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A theoretical exercise in the modeling of ground-level ozone resulting from the K–T asteroid impact: Its possible link with the extinction selectivity of terrestrial vertebrates

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ABSTRACT

The extinction pattern of the Maastrichtian indicates that long-term and short-term events contributed to the Cretaceous–Tertiary (K–T) mass extinction at 65 Ma. However, it is not clear how the impact events are linked with the extinction selectivity; e.g. non-avian dinosaurs became extinct, whereas birds survived. The post-impact air quality is discussed, and attention is focused on the then land vertebrates. Although ground-level (tropospheric) O_3 is a powerful irritant on the order of 0.1 ppm toxicity, the presence of ground-level O_3 has hardly been considered since the K–T impact theory was reported about 30 years ago. Under the post-impact conditions reconstructed by simulating the carbon cycle (including isotope balance) and impact chemistry, a trajectory model suggests that the then photochemical reactions formed ground-level O_3 whose concentration was apparently low at ~1.0 ppm, but it is much greater than the current level of ~0.04 ppm: that is, an O_3 concentration above the health-threatening level persisted on the ground after the K–T impact. All land vertebrates must have suffered from respiratory O_3 irritation at the time. However, analysis suggests that variables of O_3 characteristics – hourly variation, short half-life in water and decomposition due to catalytic effects in soil – were randomly combined with variables of lifestyle features such as habitat, torpor, etc. to form new variables (i.e. survival rates): a high survival probability for amphibians; middle/high probabilities for semi-aquatic reptiles, mammals and birds; low/middle probabilities for marsupials and terrestrial reptiles; and a zero probability for non-avian dinosaurs.

1. Introduction

It is essential to contemplate how already-known hypotheses – climate change, impact blast, acid rain, metal pollution, global wildfires due to thermal radiation, tsunami, earthquakes, etc. (review in Toon et al. (1997) and Rampino (1999)) – are linked with the Cretaceous–Tertiary (K–T) extinction (65 Ma). The main problem with most catastrophist and gradualist hypotheses lies in the selectivity of the mass extinction — about 50% survival rate for terrestrial species: e.g. non-avian dinosaurs were wiped out, while large crocodiles and small amphibians were unaffected (Sheehan and Fastovsky, 1992; Archibald, 1996). No one really understands why these animals escaped the K–T extinction (Alvarez, 1997). Several authors have grappled with this issue, but they have not yet provided an adequate explanation for it (review in Robertson et al. (2004)).

The extinction pattern of the Maastrichtian indicates long-term (gradual process) and short-term (rapid process) events contributed to the K–T mass extinction (Keller, 2001). Iridium enrichment at the K–T boundary provided the basis for the asteroid impact theory (Alvarez et al., 1980). The discovery of shocked quartz and impact spherules at the K–T boundary supports the asteroid theory (review in Smit (1999)). The Chicxulub crater of ~180 km diameter on the Yucatan Peninsula in northeastern Mexico (21°20′N and 89°30′W) is considered to be the asteroid impact site (e.g. Hildebrand et al., 1991). The ejecta layers mark the sudden mass-extinction horizon of the K–T boundary, but it is not clear how the impact event is linked with this mass extinction (review in Smit (1999)). The post-impact air quality is simulated by a theoretical exercise in modeling, and its possible link with the extinction selectivity of the then land vertebrates is discussed in this paper.

2. Stratospheric ozone vs. tropospheric (ground-level) ozone

In the stratosphere at 10–50 km altitude, ultra-violet (UV) light splits molecular oxygen into atom oxygen, and these individual atoms make a three-atom molecule (O_3) (review in Madronich (1993)). This stratospheric O_3 serves a useful function by filtering out harmful UV radiation (review in Janzen et al. (1999)). Although it has often been proposed that UV increased due to stratospheric O_3 depletion after the K–T impact (Cockell and Blaustein, 2000; Kouritidis, 2005; Birks et al., 2007), it seems difficult to explain the K–T selective extinction by this

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hypothesis. Most amphibians lay their eggs surrounded by transparent envelopes in open shallow water, and UV radiation can pass through their envelopes (Blaustein et al., 1994). High levels of ambient UV radiation can cause amphibian mortality (embryos in particular) and impair their immune systems (Blaustein et al., 2005). However, all the amphibians survived unaffected through the K–T boundary (Sheehan and Fastovsky, 1992; Archibald, 1996).

