If these arguments are correct, the amino acids that are crucial to agonist binding are in the β-subunit. Amin and Weiss find two regions of the $\beta 2$ subunit, separated by 41 amino acids, with sequences $\mathbf{Y}_{157}$GYT and $\mathbf{T}_{202}$GSY, which each appear to contribute a crucial tyrosine and threonine (indicated in bold). Conservative mutation of any of these four amino acids produced a large reduction in GABA potency, whereas mutations of several other amino acids in the region (or in the analogous regions of the $\alpha 1$ and $\gamma 2$ subunits) had relatively small effects. It is also interesting that mutations of the critical amino acids had little effect on activation of the channel by the barbiturate pentobarbitone (also known as pentobarbital): this elegantly confirms the view that GABA and pentobarbitone act on different sites.

The new findings do not exclude the possibility that GABA may bind to subunits other than the β (see, for instance, ref. 8). Indeed, expression of α, γ, δ or ρ subunits alone, or in heteromeric combinations that lack a β-subunit, can produce functional GABA-activated channels, albeit with some variability[9–11]. Each of these subunit types contains a tyrosine residue homologous with βY_{157}, and, with the possible exception of the δ subunit, at least some features of the two binding domains reported by Amin and Weiss. Whether these homologous regions in other subunits can also bind the agonist remains to be seen.

As more and more studies on mutated receptors appear, the question of whether or not mutations affect the initial binding of agonists will crop up again and again. Amin and Weiss have made a better attempt at answering it than most. □

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CRETACEOUS/TERTIARY BOUNDARY

Extinctions at the antipodes

Kirk R. Johnson

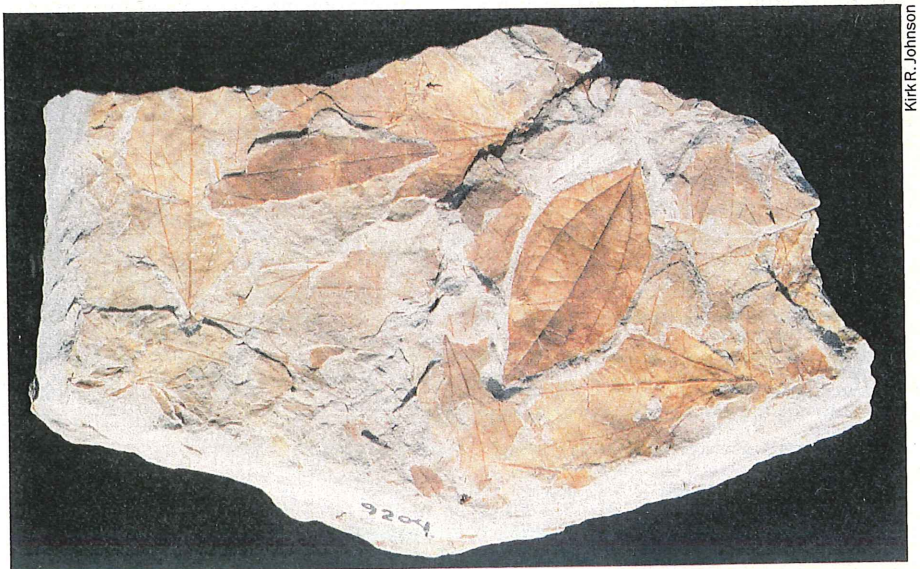
No one should expect that the second largest extinction in Earth history would turn out to be a simple affair. Although the theory that a bolide impact caused the mass extinctions at the Cretaceous/Tertiary (K/T) boundary has received wide acceptance in the 13 years since its proposal, most of the supporting data have come from mid-latitude sites, where there is evidence of the impact debris and its source crater, and detailed biostratigraphic records of large, abrupt extinctions. In contrast, the message emerging at a conference in Boston, Massachusetts*, was that the effects of the K/T event on life near the ancient South Pole were not particularly severe and, in some cases, were hardly noticeable. In addition, there is increasing evidence from a range of palaeolatitudes that large-scale plant, mollusc and nannofossil extinctions preceded the K/T boundary event by several million years.

When the impact-extinction hypothesis was first proposed, it appeared to be easily testable. In its simplest form, the hypothesis predicted stratigraphically abrupt extinctions, followed by low-diversity assemblages of surviving species. The K/T boundary record at high palaeolatitudes adds a complication to this prediction, that of the odd structure of extinct polar ecosystems. It is now generally accepted that Late Cretaceous polar regions, although subject to intensely seasonal regimes of light and dark, were nonetheless ice-free and forested[1]. There are no modern analogues for these ecosystems, and their response to an abrupt catastrophe such as a bolide impact would have been strongly affected by the time of year at which it happened. Organisms living at high latitudes in the Northern and Southern Hemisphere would have had different responses because the event would have occurred in opposite seasons.

