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This work was supported by DePaul University College of Science and Health through their funding of the Undergraduate Summer Research Program. Allen West provided the samples, along with the geographical information regarding the samples. Allen West also analyzed the carbonaceous residue samples.

Nanodiamond Extraction at a Potential Impact Location

Joel Kathan*

Department of Chemistry

ABSTRACT Meteoritic or cometary impacts create the temperature and pressure conditions necessary to form nanodiamonds (NDs). The presence of extracted NDs from rocks of the time and locations of extinctions, fires, or known environmental changes are commonly used to confirm that a theorized cosmic impact occurred to trigger those events. Samples were obtained from an archeological site described in the Old Testament of the Bible as having been destroyed by the God of the Old Testament.† To see if the historical description of Biblical events might have been triggered by a cometary impact or explosion, an attempt was made to isolate and quantify NDs from these samples. Significant quantities of the mineral gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, were present in the samples. An adjusted protocol was developed and used to extract NDs from rock samples to preferentially remove the gypsum in the hope that carbonaceous yield (containing NDs, if present) would improve. The gypsum dissolution resulted in an increase in carbonaceous residue yield ranging from 22% to 46%. However, TEM and X-ray crystallography of the carbonaceous residue indicated no NDs above the detectability limit of the procedure.

INTRODUCTION

A number of independent researchers have reported nanodiamond (ND) carbon structures in the 13,000 year-old Younger Dryas Boundary (YDB) sites (Kinzie et al., 2014), a time period

that dates to the End-Pleistocene megafaunal extinctions, which included extinction of the woolly mammoths. These diamond-like carbon samples were extracted from sediments from geographically distant sites in North America, Greenland, and Northern Europe. The Younger Dryas Boundary represents a short-lived geological period of cold climate conditions and drought during the deglacial warming of the Northern Hemisphere. It is believed that the YDB geological time period was terminated by a cosmic impact causing the observed megafaunal extinction. Similarly, NDs have also been found at the Siberian cometary impact/explosion site of Tunguska, which occurred in 1908 (Wittke et al., 2009).

† The specific site is proprietary at the time the paper was prepared. The archaeologist leading the project has requested to withhold revealing the name or location of the Biblical event until he has had an opportunity to publish his archaeological discovery.

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Various structures of diamond-like carbon were extracted from YDB sites (Figure 1). These include hexagonal lonsdaleite-like crystals and cubic diamonds, as well as the “unique carbon allotropes,” n-diamonds and i-carbon (Figure 2) (Kinzie et al., 2014). Hexagonal lonsdaleite-like crystals are composed of a graphitic hexagonal crystal structure and are shown to be formed under the force conditions imposed by a cosmic impact (Fang, 2008). Cubic diamonds form under high temperature and pressure conditions (Kennett, et al., 2009). Research suggests that the allotropes, n-diamonds and i-carbon, may be cubic diamonds with a carbon atom replaced by hydrogen or another atom (Wen et al., 2007). Because the methods of analysis used to detect the diamond-like crystals detects all forms that are shown to be associated with cosmic impacts, all of the allotropes discussed will be referred to collectively as “NDs.”

The diamond-like carbon structures are often associated with cosmic impacts due to their existence at locations of known extraterrestrial impact or cometary airburst. Various ND polytypes have been extracted from YDB sediments (Kinzie et al., 2014), Tunguska and K/T Boundary sediments (Wittke et al., 2009), as well as in meteorites that may have collided with other meteorites in the asteroid belt (Daulton et al., 1996). While the specific impact conditions vary depending on the mass and velocity of the impactor and oxygen availability, laboratory conditions necessary for the synthesis of NDs require temperatures up to 3400 °C, pressures up to 70 GPa, and an anoxic atmosphere (Kinzie et al., 2014). These conditions do not occur in natural processes on earth; they require an “outside” force to create them. Because NDs form under conditions similar to conditions present during a cosmic impact, NDs might be expected to be present in any carbon containing sediments taken from an area of a proposed impact site.

Archaeologists have tentatively identified a location as the site of a fiery, destructive cataclysm described in the Old Testament of the Bible. This particular study used an established ND extraction technique to gain insight of a

