



*Time present and time past / Are both perhaps present in time future, /
And time future contained in time past.*

T. S. Eliot, "Burnt Norton," *Four Quartets*

Paleoecotoxicology: The Impact of Chemical and Physical Stress in the Evolutionary Process

Present-day biodiversity, estimated to comprise more than 100 million species, has developed in around 4,000 million years on the basis of the ability of life forms to adapt and multiply at a rate that surpassed extinctions. Species, including humans, depend on the ecosystems that have operated with no or minimal human intervention up to recent years. Recent extinction rates are 100–1,000 times their pre-human levels in taxonomically diverse groups from widely different environments. Moreover, it is accepted that if all species currently endangered become extinct, then future extinction rates will be 10 times recent rates (1). Although chemicals are the basic units for the development of life, it seems meaningful to take into account Paracelsus' statement that "all things are poison and nothing is without poison." From this perspective it seems obvious that chemical and physical features have been considered driving forces of evolutionary processes from the beginning of recorded history. Estimates suggest that the current world production of chemicals is 400 million metric tons. Almost 11 million naturally occurring or man-made chemicals have been identified in the CAS Registry File, although only a small portion of them is commercially available. I would like to present the hypothesis of a direct link between chemical stress and a major mass extinction process, the Cretaceous-Tertiary (C-T) event, with the aim of providing a more holistic view on the potential of chemical stress on the evolutionary process.

The earliest evidence of stable continents and oceans and records thought to implicate primitive life seems to point to the late Hadean (the Dark Ages)—early Precambrian era, about 4 billion years ago. Microorganisms have flourished in the oceans since at least 3.8 billion years ago, and based on the occurrence, elemental ratios (carbon, hydrogen, nitrogen, phosphorus) and isotopic compositions of this organic matter and its host rocks indicate that microbial mats developed on the soil surface around 2.7 billion years ago. Put simply, life is a property of certain configurations of matter, an emergent phenomenon that eventually can be passed on from generation to generation and can modify itself in order to persist on longer timescales, as the environment changes. Although only a small fraction of all the potential evolutionary possibilities developed, life forms were successful enough to inhabit and even transform the Earth into a living planet—the Gaia hypothesis based on the stability of self-regulating processes such as the Earth's atmosphere during millions of years in spite of chemical disequilibrium.

Although the sampling intensity from time to time and place to place could bias our knowledge on the extant biodiversity during different periods of the Phanerozoic Era, the fossil record of non-marine tetrapods from the Devonian era (approximately 400 million years ago) onward exhibits an average of about 50 families until the last quarter of the Cretaceous period, when the number of families increased to nearly 80; the rise continued to the present 337 families



in several steps in the Tertiary period (2). A similar pattern of increase in the number of families was also found

in the record of marine invertebrates (3). Conversely, extinction throughout earth history is generally estimated to include more than 90–99% of the species that ever lived. Thus, extinction is the rule rather than the exception, and the vast majority of these extinctions are considered to be normal or background extinctions because they have occurred regularly since life originated on Earth (2–4).

The fossil record of biota also reveals mass extinctions as distinct phenomena that resulted in a succession of family assemblages that dominated for a time and then were replaced. Mass extinctions may be identified at first by a drop in biodiversity that reflects exceptional ecologic crisis, usually considered as devastating the biosphere. For example, at the end of the Permian era, some 250 million years ago, approximately 80% of species became extinct. Based on a detailed census of the end of the Permian event and the C-T mass extinction, everything from microscopic foraminifera to tetrapods seems to have vanished in an extremely short period (3,5). The C-T episode is not the only major mass extinction phenomenon during the last 540-million-year period for which abundant fossil remains were found, but the fact that it led to the transition from the age of the dinosaurs to the age of mammals about 65 million years ago puzzled both scientists and the public for more than a century. Although more than 60 theories have been developed to explain this mass extinction event, the selectivity of the mass extinction for dinosaurs and their contemporary vertebrates and invertebrates remains unexplained. For example, among the 12 major vertebrate clades, extinctions were concentrated in seven of them; sharks, ornithischians, pterosaur, saurischians, non-trilasgemic mammals, lizards, and marsupials accounted for about 75% of the extinctions (4). This demonstrates that the C-T extinctions were highly selective. Moreover, survivorship at least for the lizards and marsupials varied significantly in different geographic regions. The same pattern of concentrations in certain families is also the main feature in the paleocene floral diversities and turnover events at that time (6). Therefore, any theory of extinction must account for this selectivity as well as for the diachroneity found in the biological record during the late Cretaceous/early Tertiary period. My hypothesis for the cause of mass extinction during the C-T period is that selective toxic effects from an exceptionally high environmental pollution occurred at that time.

