

# *Sulfur isotopic compositions across terrestrial Cretaceous-Tertiary boundary successions*

**Teruyuki Maruoka**  
**Christian Koeberl**

*Institute of Geochemistry, University of Vienna, Althanstrasse 14, A-1090 Vienna, Austria*

**Jason Newton**

*Institute of Geochemistry, University of Vienna, Althanstrasse 14, A-1090 Vienna, Austria, and Department of Earth Sciences, University of California, Santa Cruz, California 95064, USA*

**Iain Gilmour**

*Planetary Science Research Institute, Open University, Milton Keynes MK7 6AA, UK*

**Bruce F. Bohor**

*U.S. Geological Survey, MS 926A, Denver Federal Center, Denver, Colorado 80225-0046, USA*

## ABSTRACT

**Isotopic compositions of sulfur and concentrations of sulfur and carbon have been measured for sedimentary rocks across terrestrial Cretaceous-Tertiary (K-T) boundary successions that originated from flood-plain and backswamp environments. Organic carbon contents are relatively constant below the boundary (26 cm for the Dogie Creek section and 9 cm for the Brownie Butte section), but change abruptly at the K-T boundary. At the K-T event, a high input of sulfate to the freshwater wetlands might have resulted from the melt ejecta and/or acid rain. We interpret the low ratio of organic C to nonorganic S at the melt ejecta layer and sulfur isotopic data as consistent with this hypothesis; however, additional analyses across a thicker interval are necessary to rule out alternative hypotheses.**

## INTRODUCTION

Most sulfides present in sediments originate from H<sub>2</sub>S produced by sulfate-reducing bacteria (e.g., Berner, 1984). This process is accompanied by a fractionation of the sulfur isotopes that results in sulfide being <sup>34</sup>S depleted with respect to the parent sulfate. The extent of isotopic fractionation between sulfate and sulfide is dependent on the kinetics of the sulfate reduction reaction (e.g., Kaplan and Rittenberg, 1964; Chambers and Trudinger, 1979), which, in turn, is affected by the environment of deposition. Consequently, the isotopic composition of sulfide can be used as a proxy for environmental conditions such as the temperature of water, sulfate abundance, and types of electron source.

Holser et al. (1988) observed that  $\delta^{34}\text{S}$  values of sulfides

and sulfate in marine sediments have not changed much since the end of the Cretaceous. However, there have been relatively few studies of sulfur across the Cretaceous-Tertiary (K-T) boundary. Schmitz et al. (1988) reported  $\delta^{34}\text{S}$  values of  $-31.5\%$  in metal-rich pyrite spherules that occur in the basal Fish Clay from the marine K-T succession at Stevns Klint, Denmark. Heymann et al. (1998) observed native sulfur in a spherule-bearing unit from marine K-T successions around the Gulf of Mexico with  $\delta^{34}\text{S}$  values of  $-24.9\%$ . Both these  $\delta^{34}\text{S}$  values are similar to those observed in Late Cretaceous sedimentary rocks, and suggest that the geological record provides no indication of major perturbations in the microbiological utilization of sulfur across the K-T boundary. However, Kajiwarra and Kaiho (1991, 1992) observed a temporary and marked increase in pyrite  $\delta^{34}\text{S}$  values across the K-T boundary in the

marine succession at Kawaruppu, Hokkaido, Japan, and suggested an anoxic depositional environment immediately after the K-T boundary as an explanation for the variation in  $\delta^{34}\text{S}$  values.

Holmes and Bohor (1994) observed an increase in  $\delta^{34}\text{S}$  values in the terrestrial K-T boundary claystone unit at the Sugarite site in the Raton Basin, New Mexico (Pillmore and Flores, 1987). The  $\delta^{34}\text{S}$  value increases by 3.5‰ and the  $\delta^{13}\text{C}$  value of the organic matter is also  $\sim 2\text{‰}$ – $3\text{‰}$  heavier in the boundary claystone unit (fireball and melt ejecta layer) than in the surrounding coal. They suggested impact-derived carbon and sulfur from vaporized marine target rocks as the origin of the isotopically heavier S and C in the boundary claystone. The terrestrial environment is suitable for the detection of an impact-derived sulfate input because the concentrations of sulfate in terrestrial environments are generally low relative to marine environments, and the perturbation effects are minimal in terrestrial environments. However, it is important to distinguish isotopically heavy S originating from vaporization of target rocks from that associated with environmental change caused by the K-T event. In this study we determined S contents and  $\delta^{34}\text{S}$  values in sedimentary rocks across two K-T boundary sequences and used these data to examine paleoenvironmental conditions of terrestrial successions across the K-T boundary from the Western Interior of the United States.

## SAMPLES

### *Dogie Creek, Wyoming*

We analyzed 17 samples from 26 cm below the boundary to 16 cm above. They include Upper Cretaceous carbonaceous shale, melt ejecta layer (boundary claystone), fireball layer (magic layer), and lower Tertiary clay-shale and lignite (Bohor et al., 1987).

### *Brownie Butte, Montana*

A series of 11 samples in 2 cm intervals from 9 cm below the boundary to 12 cm above was analyzed (Bohor et al., 1984). At the time of the terminal Cretaceous event, this locality was part of a large area consisting of flood plains and backswamps, allowing the deposition of sandstones interlayered with coal, mudstone, carbonaceous shale, and siltstone (Tschudy, 1970).