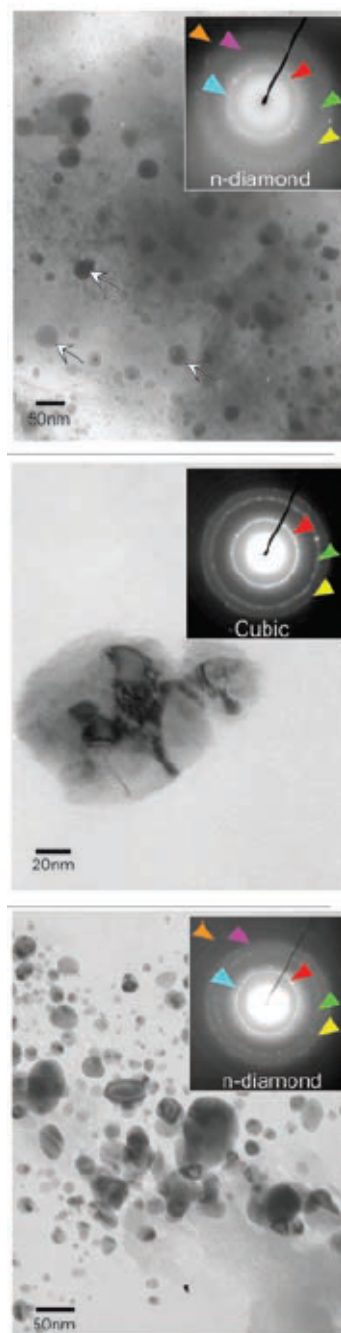


Figure 1: TEM photomicrographs of n-diamonds and cubic diamonds are shown. The NDs were extracted from the YDB sites (A) Lake Hind, MB, Canada; (B) Bull Creek, OK; and (C) Murray Springs, AZ (Kennett et al., 2009).

historic, geographical location that is purported to have been destroyed by the God of the Old

Testament. The detection of NDs in the sediment from the geographical area of the proposed destruction would be one source of evidence of a cosmic impact occurring at the geographical location.

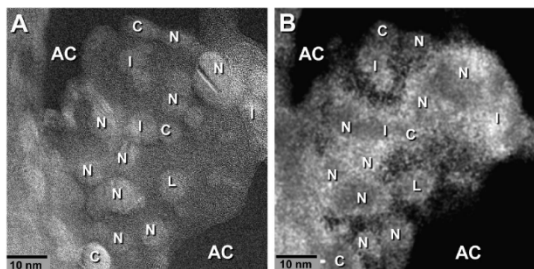


Figure 2: AN EFTEM image of NDs from Lake Cuitzeo (YDB site) is shown. ND types are labeled as N = n-diamond; I = i-carbon; C = cubic diamond; L = lonsdaleite-like crystal; AC = amorphous carbon grid film (Kinzie *et al.*, 2014).

Unlike previously extracted samples, the samples used in this experiment were known to be “gypsum-rich” (Allen West, personal communication). Gypsum is one form of calcium sulfate. Calcium sulfate exists in three different forms: dihydrate, hemihydrate, and anhydrate. Factors such as pH, temperature, and formation conditions yield the different types of calcium sulfate. The form of calcium sulfate typically found in nature is the dihydrate form, commonly referred to as gypsum. Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, has a high solubility (Al-Khaldi, *et al.*, 2011), and is thus formed when calcium and sulfate ions are present in body of water where evaporation rates are relatively high and sea level is low. Gypsum is predominately formed in temperatures less than 98°C (Al-Khaldi *et al.*, 2011). Due to the possibility that NDs were encapsulated by gypsum as it formed, a gypsum dissolution was necessary to ensure all of the NDs are removed from gypsum binding and thus free to be extracted. Thus the normal ND extraction protocol was adjusted for a gypsum removal procedure.

The purpose of this study was two-fold: (1) to design a revision to the ND extraction protocol to incorporate the need to dissolve gypsum, and (2) to apply the revised protocol to the set of archaeologically significant samples in order to determine whether measurable amounts of NDs were present. Gypsum dissolution conditions

were determined by consulting the data in Al-Khaldi *et al.* (2011), which shows that the solubility of gypsum increases in the presence of H_2SO_4 . Temperature conditions and H_2SO_4 concentrations reported by Al-Khaldi *et al.* (2011) for optimal gypsum solubility were used.

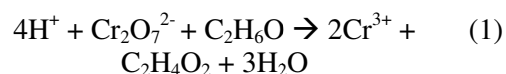
METHODS

THEORY

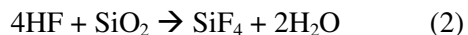
A general protocol used to isolate YDB NDs has been developed and used successfully at several dozen sites (Kinzie *et al.*, 2014). The developed protocol was used in this experiment and is shown in Figure 3. The significance of each step in the protocol is discussed below.

NaOH: It has been shown that NDs (in particular those in the YDB layer) contain organic functional groups on their surface (Shenderova *et al.*, 2002). Due to the large amounts of carboxylic acid groups on the surface, the NDs’ aqueous solubility can be altered by deprotonation of the carboxyl groups. The NDs’ aqueous solubility increases at a $\text{pH} > 7$. Thus the solution containing the suspended NDs can be extracted. After the supernatant (containing NDs if NDs are present in the samples) was collected, the samples were acidified to remove the carboxyl groups on the surface of the NDs through decarboxylation. As a result, the NDs were no longer suspended, and the samples were centrifuged to collect carbonaceous material.

