Chemistry of Jurassic seas and its bearing on the existing organic life

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ABSTRACT:

GRUSZYŃSKI, M. 1998. Chemistry of Jurassic Seas and its bearing on the existing organic life. *Acta Geol. Polon.,* **48** (1), 1-29. Warszawa

Study of Jurassic seawater chemistry comprised has revealed two successive stages of water mass organisation. The first stage, the unstable development of stratified zones, lasting until the mid Oxfordian, was characterised by large fluctuations of sea water temperatures and was interrupted by two episodes of opposite nature. The early Toarcian episode was related to expansion, whereas the Bajocian-Bathonian (B-B) episode was connected to temporary mixing of stratified seawater zones. The next stage, the breakdown of the stratified zones was characterised by stable, relatively warm seawater temperatures; it was also interrupted by boundary events, and depended, increasingly with time, on oceanic circulation. The presence, development and retreat of stratified zones was manifested by massive $CaCO_3$ precipitation and $CaCO_3$ precipitation crises. Thus, interpretation of $\delta^{13}C$ in terms of burial and reburial of C_{org} in the sea, which requires existence and mixing of stratified seawater zones resulted in secular changes of $CaCO_3$ saturation states. This led to the picture of a Jurassic "aragonitic sea", contrary to the generally accepted model. Those $CaCO_3$ precipitation crises, emphasised by omission surfaces and specific mineral parageneses, suggested that Phanerozoic carbonate seas could have been suitable sites for "reverse" weathering.

Although geochemical perturbations did not coincide with the major mass extinctions postulated for the Jurassic, they expressed changes, of primary productivity, and in the structure of organic assemblages. These changes as well as detailed palaeoenvironmental conditions, may be monitored by the elemental tracer *i.e.* Ba concentrations.

"For I am a Bear of Very Little Brain, and long words Bother me"

Winnie-the-Pooh

INTRODUCTION

I forget the name of the professor who taught his students that oceanography was a very shallow science on a very deep sea. I have followed the professor's example, scrupulously treating palaeooceanography as the shallowest and most troublesome science on the "undiscovered ocean of truth". However, assuming chemical and physical process-es to be "A Key to the Present and to the Past", some models relating to palaeochemical properties of seawater, palaeoclimate and oceanic circulation might be established, either on a local or on a global scale.

Despite much study, the details of Jurassic palaeooceanography are insufficiently well described from the isotope-geochemical point of view. This study, therefore, is an attempt to show some aspects of Jurassic seawater chemistry and its relation to changes in the structure of the marine biota. To achieve a coherent model, the research methods of isotope and elemental geochemistry have been used in an attempt to extract palaeo-
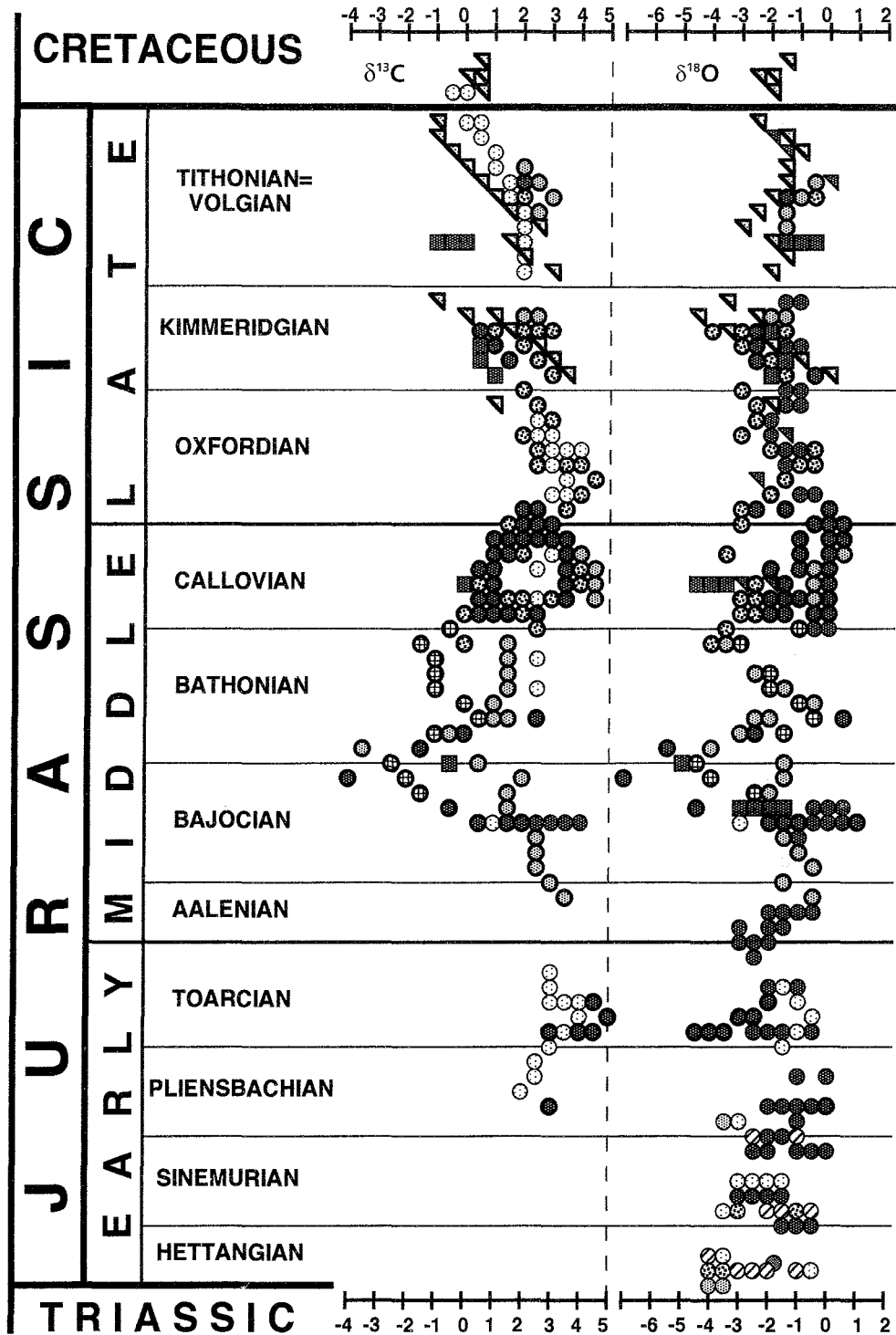
Fig. 1. General pattern of $\delta^{13}C$ and $\delta^{18}O$ values for skeletal and non-skeletal particles throughout the Jurassic; thick outlines of the symbols denote complete geochemical results, both isotopic and elemental; symbols for the different analysed material from different part of the world, are as follows: European (Tetyan and Boreal) Province: ⊘ echinoderm skeletal remains; ☉ whole rock samples; ⊛ bivalve shells; ⊕ nektonic (ammonite and nautiloid shells, belemnite rostra) skeletal remnants; ⊕ brachiopod shells; ⊕ foraminifera tests; Australo-New Zealand Province: ⊞ belemnite rostra; American Province: ◥ belemnite rostra; ◺ whole rock samples; isotope values for the arago-nitic phragmocone of Bajocian *Megatheutis* (SPAETH & al. 1971) are excluded, for they are very negative, outside the presented scale

oceanographic markers (*sensu* ELDERFIELD1990) for reconstruction of the general evolution of seawater geochemistry and circulation, seawater palaeotemperatures, palaeoproductivity, and the geochemical structure of the water column.

EVOLUTION OF JURASSIC SEAWATER GEOCHEMISTRY RECORDED BY THE δ^{13}C AND δ^{18}O CURVES

An attempt to present a general chemical palaeo-oceanographic picture has been based on all the available results of isotope studies, initially concentrated on the δ^{18}O composition of belemnite rostra (BOWEN 1961, BOWEN & FRITZ 1963, FABRICIUS & *al*. 1970, FRITZ 1965, SPAETH & *al*. 1971, BERLIN & KHABAKOV 1970, STEVENS & CLAYTON 1971, TAN & *al*. 1970, TEIS & *al*. 1968) and, to a smaller extent, of ammonite septa (STAHL & JORDAN 1969, JORDAN & STAHL 1970), which were considered as palaeotemperature proxies according to pioneering works by UREY and his students (UREY & *al*. 1951, EPSTEIN & *al*. 1953). This enthusiasm for palaeotemperature determinations decreased rapidly when it became obvious how misleading isotope results could be, that had been obtained from samples which had been diagenetically altered (VEIZER 1974, VEIZER & FRITZ 1976). Fortunately, this did not stop all the isotope investigations within the Jurassic sedimentary sequences. Although some of those studies concentrated only on interpretation of the δ^{13}C record (JENKYNS & CLAYTON 1986, JENKYNS 1988, WEISSERT & CHANNELL 1989, JENKYNS & *al*. 1991, JENKYNS 1996), other investigations attempted to interpret both the δ^{13}C and δ^{18}O record (GRUSZCZYŃSKI & *al*. 1990b, HOFFMAN & *al*. 1991b, PISERA & *al*. 1992, ANDERSON & *al*. 1994, SÆLEN & *al*. 1996, JENKYNS & CLAYTON 1997).

The results illustrated here (Text-fig. 1) are mostly from the European Province, with additional samples from the American (almost all from North and Caribbean parts) and Australo-New Zealand provinces. There are two levels of reliability of isotope results, which means that the more valuable data for interpretation deal with samples for which both isotopes and elements were analysed (BRAND & VEIZER 1980, 1981; *also* VEIZER 1983), in order to estimate the extent of diagenetic alteration. Diagenetic alteration is related, apart from the well known influence of meteoric waters, to the general process of microbial degradation of organic matter within postoxic (=suboxic) and anoxic zones (FROELICH & *al*. 1979, BERNER 1981) within bottom sediments. These dissolution-reprecipitation processes change the original isotope composition (HUDSON 1977, COLEMAN 1985, *see also* MARSHALL 1992). Apart from diagenesis, isotope values obtained from skeletal portions of molluscs, especially nektonic (belemnites, ammonites, nautiloids), might be altered because of the so-called "vital effect". According to detailed geochemical reconstruction of the ontogenetic stages of certain molluscs, the most reliable isotope values are those for the terminal portions of ammonite shells and the outer layers of belemnite rostra.

General characteristics of Jurassic δ^{13}C and δ^{18}O curves

To start with description of changes in the carbon and oxygen isotope compositions throughout the Jurassic, the author must admit that many gaps remain to be filled, especially in the case of δ^{13}C results. There are apparently no data so far on δ^{13}C values for both shells and whole rock samples belonging to the first two stages of the Early Jurassic, *i.e.* Hettangian and Sinemurian. δ^{13}C values for the Pliensbachian obtained both from whole rock samples and ammonite shell portions, oscillate around 3‰. These values increase to 4.5‰ for whole rock samples, and to more than 6‰ for belemnite rostra during the Early Toarcian, and then fall to the average Pliensbachian level (3‰). The δ^{13}C values become higher than 3‰ at the end of the Aalenian, shifting slightly towards less positive values across the Aalenian-Bajocian boundary, and then stabilize around value of 2.0‰. There is a negative shift in the δ^{13}C values in the Late Bajocian, reaching the absolute Jurassic minimum of –4‰ for the ammonite shells at the Bajocian-Bathonian boundary. Some belemnite samples from the Australo-New Zealand Province show more positive δ^{13}C values, around 0‰. In the case of Europe, less negative δ^{13}C values (–2.5‰) than the values for the ammonite shells, are observed for the shells of benthic foraminifera. This trend is followed by the δ^{13}C values for the benthic bivalve shells, which rise to 2.5‰ towards the Bajocian-Bathonian boundary, and then fall to –3‰ in the earliest Bathonian. After that, δ^{13}C values rise again, and remain stable within a range of –1 to 1‰, with foraminifera samples approaching the negative, and bivalve samples oscillating around the positive limit of this range. Surprisingly, the δ^{13}C values for some whole rock samples are more posi-

tive, oscillating between 2 and 3‰ towards the Bathonian-Callovian boundary. The values for whole rock samples stay more or less the same for the Callovian Stage, whereas $\delta^{13}C$ values for representative nektonic shells show two separate trends, one oscillating within the range 1 to 2‰ and the other within the 3 to 4‰ range. Interestingly, $\delta^{13}C$ values for benthic bivalve shells are more positive, reaching the highest values of 4.5‰ in the mid-Callovian, and decreasing gradually during the Late Callovian, whereas the $\delta^{13}C$ values for benthic brachiopods show two separate trends, similar to those for nektonic skeletal remains. $\delta^{13}C$ values become uniform for all the analysed samples at the Callovian-Oxfordian boundary. These uniform $\delta^{13}C$ values rise to 4.5‰ in the early mid-Oxfordian, and then fall gradually, oscillating between 2.5 and 3‰ at the end of the Oxfordian. This makes the Oxfordian the stage with the relatively "heaviest" $\delta^{13}C$ values in the whole Jurassic. $\delta^{13}C$ values then fall gradually through the Kimmeridgian for both nektonic (ammonite) and benthic (brachiopod and bivalve) skeletons, and more profoundly for the whole rock samples. It is noteworthy that the average $\delta^{13}C$ values for nektonic belemnite samples from New Zealand show a similar shift, but the starting point is of 1‰ lower. The trend in $\delta^{13}C$ values to decrease continues during the Tithonian (=Volgian), although an episodic opposite shift of $\delta^{13}C$ values at the Kimmeridgian – Tithonian transition has been observed. A shift of the same characteristics, towards more positive $\delta^{13}C$ values, is observed across the Tithonian-Berriasian transition, *i.e.* the Jurassic-Cretaceous boundary.

$\delta^{18}O$ values show a chaotic pattern for benthic (brachiopod, crinoid, and bivalve) skeletal remains and for whole rock samples, and a directional trend for nektonic (belemnite, ammonite and nautiloid) skeletons, during the Early Jurassic. The chaotic pattern is characterised by $\delta^{18}O$ values within a range of –4 to –1‰ until the Early Pliensbachian. The average $\delta^{18}O$ values for the whole rock samples shift slightly towards more negative values through the Hettangian – Pliensbachian. Then, in the Early Toarcian, $\delta^{18}O$ values follow the same trend as the $\delta^{13}C$ values, starting with –1.5‰, reaching a maximum of –0.5‰, and then dropping again to the initial values. The average $\delta^{18}O$ values for belemnite rostra rise from –2 to –1‰ to the end of the Hettangian, then drop to –2.5‰, and rise again at the Sinemurian-Pliensbachian boundary. A continuous rise of $\delta^{18}O$ values culminates in a Pliensbachian maximum of 0.5‰. After reaching that maximum,

$\delta^{18}O$ values fall gradually to –2.5‰ at the Toarcian-Aalenian transition. During the Middle Jurassic $\delta^{18}O$ values for belemnite rostra increase gradually up to 0‰ in the mid-Bajocian and then rapidly drop to the Jurassic absolute minimum, of almost –8‰, close to the Bajocian-Bathonian boundary, thus reflecting the same trend as seen in the $\delta^{13}C$ values. The observed trend is also evident in $\delta^{18}O$ values for belemnite rostra from the Australo-New Zealand Province, reaching –5‰ at the Bajocian-Bathonian boundary. Similarly, $\delta^{18}O$ values for shells of benthic foraminifera fall gradually in the Late Bajocian, also reaching –5‰ at the same stratigraphic boundary. On the other hand, $\delta^{18}O$ values for benthic bivalves do not change across the Bajocian-Bathonian boundary, but then drop to –4‰ in the earliest Bathonian. $\delta^{18}O$ values for all of the sampled skeletal portions rise again approaching 0.5‰ in mid-Bathonian, and then fall constantly to the average value of –4‰, below the Bathonian-Callovian transition. Those trends separate substantially at the actual Bathonian-Callovian boundary itself, being –3.5‰ for the brachiopod shells, –1.5‰ for foraminifera tests, and –0.5‰ for belemnite rostra. This discrepancy stays through the Callovian, when the average $\delta^{18}O$ values for belemnite rostra oscillate around –0.5‰ (although with some more negative values occur in the lower portions of the Callovian), and approach a maximum of 0.5‰ at the Callovian-Oxfordian boundary. Otherwise, $\delta^{18}O$ values for brachiopod shells are 2-3‰ more negative, reaching a minimum of –4‰ in the Late Callovian, and increase to –3.5‰ at the Callovian – Oxfordian boundary. ^{18}O values for the belemnite rostra from the Australo-New Zealand Province are more negative, about –4‰ on average, than those for the belemnite rostra from the European and American Provinces in the Middle Callovian. Oxfordian shell samples show significant changes in $\delta^{18}O$ values throughout the stage, with the average values for brachiopod shells rising to –0.5‰ in the mid Oxfordian, and then falling to –3‰ at the Oxfordian-Kimmeridgian boundary. The average ^{18}O values for belemnite rostra fall gradually to –2‰ in the Late Oxfordian, and then rise up to 1‰ at the Oxfordian-Kimmeridgian transition. The latter trend corresponds to values for belemnite rostra from the American Province, which reach values of –2.5‰ in the mid Oxfordian, and then rise to –1.5‰. $\delta^{18}O$ values for both ammonite and brachiopod shells, after a sudden rise in the earliest Kimmeridgian, shift towards more negative values, reaching –2‰ for ammonite and –3‰ for brachiopod shells in the Late Kimmeridgian. $\delta^{18}O$ values for

ammonite shells then rise slightly, by 1‰, towards the Kimmeridgian-Tithonian boundary. It is worthy of note that a comparable trend is also found in the $\delta^{18}O$ values for whole rock samples from the American Province. The drop in $\delta^{18}O$ values for whole rock samples is substantial, being 0‰ in the earliest Kimmeridgian, and -4.5‰ in the Late Kimmeridgian. After that, $\delta^{18}O$ values rise to -2‰ across the Kimmeridgian-Tithonian (=Volgian) boundary. $\delta^{18}O$ values for bivalve shells then rise gently, starting from -1.5‰ at the begining of the Tithonian (=Volgian), and are followed by the values for ammonite and brachiopod shells in the mid Tithonian (=Volgian). The average $\delta^{18}O$ values for belemnite rostra from the Australo-New Zealand Province are around -1‰ in the Early Tithonian (=Volgian), thus slightly more positive than those for bivalve shells. On the other hand, $\delta^{18}O$ values for whole rock samples from the American Province fluctuate around -3‰ in the Early Tithonian, then rise to -1.5‰ in the mid Tithonian, and fall continuously, reaching -3‰ again at the Tithonian-Cretaceous boundary. This trend is followed by the $\delta^{18}O$ values for belemnite rostra from the same Province with a starting point of 0.5‰ in the mid Tithonian. The $\delta^{18}O$ values for whole rock samples from the American Province show an episodic positive shift of 1‰, similar to the tendency in $\delta^{13}C$ values, across the Jurassic-Cretaceous boundary.

