Acid-neutralizing scenario after the Cretaceous-Tertiary impact event

Teruyuki Maruoka*
Christian Koeberl* } Department of Geological Sciences, University of Vienna, Althanstrasse 14, A-1090 Vienna, Austria

ABSTRACT

Acid rain from the Cretaceous-Tertiary (K-T) boundary impact event should have caused significant damage to freshwater life, but only minor extinctions of freshwater species are actually observed. We propose a mechanism to neutralize the acid using larnite (β-Ca₂SiO₄), produced as a result of the specific lithology at the Chicxulub impact site. The impact vapor plume must have been enriched in calcium from the carbonate-rich target, leading to the crystallization of larnite. The acid-neutralizing capacity of the larnite grains would have been high enough to consume acid produced after the K-T event within several hours, reducing it to a level at which freshwater life would not have been affected, even if all the acid had precipitated instantaneously after the K-T impact. This scenario can explain some of the extinction selectivity at the K-T boundary.

Keywords: impacts, K-T boundary, acid rain, mass extinction, Chicxulub crater.

INTRODUCTION

Acid rain has been proposed to account for some observations at the Cretaceous-Tertiary (K-T) boundary, such as destruction of calcareous plankton in oceans (e.g., Brett, 1992), excursion of seawater $^{87}Sr/^{86}Sr$ ratio (e.g., MacLeod et al., 2001; Lyons and Ahrens, 2003), and etched pits on the surface of spinels (Preisinger et al., 2002). The acid rain would be expected to have more seriously affected freshwater environments than marine environments, as is observed today in highly polluted areas (e.g., Gorham, 1998); however, only a minor extinction of freshwater species at the K-T boundary is evident. Sheehan and Fastovsky (1992) inferred 10% extinction for freshwater vertebrates, but 88% extinction for land-dwelling vertebrates. Animals in freshwater ecosystems, including crocodiles, champsosaurs, and turtles, generally survived the extinction (e.g., Hutchison, 1982). Cavin (2001) showed a high survival rate for freshwater species based on analyses of bony fish occurrences across the K-T boundary. The extinction selectivity implies that either the acid rain was not severe enough to damage freshwater environments, or that an acid-neutralization mechanism existed only right after the K-T impact event. Given the evidence that acid rain was produced by the K-T impact, we propose here a mechanism to neutralize the acid produced at the K-T event.

PREDICTED FRESHWATER EFFECTS OF ACID RAIN FORMED BY THE K-T EVENT

Anhydrite is part of the target at the K-T age Chicxulub impact structure (e.g., López-Ramos, 1975). The amount of sulfur released from the target as SO_2 or SO_3 gases at the K-T event is estimated at 45–75 and 76–127 Gt S for asteroids of 10 and 15 km in diameter, respectively, impacting Earth at 20 km/s (Table 1; Pierazzo et al., 1998, 2003). In addition, a carbonaceous chondritic projectile (the type derived by Kyte, 1998; Shukolyukov and Lugmair, 1998) of 10 and 15

*E-mail addresses: Maruoka—teruyuki@wuphys.wustl.edu; Koeberl—christian.koeberl@univie.ac.at. Present address: Maruoka—Laboratory for Space Sciences, Physics Department, Washington University, Campus Box 1105, One Brookings Drive, St. Louis, Missouri 63130-4899, USA.

km diameter contains 33–42 and 82–106 Gt of S, respectively (Table 2). After the impact event, the sulfur released into the stratosphere as SO_2 or SO_3 would have converted to sulfuric acid aerosol, which should have caused considerable cooling of Earth's surface (e.g., Brett, 1992; Pierazzo et al., 1998). The aerosol would then fall back to the surface as acid rain. Moreover, 0.35×10^{15} and 0.59×10^{15} moles of NO (Table 2) should also have been produced after the impact of a 10 or 15 km projectile, respectively, by interaction of the atmosphere with the impact plume and by reentry of the ejecta into the atmosphere (Lewis et al., 1982; Prinn and Fegley, 1987; Zahnle, 1990). The NO would convert to NO_2 on a time scale of minutes to hours, then to nitric acid on a time scale of about a week (e.g., Crutzen, 1979).

