

E. Gileadi, in *Electrosorption*, E. Gileadi, Ed. (Plenum, New York, 1967), chap 1. However, each of the chelating diamines has a nonchelating diamine counterpart with similar or smaller solubility. Thus, 1,6-hexanediamine is similar in solubility to en, but en has a much larger K value; and use of p -phenylenediamine, a less soluble isomer of opda that cannot chelate, yields PL changes that have not saturated by the solubility limit, evidencing a much smaller value for K than was found for opda.

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31. We are grateful to the Pew Mid-States Science and Mathematics Consortium for summer support of G.C.L. and R.L.P., and to W. R. Grace and Company for support of C.J.M. as a 1989–1990 fellow. This work was supported by the Office of Naval Research and the 3M Company. We thank L. F. Dahl, D. F. Gaines, C. P. Casey, S. H. Langer, and P. M. Treichel, Jr., for helpful comments.

12 December 1989; accepted 1 March 1990

Proximal Cretaceous-Tertiary Boundary Impact Deposits in the Caribbean

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Trace element, isotopic, and mineralogic studies indicate that the proposed impact at the Cretaceous-Tertiary (K-T) boundary occurred in an ocean basin, although a minor component of continental material is required. The size and abundance of shocked minerals and the restricted geographic occurrence of the ejecta layer and impact-wave deposits suggest an impact between the Americas. Coarse boundary sediments at sites 151 and 153 in the Colombian Basin and 5- to 450-meter-thick boundary sediments in Cuba may be deposits of a giant wave produced by a nearby oceanic impact. On the southern peninsula of Haiti, a ~50-centimeter-thick ejecta layer occurs at the K-T boundary. This ejecta layer is ~25 times as thick as that at any known K-T site and suggests an impact site within ~1000 kilometers. Seismic reflection profiles suggest that a buried ~300-km-diameter candidate structure occurs in the Colombian Basin.

ALTHOUGH AN ARRAY OF STRATIGRAPHIC, mineralogical, chemical, and isotopic evidence (1) has accumulated in support of the theory (2) that the Cretaceous Period was terminated by an impact of a large (~10 km) asteroid or comet, a suitable crater has not yet been found. Several craters with ages of ~65 million years are known (3), but they appear to be too small. The crater might have been destroyed, because half of the then existing ocean floor has been subsequently subducted (4). In this report, we (i) describe a thick ejecta unit and impact-wave deposits in the Caribbean that, in conjunction with stratigraphy at nearby sites, suggest that the impact occurred between North and South America, and (ii) identify a possible impact site in the Colombian Basin of the Caribbean Sea.

The clay layers at the K-T boundary compose a couplet. An upper layer ~3 mm thick occurs globally and contains anomalously large amounts of siderophile (5) and chalcophile (6) trace elements, shocked minerals (7), spherules with spinels (8), soot (9), isotopic anomalies (10, 11), and anomalously low amounts of incompatible lithophile elements like the rare-earth elements (REE)

(12, 13). We call this the fireball layer, implying that it was dispersed by the impact fireball formed by vaporization of the projectile and target (14). On and near North America, a clay layer ~2 cm thick and containing similar evidence for an impact (12, 15–18) underlies the fireball layer. This layer (ejecta layer) may represent a geographically restricted facies of less energetic impact ejecta (19).

The Sm-Nd and Rb-Sr isotopic systematics and the incompatible trace element compositions of both layers (11, 15, 20) can be modeled as a mixture of ~20% oceanic crust, ~70% depleted mantle, and only ~10% continentally derived material (12). In addition, 10 to 15% of the fireball layer must be derived from an extraterrestrial object to account for its siderophile trace element abundances (5). The presence of pyroxene spherules and possibly shocked chromite grains in the fireball layer (21) is also suggestive of an oceanic impact site.