Interpretation of Jurassic $\delta^{13}C$ and $\delta^{18}O$ curves

The isotope characteristics presented here depict two successive long-term trends. The initial, rather unstable trend, lasting until the mid-Oxfordian, begins with two episodes in the Early Toarcian and in the Bajocian-Bathonian transition. The next, more stable trend, ending at the Jurassic-Cretaceous boundary, is interrupted only by events at the Oxfordian-Kimmeridgian and the Kimmeridgian-Tithonian boundary. Understanding the nature of those trends requires an explanation of the Early Toarcian and the Bajocian-Bathonian episodes.

Early Toarcian episode

The Early Toarcian episode has been exhaustively interpreted as the development of anoxic conditions in the bottom waters and at the sea floor (JENKYNS 1988, JENKYNS & al. 1991, SÆLEN & al. 1996), expressed by the virtually global occurrence of black clays (JENKYNS 1988). Toarcian surface seawaters are believed to have been up to 5‰ less saline than contemporaneous normal seawater (SÆLEN & al. 1996). Those suboxic or anoxic conditions might have caused a regional excess of carbon burial and a subsequent climatic deterioration triggered by drawdown of atmospheric carbon dioxide (JENKYNS & CLAYTON 1997).

According to the model of a stratified ocean (HOFFMAN & al. 1991a), that was applied to the late Permian seas (GRUSZCZYŃSKI & al. 1989, 1990a, MAŁKOWSKI & al. 1989), the Early Toarcian event represented the expansion of stratified seawater zones thereby increasing primary productivity and the burial rate of organic matter, consequently driving ^{13}C for the seawater carbonate system toward more positive values. That might have been caused by either a natural tendency for stratified seawater zones to expand (HOFFMAN & al. 1990) or a *socalled* dense saline water downwelling because of enhanced evaporation in the upper box of the stratified seawater zones. This process might increase availability of iron consuming excess hydrogen sulphide in the form of pyrite, and vigorous growth of populations of sulphate reducing bacteria. What might stop such a vigorous expansion of the stratified system was the deficency in iron supply (*cf.* MAŁKOWSKI & al. 1990).

Bajocian – Bathonian (B-B) episode

The next, Bajocian-Bathonian (B-B) episode appears to be more profound. A very clear pattern of $\delta^{13}C$ and $\delta^{18}O$ values at the B-B transition shows a perturbation of 6-8‰ for the inital negative and the following positive shifts in both isotopic curves. Such a perturbation is much larger than the early Toarcian episode, and is thus the largest event for the whole Jurassic.

The B-B episode should not be considered as a local event. Theoretical simulations (unpublished) show that only positively correlated segments of the $\delta^{13}C$ and $\delta^{18}O$ curves could be regarded as reflecting global geochemical perturbations. This is exemplified by the trend of the $\delta^{13}C$ and $\delta^{18}O$ curves, which are truly congruent at almost all major isotopic events through geological time. Wherever the carbon either falls or rises substantially, the oxygen curve does exactly the same (HOFFMAN & al. 1991a). This congruence occurs at the Precambrian-Cambrian transition (AHARON & al. 1987), at the Permian-Triassic boundary (GRUSZCZYŃSKI & al. 1989, 1990a, *unpublished*), and during the mid-

Cretaceous event (JARVIS & al. 1988). Such covaria-
tion has also been documented in the Late
Ordovician (MARSHALL & MIDDLETON 1990) and
Early Jurasssic (JENKYNS & al. 1991).

Thus, the congruence of $\delta^{13}C$ and $\delta^{18}O$ curves for
the oceanic carbonate system is quite pervasive in
the Phanerozoic, with the exception of the Cenozoic
where these curves show negative correlation
(SHACKLETON 1977, BROECKER 1982).

Covariation of the carbon and oxygen isotope
curves might be easily attributed to diagenesis, i.e.
disturbance of the original isotope composition due
to aerobic and anaeorobic oxidation of organic mat-
ter within bottom sediments, during early and burial
diagenesis (IRWIN & al. 1977, IRWIN 1980, for
review see COLEMAN 1985). Congruence of $\delta^{13}C$ and
$\delta^{18}O$ values could also be attributed to the carbonate
system of brackish environments (ANDERSON &
ARTHUR 1983). However, it occurs in the geological
record far too commonly, under widely different cir-
cumstances, to be simply dismissed as reflecting a
diagenetic overprint or evidence of peculiar environ-
ments, unless of course we are ready to accept that
all $\delta^{13}C$ and $\delta^{18}O$ data are so severely biased by dia-
genesis as to be practically worthless. Moreover, the
B-B event is recorded by isotope values obtained
from different skeletal carbonate material –
foraminifera, bivalve and ammonite shells – all of
which were tested elementally and are believed to

have been unaffected by diagenetic alteration.
However, the phenomenon most certainly exists,
and it demands an explanation.

This explanation might be very complex and diffi-
cult involving many different interacting terrestrial
and extraterrestrial factors (HOLSER 1984). The most
common factor seems to be climatic changes result-
ing in sea level fluctuations. This might cause an
enhanced storage of C_{org} during transgression, there-
by shifting $\delta^{13}C$ for the oceanic carbonate system
towards more positive values. On the other hand,
regression might provide the oceanic carbonate sys-
tem with a vast amount of soil-derived CO_2 from an
extensive runoff, thereby shifting $\delta^{13}C$ toward more
negative values. However, a transgression is not only
the result of climatic warming which melts polar ice
caps, but it is also an effect of enhanced ocean-floor
spreading resulting in acceleration of submarine
hydrothermal and volcanic activity. If so, however,
enhanced runoff which is an effect of climatic warm-
ing provide the Earth exosystem with isotopically
"light" carbon and oxygen, whereas volcanic emana-
tions also provide this system with isotopically
"light" carbon, but "heavy" oxygen (HOEFS 1987,
MUEHLENBACHS 1986, see also MUEHLENBACHS &
CLAYTON 1976). Thus, during transgression, the
change of $\delta^{13}C$ to more positive values has to reflect
the effect of a C_{org} storage more profound than the
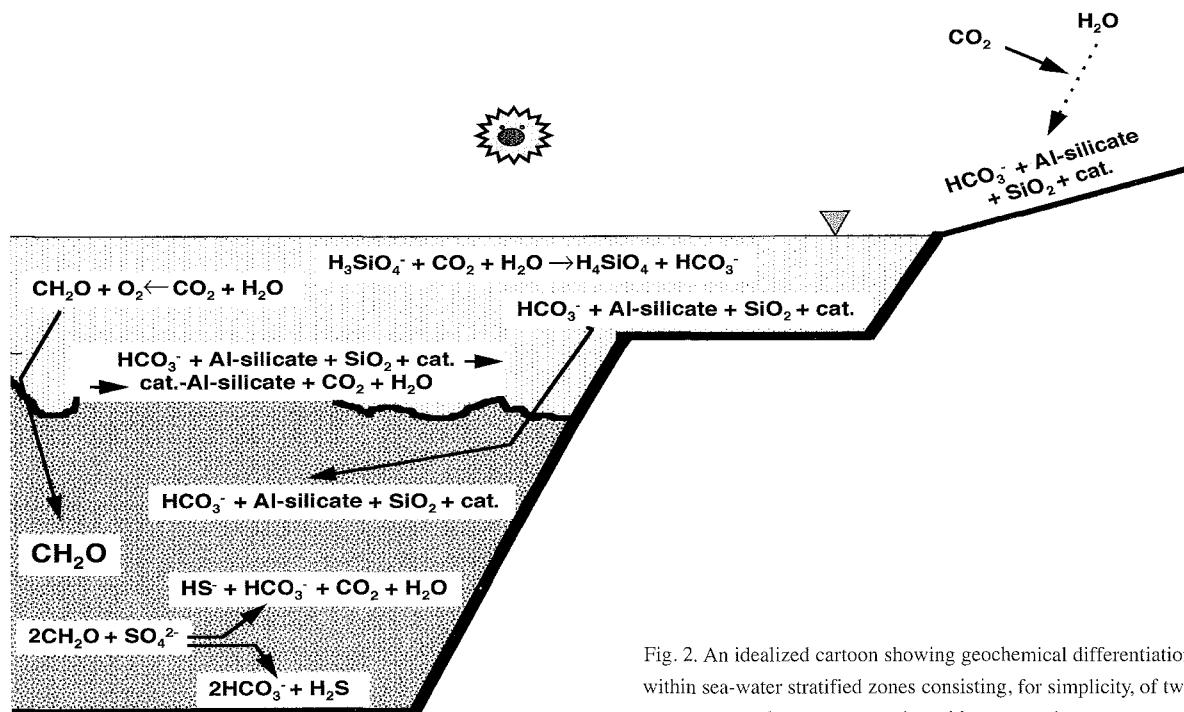united effect of runoff and volcanic emanations.

Fig. 2. An idealized cartoon showing geochemical differentiation
within sea-water stratified zones consisting, for simplicity, of two
boxes: upper oxic and lower anoxic

In turn, the change of $\delta^{18}O$ to more positive values during transgression, has to reflect the effect of evaporation (EPSTEIN & MAYEDA 1953, *also* EPSTEIN 1959) and volcanic emanations greater than the effect of enhanced runoff including water input from melting ice caps. A regression episode might create a simpler picture because the effect of enhanced erosion providing runoff with isotopically "light" carbon and oxygen has to predominate.

Going back to the B-B isotope record, the negative shift in the $\delta^{13}C$ curve in the latest Bajocian is definitely too large to be accounted for by the standard explanation relating to changes in partitioning of carbon burial betwen the $C_{carbonate}$ and C_{org} reservoirs (BROECKER 1970, HOLSER & *al.* 1988). This explanation could also not have been applied to the much smaller mid-Cretaceous perturbation (SCHOLLE & ARTHUR 1980). Consequently, another explanation must be sought. To calculate how much carbon from different reservoirs of different isotopic composition should be added or withdrawn from the monitored sea-water carbonate system to cause the recorded changes, it was necessary to use the SPITZY & DEGENS (1985) equation:

$$N_B = N_A \ \frac{[1+ \delta_{std.} \ (1+ \delta_B/1,000)] \ (\delta_A - \delta_M)}{[1+ \delta_{std.} \ (1+ \delta_A/1,000)] \ (\delta_M - \delta_B)}$$

where N_A is the initial reservoir mass of carbon, N_B is the perturbing mass and δ denotes the isotopic compositions in standard notation, with subscripts indicating (A) initial, (B) perturbing, (M) resulting and the reference standard (std.) values.

In the case of the B-B phenomenon, assuming that the perturbation was affecting a seawater carbonate system containing the same amount of carbon as in the present ocean, which is $4000 \times 10^{15}g$ (HOLLAND 1978, SUNDQUIST & BROECKER 1985), one may calculate how much carbon depleted in ^{13}C would need to have been supplied to the oceanic carbonate system in order to change its $\delta^{13}C$ from $+3‰$ to $-4‰$. Either, volcanic activity ($\delta^{13}C = -5‰$, HOEFS 1987), would have to have been increased by almost six orders of magnitude greater than at present, or a mass of C_{org} ($\delta^{13}C = -25‰$, DEGENS 1969) over 50 times greater than the whole living biosphere today (HOLLAND 1978, SUNDQUIST & BROECKER 1985) would have to have been oxidized to cause the recorded negative shift in $\delta^{13}C$. The observed pattern may simply mean that a huge mass of organic carbon rapidly underwent oxidation in the sea. On the other hand, the rapid rise of the $\delta^{13}C$ values immediately

following the latest Bajocian minimum reflected, according to previous calculations, a mass of C_{org} ($\delta^{13}C = -25‰$) 30 times greater than the standing crop today stored in the sea and/or on land.

The mass of oxidized C_{org} was so enormous, that the only mechanism one can possibly envisage is that the epicontinental seas contained large anoxic reservoirs where vast amounts of organic carbon could accumulate over geological time. Well-oxygenated water then somehow obtained access to these anoxic basins and oxidized the accumulated C_{org}.

This mechanism could work only if the Bajocian seas were distinctly different from the modern ocean. They must have included largely stagnant and stratified zones, subdivided into distinct boxes – oxic at the top and anoxic at the bottom (Text-fig. 2), with, in some cases, another oxic box below – separated by the chemo-redoxcline. In the upper, oxic box, photosynthesis took place, and hence production of organic carbon. This implies that carbon dioxide was being used up by the living biosphere. In the lower, anoxic box, decaying organic matter accumulated, and sulphates underwent bacterial reduction to sulphides. As a result, there was plenty of bicarbonate (HCO_3^-) and carbon dioxide (CO_2), as well as bisulphide (HS^-) and hydrogen sulphide (H_2S). In the upper box, intensive CO_2 utilisation, and "reverse" weathering (MACKENZIE & GARRELS 1966a, 1966b; *also* HOLLAND 1978) took place at the chemo-redoxcline. On the other hand, low pH in the lower box would have prevented intense "reverse" weathering (VON DAMM & EDMOND 1984), thereby allowing accumulation of degraded aluminosilicates and various cations (Ca^{2+}, K^+, Na^+, Fe^{2+}). This difference in the hydrochemical characteristics of the two boxes must have resulted in substantial differences in the isotopic compositions of the carbonate systems in these boxes (Text-fig. 3).

Let us first consider the carbon isotopes. In the upper, oxic box, the light (^{12}C) isotope of carbon was being taken away from the carbonate system. It was put into the living biomass and then removed from the oxic box. Hence, $\delta^{13}C$ values might have been relatively high. By contrast, organic matter rich in the light isotope of carbon accumulated in the lower, anoxic box, where it partly underwent bacterial decay. Hence, $\delta^{13}C$ values here were low (HOFFMAN & *al.* 1991a; Text-fig. 3). This is, in fact, what is observed in the Black Sea (DEUSER 1970, GOYET & *al.* 1991) and in the quasi-marine Satonda Crater Lake (KEMPE & KAŻMIERCZAK 1993).

Concerning the oxygen isotopes – in the upper, oxic box, intensive evaporation took place, prefer-
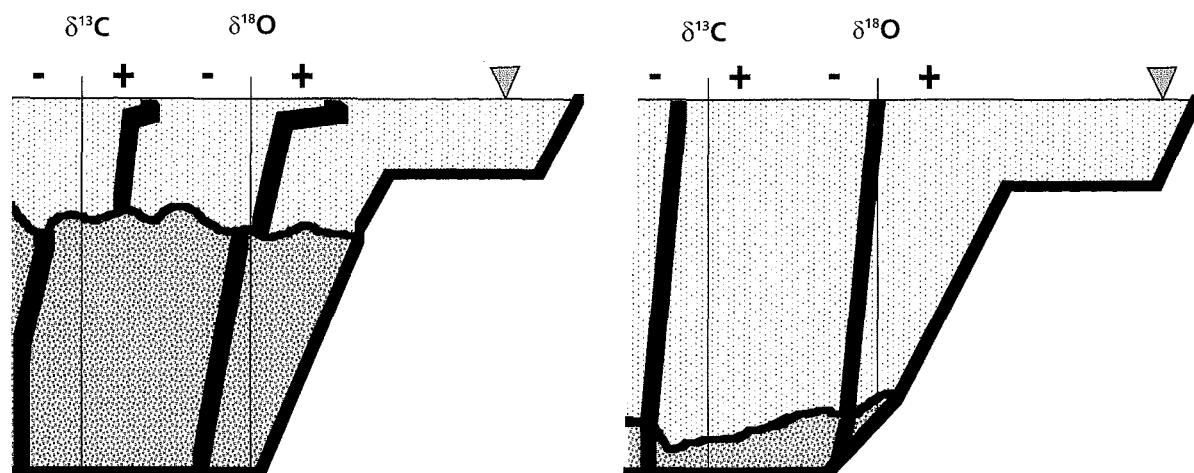
Fig. 3. Schematic cartoon showing differentiation of carbon and oxygen isotope compositions of the carbonate system (a) in the oxic and anoxic boxes of stratified sea-water zones and (b) the trends in carbon and oxygen isotope compositions of the carbonate system after destratification

entially removing the light (^{16}O) isotope of oxygen from seawater. Precipitation brought the evaporated water back to the ocean, but substantial amounts participated in chemical weathering on land. Thus, seawater in the upper box might have become gradually depleted in the light isotope. However, since the oceanic carbonate system, is generally in isotopic equilibrium with seawater, the $\delta^{18}O$ values of the carbonate system might have been relatively high in the oxic box. By contrast, the light isotope of oxygen was partly released in the lower, anoxic box, due to reconstitution of clay minerals *via* intensive "reverse" weathering at the chemo-redoxcline, and anaerobic oxidation of stored organic matter. Hence, $\delta^{18}O$ values might have been relatively low here (Text-fig. 3).

During the mixing of stratified zones some water masses of low oxygen values moved up, and a huge amount of carbon dioxide and bicarbonate, both immensely depleted in "heavy" carbon and oxygen isotopes, appeared in the carbonate system of the surface waters. This drove the surface seawater carbonate system towards negative values of $\delta^{13}C$ and $\delta^{18}O$. This destratification is believed to have been a temporary event, for $\delta^{13}C$ and $\delta^{18}O$ values for the surface seawater carbonate system susequently increased again to approximatcly the initial values.

Some independent evidence, strontium isotopes, may be used to test the internal consistency of the model. Assuming the conditions of stratified seawater, strontium from terrestrial runoff should have remained in relatively higher concentration in the upper box, simply because of inhibited water circulation. Hence, the upper box should have been relatively enriched in radiogenic strontium ^{87}Sr, while the opposite should have been true of the lower box. Thus, seawater destratification should have driven the strontium isotopic curve toward lower values. This is what is observed at the Permian-Triassic boundary, where the results of strontium isotope analyses show the pattern to be exactly as predicted (GRUSZCZYŃSKI & al. 1992).

