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The Cretaceous/Tertiary boundary in the Gurnigel Flysch (Switzerland)

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ABSTRACT

A complete Cretaceous/Tertiary boundary [K/T] section has been found in the Gurnigel Flysch in the Martisgraben (Kanton Bern, Switzerland) near Zollhaus. Biostratigraphically, both the uppermost Maastrichtian *Micula prinsii* calcareous nannofossil Zone and the lowermost Danien *Markalius inversus* (NP1) Zone are present. The extremely thin Boundary Clay is geochemically characterized by an Ir-anomaly which reaches a maximum of nearly 5 ppb in the Boundary Layers five millimeters above the lithological boundary. The concordance of a negative $\delta^{13}C$ isotopic shift with the enrichment in iridium and a general decline of the $\delta^{18}O$ isotopic ratios clearly define the K/T boundary of this section. Additionally, diagenetically formed goethitic spherules occur in the samples from the Boundary Clay but no potassium-feldspar spherules and no shocked quartz were found. The Martisgraben section is the first statigraphically complete K/T boundary in Switzerland and the first flysch section containing this boundary sequence known to date. The depositional situation of this profile enables the observation of the effects of the terminal Cretaceous events in a deep-sea environment. A new model of the tectonic situation and the structure of this part of the Gurnigel nappe is presented.

RÉSUMÉ

Une section complète de la limite Crétacé/Tertiaire [K/T] a été découverte dans le flysch de la nappe du Gurnigel, dans le Martisgraben (Canton de Berne, Suisse) près de Zollhaus. Du point de vue biostratigraphique, les deux zones de nannofossiles calcaires, la zone à *Micula prinsii* du Maestrichtien terminal et la zone à *Markalius inversus* (NP 1) du Danien inférieur sont présentes. L'argile, très mince, de la limite (Boundary Clay) se caractérise géochimiquement par une anomalie en iridium, qui atteint presque un maximum de 5 ppb dans les niveaux à cinq millimètres au-dessus de la limite lithologique. La concordance d'un pic isotopique négatif de $\delta^{13}C$ avec l'enrichissement en iridium, et d'une tendance générale à une diminution du rapport isotopique $\delta^{18}O$ définit clairement la limite K/T de cette section. Des sphérules de goethite, d'origine diagénétique, ont été trouvées dans les échantillons des niveaux de la limite K/T (Boundary Clay). Ces niveaux n'ont fourni ni sphérules de feldspaths potassiques ni quartz choqués. La section du Martisgraben est la première limite K/T, stratigraphiquement complète, découverte en Suisse et la première section de flysch contenant cette limite, décrite à ce jour. Le milieu de dépôt de ces sédiments permet d'étudier les perturbations créées par les événements du Crétacé terminal dans un environnement de mer profonde. Un nouveau modèle de la situation tectonique et de la structure de cette partie de la nappe du Gurnigel est présenté.

ZUSAMMENFASSUNG

Ein vollständiges Kreide/Tertiär [K/T] Grenzprofil wurde im Gurnigel Flysch im Martisgraben (Kanton Bern/ Schweiz) nahe Zollhaus gefunden. Biostratigraphisch gesehen ist sowohl das oberste Maastrichtian (Coccolithen Zone von *Micula prinsii*) als auch das unterste Danian (*Markalius inversus* Zone, NP 1) vorhanden. Die sehr dünne

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Grenztonschicht ist geochemisch durch eine Ir-Anomalie gekennzeichnet, die 5 mm über der basalen Grenzlage ein Maximum von fast 5 ppb erreicht. Diese Lage ist weiterhin durch einen negativen Ausschlag in $\delta^{13}C$ und einen allgemeinen Rückgang in den $\delta^{18}O$ Isotopen-Verhältnissen charakterisiert, wodurch die K/T Grenze eindeutig geochemisch definiert ist. Ferner wurden im unteren Teil des Grenztones diagenetisch entstandene goethithische Kügelchen gefunden, jedoch keine Kalifeldspat-Partikel und keine geschockten Quartze. Das Profil im Martisgraben ist das erste stratigraphisch vollständige K/T Profil in der Schweiz und das erste Flyschprofil mit einer vollständigen K/T Grenze überhaupt. Die Ablagerungsgeschichte dieses Profils ermöglicht ein genaues Studium der Ereignisse gegen Ende der Kreide in der Tiefsee. Ein neues Modell über die tektonische Situation und die Struktur jenes Teils der Gurnigel Decke, in welchem sich das untersuchte Profil befindet, wird vorgestellt.

1. Introduction

The intensified search for sections with more or less continuous accumulation over the Cretaceous/Tertiary (K/T) boundary was triggered at the beginning of this decade by the discussion about the event(s) at the end of the Cretaceous period which severely affected the biosphere and led to the extinction of the dinosaurs, ammonites, belemnites, rudists and many species of the calcareous zoo- and phytoplankton. At the symposium "Cretaceous/Tertiary Boundary Events" in Copenhagen in 1979, Alvarez et al. (1979a, b) reported anomalous iridium levels at the K/T boundary in Gubbio (Italy) attributing them to a source from the solar system rather than from a supernova, as they had suggested earlier that year. At the same symposium, Van Stuijvenberg et al. (1979) commented about the K/T boundary in Switzerland: "although Upper Maastrichtian and Lower Danian sediments are shown to be present in the Gurnigel Flysch and in the Schlieren Flysch and can be dated by calcareous nannofossils and dinoflagellates, no outcrop with an undisturbed section including a biostratigraphically well recognisable K/T boundary has yet been found".

Fieldwork carried out by De Kaenel (1986) in the Gurnigel Flysch led to the need for dating, by calcareous nannofossil biostratigraphy, of the various units in the structurally complex Schwyberg-Hällstett area. It was then realised that the uppermost Maastrichtian *Micula prinsii* Zone was present at the same locality as the lower Danian *Cruciplacolithus tenuis* Zone. The following search for the actual boundary with its typical Boundary Clay was immediately successful and reported upon by De Kaenel at the meeting of the Swiss Geological Society on Oct. 4th, 1985. This presentation of the results of our investigations is an interesting detail in Swiss geology rather than a contribution to or a review of the discussion about the K/T boundary events and their cause(s), which can be found in papers by Smit & Romein (1985), Alvarez (1986), Hallam (1987), Officer et al. (1987) and many other authors quoted therein.

2. Site location

The region studied is located 15 km SE of Fribourg and 30 km SW of Bern. The studied K/T section is situated between the Hällstett and the Schwyberg summits, near Zollhaus, along the Martisgraben, on its left bank, (Figs. 1 and 2); topographical map 1:10,000, sheet no. 1206.3, coordinates 590.08/174.52, altitude 935m (map 1:25,000, sheet Guggisberg, no. 1206).

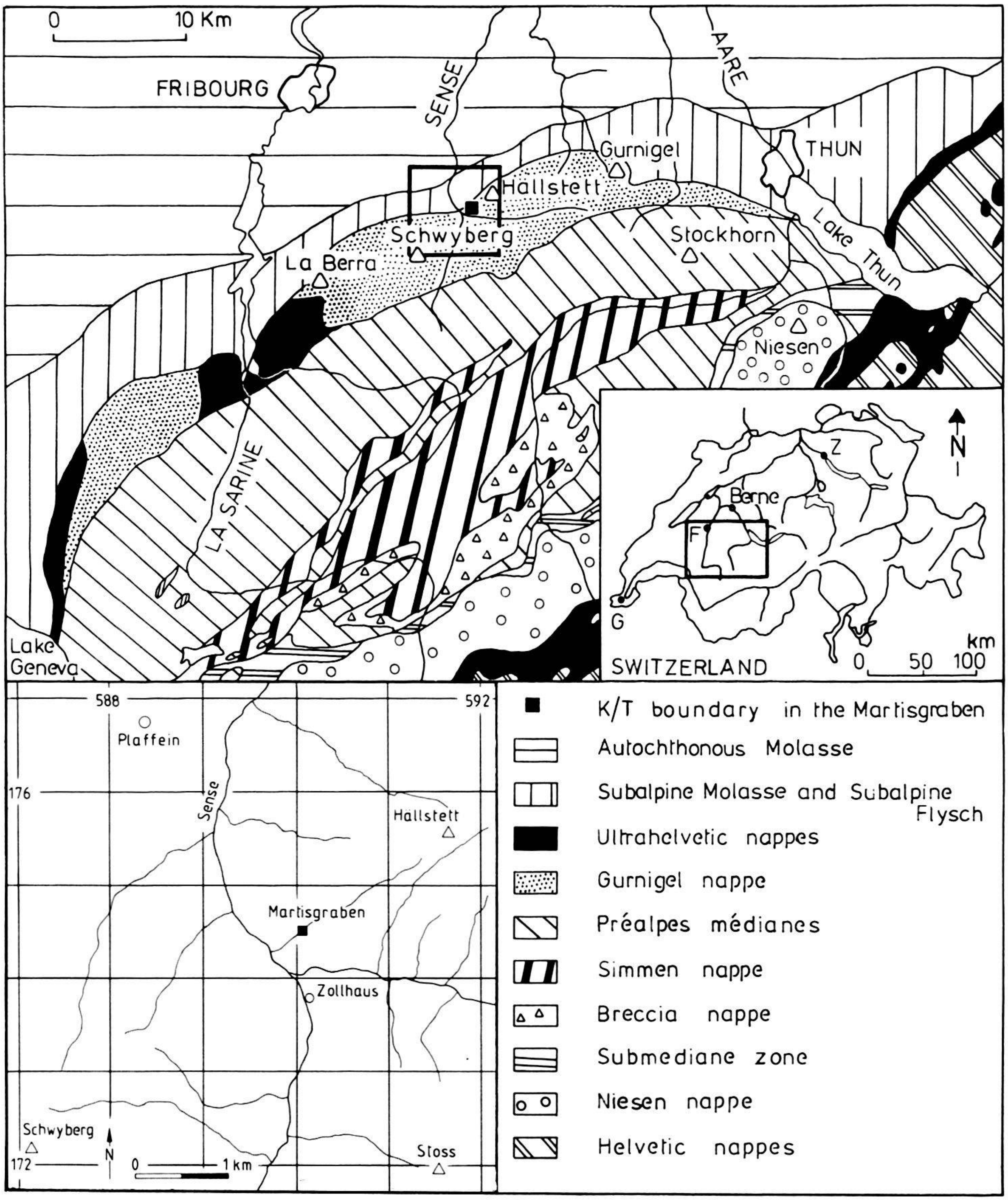


Fig. 1. Tectonic diagrammatic map of the Prealps (in part after SPICHER, 1972) and geographical situation of the K/T boundary in the Martisgraben (Gurnigel nappe), South-East of Fribourg.