## EXPERIMENTAL METHODS

### *Mass spectrometry*

Concentrations and isotopic compositions of sulfur were measured in bulk sediments and 5 M HCl-treated residues using a helium-gas continuous flow isotope ratio mass spectrometer (CF-IR-MS; Micromass Optima; Giesemann et al., 1994). The concentrations of carbon were measured using a thermal conductivity detector (TCD; Carlo Erba) with a combustion fur-

nace, followed by measurement in the mass spectrometer. The samples were weighed into  $12 \times 5$  mm tin capsule with a mixture of  $\text{V}_2\text{O}_5$  and  $\text{SiO}_2$  to promote full combustion (Yanagisawa and Sakai, 1983).

The  $\delta^{34}\text{S}$  values were calculated relative to Canyon Diablo Troilite (CDT) based on comparison with the analyses of two silver sulfide standards of International Atomic Energy Agency (IAEA) (IAEA-S-1,  $-0.3\text{‰}$  CDT; IAEA-S-2,  $+22\text{‰}$  CDT; Coplen and Krouse, 1998) and determined with a measured precision of  $\pm 0.4\text{‰}$  ( $1\sigma$ ). The reference sulfides were also used in the calibration of the sulfur contents. The contents of S were determined with a precision of  $\sim \pm 5$  rel%. An elemental standard (Acetanilide Standard, ThermoQuest Italia S.p.A.) was used in the calibration of the C contents. The contents of C were determined with a precision of  $\sim 1$  rel% for 2 mg C and 10 rel% for 0.2 mg C.

### *Acid treatment*

For each sample, we treated  $\sim 100$ – $200$  mg of powdered rock for 30 min (including 20 min for centrifugation) in  $\sim 5$  mL of 5 M HCl to eliminate sulfate and carbonate in the samples. Treatment of pure pyrite and gypsum test samples resulted in 86% and 16% recovery yields, respectively. For some samples, the sulfate was collected in the form of  $\text{BaSO}_4$  by precipitation from the solutions through the addition of  $\sim 5$  mL of  $\text{BaCl}_2$  (2 M) to the solutions.

## RESULTS AND DISCUSSION

Concentrations of carbon and sulfur together with isotopic compositions of sulfur in bulk samples and 5 M HCl residues are given in Table 1. Figure 1 shows  $\delta^{34}\text{S}$  values against C/S ratio in the 5 M HCl residues. The  $\delta^{34}\text{S}$  values are positively correlated with the C/S ratios, indicating that the organic-rich rocks contain abundant organic matter with respect to S. The organic sulfur has a high C/S ratio and high  $\delta^{34}\text{S}$  value and disulfide sulfur (acid nonvolatile sulfur, which mainly consists of pyrite) with a low  $\delta^{34}\text{S}$  value. The  $\delta^{34}\text{S}$  value of the 5 M HCl residue of LC-86-1-A ( $-1.95 \pm 0.46$ ) is the same as that of the bulk sample ( $-1.64 \pm 0.50$ ), although the C/S values vary from 29.0 to 6.1 (Fig. 2). The  $\delta^{34}\text{S}$  value of the 5 M HCl residue of BB-3 ( $-1.16 \pm 0.13$ ) is the same as that of the bulk sample ( $-0.97 \pm 0.15$ ), although the C/S values vary from 20.3 to 12.0 (Fig. 2). These observations indicate that the presence of organic sulfur does not severely affect the  $\delta^{34}\text{S}$  in the samples having these ranges of the C/S ratio (i.e.,  $<30$  for Dogie Creek samples and  $<20$  for Brownie Butte samples). However, the  $\delta^{34}\text{S}$  values of the 5 M HCl residue with C/S ratios exceeding these values become higher than that of the bulk sample due to the effect of organic sulfur (Fig. 3; e.g., 5 M HCl residues of LC-86-K and L, residue and bulk sample of BB-6, BB-7, and BB-8). Therefore, the  $\delta^{34}\text{S}$  values with C/S ratios of less than the values mentioned here can be regarded as repre-