The occurrence of shocked and unshocked grains of quartz, alkali feldspar, and other felsic rock fragments in the fireball layer has often been cited as evidence of a continental impact (7, 22). However, the small amount [$<1\%$ globally averaged (22)] of such material is consistent with an impact into an ocean basin. The ejecta layer contains at least one order of magnitude fewer

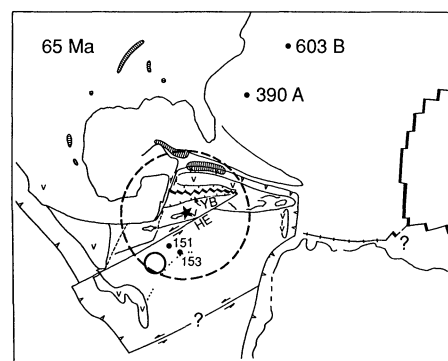


Fig. 1. A plate tectonic reconstruction of the Caribbean area at 65 million years ago [modified from (43)]; HE, Hess Escarpment; YB, Yucatan Basin. The lined areas show regions where impact-wave deposits occur. Impact-wave deposits also occur at DSDP sites 151, 153, and 603B. The star marks the position of the Beloc, Haiti localities. The dashed line is at a distance of 1000 km from those sites and corresponds to the inferred distance to the crater. The solid circle is a 300-km-diameter subcircular structure on the floor of the Colombian Basin. The positions of this structure and sites 151 and 153 and their distance to the Hess Escarpment and the Panama-Costa Rica arc have remained unchanged in this restoration. Oceanic crust south of the dotted line has since been subducted under South America.

shocked felsic minerals than the fireball layer (18).

Three lines of evidence indicate that the K/T impact was located near, and probably between, North and South America:

1) The maximum concentration of shocked mineral grains and the largest grains occur in North America (7, 22).

2) Probable impact-wave deposits have been reported at the K-T boundary (23, 24) only from the Caribbean and southern North America. (Fig. 1). Coarse deposits occur from shallow water to outer shelf environments along the southern margin of North America. A coarse boundary deposit also occurs at a continental shelf boundary in New Jersey (25). Offshore, at DSDP site 603B on the continental rise, a turbidity current deposited or reworked the ejecta layer (17, 26). The thickest, impact-wave deposits may occur in western and central Cuba, where Pszczolkowski (27) described a single graded bed from 5 to 450 m in thickness, occurring across 500 km and containing 500 km³ of sediment. The bed contains clasts up to 1.5 m in diameter at its base, many of which came from shallow water regimes, even though they were apparently deposited in a deep trough between the Bahamas platform and the Cuban island arc.

The only known abyssal K-T boundary sections showing coarse boundary deposits, which overlie stratigraphic gaps in the Upper Cretaceous, are DSDP sites 153 and 151 (Fig. 1) (28). At site 153, a ~15-cm-thick

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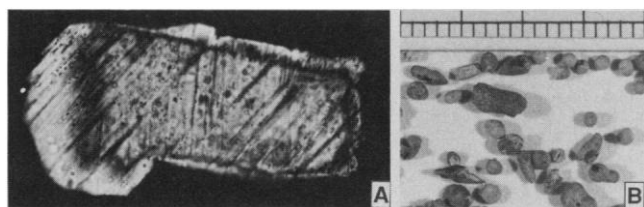


Fig. 2. (A) A 0.23-mm-long, shocked quartz grain from the thick K-T ejecta layer near Beloc, Haiti. This orientation shows two strong sets of shock lamellae. Such shocked grains are relatively common, but constitute much less than 1% of

the bulk layer. [Photo courtesy of G. Izett] (B) Altered, splash-form tektites and microtektites from the base of the ejecta layer. The finest division of the scale bar is 1 mm. The majority of the specimens are spherules, but discs, ovoids, teardrops, ellipsoids, dumbbells, rods, and irregular shapes also occur. Complete 7-mm specimens and fragments of objects up to an estimated size of 1 cm also occur.

