



Scenarios of Proterozoic and Paleozoic Catastrophes: A Review

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9 Text-Figures and 1 Table

*Catastrophe
Proterozoic
Phanerozoic
Mass extinction
Stable isotopes
Geochemistry
Extraterrestrial impact
Carnic Alps*

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Proterozoische und paläozoische Katastrophen: Eine Übersicht

Zusammenfassung

Der gegenwärtige Stand über Massensterben und Katastrophenereignisse im Proterozoikum und Paläozoikum wird referiert. Soweit vorhanden, werden auch Ergebnisse aus dem alpinen Raum mitberücksichtigt. Mit Ausnahme der Verhältnisse an der Frasn/Famenne-Grenze im Oberdevon (und an der Kreide/Tertiär-Grenze) fehlen eindeutige Indizien, die für extraterrestrische Ursachen als Auslöser von Massensterben sprechen. Wahrscheinlicher sind hingegen erdgebundene, tellurische Ereignisse von längerer Dauer, die nicht nur negative Folgen für die Organismenwelt haben, sondern auch positive Entwicklungsschübe auslösen können. Die alles entscheidende Rolle scheint hierbei der wechselnde Gehalt des Treibhausgases Kohlendioxid in der Atmosphäre zu spielen.

Abstract

In this paper we review the present knowledge about mass extinctions and other catastrophic events for the Late Proterozoic and Phanerozoic eras. Special emphasis is drawn on relevant results from the Alps. With exception to the Frasnian/Famennian boundary in the Upper Devonian (and the K/T-boundary) there are obviously no clear indications for extraterrestrial causes triggering mass extinctions. Although the newly found Alamo event of the early Upper Devonian may also have been originated by an impact it is not considered as cause of a major biological catastrophe. More likely are instead long-term Earth-bound telluric effects being responsible not only for unfavourable conditions affecting many groups of organisms but also establishing such positive environmental parameters which promote other lines of evolutionary steps. In agreement with other authors we finally conclude that on a global scale the marine and terrestrial developments are more likely to have been linked to the varying content of atmospheric CO₂ with its global impact on climate and hence, production of biomass.

1. Introduction

Natural catastrophes**) occur in the geo- and biosphere and may be of variable dimensions. Volcanic eruptions may release hundreds to thousands of cubic kilometers of magma, as well as large amounts of poisonous gasses, especially CO₂, SO₂, H₂S and NO_x. For example, about 800.000 km³ of basalt and rhyolite were erupted in the

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**) The word catastrophe is derived from the Greek "to overturn". In the Greek drama the catastrophe marks a critical point when the action either tragically unravels or a happy ending becomes possible. This double meaning also seems to apply to all large catastrophes in the Earth's history. Here we are discussing geological catastrophes – extreme natural processes, powerful incisions, which affect the Earth's surface and its inhabitants almost instantly.

Parana province in South America during the opening of the South Atlantic; even larger quantities of about 1 to up to 3 km³ were inferred for the Indian Dekkan basalts and the basalts of northern Siberia (Table 1). For the eruption of the Toba volcano in Indonesia about 75,000 years ago, it was calculated that between 900 million to 5 billion tons of sulfuric acid were released (C. OFFICER et al., 1987). The total volcanic SO₂ emissions are estimated at 13 billion tons per year, which, however, amounts to only about 5 to 10 % of the anthropogenic addition of sulfur to the atmosphere (G.J.S. BLUTH et al., 1993).

Table 1.
Volcanism in the younger history of the Earth.

	Age	Area [km ²]	Extrusion [km ³]
Columbia River basalt (USA)	17±1 Ma	200.000	> 700
Ethiopia basalts	35±2 Ma	750.000	
British-Arctic basalts	62±3 Ma	>100.000	1–2×10 ⁶
Dekkan plateau basalts	66±2 Ma	>500.00	1×10 ⁶
Rajmahal basalts (India)	110±5 Ma	>200.000	
Paraná basalts (South America)	130±5 Ma	2×10 ⁶	800.000
Namibia basalts	135±5 Ma	500.000	
Antarctic basalts	170±5 Ma	>100.000	
Karoo basalts (South Africa)	190±5 Ma	>1.5×10 ⁶	
Basalts in eastern North America	200±5 Ma	>100.000	
Siberian basalts	250±0.3 Ma	>2×10 ⁶	2–3×10 ⁶
Bozen quartz porphyry (Italy)	270–280 Ma	>2.000	>2.000
Blasseneck porphyry (Austria)	468±5 Ma (?)	>2.000	>1.000
Toba (Indonesia)	75.000 a	20.000	2–3.000
Tambora (Indonesia)	10/11-4-1815	4,5×10 ⁶	100–1.000
Krakatau (Inonesia)	26./27-8-1883		10
Mt. St. Helens (USA)	18-5-1980	>500	>2.7

Giant rock avalanches, which are mass movements that were first described in 1932 by the Swiss geologist Albert Heim, do not reach such magnitudes, but still constitute a potential danger on land. In such processes, rock volumes of about 5×10¹⁰ m³ can be moved. Recently, it was found that similar phenomena have occurred also on the Moon and on Mars (H.J. MELOSH, 1990).

Other examples of natural catastrophes that affect the climate in a broad sense are catastrophic events that are related to earthquakes, such as tsunamis, rock avalanches, and related earth movements. For example, submarine mud flows were reported to be up to 200 km long and reach volumes of more than 500,000 km³ (J.G. MOORE et al., 1994).

Natural catastrophes have influenced the biosphere of our planet Earth. Already during the last centuries paleontologists recognized that suddenly a large number of species disappeared at various times. The largest mass extinctions characterize the transitions in Earth history that define the geological time scale. Until about two decades ago, such incisions were assumed to be simply phases of slower evolution, followed by periods of enhanced evolu-

tion, which were caused by competition of different organisms.

Since 1980, the so-called ALVAREZ-hypothesis provided new ideas that prompted further studies of the known large mass extinctions. Relevant questions were, on one hand, concerned with origin, timing, and extent of these events, and, on the other hand, also with generalizations and regularities. Any conclusions from such studies may also be relevant for our understanding of the future development of the Earth (see e.g., R.A. GASTALDO et al., 1996).

2. The Five Large Mass Extinctions in the History of the Earth

The five largest Phanerozoic mass extinctions are related to the following geological eras:

- End of the Ordovician
- Upper Devonian
- End of the Permian
- End of the Triassic
- End of the Cretaceous

The mass extinction in the Upper Devonian is different from the others, because this event did not happen at the end of the Devonian, but within the Upper Devonian, namely between the Frasnian and Famennian periods.

In the past few years another mass extinction was added to this list, which, however, occurred at the end of the Proterozoic about 600 million years ago. In the following paragraphs this event will be briefly reviewed, as it seems to have been very important for the development of life on Earth.

Over a duration of more than 2 billion years, early life on Earth was dominated by single-celled organisms without a nucleus. The decisive change to planktonic algae and the appearance of eukaryotes, single-celled organisms that contain a nucleus, occurred about 1.8 billion years ago. However, in the following 800 million years evolution did not progress significantly.

This situation changed about 1 billion years ago; suddenly more and more species appeared, including multicellular algae with relatively short lifetimes. Today, molecular biologists believe they know the reason and assume that at that time a fundamental genetic innovation occurred: Sexual cell division-reproduction-multiplication of the genetic combinations.

What was the reason for this advance in evolution? Was it the environment, stress due to natural selections, or maybe related to the collision of individual continents during formation of the supercontinent Rodinia? So far, clear answers and convincing evidence favouring one particular theory are missing.

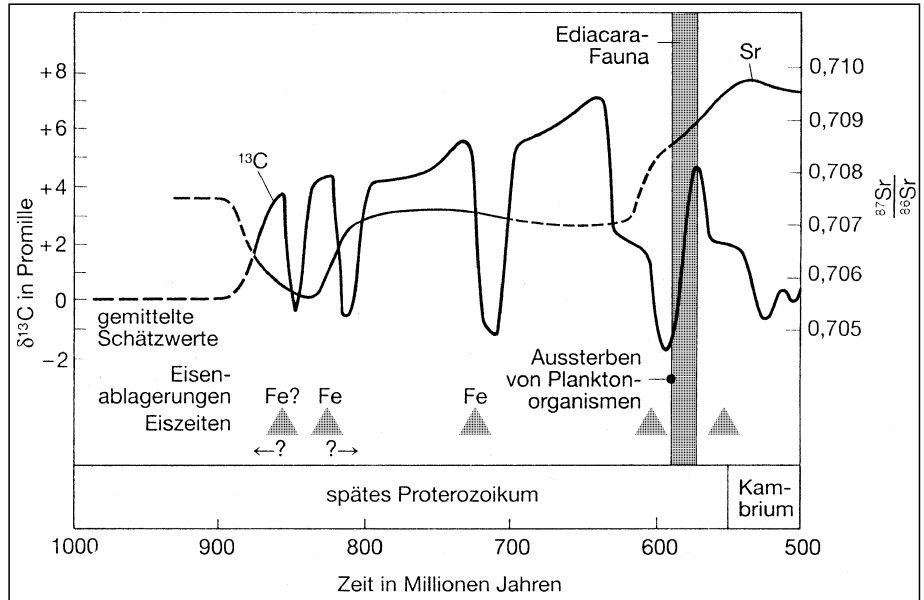
Clear indications of a mass extinction are available only 400 million years later, which was about 600 million years ago. According to our present knowledge this event was the first mass extinction in the history of the Earth. It happened immediately before the first occurrences of the Ediacara fauna (Text-Fig. 1).