What was the cause of temporary destratification of the Late Bajocian seas? One of the factors involved might have been a continuous increase of moisture and cloudiness because of enhanced evaporation from the upper box of the stratified seawater zones. The large masses of water vapour could have precipitated after cooling over uplands and mountain ranges, and then have supplied runoff with a vast amount of cool water which might, in turn, have induced mixing of seawater. This scenario seems to be not improbable, in view of the general trend for $\delta^{18}O$ values to rise continuously through the Aalenian until the mid-Bajocian. In terms of palaeotemperature, this isotope change corresponded to an increase of at least 10°C. Continental plate motion stopped in about the Bathonian period (DEWEY & al. 1973) which might have initiated a rapid reconstitution of stratified and stagnant seawater zones.

The B-B destratification episode was followed by reconstitution and development of stagnant and stratified seawater zones, which was manifested by a gradual increase of $\delta^{13}C$ within the marine carbonate system until the mid-Oxfordian.

Bathonian-Oxfordian stratified seas successive development

The Mid – to Late Bathonian seems to have been a time of initial and isolated basins that were controlled mainly by local processes. The latter may be interpreted on the basis of the separate sets of $\delta^{13}C$ values, whereas the $\delta^{18}O$ values show an uniform rise, which might be interpreted as reflecting regional warming. Callovian seas still showed some degree of isolation which may be exemplified by the Boreal Realm (British seas), and the northern peri-Tethyan margin (Polish basin). They belonged to two different biogeochemical regimes according to the initial interpretation of the $\delta^{13}C$ and $\delta^{18}O$ curves (GRUSZCZYŃSKI & al. 1993b). The seawater of the Boreal Province was more productive than the peri-Tethys sea throughout the whole Callovian, especially from Early through mid-Callovian. This suggests that the Boreal seas were much more under the control of a stratified water zone system. The Late Callovian development of some stratification of the peri-Tethyan sea water, followed by temporary destratification across the Callovian-Oxfordian boundary, was paralleled in the case of the Boreal Sea. The destratification event might have been induced by enhanced circulation of water masses, whereby generally colder masses supplied the Boreal seas and warmer masses, derived from the Tethys, influenced the peri-Tethyan seas. Nevertheless, the whole picture emphasises a tendency for the development of stratified seawater zones.

Oxfordian seas are believed to have represented the maximum development of stagnant and stratified basins, inferred on the basis of the relatively highest $\delta^{13}C$ values for the whole Jurassic, and the positive correlation between $\delta^{13}C$ and $\delta^{18}O$ values (cf. GRUSZCZYŃSKI & al. 1990b, HOFFMAN & al. 1991b). It seems that the climax of such a system occurred in the mid-Oxfordian, a time for which some kind of anoxic event related to trangression has been postulated (JENKYNS 1996). This could have resulted from the regeneration of nutrients and their supply to surface waters from flooded land areas. Nevertheless, the mid-Oxfordian was a turning point at which the stratified seawater zones started to break down. This marks the onset of the succeeding long-term trend of stratified seas crisis.

Oxfordian-latest Tithonian stratified seas crisis

This interval was characterised by a constant decrease in $\delta^{13}C$ values, starting from the mid-Oxfordian maximum, and very stable $\delta^{18}O$ values, although two short-term perturbations occured at the Oxfordian-Kimmeridgian and Kimmeridgian-Tithonian (=Volgian) boundaries. $\delta^{13}C$ depletion in the late Jurassic sea water carbonate system seems not to have been the consequence only of oxidation of C_{org} and supply of carbonate species such as CO_2 and HCO_3^- from the anoxic boxes of stratified seawater zones. Some additional processes must also have been involved, such as: (i) extensive runoff carrying to the sea a vast amount of weathered material, containing dissolved carbon dioxide, bicarbonate ion of "light" carbon isotopic composition and water of prevailing "light" oxygen composition (MUEHLENBACHS & CLAYTON 1976); and (ii) the introduction to the epicontinental basins of waters of different isotopic and geochemical compositions as part of a longer term change in oceanic circulation. The first of those additional processes might have played a role in the Kimmeridgian, which is reflected in the general trend of falling $\delta^{18}O$ values following the trend in $\delta^{13}C$ values, whereas the latter process might have played an important role during the Tithonian, expressed by rather stable $\delta^{18}O$ values and gradual drop in $\delta^{13}C$ values. In addition, the boundary events are believed to have been related to turning points in oceanic circulation, expressing an influence of geochemically different water masses (HOFFMAN & al. 1991b).

In order to obtain a clearer picture of the processes that governed the geochemistry of the late Jurassic seas, we may look at the isotope record for the developing proto-Caribbean basin (COLEMAN & al. 1995; Text-fig. 4). For the Kimmeridgian, it seems likely that the main controls on isotopic compositions were oxidation of organic matter and redistribution of oxygen and carbon isotopes within the mass of diagenetically altered calcium carbonate (COLEMAN 1985). This might have been supported by an inflow of waters carrying "light" oxygen and carbon isotopes, from below the chemo-redoxcline or from below the oxgen minimum zone. At the Kimmeridgian-Tithonian boundary, the positive shift in the ^{13}C curve (Text-fig. 4), implies rapid increase in storage of C_{org}, removing isotopically "light" carbon from the carbonate species pool; this process may have been connected with the opening of the proto-Caribbean sea as the result of eustatic movements. During the whole Tithonian, except for the Jurassic-Cretaceous boundary, conditions of $CaCO_3$ precipitation became similar to those during Kimmeridgian times, whereas the water column conditions as recorded by the $\delta^{13}C$ and $\delta^{18}O$ curves

were slightly different (Text-fig. 4). It has been suggested that such an isotope record was a reflection of the occurrence of an upwelling system providing cooler, oxygenated, and nutrient-rich waters to the water column. This might have coincided with, or might have caused a change of regional climatic conditions to a more arid environment and a consequent change in the style of weathering. This hypothetical process would have created a positive feedback for introducing the light oxygen and carbon isotopes to the seawater carbonate system. However, the carbon isotope trend during the Tithonian sequence described here is similar, although more pronounced, to that recorded from the Western Tethys (in the Southern Alps – WEISSERT & CHANNELL 1989). This might suggest a common pan-regional (or global?) process: a change to more arid climatic conditions, accelerated and caused, in the case of the proto-Caribbean sea, by the

upwelling system. According to PARRISH (1992), upwelling might have occurred over the shelf region along the equator, in what is now northernmost South America or southernmost Mexico. The Jurassic-Cretaceous boundary event is marked by a positive shift in both the carbon and oxygen curves (Text-fig. 4). It is similar to the isotope record from the coeval south Mexican succession (ADATTE & al. 1992) and seems to be specific to the Caribbean region. A plausible explanation for this proto-Caribbean event could be the invasion of the Pacific ocean waters through the widened Yucatán – South America gap.

Apart from the interpretation of the $\delta^{13}C$ and $\delta^{18}O$ curves with respect to the general evolution of the Jurassic seawater geochemistry, an interpretation of the $\delta^{18}O$ record with respect to palaeotemperature might add some palaeoclimatic information to the present model.

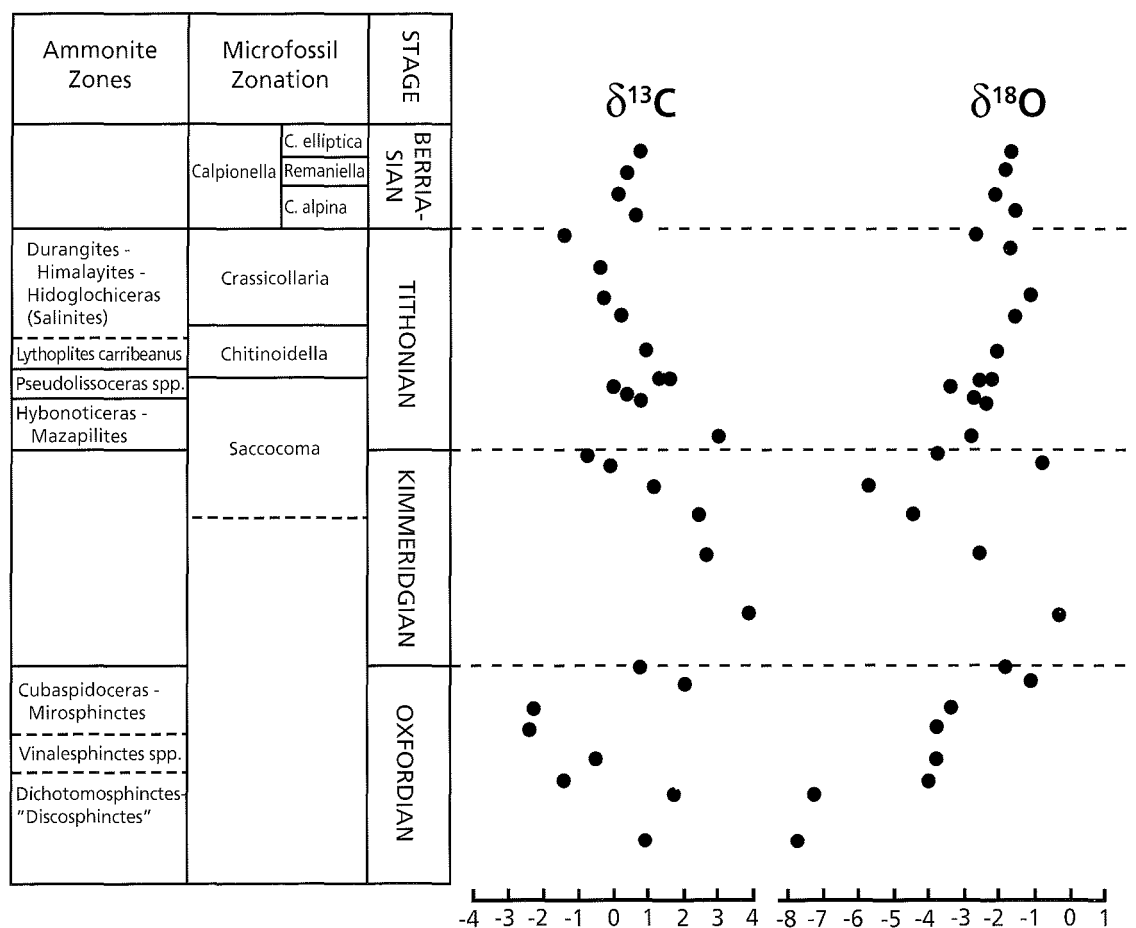Fig. 4. $\delta^{13}C$ and $\delta^{18}O$ record from the sedimentary sequence of western Cuba showing a continuous trend of $\delta^{13}C$ towards more negative values through the Kimmeridgian and Tithonian, interrupted by short-term opposite shifts at the Kimmeridgian-Tithonian and Tithonian-Berriasian boundaries (unpublished)
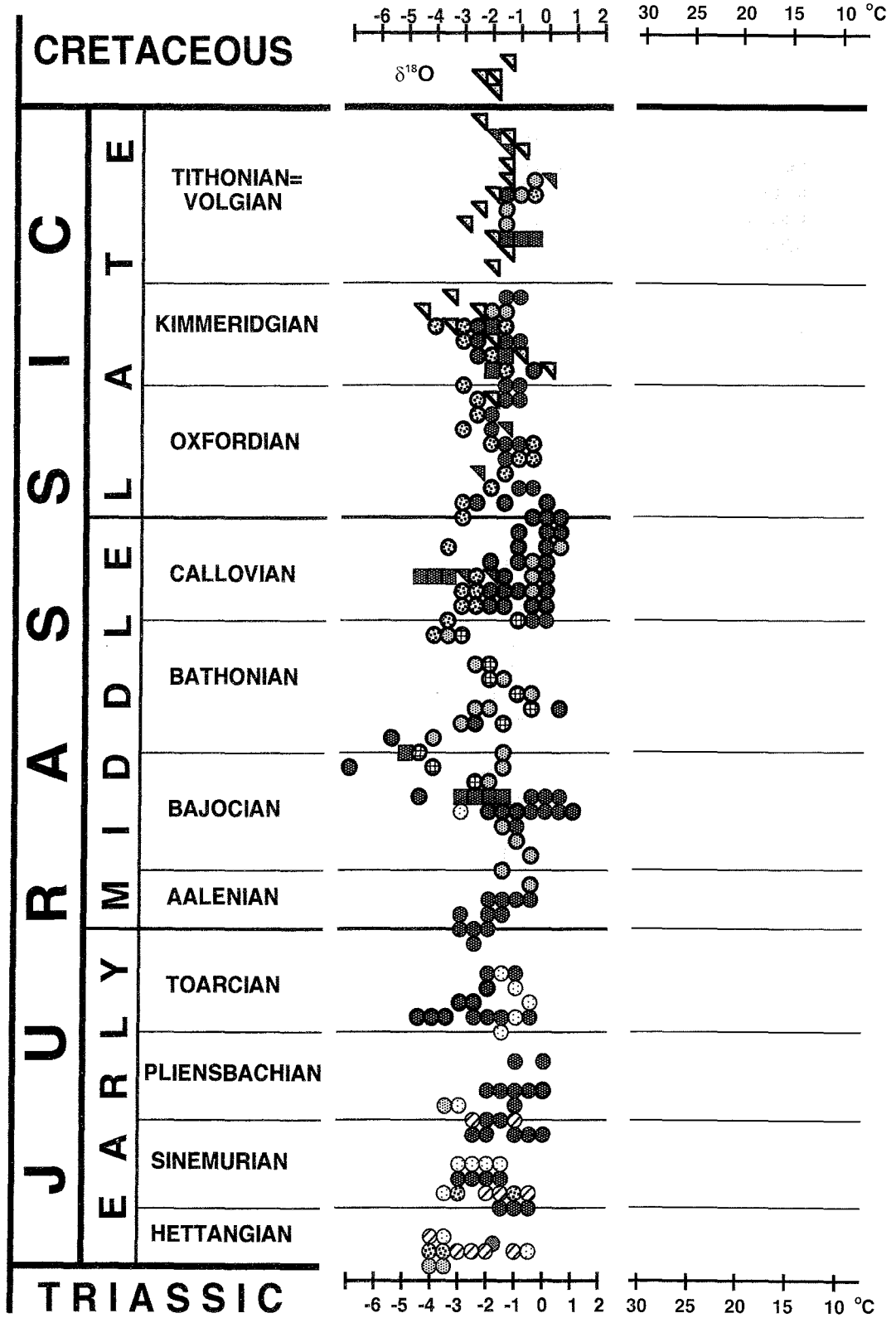
Fig. 5. The range of Jurassic seawater temperature fluctuation based on the oxygen isotope record mainly for skeletal remains, and excluding short-term episodes and boundary events

$\delta^{18}O$ Curve and palaeotemperature determinations

Interpreting $\delta^{18}O$ in terms of palaeotemperature determinations is always tricky, for oxygen is so ubiquitous in almost every chemical and physical processes on the Earth. Fortunately, however, it is not entirely impossible. Looking at the isotope results, mainly for skeletal remains in Text-fig. 1, one can find at least three or four segments of the $\delta^{18}O$ curve which might be interpreted separately from the $\delta^{13}C$ curve. Assuming the isotopic composition of Jurassic seawater $(\delta_w) = -1\%o$ SMOW (HUDSON & ANDERSON 1989), the average temperature oscillated around 26°C in the Early Hettangian, then gradually dropped to 19°C in the Late Pliensbachian, rose again to 28°C at the Toarcian-Aalenian transition, then dropped to 16°C in the mid-Bajocian, and rose once again to 28°C from the mid-Bathonian to Bathonian-Callovian boundary (Text-fig. 5). The temperature then dropped rapidly in the Callovian, which seems to have been the coolest time in the whole Jurassic, with average temperature less than 16°C. After that time, the temperature rose and stabilised at about 20°C in the Oxfordian, 24°C during the Kimmeridgian, and 22°C through the Tithonian (Text-fig. 5). Such a range of temperature oscillations are in good agreement with HUDSON & ANDERSON's (1989) scheme concerning seawater palaeotemperatures for the whole Phanerozoic. The present palaeotemperature estimations have also two points in common with the previous Jurassic palaeotemperature prediction based on $\delta^{18}O$ data (HALLAM 1975), which show a minimum at the Callovian-Oxfordian transition and a maximum at the Toarcian-Aalenian boundary. The Jurassic palaeotemperatures presented here fit well the results of detailed geochemical investigations of superbly preserved late Callovian and mid-Oxfordian fossils. These were belemnoids, nautiloids and an ammonoid in the case of the Callovian, and coral colonies with encrusting and boring bivalves in the case of the Oxfordian.

The Callovian ammonoid specimen is a macroconch of the species *Quenstedtoceras vertumnum*, preserved as pristine aragonite within concretions in dark brick clays from eastern Poland. Comparison between geochemical data and the ammonoid's ontogeny as recorded by the growth of septa, indicate that the young ammonoid remained in near-surface waters at a mean temperature of 15°C, with a seasonal range of 9°C. As it approached sexual maturity it migrated to deeper neritic waters (13±0.6°C) where it fed on nekton (COLEMAN & *al*. 1997). Temperatures of 12-13°C, based on oxygen isotope results, and of

10-12°C, based on Mg/Ca ratios (*cf*. BERLIN & KHABAKOV 1970), were determined for belemnites, and 10°C for nautiloids. All these temperatures agree very well with the general temperature predictions for the Late Callovian (Text-fig. 5).

Mid-Oxfordian corals, dominated by *Thamnasteria concinna*, showed average temperatures within a range of 19 to 21°C, calculated using the oxygen isotope palaeothermometer (GRUSZCZYŃSKI & *al*. 1990b). Using a method based on Sr/Ca ratios within coral skeletons (*cf*. BECK & *al*. 1992), the estimated temperatures were 1-2°C higher. Nevertheless, all of these temperatures, once again, are in a very good agreement with general Oxfordian temperatures (Text-fig. 5).

To summarise the above general picture of the Jurassic seawater evolution, it must be stated that there were two consecutive stages; the initial stage related to the development of stagnant and stratified seawater zones, and the subsequent stage related to the gradual breakdown of those stagnant and stratified seawater zones. The initial stage, lasting through the Early and Middle Jurassic, was characterised by short-term episodes of expansion and mixing of the stratified seawater zones, and by the creation of geochemically isolated epicontinental basins. Such a variable development of the stratified seas suggests an occurrence of several separate basins each with an independent geochemical evolution. This stage was accompanied by quite large fluctuations of sea water temperature, up to 12°C. Subsequent decline of the stratified seawater component during the Late Jurassic was characterised by increasing influence of oceanic circulation on epicontinental sea water geochemistry. This stage was characterised by stable temperatures, varying in a range of 4°C.

