



1992

# Analysis of Carbon across the Cenomanian-Turonian Boundary

Andrew J. Carr '92

*Illinois Wesleyan University*

---

## Recommended Citation

Carr '92, Andrew J., "Analysis of Carbon across the Cenomanian-Turonian Boundary" (1992). *Honors Projects*. Paper 24.  
[http://digitalcommons.iwu.edu/chem\\_honproj/24](http://digitalcommons.iwu.edu/chem_honproj/24)

This Article is brought to you for free and open access by The Ames Library, the Andrew W. Mellon Center for Curricular and Faculty Development, the Office of the Provost and the Office of the President. It has been accepted for inclusion in Digital Commons @ IWU by the faculty at Illinois Wesleyan University. For more information, please contact [digitalcommons@iwu.edu](mailto:digitalcommons@iwu.edu).

©Copyright is owned by the author of this document.

ANALYSIS OF CARBON  
ACROSS THE CENOMANIAN-TURONIAN BOUNDARY

Andrew J. Carr  
Wendy Wolbach  
Chemistry 499 Thesis  
Illinois Wesleyan University  
May 7, 1992

Approval Page

ANALYSIS OF CARBON  
ACROSS THE CENOMANIAN-TURONIAN BOUNDARY

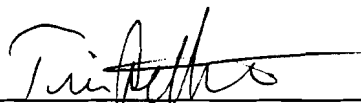
by Andrew J. Carr

A PAPER SUBMITTED IN PARTIAL FULFILLMENT OF THE  
REQUIREMENTS FOR CHEMISTRY 499 AND HONORS IN  
CHEMISTRY.

Approved, Honors Committee:



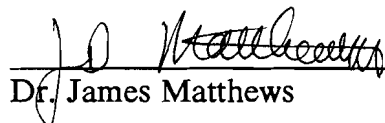
Dr. Wendy Wolbach, Research Advisor



Dr. Tim Rettich



Dr. David Bailey



Dr. James Matthews

Illinois Wesleyan University  
1992

**Index:**

Abstract .....	1
Background .....	2
Theory .....	7
Experimental .....	13
Results and Discussion .....	16
Future Work .....	33
References .....	34

## List of Figures:

1. Oxidation of carbon in sediments .....	9
2. Location of sample sites .....	17
3. % Bulk Carbon Residue vs Depth, Red Wash Creek, New Mexico .....	22
4. % Bulk Carbon Residue vs Depth, Chispa Summit, Texas .....	23
5. Isotopic Composition vs Depth, Red Wash, New Mexico .....	28
6. Reduced Carbon vs Depth, Red Wash, New Mexico .....	31
7. % Carbon vs Depth, Red Wash, New Mexico .....	32

## List of Tables:

1. Raw Carbonaceous Residue Data for C-T boundary Samples .....	18
2. Carbon Residue Data for England-bound Samples .....	19
3. Average Percent Bulk Carbon Residue .....	20
4. Carbon Residue Etching Data for C-T Boundary .....	25
5. Mass of Carbon Residue Remaining vs. Time of Etching .....	26
6. Isotopic Analysis of Bulk Residue from Red Wash, New Mexico .....	27

**Abstract:**

Following the work of Wolbach *et al.*, who studied reduced carbon across the 65 Ma-old Cretaceous-Tertiary extinction boundary, a study was conducted to analyze reduced carbon across the 92 Ma-old Cenomanian-Turonian (C-T) extinction horizon, in the hope that evidence could be gathered which might support a particular mechanism for these extinction events.

Currently two sample sites are being analyzed for reduced carbon content at the C-T boundary: Red Wash, New Mexico and Chispa Summit, Texas. Both sample sites are from the Western Interior Basin of North America. During the time of the extinctions 92 million years ago, the basin was an inland sea. Preliminary data suggest a decrease in the amount of carbonaceous residue found at the boundary at both sample sites. This would indicate that the extinction event was not rapid, as lower amounts of reduced carbon are generally more characteristic of extinctions caused by slow changes in climate vs sudden changes caused by catastrophic events. Slow climate changes would allow microorganisms time to digest (oxidize) the carbon in dead plankton before sedimentation, thus decreasing the amount of reduced carbon preserved in the rock.

A mechanism for the C-T extinctions consistent with previous data as well as preliminary results obtained in this study is the opening of deep sea fissures at the ocean floor, increasing certain metal concentrations in seawater, and, more importantly, increasing water temperatures. Plankton unable to adapt to these new conditions would become extinct.

**Background:**

There is evidence for mass extinctions throughout the geological record. Over the past 250 million years, the mass extinctions seem to occur at a periodic interval of approximately 26 million years<sup>1</sup>. Several explanations have been proposed to account for these extinctions, including the possibility of periodic meteorite impacts with the Earth<sup>1,2</sup>. The probability of the Earth being struck by a meteorite large enough to cause extinctions is small, however several mechanisms have been proposed that could account for such a periodic increase in meteor activity in the inner solar system. Any increase in meteor activity near Earth would lead to an increased probability of the Earth being struck. One mechanism proposes a companion star to the sun having a 26 million year orbit. As this star enters perihelion, it could disrupt the cometary cloud known as the Oort cloud, causing a comet storm in the inner solar system<sup>1</sup>. Other mechanisms include the gravitational distortion of the Oort cloud by a theorized tenth planet, and the oscillation of the sun above and below the plane of the galaxy as it revolves about the galactic center<sup>2</sup>.

When a large meteorite hits the Earth, evidence of the event can be preserved in stratigraphic layers of sedimentary rock deposited at the time. The evidence left by a meteorite can take on many forms, from the obvious crater to an increase in iridium concentration on the scale of parts per billion, depending on the Ir content of the meteorite and its size<sup>2</sup>. Iridium is rare in the Earth's crust, but relatively abundant in meteorites. The appearance of microspherules of

glass and shocked quartz also indicate a large impact (meteorite  $\geq 1\text{km}$ ).

Another piece of evidence consistent with an impact is the presence of soot in the geological record<sup>3</sup>. In the case of recent work by Wolbach *et al.*<sup>3</sup>, an impact is associated with mass extinctions which occurred approximately 65 million years ago, at the end of the Cretaceous/beginning of the Tertiary geologic periods.

At the Cretaceous-Tertiary (K-T) boundary 65 million years ago, approximately half of the living genera perished<sup>4</sup>. The cause of this extinction event is believed to be the impact of a meteorite, about 10km in diameter, that devastated the worldwide ecosystem<sup>1</sup>. Computer modeling of such an impact indicates that the meteorite would have<sup>5</sup>:

1. The kinetic energy equivalent of  $2.6 \times 10^{30}$  ergs equivalent to  $6.2 \times 10^7$  megatons of TNT;
2. Enough energy to cause a 12.4 earthquake on the Richter scale;
3. The power to excavate  $105\text{km}^3$  ( $9 \times 10^{15}$  tons) of rock and propel it to a height of 100km, with about 10-20% remaining in the atmosphere for months;
4. A jacket of air with a temperature of approximately 20,000K.

The environmental changes resulting from these physical effects could easily have caused the extinction of many species, including dinosaurs, flowering plants, plankton, and invertebrates. Studies indicate that land vertebrates over 25kg, or 55lbs, did not survive the event because of the limited food supply<sup>4</sup>.