About 600 million years ago, the increase in diversity of large morphologically complex acritarchs to the large numbers in the Cambrian was suddenly interrupted. An abrupt collapse occurred, which was manifested by the disappearance of about 75 % of all planktonic organisms. It is noticeable that this mass extinction is coeval with ice

Text-Fig. 1.
Key events in the late Proterozoic and at the turn to the Cambrian.
After A.H. KNOLL (1991).

ages (Varanger- and Ice Brook ice ages between 653 and 575 Ma*), which indicates a connection between these two events. The Varanger ice age is thought to represent the most intense cooling during the history of the Earth. It should be noted that this ice age occurred mainly in the lower to middle latitudes (N.M. CHUMAKOV & D.P. ELSTON, 1989; W.B. HARLAND, 1989; P.W. SCHMIDT et al., 1991; C. MCA. POWELL et al., 1994; T.H. TORSVIK et al., 1995; and others).

According to A.H. KNOLL (1991) and A.H. KNOLL & M.R. WALTER (1992), significant global changes occurred on Earth at that time (Text-Fig. 1). This assumption is supported by the following observations: Distinct negative excursions of the carbon isotope curve, indicating diminished deposition of organically bound carbon, the temporary formation of iron-rich sediments (Itabirites, banded iron formations), as well as significant changes in

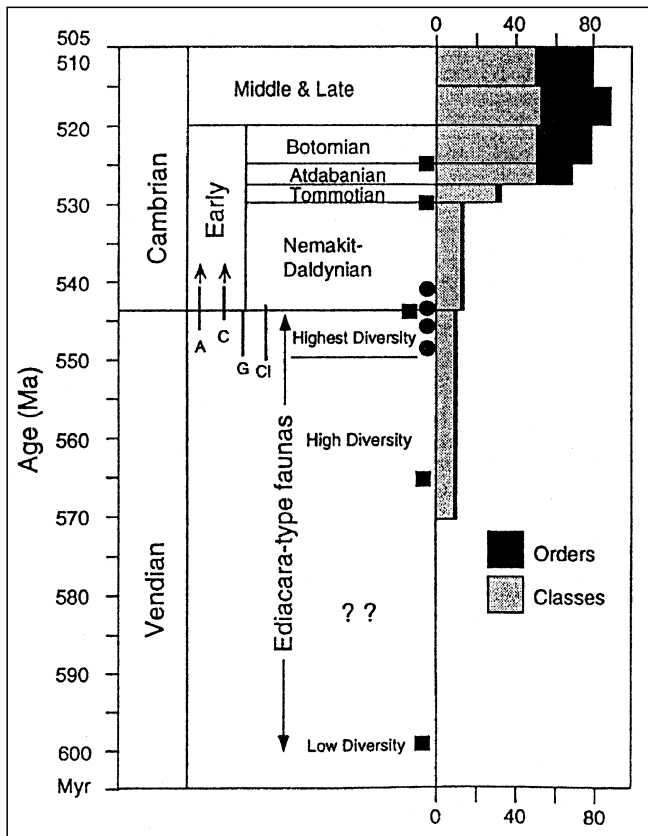


the strontium isotope ratio $^{87}\text{Sr}/^{86}\text{Sr}$, which suddenly changed from unusually low to high ratios. On one hand, they result from increased hydrothermal activities due to rifting, which affected the supercontinent Rodinia from about 725 Ma, and on the other hand they are due to a different distribution of the continental plates resulting from the formation of East Gondwana around the end of the Proterozoic. High drift rates of up to 20 cm per year and significant rotation of the individual plates, however, still hinder the exact reconstruction of the path of the individual plates (M. GURNIS & T.H. TORSVIK, 1994; T.H. TORSVIK et al., 1996).

According to J.P. GROTZINGER et al. (1995), the Ediacara fauna has (in contrast to previous assumptions) a relatively young age, just preceding the Precambrian/Cambrian boundary, for which, at present, an age of 544 Ma is assumed (Text-Fig. 2). About 565 Ma ago, organisms with a high degree of complexity appeared (A.P. BENUS, 1988), with predecessors that also belong to the Ediacara fauna that was already present at about 600 Ma. The latter are found in the Mackenzie Mountains in Canada, where they underlie tillites of the Varanger ice age (H.G. HOFMANN et al., 1990).

Considering the new age dates mentioned above, the main period of the development of the Ediacara fauna took about 20 Ma, namely from 565 to 545 Ma. During this time the planktonic acritarchs suffered a crisis that led to their restriction to a few simple forms (B.S. SOKOLOV & A.B. IWANOWSKI, 1990). After the preceding mass extinction, they were living together with more specialized Metazoa, including some Evertabrata that contain, for the first time, skeletal parts. Thus, the first mass extinction seems to have happened between 600 and about 570 Ma.

One of the mysteries in the history of life on Earth is the so-called Cambrian explosion. At the beginning of the Cambrian (Manykay or Nemakit-Daldyn period), at about 540 to 545 Ma (G.S. ODIN et al., 1983; W. COMPSTON et al., 1992; R.D. TUCKER & W.S. MCKERROW, 1995), there were already a number of small organisms with shells, marking the appearance of biomineralization (compare J.P.



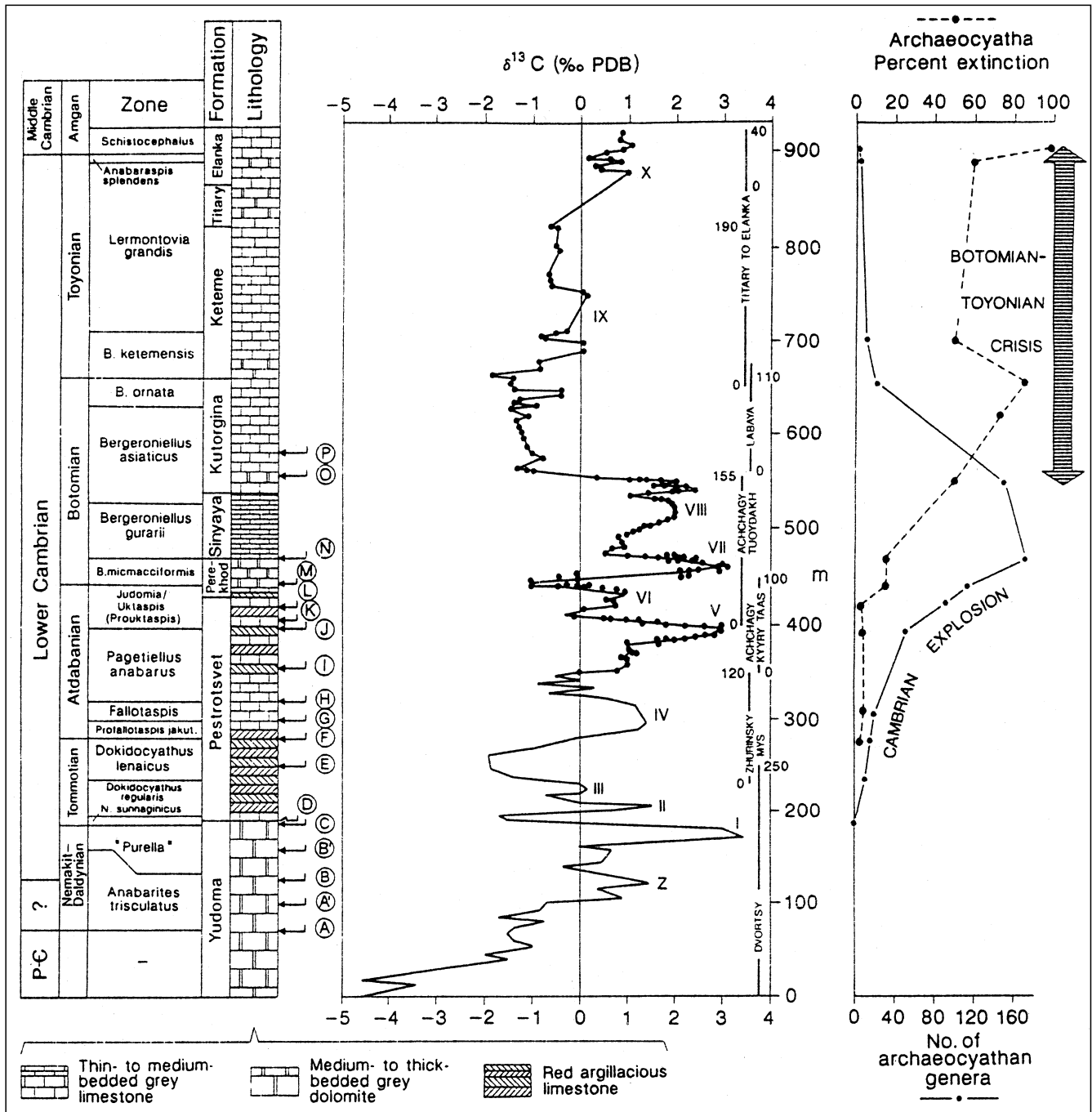
Text-Fig. 2.
Revised time table of the Vendian and the Cambrian, including faunal diversity data.
After J.P. GROTZINGER et al. (1995), J.J. SEPKOSKI (1992) and G.M. NARBONNE et al. (1994).
Filled circles and squares represent U-Pb zircon ages.
Ranges of skeleton-bearing genera: A = Anabarites; C = Cabrotubulus; CI = Cloudina; G = goblet-shaped fossils of the Nama group.