silicified, intraformational limestone breccia occurs at the boundary overlying Middle Maastrichtian foraminiferal limestone. After a break in the core, the breccia is overlain by argillaceous nannoplankton marl of Early Paleocene age. At site 151, a more complex section is interrupted by gaps in core recovery. A polymict breccia 12 m thick lies on top of the basaltic basement. This breccia is soft and was probably produced by drilling disturbance. After a 50-cm gap, this breccia is overlain by ~50 cm of calcarenite containing redeposited Santonian (Upper Cretaceous) foraminifera and partly graded beds 2 to 3 cm thick. Above a small break in the core is an 18-cm-thick, competent, rusty silica deposit; this deposit is overlain by ~20 cm of foraminiferal calcarenite of the lower Paleocene *Globorotalia trinidadensis* foramin zone followed by a thick sequence of nannoplankton chalk.

Ahrens and O'Keefe (29) showed that giant waves produced from a large projectile, initially 4 to 5 km high for a typical ocean basin and declining inversely with distance, should cause significant erosion of the deep ocean floor only within a few crater radii of the impact site. Farther away, erosion will primarily occur where the wave runs up onto shallow margins; coarse deposits can be produced on platforms, slopes, and adjacent basins. The thick boundary deposits in Cuba suggest a nearby site, but only place the impact between the Americas. The boundary stratigraphy at sites 151 and 153 suggests an impact within ~1000 km (29), or less if these sites were shielded from the impact by islands or shallow water banks. The breccia and unconformity at site 153 may represent the minor effects of an impact wave. The stratigraphy at site 151 may represent a more proximal setting where a thicker sequence of upper Cretaceous sediments were eroded, and thin graded beds were deposited while the current regime returned to normal. Silicification is a possible consequence of alteration of a nearby sea floor crater (30).

3) The ejecta layer is known only from North America locales (24), and this distribution suggests a nearby impact (31). It has

not been found in Europe, Asia, the Pacific, nor New Zealand, although a minor component may be present in the fireball layer at some of these other sites (32).

The nearest known surface exposure of the K-T boundary to sites 151 and 153 is on the southern peninsula of Haiti. This section includes an unusual coarse mafic deposit, which Maurrasse interpreted (33) as an intraformational volcanogenic turbidite. The boundary is in the Beloc Formation, a thick monotonous sequence of deepwater marine limestones. We studied exposures at six sites occurring across ~2 km. All sites have been affected by weathering and tectonism. A coarse greenish-brown clay layer, ranging from 46 to 124 cm thick, occurs at the paleontological K-T boundary. The true thickness is probably 46 cm, that observed at the only site where a single, upwards-fining, graded bed is present; other sites show evidence of reworking. This unit is underlain by chalk containing the uppermost Cretaceous foraminiferal zone *Abathomphalus mayaroensis* and overlain by similar, lighter gray chalk containing the lowermost Paleocene index forams *Globigerina eugubina* and *Guembelitria cretacea* (33). At the type locality, this layer occurs immediately below a ~5-mm-thick gray clay layer that probably represents the fireball layer. The maximum Ir value from this section, 2.3 ppb (34), was measured in a weathered sample which included this gray clay. This gray clay and adjacent units have been extensively disturbed by bioturbation.

We interpret this greenish-brown unit as a thick ejecta layer, because it contains shocked quartz grains (Fig. 2) (35), has an Ir anomaly, and is depleted in incompatible elements (Fig. 3). The REE pattern of the layer's components (described below) is the characteristic U-shaped pattern exhibited by oceanic harzburgites with an approximately chondritic abundance level at the upper end of the harzburgite range (36). If this pattern does not reflect alteration, these REE data indicate an oceanic mantle provenance for the Haitian ejecta layer. Other lithophile incompatible elements, such as Rb, Cs, Th and U, also show severe depletions relative