TABLE 1. CONCENTRATION OF CARBON AND SULFUR AND ISOTOPIC COMPOSITION OF SULFUR IN CRETACEOUS-TERTIARY BOUNDARY SEDIMENTS

Sample	Depth from		Description	Bulk analysis			Analysis after 5 M HCl			Sulfate	
	Bottom (cm)	Top (cm)		C (wt%)	S (wt%)	$\delta^{34}\text{S}$ (‰)	C (wt%)	S (wt%)	$\delta^{34}\text{S}$ (‰)	S Yield (wt%)	$\delta^{34}\text{S}$ (‰)
Dogie Creek											
LC-86-10	14	16	Carbonaceous shale	2.54 ± 0.28	0.219 ± 0.031	-3.87 ± 0.39	2.58 ± 0.32	0.134 ± 0.008	-5.79 ± 0.37	n.d	
LC-86-1N	8	11	Lignite	23.17 ± 1.37	0.631 ± 0.037	0.49 ± 0.38	27.19 ± 1.47	0.576 ± 0.099	0.68 ± 0.55	n.d	
LC-86-1M	4	6	Clay-shale	5.43 ± 0.43	2.618 ± 0.302	-3.80 ± 0.34	4.92 ± 1.23	1.805 ± 0.209	-5.52 ± 0.74	0.216	-2.82 ± 0.13
LC-86-1L	2	4	Clay-shale	1.15 ± 0.16	0.051 ± 0.012	0.57 ± 0.56	1.04 ± 0.08	0.024 ± 0.003	3.17 ± 0.59	n.d	
LC-86-1K	0	2	Clay-shale	0.99 ± 0.17	0.051 ± 0.002	-0.30 ± 0.51	1.02 ± 0.14	0.020 ± 0.003	2.87 ± 0.50	n.d	
Fireball Layer			Smectitic claystone	4.57	1.462 ± 0.033	-4.60 ± 0.79	4.09 ± 0.22	1.256 ± 0.030	-6.58 ± 0.26	0.078	-5.89
Melt Ejecta Layer			Kaolinitic claystone	2.92	1.318 ± 0.033	-3.33 ± 0.65	3.36 ± 0.16	0.864 ± 0.088	-4.99 ± 0.20	0.049	-4.67 ± 0.22
LC-86-1H	-2	0	Carbonaceous shale	0.50 ± 0.10	0.054 ± 0.015	-2.85 ± 0.57	0.54 ± 0.01	0.039 ± 0.001	-4.54 ± 0.34	n.d	
LC-86-1G	-4	-2	Carbonaceous shale	0.60 ± 0.10	0.206 ± 0.059	-2.53 ± 0.86	0.71 ± 0.11	0.115 ± 0.004	-3.24 ± 0.76	0.009	-2.17
LC-86-1F	-6	-4	Carbonaceous shale	0.56 ± 0.02	0.062 ± 0.004	-2.61 ± 0.28	0.71 ± 0.07	0.044 ± 0.002	-2.19 ± 0.26	n.d	
LC-86-1E	-10	-8	Carbonaceous shale	0.64 ± 0.11	0.085 ± 0.009	-2.44 ± 0.59	0.72 ± 0.05	0.043 ± 0.002	-2.51 ± 0.08	n.d	
LC-86-1D	-14	-12	Carbonaceous shale	1.71	0.416 ± 0.258	-2.32 ± 0.38	0.81 ± 0.17	0.136 ± 0.011	-4.06 ± 0.64	0.009	-1.67 ± 0.03
LC-86-1C	-18	-16	Carbonaceous shale	0.72 ± 0.11	0.105 ± 0.000	-3.39 ± 0.25	0.83 ± 0.04	0.070 ± 0.003	-3.54 ± 0.42	n.d	
LC-86-1B	-22	-20	Carbonaceous shale	0.65 ± 0.15	0.175 ± 0.018	-0.54 ± 0.29	0.67 ± 0.08	0.029 ± 0.001	0.07 ± 0.46	0.012	-1.25 ± 0.10
LC-86-1A	-26	-24	Carbonaceous shale	0.50 ± 0.03	0.083 ± 0.007	-1.64 ± 0.50	0.62 ± 0.03	0.021 ± 0.001	-1.95 ± 0.46	n.d	-1.62
Brownie Butte											
BB-11	10	12	Gray shale	0.70 ± 0.10	0.246 ± 0.008	-3.15 ± 0.29	0.40 ± 0.07	0.069 ± 0.004	-3.69 ± 0.19	n.d	
BB-10	8	10	Gray shale	0.68 ± 0.02	0.204 ± 0.003	-2.99 ± 0.39	0.56 ± 0.10	0.047 ± 0.002	-1.33 ± 0.20	n.d	
BB-9	6	9	Carbonaceous shale	9.92 ± 1.22	0.899 ± 0.017	1.20 ± 0.11	8.41 ± 0.10	0.275 ± 0.002	5.52 ± 0.16	0.291	-1.58 ± 0.11
BB-8	4	6	Lignite	38.45 ± 3.36	1.463 ± 0.021	5.40 ± 0.23	38.98 ± 1.00	0.828 ± 0.028	12.91 ± 0.67	n.d	
BB-7	2	4	Lignite	44.50 ± 3.29	2.177 ± 0.014	6.00 ± 0.35	48.76 ± 5.44	1.204 ± 0.275	11.10 ± 0.68	n.d	
BB-6	0	2	Lignite	20.72 ± 8.35	1.587 ± 0.245	1.72 ± 0.23	15.74 ± 1.04	0.737 ± 0.024	3.82 ± 0.26	0.292	-3.36 ± 0.49
BB-14			Fireball	4.19 ± 0.41	0.377 ± 0.016	-1.85 ± 0.39	n.d.				
BB-13			Melt ejecta	0.75	0.344 ± 0.010	-0.83 ± 0.30	0.82 ± 0.43	0.113 ± 0.019	-0.19 ± 0.34	0.041	-1.30 ± 0.04
BB-5	-2	0	Gray shale	0.81	0.236 ± 0.004	-1.62 ± 0.29	0.60 ± 0.06	0.082 ± 0.002	-2.25 ± 0.42	0.042	-2.49 ± 0.17
BB-4	-4	-2	Carbonaceous shale	4.50 ± 0.89	0.491 ± 0.002	-1.39 ± 0.26	3.16 ± 0.11	0.221 ± 0.013	-1.77 ± 0.16	n.d	
BB-3	-6	-4	Carbonaceous shale	4.01 ± 0.28	0.334 ± 0.010	-0.97 ± 0.15	3.33 ± 0.32	0.164 ± 0.006	-1.16 ± 0.13	n.d	
BB-2	-8	-6	Carbonaceous shale	3.94 ± 0.49	0.281 ± 0.003	-0.18 ± 0.43	3.50 ± 0.29	0.098 ± 0.009	0.93 ± 0.23	n.d	
BB-1	-9	-8	Carbonaceous shale	4.08 ± 0.63	0.325 ± 0.010	1.43 ± 0.26	3.29 ± 0.28	0.107 ± 0.005	1.86 ± 0.10	0.034	0.65