The presence, expansion and decline of Jurassic stratified basins must have had an impact, not only on isotope and chemical compositions within the surface seawater carbonate system, but also on the structure of that carbonate system in terms of the relative abundance of its components.

SEA WATER CARBONATE SYSTEM AND STRATIFIED BASINS

Generally, the presence of stagnant and stratified epicontinental sea zones implied the storage of CO_2 and C_{org} in the lower box, as well as various cations and degraded aluminosilicates. Moreover, the water masses in the lower box must have exhibited high

titration alkalinity (T_A= [HCO_3^-] + 2[CO_3^{2-}] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [HS^-] + 2[S^{2-}] + [$Si(OH)_3^-$] + [NH_3] + [OH^-] + [H^+]) and carbonate alkalinity (A_C= [HCO_3^-] + 2[CO_3^{2-}]). Some of the above features have been reported from the stratified Black Sea and quasi-marine lakes (DYRSEN 1986, GOYET & al. 1991, FRY & al. 1991, KEMPE & KAŹMIERCZAK 1993). It seems, that introduction of waters from the stagnant zones by diffusion must have had an influence on the surface carbonate system and thus on $CaCO_3$ precipitation. This was because of two factors that created a positive feedback: a) contributors to T_A i.e. dissolved nitrogen and phosphorus species, which were necessary nutrients causing enhanced photosynthesis, and b) a moderate excess of A_C. Increased photosynthesis took out CO_2 from the surface carbonate system and caused $CaCO_3$ precipitation, and an excess of A_C increased the saturation state with respect to $CaCO_3$. Thus, development of stagnant and stratified seawater zones would have raised the saturation state within surface waters to such a high level that it would have caused sponta-

neous $CaCO_3$ precipitation, of both calcite and aragonite (Text-fig. 6a). On the other hand, mixing of stagnant zones would have brought of a high ΣCO_2 – T_A system which simply means a high P_{CO_2} and low pH, into shallow shoals. This would have caused a crisis of $CaCO_3$ precipitation and temporary dissolution of $CaCO_3$ sediments (Text-fig. 6b).

The most intriguing suggestion is that a high saturation state with respect to both calcite and aragonite might have been achieved due to the presence and development of stratified seawater zones. In turn, those stratified sea-water zones could exist only due to storage of a vast amount of C_{org} in the sea. Since the magnitude of C_{org} burial is reflected by secular changes in oceanic $\delta^{13}C_{carbonate}$, these secular trends can be interpreted in terms of $CaCO_3$ saturation states, and consequently secular trends in calcite and aragonite precipitation.

Up to now, a rather mechanistic model concerning mineralogical variations of $CaCO_3$ precipitation throughout Phanerozoic has been established. Marine ooids and cements were selected to be the
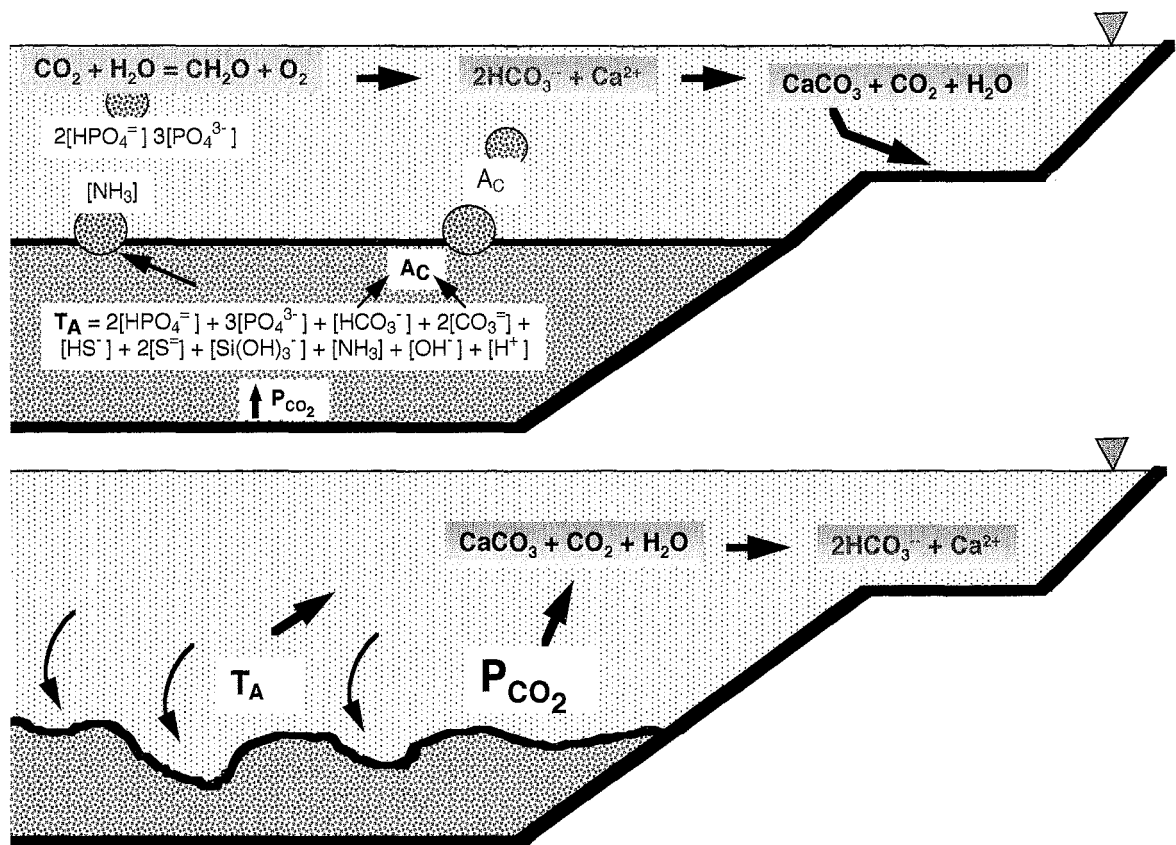

Fig. 6. Schematic cartoon showing (a) the tendency for spontaneous $CaCO_3$ precipitation within surface waters due to the presence and development of stratified seawater zones; and (b) the $CaCO_3$ precipitation crisis caused by destratification of these zones

most suitable for establishing a model of secular variations in the mineralogies of calcium carbonate precipitates in Phanerozoic seas, and a general trend of alternating "aragonitic seas" and "calcitic seas" has been proposed (SANDBERG 1983, 1985a; WILKINSON & al. 1985; WILKINSON & GIVEN 1986).

Increase of global tectonic activity led to rising atmospheric P_{CO_2}, earth surface temperatures and oceanic water level. This caused lowering of carbonate ion (CO_3^{2-}) concentration, calcium carbonate saturation states (Ω_c), and Mg/Ca ratios for seawater, all of which resulted in the preferential pre-
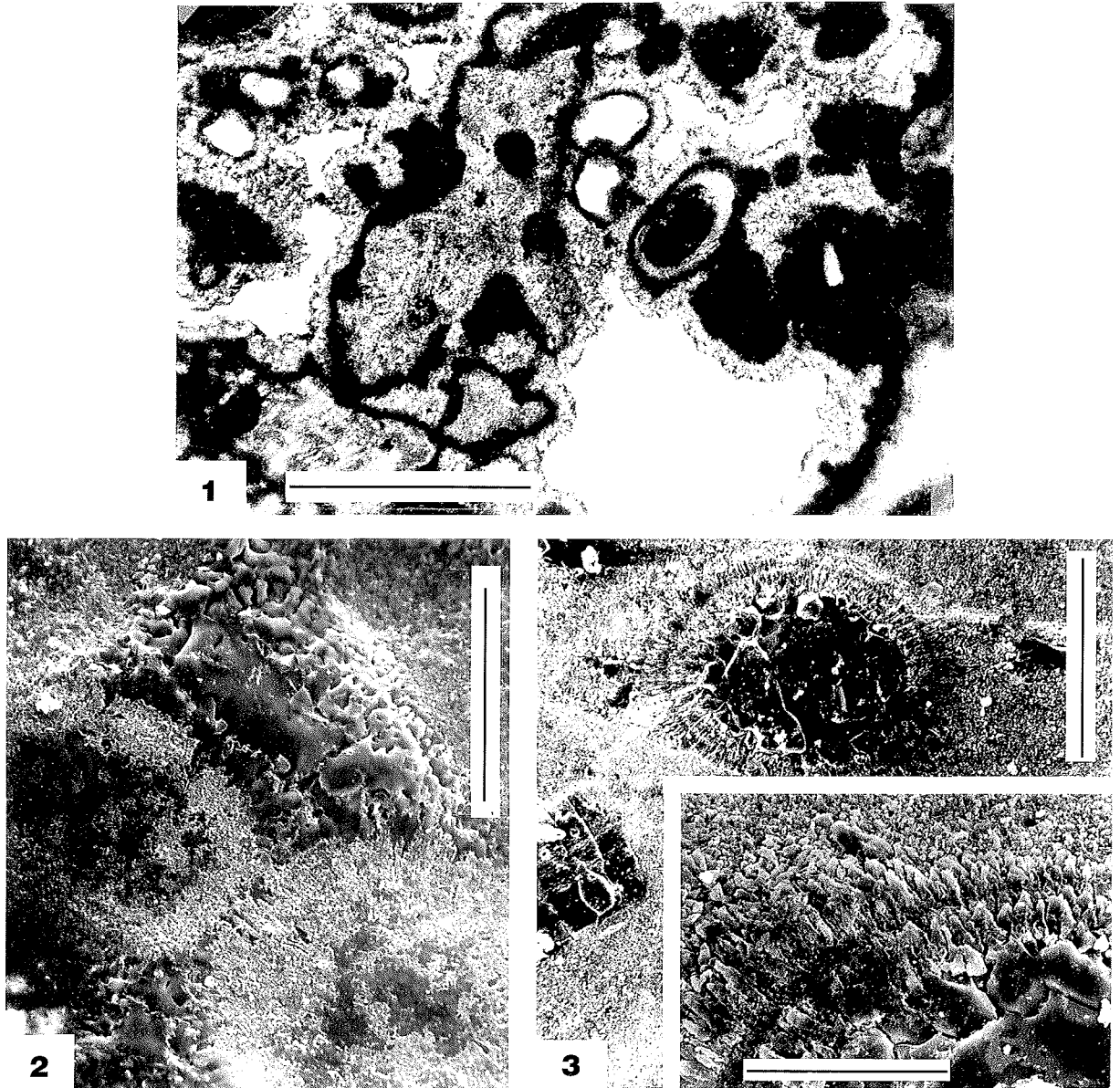

Fig. 7. Examples of Jurassic unaltered and altered aragonite precipitates; a) Aragonite cement fringes around ferruginous grains and skeletal remains of mid Oxfordian sediment occurring as glacial erratics within fluvial sands and gravels in the north-western part of Poland; the photograph was taken from a thin section. Scale bar - 300 m. b) and c) Secondary electron images of Early Kimmeridgian oolitic textures consisting of: b) calcitic finely crystalline patches embedded in a calcite mosaic replacing primary aragonite; scale bar -100 m; and c) an outer rim of radially arranged calcite crystals around the central coarse calcite mosaic replacing primary aragonite; the outer crystalline rim passes gradually into fibrous cement fringe around the ooid; scale bar - 100 m; a close up view of radially arranged calcite crystals passing gradually into fibrous cement fringe in the inset; scale bar - 30 m

cipitation of low-Mg calcite. Moreover, the large carbonate platforms that existed during periods of sea level highstand are believed to be pervaded by widespread dolomitization (GIVEN & WILKINSON 1987). The reverse conditions of moderate global tectonic activity caused a reduction in atmospheric P_{CO_2} and earth surface temperatures, resulting in a fall in oceanic water level, increase of Mg/Ca ratios, and increase of carbonate ion (CO_3^{2-}) concentration and calcium carbonate saturation states (Ω_c) for seawater. This all favoured the precipitation of high-Mg calcite and aragonite. An alternation of calcium carbonate mineralogies, had been initially suggested to be unidirectional from early Phanerozoic "calcitic seas" to the late Phanerozoic "aragonitic seas" (MACKENZIE & PIGGOT 1981). Subsequently opinion changed, assuming such an alternation to have been rather oscillatory (SANDBERG 1983). Since then the model has been only slightly modified (SANDBERG 1985a, WILKINSON & al. 1985, WILKINSON & GIVEN 1986). According to the model, "aragonitic seas" existed in the latest Precambrian and Early Cambrian, then from the Middle Carboniferous to the earliest Jurassic, and finally from the latest Cretaceous to the present days. On the other hand, "calcitic seas" developed from the Middle Cambrian until the Middle Carboniferous, and later throughout the Jurassic and Cretaceous.

Contrary to this model, a lot of evidence has been found for an "aragonite sea" in the presumed "calcitic seas" of the Jurassic (GRUSZCZYŃSKI & al. 1995). In illustration of this, it will suffice to point out the existence of aragonitic cement around grains (Text-fig. 7a) within the Middle Oxfordian fossiliferous, ferruginous and porous sediment. There is also a lot of evidence for bimineralic aragonite-calcitic grains within the Early Kimmeridgian succession, recognizable by petrographic features (SANDBERG 1985b, HEYDARI & MOORE 1994), such as finely crystalline patches embeded within coarsely crystalline (Text-fig. 7b), or a central coarse calcite mosaic with an outer rim of radially arranged fibrous crystals which pass gradually into a fibrous crystalline cement fringe around the ooid grain (Text-fig. 7c). From the general picture of Jurassic sea water geochemistry, one can remember that the mid-Oxfordian was a time of maximum development of stratified zones, whereas the Early Kimmeridgian represents the initial stages of the breakdown of theses zones.

A new concept of interpretation of $\delta^{13}C_{carbonate}$ secular trends in terms of $CaCO_3$ supersaturation states, which might be achieved due to the presence and development of stratified seawater zones, depends on an assumption about the magnitude of C_{org} burial in the sea. This assumption has been made arbitrarily in the belief that C_{org}, equivalent to 10 recent biospheres, that amount of C_{org}, stored in ancient seas, supplied to maintain domination of the stagnant and stratified seawater zones. According to calculations from the SPITZY & DEGENS (1985) formula, burial of such an amount of C_{org} would cause an increase of oceanic $\delta^{13}C_{carbonate}$ from 0 to 2‰. This +2‰ in $\delta^{13}C$ has been indicated on the general $\delta^{13}C_{carbonate}$ curve for the Phanerozoic (after BERNER 1987), modified to take account of the present Jurassic data, as well as Late Permian (GRUSZCZYŃSKI & al. 1989, 1990a), and some Neoproterozoic (BRASIER & al. 1996) data. Looking at the secular trends in the Phanerozoic $\delta^{13}C_{carbonate}$ one can see that after the late Precambrian-early Cambrian "aragonite seas", "calcite seas" predominated until the latest Devonian, and then occurred only sporadically, as minor interruptions, during the period of "aragonitic seas" that obtained throughout the rest of the late Palaeozoic and the whole of the Mesozoic (Text-fig. 8).

To summarise, the suggested model of early Palaeozoic (except the early Cambrian) "calcitic seas" and late Palaeozoic and Mesozoic "aragonitic" seas, albeit interrupted by some "calcitic" events, goes back to the earlier model of unidirectional change from early Phanerozoic "calcitic seas" to late Phanerozoic "aragonitic seas" (MACKENZIE & PIGGOT 1981).

The crises of $CaCO_3$ precipitation, that were caused by the mixing of stagnant zones, were manifested by hardgrounds and other omission surfaces. Detailed analysis of these sedimentary structures, revealed processes controlling the geochemistry of shallow water carbonate sediment and the marine biota inhabiting such a substrate (unpublished). This has given an insight into the nature of the crises of $CaCO_3$ precipitation.