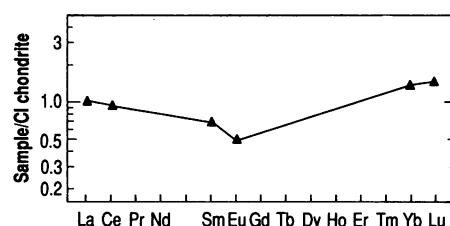


Fig. 3. Chondrite-normalized (62) neutron activation data for the REE from a single, altered tektite from the Haitian ejecta layer. Similar patterns and abundances are shown by two other altered tektites and a matrix sample, all from the base of the layer.

to typical continental crust. The abundances are an order of magnitude lower than those at any other K-T site, and thus the composition of the ejecta layer may have varied with distance. The thickness of the Haitian ejecta layer, ~25 times that of the thickest K-T ejecta layers from other areas, suggests that the impact site is nearby.

This layer contains many pelletal objects up to 1 cm in size (Fig. 2B). The objects are most abundant and largest at the base of the unit, but occur throughout. They are completely replaced by poorly ordered, smectitic, high Mg clay (37) and are both hollow and solid. Similar objects have been described from other K-T boundary layers (both marine and nonmarine), where they have been interpreted as altered microtektites (17, 38). The objects in the Haiti section are morphologically identical (39) but are larger and cross the arbitrary 1-mm size division between microtektites and tektites. They probably formed by alteration of mafic to ultramafic glass produced during the impact process and thus do not satisfy the conventional petrologic definition of microtektites because they were not siliceous. We refer to all sizes as altered tektites. We assume that the K-T tektites were altered, in contrast to most described microtektites, both because they are older and because of their mafic composition. Volcanic ejecta do not have the same range of morphologies (40), and volcanic processes cannot disperse such large objects over the observed range of ~4000 km. Prasinophyte algae (41) cannot produce objects of such shapes and sizes. The relatively large size of the altered tektites suggests a nearby impact site.

The ejecta layer in southern Haiti and the coarse boundary deposits in DSDP holes 151 and 153 are today near the northeastern margin of the Colombian Basin. The southern Caribbean has experienced a complicated plate-tectonic history (42). Most of the crustal elements of the southern Caribbean have probably moved 1000 to 2000 km northeastward relative to North and South

America since the end of the Cretaceous [Fig. 1 (43)]. Using an ejecta scaling relation (44), we show on Fig. 1 the approximate distance to the postulated progenitor crater from the Beloc localities. Possible target areas are the southern Gulf of Mexico, the trough between the Bahamas bank and the Cuban arc, the Yucatan Basin, and the larger basin between the Hess Escarpment and South America. The southern Gulf of Mexico is unlikely to be the impact locale because the geology is relatively well known and the Gulf Coast localities and DSDP site 390A, which are at roughly the same distance from this site as the Beloc localities, should also have thick ejecta layers, which they do not. The latter objection also applies to the now destroyed trough between the Bahama platform and the Cuban arc. Both of these regions are also inconsistent with the location constraint provided by the deposits at DSDP sites 151 and 153 (Fig. 1). The Yucatan Basin may be too close to the Beloc localities for the observed ejecta thickness. It is quite small, and enough is known about its geology (45) to make the occurrence of a large unidentified crater unlikely, although

subsequent tectonic activity has complicated the area. Much of the plate forming the ocean basin between the Hess Escarpment and South America has been subducted under South America; thus the impact site may have been destroyed. Remnants under the Venezuelan and Colombian basins. The only possible candidate we have found in the area is a craterform structure ~300 km in diameter in the Colombian Basin (Fig. 4), which has been described (46) as a basin underlain by typical ocean crust surrounded by basalts of an oceanic plateau.