Note: n.d. — not determined; KTB — Cretaceous-Tertiary boundary

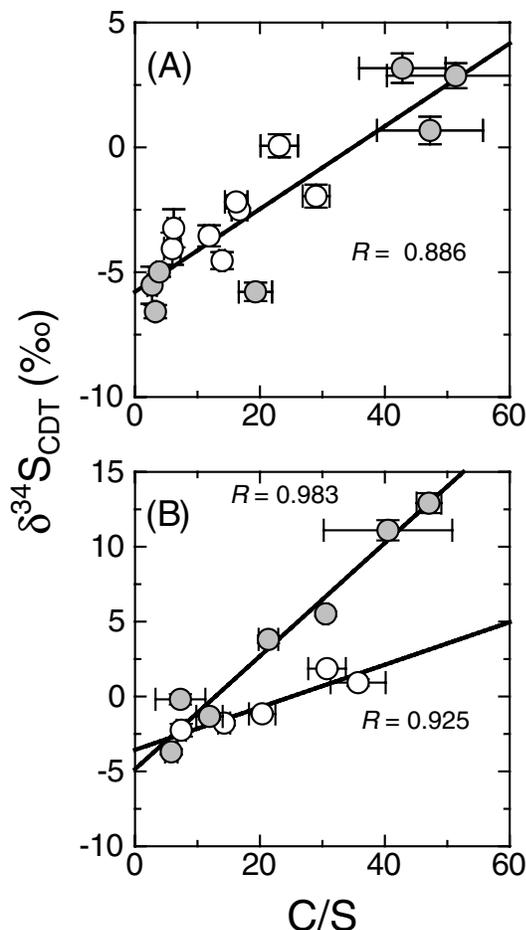


Figure 1. Isotopic compositions of sulfur against C/S ratio in 5 M HCl residue of sediments from (A) Dogie Creek and (B) Brownie Butte. Open and gray circles represent data below and above Cretaceous-Tertiary boundary, respectively. Solid lines represent regression lines. For Brownie Butte samples, two lines can be obtained from data of post- and pre-boundary sediments. Isotopic compositions are given as deviation from that of Canyon Diablo Troilite (CDT).

senting the  $\delta^{34}\text{S}$  values of nonorganic sulfur. For all samples, except for the coal-bearing samples (i.e., Dogie Creek sample LC-86-N and Brownie Butte samples BB-6, BB-7, and BB-8), the C/S ratios of the bulk samples are less than these critical values. Therefore, the  $\delta^{34}\text{S}$  values of the bulk samples of non-coal sediments can be used for our discussion.

Weathering causes the oxidation of sulfide to sulfate, such as barite and celestite, as suggested by Schmitz (1989). For most of the samples with a C/S ratio lower than the limit stated in the preceding, no difference of the  $\delta^{34}\text{S}$  values between the 5 M HCl residue and the bulk is observed, suggesting that the oxidation did not severely affect the  $\delta^{34}\text{S}$  values. However, the  $\delta^{34}\text{S}$  values of the 5 M HCl residue of such samples as LC-86-D, LC-86-H, LC-86-M, and LC-86-O, fireball, and melt eject layer, for the Dogie Creek samples, are different from those of the bulk samples. These differences could indicate that

the oxidation of sulfide affected the  $\delta^{34}\text{S}$  values of sulfide for these samples. Although some fraction of the sulfur might be lost during weathering, the  $\delta^{34}\text{S}$  value of the initial sulfide may be restricted between that of the residual component (i.e., bulk sample) and that of the lost component. The latter component can be represented by the  $\delta^{34}\text{S}$  value of the acid-volatile sulfate (Table 1), because some of the acid-volatile sulfate might be dissolved during weathering. However, because the  $\delta^{34}\text{S}$  values of the acid-volatile sulfate are generally similar to those of the bulk samples (Fig. 3), the loss of sulfur is probably not significant and should not affect the  $\delta^{34}\text{S}$  values of the bulk samples.

#### *C and S concentrations and S isotope compositions across the boundary*

**Below the K-T boundary.** Concentrations of total organic carbon (calculated using the carbon content in the 5 M HCl residue and mass losses during 5 M HCl treatment; Table 1) and total sulfur (equivalent to the sulfur content in the bulk sediment) are shown in Figure 4.

The concentrations of organic carbon are relatively constant below the K-T boundary ( $0.72\% \pm 0.07\%$  from 26 cm to 2 cm below the boundary for the Dogie Creek sediments;  $3.32\% \pm 0.14\%$  from 9 cm to 2 cm for the Brownie Butte sediments). Organic carbon burial efficiency (the ratio of the carbon burial rate and the carbon flux to the sediment surface) was shown to be a function of sedimentation rate (Henrichs and Reeburgh, 1987). At higher sedimentation rates, labile and metabolizable organic material undergoes a shorter period of oxic and suboxic degradation in the surface of sediments. Therefore, the constancy of the organic carbon concentration (i.e., the ratio of the carbon burial rate to the sedimentation rate) implies that the carbon flux should be expressed as a function of sedimentation rate. We have no reason to assume that the carbon flux is affected by the sedimentation rate, because of the difference of origin between the carbon flux and the sediments. The former originates from the biogenic activity and the latter is dominated by the influx of lithic material. Therefore, it is likely that both parameters, carbon flux and sedimentation rate, were constant over the short interval analyzed.