A "critical load" is defined as "the highest deposition of acidifying compounds that will not cause chemical changes leading to long-term harmful effects on ecosystem structure and function according to present knowledge" (Nilsson and Grennfelt, 1988, p. 12). Values for such a critical load of wet SO_4^{2-} have been estimated to range from 0.6×10^{-3} to 2×10^{-3} kg·m^{-2}·yr^{-1} for freshwater lakes (e.g., Jeffries et al., 1999). If the acid content reaches a value higher than the critical load, the biota of the acidified lakes might not recover completely even after recovery of the water chemistry (e.g., Keller et al., 1992). Sulfur amounts released from the target and projectile after the K-T impact event are estimated at 120 and 230 Gt for asteroid diameters of 10 and 15 km, respectively (Tables 1 and 2); given a value of 5.1×10^8 km^2 for surface of Earth, these sulfur tonnages result in a sulfuric acid amount of 0.69–1.4 kg/m^2. Acid rain after the K-T event would have also affected the least sensitive environments (those with critical loads of 2×10^{-3} kg·m^{-2}·yr^{-1}), if it takes <300 and <700 yr to wash out the sulfuric acid aerosol of 0.69 and 1.4 kg/m^2, respectively. Although the sulfur released as SO_2 would have converted slowly to aerosols due to the rate-limiting oxidation of SO_2 in the stratosphere, the stratospheric residence time has been estimated at 4–10 yr (e.g., Pierazzo et al., 2003). Also, acid rain from nitric acid (equivalent to ~10% of the sulfuric acid) should have affected freshwater environments, because the formation of nitric acid cannot be delayed for decades. If acid rain similar to that inferred for the K-T event fell today, the present freshwater environment would be damaged.

MECHANISM TO SAVE FRESHWATER SPECIES FROM K-T ACID RAIN

Here we propose a possible mechanism that explains the lack of harmful effects from acid rain on freshwater organisms after the K-T event. In our model the acid is neutralized by silicate minerals that were produced in the impact vapor plume. Ebel and Grossman (1999) reported that Ca- and Si-rich liquids in the plume crystallize to form silicates, such as larnite (β-Ca₂SiO₄), melilite, hatrurite (Ca₃SiO₅), or Ca-rich pyroxene. Because the target at Chicxulub contains abundant carbonate, the plume vapor would have been enriched in calcium. Magnesium and iron are incorporated in spinel, which condenses at a higher temperature than that of Ca-rich silicate (Ebel and Grossman, 1999). Therefore, Fe and Mg would not have been available to enter the structure of the Ca-rich silicate. In the following, we examine the neutralizing capacity of larnite. Although other silicates and oxides also settled after the K-T event, they do not have acid-neutralizing capacities

TABLE 1. ESTIMATES OF SULFUR RELEASED FROM THE TARGET AND NO PRODUCED DURING THE CRETACEOUS-TERTIARY (K-T) IMPACT EVENT

Projectile		S from the target (Gt)*	S from the target (10^{15} moles)	NO produced during the KT event (10^{15} moles)[#]
Diameter (km)	Density (g/cm^3)			
10	3.32	45–75[†]	1.41–2.34	0.35
15	2.49	76–127[§]	2.38–3.97	0.59
20	1.66	117–197[§]	3.66–6.16	0.76

*Maximum and minimum mass represent released sulfur from target consisting of 50%–50% and 70%–30% mixture of carbonate and evaporate, respectively.
[†]Estimates from Pierazzo et al. (1998).
[§]Estimates from Pierazzo et al. (2003).
[#]Values determined from Figure 11 in Zahnle (1990).