Evidence supporting the meteorite impact scenario has been found worldwide. There is a sudden increase in iridium of at least two orders of magnitude above background levels in rocks dating to the time of the extinction relative to those deposited prior to the impact. Some theories have suggested hot



spot volcanism as a cause of the extinction, however this cannot explain the change in other isotopic signatures<sup>2</sup>. Microspherules, soot (the increase of soot is 210 times that of the background levels of 22ppm<sup>6</sup>), and shocked quartz have also been discovered<sup>6</sup>. An important piece of evidence needed to support the impact theory is the still undiscovered crater, although recent evidence supports the possibility that the impact occurred in the Yucatan<sup>7</sup>.

The large amount of soot found at the K-T boundary is believed to have come from wildfires triggered by the impact of the K-T meteorite. These wildfires would have had to be on a continental or global scale to account for the observed increase in carbon. The addition of soot to the already dust-filled atmosphere from the ejected material of the impact crater would block out the sun even more effectively as soot has a large optical depth. The lack of sunlight would stop photosynthesis, killing most of the plant life and other organisms higher on the food chain. This phenomenon, nuclear winter, would also lower the Earth's average temperature due to the lack of solar heating, creating another biohazard<sup>4</sup>. The addition of the soot into the stratosphere would thus increase the duration of the cooling and darkness, exacerbating both.

Another mass extinction event occurred 92 million years ago. Though the event was smaller, the Cenomanian-Turonian (C-T) boundary fits the 26 million-year extinction cycle. At this extinction horizon, there was a radical decrease in the diversity of planktonic organisms<sup>8</sup>. This event corresponds to an increase in

the amount of iridium, manganese, and  $\delta^{13}\text{C}^a$ , found in the sedimentary record<sup>9</sup>, and can be correlated globally<sup>10</sup>. The cause of this event is still unknown.

There are three possible generally accepted explanations for the extinction. First is an impact scenario because of the slightly increased level of iridium at the time of the event (2x background levels in some areas and as much as 5x background levels in others). However, other elements that are typically associated with a meteoritic impact are either missing or occur at lower concentrations than expected from a major impact. A hot spot volcano might be a second cause, as might an increase in circulation of metal-rich water from the deep Atlantic might be the third<sup>9</sup>.

The stratigraphic samples at this horizon are not as uniform in color or thickness on a worldwide basis as the K-T boundary samples are, which suggests a more localized event than that of a large meteoritic impact<sup>9</sup>. Additionally, no impact crater has been found, nor is there evidence of shocked quartz or microspherules<sup>9</sup>.

In order to determine the cause of this extinction event, more data are needed. If the extinction occurred as a result of a meteorite impact, then it is possible that soot was produced at the C-T boundary as it was at the K-T boundary. This would be consistent with an impact scenario on the order of the impact 65 million years ago. An absence of soot in the C-T boundary would be

---

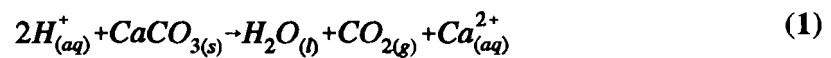
<sup>a</sup> Definition on page 11.

consistent with either a smaller impact or none at all. If so, slower processes such as gradual climate changes might have caused the C-T extinctions.

### Theory:

The separation and identification of water insoluble carbon from sedimentary rocks has been conducted on K-T boundary samples by Wolbach *et al.*<sup>11</sup> Carbon within the rock samples exists primarily in three forms: soot (relatively inert elemental carbon, whose particles have the morphology of a bunch of grapes), kerogen (defined as slow-reacting organic material), and organic carbon (fast-reacting material).

The separation of carbonaceous material from rock follows a standard procedure. Carbonate,  $\text{CO}_3^{2-}$  (limestone, i.e.  $\text{CaCO}_3$  or  $\text{MgCO}_3$ ), reacts with hydrochloric acid, producing carbon dioxide gas and water, according to eq. 1:

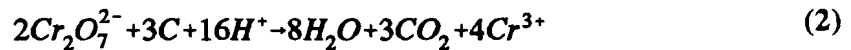


Silicates,  $\text{SiO}_4^{4-}$  present in rock, are destroyed with HF which attacks Si-O bonds. The addition of HF to the rock sample after HCl treatment can cause the precipitation of calcium fluoride and/or magnesium fluoride ( $\text{CaF}_2$ ,  $\text{MgF}_2$ ). In order to avoid this, the sample must be rinsed repeatedly with water to lower the concentration of the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions remaining in the solution to negligible levels. From the  $K_{sp}$ <sup>b</sup> of  $\text{CaF}_2$  and  $\text{MgF}_2$  and the nominal concentration of HF used, the number of washings is expected to be on the order of ten.

---

<sup>b</sup>Solubility product constant: e.g. for  $\text{CaF}_{2(s)} = \text{Ca}^{2+}_{(aq)} + 2 \text{F}^{-}_{(aq)}$ ,  
 $K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2$

After destruction of the rock portion of the sample, only carbonaceous material and small amounts of inert minerals such as TiO<sub>2</sub> remain. The carbon isotope composition of this bulk carbonaceous residue is determined. Oxidation is carried out using K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in H<sub>2</sub>SO<sub>4</sub><sup>11</sup>. The Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> solution oxidizes reactive carbon, producing CO<sub>2</sub> and water soluble organic species<sup>11</sup>. The total oxidation reaction for elemental carbon is shown below.



By plotting the mass fraction of carbonaceous residue remaining as a function of time of oxidation, it is possible to monitor the amount of each carbon phase (both organic and elemental) still present in the sample and assign each phase (fast oxidation = organic carbon, slow oxidation = elemental carbon) on the basis of its oxidation rate<sup>11</sup>. The assignment is made by determining the "half-lives" for oxidation of each carbon component in the sample. A characteristic and reproducible plot of this for the K-T boundary is shown (Fig. 1)<sup>11</sup>.

Oxidation of carbonaceous material follows first order kinetics<sup>11</sup>.

$$A_i = A_o e^{-\lambda t_i} \quad (3)$$

# Oxidation of carbon in sediments

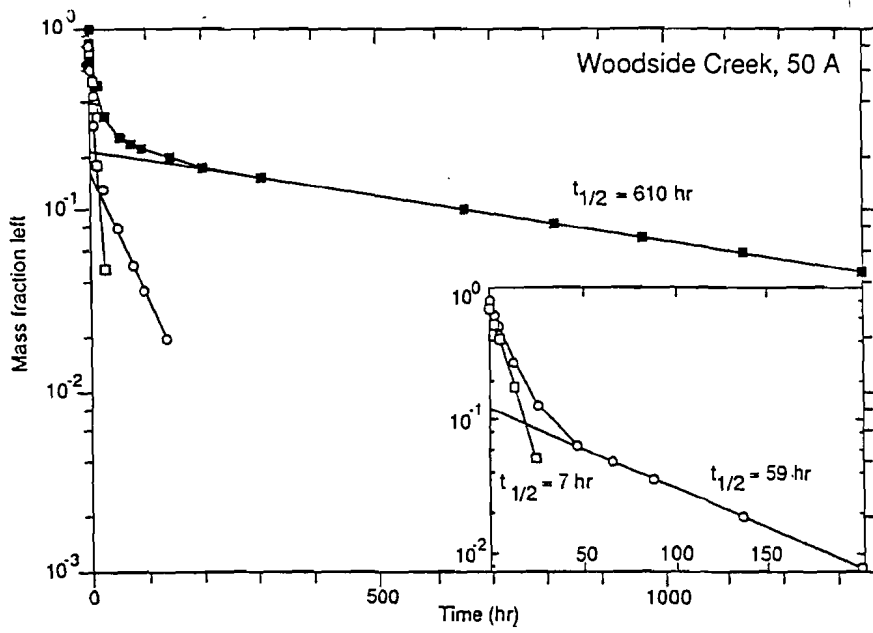


Figure 1. Mass loss curve can be resolved into 3 components, of half-life 610 hr, 59 hr, and 7 hr. They apparently represent elemental C, reactive kerogen, and organic carbon. The amounts of these 3 components can be determined from their intercepts. The sample is from the Cretaceous-Tertiary Boundary at Woodside Creek, New Zealand.

