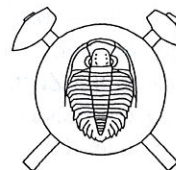


Chemical composition of the crinoid skeletal remains (Echinodermata) in weathered limestones of the Bohemian Lower Devonian (Barrandian area)



Chemické složení kosterních elementů krinoidů (Echinodermata) ve zvětralých partiích vápenců českého spodního devonu (Barrandien) (Czech summary)

(1 text-fig., 48 graphs)

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The authors give a brief report on the chemical composition of Lower Devonian crinoid skeletal remains and a preliminary interpretation of it. An enormous body of isolated crinoid ossicles from various localities of the Barrandian "white beds" was collected and 40 samples were prepared for chemical analysis. It was proved that the fossil crinoid ossicles are uniformly low-Mg calcite regardless their stratigraphical position or regional geological condition. In the samples the Fe, Pb, Zn, Cu, Mn, Sr, Li, Na, K, MgO, CaO contents and the insoluble residue were established. A simple evaluation of modern anthropogenic contamination by heavy metals was made using samples derived by previous investigators at the same localities. The possible progressive pollution with heavy metals in relation to the beginning of this century was confirmed in no sample (some samples show even a slight decrease in the heavy metal concentrations). In each sample, independent measurements of element contents were recorded for the skeletal ossicles of the crinoid pelma (esp. columnals) as well as of the crown (esp. brachials). The differences between trace element contents in pelma and crown of the crinoids turned to be too large that they cannot be caused by analytical error. The latter observation had verified that some parts of the living Palaeozoic crinoid body had accumulated certain trace metals. Results of the analyses convincingly demonstrated that the Barrandian crinoids exhibited biomagnification of certain elements and were probably very important in the cycling of trace metals in the sea. Finally, 12 stable isotopic samples (40 measurements), were analyzed, including crinoid brachials, crinoid columnals, brachiopod shells and samples of the rock. No palaeotemperature records were established. From our results it seems that an alteration of the original isotopic signal in a diagenetic environment open to meteoric water could explain the relatively low $\delta^{18}\text{O}$ and high $\delta^{13}\text{C}$ (related to the PDB standard). However, the geochemical as well as the stable isotopic interpretations are only preliminary and left open to question.

Introduction

In the Lower Palaeozoic of the Barrandian area, an enormous body of crinoid ossicles comes from highly weathered carbonates, among specialists known as "white beds". Curiously, these "white beds" may be white, bright yellow, brown, grey, reddish or distinctly pink. They originated from time-dependent weathering of fine-grained Upper Silurian and Lower to Middle Devonian limestones along zones of tectonic faulting, very probably by ground water solution. The original rock is predominantly formed of fossil skeletons and cement. The latter is now highly weathered, disintegrated and decalcified. On the other hand, all crinoid skeletal elements are hard low-Mg calcite. The "true" Barrandian "white beds" are characterized by the presence of extremely well-preserved echinodermal ossicles, including especially those of Crinoidea, Echinoidea, Ophiocistoidea, Cyclocystoidea, Holothuroidea, Asteroidea, Ophiuroidea, and Cystoidea. These echinodermal remains, as the most abundant fossils here, frequently show the original stereom, a lattice-like calcitic meshwork of which all echinodermal skeletal plates are constructed (see below the Chapter "General characteristics of echinodermal stereom"). The preservation of stereom is of great importance for palaeobiology be-

cause its microstructure reflects particular kinds of original soft tissue in thecal plates. Although such a "natural developing" of ancient stereom is very probably a worldwide phenomenon, practically no attention has been paid to it outside Bohemia. In other countries, "white beds" are often unknown or supposed to be extremely exceptional. In the U.S.A., for example, palaeontologists sought to develop the stereom of fossil crinoids in the laboratory by etching the plates with dilute acid solution. The best results were obtained with formic acid solution (see Lapham - Ausich - Lane 1976 and references therein).

A larger part of the crinoid fauna from the Barrandian localities is described in works of Bouška (1942-1956), Prokop (1967-1992), Petr (1983-1984), and Prokop - Petr (1986-1995). Interestingly, from the geochemical point of view the "white beds" were not studied in this century. However, two important works of Friedrich Katzer (see Katzer 1886, 1888) gave chemical analyses from the Barrandian area. The latter one compared the composition of a weathered and non-weathered limestone and represents so far the only study published on the Barrandian "white bed" composition in the history of the Czech geology. Katzer (1888) has analyzed two localities from which the first one was in the Koněprusy Limestone of the "Císařský lom" quarry near Koněprusy (it could be dedu-

ced from Katzer's determination of fossils and from the limited number of quarries in Katzer's times), the second one in the Zlíchov Limestone (basal portions) of the so-called "Chapel Coral Horizon" at Praha-Zlíchov. For example, Katzer (1888) gave us the composition of a non-weathered Koněprusy Limestone (in %):