Two multichannel (MCS) (46) and several single channel reflection seismic (SCS) profiles (47) across the subcircular structure indicate that it is an acoustic basement depression with a rough floor characterized by hyperbolic seismic diffractions (Fig. 5). A 30-km-wide annulus of generally inward-dipping normal faults, cutting smoother, layered basement surrounds the rough acoustic basement. The floor of the basin lies 500 to 1000 m below the level of the surrounding basement. The structure is now buried by 2 to 3 km of sediment. The central depression is ~125 km in radius. The sedi-

mentary cover of the Magdalena fan thickens to the southeast so that the southeast margin of the structure is unresolved and thus the size of the structure is uncertain by ~20 km. The surrounding crust has thicknesses of 10 to 18 km (48), but the crust is only ~8 km thick within the structure on the basis of two determinations at its margins (49). The crustal layering and velocities underneath the structure are also different from that in the surrounding crust and the seismic velocities are greater (49, 50).

If this structure is a crater, the rough terrain of the basement may be the surface of the impact breccia. The marginal faulting may represent relaxation slumping. The enlargement of the crater due to the observed annulus of slumping would be ~25%, which is less than observed at other large craters (51). An impact structure of this size would be a complex crater, and the seismic data does record an inner concentric ring ~10 km inside the perimeter of the rough terrain, but any topography, including the crater rim itself, should be severely modified by the giant backwash of the ocean as it filled the cavity. Other peaks are evident on the surface of the rough terrain, but do not form any obvious rings.

McKinnon (30) discussed the expected geophysical signature of a ~100-km-diameter impact crater on the seafloor, predicting a complex magnetic signature because of resetting and the effects of cooling and hydrothermal alteration. Magnetic anomalies over the central basin are broad and roughly oriented east to west and roughly define the basin margins (52). Magnetic anomalies in the surrounding crust also show some evidence of arcuate patterns concentric to the structure. The forebulge of the subduction zone to the southeast creates a large regional gravity anomaly that masks any local signature. A small positive anomaly does occur in the center of the structure (53), but is similar to other local anomalies in the Colombian Basin. The crater lies in a geologically unmapped area (54). The age of the crust in the Colombian basin is not well constrained; Bowland and Rosencrantz (46) suggested that it had a probable pre-Campianian crustal age (>85 Ma).

The center of the structure currently lies ~400 km from DSDP site 151, and ~450 km from site 153. Sites 151 and 153 may retain close to their original positions relative to the structure, although uplift has occurred for site 151 on Beata Ridge and many faults are known near both sites (54). These distances are consistent with erosion of the ocean floor by the initial giant wave as discussed above. The southern peninsula of Haiti has almost certainly undergone significant motion relative to the Colombian Basin

Fig. 4. Bathymetry of the eastern Colombian Basin, location of seismic studies, and location of candidate impact crater [bathymetry from (54)]. We have shown the boundary of the concentric zone of slumping only where the normal faults may be resolved within the basement; the two multichannel lines (Fig. 5) provide the best resolution of the acoustic basement. The acoustic basement is not resolved in some parts of the plotted seismic lines, especially toward the southeast. Additional seismic profiles have been taken across the structure, but much of the data does not penetrate to the acoustic basement within the structure. Some of the profiles do define the abrupt basement drop at the margin of the structure, however.