TABLE 2. ESTIMATES OF SULFUR RELEASED FROM THE PROJECTILE OF THE CRETACEOUS-TERTIARY (K-T) IMPACT EVENT

Meteorite type*	Density (g/cm^3)	S concentration		Diameter (km)	Sulfur release	
		(wt%)[†]	(wt%)[§]		(Gt)[#]	(10^{15} moles)
CV	3.42	2.2	2.1	10	39**	1.23
				15	100[††]	3.12
				20	158[§§]	4.92
CO	3.63	2.2	2.0	10	42**	1.31
				15	106[††]	3.31
				20	167[§§]	5.23
CR	3.27	1.9		10	33**	1.02
				15	82[††]	2.57
				20	130[§§]	4.07

*Projectile types inferred by Kyte (1998).
[†]Data from Lodders and Fegley (1998).
[§]Data from Kring et al. (1996).
[#]Values determined using S concentrations compiled by Lodders and Fegley (1998).
**Projectile porosities assumed to be 0%.
[††]Projectile porosities assumed to be 25% (Pierazzo et al., 1998, 2003).
[§§]Projectile porosities assumed to be 50% (Pierazzo et al., 1998, 2003).

similar to those of larnite. For example, the acid-consuming rates of monticellite (CaMgSiO$_4$) and forsterite (Mg$_2$SiO$_4$) are approximately two and four orders of magnitude, respectively, lower than that of CaSiO$_4$ (Westrich et al., 1993).

So far larnite has not been found in K-T boundary rocks; this is not surprising because larnite dissolves or is converted to clays even in neutral water. However, Martinez et al. (1994) reported the presence of larnite at the Haughton impact crater, which also involved a carbonate-dominated target. Larnite precipitates from a liquid with a narrow range of CaO/SiO$_2$ ratios—from 1.5 to 2.5 (Zharikov and Shmulovich, 1969); this is similar to the range of CaO/SiO$_2$ ratios predicted by Ebel and Grossman (1999) for the impact of a 10-km-diameter asteroid, whereas the impact of a 20-km-diameter asteroid results in different ratios. The Ca concentration in the liquid decreases with increasing projectile diameter because a larger impact penetrates the target to a greater depth, incorporating a larger amount of basement rocks. A diameter of 10–15 km for the K-T projectile is considered the most plausible value (e.g., Smit, 1999).

Orthosilicate minerals are the fastest acid buffers because of their crystal structure (Schuiling et al., 1986; Westrich et al., 1993). During dissolution of orthosilicates (M$_2$SiO$_4$) in acid, M^{2+} ions are replaced by H$^+$, yielding Si(OH)$_4$ monomers and M^{2+} ions in solution. In particular, γ-Ca$_2$SiO$_4$ (Ca-olivine) has the highest dissolution rate among orthosilicates (Westrich et al., 1993). No data are available on the dissolution rate of β-Ca$_2$SiO$_4$ (larnite), which is produced by rapid cooling of melt; therefore, we use the rate for γ-Ca$_2$SiO$_4$ for the following discussion. This approach is reasonable because the dissolution rate of orthosilicates is controlled by the strength of bonds between divalent metals and oxygen rather than by the lattice energy and the lattice substructure (e.g., olivine and willemite class; Westrich et al., 1993).

The exact amount of Ca$_2$SiO$_4$ produced depends on physical parameters including the porosity of the target and the cooling rate of the vapor plume (Ebel and Grossman, 1999). Most of the calcium and sulfur in the vapor plume originated from the target rocks at Chicxulub, where carbonate (i.e., dolomite and calcite) was more abundant than anhydrite (35–40% [by mass] dolomite, 25–30% calcite, 25–30% anhydrite, and 3–4% sandstone and shale; Ward et al., 1995). Incipient and complete devolatilization of nonporous anhydrite occurs at 32.5 ± 2.5 GPa and 122 ± 13 GPa, respectively (Gupta et al., 2001), at pressures much higher than in carbonates (~10 and 100 GPa, respectively; Love and Ahrens, 1998). Although experimental data for the shock pressure of incipient decarbonation show a range from 10 to 60 GPa (e.g., Ivanov et al., 2002; Skála et al., 2002), the degree of devolatilization of anhydrite is always lower than that of carbonate. Therefore, the amount of calcium released from the devolatilization of carbonate and anhydrite in the vapor volume always exceeds the amount of sulfuric acid produced mainly from anhydrite. The nitric acid produced after the K-T impact was equivalent to ~10% of the sulfuric acid. This amount of nitric acid would not induce a deficiency of larnite.