*) New results of C.A. KAYE & R.F. ZARTMAN (1980) and T.E. KROGH et al. (1988) indicate that the Varanger ice age happened later; J.P. GROTZINGER et al. (1995) interpret the available data to represent ages of about 600 million years.

GROTZINGER et al., 1995). However, all later taxa appeared, with just one exception, in the Atdabanian period (Text-Fig. 2). At this time, the evolutionary productivity of the invertebrates (J.J. SEPKOSKI, 1988, 1992; J.W. VALENTINE et al., 1991) and of trace fossils (P. CRIMES, 1989) suddenly increased, as did the intensity of bioturbation (M.L. DROSER and D.J. BOTTJER, 1988). It is unusual that this development occurred within only 5 to 6 (10) million years, i.e., during the time marking the duration of the Tommotian and Atdabanian periods of the early Cambrian (S.A. BOWRING et al., 1993).

Recently, there have been repeated attempts to explain this two-phase evolution and to provide supporting arguments. The explanations range from a change in atmo-

spheric composition to changes in the distribution of plates and physiological modifications of the fauna. According to M.D. BRASIER (1992), the lower Vendian was characterized by a cold age or ice age. In contrast, the lower latitudes had a warm climate during the lifetime of the Ediacara fauna, which continued into the Cambrian. The boundary itself is characterized by sea level changes, the formation of evaporites and phosphorites, and unusual anomalies in the ¹³C to ¹²C carbon isotope ratio (Text-Fig. 3). The positive signal of the carbon isotope ratio immediately above the Precambrian/Cambrian boundary has been interpreted as an indication of a high rate of primary biomass production, eutrophication, and removal of carbon dioxide from the atmosphere with simultaneous



Text-Fig. 3. $\delta^{13}\text{C}$ curve across the Precambrian/Cambrian boundary, and the Lower Cambrian of the Siberian Platform. The column on the right side shows data for archaeocyaths and represents crises of the reef-fauna. After M.D. BRASIER et al. (1994).

increase of the oxygen content and a short cooling period. However, the curve shows six excursions during the lower Cambrian, with durations of about 1 to 2 million years each. It is possible that these fluctuations are caused by variable greenhouse conditions (M.D. BRASIER, 1992; M.D. BRASIER et al., 1994). On the other hand, significant negative values of the carbon isotope ratio during the Botomian period have been interpreted as a crisis of the archaeocyathids, combined with a lower production of organic carbon.

A comparison of the carbon isotope curve at the Precambrian/Cambrian boundary with that at the Permian/Triassic boundary, i.e. 251 million years ago shows an almost identical behavior. It is well known that the most significant change in the development of life on Earth occurred at the turn of the Paleozoic to the Mesozoic (see comment of R.A. KERR, 1993). Analyses of fauna and flora indicated that at that time at least 80 %, probably even up to 90 % of all marine species became extinct (compare D.H. ERWIN, 1993, 1994, 1996 and others), but also insects and the terrestrial flora were strongly affected (Y. ESHET et al., 1995; G.J. RETALLACK, 1995; G.J. RETALLACK et al., 1996; C.C. LABANDEIRA & J.J. SEPKOSKI, 1993). Slightly less severe were the changes for non-marine tetrapods (W.D. MAXWELL, 1992). The origin of this catastrophe was the subject of an intensive debate, as well as the question if it occurred instantaneously or over a long period of time (compare P.B. WIGNALL & A. HALLAM, 1992; A. HALLAM, 1993).

According to a study published by S.M. STANLEY & X. YANG (1994), two mass extinctions may have occurred within 5 million years at the end of the Permian. The first one supposedly happened at the end of the Guadalupian stage, when 58 % of all marine species disappeared, and the second one at the end of the following Tatarian stage, when 61 % of all species became extinct. All together, 80 % of all marine species were supposedly affected during both of these crises.

In contrast, the astrophysicist D.N. SCHRAMM (1995) interpreted the extinction at the Permian/Triassic boundary as the result of an extraterrestrial event. According to his theory, the explosion of a supernova was the main cause of the vast extinctions 251 million years ago. The radiation from this explosion supposedly led to severe damage of the protective ozone layer of the Earth's atmosphere, so that almost all life was destroyed.

The list of possible reasons for the events at the Permian/Triassic boundary has been extended considerably during the last few years. Today, a fatal combination of various severe environmental changes are thought to be the most likely reason, and not a single event, such as an asteroid impact, for which no evidence is presently available (compare D.H. ERWIN, 1993, 1994, 1996; R.A. KERR, 1993). Thus, a combination of the following events led to an accumulation of negative environmental effects that resulted in the immense extinctions 251 million years ago:

- Regression/Transgression
- Volcanism
- Climatic changes (temperature increase/decrease)
- Ocean poisoning ("Strangelove Ocean")
- Changes in salinity?

As a result of the assembly of the continental plates during the Permian, the supercontinent Pangaea was formed. About 40 % of the surface of Pangaea were flooded by a shallow ocean due to the high sea level at that time. The

largest part of Pangaea was situated at lower latitudes; thus, a warm climate was predominant during most of the Permian.

At the end of the Permian the climatic conditions changed, probably due to significant regression, which may have been the result of the formation of a mantle plume preceding the onset of the Siberian Trap volcanism. This, in turn, led to a change in the environmental conditions for a number of organisms and species with a low level of tolerance (e.g., corals, brachiopods).

Following these environmental changes, the onset of the extensive volcanic eruptions in Northern Siberia provided the final blow. During the volcanic activity, 2 to 3 million km³ of magma were erupted during a period of only 1 million years, covering an area of 2.5×10⁶ km² (P.R. RENNE et al., 1995). According to published ages, the time of this most powerful volcanic eruption of the entire Phanerozoic corresponds, within errors, to that of the Permian/Triassic boundary. This observation supports the earlier suspicion that there is a causal relation between the mass extinction and the coeval volcanic activity at this boundary (V.E. COURTILOT et al., 1986; M.R. RAMPINO et al., 1988; V.E. COURTILOT, 1994). We can only speculate about further effects, such as the release of sulfate aerosols and carbon dioxide, which resulted in climatic changes, including cooling, glaciation of the polar caps, and possible greenhouse effects. It cannot be excluded that these events were related to observed anomalies in the C, S, and Sr-isotopic ratios (compare W.T. HOLSER et al., 1989; Y.G. LIU & R.A. SCHMITT, 1992; A. HALLAM, 1993; K. WANG et al., 1994, and others).

Death by suffocation: This was the conclusion of P.B. WIGNALL & A. HALLAM (1992), A. HALLAM (1993), and P.B. WIGNALL & R.J. TWITCHETT (1996) in their studies of the dramatic events affecting life at the Permian/Triassic boundary. One of the main reasons for these extinctions could have been an abrupt sea level increase, which is documented in sedimentary rocks. During this period of increasing stagnation, oxygen-poor water from great depths flooded the shelf areas and terminated all life. The oxygen content of the atmosphere actually decreased from 35 % O₂ at the end of the Carboniferous to 15 % O₂ at the end of the Permian, compared to today's value of 21 % O₂ (J.B. GRAHAM et al., 1995). While not all species were able to adapt to these changes, a connection with the Permian/Triassic mass extinction is rather unlikely. On the other hand, the CO₂ content of the atmosphere started with values similar to those of today's atmosphere during the Upper Carboniferous and Lower Permian and increased in the Permian to a level that was three-times higher than today, with even further increases during the Triassic.

Another hypothesis for explaining the mass extinction is ocean poisoning, as suggested by A.H. KNOLL, R.A. BAMBACH & J.P. GROTZINGER (1995, 1996; compare R.A. KERR, 1995). According to this hypothesis the Permian oceans were dominated by long-lasting stagnating conditions. At the same time, atmospheric CO₂ was extracted by phytoplankton and was changed into organic biomass. This resulted in an increase of the CO₂ content at depth, as well as reduction of the atmosphere greenhouse effect, leading to an ice age. The global cooling restarted the oceanic circulation, which had previously slowed down, bringing CO₂-rich water from great depths to the ocean surface, with catastrophic effects similar to the turnover at Lake Nyos in Cameroon in 1986.