CO ₂	44.23
CaO	51.78
MgO	2.64
insoluble residue	0.84

From the above given table Katzer (1888) calculated the CaCO₃ and MgCO₃ content (in %):

CaCO ₃	92.45
MgCO ₃	5.6

Katzer (1888) assigned therefore the Koněprusy Limestone to a category of a dolomitic limestone. The same author further analyzed the chemical composition of the weathered portions of the Koněprusy Limestone (in %):

CO ₂	14.33
CaO	18.13
MgO	0.28
Fe ₂ O ₃ and Al ₂ O ₃	5.94
K ₂ O and Na ₂ O	0.7
H ₂ O	5.53
insoluble residue	0.84

Similarly, from these results Katzer again calculated the CaCO₃ and MgCO₃ content of the weathered Koněprusy Limestone (in %):

CaCO ₃	32.37
MgCO ₃	0.58

Moreover, Katzer (1888) stressed that in both cases the insoluble residue represents the same material and calculated the amount of CaCO₃ and MgCO₃ content in the non-weathered and weathered limestone against the same amount of insoluble residue:

	CaCO ₃	MgCO ₃	insoluble residue
hard limestone	5916.8	359.04	54.11
residue	32.37	0.58	54.11

Therefore, Katzer (1888) logically concluded that 1 kg of the weathered limestone (or residue) evolve from 72.7 kg of the non-weathered (hard) Koněprusy Limestone. In fact, his interesting results have no counterpart in the more recent studies because the work of Svoboda, Prantl - Kukal (1957) gives only the compositions for the non-weathered Koněprusy Limestone (MgO 1.19 %, CaO 53.84 % and insoluble residue 0.76 %).

However, neither Svoboda, Prantl and Kukal, nor Friedrich Katzer have studied chemical compositions of Barrandian fossils themselves. Curiously, we have at our disposal only three pioneering chemical analyses published by J. Obrhel (see Obrhel 1976a,b, 1979).

Obrhel (1976a) presented analyses of the Koněprusy

Limestone and stressed that in the non-stromatolite limestone the average MgO content is 1.34 % (= 2.8 % MgCO₃) while in the oncolites (stromatolites s.l.) it is considerably higher (11.4 % MgO = 23.84 % MgCO₃). Within the oncolites high-Mg calcite has been proved. Also in the red alga *Parachaetetes bohemicus* (Němejc, 1942) Johnson & Konishi 1958 a higher content of magnesium (also in the form of high-Mg calcite) has been proved: CaO 45.92 %, MgO 8.62 % and CO₂ 44.20 % (see Obrhel 1976b). In both the latter cases Obrhel pointed to the possibility that an original chemical composition is preserved in the fossils from the Koněprusy Limestone. He also studied (Obrhel 1979) the chemical composition (main elements Si, Fe, and P, as well as trace elements Na, Mn, Al, Cu, V, and Sr) of nodules of the calcareous red alga *Solenopora filiformis* Rothpletz (Silurian, Kozel syncline, Šanův kout between Srbsko and Beroun) and found that the Mg content is lower than in the Devonian red alga *Parachaetetes bohemicus*. He concluded that "the Silurian *Solenopora filiformis* was in an initial stage of incorporating Mg into its skeleton (in this alga an ecological protective function of biostromes was still undeveloped), whereas in *Parachaetetes bohemicus* the concentration of Mg had already made major progress, obviously in connection with the development of the ecological protective function of the Koněprusy bioherms".

Although the above given results have been deeply questioned by recent investigators (Kukal, personal communication), the Obrhel's interest established the foundation for an extensive geochemical research of Barrandian fossils. It is surprising that so many years have passed without almost anything in this way, except several unpublished studies (Kukal, personal communication) and except some reports in press (Žák, personal communication). Therefore, the most important purpose of the present study is to determine how the chemical content of the crinoid skeletal ossicles was controlled by both the palaeoenvironmental conditions and recrystallization processes.