3. Geological situation

The Gurnigel nappe forms part of the external Swiss Prealps (Fig. 1). The Gurnigel Flysch series, consisting mainly of sandstones, pelitic turbidites and hemipelagic pelites, are more than 1000 m thick. Most of the flysch is Middle Maastrichtian to

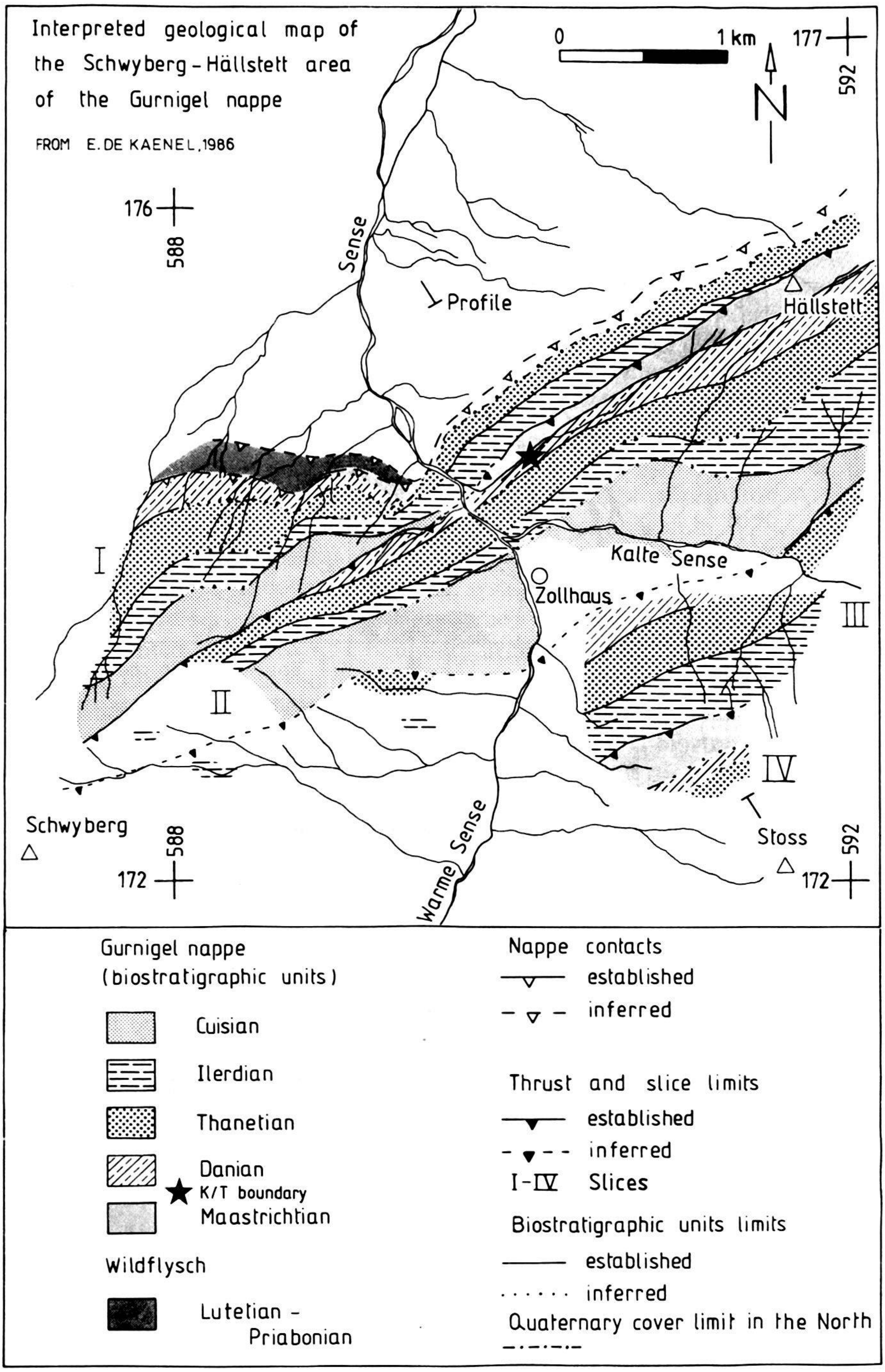


Fig. 2. Interpreted geological map of the Schwyberg-Hällstett area (after De Kaenel 1986).

Middle Eocene in age and was deposited in an abyssal to bathyal environment, its paleogeographical origin being the South Penninic-Ligurian ocean (STUIJVENBERG 1979). The facies indicates an evolution of the sedimentation from a deep-sea basin setting to a deep-sea fan set at the lower part of the continental slope. This evolution, beginning with the Lower Danian sediments, is determined by the tectonic movements taking place in the basin and by global negative eustatic movements.

The nappe consists of several imbricated thrust sheets (Fig. 2) which form a duplex type structure (DE KAENEL 1986). Heading south from the thrusted Subalpine Molasse, the following units are successively encountered [zonations of SISSINGH (1977, Maastrichtian) and MARTINI (1971, Tertiary)]:

- the wildflysch, Middle to Late Eocene in age (NP 16–18).
- four imbricated thrust sheets of the Gurnigel nappe, which are often incomplete with respect to the full stratigraphic range involved:
  - I. Gebrannte Egg slice: Thanetian to Ilerdian in age to the east (NP 5–10) and Late Cretaceous to Eocene in age to the west (CC 25- NP 14).
  - II. Hällstett slice: Maastrichtian to Cuisian in age (CC 25- NP 14).
  - III. Schafera slice: Danian to Ilerdian in age.
  - IV. Erlenbruch slice: beginning with sediments of Maastrichtian age and reaching the Eocene at the Stoss.

The K/T boundary section described in this study lies in the Hällstett slice.

4. Structural geology

The Gurnigel nappe is the most external unit of the Prealpine nappes and forms their western and northern front. For understanding the structure of the Gurnigel nappe, it is important to know that its origin is considered to lie South of the main Prealpine units (CARON et al. 1980). It is therefore postulated that the Gurnigel nappe was thrust over the entire Prealpine area to be emplaced onto Subalpine Molasse.

It consists of several imbricate thrust sheets and of duplexes (Fig. 3) having a lateral extension of several km.

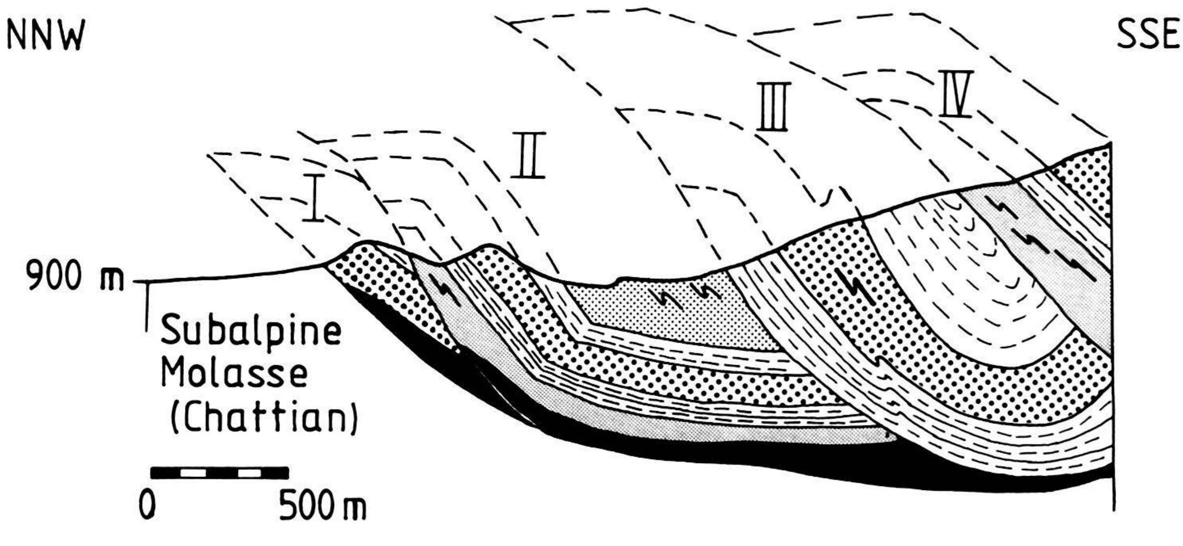


Fig. 3. Geological profile through study area (same legend as Fig. 2, except for the wildflysch in black).

The internal structure of the nappe is best described as a duplex structure characterised by an alternating ramp-flat morphology (De Kaenel 1986). This was documented by various methods, such as the construction of isohypse contours of the limits between different units and of the thrust faults (see Butler 1982; Boyer & Elliot 1982 for theoretical explanations).

Many units pinch out (Fig. 2) at inflexions of the thrust planes. The lateral ramps of the sheets are also the cause of this phenomenon and, for this reason, individual imbricates are lense shaped. Hence, the pinching-out is due to the structure of the sheets.

In the study area, the main thrust and minor thrust planes plunge to the SE (Fig. 3). Cleavage and axial planes of folds are roughly parallel to the thrust planes. Generally fold axes are oriented NE-SW. Close to the thrust planes bedding is reoriented and fold axes change direction, becoming parallel to the transport direction of the nappe.

In the southern region, in contact with the Prealps Medianes Plastiques, the most internal slice of the Gurnigel nappe is in an overturned position. This situation is explained by a late reactivation of an "out of sequence thrust" bringing the Prealps Medianes over the internal part of the Gurnigel nappe. The duplex-formation predates this event. Obviously, the structure described here may be faulted as a consequence of continued thrusting. This hangingwall structure is explained as a result of a piggy-back thrust propagation (Butler 1982; Ori & Friend 1984).

5. Lithology and sedimentology

The lithologies and sedimentary facies of the Upper Maastrichtian/Lower Danian are shown in the profiles (Figs. 5, 6 and 7). The section is subdivided into 16 individual sequences (Fig. 7), numbered according to a prominent bed at the base of each sequence (numbers 20 through 35). Sample numbers are systematically composed of two leading digits indicating the corresponding sequence and may be completed by (either) a third digit or letter.

5.1 Upper Maastrichtian

This first part of the Upper Maastrichtian studied (up to bed 27) consists of alternating fine grained sequences (Fig. 7), comprising:

a) Pelitic turbidites (mudstones), which are the dominant lithology in volume; beds 2–100 cm thick, containing 8 to 38% carbonates.
b) Fine-grained limestone arenites (sandstones), in thin beds, 2–20 cm thick.
c) Silty micritic limestone, beds 30 cm thick, blue-brown in color but with a yellowish color due to alteration. They are found at the bottom of the outcrop, some 15 m below bed M 20.
d) Green hemipelagic pelites, containing 5 to 15% carbonates. They form the upper part of many sequences and are generally 2–3 cm thick.

The turbiditic sequences were deposited in a pelitic-sandstone facies. The facies-types D3, D2 and G of Mutti & Ricci Lucchi (1975) are dominant in the lower section and reach bed M 27. These turbidites form cycles that are generally fining and thinning upwards, which end at the top with hemipelagic layers of facies-type G.