$$\frac{A_i}{A_o} = e^{-\lambda t_i} \quad (4)$$

$$\ln\left(\frac{A_i}{A_o}\right) = -\lambda t_i \quad (5)$$

$$\ln(A_i) = -\lambda t_i + \ln(A_o) \quad (6)$$

Where:

$A_o$  = initial mass of carbon sample

$t_i$  = time of oxidation

$A_i$  = mass of carbon sample at  $t_i$

$-\lambda$  = slope of line

Equation 6 describes the equation for a straight line. This equation is used to determine  $\lambda$ , and thus the  $t_{1/2}$  for each carbon component according to equation 7.

$$t_{1/2} = \frac{\ln(2)}{\lambda} \quad (7)$$

Since first order kinetics applies, the half-life of the individual components can be resolved if the half-lives of the components differ by a factor of two or more<sup>11</sup>. As can be seen from the plot, three components are present in the K-T example.

The half-lives of the components are calculated, along with the mass fraction of each component. This is done using linear regression of the longest-lived species (elemental carbon), and extrapolating to time zero. The intercept is the initial mass fraction of elemental carbon in the residue. The equation of the line is then used to determine the amount of elemental carbon present at each

line is then used to determine the amount of elemental carbon present at each data point. Subtraction of these values from the total fraction of residue yields the next longest living component's mass fraction; its half-life can be determined in an analogous manner to that for the longest-lived component. The procedure can be used for as many components that are in the sample and resolvable by this technique<sup>11</sup>.

The duration of oxidation is determined once half-lives have been calculated for all components present. An etch duration is chosen to maximize destruction of organic carbon while leaving elemental carbon. Isotopic measurements of <sup>13</sup>C/<sup>12</sup>C of this elemental carbon are performed. These data, together with similar isotopic data for the bulk carbonaceous residue, allow isotopic composition of the oxidized (organic) fractions removed to be calculated by mass balance. The isotopic composition is generally reported in parts per thousand according to:

$$\delta(\text{‰}) = \left[ \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right] * 1000 \quad (8)$$

Where:

- δ(‰): C isotope composition of sample
- R<sub>sample</sub>: <sup>13</sup>C/<sup>12</sup>C of sample
- R<sub>standard</sub>: <sup>13</sup>C/<sup>12</sup>C international reference (National Bureau of Standards)



The isotopic composition of the organic material can yield interesting information regarding the type of plants living at the time of the extinction. There are two major varieties of plants<sup>13</sup>. One type, called C3 plants, has a low <sup>13</sup>C/<sup>12</sup>C ratio, while the other type, C4, has a higher ratio because of their different metabolic pathways. The majority of plankton living prior to the C-T extinction show C3 properties. The <sup>13</sup>C/<sup>12</sup>C ratio is also temperature dependent; a higher <sup>13</sup>C/<sup>12</sup>C ratio is generally observed in warm water regions<sup>13</sup>. Clues regarding temperature changes in the environment may thus be learned from an isotopic study of C-T and related samples.

If soot is present in the samples, it can be identified using a scanning electron microscope (SEM). At high magnification, soot particles display an easily-recognizable morphology: that of a bunch of grapes.

**Experimental:**

Rock specimens from two C-T boundary sites at Red Wash, New Mexico and Chispa Summit, Texas were obtained. Samples having a mass between 1 and 2 grams were placed in pre-marked polypropylene tubes (Nalge Company Centrifuge Ware, round bottom 15ml). Samples were dissolved by adding 9M HCl (Fisher Scientific reagent grade) dropwise, to minimize violent bubbling. If the neutralization reaction became too vigorous, a few milliliters of distilled water (Culligan, reverse osmosis unit) were added. Over the course of several days, sufficient acid was added to the samples to neutralize the carbonate present. In order to insure complete mixing of the acid with the sample, the test tube containing the sample was vibrated on a vortex (Scientific Industries Inc. Vortex-Genie model K-550-G).

Samples were centrifuged (Fisher Scientific Centrifuge model 228) for 15 minutes and the supernatant decanted from the residue. The residue was washed five times with distilled water. At this point the supernatant removed from the residue did not form a precipitate with concentrated HF (Fisher Scientific reagent grade). Concentrated HF was added because of the apparently high fraction of clay in the rock samples. The samples were vortexed and left to react for approximately two weeks. The supernatant was removed and fresh HF added; samples were again left to react for two weeks. The samples were rinsed five times with distilled water. Some of the organic fraction of the rock did not settle out upon centrifuging, so approximately 1ml of 9M HCl was added to aid in

sample coagulation, and samples were centrifuged (Damon IEC Division IEC model K centrifuge with swinging bucket rotor) until complete settling of carbon occurred.

The remaining residue once again was treated with 9M HCl, alternating with HF, then 9M HCl (each reaction interspersed with copious rinsing with water) until all that remained in the residue was elemental and organic carbon and a tiny fraction of insoluble minerals.

When the amount of residue was large enough, the samples were divided into three fractions: one-third for bulk  $^{13}\text{C}/^{12}\text{C}$  isotopic analysis, another third for dichromate oxidation and the remaining third for back up. The residue was fractionated by volume; samples were suspended as thoroughly as possible in 12ml of water by ultrasonic dispersion and vortex stirring. Three of the samples were pitch black, making it difficult to determine how uniform the suspension was. Four milliliters of each suspended sample were added to a clean, pre-weighed glass test tube [previously washed in warm concentrated nitric acid (Fisher Scientific reagent grade) rinsed and dried]. Four milliliters were poured into labelled Nalgene tubes for storage. The remaining 4ml were transferred to preweighed 0.3 ml sample vials. This was accomplished by adding the suspension dropwise to the vial and centrifuging to remove water until each sample was transferred quantitatively to a vial. The vials were dried, weighed, and shipped to England (The Open University) for carbon isotope analysis.

Samples to be oxidized were dried and weighed. To the samples  $\geq 5$ ml  $0.10\text{M}$   $\text{K}_2\text{Cr}_2\text{O}_7$  in  $2\text{M}$   $\text{H}_2\text{SO}_4$  (Fisher Scientific reagent grade) were added, depending on amount of carbonaceous material present. Samples were ultrasonicated to break up dried carbon clumps and placed in a  $50^\circ \pm 3^\circ\text{C}$  water bath (bath container was made from a turkey roaster). After several hours, the samples were removed from the bath and water was added to dilute the dichromate. The samples were centrifuged. If some carbon material remained suspended, removal of some of the liquid was achieved using a Pasteur pipet. The residue was washed with water until the orange color of the dichromate disappeared. The residue was then dried and weighed. The procedure was repeated at each stopping point for the duration of the oxidation.

