of mortar and pestle, and approximately 2 g of rock powder were extracted with an organic solvent mixture of methylene chloride/methanol (3:1, v/v), using microwave assisted extraction (Kornilova and Rosell-Melé 2003). Along with the samples, a

laboratory blank was run. Extracts were hydrolyzed overnight with a solution of 8% KOH in methanol, and the neutral lipid fraction was recovered with hexane by liquid extraction. The solvent was removed by vacuum rotary evaporation and the samples were redissolved in *n*-hexane/*n*-propanol (99:1, v/v), and filtered through 0.45 μm Millipore PVDF filters. All solvents used in the laboratory process were of high purity (Suprasolv® or Lichrosolv®, Merck).

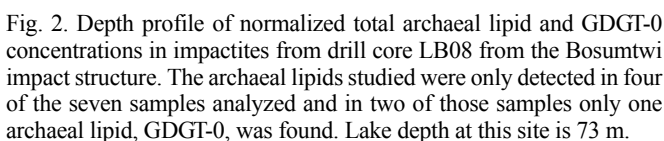
The target archaeal lipids were separated by means of high performance liquid chromatography (HPLC) using an Agilent 1100 HPLC instrument. Sample extracts were eluted using a Nucleosil Cyano column (4 \times 150 mm, 5 μm ; Tracer) at 30.0 $^{\circ}\text{C}$ in a gradient flow using a mixture of hexane/*n*-propanol. Flow rate was 1 $\text{ml}\cdot\text{min}^{-1}$ and 10 μl of sample were injected. The lipids were detected and identified by mass spectrometry (MS), using a Bruker ion trap Esquire 3000 MS with an APCI (Atmospheric Pressure Chemical Ionisation) interface. For mass spectrometry, positive ion spectra were generated with the following parameters: corona voltage 5000 V, capillary voltage 4200 V, vaporizer temperature 300 $^{\circ}\text{C}$ and dry N_2 flux at 250 $^{\circ}\text{C}$. The target GDGTs were monitored at m/z 1302 (I), 1300 (II), 1298 (III), 1296 (IV), 1292 (regioisomers V and VI), 1050, 1036, and 1022.

RESULTS AND DISCUSSION

Archaeal lipids were detected in four of the seven impactite rock samples analyzed (i.e., at 235.77, 240.04, 283.50, and 382.17 m) and none of the target lipids was detected in the laboratory blank. The highest concentration of GDGT lipids was found at 382.17 m depth. By comparison with external standards, we can estimate that the concentration of GDGTs in some samples is at most a few ng/g. However, given the reproducibility of the mass spectrometric method to quantify GDGTs (approximately 10% relative precision) and that internal standards were not used for this exploratory study, normalized concentrations

The rock samples analyzed in the laboratory come from the inner part of the cores and we can also rule out laboratory contamination. Thus, we infer that archaeal presence in the Bosumtwi crater is revealed by the occurrence of typical biomarker lipids, GDGTs, in the impactite rocks of this geological structure. The origin of the archaeal community is however difficult to evaluate at this time given the available data. Little information can be derived from the distribution of the detected GDGTs: GDGTs 0–3 (see Fig. 1) have been described in environmental samples including soils and lakes and ascribed to mesophilic Archaea (e.g., Powers et al. 2004; Weijers et al. 2004), but the same structures have been also observed in membranes from thermoacidophilic species (e.g., Shimada et al. 2002). Conversely, crenarchaeol is considered a marker for mesophilic Archaea, especially abundant in aquatic environments although it has also been observed, in less abundance, in soil samples (e.g., Weijers et al. 2004). However, those bacterial GDGTs that are ubiquitous in soils (Weijers et al. 2006) were not detected. The relatively high abundance of GDGT-0 in the studied Bosumtwi samples is more unusual and can provide more insights on the origin of the lipids, as discussed below.

First, it can be considered that lipids found in the rocks are from pre-impact archaeal lipids, accumulated in surface soils older than 1.07 Myr that have survived the impact event originating the Bosumtwi crater. Archaeal lipids have been found in sedimentary rocks as old as 112 Myr (Kuypers et al. 2001) and therefore, it is plausible that the lipids detected are fossil remnants of the archaeal cells that dwelled in former soils. Signatures of fossil biological activity have been found in other impact craters. For instance, in the Haughton impact structure (Nunavut, Canada) several biomarkers were identified in the melt breccias and are considered to have survived the impact event and the ensuing relatively high



temperatures (around 210 °C) that lasted for ~5 kyr (Parnell et al. 2005; Lindgren et al. 2006). However, temperature effects on GDGT stability should also be taken into account. There is evidence from pyrrhotite deformation in the impact rocks of Bosumtwi suggesting peak shock temperatures at the drilling site around 250 °C (Kontny et al. 2007). There is also evidence of a moderately high-temperature post-impact hydrothermal alteration event near the central uplift, with calculated temperatures not higher than 300–350 °C (Petersen et al. 2007), although geochemical analysis suggests that this did not produce a particularly severe alteration or involved a limited volume of fluid percolating through the impacted breccias (Ferrière et al. 2007). Thus we might consider the possibility that Archaea were present in the impact target soils and they were in contact with high-temperature fluids during a relatively long time, of a few thousand years. Schouten et al. (2004) investigated the thermal maturation of GDGTs using hydrous pyrolysis and found that GDGTs exposed to temperatures above 240 °C for 72 h decreased rapidly and they were virtually completely degraded at 300 °C. Given that these values seem to be the peak temperatures reached during the impact event and post-impact hydrothermal processes, it is difficult to ascertain whether GDGTs were able