These mudstones with fine-grained current-laminated sandstones were deposited by diluted turbidity currents.

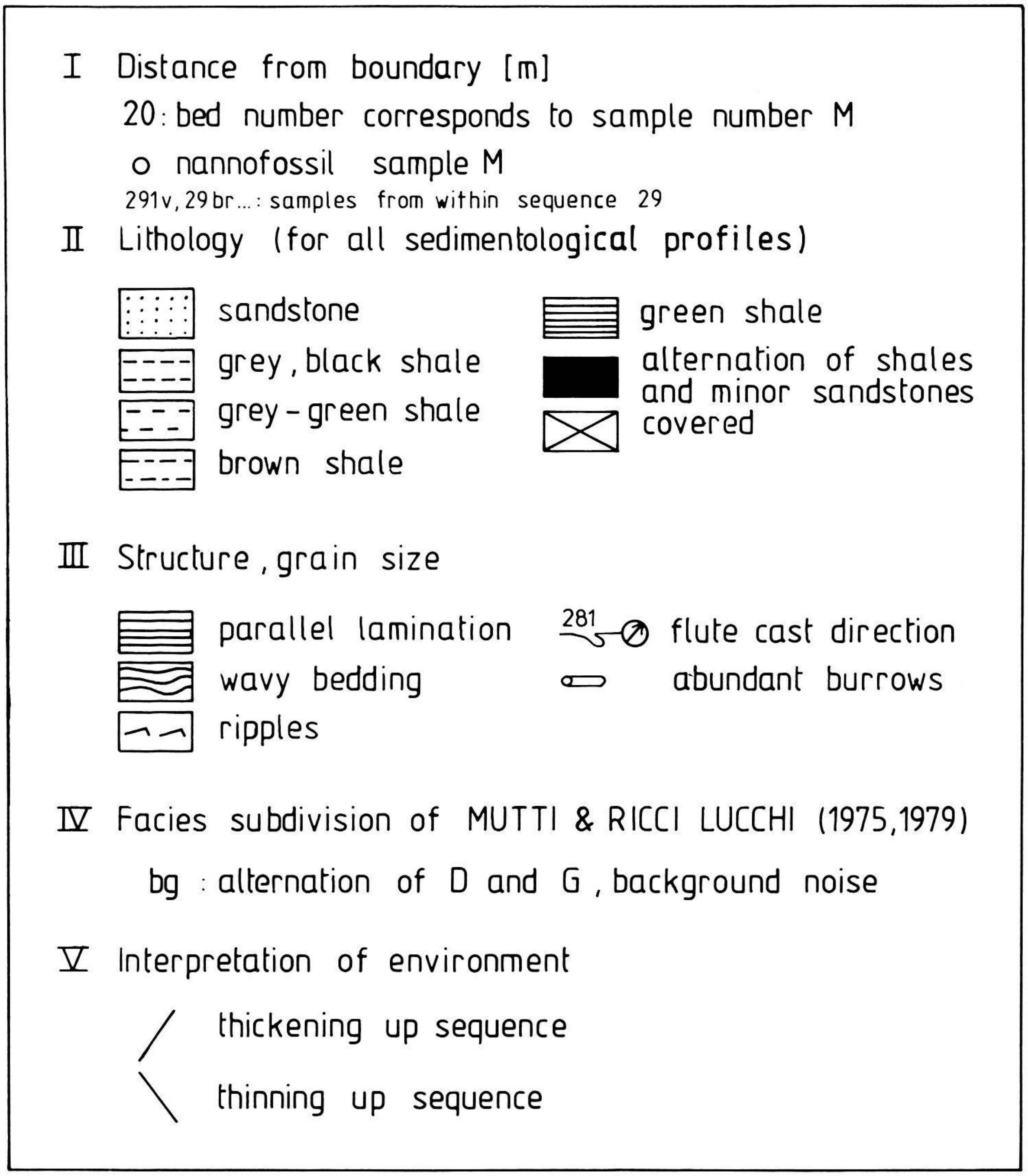


Fig. 4. Legend of sedimentological sections (Figs. 5, 7 and 9).

In the hemipelagic intervals of individual turbidites the presence of siliceous agglutinated foraminifera (*Rhabdamina*-faunas) indicates that the sedimentation took place below the CCD (Van Stuijvenberg 1979, Winkler 1983, 1984). Planktic calcareous foraminifera, *Globotruncanita stuarti* (M 6) were found in turbiditic deposits, but never in hemipelagic deposits, where *Rhabdamina sp.* was predominant. Debris of algae *(Lithothamnium),* bivalves and echinoderms were found in the sandy turbiditic intervals.

The presence of turbiditic limestone deposits could be explained by very high rates of $CaCO_3$ production by planktic foraminifera and calcareous nannoplankton. It

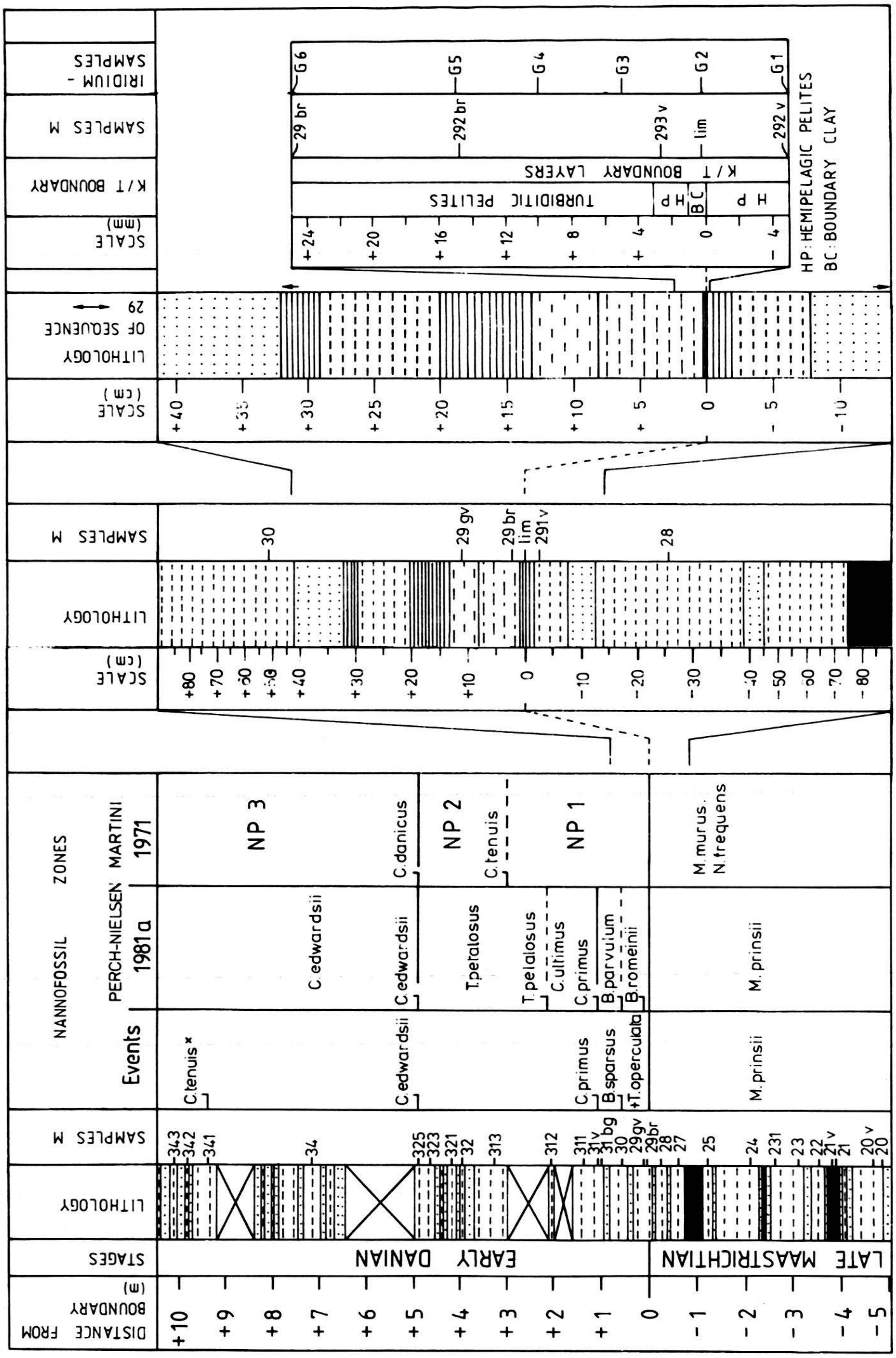


Fig. 5. Lithology, biostratigraphy and chronostratigraphy of the Cretaceous/Tertiary boundary of the Gurnigel Flysch of the Martisgraben section (legend Fig. 4).