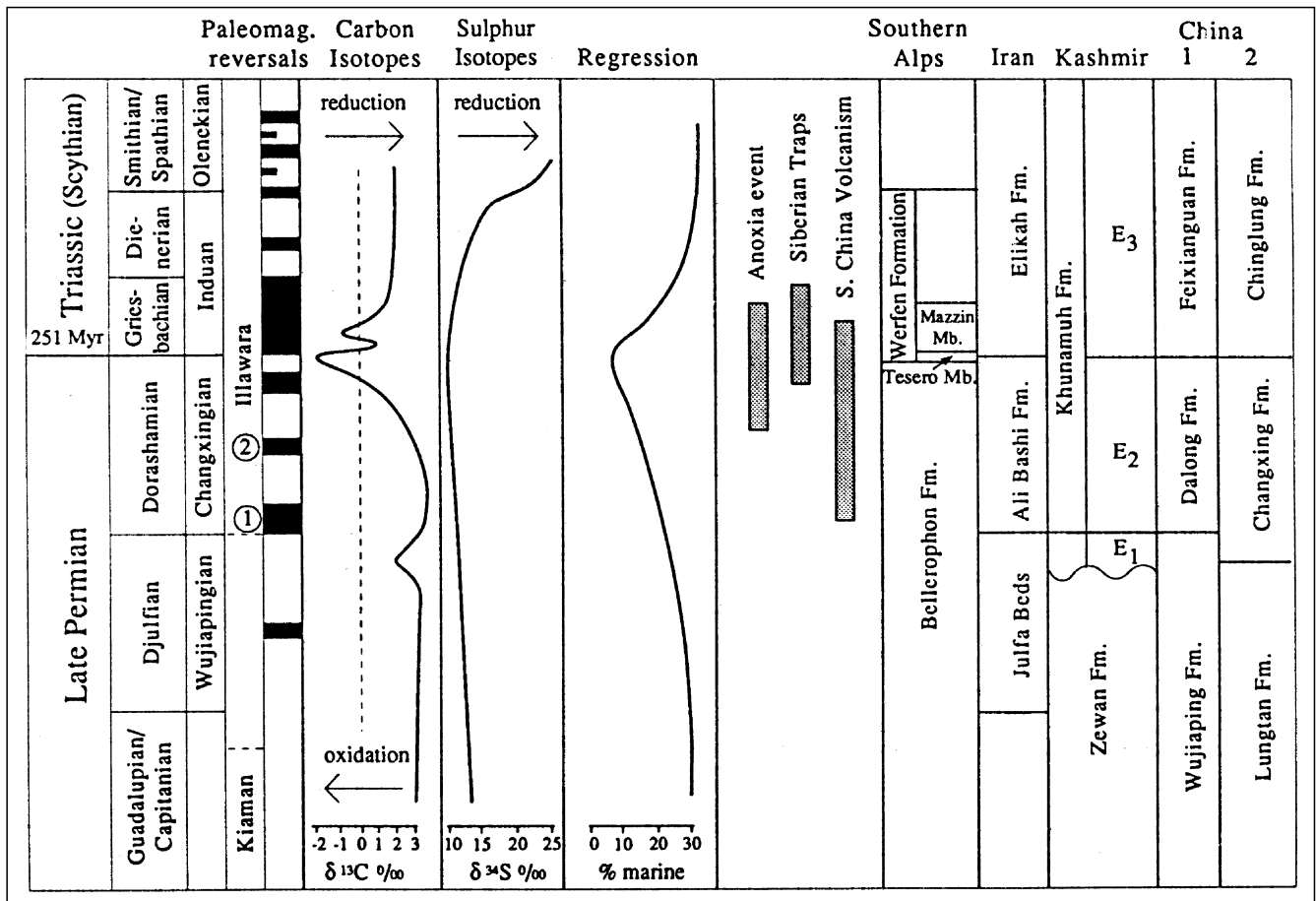
The results of a working group analyzing the events at the Permian/Triassic boundary at Nassfeld, Carnic Alps, also provided evidence for a complex ecological disaster (W.T. HOLSER & H.P. SCHÖNLAUB [eds.], 1991). After the evaluation of the drilling and outcrop studies these authors strongly concluded that the productivity in the oceans strongly decreased at the end of the Permian, while, at the same time, the partial pressure of CO₂ in the atmosphere increased. This led to an occasional greenhouse climate. The Mazzin Member showed indications of sapropelitic deposits with relatively high contents of organic carbon, which coincide with negative carbon excursions and are situated slightly above some weak iridium anomalies. They may represent the anoxic events described by P.B. WIGNALL & A. HALLAM (1992) from South Tyrol. However, there are also indications of isolated volcanism, such as in the basal part of the Mazzin Member, a few meters above the Tesero horizon (A. FENNINGER, 1991). In addition, the carbon isotope curve shows some repeated oscillations over a period of about 3 million years just above the Permian/Triassic boundary.

This behavior of the isotopic ratios, which is, so far, only known from the southern Alps, is confirmed in some recent analytical results from the Bükk mountain range in northern Hungary.

In today's knowledge, the question regarding the real reason(s) of the mass extinction 251 million years ago cannot be exhausted in just one answer. Rather, the tendency is to single out not just an individual event, as at the Cretaceous/Tertiary boundary, but a series of events – that all have negative consequences for fauna and flora –

as the causes for this environmental catastrophe (Text-Fig. 4):

- 1) After the high sea level in the earliest Permian, a global regression led to the loss of many coastal environments in the Upper Permian.
- 2) The supercontinent Pangaea was characterized by a relatively unstable climate.
- 3) This instability was amplified by locally intense volcanism (Siberia, China), leading to a significant increase in the CO₂ content of the atmosphere and related global warming, which exceeded the levels of tolerance for most species on land and in the sea. This ecological collapse was further amplified by acid rain and other environmental poisons that were flushed into the oceans.
- 4) In the course of the transgressions that began in the lowest Triassic, occasionally disaerobic water from the deep ocean flooded the continental shelves and inhibited the rapid growth of fauna and flora.
- 5) The repeated fluctuations of the carbon isotopic values at the beginning of the Triassic may be understood as an indication of "flurries in biological activity in a changing setting" (M.D. BRASIER, 1994), in analogy to the conditions at the Precambrian/Cambrian boundary. They represent variably successful attempts of life to adapt physiologically to its new environment with the dominating physical and chemical conditions.
- 6) There is, however, no evidence for an extraterrestrial component contributing to the mass extinction.



Text-Fig. 4. Summary of geological events across the Permian/Triassic boundary and correlation of important boundary profiles. After D.H. ERWIN (1994).

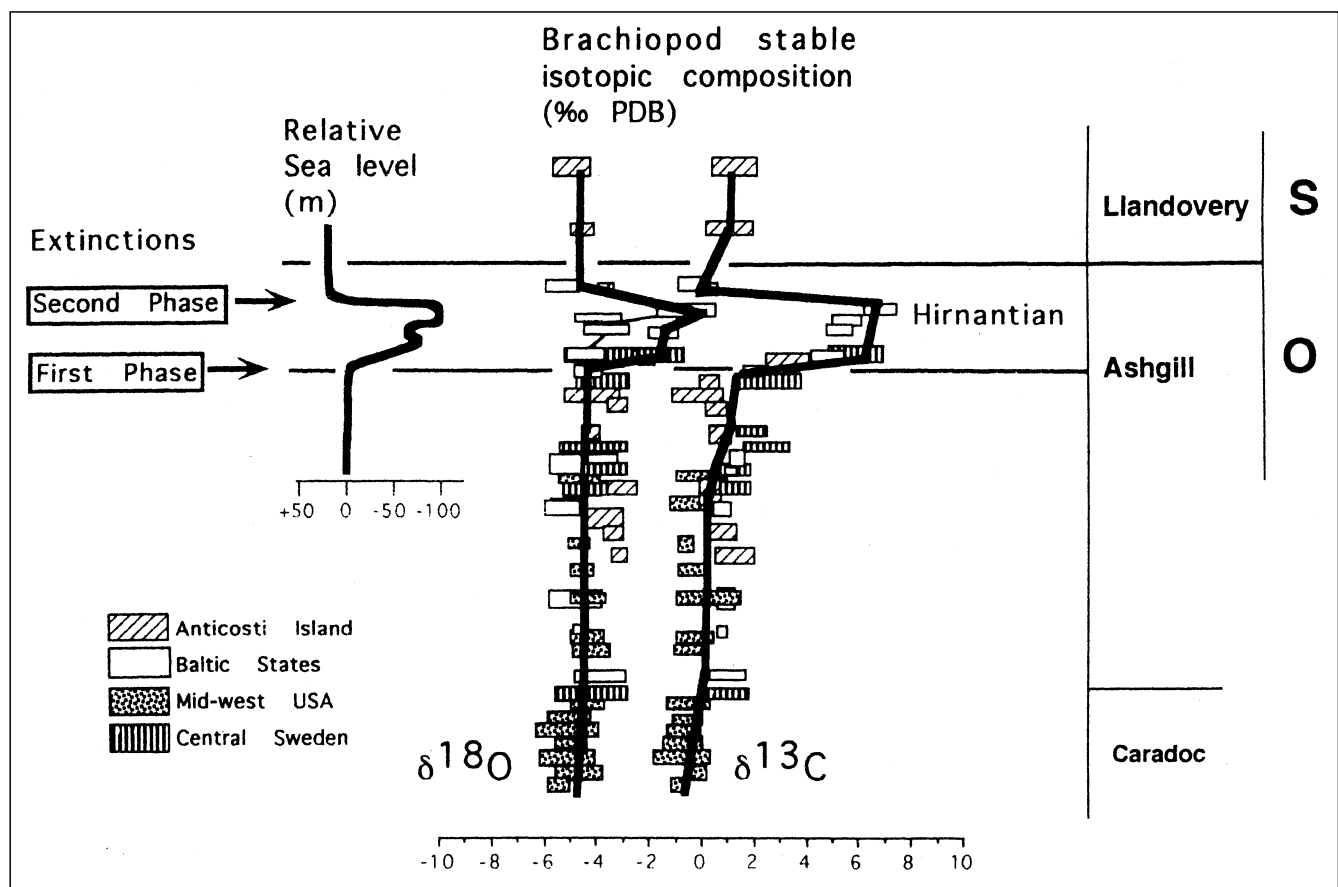
The mass extinction at the end of the Ordovician led to the disappearance of about 100 families, which represented about 22 % of all marine families (J.J. SEPKOSKI, 1982, 1993). However, other species were also affected, mainly trilobites, brachiopods, echinoderms, stromatoporoids, corals, bryozoans, ostracods, bivalves, cephalopods, graptolites, conodonts, chitinozoa, and acritarchs (N.D. NEWELL, 1967; P.J. BRENCHELEY, 1989, and others). In comparison to the great dying at the Permian/Triassic boundary, this was the second-largest catastrophe in the Phanerozoic. A number of explanations have been suggested for this extinction, such as the species/area-effect as a negative consequence of a global ice age with an associated regression (P.J. BRENCHELEY, 1995; D.A.T. HARPER & R. JIA-YU, 1995; A.W. OWEN & D.B.R. ROBERTSON, 1995), increased sedimentation with related pollution due to a significant sea level decrease (A.R. WYATT, 1995), or changes in the composition of sea water and precipitates (C.J. ORTH et al., 1986; P. WILDE et al., 1986; M.J. MELCHIN et al., 1991; W.D. GOODFELLOW et al., 1992; K. WANG et al., 1992, 1993a,b, 1995; D.G.F. LONG, 1993). In a few areas, such as South China, the Canadian Arctic, on the island Anticosti, and in South Scotland (Stratotype Dob's Linn), elevated Ir contents were found in boundary layers. However, they have been interpreted to be of terrestrial origin (K. WANG et al., 1995).