**At the K-T boundary (melt ejecta layer and fireball layer).** The ratios of organic C to bulk S in the melt-ejecta layer ( $2.88 \pm 0.15$  for Dogie Creek site and  $2.57 \pm 1.35$  for Brownie Butte site) are similar to the mean C/S value for the marine sediments ( $1.8 \pm 0.5$  for Devonian to Tertiary marine shale; Raiswell and Berner, 1986). In normal (noneuxinic) marine sediments, where dissolved sulfate and iron minerals are abundant, organic matter is the major control on pyrite formation (Berner, 1984). In contrast, pyrite formation in nonmarine, freshwater sediments is not significantly limited by the abundance of organic matter, because abundant organic matter is available in freshwater environments (Berner and Raiswell, 1984). Therefore, the low C/S ratios, similar to the marine sediments, indicate that the sulfate concentrations in the water of the wetlands

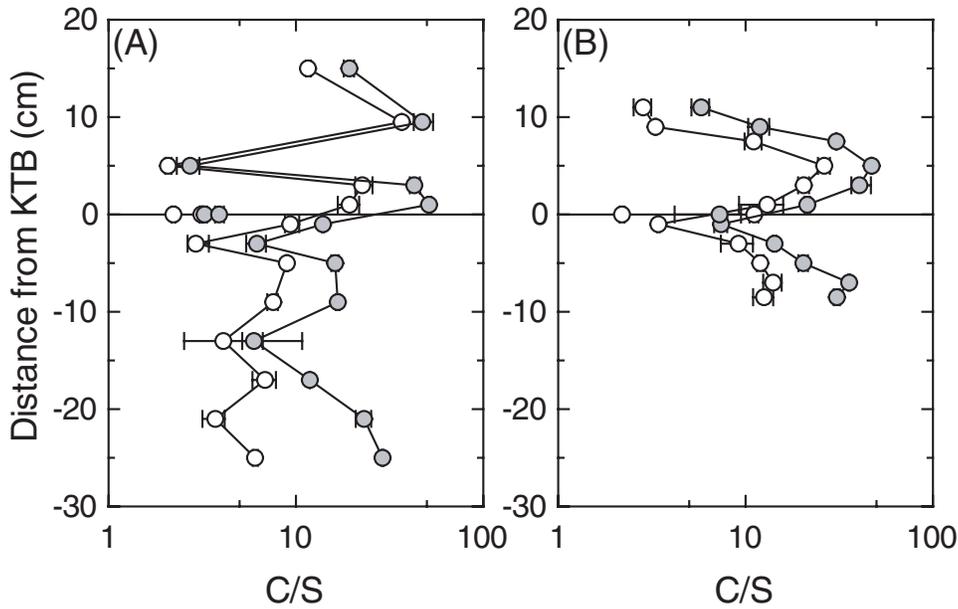


Figure 2. Ratio of organic carbon to sulfur across Cretaceous-Tertiary (K-T) boundary (KTB) at (A) Dogie Creek and (B) Brownie Butte. Open and gray circles represent data for bulk sample and 5 M HCl residue, respectively. Distances from K-T boundary are given from center of boundary layer.

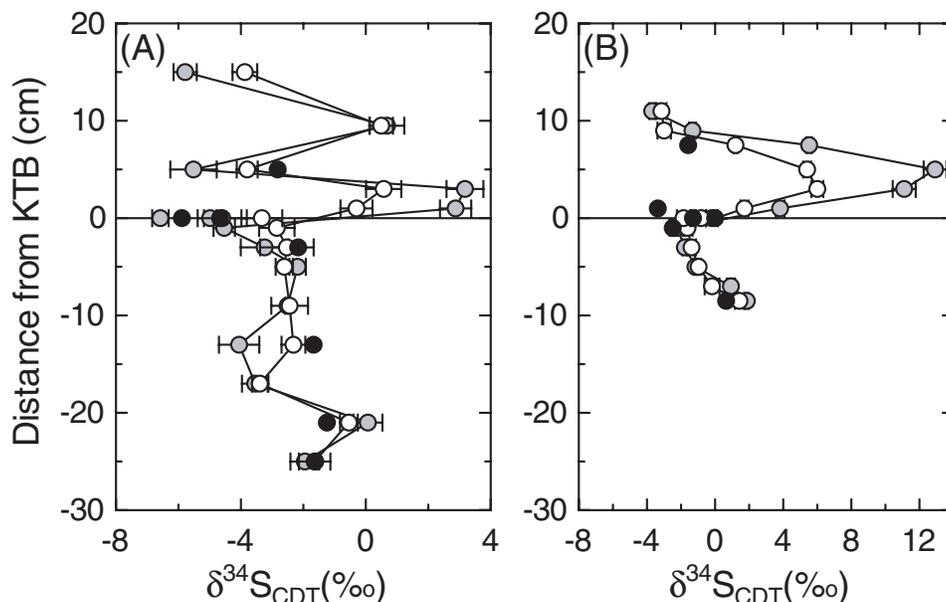


Figure 3. Isotopic composition of sulfur across Cretaceous-Tertiary (K-T) boundary (KTB) at (A) Dogie Creek and (B) Brownie Butte sites. Open, gray, and closed circles represent data for bulk sample, 5 M HCl residue, and acid-volatile sulfate, respectively. Distances from K-T boundary are given from center of boundary layer. CDT is Canyon Diablo Troilite.

at the period of melt ejecta deposition might be much higher relative to those at other periods. The accumulation of sulfides in lake sediments increases as the sulfate concentration increases (e.g., Nriagu and Coker, 1983; Fry, 1986). The melt ejecta and/or acid rain induced by the K-T impact event (Sigurdsson et al., 1992) may have led to such a higher concentration in the wetlands.