## **Results and Discussion:**

The two sample sites studied were Red Wash, New Mexico and Chispa Summit, Texas (Fig. 2). The rock samples from these two sites differed in color. The Red Wash (RW) samples were gray, while the Chispa Summit (CS) samples were yellow or orange. Upon demineralization of the samples it was observed that CS contains a higher mass fraction of carbonates and silicates while having a lower reduced carbon mass fraction, compared to RW samples.

It is apparent from the data in Table 1 that there is a difference in the amount of carbon at the two sample sites; data in Table 2 support this difference. From the values in Table 3, the average percent of reduced carbon at the entire RW site for this depth profile is 1.09% while the CS site only contains 0.17% reduced carbon. The different amounts of total reduced carbon suggest different physical sets of deposition conditions at the two sites. These conditions could have been affected by local differences in weather (eg. wind patterns), deposition of other material (eg. erosion products), distance from shore, water depth, and the redox environment. For example, the color of the rock samples alone indicate that the redox environment at the two sample sites was different. The orange color indicates  $\text{Fe}^{3+}$ , or an oxidizing environment at CS. It is natural to expect that a more oxidizing environment will lead to less preserved reduced carbon in the sediment from CS, which is apparently observed.

Table 1: Raw Carbonaceous Residue Data for C-T boundary Samples\*

Sample	Depth	Initial mass	Mass GTT	Mass GTT & CR	Mass CR to be etched	Total CR	% CR	%CR, Error
RW 10	66 to 37	1.5459	13.6631	13.6708	7.7	23.1	1.49	0.08
RW 9	37 to 0	1.6114	13.9910	13.9956	4.6	13.8	0.86	0.07
RW 8	0 to -25	1.1009	22.2104	22.2132	2.8	8.4	0.76	0.11
CS 246	11 to 8	1.2125	13.9581	13.9594	1.3	3.6	0.30	0.09
CS 245	8 to 3	1.8760	13.6955	***	***	***	***	***
CS 244	3 to 0	1.2246	14.0344	***	***	***	***	***
CS 243	-5 to -8	1.6145	13.6953	13.6957	0.4	1.2	0.07	0.07
CS 235	-52 to -55	1.3904	14.0651	14.0661	1.0	3.0	0.22	0.09
CS 234	-55 to -63	1.4471	13.9585	13.9596	1.1	3.0	0.21	0.08
CS 233	-63 to -71	1.4393	14.2126	14.2139	1.3	3.9	0.27	0.08

\* Headings are defined as follows:

RW: Red Wash, New Mexico

Chispa Summit, Texas

Depth: depth (cm) from the boundary (boundary is defined as 0cm)

[mass reported in grams +/-0.0002 unless stated otherwise]

Initial mass: mass of rock sample used (g)

Mass GTT: mass of dry glass test tube (g)

CR: carbonaceous residue

Mass GTT & CR: mass glass test tube and carbonaceous residue (g)

Mass CR to be etched: (mg) uncertainty +/-0.4mg

Total CR: total mass of carbonaceous residue [3x Mass CR to be etched] (mg)

%CR: percentage of carbonaceous residue in original rock sample

Error: propagated uncertainty of %CR (+/- value calculated)

\*\*\*: too little residue for etching

Table 2: Carbon Residue Data for England-bound Samples\*

Sample	Mass vial	Mass vial & CR	Mass CR	% CR	%CR, Error
RW 10	7.6884	7.6914	7.0	1.36	0.08
RW 9	7.9605	7.9656	5.1	0.95	0.07
RW 8	7.5068	7.8108	4.0	1.1	0.1
CS 246	8.0030	8.0041	1.1	0.3	0.1
CS 245	8.0181	8.0185	0.4	0.02	0.02
CS 244	7.7054	7.7056	0.2	0.02	0.02
CS 243	7.3062	7.3066	0.4	0.07	0.07
CS 235	7.9056	7.9068	1.2	0.26	0.09
CS 234	7.7439	7.7450	1.1	0.23	0.08
CS 233	7.3880	7.3896	1.6	0.33	0.08

\*: Samples sent to the Open Universtiy for C isotopic analysis. Headings:

RW: Red Wash, New Mexico

CS: Chispa Summit, Texas

CR: carbonaceous residue

Mass CR: (mg) mass carbonaceous residue propigated uncertainty +/-0.4mg

%CR: calculated using mass data from this table

Table 3: Average Percent Bulk Carbon Residue\*

Sample	Average Depth	Average %CR	Error
RW 10	51.5	1.43	0.08
RW 9	18.5	0.90	0.07
RW 8	-12.5	0.9	0.1
CS 246	9.5	0.3	0.1
CS 245	5.5	0.02	0.02
CS 244	1.5	0.02	0.02
CS 243	-6.5	0.07	0.07
CS 235	-53.5	0.24	0.09
CS 234	-59	0.22	0.08
CS 233	-67	0.30	0.08

\* Headings defined as follows:

RW: Red Wash, New Mexico

CS: Chispa Summit, Texas

Average Depth: distance of center of samples from boundary (cm)

Average %CR: Percent carboneous residue calculated from the 2 of the 3 fractions weighed (Tables 1 and 2)



Local differences in the depositional environment can result in vast differences in the accumulation rate of sedimentary material, including all types of carbon. Accumulation rates are normally affected most by stream run-off (input of erosion products). It is possible that CS was fed by streams carrying more erosion products than those which fed RW. If both accumulated carbon at the same rate, a lower %CR in rocks from CS would be expected as is observed.

Despite the obvious differences between the two sites, the percentage of bulk carbon vs distance from the boundary (Table 3; Fig. 3 and 4) follows a similar trend at both CS and RW. Both show a decrease in the amount of reduced carbon at the extinction boundary. Between RW 8, below the boundary, and RW 9, at the boundary, there is little change. The major shift in carbon concentration at this sample site occurs between RW 9 and RW 10, where carbon concentration increases by almost a factor of 2.

At the CS site, the decrease in the percentage of bulk reduced carbon at the boundary is much more dramatic (Fig. 4). A *decrease* in reduced carbon might not be expected at an extinction horizon where plankton became extinct; rather an *increase* would be expected from the rapid accumulation of suddenly-dead plankton at the bottom of the ocean. Rapid accumulation would enhance the preservation of reduced carbon. However, this expectation carries with it several assumptions:

# %Bulk Carbon Residue vs Depth

## Red Wash Creek, New Mexico

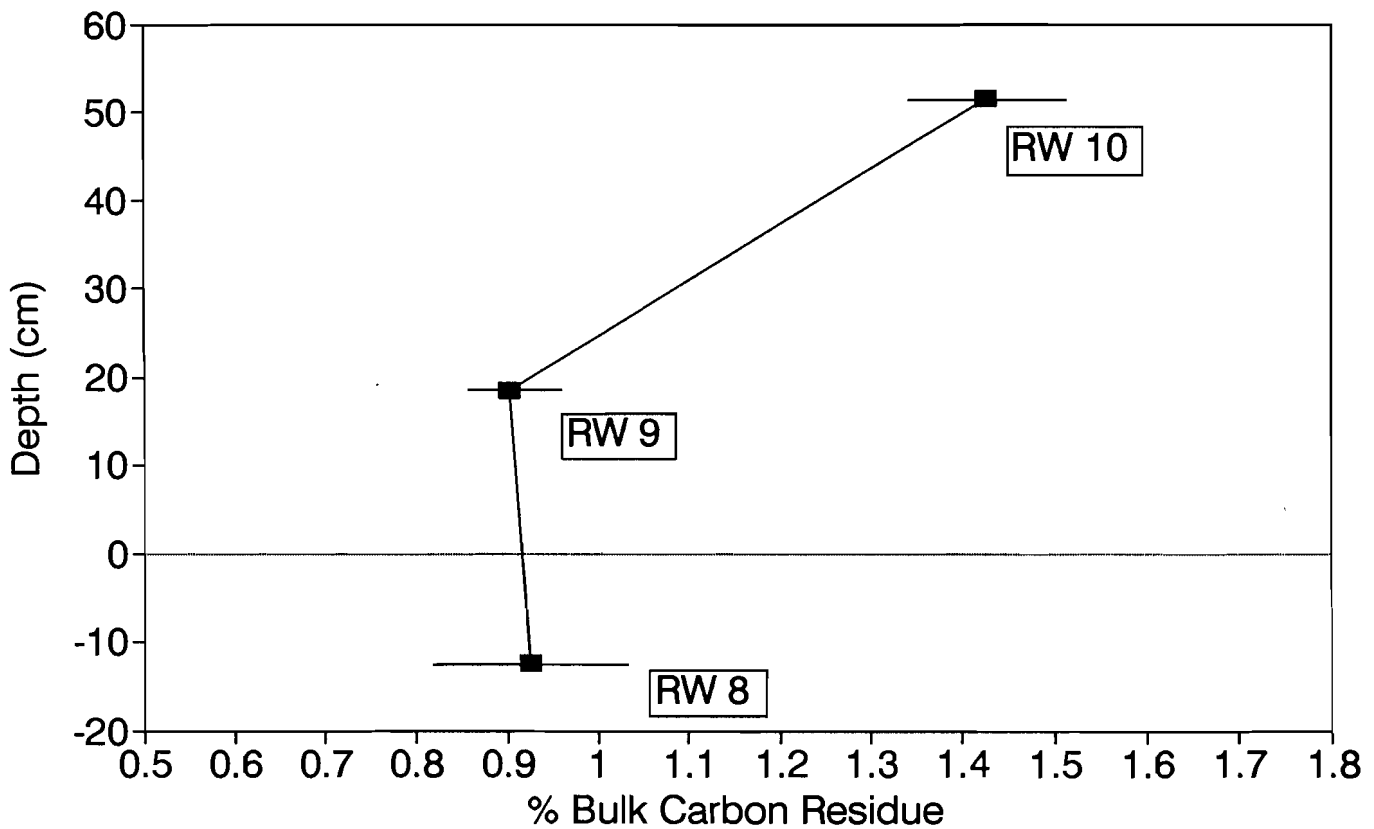


Figure 3: Amount of reduced carbon is slightly lower at the boundary than at the surrounding depths.

# % Bulk Carbon Residue vs Depth

## Chispa Summit, Texas

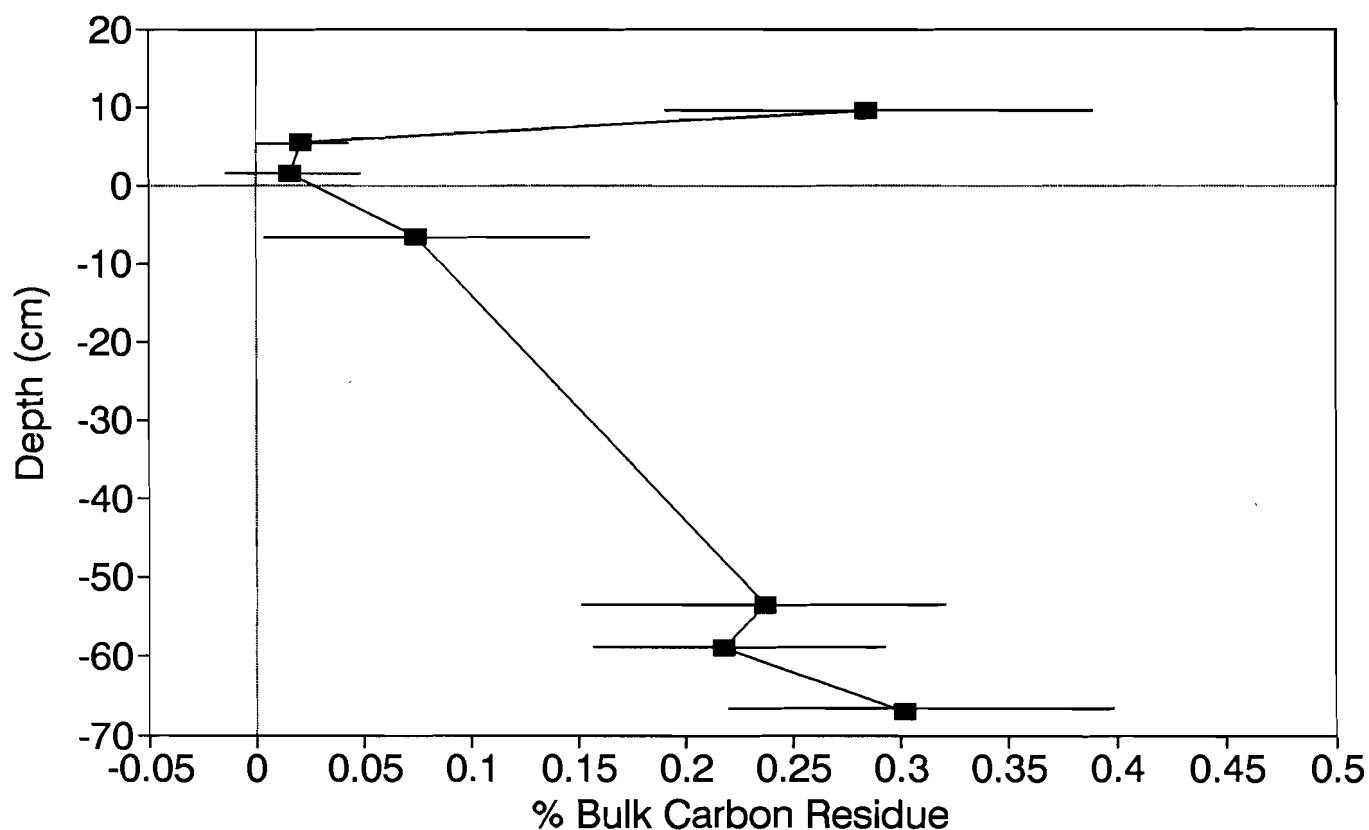


Figure 4: Amount of reduced carbon residue is 10x lower at the boundary than at surrounding depths.

1) That death was sudden and accumulation of plankton (sedimentary carbon) rapid. If the extinctions were not sudden, but gradual, such as the result of gradual climate changes, the dead plankton might not accumulate much faster than under normal conditions, in which case a sudden increase in reduced C at the boundary would not be expected.