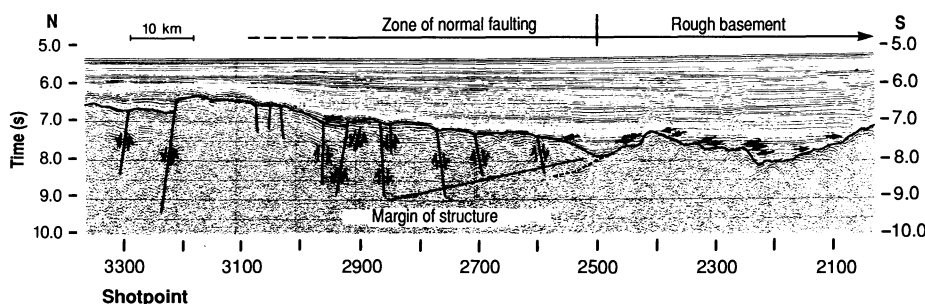


Fig. 5. Multichannel seismic reflection data [line CT1-27, from (46)] show the margin of a craterform structure in the Colombian Basin. The vertical exaggeration is seven times at the sediment-water interface; as seismic velocities increase with depth, the vertical exaggeration decreases. Topographic highs, such as at shot point 2400, form a concentric ring ~10 km in from the margin of the rough acoustic basement. The arrows indicate onlap of overlying sediments, which shows the topography is not due to faulting. This cross section is not perpendicular to the perimeter of the structure; the true width of the annulus of normal faulting is ~30 km.

crust, as it is separated from the structure by major faults (Fig. 1). The Cuban localities were at a distance of ~1500 km where the free-standing wave would still be ~500 m high. Although the structure would probably have been marginally in the eastern Pacific at K-T time, the gap between North and South America was wide enough to allow the impact waves to travel northward to the southern coast of North America. Reflection, refraction, and diffraction of the waves would allow scouring of the Gulf Coast even if a barrier, such as the Cuban island arc, were interposed.

This 300-km-diameter structure satisfies most of the trace element and isotopic provenance requirements. However, an impact at this location may not be able to supply the continental component to the boundary layers. At North American sites the proportion of shocked to unshocked grains, their cathodoluminescence, and the characteristics of their shock features (22, 55–57) are suggestive of a mixed provenance of crystalline and sedimentary targets. Some felsic components could come from altered rocks of the ocean crust (58, 59). If a continental fragment, or island arc segment, were present in the target area, it would also have been a source. Multiple simultaneous impacts, although rare events, could also account for the dual petrologic character if one of the projectiles impacted continental crust.

Regardless of whether the suggested structure is actually the K-T crater, the thick K-T ejecta layer in Haiti and the coarse boundary sediments exposed on Cuba and at Caribbean DSDP sites imply that the K-T impact occurred nearby. Other structures in the area may need further investigation; Christofferson and Hamil (60) suggested that a ~500-km-diameter zone of radial deformation occurs in the western Colombian Basin. An impact at this location, on the margin of the continental Nicaragua Rise, could easily satisfy the provenance constraints. Alternatively, the ~200-km-diameter, circular, magnetic, and gravity anomalies reported by Penfield and Camargo (61) on the continental Yucatan Platform could indicate a buried impact structure, although it probably could not alone satisfy the provenance constraints.

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19 December 1989; accepted 16 April 1990

Structural Motif of the GCN4 DNA Binding Domain Characterized by Affinity Cleaving

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The NH₂-terminal locations of a dimer containing the DNA binding domain of the yeast transcriptional activator GCN4 have been mapped on the binding sites 5'-CTGACTAAT-3' and 5'-ATGACTCTT-3'. Affinity cleaving was effected by synthetic GCN4 proteins with Fe·EDTA moieties at the NH₂-terminus. Analysis of the DNA cleavage patterns for dimers of the Fe·EDTA-proteins corresponding to GCN4 residues 222 to 281 and 226 to 281 revealed that the NH₂-termini were in the major groove nine to ten base pairs apart and were symmetrically displaced four to five base pairs from the central C of the recognition site. This result is consistent with the Y-shaped scissor grip-leucine zipper model recently proposed for a class of DNA binding proteins important in the regulation of gene expression.