An increase of  $\text{Fe}^{2+}$  ions also causes the high concentration of pyritic sulfur. However, a higher amount of  $\text{Fe}^{2+}$  ions may be accompanied with a higher  $\delta^{34}\text{S}$  value, as stated in detail in the following. Therefore, it cannot explain the low C/S ratio at the boundary.

Sheehan and Fastovsky (1992) noted only a minor extinc-

tion of freshwater taxa (10%) at the K-T boundary. This observation appears to be inconsistent with the acid rain scenario. However, acid rain does not have to cause the extinction of freshwater animals, if the acid addition did not exceed the ability of acid-neutralization of the wetlands. Moreover, olivine, which might have formed during the K-T impact, and subsequently altered to clay minerals (Evans et al., 1994), can act as an acid buffer (cf. Schuiling et al., 1986). During dissolution of olivine in acid,  $\text{Mg}^{2+}$  ions are replaced by  $\text{H}^+$ , yielding  $\text{Si}(\text{OH})_4$  monomers and  $\text{Mg}^{2+}$  ions in solution. Because the rate of neutralization depends on the geometrical surface area of the olivine grains (e.g., Jonckbloedt, 1998), small or porous grains of the condensed mafic droplets induced by the impact may

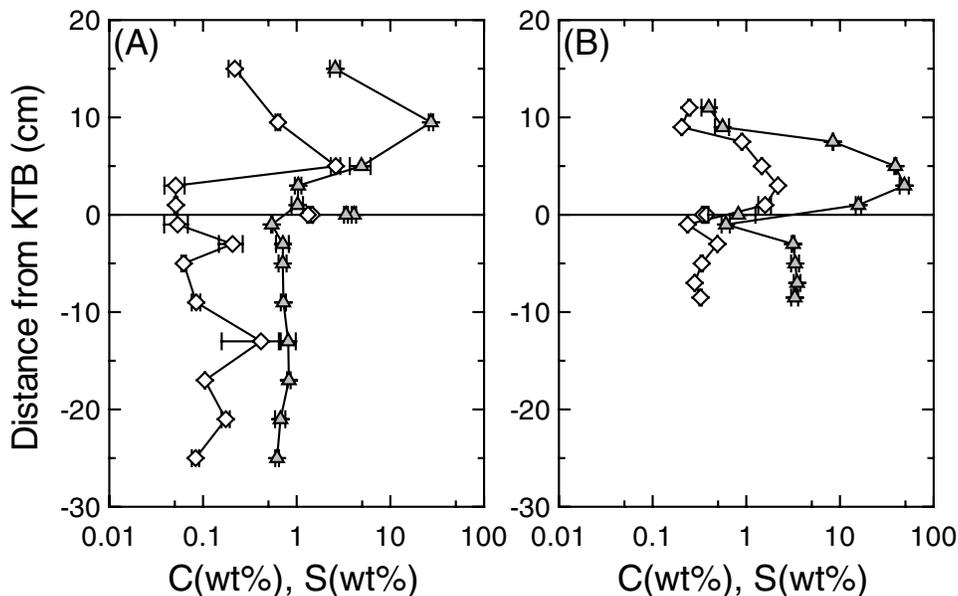


Figure 4. Concentration profiles of organic carbon and total sulfur across Cretaceous-Tertiary (K-T) boundary (KTB) at (A) Dogie Creek and (B) Brownie Butte. Triangles and diamonds represent data for carbon and sulfur, respectively. Distances from K-T boundary are given from center of boundary layer.

improve neutralization. Therefore, neutralization by olivine grains might help to prevent the extinction of freshwater animals. During neutralization, anions, such as sulfate, should remain in solution. The scenario of olivine-assisted neutralization is consistent with the high input of sulfate from melt ejecta and/or acid rains.

**Above the K-T boundary.** Concentrations of organic carbon and total sulfur reached a maximum after the K-T boundary (Fig. 4). The variation of carbon concentrations should reflect changes in the environmental factors, such as deposition rate, oxygen concentration in wetland waters, organic input, and water temperature. However, because the distance above the K-T boundary of the Dogie Creek section to the maximum in total S concentration (4–6 cm above the boundary; Fig. 4) is different from that of the organic C concentrations (8–11 cm above the boundary; Fig. 4), the environmental conditions that caused the variation of sulfur and organic concentrations might have been different.

The maximum concentration of nonorganic sulfur corresponds with minimum  $\delta^{34}\text{S}$  values above the K-T boundary (including the boundary layer) for the Dogie Creek sediments. The maxima at the melt-ejecta and fireball layer and at 4–6 cm above the boundary (LC-86-1-M) were accompanied by a minimum of the  $\delta^{34}\text{S}$  values; i.e., values are negatively correlated with the concentration of sulfur.

Under conditions in which the concentration of  $\text{Fe}^{2+}$  ions is not limited by the formation of pyrite, the higher concentration of sulfate ions results in a higher residual fraction of sulfate, reflecting the higher isotopic fractionation between sulfate and microbiological  $\text{H}_2\text{S}$  (the lower  $\delta^{34}\text{S}$  values). Sulfate reduction rate,  $R$ , can be expressed using the concentration of sulfate,  $[\text{S}]$ , as  $1/R = a/[\text{S}] + b$ , where  $a$  and  $b$  are constants ( $a, b > 0$ ) (Boudreau and Westrich, 1984). The fraction of reduced sulfate,