2) That if death was sudden, it resulted from an impact. If an impact occurred, the accumulated dust from the meteorite and crater would help preserve carbon on the bottom of the ocean by blanketing it from oxidizing bacteria in the water. There is no indication that boundary material has been derived from any weathered impact material.

The lack of increase in carbon at the boundary is consistent with no enhanced preservation.

There is more organic material in RW samples, than CS samples.

Oxidation of RW samples over time (Tables 4 and 5) shows a dramatic loss in mass compared with CS samples. With the tiny amount of carbon residue remaining in most of the samples, especially those from CS, as well as the limited data available to date, it is difficult to plot the data to find the fractions and half-lives of the carbon components of the residue.

It seems clear from the bulk carbon data, that there is no evidence of either an impact (local or global) or even a *sudden* extinction event. The fact that plankton became extinct at the C-T boundary is undisputed; however, a rapid extinction is questionable. The carbon abundance data available at this time seem to support a slow extinction scenario, as outlined above.

From the carbon isotope data (Table 6) it appears that there is an increase in  $\delta^{13}\text{C}$  from RW 9 to RW 10, while there is little change between RW 8 and RW 9 (Fig. 5). This would indicate an accumulation of isotopically heavier plankton

Table 4: Carbon Residue Etching Data for C-T boundary\*

Sample	M/0 hours	M/2.5 hours	M/6.25 hours	M/245.25 hours
RW 10	13.6708	13.6705	13.6698	13.6648
RW 9	13.9956	13.9956	13.9954	13.9917
RW 8	22.2132	22.2131	22.2125	22.2110
CS 246	13.9594	13.9584	13.9583	13.9580
CS 245	***	***	***	***
CS 244	***	***	***	***
CS 243	13.6957	13.6957	13.6956	22.0502
CS 235	14.0661	14.0659	14.0659	21.4638
CS 234	13.9596	13.9589	13.9589	23.6182
CS 233	14.2139	14.2133	14.2133	14.2130

\* Headings defined as follows:

RW: Red Wash, New Mexico

CS: Chispa Summit, Texas

M/: Mass of samples and glass test tubes/ hours of etch

Three samples transferred to thicker test tubes

Dry weight of the glass test tubes (grams):

CS 243 22.0500

CS 235 21.4635

CS 234 23.6182

Table 5: Mass of Carbon Residue Remaining vs. Time of Etching

Time/hours	Mass/mg							
	RW 10	RW 9	RW 8	CS 246	CS 243	CS 235	CS 234	CS 233
0	7.7	4.6	2.8	1.3	0.4	1.0	1.1	1.3
2.5	7.4	4.6	2.7	0.3	0.4	0.8	0.4	0.7
6.25	6.7	4.4	2.1	0.2	0.3	0.8	0.4	0.7
245.25	1.7	0.7	0.6	-0.1	0.3	0.3	0.4	0.4

Propagated uncertainty for all mass reported is +/-0.4mg

RW: Red Wash, New Mexico

CS: Chispa Summit, Texas

Table 6: Isotopic Analysis of Bulk Residue from Red Wash, Mew Mexico.\* ~

Sample	Average Depth	$\delta^{13}\text{C}(\text{‰})$	$\delta^{13}\text{C}(\text{‰})$ , Error	PPM Carbon	Actual %C	%C, Error
RW 10	51.5	-22.8	0.1	5.37E+05	0.77	0.04
RW 9	18.5	-23.6	0.1	5.64E+05	0.51	0.04
RW 8	-12.5	-23.4	0.1	5.28E+05	0.49	0.05

\* Headings defined as follows:

RW : Red Wash, New Mexico

Average Depth : Average Depth from boundary (cm).

$$\delta^{13}\text{C}(\text{‰}) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} * 1000 \quad \text{where } R = \frac{^{13}\text{C}}{^{12}\text{C}}$$

PPM Carbon: part per million carbon content of samples.

Actual %C: Bulk residues, corrected for non-carbon components.

~ : isotopic data collected at The Open University, England

# Isotopic Composition vs Depth

## Red Wash, New Mexico

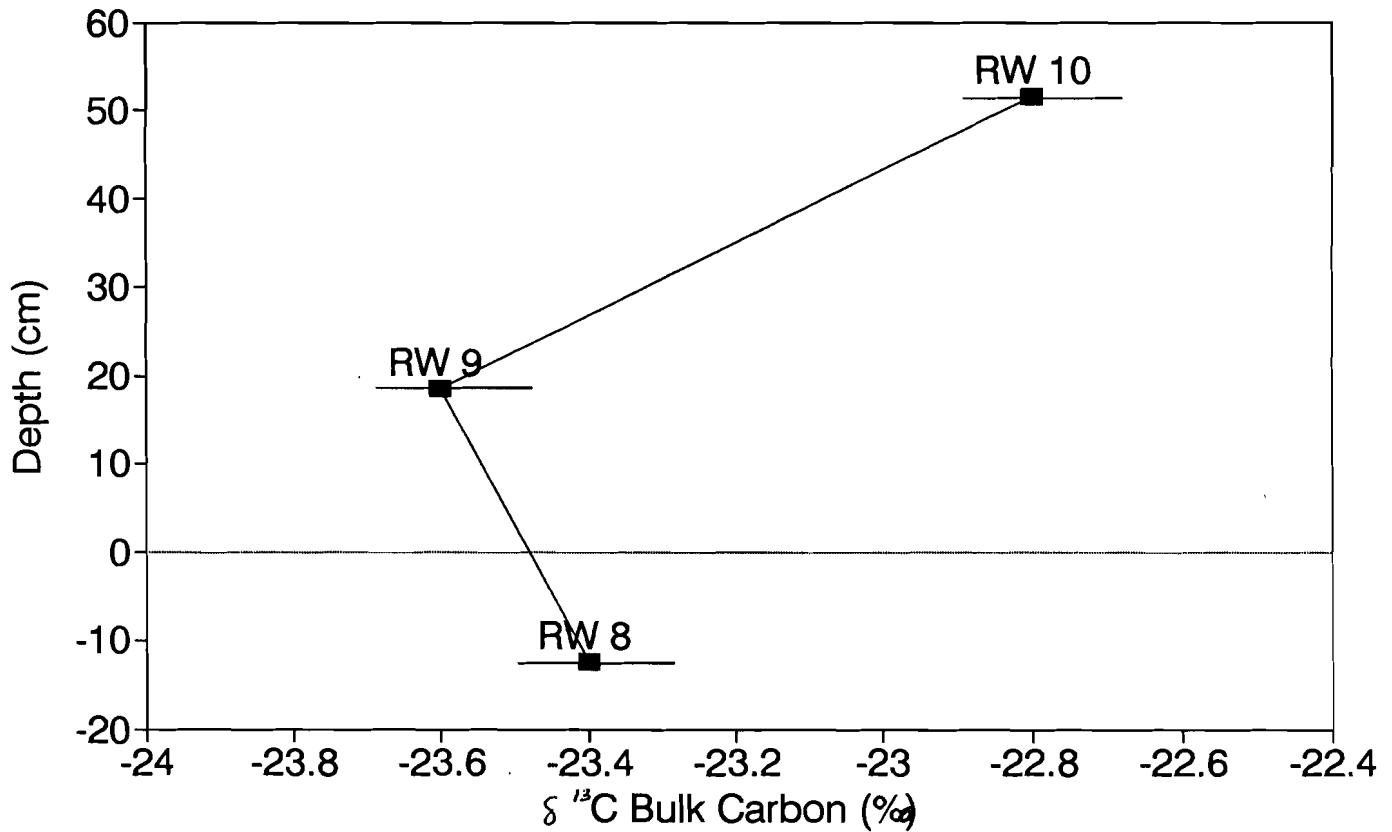


Figure 5: The  $\text{C}^{13}/\text{C}^{12}$  ratio of all reduced carbon increases above the boundary, due to the increased accumulation of an isotopically heavier species.