The global ice age at the end of the Ordovician ("the climatic paradox": P.J. BRENCHELEY et al., 1994) is unusual because it occurred at a time when the atmosphere had increased CO₂ contents and, thus, the Earth should have had a relatively stable greenhouse climate (P.J. BRENCHELEY et al., 1994). At that time the CO₂ content of the atmo-

sphere was supposedly 14 to 16 times higher than at present (R.A. BERNER, 1990, 1992, 1994; T.J. CROWLEY & S.K. BAUM, 1991; J.B. GRAHAM et al., 1995; C.I. MORA et al., 1996).

New studies seem to have clarified the long-standing question regarding the exact timing of the mass extinction at the end of the Ordovician. According to W.D. GOODFELLOW et al. (1992), this event occurred at the end of the Ordovician with the beginning of the graptolite zone of *Gl. persculptus*. In addition, these authors cited changes in the ratios of the stable isotopes of C, O, and S, which they explained as a result of biomass reduction, temperature increase, and a short-term flooding of the continental shelf with anoxic water. The latter supposedly was the cause of the mass extinction. However, an opposite trend was observed for the Hirnantian Stage in middle Sweden by J.D. MARSHALL & P.D. MIDDLETON (1990).

Based on recent stratigraphic and geochemical studies, the following scenario becomes evident for the Upper Ordovician (Text-Fig. 5): Beginning with the so-called gracilis-transgression of the older Caradoc Series, the global sea level increased until the end of the Ordovician (J.R.P. ROSS & C.A. ROSS, 1992). This second-order cycle was, however, overprinted by a regressive-transgressive trend in the late Ashgill Series for 0.5 to 1 million years, namely during the early to middle Hirnantian Stage; this trend was caused by glacio-eustatic changes and led to sea level variations of between 45 and 60 meters (P.J. BRENCHELEY et al., 1991, 1994). The glaciation of large parts of the southern hemisphere resulted in a significant decrease in average temperature, as well as in an increased productivity due to increased oceanic circulation. The latter is evident



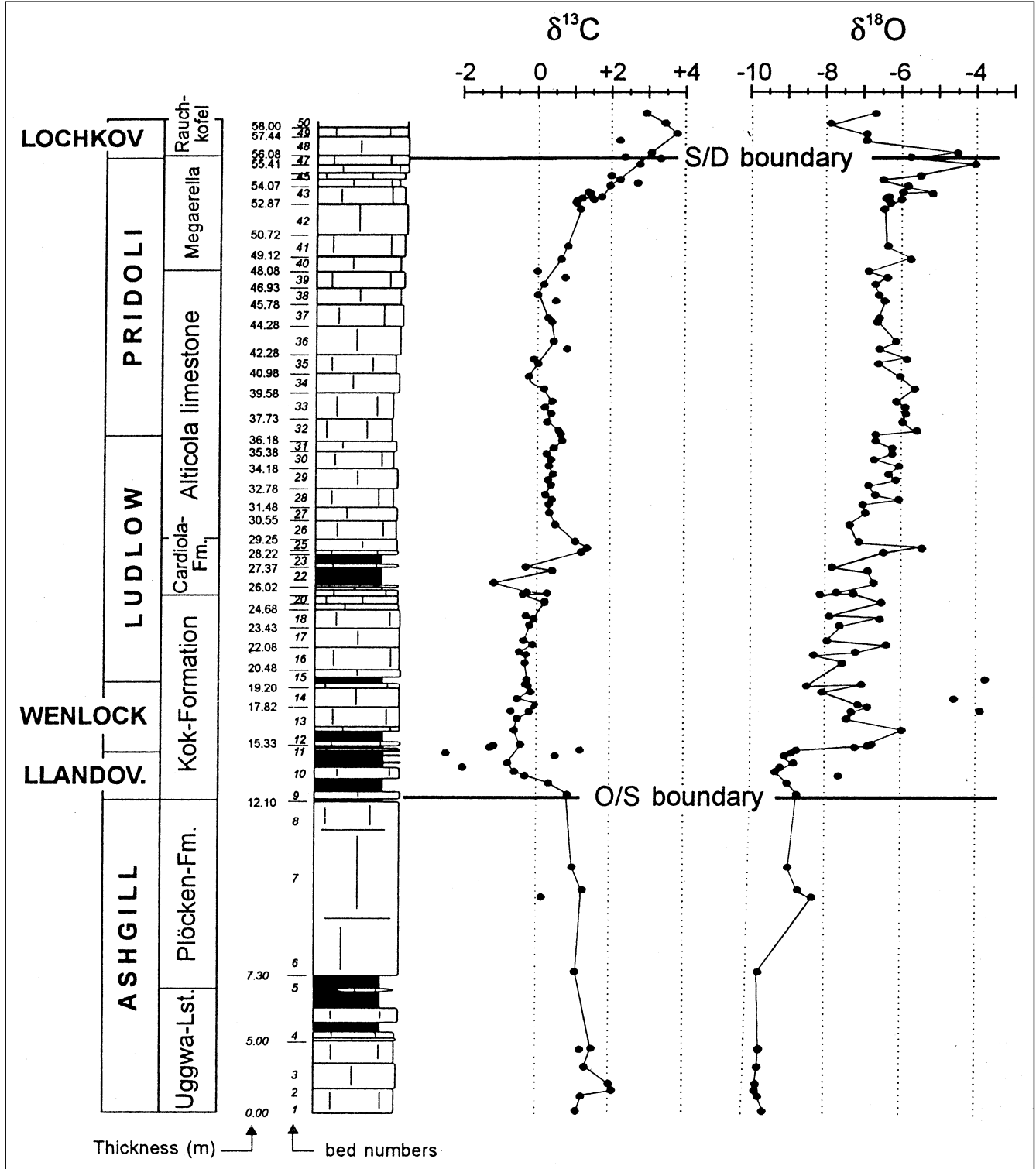
Text-Fig. 5.
Sea level variations and isotopic anomalies in the latest Ordovician.
After J.D. MARSHALL et al. (1994).

from anomalies in the oxygen and carbon isotopic ratios of marine carbonates and in the organic carbon reservoir. J.D. MARSHALL & P.D. MIDDLETON (1990) concluded that an inverse greenhouse effect was present as a result of a short-term decrease of the CO₂ partial pressure in the atmosphere and oceans.

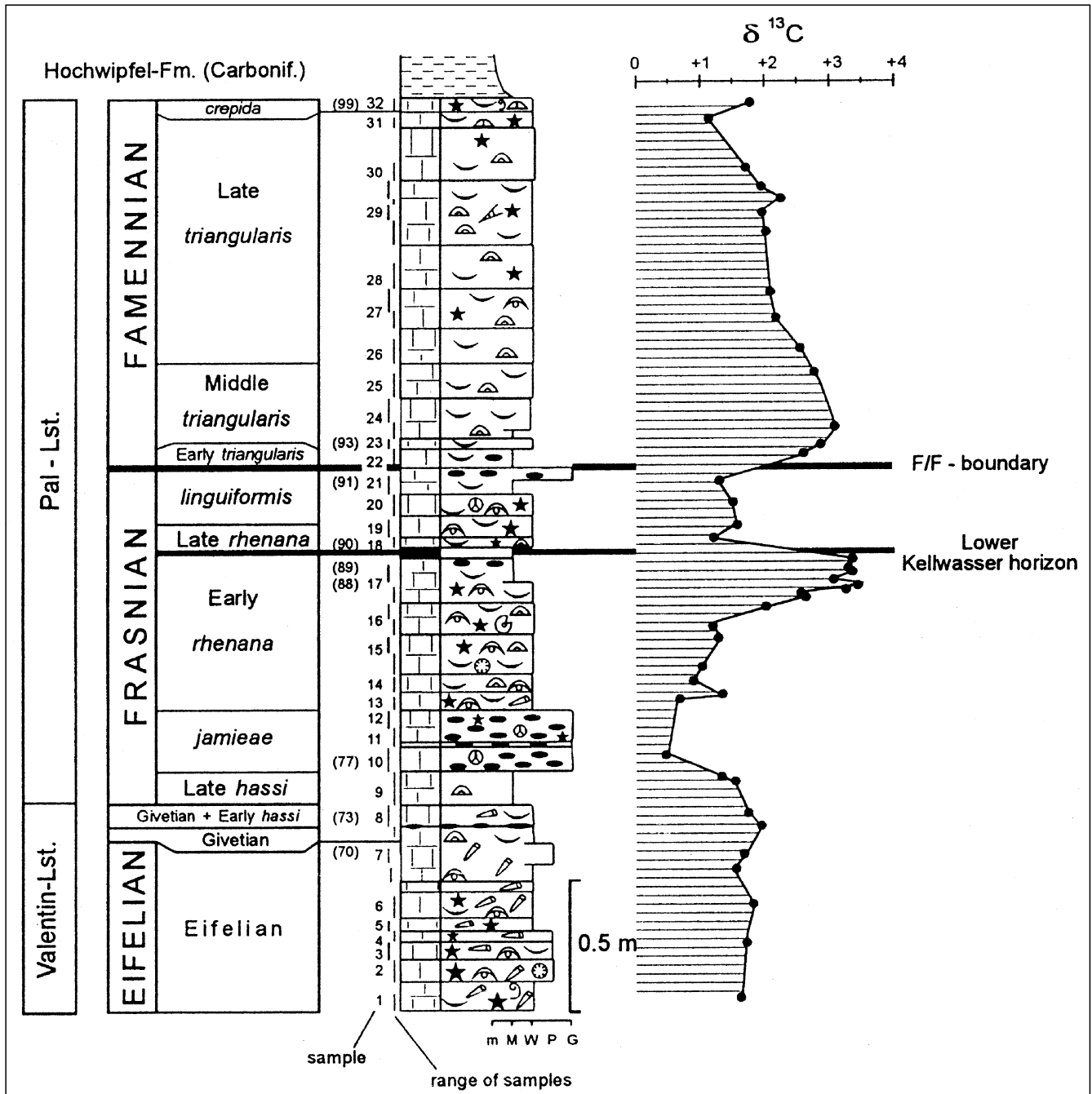
At the base of the graptolite zone of *Gl. persculptus*, both curves show an opposite trend (J.D. MARSHALL et al., 1994; P.J. BRENCHELY et al., 1994; K. WANG et al., 1994). It is assumed that this signal indicates the end of the glacia