Iridium, a well-known tracer of the C-T boundary during the turnover of biodiversity, can be used to check the hypothesis that global chemical stress is a significant cause of the loss of biodiversity and selectivity during C-T mass extinction. The iridium anomaly seems to be related to a large quantity of siderolite material most

likely from a 10-km asteroid that struck Earth 65 million years ago. This theory is supported by a crater 180 km across located in the Yucatan Peninsula (Chicxulub), as well as shocked quartz and the presence of double lamellae structure at the Earth's surface corresponding to the C-T level. Large amounts of iridium were found at the C-T level in all of the geographic regions evaluated from Europe to Antarctica, which clearly shows that the materials from the asteroid had worldwide distribution, probably by means of atmosphere (5) and water-bound transport. In contrast, the impact of a large asteroid would inject about 60 times the object's mass into the atmosphere as pulverized rock, an estimated 6.8×10^{18} g of material. Compared to the annual global mine production for well-known toxic substances [e.g., 5.3×10^9 g Hg, 1.8×10^{10} g Cd, 3.4×10^{12} g Pb (7)], the estimates of ejected chemicals due to the asteroid impact were one order of magnitude higher. Iridium at the C-T boundary is up to 160 times the background crust abundance of this substance, and the anomalies in the concentrations of many other chemicals found at the C-T boundary (5) are also among the different lines of evidence that support the hypothesis of a worldwide chemical stress scenario devastating biota toward a mass extinction phenomenon.

The immense amount of pulverized material injected into the environment would have generated an exceptionally high level of air pollution (tiny particles of dust and soot), which could have potentially caused adverse effects including death, as has been reported for particulate matter in current air pollution conditions (8). In contrast, the sudden, high amount of pulverized chemicals injected into the environment could exceed the controlling factors (biotic and abiotic) involved in the storage and purification of the ecosystem before bioavailable concentrations could adversely affect biodiversity. Several hazard and risk assessment studies using different species and environmental scenarios document the adverse effect of crust and siderophile substances to the biota. For example, aluminum, a common substance in the earth's crust, is toxic (9). Its toxicity and bioavailability increase in a low pH, such as with acid rain. Other elements, such as nickel, lithium, copper, mercury, cadmium, cobalt, chromium, arsenic, and zinc, are all well known to be highly toxic (10,11), but additive and synergistic effects of several of these substances in living organisms could result in serious health effects in the existing biota at the C-T boundary. Iridium is not a priority substance for current environmental conditions, but the results obtained using the AMPHITOX test (12) (e.g., lethal to 100%, 24 hr: 0.2 mg Ir³⁺/L; no-observed-effect concentration, 7-day exposure: 0.14 mg Ir³⁺/L; bioconcentration factor = 9) indicate that it is a very toxic substance. Because amphibians survived the C-T mass extinction, the exposure scenario was probably at concentrations below those exerting adverse effects in laboratory conditions.

The different sources of chemical contamination of the biota during the C-T event can be summarized as follows (13): Direct bioaccumulation of chemicals from the air, water, soil, and sediments, and eventual incorporation into the food web could be of major importance for biomagnification processes that contribute to adverse effects. This could occur not only in species with higher susceptibility but also in those with high exposure due to different circumstances as a result of transport and fate features of environmental pollutants, ecologic complexity factors (14), and species-linked features from age-dependent uptake of chemicals to food preference. For instance, ptarmigans in Colorado are poisoned by cadmium due to a biomagnification process in one particular genus of willows (*Salix* spp.), which is a primary food of ptarmigans (15). Larison et al. (15) point out that even the ingestion of trace quantities of cadmium by these birds can influence not only the physiology and health of individual organisms but also their demographics and distribution. Other species within the same habitat that do not feed on willows do not exhibit

adverse effects due to cadmium. Many other plants and animals hyperaccumulate certain chemicals; for example, the brake fern can take up about 16,000 ppm of arsenic in 2 weeks (16). Besides regional differences related to transport and fate of the pollutants, reflected to some extent by the abundance of iridium and other elements found in different geographic regions (5), the species with higher resistance to chemical stress, with less limited geographic range as habitat, or better adapted to more environmental and feeding conditions have a better chance of survival.