C4 type plants in the sediment following the extinction event, possibly due to the evolution of new species or a change in the distribution of pre-existing plant species at this site. Since these data reflect bulk carbon composition (organic plus elemental carbon) and not simply the organic fraction of each sample, their interpretation may change as data for the isotopic composition of elemental carbon become available.

If, as the carbon data indicate, the extinction event 92 Ma ago was gradual, what possible mechanisms might have triggered the extinctions? A possible mechanism could involve the opening of deep sea fissures, allowing for metal-rich magma (molten rock) to break through the ocean floor, thereby heating the water. This explains the increase of Ir and other metals found at the extinction boundary and provides a way to kill plankton. The fissures would heat the surrounding water and that water would change ocean circulation patterns, carrying the metals into pre-existing currents and spreading the metals around the globe. This mechanism is supported by the global correlation in metal abundance at the C-T boundary. The added heat from the fissure could lead to the extinction of plankton, if they were not able to adapt to the new water temperature. This scenario is also supported by the fact that isotopically *heavier* plankton increase in abundance after the extinction: C4 plants prefer warmer water.

Combustion analysis of the carbonaceous residue from RW (performed while doing  $^{13}\text{C}/^{12}\text{C}$  determinations) has also revealed that there is a  $\approx 3\%$  higher percentage carbon at the extinction boundary compared with samples above and

below it (Table 6, Figure 6). This increase in the amount of atomic carbon present at the boundary could be the result of slightly more reducing conditions at the time of extinction at this site. It could also be due to a slight influx of more reduced (less aliphatic) carbon from an unknown source. Again, since these data reflect both elemental and organic carbon abundances (unseparated), any interpretation is open to later modification once data for elemental carbon have been acquired.

If the slight increase in %C in the boundary is due to an influx of reduced carbon, one possible source might be soot. Soot is essentially aromatic carbon; the only hetero atoms that are part of a soot molecule are on the exposed edge. This makes the percentage of carbon in soot exceed 70%. The accumulation of any significant amount of soot could account for the difference in the concentration of carbon in the boundary sample. This possibility cannot be checked, of course, until oxidation of bulk residues is complete. Despite the real differences (up to 3%) in %C in CR samples across the boundary, the magnitude of these differences is still small enough not to significantly alter the CR profile (Figure 3) when CR samples are corrected for non-carbon components (Figure 7).

# Reduced C vs Depth

## Red Wash, New Mexico

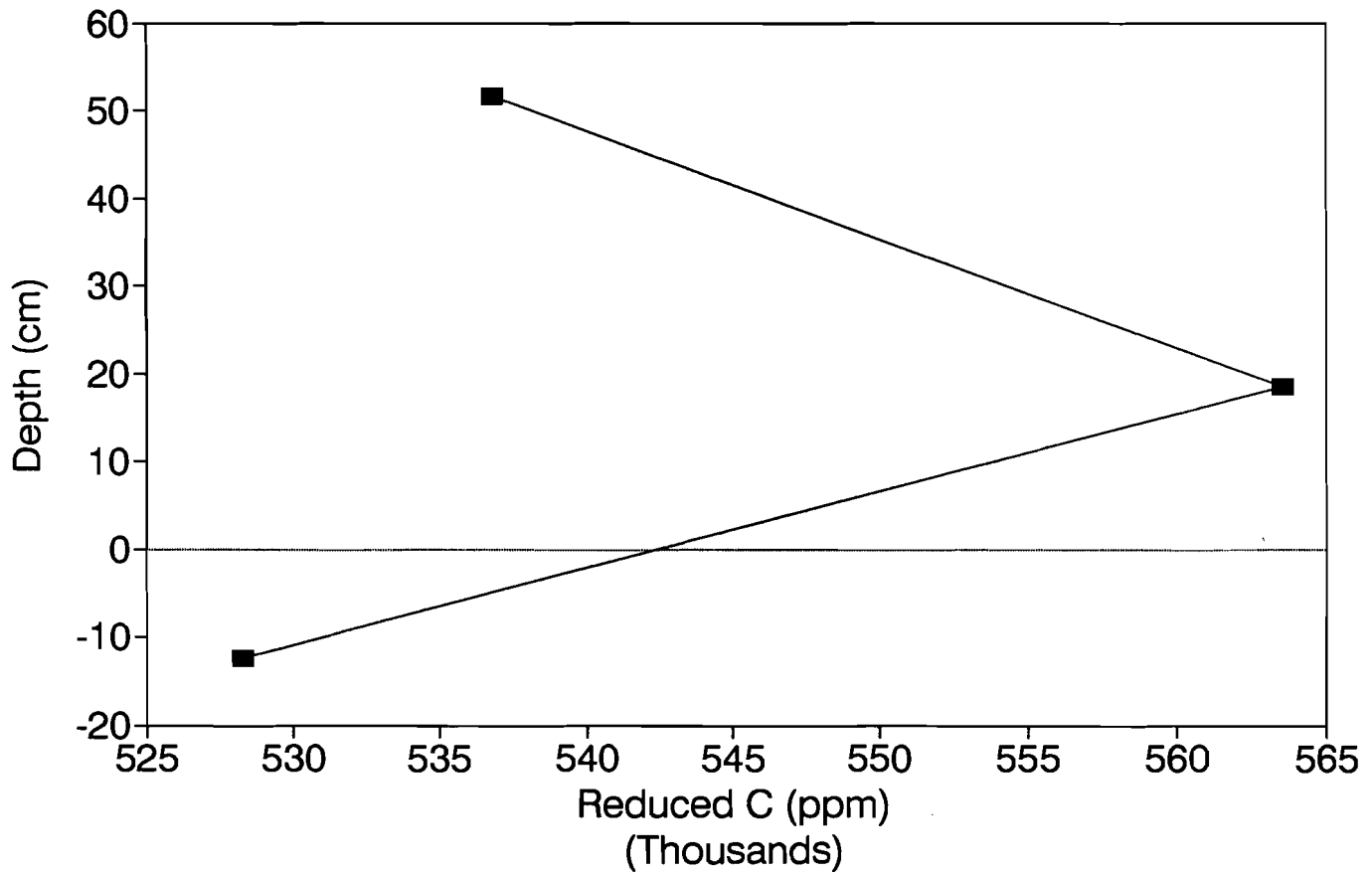


Figure 6: Actual ppm concentration in bulk residue across the C-T boundary, at Red Wash, New Mexico. C concentration increases  $\sim 3\%$  at the boundary.