O_3 also occurs in the troposphere (lower atmosphere), and it is designated ground-level O_3 in this paper. Ground-level O_3 acts as a powerful respiratory irritant (Office of Air and Radiation, 1999). The probable toxic effect of gas released by the Chicxulub impact has been listed (Gerasimov, 2002), but lethal concentrations (LC) of the listed gases are very high — i.e. weak toxicities: 32,000 ppm LC for benzene C_6H_6, 1000 ppm for carbonyl sulfide COS, 1000 ppm for sulfur dioxide SO_2, 220 ppm for carbon sulfide CS_2, 100 ppm for hydrogen sulfide H_2S and 100 ppm for hydrogen cyanide HCN (Wexler, 1998). Ground-level O_3 is not on this list. Ground-level O_3 currently presents at low abundance of 0.03–0.04 ppm (cf. Janzen et al., 1999), but the permissible human exposure is set to 0.1 ppm (NIOSH, 1997). Although a slight variation of ground-level O_3 on the order of 0.1 ppm is a menace to life, the occurrence of ground-level O_3 in the K–T period has hardly been discussed since the asteroid impact theory was presented about 30 years ago.

3. Approach to reconstruct the K–T concentration of ground-level O_3

Terrestrial mass-independent stable isotope fractions (MIF) in oxygen and sulfur isotopes originate during photochemical reactions induced by sunlight (UV) in the atmosphere; this MIF technique makes it possible to measure the ancient concentration of ground-level O_3 (Thiemens, 2001). However, the known record of oxygen isotope MIF extends only to the Miocene at ~23 Ma (Rumble, 2003).

Since the MIF record cannot extend to the end Cretaceous at ~65 Ma, it is necessary to simulate the then concentration of ground-level O_3 in order to assess the link between ground-level O_3 and the K–T extinction. The input parameters for this simulation are perhaps seemingly unrelated, so they are summarized in Fig. 1 in order to clarify the description. Ground-level O_3 is produced through hydrocarbon-related photochemical reactions in the presence of sufficient nitrogen oxides (Madronich, 1993): that is, three main parameters are required in the K–T atmosphere: hydrocarbons, nitrogen oxides (NO_x), and sunlight.

4. Preparation of main input parameters

As the issues shown in Fig. 1 are numerous, it is attempted to provide each description (hydrocarbon, NO_x and sunlight) as simply as possible in order to consistently follow key concepts.

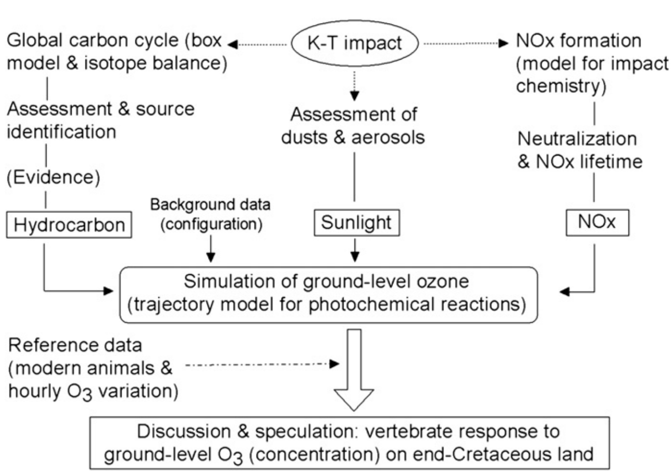

Fig. 1. Global scheme for evaluating responses of terrestrial vertebrates to K–T ground-level ozone.