A further snag with high-latitude K/T sections is that the distance from well-studied mid-latitude sections makes biostratigraphic correlation tenuous. One piece of good news at the conference was that the discovery of a significant iridium anomaly (R. Askin, University of California, Riverside) in fossil-rich sections on Seymour Island near the Antarctic Peninsula allows this site to be correlated to the K/T event. Among fossil dinoflagellates in this nearshore marine sequence, there is a decrease in the relative abundance of the dominant species above the iridium-bearing level, but there are only minor extinctions. The terrestrial pollen and spore record from this same section marks the boundary with the disappearance of only a few, rare taxa[2]. To be sure, caution should be exercised in the interpretation of terrestrial palynomorphs in marine sediments, but a similar pattern of low palynofloral extinction has been observed at the K/T boundary in terrestrial deposits in New Zealand[3]. This contrasts strongly with the pattern in the mid-latitude Northern Hemisphere (D. Nichols, United States Geological Survey) of high palynofloral extinction, where loss of roughly 30 per cent of species coincides with the iridium anomaly.

At the other end of the globe, a stratigraphic sequence from Alaska's North Slope (L. Marincovich, United States Geological Survey) shows apparent survival of some Cretaceous molluscs (not including ammonites or inoceramids) into the Palaeocene. But this pattern may have as much to do with the disputed position of the K/T boundary in the Colville River section as with mollusc survival[4]. In the pollen record for this sequence, the boundary is defined by high levels of extinction in the *Wodehouseia spinata* assemblage and occurs above the level of the putative Palaeocene molluscs[4].

The indisputably Cretaceous portion of



Kirk R. Johnson

Survivors — fossil leaves from the Lauraceae family, found in Nelson, New Zealand, represent one species that survived the K/T boundary event.

*The Cretaceous/Tertiary Boundary Event: Biotic and Environmental Changes, Geological Society of America National Meeting, Boston, Massachusetts, 27 October 1993.

this section holds the remains of dinosaurs[5], as do Early Cretaceous sites from high-palaeolatitude Australia[6], indicating that dinosaurs were able to survive in polar light regimes. This has been offered as evidence that the impact-induced darkness and cold would not necessarily have killed off the dinosaurs[5,6], but such hypotheses fail to account for the extreme seasonality of ancient polar climates. The dinosaurs could survive a polar winter that followed a highly productive polar summer. Remove the summer light with bolide dust and follow it with another dark winter, and things look considerably tougher.

Does the observed pattern of high K/T extinction in the Northern Hemisphere and low K/T extinction in the high latitudes of the Southern Hemisphere suggest that the Chicxulub bolide arrived in the boreal spring? Or is the geographical pattern of extinctions still too poorly known for us to speculate? These questions will only be answered by a greater geographical diversity of high-resolution K/T boundary studies. At the conference, alongside the suggestions of unexpected survivals ran a parallel thread of evidence for substantial extinctions well before the K/T event. Belemnites and inoceramid bivalves from the Seymour Island section disappeared near the Campanian/Maastrichtian boundary, several million years earlier (W. Zinsmeister, Purdue University). Ammonites from this section, once thought to extend into the Palaeocene[7], are not found *in situ* above the K/T iridium anomaly but do appear to decline in diversity towards the end of the Cretaceous period. At low palaeolatitudes, reef-building rudist bivalves disappeared about 1.5 million years before the boundary (C. Johnson, Pennsylvania State University).

Add these observations to other recently discovered events during the mid-Maastrichtian age, such as the major floral extinctions on land[8] and inoceramid[9] and nannofossil[10] extinctions at sea, and it looks as though a bolide impact alone cannot explain the whole of the biotic crisis at the end of the Cretaceous. □