to survive the thermal conditions in the recent Bosumtwi impact structure. However, it is interesting to note that Schouten et al. (2004) also found that GDGT-0 seemed more thermally stable than the other GDGTs investigated, which is consistent with our results, where lipid distribution in rock samples is dominated by GDGT-0. The distribution of GDGTs in the sample from 283.50 m could just reflect the lipid distribution in pre-impact soils, in accordance with soil samples investigated so far (e.g., Weijers et al. 2006). But the clear dominance of GDGT-0 in the other samples, including the one at 235.77 m where little amounts of other lipids were detected, suggests an additional source for this lipid. Thus, a third explanation for the dominance of GDGT-0 within the set of investigated archaeal lipids is a large contribution of methanogenic Archaea, which are known to contain high amounts of GDGT-0 in their membranes (Koga et al. 1993).

Alternatively, the GDGTs could be of post-impact origin. Although the process of biological recovery after an impact is unique for each event and site, Cockell and Lee (2002) proposed a generalized sequence of post-impact succession. The three stages the authors distinguish after an impact event, which can include partial sterilization of the area, are (i) phase of thermal biology, characterized by thermal activity and associated microbial ecology, (ii) phase of impact succession and climax, when greater colonization of the impact crater takes place, and (iii) phase of ecological assimilation, which culminates with the erosion or burial of the impact structure. Based on studies of Haughton impact crater (about 24 km wide), the duration of the phase of thermal biology would be of the order of several thousands of years, although this will scale with the dimension of the event (Cockell and Lee 2002). Although there is a lack of global data on biological signatures which can be unequivocally associated with this phase of development of any impact crater, it can be reasonably argued that at this stage at Bosumtwi crater, the transient hydrothermal system generated provided an ideal habitat for thermophilic Archaea. Thus, the GDGTs could be remnants of this relatively recent hydrothermal system.

Otherwise, the GDGTs could be of even more recent origin. During the second phase of succession and climax proposed by Cockell and Lee (2002), crater lakes typically develop in the impact craters. In this scenario, recolonization of crater surface rocks and crater lakes can take place very rapidly, in some cases within a few months (see Cockell and Lee (2002), and references therein), with organisms that can be wind-borne, for instance. Since the meteorite impact took place (1.07 Ma), arguably enough time has passed by for prokaryotic communities (Bacteria and Archaea) to have developed in the surface of former air-exposed breccias and the lake filling the crater. The GDGTs present in the deep rocks of the Bosumtwi structure could have been carried by the water percolating from the sediments and of the lake above. In fact, mesophilic Archaea occur ubiquitously in the water column and sediments of lakes (e.g., Powers et al. 2005;

Escala et al. 2007), and seismic reflection data from Bosumtwi structure suggest highly fractured impact material and water-saturated lake sediments (Scholz et al. 2007). In the same context, post-impact soils from the crater rim could be a likely source for the archaeal lipids, given that there is hydrological contact between the brecciated crater-rim rocks and the sub-lake breccias. However, the surface of the crater rim is very small compared to the size of the lake and thus the contribution of these soils in comparison to the production of GDGTs in the lake is probably not very significant. Furthermore, those GDGTs typically present in soils (Weijers et al. 2006) were not detected in the samples. If the lake waters are indeed the source of the archaeal lipids in the breccias, the high relative abundance of GDGT-0 could be explained by the presence of archaeal methanogens in sediments, which could produce the CH₄ observed in surface sediments and deep water in the Bosumtwi lake (Koeberl et al. 2007).

The lack of correlation of GDGTs concentration with depth could be explained in this case by the vertical heterogeneity in lithology and grain size that has been reported for this core (Ferrière et al. 2007). For instance, high concentrations of GDGTs in the shallowest sample (235.77 m) just below the lake sediment can be connected to the presence of carbon-rich shale clasts in the upper meters of the impactite rocks. The depth-independent concentration of archaeal lipids is also consistent with the reported vertical structure in microbial distribution in the Chesapeake Bay impact structure, which is attributed to processes of sterilization and microbial recolonization linked to the impact cratering (Cockell et al. 2007).

SUMMARY AND CONCLUSIONS

Seven samples of impact breccia from the central uplift of the Bosumtwi crater were analyzed for the presence of typical archaeal membrane-lipids (GDGTs). These have been detected in four of the samples, at a maximum depth of 382 m below lake level, and the distribution of the analyzed GDGTs is dominated by GDGT-0. The origin of these lipids is discussed and three hypotheses are considered as possible explanations: (i) pre-impact lipids in soil that survived the impact event, (ii) lipids synthesized by hyperthermophilic Archaea in the post-impact hydrothermal system, and (iii) lipids synthesized by Archaea thriving in the lake and/or crater-rim rocks that have percolated into the impactites. Additional data are needed to discriminate between these possible modes of origin for these lipids, but our preliminary results suggest that studies on the microbial community in the deep interior of the Bosumtwi structure would be rewarding.

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