The hypothesis of a worldwide chemical explosion scenario at the C-T boundary caused by the asteroid impact probably received inputs from other concomitant and concurrent phenomena at that time that could also threaten biota, such as:

- Massive eruption of flood basalts called the Deccan Traps occurred on the Indian subcontinent, with a volume of material estimated at 13×10^{10} m³ (17,18). This eruption occurred over 4 million years, and the resulting climatic changes and acid rain have been argued as proximate causes for mass extinction at the C-T boundary.
- Marine regression resulted in draining of epicontinental seas (19). An estimated 29 million square miles of land (approximately the size of Africa) were exposed during this interval, with major loss of low coastal plain habitat, establishment of land bridges, extension of freshwater systems, and climatic change with a general trend toward cooling of the planet.
- The asteroid impact led to the theory developed by Alvarez et al. (5) that the ejecta and plume spread around the globe blocked out the radiation from the Sun, resulting in cessation of photosynthesis and leading to death and extinction of plants, the herbivores, and then the carnivores that fed upon the herbivores. Other effects attributed to the asteroid impact were acid rain, global wildfire, sudden temperature increases and decreases, tsunamis, and strong hurricanes.
- Panzootic outbreaks of disease were possible (however, there is no evidence of an episode that exerted lethality in all living forms, from unicellular to the largest tetrapods, as occurred during the C-T and other mass extinction events).

Although these phenomena do not explain the selectivity in the mass extinction event, which is most conspicuous during the C-T boundary (2–4,20,21), a reduction in, for example, the radiation from the Sun, climate changes, increased volcanic activity, marine regression, and acid rain (5,22–24) could contribute to disturbances in biota and could modify exposure and xenobiotic toxicity (25); organisms under chemical or other environmental stress could be more vulnerable to pathogens as well (26). Moreover, even slight changes in nutrient supply, an expected condition during a severe environmental pollution situation, could result in extinction of species (27).

The capability to adapt to environmental stress is an inherent property of life (28), and it is well known that, by means of an acclimation protocol, an enhanced resistance to lethal chemical stress can be achieved (29). This enhanced capability to resist toxic effects could be viewed also as the persistence of information within an ecologic system following a toxicologic stressor. Therefore toxicant-stressed communities and species could evolve resistant organisms or be replaced by pollution-tolerant invaders. As a whole, the chemical stress hypothesis seems to contribute to better understanding of the selective mass extinction phenomena at the C-T boundary. It is also conceivable that chemical stress was involved, at least to some extent, in other mass extinction episodes during the Phanerozoic era. For instance, smaller iridium enrichments are coincidental with previous extinction horizons (30,31), which could be viewed as evidence of an increased resistance in the surviving species to chemical stress as the evolutionary process advances. From that perspective, the variability in the resistance of different species and strains to chemical and physical stress could reflect the environmental challenges during their evolution.

It can be inferred from the stratigraphic evidence of the thin iridium-enriched layer constituting the C-T boundary (5) that the environment recovered in a relatively short time after the chemical storm and that the surviving species, with less competition than ever before, had an excellent opportunity to multiply, radiate, and recolonize the Earth. The global extinction of species is currently occurring at such a high rate that, according to some experts, it could become the worst disaster in human history because the extinction of other species threatens our own survival; that is, the ecosystem services are essential to the quality of the environment and human life (32). The dynamics of biodiversity are influenced by a series of processes related to human activity, such as land-use changes and emission of pollutants (33). Paleocotoxicology could contribute to a holistic view on the role of chemical and physical stress on the evolutionary process, from the origination to the extinction of biodiversity on the planet.

Jorge Herkovits

Instituto de Ciencias Ambientales y Salud
Fundacion PROSAMA
Buenos Aires, Argentina
E-mail: herkovit@mail.retina.ar