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QUANTUM CHEMISTRY

The elusive signature of CH_5^+

Gustavo E. Scuseria

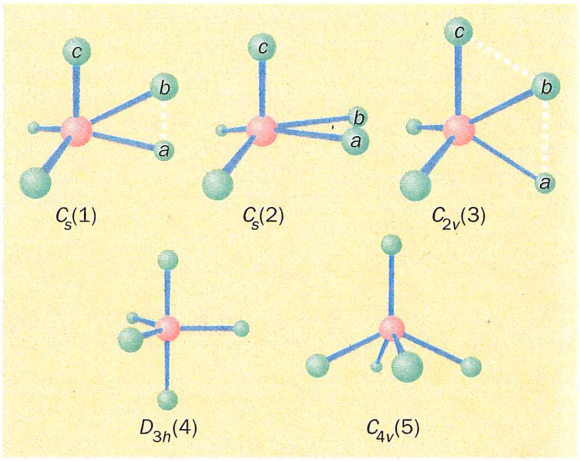
Do all molecules possess a definite equilibrium geometry? Although many molecules exist in multiple isomeric forms, usually a structure can be identified as the lowest in energy and assigned as the ground-state geometry conformation. But, in a paper entitled "CH_5^+: The never-ending story or the final word?", Schreiner *et al.*[1] conclude that protonated methane may be an exception to the rule.

Known since the 1950s and now a common gas-phase reagent for chemical ionization mass spectrometry, protonated methane's small size makes very-high-level quantum mechanical calculations computationally feasible, and its penta-coordinated carbon atom gives a special importance to establishing its structure. CH_5^+ is the smallest member and perhaps the prototype of the class of protonated alkanes or nonclassical carbonium ions, which play important roles as intermediates in acid-catalysed transformations of hydrocarbons and in many electrophilic reactions[2]. Yet despite the interest in protonated methane, a high-resolution infrared spectrum remains elusive. Attempts made by top practitioners such as Saykally (University of California, Berkeley) and Oka (University of Chicago) have so far been unsuccessful.

The conventional view of the structure of CH_5^+, shown as $C_s(1)$ in the figure, corresponds to a CH_3^+ unit strongly bound to a H_2 molecule by an energy of about 40 kcal mol^{-1}. This picture, supported by recent theoretical studies[3,4], is consistent with that of the nonclassical carbonium ions, which are known for forming three-centre/two-electron bonds[5]. Other isomers, such as $C_s(2)$, $C_{2v}(3)$, $D_{3h}(4)$ and $C_{4v}(5)$, have also been thought plausible candidates for the lowest-energy conformation. Previous calculations indicate that the $C_{4v}(5)$ structure is higher in energy than $C_s(1)$ by about 1 kcal mol^{-1}, and that the trigonal bipyramid $D_{3h}(4)$ isomer is unfavourable.

In the latest twist to the CH_5^+ story, Schreiner and co-workers have made high-level calculations demonstrating that although the $C_s(1)$ structure is the best candidate for the global energy minimum in the potential energy surface, the $C_s(2)$ and $C_{2v}(3)$ structures are transition states for hydrogen scrambling with remarkably small activation barriers. From calculations using large basis sets in conjunction with the coupled-cluster method[6,7], they conclude that the $C_s(2)$ and $C_{2v}(3)$ structures lie above $C_s(1)$ by 0.1 and 0.9 kcal mol^{-1}, respectively. If zero-point vibrational energy corrections are included, the energy differences among these three structures become essentially negligible.

These state-of-the art theoretical predictions, based on what is widely accepted as one of the most accurate *ab initio* computational quantum chemistry methods[8,9], are significant because they clearly indicate that for all practical purposes CH_5^+ does not have a unique, stable equilibrium structure. The hydrogen atoms are predicted to scramble almost freely among multiple equivalent minima. This effect, usually known as 'pseudorotation', yields very complicated spectra, which could be a true nightmare for experimentalists and may be already responsible for the spectroscopic elusiveness of CH_5^+. If the theoretical predictions turn out to be correct, attempts to interpret the experimental data based on a single structure may be doomed to fail.



Five possible structures for CH_5^+. (1) Lowest-energy minimum in the CH_5^+ potential energy surface. This structure corresponds to a hydrogen molecule (H_aH_b) strongly bound to a CH_3^+ unit. (2) Transition state for rotating H_a–H_b about the CH_3^+ unit leading to exchange of H_a with H_b. (3) Transition state for hydrogen scrambling that switches H_b and H_c, resulting in a H_bH_c molecule attached to CH_3^+. Because (2) and (3) are low-lying in the potential energy surface, all five C–H bonds are essentially equivalent and exchange dynamically very rapidly. (4), (5) Higher-energy isomers of CH_5^+.

Just a few months ago, Boo and Lee[10] attempted to stabilize CH_5^+ by attaching to it a weakly bound neutral species such as H_2. In this experiment, the idea is to assess the structural features of CH_5^+ indirectly by 'freezing' it with another small molecule which ideally stops the hydrogen