A CLASS OF SEQUENCE-SPECIFIC DNA binding proteins important in the regulation of gene expression has been proposed to bind DNA through a bipartite structural motif consisting of a DNA binding domain, termed the "basic region," and a dimerization domain, termed the "leucine zipper" (1). These proteins recognize binding sites on DNA that consist of abutted inverted repeats. An evaluation of conserved amino acids within the basic region of several sequences from plant, mammalian, and fungal proteins located at invariant distances from the leucine zipper (bZIP proteins) has led to a provisional "scissor-grip" model for DNA binding (2). Vinson, Sigler, and McKnight propose that two polypeptide chains join to form a Y-shaped molecule (2). The stem of the Y is the dimer-forming region and corresponds to a coiled pair of amphipathic α helices, 30 amino

acids long (1). The bifurcating arms of the Y emerge from the paired α helices and begin tracking each half site in opposite directions along the major groove of the DNA (2). The bZIP model predicts that a rotationally symmetric dimer forms and that the NH₂-terminal extensions of the leucine zipper bend to grip around the major groove of DNA on the side opposite to their initial approach (2).

Although footprinting studies are consistent with symmetrical contacts in the major groove, there is little other structural data concerning the basic region of bZIP proteins bound to DNA (2). Neither x-ray diffraction nor two-dimensional nuclear magnetic resonance studies have been reported on this class of DNA binding proteins. Remarkably, the Y-shaped motif has been derived mostly from model building (2).

We report affinity cleaving studies designed to investigate the structure of the DNA binding domain of the yeast transcriptional activator GCN4, a putative basic region-leucine zipper (bZIP) protein. GCN4 is necessary for the coordinate induction of

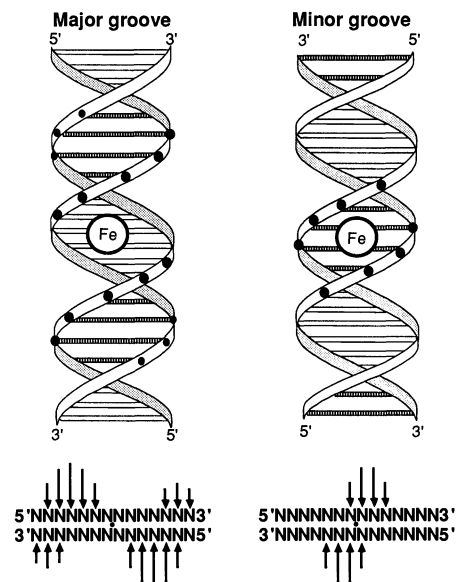


Fig. 1. Cleavage patterns produced by a diffusible oxidant generated by Fe·EDTA located in the major and minor grooves of right-handed DNA. Filled circles represent points of cleavage along the phosphodiester deoxyribose backbone. Sizes of circles represent extent of cleavage.

30 to 50 proteins involved in the biosynthesis of amino acids in response to amino acid starvation (3). A functional dissection of GCN4 has demonstrated that the 60 amino acids at the COOH-terminus, residues 222 to 281, contain the specific DNA binding activity; however, 37 residues (245 to 281) at the COOH-terminus were shown to be insufficient for DNA binding (4). GCN4 exists as a dimer and the 60 residues at the COOH-terminus are sufficient for dimerization (5). The optimum DNA binding site for GCN4 is 5'-rrTGACTcatt-3' (6). Struhl and co-workers have proposed that this pseudosymmetric site behaves as two half-sites, noting that mutation of the naturally occurring GCN4 binding site 5'-TGACTCT-3' to the symmetric 5'-TGACTCA-3' increases the affinity of the protein for the DNA, whereas all other mutations in this region lead to unchanged or decreased affinity. However, mutation of the TGACT bases leads to the greatest reduction in binding affinity, and mutation of the central C to G abolishes activity, implying that the protein-DNA interactions at each half site are not equal (6).

Incorporation of the DNA cleaving moiety, Fe·EDTA, at discrete amino acid residues within a protein allows the positions of those residues in the protein-DNA complex relative to the DNA bases to be mapped to nucleotide resolution (7). After chemical activation with a reducing agent such as dithiothreitol (DTT), Fe·EDTA localized at a specific DNA binding site cleaves both DNA strands, typically over four to six base

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