The acid neutralization rate depends on the activity of the acid

and the geometric surface area of the larnite grains (Westrich et al., 1993). In order to test the reliability of our scenario, we need to discuss the amount of larnite grains, the grain-size distribution, and the duration of the acid deposition, which would be controlled by the SO$_2$/SO$_3$ ratio of the vapor plume. Here we discuss the speed of acid neutralization in a worst-case scenario, using the minimum amount of larnite required to neutralize the sulfuric and nitric acid produced after the K-T event, maximum grain size (i.e., minimum surface area), and immediate production of the sulfate aerosols.

The H$^+$-consuming rate, R (in units of mol·cm^{-2}·s^{-1}), of γ-Ca$_2$SiO$_4$ at a temperature of 25 °C can be expressed as

$$R/S = (5.5 \pm 2.8) \times 10^{-8} \times 10^{-0.42[\text{pH}]}$$
$$= (5.5 \pm 2.8) \times 10^{-8}[\text{H}^+]^{0.42}, \quad (1)$$

where S is the sum of the surface area of the larnite grains (m^2) per square m of Earth (Casey and Westrich, 1992; Westrich et al., 1993). During dissolution of the larnite grains, radius decreases with time. Thus, the larnite grain volume (and the radius) should be related to the number of residual H$^+$ ions. Assuming that the amount of larnite was equal to the minimum amount required to neutralize the acid, we obtain

$$[\text{H}^+]/[\text{H}^+]_0 = r^3/r_0^3, \quad (2)$$

where $[\text{H}^+]_0$ and r_0 are the initial concentration of H$^+$ ions and initial radius of the larnite grains, respectively, and $[\text{H}^+]$ and r are concentration of H$^+$ ions and radius of the larnite grains, respectively, after time t. The H$^+$-consuming rate can be expressed as follows:

$$R_0 = A[\text{H}^+]_0^{0.42}4\pi r_0^2 \quad \text{and} \quad (3)$$
$$R = A[\text{H}^+]^{0.42}4\pi r^2, \quad (4)$$

where A is a constant value, R_0 is the initial rate, and R is the rate after the time t. From equations 2, 3, and 4, we obtain

$$R/R_0 = ([\text{H}^+]/[\text{H}^+]_0)^{0.42} \times ([\text{H}^+]/[\text{H}^+]_0)^{2/3} \sim ([\text{H}^+]/[\text{H}^+]_0)^1. \quad (5)$$

The acid-consuming rate is defined as follows:

$$R = -V \times d[\text{H}^+]/dt, \quad (6)$$

where V is the volume of water that exists on the concerning unit area of a freshwater environment. Using equations 5 and 6, we obtain a differential equation:

$$d[\text{H}^+]/dt = -\{R_0/([\text{H}^+]_0 V)\} \times [\text{H}^+]. \tag{7}$$

Solving equation 7, we obtain

$$[\text{H}^+] = [\text{H}^+]_0 \times \exp\{-(R_0/([\text{H}^+]_0 V)) \times t\}. \tag{8}$$

Assuming that the sulfur liberated at the K-T event was converted to sulfuric acid and precipitation occurred immediately after the impact event—which is the worst case scenario for life in the freshwater environment—then the total initial input (i.e., $[\text{H}^+]_0 V$) to the freshwater is equivalent to the total amount of acid deposited onto the unit area.