# Actual %Bulk C vs Depth

## Red Wash, New Mexico

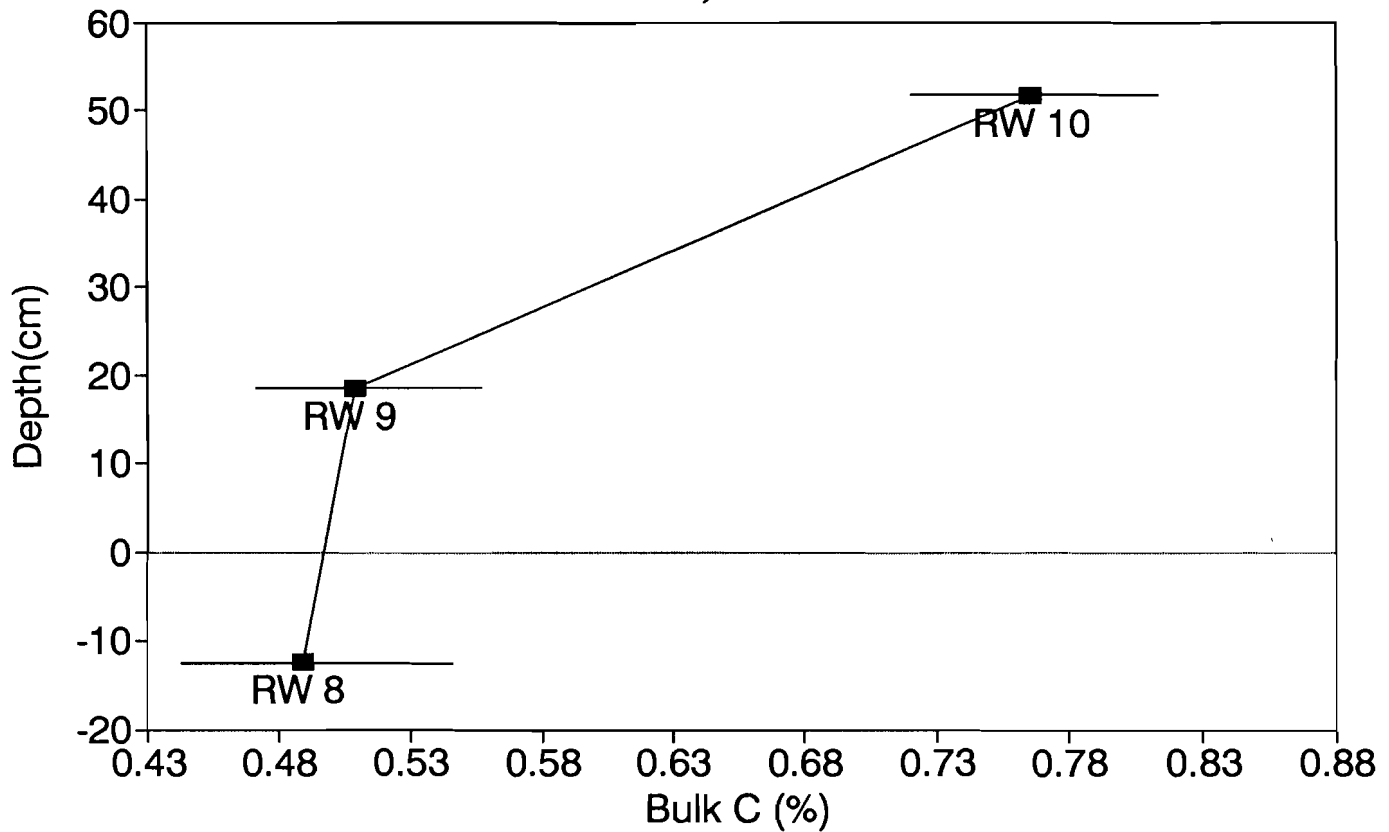


Figure 7: The %Bulk Carbon profile (Fig. 3) has been corrected for non-carbon components, because the %C in the bulk residue is  $\sim 3\%$  higher at the boundary (RW 9), than below it (RW 8).

**Future work:**

Isotopic analysis is currently being done on the bulk reduced carbon portion of all samples. Oxidation of the samples is in progress and will continue until all reactive organic material has been removed. The remainder of the fraction containing elemental carbon and insoluble minerals will be looked at closely under the SEM to determine if soot is present. Also isotopic analysis of the elemental carbon will be done.

## References:

- <sup>1</sup> Raup, David M. and Sepkoski, John Jr., Periodicity of extinctions in the geological past, *Proceedings of the National Academy of Sciences USA*. Vol 18, pp. 801-5, 1984.
- <sup>2</sup> Alvarez, Walter, Toward A Theory of Impact Crises, *Eos*, Vol 67, no. 35, pp. 649, 653-655, 658, 1986.
- <sup>3</sup> Wolbach, Wendy S., Lewis, Roy S., and Anders, Edward, Cretaceous Extinctions: Evidence for Wildfires and the Search for Meteoritic Material, *Science*, Vol. 230, pp. 167-170, 1985.
- <sup>4</sup> Alvarez, Luis, Alvarez, Walter, Asaro, Frank, and Michel, Helen V., Extraterrestrial Cause for the Cretaceous-Tertiary Extinction, *Science*, Vol. 208, no. 4448, pp. 1095-1108, 1980.
- <sup>5</sup> McLaren, Digby J. and Goodfellow, Wayne D., Geological and Biological Consequences of Giant Impacts., *Annual Review of Earth and Planetary Science*, Vol. 18. pp. 123-71, 1990.
- <sup>6</sup> Wolbach, Wendy S., Gilmour, Iain, Anders, Edward, Orth, Charles J., and Brooks, Robert R., Global fire at the Cretaceous-Tertiary boundary, *Nature*, Vol. 334, no. 6184, pp. 665-9, 1988.
- <sup>7</sup> Smit, J. *et al.*, Tektite-bearing, deep-water cluster unit at the Cretaceous-Tertiary boundary in northeast Mexico, *Geology*, vol. 20, pp. 99-103; 1992.
- <sup>8</sup> Orth, C. J., Attrep, M. Jr., and Mao, X. Y., Iridium Abundance Maxima in the Upper Cenomanian Extinction Interval, *Geophysical Research Letters*, Vol. 15, no. 4, pp. 346-9, 1988.
- <sup>9</sup> Orth, C. J., Attrep, M. Jr., Quintana, L. R., Elder, W. P., Kauffman, E. G., Diner, R., and Villamil, T., Elemental Abundance Anomalies in the Late Cenomanian Extinction Interval: A Search for the Source(s), *Geological Society of America Bulletin*, Submitted
- <sup>10</sup> Hart, Malcolm B. and Leary, Paul N., Stepwise mass extinctions: the case for the Late Cenomanian event, *Terra Nova*, Vol. 3, pp.142-7, 1990.
- <sup>11</sup> Wolbach, Wendy S. and Anders, Edward, Elemental carbon in sediments: Determination and isotopic analysis in the presence of kerogen. *Geochimica et Cosmochimica Acta*, Vol. 53, pp.1637-47, 1989.

<sup>12</sup> Arneth, J., Matzigkeit, U., and Boos, A., Carbon isotope geochemistry of the Cretaceous-Tertiary section of the Wasserfallgraben, Lattenbirge, southeast Germany. *Earth and Planetary Science Letters*, Vol. 75, pp.50-8, 1985.

<sup>13</sup> Deines, P., The isotopic composition of reduced carbon in the terrestrial environment. *Handbook of Environmental Isotope Geochemistry*, pp. 329-407, 1980.