Initially, the effect of waters coming from the stagnant zones was a change in calcium carbonate saturation toward undersaturation, $\Omega_c \leq 1$, where $\Omega_c = IAP/K_{sp}$. The ion activity product $IAP = a_{Ca}*a_{CO_3}$ (a denotes ion activity), which is determined by the calculation of a_{Ca} from GARRELS & THOMPSON's model (GARRELS & THOMPSON 1962), and a_{CO_3} using carbonate equilibrium calculations (see for review MORSE & MACKENZIE 1990) and any two of the four measurements A_C, ΣCO_2 ($=TCO_2$), pH, P_{CO_2}, may not be the same as the calcite stochiometric solubility constant K_{sp} ($=a_{Ca}*a_{CO_3}$), which is calculated the-
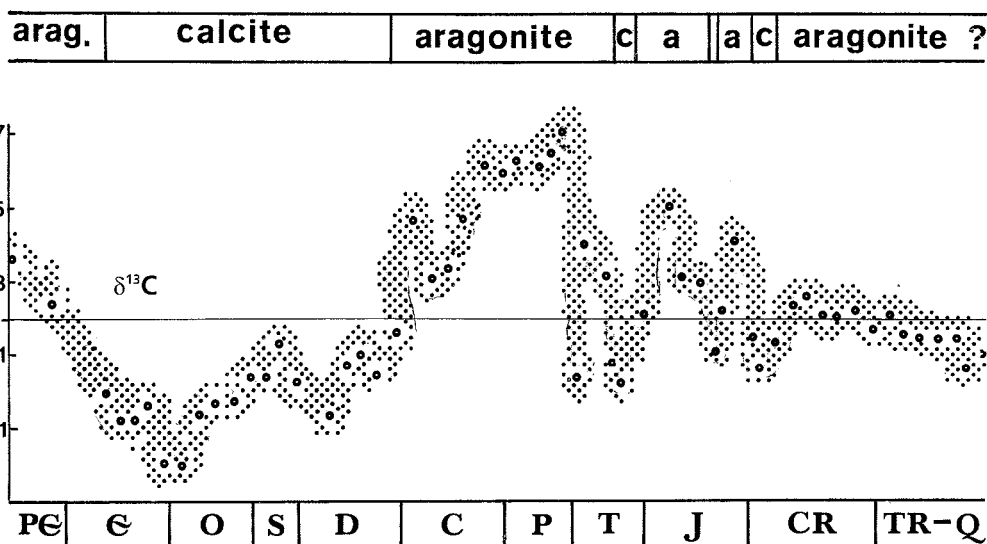
Fig. 8. Proposed occurrence of predominant low-Mg precipitates and their high-Mg calcite and aragonite counterparts in accordance with the general course of $\delta^{13}C_{carbonate}$ throughout the Phanerozoic; the $\delta^{13}C_{carbonate}$ curve was compiled from the results published by BERNER (1987), BRASIER & al. (1996) for the Neoproterozoic, GRUSZCZYŃSKI & al. (1989, 1990) for the Late Permian, and the present data for the Jurassic
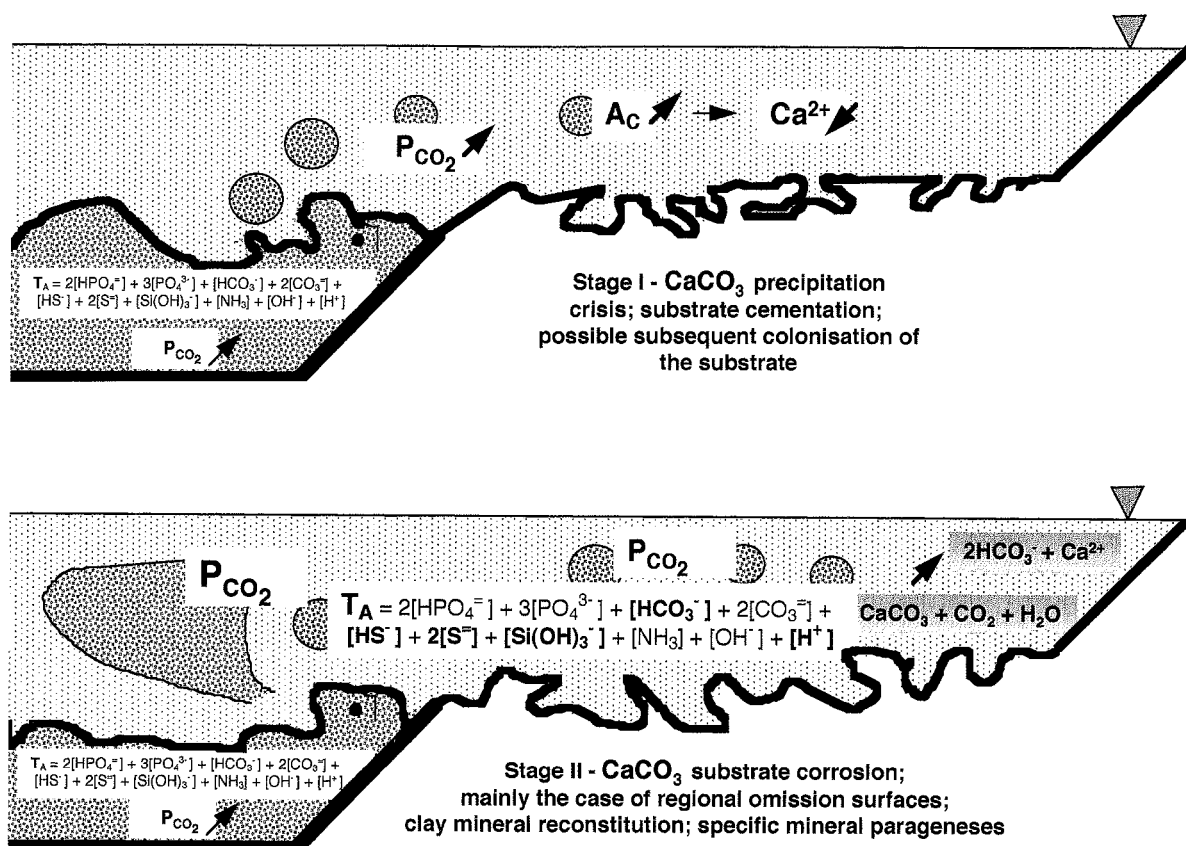

Fig. 9. An idealised scheme of chemical perturbations within shallow water carbonate sediments during $CaCO_3$ preciptation crises caused by the destratification of adjacent sea zones; such perturbations created local and regional omission surfaces, then controlled substrate colonisation and finally caused termination of the omission surfaces

oretically from free-energy data (*cf*. BERNER 1971) or measured at equilibrium under conditions of different salinities and temperatures, in the laboratory (*cf*. MUCCI 1983).

In the case of examined Early Kimmeridgian hardgrounds for the IAP_c calculations, two interacting processes influencing a primary Ω_c were considered: (i) introduction of a high amount of CO_2 stored in stagnant seawater into the carbonate shoals; a recent quasi-marine example shows a CO_2 concentrations under the chemo-redoxcline 100 times greater than that in Recent seawater (KEMPE & KAŹMIERCZAK 1993) and (ii) a large increase in A_C because of sulphate reduction using carbohydrates and ammonia formation from amino acids in anoxic waters (BERNER & *al*. 1970) of stagnant zones (Text-fig. 9). Increase in A_C coincides with a decrease in free Ca^{2+} according to thermodynamic calculations (KEMPE & KAŹMIERCZAK, 1994, using the WATMIX model, WIGLEY & PLUMMER 1976). Some simple calculations, assuming a 50% increase of A_C (the highest A_C increase under anoxic conditions postulated by BERNER & *al*. 1970), resulted in initial undersaturation of $\Omega \approx 0.65$-0.75, assuming, respectively, maximal and minimal CO_2 input, estimated from the $\delta^{13}C$ record in examined hardgrounds, according to calculations from the SPITZY & DEGENS (1985) formula.

The cessation of carbonate sedimentation allowed sea bottom colonisation by burrowing organisms, and subsequently, with progressive cementation, by boring and encrusting faunal assemblages. Cementation was promoted by aerobic and anaerobic oxidation of organic matter within the sediment, and could have been very fast, prohibiting a complete ecological succession of hardground assemblages (GRUSZCZYŃSKI 1986). Colonisation of many of the developing hardgrounds was interrupted by episodes of substrate corrosion (GRUSZCZYŃSKI 1979). This suffered from mixing of the stagnant zones bringing the waters of a high P_{CO_2} and relatively low pH. Finally, that short-term mixing terminated the existence of the hardground (Text-fig. 9). Some estimations of the chemical parameters of that fatal event resulted in $P_{CO_2} = 10^{-2}$, $\Omega_c \approx 0.2$, and pH ≈ 6.7. This induced $CaCO_3$ dissolution, which in turn caused an increase in Ca^{2+} concentration, initiating the precipitation of gypsum in some places. Subsequent loss of T_A, accompanied by the presence of various cations and aluminosilicates, should result in extensive silicification, supported by a natural tendency for the concentration of dissolved silica to increase (MACKENZIE & *al*. 1967, LERMAN 1979),

and for the precipitation of phosphate, magnesium and calcium silicate, other silicates, variable aluminosilicates, and iron minerals (GRUSZCZYŃSKI & *al*. 1993a; Text-fig. 9). When the Ca^{2+} had been exhausted, halite and potassium chloride started to precipitate. Thus, generally, in epicontinental seas with a predominance of stagnant and stratified zones, carbonate shoals may have been important places for mineral reconstitution, and therefore "reverse weathering" (MACKENZIE & GARRELS 1966a, b). Hence, it might also suggest that the UREY reaction $CaCO_3 + SiO_2 = CaSiO_3 + CO_2$ (UREY 1956, *see also* UREY 1951), believed to be a result of the weathering-metamorphism cycle (BERNER & *al*. 1983, LASAGA & *al*. 1985), may be replaced by the weathering-reconstitution cycle throughout the Phanerozoic.

The renewal of sedimentation after $CaCO_3$ precipitation crises sometimes took place under conditions where the surface waters were still controlled by stratified seawater zones, leading to sediment colonization by almost entirely monospecific biota, *e.g*. cyanobacterial mats. This suggests that Jurassic sea water geochemistry might have strongly affected the existing organic life, creating very specific structures of marine biotas. The question then arises whether any other coincidence of Jurassic seawater geochemistry and structure of marine biotas was recognizable, especially at the time of general biological catastrophes – mass extinctions?

MASS EXTINCTIONS, STRUCTURE OF MARINE BIOTA IN THE CONTEXT OF JURASSIC SEAWATER GEOCHEMISTRY

After protracted calculations on survivorship of genera and families which do not exactly fit the model of the periodicity of mass extinctions (RAUP & SEPKOWSKI 1984), at least three mass extinctions are postulated for the Jurassic: Pliensbachian, Early Bajocian, and Late Tithonian. As one can see, none of these mass extinctions seems to coincide with either short-term episodes or boundary geochemical events. However, one can try to correlate the Pliensbachian and Early Bajocian extinction peaks with short-term geochemical episodes. For example, "The Pliensbachian peak probably reflects the event documented ... in the lowest zone of the Toarcian, with global extinction records smeared backward into the Pliensbachian as a result of incomplete sampling..." (SEPKOWSKI 1989). Simlarly, the Early Bajocian peak might reflect the event documented at
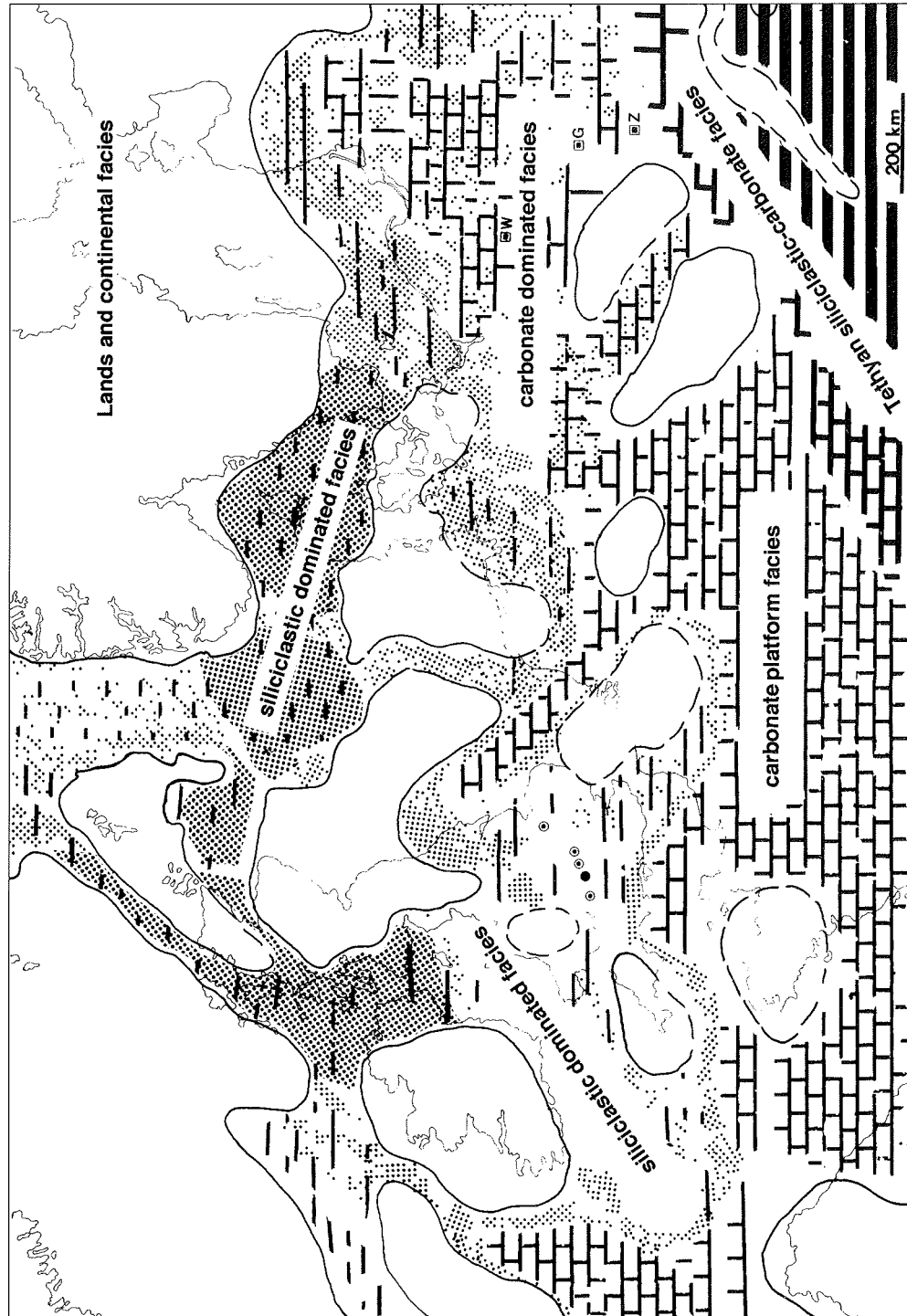
Fig. 10. Palaeogeographical map (ZIEGLER, 1990; Bradshaw & Cripps, 1992) with hypothetical facies distribution at the end of Callovian time showing four localities in Britain (open circles), from which Early and Middle Callovian belemnite rostra were analysed isotopically (Anderson et al., 1994), and another British site in the vicinity of Stanton Harcourt (solid circle), from which Late Callovian-Early Oxfordian belemnite rostra were analysed isotopically (this paper); Callovian-Oxfordian sections in Poland, examined geochemically (unpublished), are denoted by squares and letters (Z -Zalas, for the most condensed succession, and G - Gnieździska and W - Wojszyce for the less condensed successions); Britain belonged to the Boreal Province, whereas Poland was a part of the peri-Tethyan Province during Callovian times

the Bajocian-Bathonian transition. This brings to light an example of local extinction correlated directly to a geochemical event at the Callovian-Oxfordian transition (GRUSZCZYŃSKI & al. 1994).

A Deceptive Callovian-Oxfordian extraterrestrial impact and mass extinction

Since the onset of the debate on the influence of extraterrestrial impacts on life on Earth (ALVAREZ & al. 1980), the periodicity of appearance of terrestrial impact craters (ALVAREZ & MULLER 1984 SHOEMAKER & WOLFE 1986), and their close relationship with comet showers (ALVAREZ 1986, HUT & al. 1987) and the periodicity of Mass Extinction Events (RAUP & SEPKOWSKI 1984, 1986; SEPKOWSKI 1989), a lot of work has been done to find evidence for a catastrophic event at the Callovian/Oxfordian transition. Magnetic spherules of cosmic origin, shocked quartz, and enrichment in Ir, Ni, Co, REE and other metals (BROCHWICZ-LEWIŃSKI & al. 1986) within Late Callovian sediments from Poland, France and Spain led to belief in a global, catastrophic, cosmic event (BROCHWICZ-LEWIŃSKI & al. 1989).

To check such a possibility, in other words to find some arguments for or against extraterrestrial impact at the Callovian-Oxfordian transition, several sections from the peri-Tethys (*i.e.* Poland) and Boreal (*i.e.* Britain ANDERSON & al. 1994) provinces were analysed isotopically. The most southern peri-Tethyan section representing the whole Callovian succession, compressed to several meters in thickness and with many omission surfaces and stratigraphic gaps approaching the Callovian-Oxfordian transition (KOPIK 1979, RÓŻYCKI 1953) is located at almost the same palaeolattitude as its Boreal equivalents (Text-fig.10). Facies characteristics in both areas suggests siliciclastic-dominated and carbonate-siliciclastic sedimentation on epicontinental sea shelfs. The remaining two peri-Tethyan sections, from middle and north-western Poland respectively (Text-fig. 10), represent a less extremely condensed Callovian succession.

For simplicity, only isotope analyses for belemnite rostra were considered; belemnite rostra which had been previously tested to establish the degree of diagenetic alteration (ANDERSON & al. 1994). Generally, the $\delta^{13}C$ values for the Boreal Province obtained from the English Oxford Clay show a wide range variation of 0.5 – 3.5‰, and a very slight shift towards more negative values from Early through Middle Callovian (ANDERSON & al. 1994; Text-fig. 11). $\delta^{18}O$ values for Oxford Clay belemnites varying

from –2.0‰ to 0‰, shift very slightly towards more positive values during the Early through Middle Callovian (ANDERSON & al. 1994; Text-fig. 11). For successively younger samples, the $\delta^{13}C$ curve representing peri-Tethys seawater shows a weak general trend towards more positive values, the average being initially 0.5-1‰. The $\delta^{18}O$ values of the oldest samples maintain a narrow range between –2.0 and –1‰ for the most southern section, and between –1 and 0‰ for the remaining two sections (Text-fig. 11). Towards the transition zone, the $\delta^{13}C$ curve for the Boreal Province shows an initial negative, and then a gradual positive shift towards the Callovian-Oxfordian transition, followed by a sudden drop across the boundary. The $\delta^{18}O$ curve follows the $\delta^{13}C$ curve until the end of the Callovian, whereas across the Callovian-Oxfordian boundary it increases in contrast to the $\delta^{13}C$ curve (Text-fig. 11). On the other hand, $\delta^{13}C$ curve for the peri-Tethyan Province displays a continuous shift towards more and more positive values towards the transition zone, and then decreases across the Callovian/Oxfordian boundary. The $\delta^{18}O$ curve for the section from central Poland (Text-fig. 11, section G) also displays a gradual course to more and more positive values after a slight negative shift, and then drops slightly across the Callovian/Oxfordian boundary. By contrast, the $\delta^{18}O$ curve for the most northern Polish section stays rather constant and than rises across the Callovian-Oxfordian boundary (Text-fig. 11, section W). The above characteristics reveals a distinctive boundary event at the time of unstable development of stratified seawater zones.