tion period, as well as a decreased production of biomass. This condition seems to have been the reason for a further mass extinction shortly before the end of the Ordovician.

New data from Anticosti Island (Canada) add considerably to the understanding of the step-wise pattern of these events. According to G. RADCLIFFE & H.A. ARMSTRONG (1966) sea-level fall (= early glacial phase) was initiated within the Richmondian Stage of the middle Ashgill Series. The glacial maximum phase was reached during



Text-Fig. 6. Carbon and oxygen isotope data across the Upper Ordovician and Silurian part of the Cellon section in the Carnic Alps. After M.M. JOACHIMSKI & W. BUGGISCH in H.P. SCHÖNLAUB & L.H. KREUTZER (1994).



Text-Fig. 7. $\delta^{13}C$ anomaly at the Frasnian/Famennian boundary, Wolayer glacier section, Carnic Alps. After M.M. JOACHIMSKI, W. BUGGISCH & T. ANDERS (1994).

the *C. extraordinarius* Biozone and is represented by the Oncolite Platform Bed. The late glacial phase started in the *Gl. persculptus* Biozone and corresponds to the bioherms of the Ellis Bay Formation; their growth was terminated in the *A. acuminatus* Biozone at the base of the Becscie Formation indicating the post-glaciated highstand.

Facies sequence data from later Ordovician deposits in the Carnic Alps also indicate regressive-transgressive sedimentation conditions at the beginning of the Hirnantian Stage (H.P. SCHÖNLAUB, 1988). The regressive trend begins in the upper part of the Uggwa Limestone and reaches its maximum in the bioclastic Plöcken-Formation. The few isotopic data presently available indicate fluctuations of the oxygen and carbon isotopic ratios, but, so far, no conclusive comparison with results from other locations is possible (Text-Fig. 6).

At the beginning of the Upper Devonian, a new crisis in the biosphere became apparent. Increased extinction rates of various groups of organisms occur at the Givetian/Frasnian and also at the Devonian/Carboniferous boundary. A significantly larger mass extinction happened, however, within the Upper Devonian. This extinction is different from all others, inasmuch it did not occur at the end of a geological era, but between the Frasnian and Famennian Periods in the Upper Devonian, about 368 million years ago.

Already in 1970 a connection was suggested between the impact of an extraterrestrial object and the mass extinction in the Upper Devonian – 10 years before Louis ALVAREZ and his son Walter tried to find evidence for a similar scenario at the Cretaceous/Tertiary boundary (D.J. McLAREN, 1970). According to J.J. SEPKOSKI (1986), this

crisis affected about 21 % of all marine families and about 50 % of all genera; about 75 to 82 % of all species became extinct at that time. A peculiarity of this extinction is that it did not happen over night, but in several phases of about 2 to 3 million years (G.R. MCGHEE, 1989, 1994; T.R. BECKER et al., 1991). A first extinction occurred in the Upper rhenana-conodont Zone of the youngest Frasnian, with a second, more intense one, following in the linguiformis Zone at the end of the Frasnian.

A decrease in global temperatures was suggested in early paleoenvironmental studies as a reason for this extinction (P. COPPER, 1977, 1986; H.H.J. GELDSETZER et al., 1987; G.R. MCGHEE, 1982, 1989, 1991; S.M. STANLEY, 1987). The impact of an asteroid, with prolonged environmental effects, did not fit this scenario. Thus, multiple impact events were suggested as an alternative theory (G.R. MCGHEE, 1982, 1994; C.A. SANDBERG et al., 1988). There appears to be some evidence for this view, in the form of impact craters as well as microtektite-bearing layers, which were found in China and in two locations (90 km apart) in Belgium (P. CLAEYS et al., 1992; K. WANG, 1992; P. CLAEYS & J.-G. CASIER, 1994). According to P. CLAEYS and J.-G. CASIER (1994), the Belgium microtektites could have been derived from the 52 km-diameter Siljan Crater in Sweden, which has an age of 368 ± 1 Ma (R.A.F. GRIEVE et al., 1988, 1995). The 46 km-diameter Charlevoix crater in Quebec is, however, an unlikely source crater, because its age of 360 Ma seems too young (and is not well constrained). The microtektites in South China are found in Quidong and occur in the crepida conodont Zone at the beginning of the Famennian and are, thus, about 1.5 million years younger than those in Belgium. These microtektites were suggested to be related to the about 70 km-diameter Lake Taihu structure in China, which is about 900 km NE of their finding location, but has not been confirmed as an impact crater (pers. comm. C. KOEBERL).

So far, geochemical studies of the boundary layers that are related to the mass extinctions show no clear indications for an extraterrestrial event as the cause of this mass extinction (with exception of the work of, e.g., D.J. OVER et al., 1996). This includes especially reports related to biological activities (P.E. PLAYFORD et al., 1984; G.R. MCGHEE, 1989; C.J. ORTH, 1989).

The stable isotope data for carbon show obvious positive and negative anomalies (Text-Fig. 7) at many locations, including the Carnic Alps; similar signals were also observed for oxygen and sulfur isotopes (H.H.J. GELDSETZER et al., 1987; W.D. GOODFELLOW et al., 1988; M.M. JOACHIMSKI & W. BUGGISCH, 1993, 1994; M.M. JOACHIMSKI et al., 1994; K. WANG et al., 1996). These values have been interpreted as changes in the isotopic composition of the total carbon that is dissolved in the oceans ("TDC"). According to this, a short-time sea level increase resulted in an extension of the O-minimum-zone at the shelf and in increased deposition of sediments that were rich in organic carbon (i.e., ^{12}C), in the lower and upper Kellwasser horizons, leading to an increase in the ^{13}C signal.

According to these explanations, the main reason for the increased amount of organic carbon is not increased productivity, but the beginning of anoxic reducing conditions in the youngest Frasnian. This is supported by the predominance of black layered sediments missing bioturbation, an increase in the concentrations of chalcophile elements such as S, Zn, As, and Sb, as well as increased $\delta^{34}\text{S}$ due to preferential extraction of the lighter sulfur isotope ^{32}S from sea water during formation of pyrite.

According to M.M. JOACHIMSKI & BUGGISCH (1993, 1994), M.M. JOACHIMSKI et al. (1994) and K. WANG et al. (1996), the positive signal of the stable carbon isotope ratio is overprinted at the Frasnian/Famennian boundary by a short-term negative anomaly. These authors interpret this anomaly as an indication of a significant reduction of the productivity and biomass formation in the upper water layers, which they explain as being due to the mass extinction mentioned above.

According to the opinion of M.M. JOACHIMSKI et al. (1994), which is, however, not undisputed, the increased removal of carbon in water near the surface caused a change in the CO_2 content of the atmosphere. Climatic consequences ensued, which further burdened the already stressed fragile eco-system. According to U. BRAND (1989) and B. LUZ et al. (1984), the Frasnian/Famennian boundary was characterized by extremely high temperatures and a distinct greenhouse climate, which was close to the level of tolerance for many organisms (J.B. THOMPSON & C.R. NEWTON, 1988; R.T. BECKER & M.R. HOUSE, 1994). The final collapse came after flooding of large areas of continental shelves by oxygen-poor deep water and short-term climate changes – most probably resulting from the impact of an extraterrestrial body (K. WANG et al., 1996).

In an endogenous hypothesis for the mass extinction at the Frasnian/Famennian boundary, T.J. ALGEO et al. (1995) proposed that the extinction occurred due to suffocation that resulted from increased introduction of nutrients into the oceans. According to this hypothesis, the formation rate of soil, physical and chemical weathering, and the production rate of biomass have increased as a result of the development of the tree-forming vascular plants, e.g., progymnosperms, genus *Archaeopteris* during the late Middle Devonian. This increase led to a massive flux of nutrients into the ocean, which used up all the available oxygen, and, in turn, resulted in the decline of the marine fauna. According to this scenario, eutrophication, blooming of algae, and the formation of black shales were primarily responsible for the mass extinction. The decrease of the atmospheric CO_2 content and the global climate change were supposedly only secondary effects*).