4.1. Hydrocarbon input to the post-impact atmosphere

Consideration of the carbon cycle is a clue to making an estimate of atmospheric hydrocarbon. In order to predict the then carbon cycle, a box model simulation is combined with data obtained from the Deep Sea Drilling Project and the Ocean Drilling Program (review in Ivany and Salawitch (1993)): (i) a 1.4‰ $\delta^{13}C$ value before the K–T boundary and a −0.4‰ $\delta^{13}C$ value afterwards are given by calculating the average paleoceanic $\delta^{13}C$ gradients between surface water and deep water; (ii) the negative degree of the planktonic $\delta^{13}C$ gradient provides a lower limit to the amount of isotopically light carbon which must be added on condition that near cessation of primary productivity is sufficient to bring its gradient value to zero; the limit value (−0.4‰) is therefore more realistic than zero for estimating the carbon amount; (iii) normal factors (exchange frequency = 58.6^{-1} $year^{-1}$ and isotopic fraction for transfer = 1.0) are applied in this model simulation; and (iv) the impact-related materials presented in the Introduction indicate that the K–T boundary is associated with the asteroid event but not the Deccan Traps volcanism (Smit, 1999): cf. this volcanism did not release isotopically light carbon (Sheth, 2005).

A simulation run cannot reconstruct the lower limit (a $\delta^{13}C$ gradient of −0.4‰) on the applied conditions because of the isotopic imbalance between ^{12}C and ^{13}C in each reservoir (Fig. 2A); that is, a negative excursion in $\delta^{13}C$ means that isotopically light carbon (e.g. biogenic carbon) was delivered to the K–T atmosphere. Taking the isotopic balance into account, the simulation results when carbon is supplemented (on biomass base) are illustrated in Fig. 2B.

4.1.1. Input of biogenic carbon to the K–T atmosphere

It is necessary to consider where a great amount (1.3×10^{17} g of carbon at least) of isotopically light carbon (biogenic carbon) came from: (i) the Deccan Traps volcanism at ~65.4 ± 0.7 Ma (Hofmann et al., 2000) could not have accounted for the depletion in paleoatmospheric $\delta^{13}C$ necessary to change the isotopic gradients of planktonic carbonates in the shallow ocean because flood basalts of the Deccan Traps did not originate from a subduction zone (Sheth, 2005) — seafloor-altered basalts containing oceanic materials (i.e. isotopically light carbon), and hence a main factor for the negative $\delta^{13}C$ shift in the K–T atmosphere, was not the Deccan Traps volcanism; (ii) the impact-induced release of CO_2 from carbonate is a possible source of the increased atmospheric CO_2, but an experimental study shows that reverse reaction ($CO_2 + CaO \leftrightarrow CaCO_3$) occurs on a similar time scale (Agrinier et al., 2001); (iii) it is possible to consider the atmospheric input of marine carbon from the acidified ocean; however, it is reported that ocean acidification was local (Toon et al., 1997) and the amount of larnite grains (β-Ca_2SiO_4) contained in the impact plume also helped to neutralize the produced acids (Maruoka and Koeberl, 2003); and (iv) atmospheric injection of photosynthetic carbon (as CO_2) can be caused by biomass burning associated with global wildfires (Wolbach et al., 1985; Kring and Durda, 2002). The record in the K–T rocks suggests that the morphology of soot (i.e. aciniform type) (Harvey, 2004) is more consistent with a source from pyrolysis/combustion of organic-rich clays and rocks (Dypvik et al., 2005) rather than biomass burning (Belcher, 2006). Furthermore, if a lot of terrestrial vegetation were burned, a lot of charcoal would be expected on land. A field study shows that rocks laid down at the time contain little charcoal (Belcher et al., 2003).

4.1.2. Hydrocarbon (methane) and naturally occurring gas hydrate

Methane (CH_4) originating in natural gas hydrate (GH) is predominantly biogenic (Kvenvolden, 1993). The worldwide distribution of methane hydrates in outer continental margins of oceans is significant (Kvenvolden, 1998), and current estimates of CH_4 in the world's GH deposits are about 10,000 Gt of carbon (Kvenvolden, 1998). CH_4 commonly ponds and forms large deposits of free gas below a hydrate stability field, and the amount of this free gas is