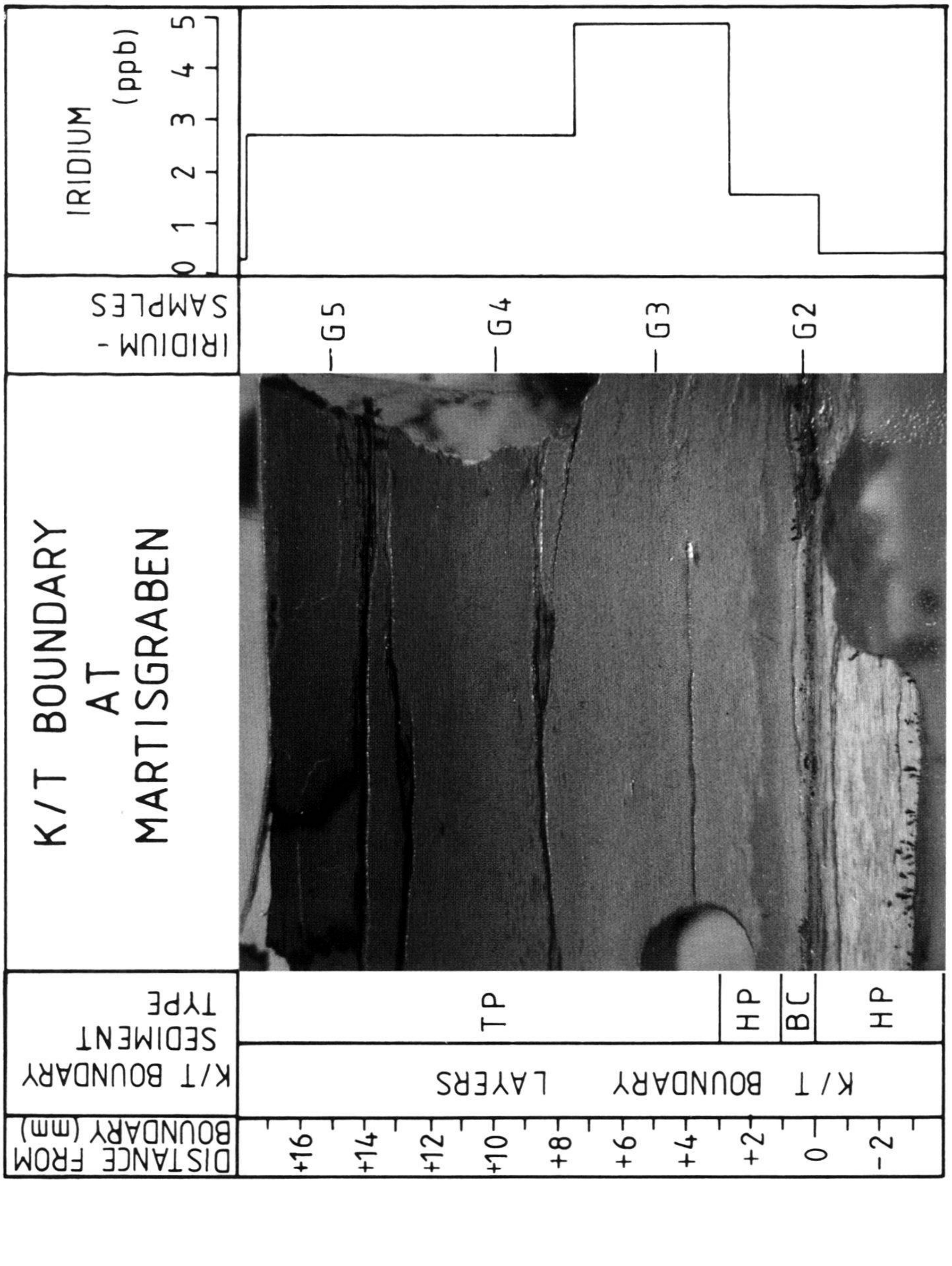


Fig. 6. Detailed section, sedimentology and Iridium distribution of the K/T boundary interval at Martisgraben. TP: Turbiditic Pelites, HP: Hemipelagic Pelites, BC: Boundary Clay.

seems, in our opinion, more probable that these lime turbidites were deposited very rapidly, inhibiting the deep waters (which are undersaturated in $CaCO_3$) from dissolving the carbonate. This type of facies, dominated by the grey pelitic turbidites but containing several hemipelagic limestone pelitic layers, suggests an environment of sedimentation characteristic of a deep-sea plain (MUTTI et al. 1975; MUTTI 1985), encroached at the end of the Maastrichtian by the continental slope and therefore influenced by a lobe of a deep-sea fan.

5.2 The K/T Boundary Interval: K/T Boundary Layers and Boundary Clay

Sequence 29, which contains the K/T Boundary Interval, has a total thickness of 47 cm (Fig. 5). This sequence is composed of three turbidites, which have thicknesses of 14, 20 and 13 cm respectively. Each of these three turbidites is characterized by a bed of hemipelagic calcareous pelites.

The base of the K/T Boundary Layers is represented by sample G1 (0.43 ppb Ir at −0.5 cm; Fig. 5) and the top is marked by sample G6 (0.3 ppb Ir at +2.5 cm). Lithologically, a separation into two subunits is possible within the K/T Boundary Layers: a green hemipelagic, pelitic layer (HP) marks the basal part (−0.5 cm to +0.3 cm) and is overlaying by brown turbiditic, pelitic layers (TP; from +0.3 cm to +2.5 cm; Fig. 5).

The K/T boundary is defined by a 1 to 2 mm thick, yellow-grey layer, the Boundary Clay (BC). This layer lies within subunit HP, some 2 mm below subunit TP, which itself belongs to the basal part of the second turbiditic-sequence described above (Fig. 6). The rust-coloured Boundary Clay is laterally discontinuous and stands out among the greenish colours of subunit HP. Inspection of sequence 29 revealed an abrupt change in colour at the K/T boundary (Fig. 6). Responsible for this rusty colour are marked contents in iron and the high clay-contents (e.g. low contents in $CaCO_3$). Although this Boundary Clay is free of calcareous nannofossils (sample M lim), we have still measured 9% $CaCO_3$ in this layer. Compared to the contents in carbonate below and above, the Boundary Clay is clearly defined by a minimum in calcite. Other K/T boundary layers, however, are known to be entirely free of calcite or contain only 1 or 2% of carbonate. Thus, the Boundary Clay of this section has, on a global scale, relatively high amounts in $CaCO_3$.

This bed (BC) is defined as the K/T boundary although the maximum iridium enrichment (sample G3) appears 3–4 mm above at the base of the subunit TP (Figs. 5 and 6). The 2 mm of hemipelagic pelites between the Boundary Clay and the brown turbiditic pelites are the result of normal autochthonous sedimentation and may represent about 7000 years (sedimentation rate in green pelites: 0.3 mm/1000 years; KAPELLOS 1973; STUIJVENBERG 1979).

The base of the K/T Boundary Clay is used as a reference level for all measurements.

The Boundary Clay and the basal subunit TP contain small rust-coloured goethitic spherules (Fig. 6), which are described below.

5.3 Lower Danian

Several changes appear very rapidly, beginning at sequence 29 (Fig. 7):

a) The pelitic turbiditic intervals become darker (grey-black) and the content of carbonates greatly diminishes (0–20% $CaCO_3$). Many beds are free of $CaCO_3$.

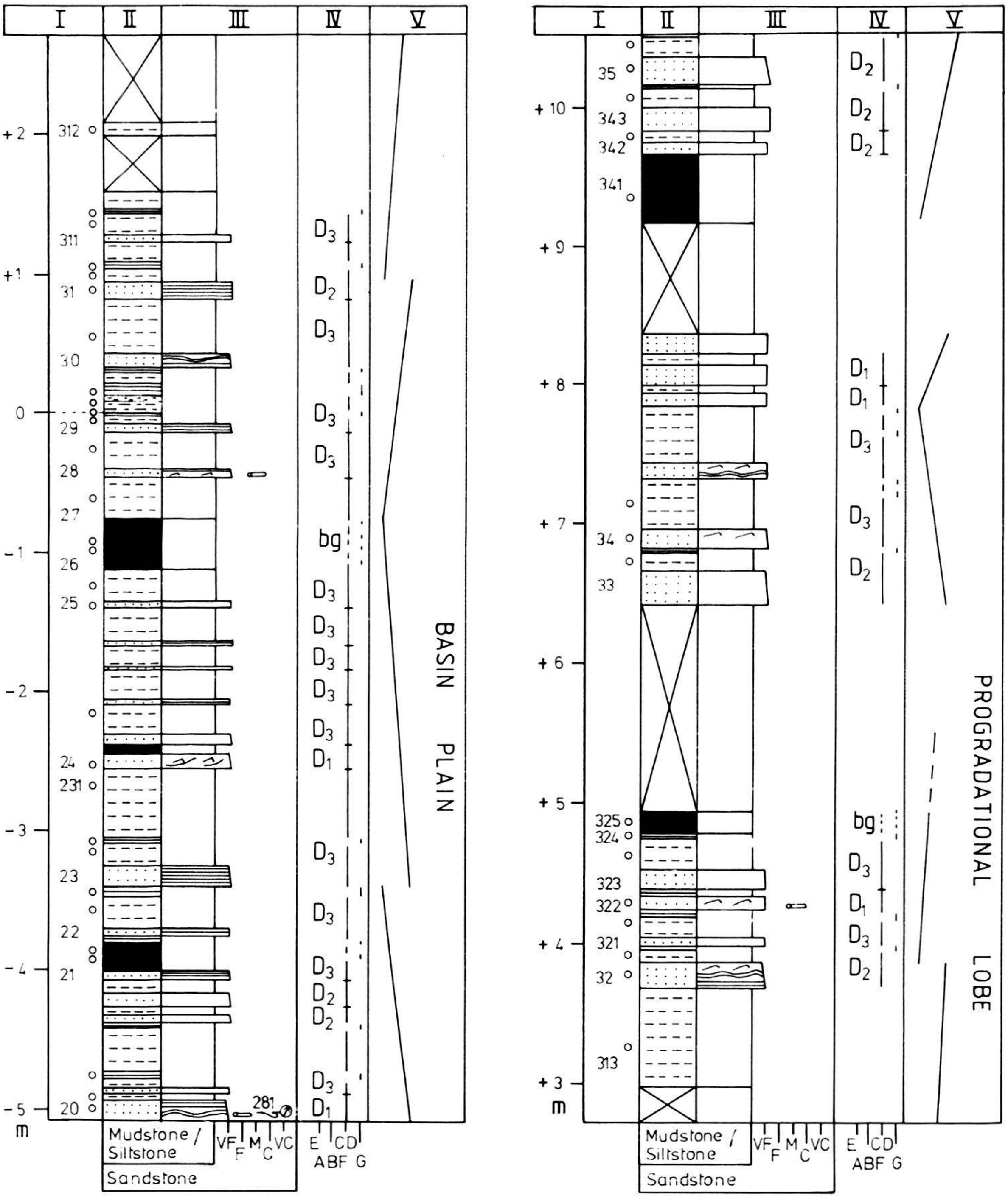


Fig. 7. Martisgraben: sedimentological section below and above the K/T boundary (0 m) (legend Fig. 4).

b) The hemipelagic intervals are mostly free of carbonates (0–6% $CaCO_3$).
c) The sandstone layers are always fine grained but they are thicker and closer to each other than in the Maastrichtian.
d) From bed M 38 upwards (14 m above the K/T boundary) the thickness of the layers becomes greater than 100 cm. Poor outcrop conditions above M 35 did not allow further detailed studies.

The fine grained turbiditic beds having varying amounts of pelites (facies D3, D2, D1 after Mutti & Ricchi Lucchi 1975) are associated with green hemipelagic shales of facies G.

Agglutinated benthic foraminifera were found in hemipelagic shales, M 29: *Rhabdamina sp., Glomospira sp., Saccammina sp.;* M 32: *Ammodiscus sp.;* M 323: *Trochammina sp.*.

The turbidites tend to form thickening upwards cycles. This tendency becomes more important in the Upper Danian strata (NP 4, about 29 meters above the boundary, sample M 40). These cycles are considered to indicate a sedimentary environment on the fringe of a lobe (from bed M 27) towards an external lobe of a deep-sea fan corresponding to type I, unchannelled sandstone lobes of Mutti 1985.

The progradation of this deep-sea fan could explain the decrease and absence of the carbonates in the pelites by dilution of the calcareous nannofossils and of the planktic foraminifera.

An alternative explanation of the Martisgraben section could be found in relative sea-level changes (Haq et al. 1987; Vail et al. 1987).