In 1991, J.E. WARME described the Upper Devonian "Alamo event", in which tsunamis and submarine mass flows occurred in southern Nevada, probably as the result of an extraterrestrial event, such as the impact of an extraterrestrial body. In this event, a limestone megabreccia was formed, which is supposed to represent the largest such mass flow preserved on land. It consists of more than 250 km^3 of debris from limestone platforms, which have an average thickness of 70 m and are distributed over an area of about 4000 km^2 (J.E. WARME & C.A. SANDBERG, 1995, 1996). The presence of shocked quartz and an iridium anomaly has been cited as confirming evidence for an impact origin (H. LEROUX, J.E. WARME & J.-C. DOUKHAN, 1995; J.E. WARME & C.A. SANDBERG, 1996). The impact

*) According to the opinion of geochemists, the global carbon cycle and, therefore, the atmospheric composition during the Phanerozoic, provide a mirror image of the development of the terrestrial flora (H.D. HOLLAND, 1972; R.A. BERNER, 1989, 1992, 1994). It controls the chemical weathering rate, which is a process in which CO_2 is taken out of the atmosphere, thus reducing or preventing greenhouse conditions. The balance resulting from this process has been disturbed several times in the past, e.g., in the glaciation period in the late Ordovician. After the appearance of vascular and seed plants during the Carboniferous and Permian, the CO_2 content of the atmosphere decreased, resulting in an inverse greenhouse climate.

Text-Fig. 8. Carbon and oxygen isotope data across the Devonian/Carboniferous boundary, Grüne Schneid and Kronhofgraben sections, Carnic Alps. After H.P. SCHÖNLAUB et al. (1992), changed from M.M. JOACHIMSKI & W. BUGGISCH in H.P. SCHÖNLAUB & L.H. KREUTZER (1994).

supposedly happened during the *P. punctata* conodont Zone (= middle *A. asymmetricus* Zone of the older system), which is only a few 100,000 years after the beginning of the Frasnian Stage in the Upper Devonian.

So far, no detailed conclusions can be made regarding the true extent of the Alamo event, except for local consequences in Nevada. It is interesting, however, that, at the same time, some limestone breccias, hiatuses, and mixed conodont faunas exist in various areas of the Eastern and Southern Alps. So far, they have been attributed to extensive tectonic movements related to the Variscan orogeny (C. SPALLETTA & C. VENTURINI, 1994). Examples exist in the Carnic Alps, the eastern Karawanken Alps, and in central Carinthia (H.P. SCHÖNLAUB, 1971, 1986; P. PÖLSLER, 1969; B. MOSHAMMER, 1989). Are these breccias perhaps related to the Alamo-event?

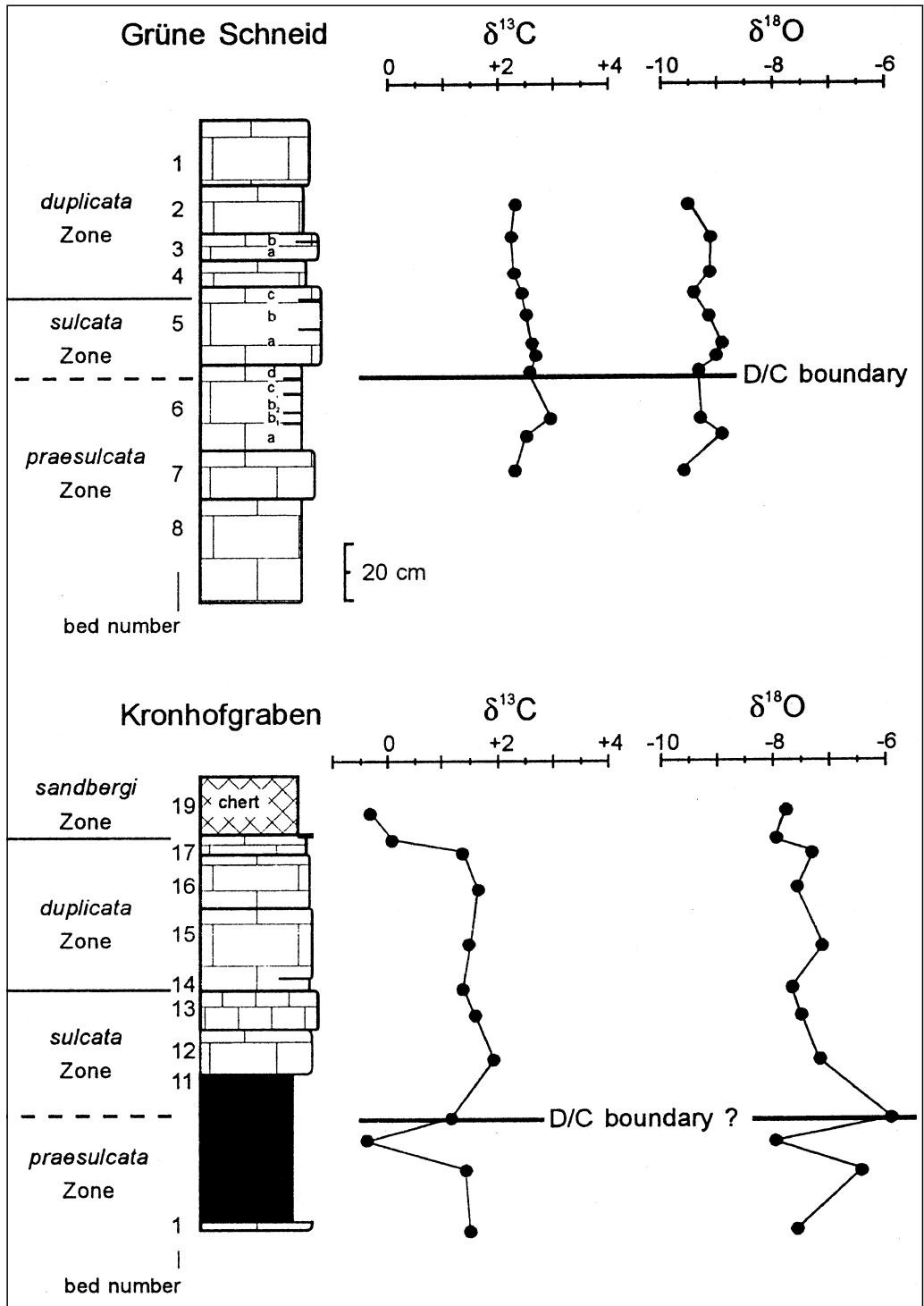
The extinction at 354 Ma, at the Devonian/Carboniferous boundary, the so-called "Hangenberg event" is, compared to the five large mass extinctions, only of secondary importance. This event affected mainly pelagic organisms, such as conodonts, ammonites, and trilobites, and, to a lesser degree, ostracods, foraminifera, and corals. A detailed description of this event at the Carnic Alps, including data on biofacies and geochemical composition, is given in H.P. SCHÖNLAUB et al. (1992) and H.P. SCHÖNLAUB & L.H. KREUTZER (1994) (with contributions on the Drewer quarry, Rheinisches Schiefergebirge, by M.M. JOACHIMSKI & W. BUGGISCH). As there do not seem to be any significant changes in trace elements or isotope composition across the Devonian/Carboniferous boundary, these authors concluded that uniform sedimentation, dictated

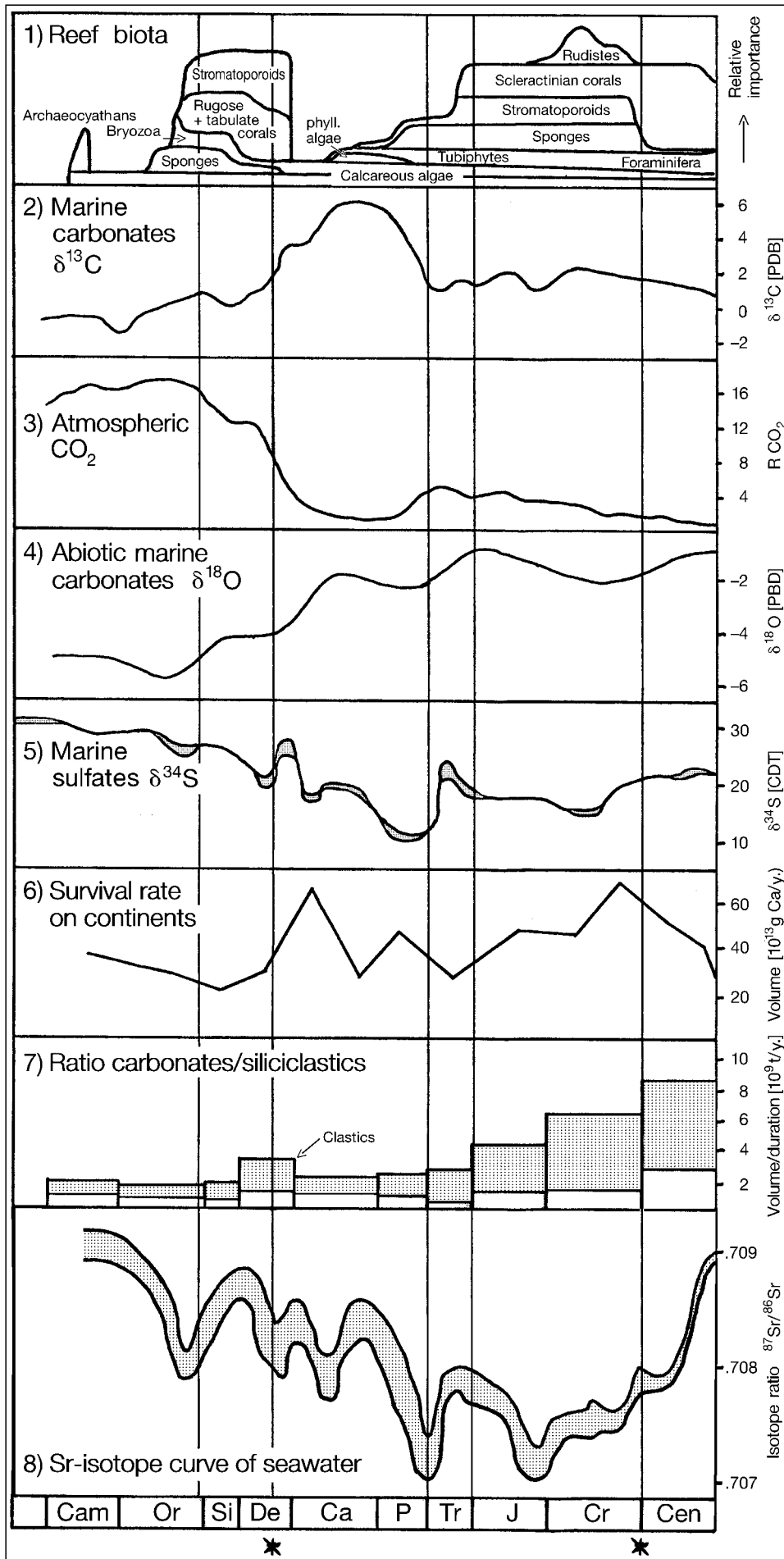
by regressive-transgressive conditions, took place (Text-Fig. 8). There is no evidence for an extraterrestrial event.