The drop in the $\delta^{13}C$ values across the Callovian-Oxfordian boundary in all the examined examples might be potentially interpretable in many ways, but a simultaneous drop or rise in the $\delta^{18}O$ values makes two explanations untenable: (i) extensive weathering of meteoritic remnants and cosmic dust transported to the seas and suspended in the sea should change the isotopic composition of oxygen, shifting $\delta^{18}O$ towards very positive values (HOEFS 1987); and (ii) a possibility of increased flux of weathering products, enriched in isotopically "light" carbon (DEINES 1980) and oxygen (MUEHLENBACHS & CLAYTON 1976), by runoff due to marine regression (or meteoritic bombardment?). For the latter explanation, calculating from the SPITZY & DEGENS (1985) formula, in order to compensate for the drop in the range of $\delta^{13}C$ values across the Callovian-Oxfordian boundary, 5 at minimum and 15 at maximum present day biospheres (HOLLAND 1978, SUNDQUIST & BROECKER 1985) would need to have been oxidised.
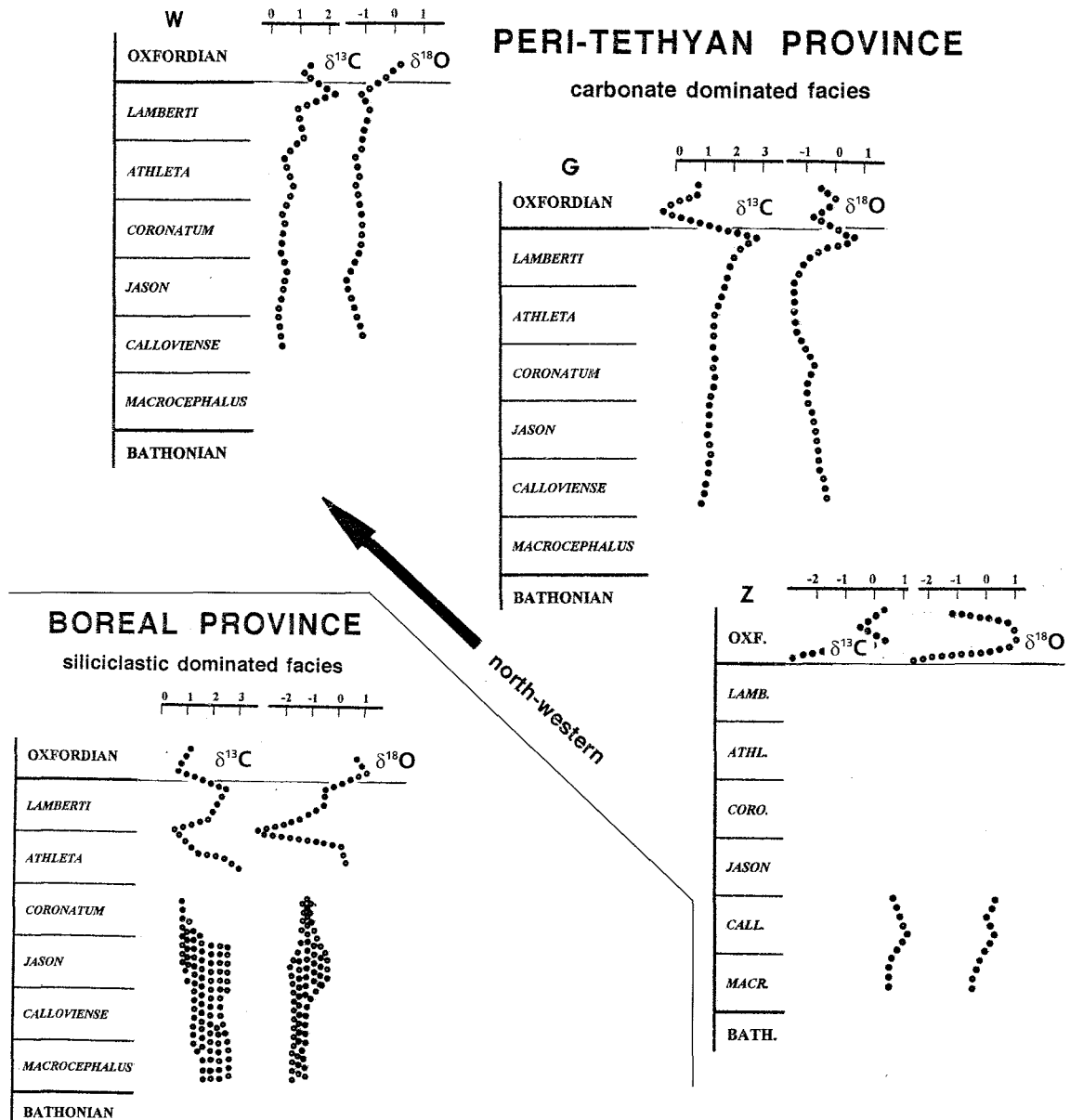
Fig. 11. Simplified δ¹³C and δ¹⁸O isotope age curves for the Callovian and Early Oxfordian plotted according to the results obtained from belemnite rostra for the Boreal Province (ANDERSON & al. 1994; this paper) and peri-Tethyan Province (this paper; letters indicate particular sections) showing an obvious geochemical event at the Callovian-Oxfordian boundary

This seems to eliminate a change in isotopic regime by wildfire activity as a plausible explanation. Also, using the MACKENZIE & MORSE (1992) figure for the total riverine flux during Jurassic times, with the assumption that apart from the dissolved carbonate, the remainder was of particulate organic carbon (POC), and dissolved organic carbon (DOC) composition, that flux would have had to have increased at least ten times. Moreover, there is no evidence for a regression during the Mid-Late Jurassic. In fact, it

seems to be the reverse (HALLAM 1984). The most plausible explanation is again that episodic destratification of some seawater zones drove δ¹³C for the carbonate system towards more negative values. This might have been driven by the enhanced hydrothermal activity that is postulated to have occurred at the Callovian-Oxfordian boundary (JONES & al. 1994; unpublished). Moreover, enhanced volcanism, producing isotopically "light" carbon, also would have produced isotopically

"heavy" oxygen at the same time (MUEHLENBACHS 1986).

There is thus no need to invoke an extraterrestrial catastrophe in this model, however it does predict a local extinction event which is evident for some ammonite groups (WESTERMANN 1993). In addtion, it seems that a geochemical impact on the organic life was unquestionable, but only in a few cases could also be recognisable using other evidence. The case of the Tithonian upwelling circulation within the proto-Caribbean sea which was postulated according to interpretation of $\delta^{13}C$ and $\delta^{18}O$ curves (Text-fig. 4), is given here as an example.

A note on the Tithonian upwelling circulation

This suggestion corroborates BAUMGARTNER's (1987) opinion that off-shore winds created upwelling and high fertility in the surface waters of the Late Jurassic "Caribbean Tethys", and also ROSS & al's. (1992) opinion regarding a strong correlation between Kimmeridgian and Tithonian wind-driven coastal upwelling. It also is supported by some indications, in the sedimentary succession from Cuba, of increased fertility in the proto-Caribbean sea surface waters related to the upwelling circulation. These are: (i) radiolarian microfacies gradually replacing the *Saccocoma* microfacies that predominated during the Early Tithonian; and (ii) higher content of phosphatic grains, mainly fish debris (bones, scales, and teeth) within the Late Tithonian limestones. Morover, it should be possible to estimate the sea current direction because of the occurrences of some bivalves belonging to the genera *Anopea* and *Buchia*. The occurrence of these characteristic high latitude bivalves might suggest the upwelling of cold, deeper waters in the northern (or NW) part of the proto-Caribbean sea, between the Yucatán and the Florida-Bahamas block.

This is an unique example. In many cases, however, additional geochemical studies are required in order to investigate palaeoenvironmental impact on marine biota. One of the geochemical tracers, that has been recently used for the palaeoenvironmental reconstructions, is barium.

Ba concentrations and Ba/Ca Ratios as tracers of biogenic productivity and palaeoenvironment

As far as it is known, decaying organic matter such as phytoplankton cells and faecal pellets cause pre-

cipitation of minute barite crystals (DEHAIRS & al. 1980, BISHOP 1988) in those microenvironments. This is a result of either sulphate regeneration from organic sulphur (DEHAIRS & al. 1980, BISHOP 1988) or release of barium from the dissolution of acantharian-derived celestite (BERNSTEIN & al. 1992). These barite crystals appear to be the main mean of transport of Ba from surface to deeper waters (DEHAIRS & al. 1990), where higher barite accumulation seems to be directly related to higher primary productivity within surface waters (DEHAIRS & al. 1992).

In the case of the proto-Caribbean sea, the positive shift of the $\delta^{13}C$ curve at the Kimmeridgian-Tithonian boundary, implying rapid increase in storage of C_{org}, coincides with a positive excursion of the Ba/Ca ratios (Text-fig. 12a). Of course, it has to be calculated how much barium can be introduced to the sea floor by detrital aluminosilicates responsible for the non-barite Ba (DYMOND & al. 1992, MCNEILL 1933). Moreover, it must be recognised that the non-barite Ba is scavenged or diagenetically transfered to the Fe-oxide component (SCHROEDER & al. 1997). In the sediments examined, the non-barite Ba input was 50 ppm at the point of maximum barium enrichment, whereas the Fe concentration was very stable for the whole Kimmeridgian. Thus, one might treat the positive Ba/Ca excursion as a proxy of palaeoproductivity, and calculate the flux of bio-Ba and an amount of "new" production. Neglecting figures for the dissolved Ba concentration, which is believed not to be an important factor controlling the flux of bio-Ba to the seafloor (FRANCOIS & al. 1995), a simplified DYMOND & al. (1992) formula is used to estimate the "new" production. For the end of the Kimmeridgian an increase in the primary productivity of 10-20 Gt was obtained. This is quite substantial, one-fiftieth to one-twentieth of the whole standing crop today (HOLLAND 1978, SUNDQUIST & BROECKER 1985).

In the case of the Callovian-Oxfordian transition, the observed positive trend in $\delta^{13}C$ coincides with a sudden drop in the Ba concentration (Text-fig. 12b). Since the Ba content was measured within belemnite rostra, it might be assumed that the Ba concentration in these rostra was proportional to the Ba concentration in the seawater, and that the response for Ba incorporation was linear, as in the case of foraminiferal tests (LEA & SPERO 1992). Thus, the rapid drop in Ba concentration basically means that a fraction of the barium was involved in enhanced settling of POC due to increased productivity and C_{org} burial. It is highly intriguing that the most characteristic sedimentary features at the Callovian-Oxfordian transition are stromatolitic buildups, *i.e.*

remains of cyanobacterial mats. Those cyanobacterial mats were almost the only component of the marine biota that was widespread over vast areas of the seafloor. It might be suggested that an excess of A_C accompanying the expansion of the stratified system due to enhanced primary production and C_{org} burial could induce the appearance of such specific microbiota.

In addition, a Ba tracer seems to be very useful in more detailed studies. By analogy that Ba incorpora-

tion into foraminiferal tests is linearly proportional to the barium concentration in seawater (LEA & SPERO 1992), the same might be assumed in the case of the ammonoid shells. Prior to sexual maturation, ammonoid septa showed a cyclic variability of $\delta^{18}O$ values, implying seasonality of the surface waters, and a continuous decrease of $\delta^{13}C$ values towards younger ammonite stages, together with the opposite trends in Ba/Ca ratios (Text-fig. 12c). Of course, one might say that elemental ratio perturbations are due
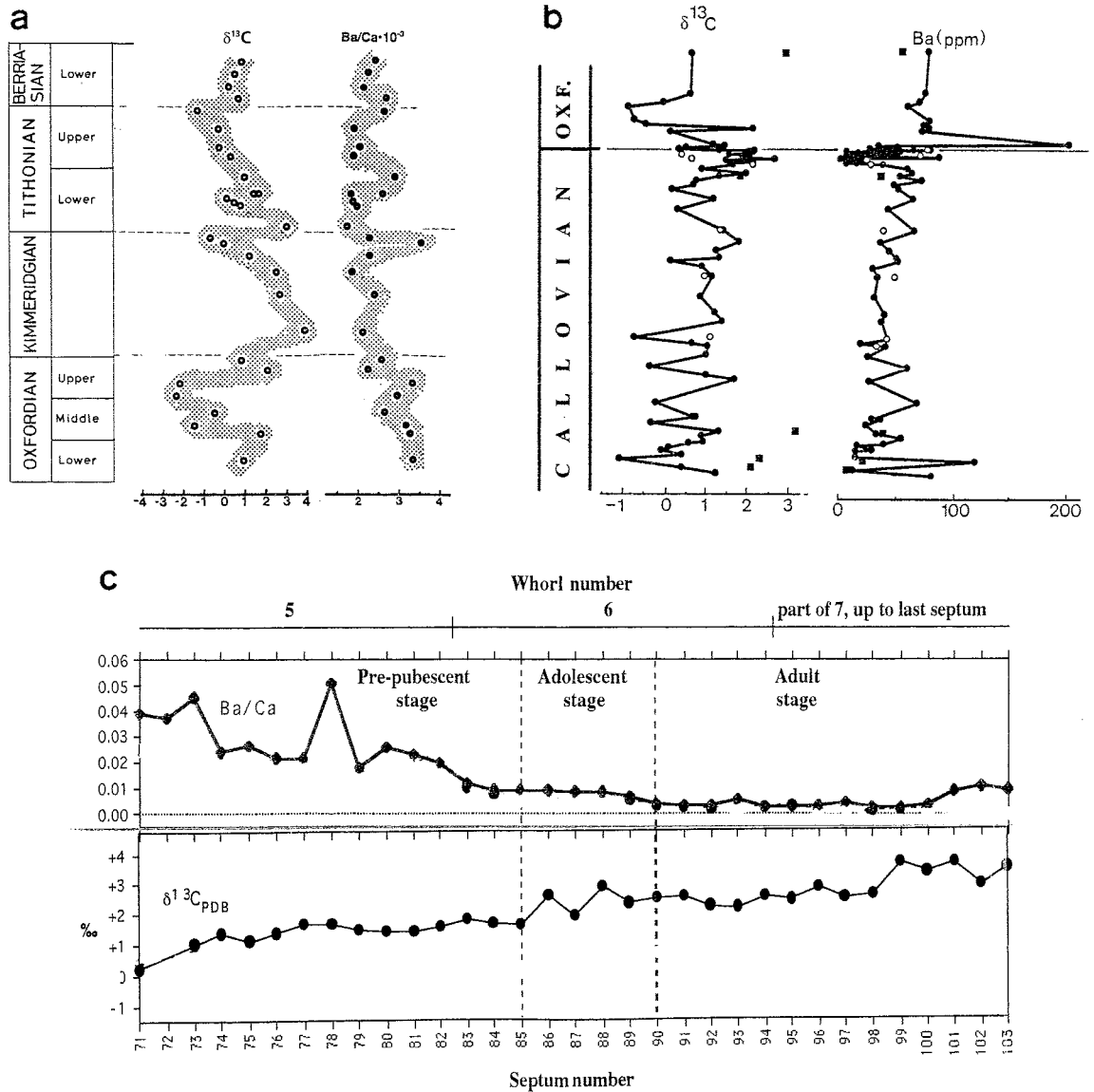
Fig. 12. Combined plots of $\delta^{13}C$ values against Ba/Ca ratios or Ba concentrations showing the interpretational potential of the Ba record in palaeoproductivity estimations, predictions, and detailed palaeoenvironmental reconstructions; in case (a) the Ba/Ca ratios were measured in carbonate sediment, whereas in cases (b) and (c) the Ba concentrations and Ba/Ca ratios were measured in belemnite rostra and ammonite septa respectively

to the lack of physiological control, which is a common explanation for magnesium and strontium enrichment in Recent juvenile nautiloid shell structures (CRICK & MANN 1987). However, it is highly probable that changes of Ba/Ca ratios expressed changes of the palaeoenvironmental conditions. Simple calculations give a Ba/Ca concentration in the seawater of 1-3 mmole/mole after sexual maturation, which is slightly more than that in the present seawater (LEA & SPERO 1992), increasing ten-fold, at least, before that episode. It seems, that there is only one possible explanation of the increase in Ba concentration, namely, barite recycling. Dissolution of barite particles because of sulphate reduction in anoxic waters (FALKNER & al. 1993), and/or from the aluminosilicate rearrangement in anoxic sediments (DYMOND & al. 1992) provides a very high concentration of recycled Ba cation across the redoxcline (FALKNER & al. 1993). Thus, the young ammonoid would have lived in shallow waters in the proximity of the anoxic sea floor and/or chemo-redoxcline in sea water. This might be supported by the trend in $\delta^{13}C$ values, interpreted not only as a change of diet from zooplankton of "lighter" carbon isotopic composition to fine nekton of "heavier" carbon isotopic composition (FRY & SHERR 1984), but also as an input of light carbon isotope from anoxic sea floor or seawater. In conclusion, it seems that the Ba tracer may be a very efficient tool in general estimations of palaeoproductivity, as well as in detailed palaeoenvironmental reconstructions.

CONCLUSIONS

Almost all the available geochemical data have been gathered to interpret Jurassic sea water chemistry and its influence on marine organic life. Two stages has been postulated for the geochemical evolution of Jurassic seas:

(1) The initial stage comprised the development of stagnant and stratified sea-water zones where enhanced C_{org} burial could take place. Such a development was unstable, emphasised by two short-term episodes of opposite nature. The older, Early Toarcian episode marked a rapid expansion, followed by a retreat, to the initial point, of a stratified system. This phenomenon might have been triggered by the downwelling of dense saline water because of enhanced evaporation in the upper box of the stratified sea-water zones, and moderated by the availability of iron. The availability of iron might have terminated the Early Toarcian episode because defi-

ciency in iron could have caused an excess of H_2S and H^+ below the chemo-redoxcline, and a strong limitation to the existence of sulphate-reducing bacteria. By contrast, the Bajocian-Bathonian (B-B) episode expressed a temporary mixing of stratified seawater zones. This mixing seems to have been caused by the deep water circulation, because of the sinking of cold waters due to the general climate cooling. An onset of the reconstitution of the stratified system was induced by a cessation of continental plate movements.

This unstable development of stratified seas, which approached its maximum in the mid-Oxfordian, was accompanied by large seawater temperature fluctuations. The general temperature estimations for a large set of isotope data resulted in acceptable figures, which are quite similar to those for the perfectly preserved fossils, and obtained from very detailed geochemical investigations.

(2) The following stage, was one of gradual destratification and breakdown of the stratified seawater zones. The gradual destratification was interrupted by short-term (boundary) events of increasing C_{org} burial; these could have been triggered by changes in oceanic circulation, which implies the influence of water masses of different geochemical characteristics. The controlling role of oceanic circulation increased with time throughout the period of the destratification of the Jurassic seas, being undetectable in the Oxfordian, present during the Kimmeridgian, and predominant throughout the Tithonian (=Volgian). This stage is characterised by stable, warm seawater temperatures throughout.

This model, assuming the presence of seawater zones which are divided into at least two boxes of different hydrochemistry and isotopic composition, creates the essential mechanism controlling the carbonate system of the surface waters. Generally, the presence of stagnant and stratified epicontinental sea zones implied the storage of CO_2 and easily mobilized C_{org}, as well as, various cations and degraded aluminosilicates, in the lower box. Moreover, the lower box also exhibited high titration alkalinity (T_A) and carbonate alkalinity (A_C). Introduction of waters from the stagnant zones by diffusion influenced the surface carbonate system, inducing spontaneous $CaCO_3$ precipitation in the form of both calcite and aragonite, because of positive feedback of enhanced photosynthesis and a slight excess of A_C. On the other hand, the crises of $CaCO_3$ precipitation manifested by hardgrounds and other omission surfaces were caused by mixing of stagnant zones, bringing the waters of a high $\Sigma CO_2 - T_A$ system into

shallow shoals, which simply means a high P_{CO_2} and low pH, and also an excess of H^+ (due to oxidation of reduced sulphur species – contributors to T_A) in surface waters.