Three subunits are distinguished:

1) The upper Maastrichtian up to sequence 27 (Fig. 7) is characterized by a thinning upward trend and facies-type D3 of Mutti & Ricci Lucchi (1975) indicating a relative rise of sea-level and phase of transgression.

2) Sequence 27 through 32, characterized by a thickening upward trend but still dominated by facies-type D3 of Mutti & Ricci Lucchi (1975) points to a decelaration in relative sea-level rise indicating the beginning of a regression.

3) Sequence 32 situated in NP 2 (early Danian) marks the beginning of a relative sea-level fall, with thickening upward trend and facies-types D1/D2 of Mutti & Ricci Lucchi (1975). The rate of sea-level fall must have been slow, since no channel-levee deposits developed during the Danian. Moreover this facies cyclicity of type I of Mutti 1985 is related to small scale fluctuations of sea-levels (Mutti 1985).

In conclusion this points to a relative rise of sea-level during the late Maastrichtian, the K/T boundary interval and a slow sea-level fall from NP 2 to NP 4.

6. Biostratigraphy

The fossils best suited for a biostratigraphic subdivision of Cretaceous and Tertiary flysch sequences are often the calcareous nannofossils, since they can be present in sediments deposited below the depths from where planktic foraminifera are preserved. The planktic foraminifera at Martisgraben were not studied in detail, since most samples contained no specimens. No studies were made of the dinoflagellates and pollen.

A marked change in the calcareous nannofossil assemblage at the Cretaceous/Tertiary boundary was first described by Bramlette & Martini (1964). It has since been prooved that vanishing Cretaceous species as well as persistant survivors continue along with the newly evolving Danian species into the Tertiary (Perch-Nielsen 1969, 1981, 1985a, b; Percival & Fischer 1977; Thierstein 1981, 1982; Jiang & Gartner 1986 and others) in many K/T boundary sections.

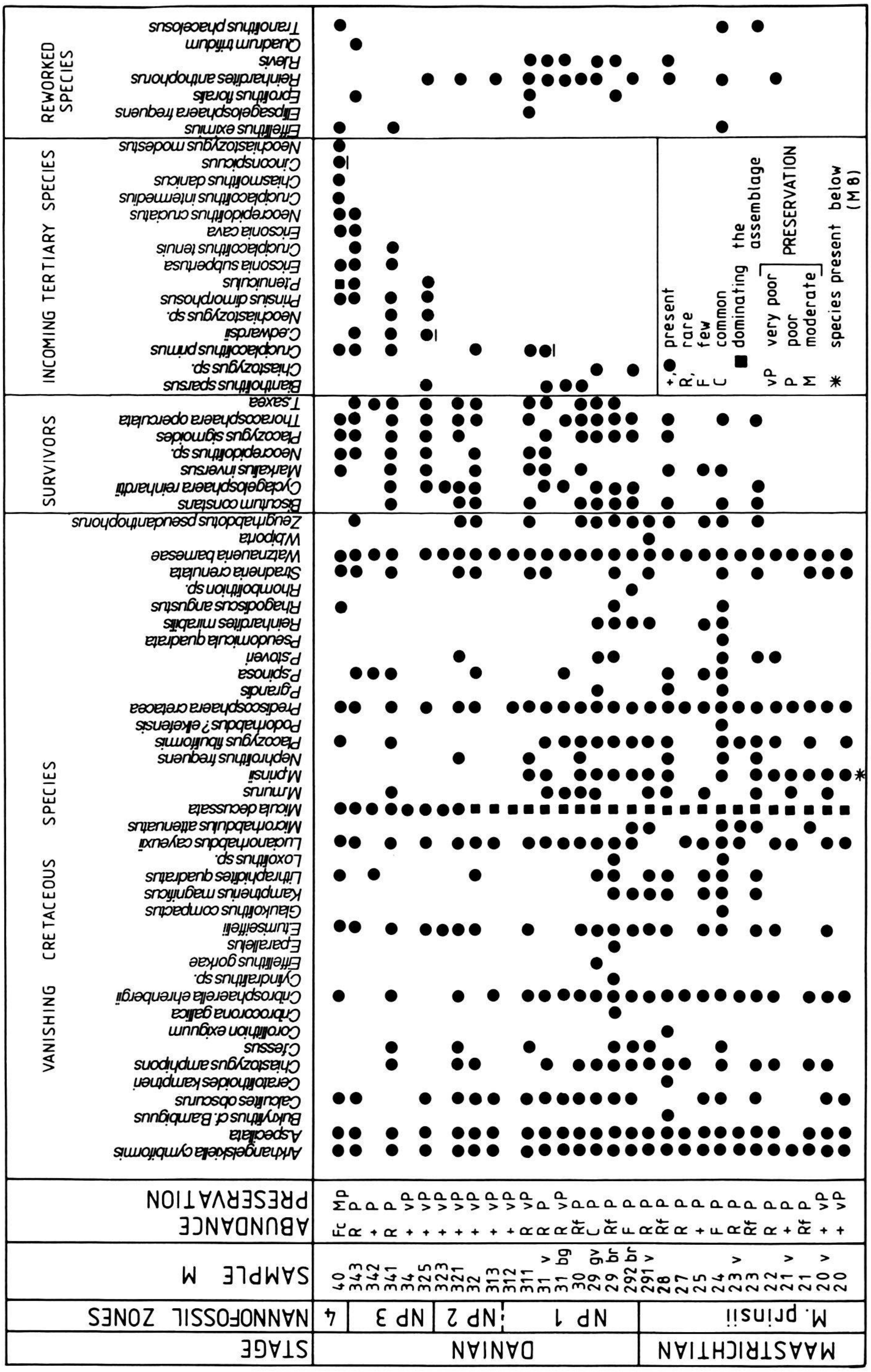


Fig. 8. Distribution of calcareous nannofossils at the Cretaceous/Tertiary boundary at Martisgraben.

The section at Martisgraben is no exception to this general picture. However, due to the deposition close to or below the CCD, coccoliths are absent or very rare in parts of this turbiditic sequence. Some planktic foraminifera were found in the Upper Maastrichtian. *Globotruncanita stuarti* in sample M6, 20 m below the K/T boundary, indicates a Maastrichtian age.

6.1 Upper Maastrichtian

The Maastrichtian calcareous nannofossil assemblage includes numerous *Micula prinsii,* the marker species for the uppermost Cretaceous, down to at least sample M 8, about 19 m below the K/T boundary. The assemblage is quite rich and includes forms reworked from the Lower Maastrichtian or below (Fig. 8), despite the fact of being dominated by *Micula decussata,* a solution resistant form.

6.2 The K/T boundary interval

From a micropaleontological standpoint, samples M 291 v and M 29 br enclose the K/T Boundary Layers. The persistant nannoplankton species *Thoracosphaera operculata, Placozygus sigmoides, Markalius inversus, Thoracosphaera saxea, Biscutum constans* and *Cyclagelosphaera reinhardtii* are present below and above the Boundary Clay (Fig. 8). *Biantholithus sparsus* appears in sample M 30 and *Cruciplacolithus primus* in sample M 31 v. The persistant and the new Danian forms play a minor part in the coccolith assemblage which is dominated by vanishing Cretaceous species, and here again by the solution-resistant *Micula decussata.*

6.3 Danian

Samples M 29 br to M 31 bg, the latter nearly one meter above the K/T boundary, include assemblages which are dominated by vanishing Cretaceous species and rare persistant forms. The fine subdivision of this interval which is possible in sections with more common and better preserved calcareous nannofossils as El Kef (Tunisia), cannot be found in this section. The first *Cruciplacolithus primus* occurs in M 31 v, the first *C. edwardsii* in sample M 325, about 5 m above the K/T boundary. Other Danian species are equally rare and the first typical *Chiasmolithus danicus* was not found in sample M 343 (about 15.3 m above the boundary) but in sample M 40, some 29 meters above it. It is accompanied by *Prinsius tenuiculus* and *Neochiastozygus modestus,* indicating the presence of Zone NP 4 of Late Danian age. Most assemblages are again dominated by the solution resistant Cretaceous form *Micula decussata.*

7. Geochemical and Mineralogical changes

7.1 Introduction

Anomalies in the carbon and oxygen isotopic ratios and noble metals, as well as siderophile and chalcophile elements have been reported from many K/T boundary sections worldwide (Alvarez 1986; Perch-Nielsen et al. 1982; Zachos & Arthur

1986; ZACHOS et al. 1989). The findings of quartz grains with a "shocked matrix" (BOHOR et al. 1984, 1987) and of micro-spherules at the base of the K/T boundary clays (MONTANARI et al. 1983; SMIT & KYTE 1984; IZETT, 1987) are, besides these geochemical anomalies, additional criteria used to define the K/T boundary and support the impact hypothesis.

In this study the contents in total organic carbon (TOC) and $CaCO_3$ of the bulk sediments across the K/T boundary have been measured. Due to the scarcity of planktic and benthic forminifera we have measured the carbon and oxygen isotopic ratios of bulk sediment calcite. Geochemical and mineralogical studies were extended to measurements of Ir by Neutron Activation Analysis (NAA), Atomic Absorbtion Spectrophothometric analysis (AAS), X-Ray Diffractometric analyses (XRD) and SEM studies with an energy dispersive system (EDAX). The results of these studies are shown in Figs. 9, 10 and 11.

7.2 Carbonate and total organic carbon (TOC) content

The $CaCO_3$ content was determined with a Coulometric 5030 Carbonate-Carbon-Aparatus and the TOC content with a CNS analyser at the ETH-Zurich. The instrumental precision is better than ±3.5% and ±5% respectively. EDAX analyses have been performed with the SEM Jeol SM 840 at the Labor für Elektronen-Mikroskopie at the ETH-Zurich.

The $CaCO_3$ content of the sediment in the upper Maastrichtian varies from 9% to 35% due to the changes in lithology. The Boundary Clay which is lithologically defined by a 1–2 mm yellowish rust coloured layer (Fig. 6), surprisingly contains nearly 9% $CaCO_3$. Reinspection of smearslides showed that the carbonate occurs as finely disseminated matrix material. These observations were qualitatively confirmed by EDAX and XRD analyses. The carbonate content keeps varying in the basal Paleocene between this value and reaching nearly 30% in sample M 30. Above this level, it drops again to less than 2% and stays low in many beds for the remainder of the Danian investigated. However, certain beds, as M 32, in which calcareous nannofossils have been found, may contain as much as 10% and up to 20% $CaCO_3$.

TOC values are low in the upper Maastrichtian and lower Paleocene samples and have an average value of 0.2%. The sharp increase in TOC concentration found at other stratigraphically complete K/T boundary localities (WOLBACH et al. 1985, 1988; PREISINGER et al. 1986; LINDINGER 1988) was not found in the present section. Sample GuT 03 at + 1.5 cm, however, reaches a maximum of 0.66%.