3. Summary

In the past years many questions have been posed regarding the cause and reason of the various mass extinctions mentioned above. However, apart from the events at the Cretaceous/Tertiary boundary, no clear and satisfying answers have emerged so far.

What is the relative importance of the various biological, chemical, and physical indicators that are characteristic for one or the other scenario? Or do all of these catastrophes follow a common pattern?





Text-Fig. 9. Evolutionary trends during the Phanerozoic in biosphere, atmosphere, and hydrosphere. After T.J. ALGEO et al. (1995), changed and extended.

Vertical lines indicate periods of mass extinctions around the end of the Ordovician, the Frasnian/Famennian boundary in the Upper Devonian, the Permian/Triassic boundary, the Triassic/Jurassic boundary, and the Cretaceous/Tertiary boundary. Asterisks indicate confirmed impact events.

- 1) Dominant reef-forming organisms (after N.P. JAMES, 1983).
- 2) Marine carbonate $\delta^{13}\text{C}$ (after R.A. BERNER, 1989).
- 3) CO_2 content of the atmosphere, compared with the present-day value R_{CO_2} (after R.A. BERNER, 1994).
- 4) Abiotic marine $\delta^{18}\text{O}$ (after K.C. LOHMANN, 1988).
- 5) Marine sulfate $\delta^{34}\text{S}$ (after W.T. HOLSER et al., 1989).
- 6) Fossil carbonates from continental areas ("survival rates"; after F.T. MACKENZIE & J.W. MORSE, 1992).
- 7) Ratio of carbonate mass versus clastics per period (after F.T. MACKENZIE & J.W. MORSE, 1992).
- 8) Sr-isotopic curve in seawater (after F.M. RICHTER et al., 1992).

With the exception of the Cretaceous/Tertiary boundary, and possibly the Frasnian/Famennian boundary in the Upper Devonian, no direct physical and chemical connection has – so far – been established between mass extinctions and impact events. It seems justified to assume that mass extinctions can also have endogenic – terrestrial – origins.

Text-Fig. 9 shows the anomalies of: carbon, oxygen, and sulfur (2,4,5) isotopic composition, the CO_2 content of the atmosphere (3, normalized to today's PAL value), the carbonates that are present on the continents (relative to the duration of the respective periods; 6), the ratio of carbonates versus clastics per period (7), the Sr-isotopic composition of seawater as a measure of tectonic activity during the Phanerozoic (8), and the relative abundance of reef-forming organisms (1); all during the Phanerozoic.

The sulfur isotope curve, as determined from old evaporites, indicates the degree to which sulfate dissolved in

seawater was reduced by bacterial action, as well as the available amount of carbon-rich organic sediments.

In this schematic representation, the changing CO₂ content of the atmosphere is the primary signal. It is interesting to note that all significant changes in that curve seem to correlate with the occurrences of the various mass extinctions described above. Following a maximum during the lower Paleozoic, the CO₂ content decreased during the Devonian and Lower Carboniferous to values that are similar to present-day values. However, during the Upper Permian and the Triassic, the atmospheric CO₂ content increased again to four times the present day number.

The biogeochemical carbon cycle indicates that when carbon is being removed from the atmosphere and from the oceans, mainly the lighter ¹²C isotope is removed and concentrated in sediments that are rich in organic carbon. This process leads, therefore, to an enrichment in the heavier ¹³C isotope and, in turn, to a higher δ¹³C value of marine carbonates.

Changes in the CO₂ content of the atmosphere may have climatic consequences, and also influence the temperature of the upper layers of the oceans. The ratio of the oxygen isotopes ¹⁸O/¹⁶O, which can be measured in the shells of marine organisms, is a function of the respective ambient water temperature and increases with decreasing temperature. Since the classical work by A.G. FISCHER & M.A. ARTHUR (1977), several authors have expressed the opinion that evolutionary crises may be related to changes in the ocean temperatures (compare S.M. STANLEY, 1984a,b, 1988). Indeed, several highly specialized tropical organisms have a very narrow tolerance range regarding physical and chemical parameters, such as temperatures between 24° and 28°C and poly- to euryhaline conditions (J.B. THOMPSON & C.R. NEWTON, 1987; J.D. HUDSON, 1990; P.J. BRENCHLEY, 1990; R.T. BECKER & M.R. HOUSE, 1994). If these limits are exceeded, significant consequences in the evolution are the result.

The decrease in the CO₂ content of the atmosphere at the end of the Ordovician led to global cooling, which is clearly indicated by an increase in δ¹⁸O in marine carbonates. Similar clear anomalies are also obvious at the Permian/Triassic and Triassic/Jurassic boundaries. While the unusually high temperatures of around 40°C in surface waters of the Upper Devonian (U. BRAND, 1989) are not universally accepted, the δ¹⁸O values show a distinct trend towards higher temperatures. Cooling is only obvious in the Lower Carboniferous after formation of an extensive ice cap in the southern hemisphere (T.J. CROWLEY & S.K. BAUM, 1991b; G. GONZALEZ-BONORINO & N. EYLES, 1995; N. EYLES et al., 1995, and others). This decrease in temperature also led to a reduction in the formation rate of carbonates (F.T. MACKENZIE & J.W. MORSE, 1992). The low CO₂ content in the atmosphere was an important factor in this development, which led to "icehouse" conditions on Earth.

There are various opinions regarding the origin of these remarkable variations of the atmospheric CO₂ content during the Phanerozoic (cf. S.H. SCHNEIDER, 1989; R.A. HOUGHTON & G.M. WOODWELL, 1989). According to M. JAVOY et al. (1982) and R.A. BERNER et al. (1983), a direct relation exists between volcanic CO₂ emissions and the formation rate of oceanic crust in mid-oceanic rift zones. R.A. BERNER (1990b) regards the volcanic emissions as an important contribution to the CO₂ cycle. However, as shown in recent calculations by S.N. WILLIAMS et al. (1992), this contribution is relatively small, with about

6.5 × 10¹³ g per year, which is only about 0.22 % of the anthropogenic CO₂ released into the atmosphere. Nevertheless, in periods of enhanced volcanic activity, such as during eruption of the Dekkan Traps or the Columbia River basalts, the CO₂ emissions can reach – within days – 30 % of the annual anthropogenic CO₂ emissions.

The ⁸⁷Sr/⁸⁶Sr isotope curve for seawater (Text-Fig. 9) comprises more than 1300 analyses from the Phanerozoic (W.H. BURKE et al., 1982; F.M. RICHTER et al., 1992; P.C. SMALLEY et al., 1994, and others). According to F.M. RICHTER et al. (1992), the high present-day ⁸⁷Sr/⁸⁶Sr ratio for seawater is correlated with sub-recent collisional events between the Indian plate and Asia. The collision led to increased erosion of deformed crustal rocks and, by the way of Sr dissolved in river water, influenced the seawater Sr-budget. Thus, the development of the Sr-isotope curve for seawater is assumed to mirror global orogeny in collisional zones, but excluding local minima or maxima.

The view that the Sr-isotopic curve of seawater represents an indicator for magmatic and tectonic activities, and, thus, increased or decreased volcanic CO₂ emissions in the Phanerozoic is not supported by studies of the distribution of atmospheric CO₂ in the orogenic-dominated periods from the Silurian to the Carboniferous. Thus, it may be concluded that the changes in the composition of the atmosphere are dominated by other mechanisms. In conclusion, I agree with T.J. ALGEO et al. (1985) that the evolution of the terrestrial flora is primarily responsible for the atmospheric CO₂-content.

Only combinations and linkages of individual events may trigger outstanding and dangerous environmental conditions.

In contrast to cosmic catastrophes, such as impact events, such changes do not occur instantaneously. Rather, one event prompts the next one, until interlinked conditions are significantly enhanced and finally lead to an ecological and environmental catastrophe.

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