$\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$: The samples were then suspended in $0.5\text{ M K}_2\text{Cr}_2\text{O}_7/2\text{ M H}_2\text{SO}_4$ to oxidize any remaining organic components in the ND-containing containing residue. An example redox reaction is shown in Reaction 1, where ethanol is oxidized to acetic acid.



HF/HCl: Silicate residues were then removed using a $10\text{ M HF}/1\text{ M HCl}$ solution. To dissolve fluorides that may have formed, the samples were washed with 9 M HCl . The reaction is shown in Reaction 2.



PROCEDURE

The following procedure is also depicted schematically in the flowchart of Figure 3.

Eight sediment samples (~100 g each) containing primarily sandy quartz (Allen West, personal communication) were obtained from Allen West. The samples were from different geological areas near the archaeological site of interest. The samples were massed (Table 1) and submerged in 0.1 M NaOH (30 mL/10 g) for two days. The samples were then centrifuged at 1000 relative centrifugal force (rcf) for ten minutes (Hermle K 400 Z), and the supernatant was retained for further experimentation. The remaining sediment was treated for gypsum dissolution. Approximately 10 mL of 0.1 M H₂SO₄ was added to the samples undergoing gypsum dissolution. Concentrated H₂SO₄ was then added drop-wise until the pH of each sample was 0.5-1. After five days, the samples were made basic (pH > 7) using 50% NaOH to extract any NDs liberated by gypsum dissolution. The samples were centrifuged at 2500 rcf for ten minutes. The supernatant was collected, and this set of samples was treated identically to the first set of samples for the remaining experimentation. The samples were acidified with approximately 1 mL of 12 M HCl to a pH of 0.5-1. The samples were centrifuged for one hour at 2500 rcf. The supernatant was discarded, and the carbonaceous material was collected. The samples were submerged in 20 mL of 0.5 M K₂Cr₂O₇/2 M H₂SO₄ and placed in a 70 °C water bath for twelve days. After twelve days, the samples were rinsed three times using 0.1 M HCl. After each rinse, the samples were centrifuged at 2500 rcf for thirty minutes. To destroy any silicates that may have been present, approximately 7 mL of 10 M HF/1 M HCl was added to each sample, and then approximately 3 mL of concentrated HF was added. The samples were then diluted with approximately 35 mL of

de-ionized H₂O and centrifuged at 2500 rcf for thirty minutes. To dissolve fluorides that may

have formed, approximately 10 mL of 9 M HCl was added to each sample. After two days, the samples were diluted with approximately 40 mL of 0.1 M HCl and centrifuged at 2500 rcf for one hour. This rinsing process was repeated two more times. The samples were dried and massed. The samples were sent to Allen West to be analyzed by TEM and X-ray crystallography.

RESULTS

Carbonaceous samples were analyzed by TEM and X-ray crystallography as described in Kinzie *et al.* (2014). Both methods of analysis indicated no detectable NDs in the samples in either extraction phase (i.e., either before or after gypsum dissolution) (Allen West, personal communication). Possible reasons for not observing measureable NDs include: (1) archaeological mis-identification of the city destroyed in the Bible, thus there is no reason to expect NDs; (2) if the site is correct, sample sizes were too small to provide measureable quantities of ND, which are typically detectable at concentrations of ≥ 0.1 ppm within isolated carbonaceous material; or (3) if the site is correct and the samples were of adequate size, perhaps there was no cometary airburst or other impact event at the time of the historic occurrence described in the Bible. Other possible non-ND carbonaceous components could include materials such as soot, charcoal, or metamorphosed organics (kerogen). However, the samples were not analyzed for these components.

Mass data are given in Table 1. The results show that the gypsum dissolution increased the recovery of carbonaceous material by at least 22%. The percent of carbonaceous material recovered in the total amount recovered ranged from 22% to 46%.

In order to gain further insight into the proposed cometary impact location site, more samples must be tested from both the current proposed geographical site, as well as the area surrounding the proposed site. A more comprehensive analysis will allow one of the