7.3 Carbon and oxygen isotopes

Stable isotope analyses of CO_2 gas generated from samples by the phosphoric acid method (McCREA 1950) were made with a triple collecting mass spectrometer Micromass 903C at the Geological Institute, ETH-Zurich. The carbon and oxygen isotope ratios are given as the ‰ deviation from the PDB isotopic standard. The carbon dioxide was released by reaction with 100% orthophosphoric acid at 25 °C. The analytical precision, based on double measurements, is better than ±0.2‰ for the oxygen isotopic ratios and ±0.1‰ for the carbon isotopic ratios.

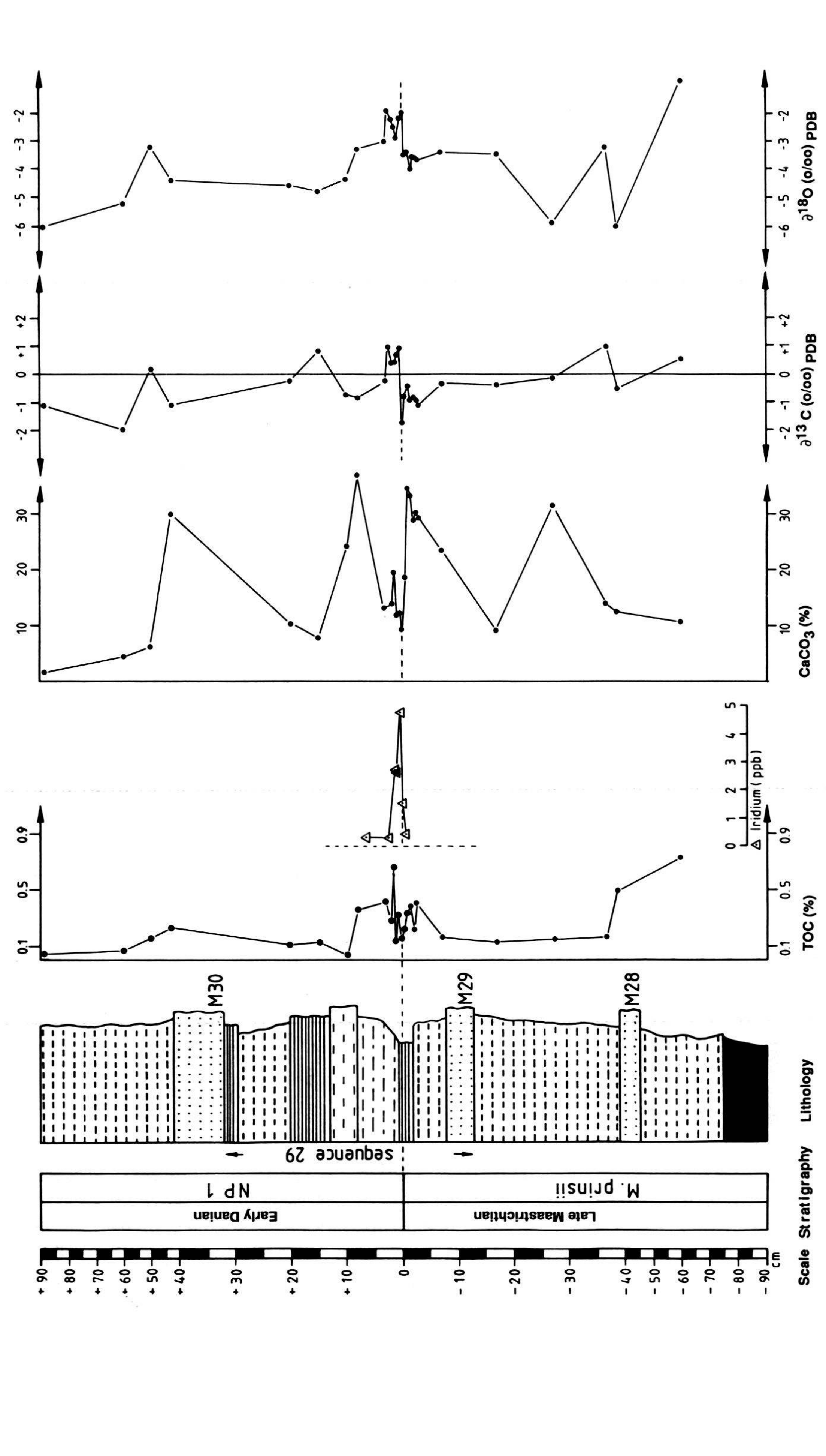


Fig. 9. Lithology and biostratigraphy with values of total organic carbon (TOC), $CaCO_3$ and stables-isotope ($\delta^{13}C$, $\delta^{18}O$) on bulk sediments of the K/T boundary at Martisgraben (geochemical data from table 1), (legend Fig. 4).

Carbon and oxygen isotopic data are now available from many K/T boundary sections worldwide. It has become generally accepted, that one of the most prominent and most constantly occurring features at the K/T boundary is the strong evidence that the productivity of phyto- and zooplankton was drastically reduced. The negative $\delta^{13}C$ isotopic shift is generally explained by a sudden breakdown of the photosynthesis-respiration mechanisms and a drastic cessation of bioproductivity in the surface waters, if diagenetic overprinting can be ruled out. This "strangelove effect" after the mass mortality resulted in the elimination of the carbon isotope gradient between the surface and the bottom-waters and a thorough mixing of the water masses (BROEKER & PENG 1982; HSÜ & MCKENZIE 1985).

Due to the scarcity or even absence of both planktic and benthic foraminifera in the present section, we had to measure bulk sediments. These are assumed to furnish data representative for the calcite produced by the calcareous nannoplankton in the surface-water, despite the presence of fine, disseminated non-biogenic calcite in the sediments, especially in the Boundary Clay. Additionally, any interpretation of bulk sediment isotopic ratios across the K/T boundary has to consider the fact that benthic species generally increase at the K/T boundary and basal Paleocene sediments (LINDINGER 1988). This observation was also made at this section.

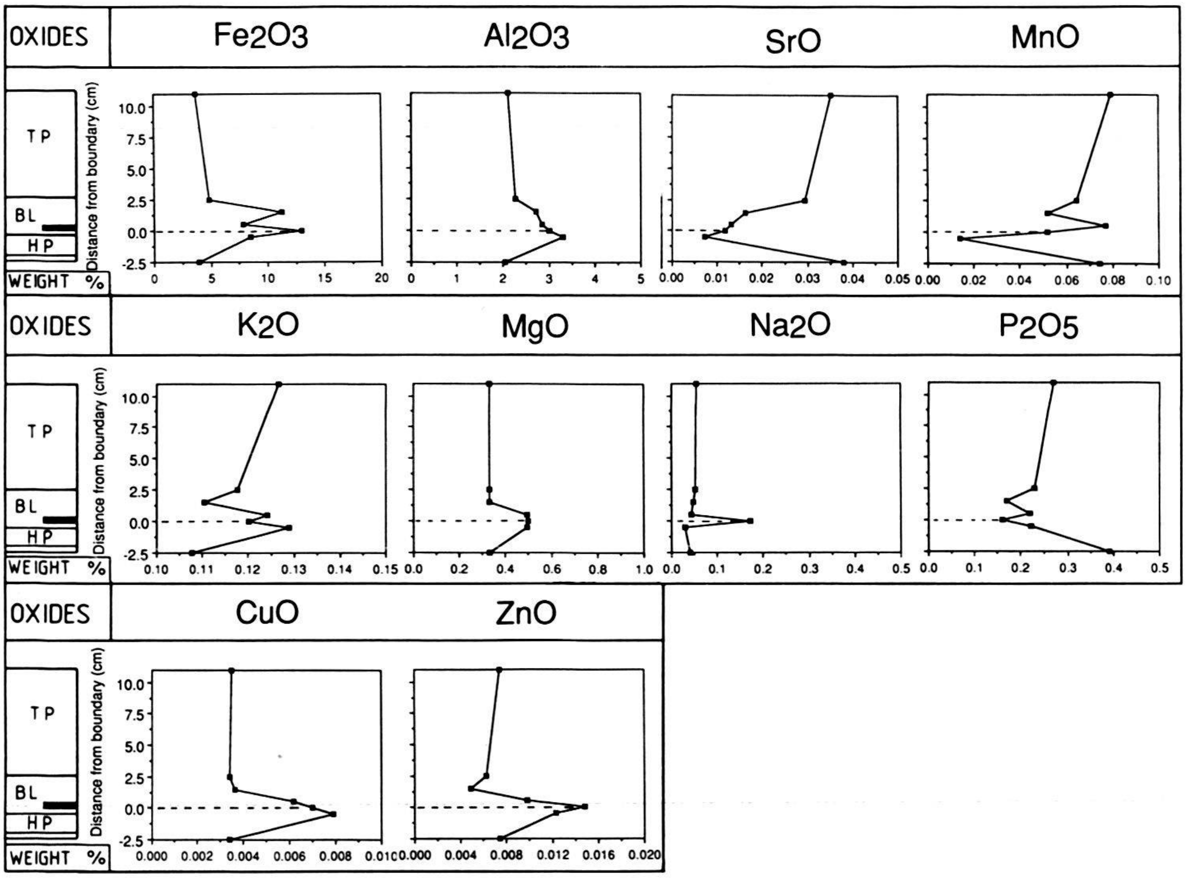
$\delta^{13}C$ isotopic ratios of bulk sediments measured show a gradual decline from +1.0‰ to about −1.0‰ in the uppermost 90 cm of the Upper Maastrichtian at the Martisgraben section. An excursion of about 1.0‰ into the negative direction is observed at the K/T boundary, immediately followed by a 2.7‰ shift towards positive values in the basal Danian (Fig. 9). About 3 cm above the Boundary Clay a second decrease of carbon isotopic values is observed. Carbon isotopic values fluctuate in the lower Paleocene sediments analyzed.

The oxygen isotopic ratios show a greater variability than do the complementary carbon isotopic values. In the upper Maastrichtian they average near −4‰. Negative minima of up to −6‰ were measured (Fig. 9). As these isotopic values are much lower than in other well preserved K/T boundary sections (KELLER & LINDINGER 1989) it is believed that these signals rather furnish diagenetic values than original paleotemperatures. At the K/T boundary a nearly 1.5‰ local increase in the oxygen isotopic ratios towards heavier values is observed. Section upwards the $\delta^{18}O$ isotopic ratios return to negative values, averaging −4.5‰. Similar increases in the isotopic ratios have been reported from other K/T boundary sections and are mostly interpreted as reflecting a global and sudden cooling of the surface-waters. The observed increase in oxygen isotopic ratios across the K/T boundary is a direct effect of the varying compositional state of the sediments below, at and above the K/T boundary (e.g. diagenesis). Based on the assumptions made above, an interpretation in terms of paleotemperature is not possible in this section.