REFERENCES AND NOTES

- Pimm SL, Russell GJ, Gittleman JL, Brooks TM. The future of biodiversity. *Science* 269:347–350 (1995).
- Benton MJ. Diversification and extinction in the history of life. *Science* 268:52–58 (1995).
- Roupe DM, Sepkoski JJ Jr. Periodic extinction of families and genera. *Science* 231:833–836 (1986).
- Archibald JD. Testing extinction theories at the Cretaceous-Tertiary boundary using the vertebrate fossil record. In: *Cretaceous-Tertiary Mass Extinctions: Biotic and Environmental Changes* (MacLeod N, Keller G, eds). New York/London:W.W. Norton & Company, 1996:373–397.
- Alvarez WA, Alvarez W, Asaro F, Michel HV. Extraterrestrial cause for the Cretaceous-Tertiary extinction. *Science* 208:1095–1107 (1980).
- Frederiksen NO. Paleocene floral diversities and turnover events in eastern North America and their relation to diversity models. *Rev Paleobot Palynol* 82:225–238 (1994).
- UNEP. *Chemical Pollution: A Global Overview*. Geneva:Earthwatch, United Nations Environment Programme, 1992.
- Kaiser J. Air pollution: evidence mounts that tiny particles can kill. *Science* 289:22–23 (2000).
- Herkovits J, Herkovits FD, Perez-Coll CS. Identification of aluminum toxicity and aluminum-zinc interaction in amphibian *Bufo arenarum* embryos. *Environ Sci* 5:57–64 (1997).
- Herkovits J, Helguero LA. Copper toxicity and copper-zinc interactions in amphibian embryos. *Sci Total Environ* 221:1–10 (1998).
- Herkovits J, Perez-Coll CS, Herkovits FD. Evaluation of nickel-zinc interactions by means of bioassays with amphibian embryos. *Ecotoxicol Environ Saf* 45:266–273 (2000).
- Herkovits J, Perez-Coll CS. Bioensayos para test de toxicidad con embriones de anfibio (ANFITOX). *Ing Sanitaria y Ambiental* 42:24–30 (1999).
- Herkovits J. Paleocotoxicology: extending environmental toxicology and chemistry to the interpretation of the fossil record. *Environ Toxicol Chem* 20:1623–1624 (2001).
- Marquet PA. Invariants, scaling laws, and ecological complexity. *Science* 289:1487–1488 (2000).
- Larison JR, Likens GE, Fitzpatrick JF, Crock JG. Cadmium toxicity among wildlife in the Colorado Rocky Mountains. *Nature* 406:181–183 (2000).
- Ma LQ, Komar KM, Tu C, Zhang W, Cai Y, Kennelley ED. A fern that hyperaccumulates arsenic. *Nature* 409:579 (2001).
- Duncan RA, Pyle DG. Rapid eruption of the Deccan flood basalts at the Cretaceous/Tertiary boundary. *Nature* 333:841–843 (1988).
- Hallam A. End-Cretaceous mass extinction event: argument for terrestrial causation. *Science* 238:237–242 (1987).
- Smith AG, Smith DG, Funnell BM. *Atlas of Mesozoic and Cenozoic Coastlines*. London:Cambridge University Press, 1994.
- Archibald JD. *Dinosaur Extinction and The End of An Era: What The Fossils Say*. New York:Columbia University Press, 1996.
- Jablonski D. Mass extinction: persistent problems and new directions. In: *The Cretaceous-Tertiary Event and Other Catastrophes in Earth History* (Ryder G, Fastovsky D, Gardner S, eds). Boulder, CO:Geological Society of America, 1996:1–9.
- Hickey LJ. Land plant evidence compatible with gradual, not catastrophic, change at the end of the Cretaceous. *Nature* 292:529–531 (1981).
- Roupe DM, Sepkoski JJ Jr. Periodicity of extinctions in the geologic past. *Proc Natl Acad Sci USA* 81:801–805 (1984).
- Benton MJ. Evolution, interpretations of mass extinction. *Nature* 314:496–497 (1985).
- Perez-Coll CS, Herkovits J, Salibian A. Teratogenic effects of cadmium on *Bufo arenarum* during gastrulation. *Experientia* 42:1174–1176 (1986).
- Bloom BR. On the particularity of pathogens. *Nature* 406:760–761 (2000).
- Earn DJD, Levin SA, Rohani P. Coherence and conservation. *Science* 290:1360–1364 (2000).
- Herkovits J. Are shape and morphogenesis independent phenomena? *Experientia* 33:510–513 (1977).
- Herkovits J, Perez-Coll CS. Increased resistance against cadmium toxicity by means of pretreatment with low cadmium/zinc concentrations in *Bufo arenarum* embryos. *Biol Trace Element Res* 49:171–175 (1995).
- Kyte FT, Zhou Z, Wasson JT. High noble metal concentrations in a late Pliocene sediment. *Nature* 292:417–420 (1981).
- Alvarez A, Asaro F, Michel HV, Alvarez LW. Iridium anomaly approximately synchronous with terminal Eocene extinctions. *Science* 216:886–888 (1982).
- Cairns J, Nierderlehner BR. Estimating the effects of toxicants on ecosystem services. *Environ Health Perspect* 102:936–939 (1994).
- United Nations Environment Programme. *The UNEP Biodiversity Programme and Implementation Strategy - A Framework for Supporting Global Conservation and Sustainable Use of Biodiversity*. New York:United Nations, 1996.



Knowledge
ehpjournal.com