$F$ , can be obtained as  $F = (\Sigma R \Delta t)/[\text{S}]_0$ , where  $[\text{S}]_0$  represents the initial sulfate concentration in the water incorporated into the sediment in which bacterial reduction occurs. The final amount of reduced sulfide will be controlled by the initial reduction rate so that the fraction of reduced sulfide is roughly correlated to  $R \times \Delta t/[\text{S}]_0 = \Delta t/(a + b[\text{S}]_0)$ , where  $\Delta t$  (time) is the interval of the deposition. Consequently, an increase in the initial sulfate concentration would cause a decrease in the fraction of reduced sulfate, reflected by an increase in isotopic fractionation between reduced products,  $\text{H}_2\text{S}$ , and initial sulfate (the decrease of  $\delta^{34}\text{S}$  values in pyrite). This process causes a negative correlation between sulfide concentrations and  $\delta^{34}\text{S}$  values. As dissolved  $\text{Fe}^{2+}$  ions are derived from the reductive dissolution of oxide phases (Canfield et al., 1996), water with saturated  $\text{Fe}^{2+}$  ions would have been anoxic during the period with S- $\delta^{34}\text{S}$  negative correlation. Therefore, reduction under anoxic conditions is likely to result in the negative correlation between S and  $\delta^{34}\text{S}$  observed above the K-T boundary. The bottom of the wetland should be anoxic, inferred from the presence of sulfur reduced by sulfate-reducing bacteria; however, the saturation of  $\text{Fe}^{2+}$  may require anoxia of some fraction of the non-bottom water to supply enough  $\text{Fe}^{2+}$  ions.

The variation of the abundance of  $\text{Fe}^{2+}$  cannot cause S- $\delta^{34}\text{S}$  negative correlation. An increase of  $\text{Fe}^{2+}$  ions promotes pyrite formation from  $\text{H}_2\text{S}$  before it reoxidizes to sulfate. Therefore, the increase in  $\text{Fe}^{2+}$  ions leads to an increase in the reduction speed, and therefore to a decrease in the amount of residual sulfate. The lower amount of residual sulfate causes the smaller isotopic fractionation between pyrite and initial sulfate, and therefore the higher  $\delta^{34}\text{S}$  in the pyritic sulfur. The high amount of reactive  $\text{Fe}^{2+}$  should cause the high concentration and high  $\delta^{34}\text{S}$  value of pyritic sulfur. Although parameters such as abundance of organic matter and oxygen also affect the re-

duction speed, their variations also may cause S- $\delta^{34}\text{S}$  positive correlation as the variation of the abundance of  $\text{Fe}^{2+}$  should cause.

After the concentration maximum of S and organic C of Dogie Creek sediments above the K-T boundary, no negative correlation between  $\delta^{34}\text{S}$  values and concentration of sulfur is observed. Therefore, the anoxic conditions may be short lived and of extraordinary nature.

## CONCLUSIONS

We have presented data for sulfur contents and isotopic compositions across two K-T boundary successions. From these results, we derived the following observations and conclusions.

The concentrations of organic carbon were constant below the K-T boundary (26 cm at the Dogie Creek and 9 cm at Brownie Butte sites), suggesting constancy of such parameters as depositional rate, oxygen concentration, and organic input to the wetland.

At the K-T boundary, sulfates in wetlands water might be much more abundant than those before and after the K-T boundary, which causes low C/S ratios, similar to those observed in marine sediments. The high input of sulfate to the wetlands may have been caused by the melt ejecta and/or acid rain, induced by the Chicxulub impact event.

Just above the K-T boundary at the Dogie Creek site, the concentrations of nonorganic sulfur are negatively correlated with the  $\delta^{34}\text{S}$  values, suggesting that the  $\delta^{34}\text{S}$  values might not be controlled by the concentration of  $\text{Fe}^{2+}$  ions. This means that the wetlands water at the Dogie Creek site might have been anoxic for the period of deposition.

After the maximum concentration of organic C and nonorganic S, the anoxic conditions of the wetland water might have ceased and returned to normal conditions.

## ACKNOWLEDGMENTS

This work was supported by the Austrian Science Foundation project Y58-GEO (to Koeberl). We thank T. Lyons, K. MacLeod, B. Schmitz, C. Pilmore, and J. Hatch for their helpful comments and critical reviews.