7.4 Spherules

The presence of different types of spherules in K/T boundary sediments has been reported to be markedly increased (BOHOR et al. 1984, 1987; MONTANARI et al. 1983; SMIT & KYTE 1984; IZETT 1987) The K/T boundary sediments of the Martisgraben section were therefore carefully studied under the microscope.

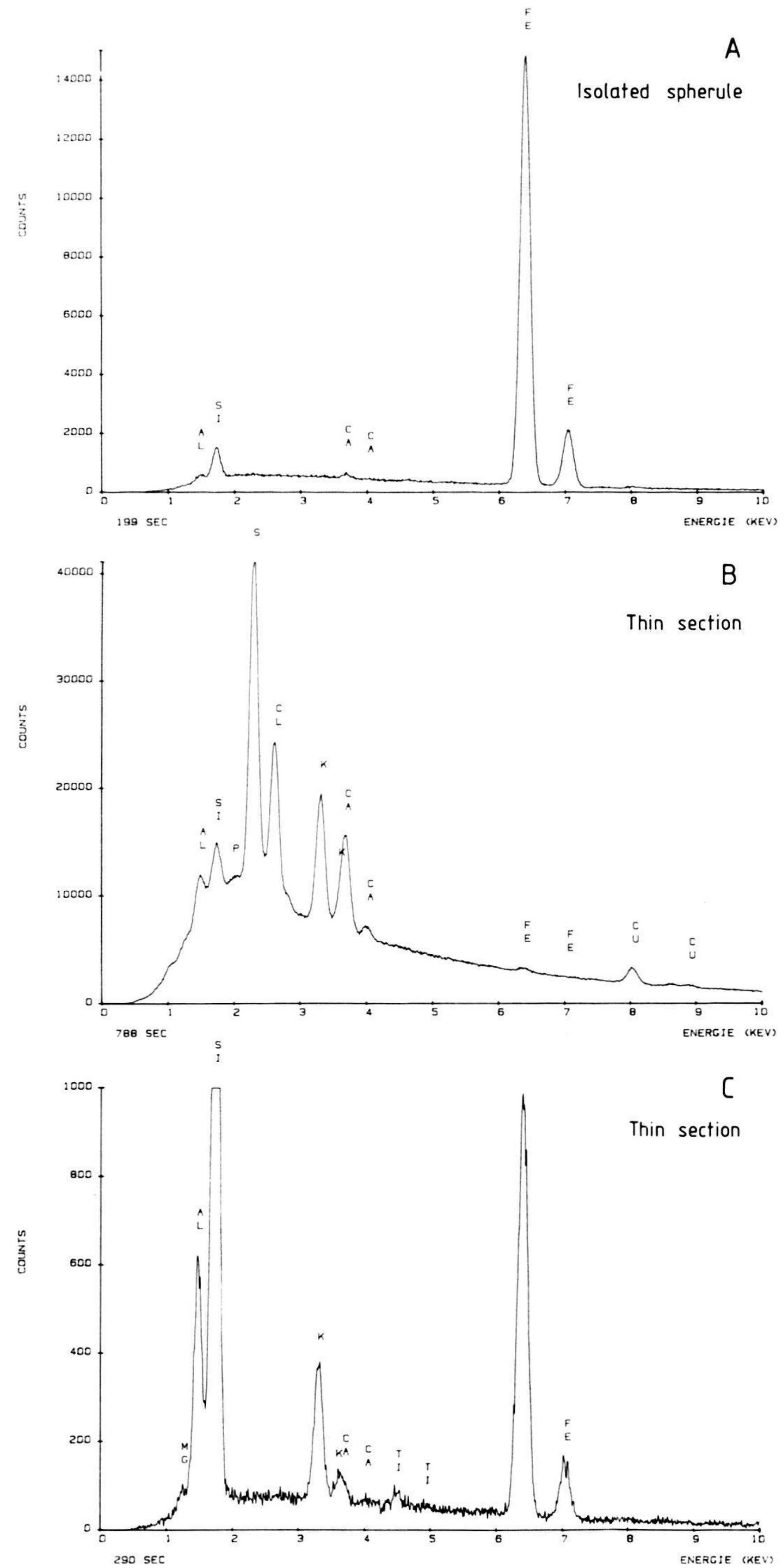
AAS measurements of the bulk sediments were performed with a Perkin-Elmer 603 Atomic Absorbtion Spectrophothometer to analyse Mg, Sr, Mn, Fe, K, Al, Na, Cu and Zn. P was analysed with a Technicon Autoanalyser II with automatic colorimetry. These measurements (Fig. 10) were done at the University of Neuchâtel.



SCALE [CM]	MGO	SRO	MNO	FE2O3	NA2O	K2O	AL2O3	CUO	ZNO	P2O5
+11.0	.3296	.0351	.0794	3.691	.0536	.1268	2.1015	.0035	.0074	.2692
+2.5	.3306	.0294	.0642	4.899	.0511	.1176	2.2585	.0034	.0062	.2285
+1.5	.3309	.0162	.0514	11.288	.0484	.1105	2.7126	.0036	.0049	.1693
+0.5	.4934	.0132	.0767	7.878	.0428	.1242	2.8463	.0062	.0098	.2185
0.0	.4967	.0118	.0515	12.978	.1723	.1202	3.0159	.0070	.0148	.1605
-0.5	.4937	.0073	.0141	8.506	.0294	.1290	3.2977	.0079	.0123	.2216
-2.5	.3299	.0381	.0743	3.978	.0402	.1077	2.0280	.0034	.0074	.3908

Fig. 10. Atomic Absorption Spectrophotometric (AAS) analyses after decalcification. Distribution of major element oxides at the K/T boundary at Martisgraben; TP: Turbiditic Pelites, BL: Boundary Layers with Boundary Clay in black, HP: Hemipelagic Pelites.

Fig. 11. EDAX analyses from the K/T Boundary Clay at Martisgraben; A. Isolated spherule, mostly Fe from goethite. B and C: EDAX analyses under the SEM from total thin section (B and C: amplification ×1700), major components found; B: Peak maximum in S, remaining signals are pyrite; C: Peak maxima in Fe and clay minerals (Si, AL, Mg, K).


A
Isolated spherule
COUNTS
14000
12000
10000
8000
6000
4000
2000
0
FE
SI
AL
CA
CA
FE
0 1 2 3 4 5 6 7 8 9 10
199 SEC
ENERGIE (KEV)
B
Thin section
COUNTS
40000
30000
20000
10000
0
S
CL
K
CA
SI
AL
P
K
CA
FE
FE
CU
CU
0 1 2 3 4 5 6 7 8 9 10
788 SEC
ENERGIE (KEV)
C
Thin section
COUNTS
1000
800
600
400
200
0
SI
AL
K
MG
CA
K
CA
TI
TI
FE
0 1 2 3 4 5 6 7 8 9 10
290 SEC
ENERGIE (KEV)

No shocked potassium feldspar, plagioclase or quartz grains have been found in the Boundary Clay of this section. A significant positive shift of Na and K, as evidenced by bulk sediment analysis with AAS could be indicative for the presence of finely disseminated feldspar particles which escaped detection under the microscope. No change in the clay mineralogy across the K/T boundary occurs (De Kaenel 1986) if compared to the adjacent and overlying sediments. Therefore it is assumed that the increase in clay mineral content at the K/T boundary might be responsible for the observed increases in Na and K, but also in Fe_2O_3, MgO and Al_2O_3 as expressed by respective peak maxima (Fig. 10). This is also expressed by a minimum in $CaCO_3$ (Fig. 9) at this level. As Mn and Sr contents (Fig. 10) are closely linked to the concentration in $CaCO_3$ of the sediments, the lowest concentration of these elements in the Boundary Clay is explainable by the lithological change observed at this level.

Well rounded and compressed, as well as disc- or oblate-shaped reddish spherules, 100 µm to 200 µm in diameter, were recovered from the Boundary Clay. EDAX analysis under the SEM (Fig. 11) indicates that they mostly consist of iron, the surface being coated with clay minerals (Al, Si, K, Mg; Fig. 11C). XRD analyses of isolated grains revealed that mineralogically they consist of goethite and hematite, whereas no pyrite could be detected. A major amount of sulfur was, however, found to be a characteristic component of these spherules, as evidenced by EDAX analyses, which has a much higher detection limit than the XRD (Fig. 11B).

De Kaenel (1986) found the K/T boundary level of this section to be characterized by a local minimum in detrital quartz contents (19%) compared to concentrations of 25% in the upper Maastrichtian and lower Paleocene sediments.

7.5 Iridium enrichment

The enrichment in Ir, characteristic for many K/T boundary sections worldwide (Alvarez et al. 1980), was also found at the Martisgraben. Neutron activation analyses for Ir have been performed by F. Grass at an ASTRA Reactor at Seibersdorf near Vienna. Neutron irridations were carried out 7–14 days on decarbonated bulk sediment samples (10% CH_3COOH). The flux rate was 6.10^{13} neutrons/cm^{-2}/s^{-1}. Absolute instrumental precision of these measurements is ± 0.5 ppb Ir, detection limit was 0.23 ppb for Ir.

The results of these measurements show the expected enrichment at the K/T boundary level of 1.53 ppb and a maximum of 4.78 ppb some 5 mm higher up (Fig. 9 and Table 1). The Paleocene sample G 5 at +1.5 cm is still slightly enriched in iridium. Background concentrations higher up in the section, however, rapidly decline to contents below 0.3 ppb Ir, matching Late Maastrichtian contents.

7.6 Interpretation

Although no monospecific planktic and benthic foraminifera have been measured, the negative shift $\delta^{13}C$ of nearly 1‰ at the K/T boundary of the Martisgraben section is in good agreement with other K/T sections worldwide (Perch-Nielsen et al. 1982; Zachos & Arthur 1986; Lindinger 1988).