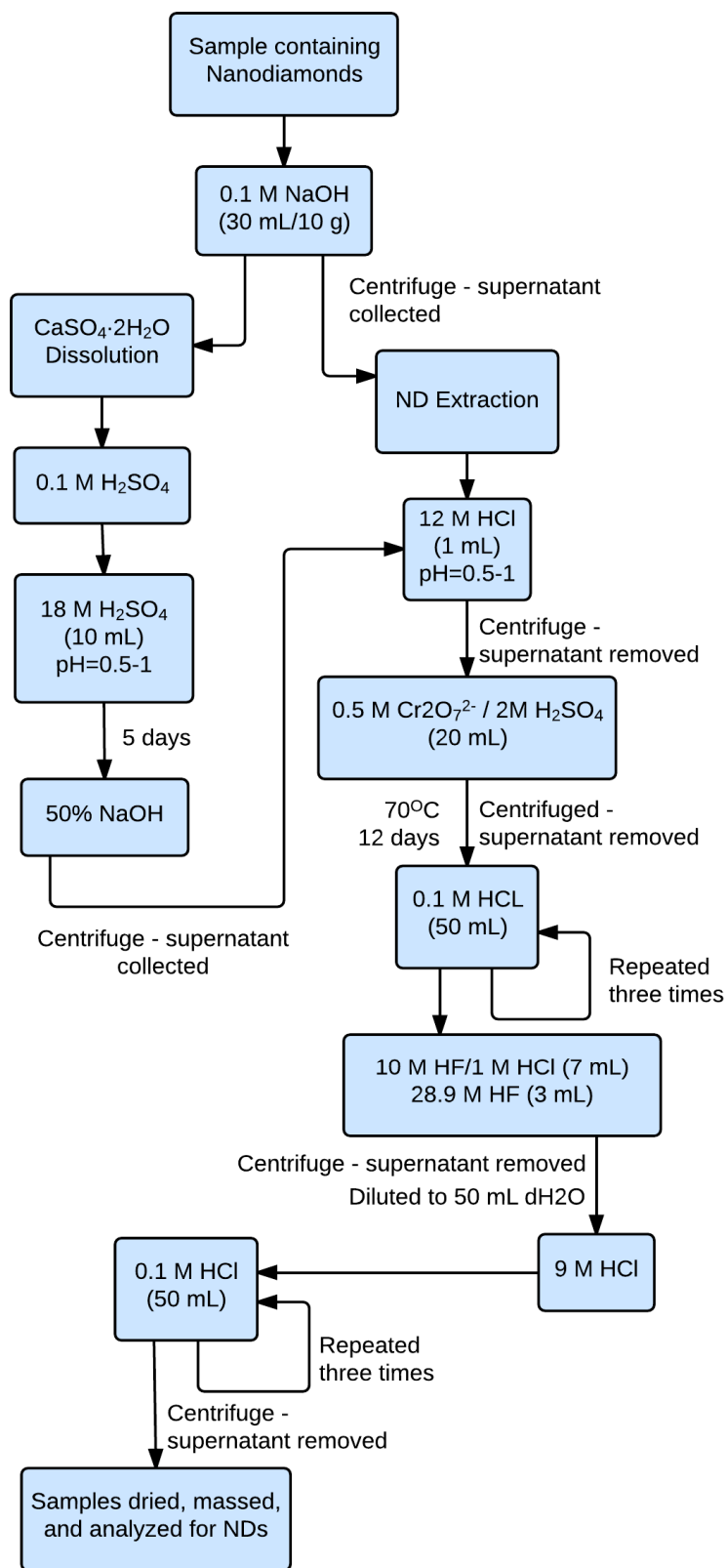


Figure 3: A flowchart showing the methods of the ND extraction is shown.

for the absence of NDs to three proposed causes hold true or be proven incorrect.

DISCUSSION

The purpose of this research project was two-fold. The first goal was to follow predetermined ND extraction protocol in order to recover NDs in samples from a proposed cometary impact location. The other goal of the experiment was to show that a gypsum dissolution of the samples would increase recovery of carbonaceous materials (and/or NDs). While no NDs were detected in the samples from the area of proposed impact, the gypsum dissolution was shown successful, increasing the total carbonaceous material up to 46%.

Table 1: Mass Data for Carbonaceous Residue Extraction and Gypsum Dissolution.

Sample	Sample Start Mass (g)	Mass of Carbonaceous Residue After Extraction (ppm)		Percent of Carbonaceous Material Released by the Gypsum Dissolution (%)
		Gypsum Dissolution Performed	Gypsum Dissolution Not Performed	
1	94.809	3.2 ± 0.4	3.8 ± 0.3	46 ± 7
2	67.995	2.1 ± 0.3	7.2 ± 0.3	22 ± 3
3	85.502	1.9 ± 0.5	3.6 ± 0.2	40 ± 10
4	85.753	2.0 ± 0.4	4.6 ± 0.2	30 ± 6
5	76.664	1.7 ± 0.3	3.8 ± 0.4	31 ± 6
6	66.437	2.0 ± 0.5	4.4 ± 0.5	31 ± 9
7	87.538	2.2 ± 0.1	2.9 ± 0.2	43 ± 3
8	87.538	1.1 ± 0.1	3.8 ± 0.4	22 ± 3

ACKNOWLEDGEMENTS

This work was supported by DePaul University College of Science and Health through their funding of the Undergraduate Summer Research Program. Allen West provided the samples, along with the geographical information regarding the samples. Allen West also analyzed the carbonaceous residue samples.

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