Interestingly, a high saturation state with respect to both calcite and aragonite might be achieved due to the presence and development of stratified seawater zones. In turn those stratified zones could exist only due to storage in the sea. Since the magnitude of C_{org} burial is reflected by secular changes in oceanic $\delta^{13}C_{carbonate}$, one can interpret those trends in terms of $CaCO_3$ saturation states, thus secular trends in calcite and aragonite precipitation. This led to the proposition that, after the latest Precambrian-Early Cambrian "aragonite seas", "calcite seas" dominated until the latest Devonian and then occurred only sporadically as interruptions during domination of "aragonitic seas" through the rest of the late Palaeozoic and Mesozoic, contrary to the well established model of an oscillatory trend of "aragonitic" and "calcitic" seas throughout the Phanerozoic. Virtually the entire Jurassic appeared to have been a time of "aragonitic sea", evidenced by numerous occurrences of aragonite cements and grains.

The proximity of stratified sea-water zones caused spontaneous $CaCO_3$ precipitation and $CaCO_3$ precipitation crises within shallow carbonate shoals. Those crises were manifested by various omission surfaces, including hardgrounds. After initial $CaCO_3$ undersaturation because of positive feedback of a high excess of A_C causing depletion of free Ca^{2+}, and higher P_{CO_2} buildup due to diffusion from the anoxic box of stratified sea-water zones, the bottom carbonate sediments were cemented. This carbonate substrate could be colonised by specific assemblages of burrowing, boring and encrusting oragnisms. The existence of regional omission surfaces was terminated by destratification pulses, supplying water masses from below the chemo-redoxcline to the shallow shoals. This allowed the formation of specific siliceous and clay mineral parageneses within the carbonate substratum. In general, the Phanerozoic epicontinental carbonate seas could have been suitable sites for "reverse" weathering.

The impact of seawater geochemistry on organic life has been established, although the geochemical episodes and events were not connected to the mass extinctions postulated for the Jurassic. Moreover, no evidence has been found to support the extraterrestrial catastrophe postulated for the Callovian-Oxfordian transition, although a local extinction of some marine biota due to a geochemical event could be proposed. Generalising again, geochemical events such as rapid C_{org} burial are usually accompanied by increase of primary productivity and A_C excess allowing domination of some specific benthic microbiota.

Among palaeo-oceanographic tracers, the present paper has demonstrated the validity of Ba for estimations of palaeoproductivity and its usefulness in detailed palaeoenvironmental reconstructions.

Finally, the model of the chemistry of Jurassic seas puts severe limits on the application of uniformitarian inference in palaeo-oceanography and allows the value of terrestrial processes as major moderators of Phanerozoic palaeo-oceanographic events to be stressed.

Acknowledgements

REFERENCES

ADATTE, T., STINNESBECK, W., HUBBERTEN, H. & REMANE, J. 1992. The Jurassic-Cretaceous boundary in the northeastern and central Mexico – a multistratigraphical approach. In: III Congreso Geologico de España y VIII Congreso Lationoamericano de Geologia, Salamanca 1992, Actas, 4, 23-29. Salamanca.

AHARON, P., SCHIDLOWSKI, M. & SINGH, I.B. 1987. Chronostratigraphic markers in the end-Precambrian carbon isotope record of the Lesser Himalaya. Nature, 327, 699-702. London.

ALVAREZ, W. 1986. Toward a theory of impact crisises. Eos, 67, 649-658. Washington.

ALVAREZ, L.W., ASARO, F., MICHEL, H.V. & ALVAREZ, W. 1980. Extraterrestrial cause for the Cretaceous-Tertiary extinction. Science, 208, 1095-1108. Washington.

ALVAREZ, W. & MULLER, R.A. 1984. Evidence from crater ages for periodic impacts on the Earth. Nature, 308, 718-720. London.

ANDERSON, T.F. & ARTHUR, M.A. 1983. Stable isotopes of oxygen and carbon and their application to sedimentologic and environmental problems. *In*: M.A. ARTHUR, T.F. ANDERSON, I.R. KAPLAN, J. VEIZER & L.S. LAND (*Eds.*), *Stable Isotopes in Sedimentary Geology*, *SEPM Short Course*, **10**, 1.1-1.151. Tulsa.

ANDERSON, T.F., POPP, B.N., WILLIAMS, A.C., HO, L.-Z. & HUDSON, J.D. 1994. The stable isotopic records of fossils from the Peterborough Member, Oxford Clay Formation (Jurassic), UK: palaeoenvironmental implications. *J. Geol. Soc., London*, **151**, 125-138. London.

BAUMGARTNER, P.O. 1987. Age and genesis of Tethyan Jurassic radiolarites. *Eclogae Geol. Helv.*, **80**, 831-879. Bern.

BERNSTEIN, R.E., BRYNE, R.H., BETZER, R. & GRECO, A.M. 1992. Morphologies and transformations of celestite in seawater: The role of acantharians in strontium and barium geochemistry. *Geochim. Cosmochim. Acta*, **56**, 3273-3279. Lancaster.

BECK, J.W., EDWARDS, R.L., ITO, E., TAYLOR, F.W., REY, J., ROUGERIE, F., JOANNOT, P. & HEINN, C. 1992. Sea-surface temperature from coral skeletal strontium/calcium ratio. *Science*, **257**, 644-646. Washington.

BERLIN, T.S. & KHABAKOV, A.V. 1970. Results of the comparison of Ca/Mg ratios and temperatures according to $^{18}O/^{16}O$ isotopes in rostra of Jurassic and Early Cretaceous belemnites. *Geokhimja*, **8**, 971-978. Moscow. [*In Russian with English summary*]

BERNER, R.A. 1971. Principles of Chemical Sedimentology, 1-240. *McGraw-Hill*; New York.

BERNER, R.A. 1981. A new geochemical classification of sedimentary environments. *J. Sedim. Petrol.*, **51**, 359-365. Tulsa.

BERNER, R.A. 1987. Models for carbon and sulfur cycles and atmospheric oxygen: application to Paleozoic geologic history. *Amer. J. Sci.*, **287**, 177-196. New Haven.

BERNER, R.A., SCOTT, M.R. & THOMILSON, C. 1970. Carbonate alkalinity in the pore waters of anoxic marine sediments. *Limnol. Oceanogr.*, **15**, 544-549. Washington.

BERNER, R.A., LASAGA, A.C. & GARRELS, R.M. 1983. The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *Am. J. Sci.*, **283**, 641-683. New Haven.

BISHOP, J.K. 1988 The barite-opal-organic carbon association in oceanic particulate matter. *Nature*, **332**, 341-343. London.

BOWEN, R. 1961. Paleotemperature analyses of Belemnoidea and Jurassic paleoclimatology. *J. Geol.*, **69**, 309-320. Chicago.

BOWEN, R. & FRITZ, P. 1963. Oxygen isotope paleotemperature analsis of Lower and Middle Jurassic fossils from Pliensbach, Würt. *Experientia*, **19**, 461-465. Bern.

BRADSHAW, M.J. & CRIPPS, D.W. 1992. Mid Callovian. *In* : J.C.W. COPE, J.K. INGHAM & P.F. RAWSON (*Eds*), *Atlas of Palaeogeography and Lithofacies*. *Geol. Soc. London, Memoirs*, **13**,1-120. London.

BRAND, U. & VEIZER, J. 1980. Chemical diagenesis of a multicomponent carbonate system – 1: Trace elements. *J. Sedim. Petrol.*, **50**, 1219-1236. Tulsa.

BRAND, U. & VEIZER, J. 1981. Chemical diagenesis of a multicomponent carbonate system – 2: Stable isotopes. *J. Sedim. Petrol.*, **51**, 987-998. Tulsa.

BRASIER, M.D., SHIELDS, G., KULESHOV, V.N. & ZHEGALLO, E.A. 1996. Integrated chemo- and biostratigraphic calibration of early animal evolution: Neoproterozoic-early Cambrian of southwest Mongolia: *Geol. Magazine*, **133**, 445-485. Cambridge.

BROCHWICZ-LEWIŃSKI, W., GĄSIEWICZ, A., KRUMBEIN, W.E., MELENDEZ, G., SQUEIROS, L., SUFFCZYŃSKI, S., SZATKOWSKI, K., TARKOWSKI, R. & ŻBIK, M. 1986. Anomalia irydowa na granicy jury środkowej i górnej. *Przegląd Geol.*, **34**, 83-87. Warszawa.

BROCHWICZ-LEWIŃSKI, W., GĄSIEWICZ, A., KRUMBEIN, W.E., MELENDEZ, G., SQUEIROS, L., SUFFCZYŃSKI, S., SZATKOWSKI, K. & ZIMMERMANN, H.D. 1989. Zdarzenia jura środkowa-jura górna i ich implikacje. *Przegląd Geol.*, **37**, 559-562. Warszawa.

BROECKER, W.S. 1970. A boundary condition on the evolution of atmospheric oxygen. *J. Geophys. Res.*, **75**, 3553-3557. Washington.

BROECKER, W.S. 1982. Ocean chemistry during glaciations. *Geochim. Cosmochim. Acta*, **46**, 1689-1705. Lancaster.

COLEMAN, M.L. 1985. Geochemistry of diagenetic non-silicate minerals: kinetic considerations. *Phil. Trans. R. Soc. London A*, **315**, 39-56. London.

COLEMAN, M.L., WALSH, J.N. & BENEMORE, R.A. 1989. Determination of both chemical and stable isotope composition in milligramme-size carbonate samples. *Sedim. Geol.*, **65**, 233-238. Amsterdam.

COLEMAN, M.L., GRUSZCZYŃSKI, M., PSZCZÓŁKOWSKI, A., MYCZYŃSKI, R. & ISAACS, M.C. 1995. Isotope and elemental record in Late Jurassic-Earliest Cretaceous sedimentary sequence of western Cuba: geochemical evolution of proto-Caribbean sea. *In*: *Ist SEPM Congress Sed Geol. Progr. Abstr.*, **1**, 41. Miami.

COLEMAN, M.L., GRUSZCZYŃSKI, M., HUDSON, J.D., KULICKI, C & ISAACS, M.C. 1997. Precise determination of seasonal temperature variation from the pre-pubescent stage of an exceptionally-preserved female, Jurassic ammonite. *In*: *Seventh Annual VM Goldschmidt Conference*. LPI contrib, 921, 53-54. *Lunar & Planetary Institute*, Houston.

CRICK, R.E. & MANN, K.O. 1987. Biomineralization and Systematic Implications. *In*: W.B. SAUNDERS & N.H. LANDMANN (*Eds*.), *NAUTILUS, The Biology and Paleobiology of a Living Fossil*, 115-134. *Plenum Press*; New York - London.

DEGENS, E.T. 1969. Biogeochemistry of stable carbon isotopes. *In*: G. EGLINGTON & J. MURPHY (*Eds*.), *Organic Geochemistry*, 304-329. *Springer-Verlag*; New York.

DEHAIRS, F., CHESELLET, R. & JEDWAB, J. 1980. Discrete suspended particles of barite and the barium cycle in the ocean. *Earth. Planet Sci. Lett.*, **49**, 528-550. Amsterdam.

DEHAIRS, F., GOEYENS, L., STROOBANTS, N., BERNARD, N., GOYET, C., POISSON & CHESELLET, R. 1990. On suspended barite and the oxygen minimum in the southern ocean. *Global Biogeochem. Cycles*, **4**, 85-102. Washington.

DEHAIRS, F., BAYENES, W. & GOEYENS, L. 1992. Accumulation of suspended barite at mesopelagic depths and export production in the southern ocean. *Science*, **258**, 1332-1335. Washington.

DEINES, P. 1980. The isotopic composition of reduced organic carbon. *In*: P. FRITZ & J.Ch. FONTES (*Eds*), *Handbook of Environmental Isotope Geochemistry*, 329-406. *Elsevier*; Amsterdam.

DEUSER, W.G. 1970. Carbon-13 in Black Sea waters and implications for the origin of hydrogen sulphide. *Science*, **268**, 1575-1577. Washington.

DEWEY, J.F., PITTMAN, W.C., RYAN, W.B.F. & BONIN, J. 1973. Plate tectonics and the evolution of the Alpine system. *Geol. Soc. Am. Bull.*, **84**, 3134-3180. Boulder.

DYMOND, J., SUESS, E. & LYLE, M. 1992. Barium in deep-sea sediment: a geochemical proxy for paleoproductivity. *Paleoceanography*, **7**, 163-181. Washington.

DYRSEN, D. 1986. Stagnant sulphidic basin waters. *Sci. Total Environ.*, **58**, 161-173. Washington.

ELDERFIELD, H. 1990. Tracers of ocean palaeoproductivity and palaeochemistry: an introduction. *Paleoceanography*, **5**, 711-717. Washington.

EPSTEIN, S. 1959. The variation of the ^{18}O /^{16}O ratio in nature and some geological implications. *In*: P.H. ABELSON (*Ed*.), *Researches in Geochemistry*, 217-240. *Wiley*; New York.

EPSTEIN, S. & MAYEDA, T. 1953. Variation of ^{18}O content of waters from natural sources. *Geochim. Cosmochim. Acta*, **4**, 213-224. Lancaster.

EPSTEIN, S., BUCHSBAUM, R., LOWENSTAM, H.A. & UREY, H.C. 1953. Revised carbonate-water isotopic temperature scale. *Geol. Soc. Amer. Bull.*, **64**, 1315-1326. Boulder.

FABRICIUS, F., FRIEDRICHSEN, V. & JACOBSHAGEN, V. 1970. Paläotemperaturen und Paläoklima in Obertrias und Lias der Alpen. *Geol. Rundschau*, **59**, 805-826. Stuttgart.

FALKNER, K.K., KLINKHAMMER, G.P., BOWERS, T.S., TODD, J.E., LEWIS, B.L., LANDING, W.M. & EDMOND, J.M. 1993. The behaviour of barium in anoxic marine waters. *Geochim. Cosmochim. Acta*, **57**, 537-554. Lancaster.

FRANCOIS, R., HONJO, S., MANGANINI, S.J. & RAVIZZA, G.E. 1995. Biogenic barium fluxes to the deep sediments: Implications for paleoproductivity reconstructions. *Global Biogeochem. Cycles*, **9**, 289-303. Washington.

FRITZ, P. 1965. $^{18}O/^{16}O$-Isotopenanalysen und Paläotemperaturbestimmungen an Belemniten aus dem Schwäb. Jura. *Geol. Rundschau*, **54**, 261-269. Stuttgart.

FROELICH, P.N., KLINKHAMMER, G.P., BENDER, M.L., LUEDTKE, N.A., HEATH, G.R., CULLEN, D., DAUPHIN, P., HAMMOND, D., HATRMAN, B. & MAYNARD, V. 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochim. Cosmocim. Acta*, **43**, 1075-1090. Lancaster.

FRY, B. & SHERR, E.B. 1984. $\delta^{13}C$ measurements as indicators of carbon flow in marine and freshwater ecosystems. *Contrib. Mar. Sci.*, **27**, 13-47. Seattle.

FRY, B., JANNASCH, H.W., MOLYNEAUX, S.J., WIRSEN, C.O. MURAMOTO, J.A. & KING, S. 1991. Stable isotope studies of the carbon, nitrogen and sulfur cycles in the Black Sea and the CariacoTrench. *Deep-Sea Res.*, **38**, 1003-1019. Woods Hole.

GARRELS, R.M. & THOMPSON, M.E. 1962. A chemical model for sea water at 25°C and one atmosphere total presure. *Amer. J. Sci.*, **260**, 57-66. New Haven.

GIVEN, R.K. & WILKINSON, B.H. 1987. Dolomite abundance and stratigraphic age, constraints on rates and mechanisms of Phanerozoic dolostone formation. *J Sedim. Petrol.*, **57**, 1068-1078. Tulsa.

GOYET, C., BRADSHAW, A.L. & BREWER, P.G. 1991. The carbonate system in the Black Sea. *Deep-Sea Res.*, **38**, 1049-1068. Woods Hole.

GRUSZCZYŃSKI, M. 1979. Ecological succession in Upper Jurassic hardgrounds from Central Poland. *Acta Palaeont. Polonica*, **24**, 429-450. Warszawa.

GRUSZCZYŃSKI, M. 1986. Hardgrounds and ecological succession in the light of early diagenesis (Jurassic, Holy Cross Mts., Poland). *Acta Palaeont. Polonica*, **31**, 163-212. Warszawa.

GRUSZCZYŃSKI, M., HAŁAS, S., HOFFMAN, A. & MAŁKOWSKI, K. 1989. A brachiopod calcite record of the oceanic carbon and oxgen isotope shifts at the Permian/Triassic transition. *Nature*, **337**, 64-68. London.

GRUSZCZYŃSKI, M., HOFFMAN, A., MAŁKOWSKI, K., HAŁAS, S., ZAWIDZKA, K. & ZENG-YONG, 1990a. Carbon isotopic drop across the Permian-Triassic boundary in SE

Sichuan, China. *N. Jb. Geol. Paläont. Mh.*, (**10**), 600-606. Stuttgart.

GRUSZCZYŃSKI, M., HOFFMAN, A., MAŁKOWSKI, K., TATUR, A. & HAŁAS, S. 1990b. Some geochemical aspects of life and burial environments of late Jurassic scleractinian corals from northern Poland. *N. Jb. Geol. Paläont. Mh.*, (**11**), 673-686. Stuttgart.

GRUSZCZYŃSKI, M., COLEMAN, M.L. & ISAACS, M.C. 1993a. Origin of hardgrounds: a step of understanding. *Terra Abstr.*, **5**, 688-689. Oxford.

GRUSZCZYŃSKI, M., COLEMAN, M.L. & HUDSON, J.D. 1993b. Callovian provinciality: a geochemical perspective. *In*: *Arkell Int. Symp. Jurassic Geology*, p. 26. London.

GRUSZCZYŃSKI, M., COLEMAN, M.L., DREWNIAK, A. & ISAACS, M.C. 1994. Mass extinction and oceanic circulation at the Middle-Upper Jurassic passage. *In*: *14th Inter. Sedim. Congress Abstr.*, p. E-11. Reciefe.