Sample	Scale (cm)	$\partial^{13}C$ (PDB)	$\partial^{18}O$ (PDB)	$CaCO_3$ (%)	TOC (%)
GuT 89	+ 89	- 1.131	- 6.093	1.75	0.05
GuT 60	+ 60	- 2.090	- 5.223	4.11	0.08
GuT 50	+ 50	+0.146	- 3.260	6.11	0.16
GuT 43	+ 43	- 1.141	- 4.390	29.75	0.23
GuT 20	+ 20	- 0.277	- 4.604	10.33	0.10
GuT 15	+ 15	+0.846	- 4.810	7.59	0.12
GuT 10	+ 10	- 0.742	- 4.343	24.15	0.04
GuT 08	+ 8.0	- 0.861	- 3.295	36.95	0.38
GuT 06	+ 3.0	- 0.261	- 2.998	13.10	0.41
GuT 05	+ 2.5	+0.961	- 1.916	---	---
GuT 04	+ 2.0	+0.415	- 2.206	13.62	0.28
GuT 03	+ 1.5	+0.413	- 2.493	19.36	0.66
GuT 02	+ 1.0	+0.648	- 2.869	11.51	0.14
GuT 01	+ 0.5	+0.923	- 2.161	11.97	0.32
Gu - Ir	+ / - 0	- 1.733	- 1.956	9.38	0.16
GuM 01	- 0.5	- 0.795	- 3.468	18.46	0.22
GuM 02	- 1.0	- 0.464	- 3.338	34.51	0.33
GuM 03	- 1.5	- 0.962	- 3.913	33.08	0.37
GuM 04	- 2.0	- 0.856	- 3.517	28.74	0.22
GuM 05	- 2.5	- 0.920	- 3.599	30.34	0.41
GuM 06	- 2.8	- 1.147	- 3.660	29.29	---
GuM 07	- 7.0	- 0.337	- 3.388	23.30	0.16
GuM 17	- 17	- 0.398	- 3.427	9.00	0.12
GuM 27	- 27	- 0.151	- 5.892	31.10	0.15
GuM 37	- 37	+0.910	- 3.231	13.68	0.16
GuM 41	- 41	- 0.571	- 6.039	12.56	0.50
GuM 60	- 60	+0.502	- 0.803	10.57	0.73
GuM 234	- 234	- 0.470	- 3.743	22.95	0.75
GuM 337	- 337	- 0.522	- 5.409	14.91	0.30

Absolute errors : $CaCO_3$: + / - 3.5 % TOC : + / - 5 %

$\partial^{13}C$: + / - 0.1 ‰ $\partial^{18}O$: + / - 0.2 ‰

Iridium - Measurements

Sample G7	0.3 ppb	+ 6.5 cm
Sample G6	0.3 ppb	+ 2.5 cm
Sample G5	2.65 ppb	+ 1.5 cm
Sample G4	2.64 ppb	+ 1.0 cm
Sample G3	4.78 ppb	+ 0.5 cm
Sample G2	1.53 ppb	K / T boundary
Sample G1	0.43 ppb	- 0.5 cm

Error : + / - 0.5 ppb ; Detection limit : 0.23 ppb

Tab. 1. Geochemical Data of the K/T Boundary at Martisgraben.

It is not clear if the observed decline in $\delta^{13}C$ isotopic ratios in the Late Maastrichtian represents a real signal or reflects the relatively high amount of non biogenic calcite found in this layer (e.g. diagenetic signal). It is generally accepted (WEIZER 1978), that diagenetic processes in marine sediments preferentially remove Sr ions from the carbonate matrix, which results in a subsequent decrease of the Sr/Ca ratio with progressive recrystallisation or replacement (LORENS 1981). Our data does not show a lowering of the Sr/Ca ratio of the bulk sediment at the K/T boundary, despite the relative high amount of non biogenic calcite at this layer. We therefore conclude, that the carbon isotopic data reflects stable conditions in the CO_2/HCO_3-system in the water. These isotopic values in the Late Maastrichtien are interpreted as reflecting high bioproductivity and stable living conditions of the phyto- and zooplankton during the Late Maastrichtian. The negative $\delta^{13}C$ could be interpreted as a direct result of the mass mortality of the phytoplankton in the surface water layers (THIERSTEIN 1981, 1982) and a drastic drop in phytoplankton productivity (TAPPAN, 1968; HSÜ et al. 1982a, b; HSÜ & MCKENZIE 1985; ZACHOS et al. 1986; ARTHUR et al. 1987). We have, however, observed that most of the carbonate found in the Boundary Layers of this section is part of the matrix. This makes the interpretation of the oxygen isotopic values highly speculative. Although we have found the characteristic increase in $\delta^{18}O$ isotopic values towards the positive direction across the K/T boundary, any interpretation in terms of a cooling of the water temperatures has to be rejected, because diagenetic overprint of the $\delta^{18}O$ signals seems to be evident. Furthermore, an increasing number of benthic specimens at this level could additionally be responsible for this shift.

In summary it can be concluded that the concordance of a negative $\delta^{13}C$ isotopic shift with the enrichments in iridium and a general decline of the $\delta^{18}O$ isotopic ratios characterize the K/T boundary transition of this section.

No well defined increase in TOC as observed from other K/T boundary sections (WOLBACH et al. 1985, 1988; PREISINGER et al. 1986; LINDINGER 1988) has been found in the Boundary Clay. The abyssal paleodepth may have prevented accumulation of the incoming organic material in the bottom sediments. But a marked increase in TOC (0.66%) appears at 1.3 cm above the Boundary Clay in sample GuT 03 (Table 1) which is situated at 1 cm above the maximum enrichment in iridium.

The presence of goethitic spherules in the Boundary Clay confirms the similar findings from the El Kef section in Tunisia (LINDINGER 1988). The break-down of the incoming organic material, debris from land and dead phytoplankton material (WOLBACH et al. 1985, 1988; HSÜ & MCKENZIE 1985), by sulfate reducing bacteria presumably led to production of H_2S and to the diagenetic formation of pyrite in the Boundary Clay at this site. This pyrites mostly would have been oxydized into iron oxides after recent exposure of the K/T boundary sediments. The presence of pyritic remainders within these spherules is indicative for oxygen reduced interstitial pore-water or bottom-water conditions. Despite the low sample resolution of our section, we follow the proposition that an increased flux of organic material (from land after devastation of forests) and admixture with biogenic organic material from the surface-waters (after a mass mortality in the surface-waters of the oceans) and organic material from other sources (organic-rich sediments which were globally distributed after an impact) led to a brief and worldwide reduced and sulfide-rich bottom-water environment (VAREN-

KAMP & THOMAS 1982; KYTE & WASSON 1985; WOLBACH et al. 1985, 1988; LINDINGER 1988).

The discovery of a local minimum in detrital quartz in the Boundary Clay can be used as indirect estimation of the sedimentation-rates. Assuming a constant supply of detrital quartz across the K/T boundary this minimum may be interpreted as indicative for a rapid deposition of the Boundary Clay, confirming respective assumptions made from other K/T boundary sections (PREISINGER et al. 1986; LINDINGER 1988) and estimates of the time of deposition of these sediments.

The Boundary Clay of this section is characterized by an anomaly in Ir. It is not yet clear in which carrier-phase this metal was deposited within the sediments. However, it is believed that the reducing conditions in the bottom-water environment led to a reduction of the residence-times of most metals and noble elements (KYTE & WASSON 1985; LINDINGER 1988). The main mineral-phases in the hydrosphere were possibly organometallic complexes and metal-sulfides. Scavenging by pyrites and processes of adsorbtion on organic mineral particles may have enhanced deposition of metals in the sediments. Diagenetic processes of alteration, dissolution and redeposition, as well as oxydation of the sediment after deposition are believed to be responsible for the difficulties in isolating a carrier-phase of Ir or other noble elements in K/T boundary sections. This interpretation has indirectly been confirmed by the discovery of metal enrichments at redox boundaries (KUCHA 1982; SCHMITZ 1985; SCHMITZ et al. 1988).

The maximum of nearly 5 ppb Ir some 5 mm above the K/T boundary is considered to be the result of sedimentation processes and not the effect of such secondary diagenetic alteration processes. It may be due to redeposition of material by the distal end of a tsunami (HANSEN et al. 1987) sweeping the shelf, which was resedimented into thin-bedded lobe fringe deposits in a deep-sea fan system in the basin. The enrichment in Ir above the K/T boundary cannot be explained by bioturbation, since no trace fossils have been observed at this level.

From a geochemical point of view, the K/T boundary section at Martisgraben is characterized by a negative shift in carbon isotopic values, oscillations in oxygen isotopic ratios and a reduction in $CaCO_3$ and detrital quartz contents. The lack of a peak in TOC in the Boundary Clay is explained by the abyssal depth of this section. Anomalies in Ir, as well as the presence of altered pyritic spherules additionally characterize the Boundary Clay. It can therefore be concluded, that despite the abyssal depth of this section and the fact that the Boundary Clay is exceptionally thin, the geochemical anomalies at this level indicate that the Martisgraben section belongs to the growing group of stratigraphically complete K/T boundary sections.

8. Discussion and conclusions

In our investigations of the Martisgraben section we have found some features typical for many marine K/T boundaries:

- the uppermost Maastrichtian *Micula prinsii* and the lowermost Danian *Markalius inversus* NP 1 Zones,
- the Boundary Clay,
- a peak in iridium of 1.53 ppb (enrichment 5 ×) in the Boundary Clay,

— the presence of goethitic spherules considered to represent diagenetically altered pyrite in the Boundary Clay.

Other characteristics were found to differ from those found in other sections.
These include:

— an enrichment in Ir in the Boundary Layers of nearly 5 ppb. The Boundary Clay, entirely lying within hemipelagic deposits, has a peak of 1.53 ppb in Ir (enrichment 5×). The maximum peak of nearly 5 ppb Ir (enrichment 16×) was found 5 mm above the K/T boundary,
— the smaller than normal negative shift in $\delta^{13}C$ across the boundary (1‰) and the immediate shift back into positive values (2.7‰). This might be due to the fact that the calcite measured is not mainly of calcareous plankton origin but is mainly detrital,
— the general decline in $\delta^{18}O$ and the characteristic increase in $\delta^{18}O$ isotopic ratios across the K/T boundary are difficult to interpret in terms of a cooling of the water temperatures. Diagenetic overprint seems to be obvious and causes perturbations in the oxygen isotopic signals,
— the increase in TOC noted by Lindinger (1987) in the Boundary Clay of the Caravaca section and by Keller & Lindinger (in press) at El Kef was not found in the Boundary Clay. A relative increase in TOC some 1.3 cm above the K/T boundary could be equivalent with the TOC peak at other shallow-water K/T boundaries. This can be interpreted as meaning that the organic carbon entering the hydrosphere and representing the mass mortality of the phyto- and zooplankton and land debris at the K/T boundary reaches the depth of deposition of this site later, after the deposition of the Boundary Clay. This interpretation, however, is highly speculative,
— a drop in carbonate content to values below 10%. This is a relatively high $CaCO_3$ content for the K/T Boundary Clay which is normally devoid of calcite or includes only 1 or 2% of it in other sections. This, again, is believed to be a result of the fact that, at our site, the calcite is essentially detrital and was transported to the site by turbidity currents and not as part of fecal pellets containing coccoliths or as settling of planktic foraminifera,
— the minimum in transported quartz (19%) is relatively high compared with other K/T boundary sections but explainable if the high amount of turbiditic detritus of the sediments is considered,
— no discordance (erosion surface due to sea level fall) has been observed. No disruption in the sedimentation occured across the K/T boundary.

The Martisgraben is the first complete K/T boundary section in Switzerland and the first flysch section containing this boundary known to date. Although this section may not be considered an ideal K/T boundary site, it is concluded that the event at the end of the Cretaceous Period was sudden and global as documented in this deep-sea section.

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