We assume that 330 and 650 Gt of Ca_2SiO_4 were present as spherules, each with a radius of 1 μm; these are the minimum amounts required to consume the sulfuric and nitric acid produced by the impact of projectiles of 10 and 15 km in diameter, respectively. The spherule size is smaller than that of melt droplets condensed from the vapor plume (10–400 μm; e.g., Montanari, 1991; Smit, 1999). However, the majority of the spherules would have consisted of a porous meshwork of minerals arranged in a dendritic texture (e.g., Smit, 1999), and the dendritic texture, which would have resulted from rapid cooling, would consist of microcrystals <1 μm in size. Dendrites should have been most abundant near the surface of melt droplets. We consider 1 μm as a reasonable maximum radius for larnite grains. This radius leads to initial total geometric surface areas of 600 and 1200 m^2 of larnite per square meter of Earth's surface for asteroid diameters of 10 and 15 km, respectively. Such a layer can consume acid at a rate (in units of $mol \cdot s^{-1} \cdot m^{-2}$) of

$$R_0 = (0.33 \pm 0.17) \times [\text{H}^+]_0^{0.42} \quad \text{and} \tag{9}$$

$$R_0 = (0.65 \pm 0.32) \times [\text{H}^+]_0^{0.42} \tag{10}$$

for impacts of asteroids of 10 and 15 km diameter, respectively.

Equations 8–10 yield the time interval required to raise the pH of the freshwater to a pH at which no harmful effects on life are caused (i.e., pH = 6; e.g., Schindler, 1988). These intervals can be estimated at, for example, 1400 ± 700 s (0.4 ± 0.2 h) and 13,000 ± 6700 s (3.7 ± 1.9 h) for initial freshwater pH values of 1 and 5, respectively. These durations are not controlled by the initial amount of the acid, i.e., the size of the asteroid. These calculations indicate that all the sulfuric and nitric acid related to the K-T impact event could have been consumed within several hours, even if all acid aerosols had precipitated instantaneously. Because mortalities of organisms in freshwater environments can occur within 1–5 days in waters with sufficiently low pH (e.g., Curtis et al., 1989), acid neutralization with Ca_2SiO_4 grains may prevent freshwater organisms from dying (Fig. 1).

The acid produced by an impact of a 10- or 15-km-diameter projectile would yield 300 and 600 g Ca^{2+}, 690 and 1400 g SO_4^{2-}, 43 and 71 g NO_3^-, and 360 and 710 g $Si(OH)_4$, respectively, per square meter of Earth in the freshwater environment. The addition of these amounts all at once to water with a depth of, e.g., 10 cm (i.e., 100 $L \cdot m^{-2}$) would lead to concentrations of 3–6 g Ca^{2+}, 7–14 g SO_4^{2-}, 0.4–0.7 g NO_3^-, and 4–7 g SiO_2 per liter. These concentrations are about three orders of magnitude higher than those observed today in river waters (world average: Ca^{2+}, 15 mg/L; SO_4^{2-}, 11.2 mg/L; NO_3^-, 1 mg/L; and SiO_2, 13.1 mg/L; Schlesinger, 1997). It may be possible (but difficult) to observe an enrichment in these elements in some terrestrial K-T boundary deposits. Actually, Maruoka et al. (2002) inferred sulfate enrichments in freshwater environments just after the K-T impact event on the basis of sulfide enrichments in terrestrial K-T boundary sediments. Those sulfide enrichments could have been induced by enhanced activity of sulfate-reducing bacteria, as observed in present-day freshwaters with anthropogenically enhanced sulfate concentrations (e.g., Fry, 1986).
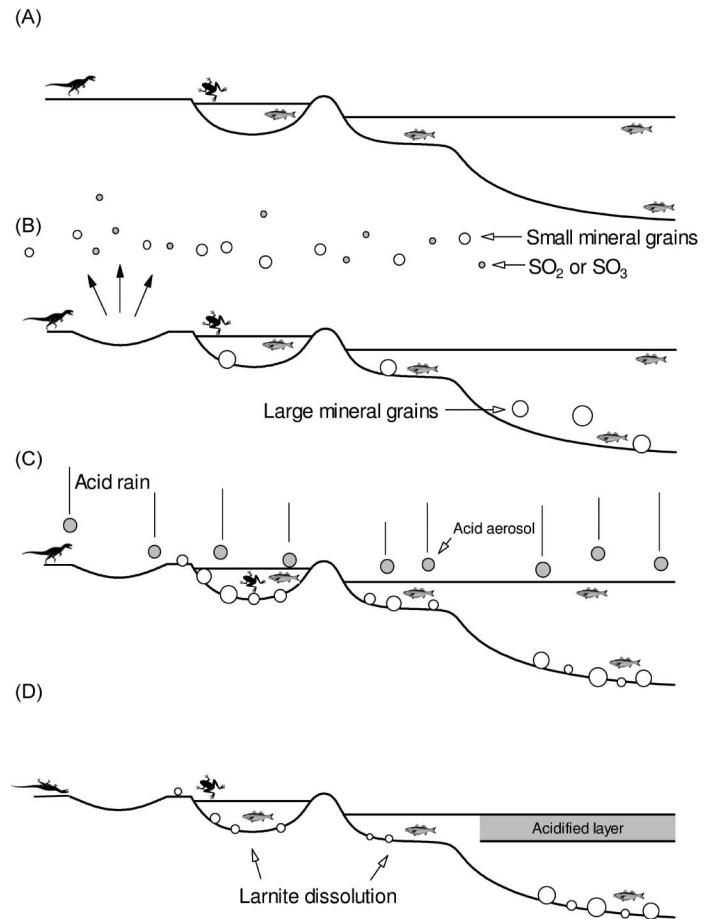