GRUSZCZYŃSKI, M., COLEMAN, M.L. & MACKENZIE, F.T. 1995. Aragonite in "calcitic" seas: interpreting $\delta^{13}C$ Phanerozoic curve once more *In*: *10th Bathurst Meeting of Carbonate Sedimentologists*, Abstracts, p. 24. Egham.

HALLAM, A. 1975. Jurassic Environnments, 1-269. *Cambridge University Press*; Cambridge.

HALLAM, A. 1984. Pre-Quaternary sea-level changes. *Ann. Rev. Earth Planet. Sci.*, **12**, 205-243. Palo Alto.

HEYDARI, E. & MOORE, C.H. 1994. Paleoceanographic and Paleoclimatic controls on ooid mineralogy of the Smackover formation, Mississipi Salt Basin: implications for Late Jurassic seawater composition. *J. Sedim. Research*, **A64**, 101-114. Tulsa.

HOEFS, J. 1987. Stable Isotope Geochemistry, 1-241. *Springer*; New York - Berlin - Heidelberg.

HOFFMAN, A., GRUSZCZYŃSKI, M. & MAŁKOWSKI, K. 1991a. On the interrelationship between temporal trends in $\delta^{13}C$, $\delta^{18}O$, and $\delta^{34}S$, in the world ocean. *J. Geology*, **99**, 355-370. Chicago.

HOFFMAN, A., GRUSZCZYŃSKI, M., MAŁKOWSKI, K., HAŁAS, S., MATYJA, B.A. & WIERZBOWSKI, A. 1991b. Carbon and oxygen isotope curves for the Oxfordian of central Poland. *Acta Geol. Polonica*, **43**, 157-164. Warszawa.

HOLLAND, H.D. 1978. The Chemistry of the Atmosphere and Oceans, 1-351. *Wiley*; New York.

HOLSER, W.T. 1984. Gradual and abrupt shifts in ocean chemistry during Phanerozoic time. *In*: H.D. HOLLAND & A.F. TRENDALL (*Eds*), *Patterns of Changes in Earth Evolution*, 123-143. *Springer-Verlag*; Berlin.

HOLSER, W.T., SCHIDLOWSKI, M., MACKENZIE, F.T. & MAYNARD, J.B. 1988. Geochemical Cycles of Carbon and Sulfur. *In*: C.B. *Gregor*, R.M. GARRELS, F.T. MACKENZIE & J.B. MAYNARD (*Eds*), *Chemical Cycles in the Evolution of the Earth* , 105-173.

HUDSON, J.D. 1977. Stable isotopes and limestone lithification. *J. Geol. Soc., London*, **133**, 637-660. Lodnon.

HUDSON, J.D. & ANDERSON, T.F. 1989. Ocean temperatures and isotopic compositions through time. *Trans. Roy. Soc. Edinburgh, Earth Sci.*, **80**, 183-192. Edinburgh.

HUT, P., ALVAREZ, W., ELDER, W.P., HANSEN, T., KAUFFMAN, E.G., KELLER, G., SCHOEMAKER, E.M. & WEISSMAN, P.R. 1987. Comet showers as a cause of mass extinctions. *Nature*, **329**, 118-126. London.

IRWIN, H. 1980. Early diagenetic carbonate precipitation and pore fluid migration in the Kimmeridge Clay of Dorset, England. *Sedimentology*, **27**, 57-591. Oxford.

IRWIN, H., CURTIS, C. & COLEMAN, M.L. 1977. Isotopic evidence for source of diagenetic carbonates formed durng burial of organic-rich sediments. *Nature*, **269**, 209-213. London.

JARVIS, I, Carson, G.A., COOPER, M.K.E., HART, H.B., LEARY, P.N., TOCHER, B.A., HORNE, D. & ROSENFELD, A. 1988. Microfossil assemblages and the Cenomanian – Turonian (late Cretaceous) oceanic anoxic event. *Cretaceous Res.*, **9**, 3-103. London.

JENKYNS, H.C. 1988. The early Toarcian (Jurassic) anoxic event: stratigraphic, sedimentary and geochemical evidence. *Amer. J. Sci.*, **288**, 101-151. New Haven.

JENKYNS, H.C. 1996. Relative sea-level change and carbon isotopes: data from the Upper Jurassic (Oxfordian) of central Southern Europe. *Terra Nova*, **8**, 75-85. Oxford.

JENKYNS, H.C. & CLAYTON, C.J. 1986. Black shales and carbon isotopes in pelagic sediments from the Tethyan Lower Jurassic. *Sedimentology*, **33**, 87-106. Oxford.

JENKYNS, H.C. & CLAYTON, C.J. 1997. Lower Jurassic epicontinental carbonates and mudstones from England and Wales: chemostratigraphic signals and the early Toarcian anoxic event. *Sedimentology*, **44**, 687-706. Oxford.

JENKYNS, H.C., GÉCZY, B. & MARSHALL, J.D. 1991. Jurassic manganese carbonates of central Europe and the early Toarcian anoxic event. *J. Geol.*, **99**, 137-149. Chicago.

JONES, C.E., JENKYNS, H.C., COE, A.L. & HASSELBO, S.P. 1994. Strontium isotopic variations in Jurassic and Cretaceous seawater. *Geochim. Cosmochim. Acta*, **58**, 3061-3074. Lancaster.

JORDAN, R. & STAHL, W. 1970. Isotopische Paläotemperatur Bestimmungen an jurassischen Ammoniten und grundsätzliche Voraussetzungen für diese Methode. *Geol. Jb.*, **89**, 33-62. Stuttgart.

KEMPE, S. & KAŹMIERCZAK, J. 1993. Satonda Crater Lake, Indonesia: Hydrochemistry and biocarbonates. *Facies*, **28**, 1-32. Erlangen.

KEMPE, S. & KAŹMIERCZAK, J. 1994. The role of alkalinity in the evolution of ocean chemistry, organization of living systems, and biocalcification processes. *In*:

F. DOUMENGE (*Ed.*), *Past and Present Biomineralization Processes. Bull. Inst. Oceanogr., Monaco, No. Spec.*, **13**, 61-117. Monte Carlo.

KOPIK, J. 1979. Callovian of the Czestochowa Jura (southwestern Poland). *Prace Inst. Geol.*, **93**, 1-69. Warszawa. [*In Polish with English summary*]

LEA, D.W. & SPERO, H.J. 1992. Experimental determination of barium uptake in shells of the planktonic foraminifera *Orbulina universa* at 22°C. *Geochim. Cosmochim. Acta*, **56**, 2673-2680. Lancaster.

LASAGA, A., BERNER, R.A. & GARRELS, R.M. 1985. An improved geochemical model of atmospheric CO_2 fluctuations over the past 100 million years. *In*: E.T. SUNDQUIST & W.S. BROECKER (*Eds*), *The carbon cycle and atmospheric CO_2: Natural variations Archean to present. American Geophysical Union Monograph*, **32**, 397-411. Washington, D.C.

LERMAN, A. 1979. *Geochemical Processes: Water and Sediment Environments*, 1-481. *Wiley & Sons*; New York.

MACKENZIE, F.T. & GARRELS, R.M. 1966a. Chemical mass balance between rivers and oceans. *Amer. J. Sci.,* **264**, 507-525. New Haven.

MACKENZIE, F.T. & GARRELS, R.M. 1966b. Silica-bicarbonate balance in the ocean and early diagenesis. *J. Sedim. Petrol.*, **36**, 1075-1084. Tulsa.

MACKENZIE, F.T. & Pigott, J.D. 1981.Tectonic controls of Phanerozoic sedimentary rock cycling. *J. Geol. Soc. London*, **138**, 183-196. London.

MACKENZIE, F.T. & MORSE, J.W. 1992. Sedimentary carbonates through Phanerozoic time. *Geochim. Cosmochim. Acta*, **56**, 3281-3295. New Haven.

MACKENZIE, F.T., GARRELS, R.M., BRICKER, O.P. & BICKLEY, F. 1967. Silica in sea water: control by silica minerals. *Science*, **155**, 1404-1405. Washington.

MAŁKOWSKI, K., GRUSZCZYŃSKI, M., HOFFMAN, A. & HAŁAS, S. 1989. Oceanic stable isotope composition and a scenario for the Permo-Triassic crisis. *Hist. Biology*, **2**, 289-309. London.

MAŁKOWSKI, K., GRUSZCZYŃSKI, M. & HOFFMAN, A. 1990. A model of oceanic controls on limestone-clay alternations in open-shelf settings. *N. Jb. Geol. Paläont., Mh.*, (**3**),165-168. Stuttgart.

MARSHALL, J.D. 1992. Climatic and oeanographic isotopic signals from the carbonate rock record and their preservation. *Geol. Mag.*, **129**, 143-160. Cambridge.

MARSHALL, J.D. & MIDDLETON, P.D. 1990. Chages in marine isotope composition and the late Ordovician glaciation. *J. Geol. Soc. London,* **147**, 1-4. London.

MCNEILL, G.W. 1993. The geochemical palaeo-oceanography and mineralogy of marine sediments from the Peruvian continental margin. *Ph.D. Thesis*, 1-280. Edinburgh.

MORSE, J.W. & MACKENZIE, F.T. 1990. Geochemistry of Sedimentary Carbonates. *In*: Developments in Sedimentology, **48**, 1-707. *Elsevier*, Amsterdam - New York.

MUCCI, A. 1983. The solubility of calcite and aragonite in seawater at various salinities, temperatures, and one atmosphere total pressure. *Am. J. Sci.*, **283**, 780-799. New Haven.

MUEHLENBACHS, K. 1986. Alteration of the oceanic crust and the ^{18}O history of seawater. *In*: J.W. VALLEY, H.P. TAYLOR, JR. & J.R. O'NEIL (*Eds*), *Stable Isotopes in High Temperature Geological Processes. Rev. Mineralogy*, **16**, 425-444. *MSA, Book Crafters, Inc*; Chelsea, Michigan.

MUEHLENBACHS, K. & CLAYTON, R.N. 1976. Oxygen isotope composition of the oceanic crust and its bearing on seawater. *J. Geophys. Res.*, **81**, 4365-4369. Washington.

PARRISH, J.T. 1992. Jurassic climate and oceanography of the Circum-Pacific region. *In*: G.E.G. WESTERMANN (*Ed.*), *The Jurassic of the Circum-Pacific. World and Regional Geology*, **3**, 365-379. *Cambridge Univ. Press*; Cambridge.

RAUP, D. & SEPKOWSKI, J.J. 1984. Periodicity of extinctions in the geologic past. *Proc. Natl. Acad. Sci. USA*, **81**, 801-805. Washington.

RAUP, D. & SEPKOWSKI, J.J. 1986. Periodic extinction of families and genera, *Science,* **231**, 833-836. Washington.

ROSS, C.A., MOORE, G.T. & HAYASHIDA, D.N. 1992. Late Jurassic paleoclimate simulation – paleoecological implications for ammonoid provinciality. *Palaios*, **7**, 487-507. Tulsa.

RÓŻYCKI, S.Z. 1953. The Upper Dogger and Lower Malm of the Kraków-Częstochowa Jura Chain. *Prace Inst. Geol.*, **17**, 1-412. Warszawa. [*In Polish*]

SÆLEN, G., DOYLE, P. & TALBOT, M.R. 1996. Stable-isotope analyses of belemnite rostra from the Whitby Mudstone Fm., England: surface water conditions during deposition of a marine black shale. *Palaios*, **11**, 97-117. Tulsa.

SANDBERG, P.A. 1983. An oscillating trend in Phanerozoic nonskeletal carbonate mineralogy. *Nature*, **305**, 19-22. London.

SANDBERG, P.A. 1985a. Nonskeletal aragonite and pCO_2 in the Phanerozoic and Proterozoic. *In*: E.T. SUNDQUIST & W.S. BROECKER (*Eds*), *The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present. A G U Monogr.*, **32**, 585-594. Washington, D.C.

SANDBERG, P.A. 1985b. Aragonite cements and their occurrence in ancient limestones. *In*: N. SCHNEIDERMANN & P.M. HARRIS (*Eds*), *Carbonate Cements. S.E.P.M. Spec. Publ.*, **36**, 33-57. Tulsa, Oklahoma.

SCHOLLE, P.A. & ARTHUR, M.A. 1980. Carbon isotopic fluctuations in Cretaceous pelagic limestones: Potential stratigraphic and petroleum exploration tool. *Amer. Assoc. Petrol. Geol. Bull.*, **64**, 67-87. Tulsa.

SCHROEDER, J.O., MURRAY, R.W., LEINEN, M., PFLAUM, R.C. & JANECEK, T.R. 1997. Barium in equatorial Pacific carbonate sediment: Terrigenous, oxide, and biogenic associations. *Paleoceanography*, **12**, 125-146. Washington.

SEPKOWSKI, J.J. 1989. Periodicity in extinction and the problem of catastrophism in the history of life. *J. Geol. Soc. London*, **146**, 7-19. London.

SHACKLETON, N.J. 1977. Tropical rainforest history and the equatorial Pacific carbonate dissolution cycles. *In*: N. ANDERSON & A. MALAHOFF (*Eds*), *The Fate of Fossil Fuel CO$_2$ in the Ocean*, 355-374. *Plenum Press*; New York.

SHOEMAKER, E.M., & WOLFE, R.F. 1986. Mass extinctions, crater ages and comet showers. *In*: R.M. SMOLUCHOWSKI, J.N. BAHCALL & M.S. MATTHEWS (*Eds*), *The Galaxy and the Solar System*, 338-386. *University of Arizona Press*; Tuscon, Arizona.

STAHL, W. & JORDAN, R. 1969. General considerations on isotopic palaeotemperature determinations and analyses on Jurassic ammonites. *Earth Planet. Sci. Lett.*, **6**, 173-178. Amsterdam.

SPAETH, C., HOEFS, J. & VETTER, U. 1971. Some aspects of isotopic composition of belemnites and related paleotemperatures. *Bull. Geol. Soc. Amer.*, **82**, 3139-3150. Boulder.

SPITZY, A. & DEGENS, E.T. 1985. Modelling stable isotope fluctuations through geologic time. *Mitteilungen Geol.-Paläont. Inst. Uni. Hamburg*, **59**, 155-156. Hamburg.

STEVENS, G.R. & CLAYTON, R.N. 1971. Oxygen isotope studies on Jurassic and Cretaceous belemnites from New Zealand and their biogeographic siginificance. *N. Zeal. J. Geol. Geophys.*, **14**, 829-897. Auckland.

SUNDQUIST, E.T. & BROECKER, W.S. (*Eds*.). 1985. The Carbon Cycle and Atmospheric CO$_2$: Natural Variations, Archaean to Present. *Geophys. Monogr. Ser.*, **32**, 1-627. *AGU*; Washington.

TAN, F.C., HUDSON, J.D. & KEITH, M.L. 1970. Jurassic (Callovian) paleotemperatures from Scotland. *Earth Planet. Sci. Lett.*, **9**, 421-426. Amsterdam.

TEIS, R.V., NAIDIN, D.P. & SAKS, V.N. 1968. Determination of Late Jurassic and Early Cretaceous paleotemperatures from the oxygen isotopic composition of belemnie guards. *In*: V.N. Saks (*Ed.*), *Mesozoic Marine Faunas of the U.S.S.R. North and Far East and their Stratigraphic Significance*. *Siberian Branch, USSR Acad. Sci., Trans. Inst. Geol. Geophys.*, **48**, 51-71. Moscow. [*In Russian*]

UREY, H.C. 1951. The origin and development of the Earth and other terrestrial planets. *Geochim. Cosmochim. Acta*, **1**, 209-277. Lancaster.

UREY, H.C. 1956. Regarding the early history of the earth's atmosphere. *Bull. Geol. Amer. Soc.*, **67**, 1125-1127. Boulder.

UREY, H.C., LOWENSTAM, H.A., EPSTEIN, S. & MCKINNEY, C.R. 1951. Measurment of paleotemperatures and temperatures of the Upper Cretaceous of England, Denmark, and the southern United States. *Bull. Geol. Soc. Amer.*, **62**, 399-416. Boulder.

VON DAMM, K.L. & EDMOND, J.M.1984. Reverse weathering in the closed-basin lakes of the Ethiopian rift. *J. Amer. Sci.*, **284**, 835-862. New Haven.

VEIZER, J. 1974. Chemical diagenesis of belemnite shells and possible consequences for paleotemperature determinations. *N. Jb. Geol. Paläont., Abh.*, **145**, 279-305. Stuttgart.

VEIZER, J. 1983.Chemical diagenesis of carbonates: theory and application of trace element technique. *In*: M.A. ARTHUR, T.F. ANDERSON, I.R. KAPLAN, J. VEIZER & L.S. LAND (*Eds*), *Stable Isotopes in Sedimentary Geology. SEPM Short Course*, **10**, 1-100. Dallas.

VEIZER, J. & FRITZ, P. 1976. Possible control of post-depositional alteration in oxgen paleotemperature determinations. *Earth Planet. Sci. Lett.*, **33**, 255-260. Amsterdam.

WEISSERT, H. & CHANNELL, J.E.T. 1989. Tethyan carbonate isotope stratigraphy across the Jurassic-Cretaceous boundary: an indicator of decelerated global cycling? *Paleoceanography*, **4**, 483-494. Washington.

WESTERMANN, G.E.G. 1993. Global bio-events in mid-Jurassic ammonites controlled by seaways. *In*: M.R. HOUSE (Ed.), *The Ammonoidea: Environment, Ecology, and Evolutionary Change. Systematics Assoc., Spec. Vol.*, **47**, 187-226. *Clarendon Press*; Oxford.

WIGLEY, T.M.L. & PLUMMER, L.N. 1976. Mixing of carbonate waters. *Geochim. Cosmochim. Acta*, **40**, 989-995. Lancaster.

WILKINSON, B.H. & GIVEN, R.K. 1986. Secular variation in abiotic marine carbonates: Constraints on Phanerozoic atmospheric carbon dioxide contents and oceanic Mg/Ca ratios. *J. Geology*, **94**, 321-333. Chicago.

WILKINSON, B.H., OWEN, R.M. & CARROLL, A.R. 1985. Submarine hydrothermal weathering, global eustasy, and carbonate polymorphism in Phanerozoic marine oolites. *J. Sedim. Petrol.*, **55**, 171-183. Tulsa.

ZIEGLER, P.A. 1990. Geological Atlas of Western and Central Europe, 1-390. *Shell Internationale Petroleum Maatschappij B.V.*; Amsterdam.