## REFERENCES CITED

- Berner, R.A., 1984, Sedimentary pyrite formation: An update: *Geochimica et Cosmochimica Acta*, v. 48, p. 605–615.
- Berner, R.A., and Raiswell, R., 1984, C/S method for distinguishing freshwater from marine sedimentary rocks: *Geology*, v. 12, p. 365–368.
- Bohor, B.F., Foord, E.E., Modreski, P.J., and Triplehorn, D.M., 1984, Mineralogic evidence for an impact event at the Cretaceous-Tertiary boundary: *Science*, v. 224, 867–869.
- Bohor, B.F., Triplehorn, D.M., Nichols, D.J., and Millard, H.T., Jr., 1987, Dinosaurs, spherules, and the “magic” layer: A new K-T boundary clay site in Wyoming: *Geology*, v. 15, p. 896–899.
- Boudreau, B.P., and Westrich, J.T., 1984, The dependence of bacterial sulfate reduction on sulfate concentration in marine sediments: *Geochimica et Cosmochimica Acta*, v. 48, p. 2503–2516.
- Canfield, D.E., Lyons, T.W., and Raiswell, R., 1996, A model for iron deposition to euxinic black sea sediments: *American Journal of Science*, v. 296, p. 818–834.
- Chambers, L.A., and Trudinger, P.A., 1979, Microbiological fractionation of stable sulfur isotopes: A review and critique: *Geomicrobiology Journal*, v. 1, p. 249–293.
- Coplen, T.B., and Krouse, H.R., 1998, Sulphur isotope data consistency improved: *Nature*, v. 392, p. 32.
- Evans, N.J., Gregoire, D.C., Goodfellow, W.D., Miles, N., and Veizer J., 1994, The Cretaceous-Tertiary fireball layer, ejecta layer and coal seam: Platinum-group element content and mineralogy of size fractions: *Meteoritics*, v. 29, p. 223–235.
- Fry, B., 1986, Stable sulfur isotopic distributions and sulfate reduction in lake sediments of the Adirondack Mountains, New York: *Biogeochemistry*, v. 2, p. 329–343.
- Giesemann, A., Jäger, H.-J., Norman, A.L., Krouse, H.R., and Brand, W.A., 1994, On-line sulfur-isotope determination using an elemental analyzer coupled to a mass spectrometer: *Analytical Chemistry*, v. 66, p. 2816–2819.
- Henrichs, S.M., and Reeburgh, W.S., 1987, Anaerobic mineralization of marine sediment organic matter: Rate and the role of anaerobic processes in the oceanic carbon economy: *Geomicrobiology Journal*, v. 5, p. 191–237.
- Heymann, D., Yancey, T.E., Wolbach, W.S., Thiemens, M.H., Johnson, E.A., Roach, D., and Moecker, S., 1998, Geochemical markers of the Cretaceous-Tertiary boundary event at Barazos River, Texas, USA: *Geochimica et Cosmochimica Acta*, v. 62, p. 173–181.
- Holmes, C.W., and Bohor, B.F., 1994, Stable isotope (C, S, N) distributions in coals spanning the Cretaceous/Tertiary boundary in the Raton Basin, Colorado and New Mexico [abs.]: U.S. Geological Survey Circular 1107, p. 141.
- Holser, W.T., Schidlowski, M., Mackenzie, F.T., and Maynard, J.B., 1988, Geochemical cycles of carbon and sulfur, in Gregor, C.B., Garrels, R.M., Mackenzie, F.T., and Maynard, J.B., eds., *Chemical cycles in the evolution of the earth*: New York, John Wiley and Sons, p. 105–173.
- Jonckbloedt, R.C.L., 1998, Olivine dissolution in sulphuric acid at elevated temperatures: Implications for the olivine process, an alternative waste acid neutralizing process: *Journal of Geochemical Exploration*, v. 62, p. 337–346.
- Kajiwarra, Y., and Kaiho, K., 1991, Sulfur isotopic data from the Cretaceous/Tertiary boundary sediments in the eastern Hokkaido, Japan: Annual Report of the Institute of Geoscience, University of Tsukuba, v. 17, p. 68–73.
- Kajiwarra, Y., and Kaiho, K., 1992, Oceanic anoxia at the Cretaceous/tertiary boundary supported by the sulfur isotopic record: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 99, p. 151–162.
- Kaplan, I.R., and Rittenberg, S.C., 1964, Microbiological fractionation of sulphur isotopes: *Journal of General Microbiology*, v. 34, p. 195–212.
- Nriagu, J.O., and Coker, R.D., 1983, Sulphur in sediments chronicles past changes in lake acidification: *Nature*, v. 303, p. 692–694.
- Pillmore, C.L., and Flores, R.M., 1987, Stratigraphy and depositional environments of the Cretaceous-Tertiary boundary clay and associated rocks, Raton Basin, New Mexico and Colorado, in Fassett, J.E., and Rigby, J.K., Jr., eds., *The Cretaceous-Tertiary boundary in the San Juan and Raton Basins, New Mexico and Colorado*: Geological Society of America Special Paper 209, p. 111–129.
- Raiswell, R., and Berner, R.A., 1986, Pyrite and organic matter in Phanerozoic normal marine shales: *Geochimica et Cosmochimica Acta*, v. 50, p. 1967–1976.
- Schmitz, B., 1989, Recent formation of barite and celestite in weathering Cretaceous-Tertiary boundary clays: International Geological Congress, 28th, Washington, D.C., Abstracts, v. 3, p. 51.
- Schmitz, B., Andersson, P., and Dahl, J., 1988, Iridium, sulfur isotopes and

- rare earth elements in the Cretaceous-Tertiary boundary clay at Stevns Klint, Denmark: *Geochimica et Cosmochimica Acta*, v. 52, p. 229–236.
- Schuiling, R.D., and van Herk, J., and Pietersen, H.S., 1986, A potential process for the neutralization of waste acids by reaction with olivine: *Geologie en Mijnbouw*, v. 65, p. 243–246.
- Sheehan, P.M., and Fastovsky, D.E., 1992, Major extinctions of land-dwelling vertebrates at the Cretaceous-Tertiary boundary, eastern Montana: *Geology*, v. 20, p. 556–560.
- Sigurdsson, H., D'Hondt, S., and Carey, S., 1992, The impact of the Cretaceous/Tertiary bolide on evaporate terrane and generation of major sulfuric acid aerosol: *Earth and Planetary Science Letters*, v. 109, p. 543–559.
- Tschudy, R.H., 1970, Palynology of the Cretaceous-Tertiary boundary in the northern Rocky Mountain and Mississippi Embayment regions: *Geological Society of America Special Paper 127*, p. 65–111.
- Yanagisawa, F., and Sakai, H., 1983, Thermal decomposition of barium sulfate-vanadium pentoxide-silica glass mixtures for preparation of sulfur dioxide in sulfur isotope ratio measurements: *Analytical Chemistry*, v. 55, p. 985–987.

MANUSCRIPT SUBMITTED NOVEMBER 3, 2000; ACCEPTED BY THE SOCIETY MARCH 22, 2001