Figure 1. Schematic drawing showing freshwater and marine ecosystems before the Cretaceous-Tertiary (K-T) impact event (A), immediately after the impact event (B), acid rain after the impact event (C), and after acid neutralization (D).

EFFECT OF ACID RAIN ON SEA- AND LAND-DWELLING SPECIES

In addition to differences in salinity, marine and freshwater environments are characterized by differences in water depth. In the ocean, solid condensates quickly settle to the bottom, whereas the acid remains near the surface (Fig. 1D) due to immiscibility of water with different salinities. Therefore, in contrast to the situation in shallow-water and freshwater environments, acid and neutralizer rapidly separate in deep-ocean settings, which leads to life being more severely affected in the near-surface layers. The fossil record shows survival of deep-sea, nearshore, and brackish-water fish species (Cavin, 2001) after the K-T impact event. Moreover, benthic foraminifera underwent less extinction at the K-T boundary than planktonic foraminifera (e.g., Culver, 2003). However, this scenario cannot explain some observations. For example, bottom life inferred from trace-fossil fabrics decreased dramatically at intermediate (200–1000 m) water depth (e.g., Smit et al., 1997). There is little evidence for acidification of the ocean surface (D'Hondt et al., 1994), which can also be explained by the higher pH buffer capacity of ocean water compared to freshwater. Thus, acid rain may not have been the primary cause for the marine K-T mass extinction.

On land, plants might have been affected by acid rain, which, in turn, would have affected herbivores (e.g., Sheehan and Fastovsky, 1992), whereas species that rely on freshwater ecosystems, such as frogs, crocodiles, champsosaurs, and turtles, would have been protected from acid rain by the acid-neutralization action of larnite (Fig. 1C). Most plant extinctions at the K-T boundary involved zoophilous

(animal-pollinated) angiosperms; however, zoophilous angiosperms in swamp and swamp-margin environments actually appear to have been unaffected by the K-T extinction (Sweet, 2001). The acid-neutralizing scenario can explain some of the extinction selectivity that occurred after the K-T event.

Work by Smit (1999) and Kring and Durda (2002) indicates that the global distribution of the Chicxulub ejecta was not homogeneous, but showed rays and regionally different patterns. The resulting heterogeneous distribution of larnite may have caused regional variations in acid-neutralizing capacity and, therefore, in the selectivity of the survival of freshwater and marine species. Unfortunately, regional survival patterns have not yet been tested due to the low number of freshwater K-T boundary sites known and studied so far.

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