Material

As illustrated in the following list, the present authors have obtained samples from all known Lower Devonian "white beds" localities of the Barrandian area, additional samples from some Silurian localities (lower part of the Kopanina Formation, quarries "Amerika" near Karlštejn, "Na rešněnách", and upper part of the Přidolí Formation, so-called "lobolith hillside" near Řeporyje) and from some Middle Devonian ones (basal part of the Choteč Limestone at Praha-Barrandov, and "white beds" from Eifel Mountains, Germany near Nollenbach - collected by Prokop in 1990). From all the 40 samples studied only the sample n. 1 (tuffitic sediments of the Kopanina Formation, "Na rešněnách" near Karlštejn) does not come from "true white beds". The samples under study are briefly listed below (abbrev. C = ossicles of the crown, predominantly brachials, P = ossicles of the pelma, predominantly columnals):

1. Upper Silurian, Ludlow, lower part of the Kopanina Formation, quarries "Amerika" near Karlštejn, "Na řeš-nách", Da/Db, sampled by Horný 1994; C + P.
2. Upper Silurian, Přídolí, upper part of the Přídolí Formation, so-called "lobolith hillside" near Praha-Řeporyje, sampled by Hanuš 1922; P.
3. Upper Silurian, Přídolí, upper part of the Přídolí Formation, so-called "lobolith hillside" near Praha-Řeporyje, sampled by Zedník 1993; C + P.
4. Lower Devonian, Lochkovian, pink biostrome layers of the Kotýs Limestone, quarry "Černá skála" near Praha-Řeporyje, sampled by Prokop 1982; C + P.
5. Lower Devonian, Lochkovian, pink biostrome layers of the Kotýs Limestone, quarry "Černá skála" near Praha-Řeporyje, sampled by Petr 1987; C + P.
6. Lower Devonian, Lochkovian, uppermost part of the Kotýs Limestone, quarry "Čížovec" near Trněný Újezd (2), sampled by Horný 1992; C + P.
7. Lower Devonian, Pragian, Koněprusy Limestone (reef periphery or talus zone), "Císařský lom" quarry near Koněprusy, sampled by Jahn 1898 (approx.); P.
8. Lower Devonian, Pragian, Koněprusy Limestone (reef periphery or talus zone), quarry "Homolák" on the Plešivec Hill near Koněprusy (B), sampled by Horný 1993; C + P.
9. Lower Devonian, Pragian, Slivenec Limestone, quarry near the junction of the Kačák Brook and the Berounka River at Srbsko near Karlštejn, sampled by Prantl 1935-1937; C + P.
10. Lower Devonian, Pragian, Slivenec Limestone, base of the section in the "Červený lom" quarry near Praha-Klukovice, sampled by Prokop 1991; C + P.
11. Lower Devonian, Pragian, lowermost part of the Loděnice Limestone in the quarry "Na Konvářce" at Praha-Smíchov, sampled by Prokop 1991; C + P.
12. Lower Devonian, Pragian, Loděnice Limestone, Praha-Smíchov, "Konvářka", filled quarry near a small viaduct, sampled by Koliha 1931-1932; C + P.
13. Lower Devonian, Pragian, Loděnice Limestone, quarry "Na Konvářce" at Praha-Smíchov, sampled by Horný 1991; C + P.
14. Lower Devonian, Pragian, Loděnice Limestone, "Červený lom" quarry near Praha-Klukovice, sampled by Prokop 1982; C + P.
15. Lower Devonian, Pragian, Loděnice Limestone, "Červený lom" quarry near Praha-Klukovice (lower portion of the sampling station C), sampled by Prokop 1991; C + P.
16. Lower Devonian, Pragian, Loděnice Limestone, "Červený lom" quarry near Praha-Klukovice (uppermost 40 cm of the sampling station C), sampled by Prokop 1991; C + P.
17. Lower Devonian, Pragian, Loděnice Limestone, "Červený lom" quarry near Praha-Klukovice (the sampling station D), sampled by Prokop 1991; C + P.
18. Lower Devonian, Pragian, Loděnice Limestone, "Červený lom" quarry near Praha-Klukovice (the sampling station E), sampled by Prokop 1991; C + P.
19. Lower Devonian, Pragian, base of the Dvorce-Prokop Limestone (directly above the boundary with the Loděnice Limestone), "Červený lom" quarry near Praha-Klukovice, sampled by Prokop 1991; C + P.
20. Lower Devonian, Pragian, basal part of the Dvorce-Prokop Limestone (about 1 to 2 m above the boundary with the Loděnice Limestone), "Červený lom" quarry near Praha-Klukovice, sampled by Horný 1991; C + P.
21. Lower Devonian, Pragian, Dvorce-Prokop Limestone, lower pit at the quarry "U kantiny" near Praha-Řeporyje, sampled by Koliha 1936; C + P.
22. Lower Devonian, Pragian, Dvorce-Prokop Limestone, upper pit at the quarry "U kantiny" near Praha-Řeporyje, sampled by Koliha 1936; C + P.
23. Lower Devonian, Pragian, Dvorce-Prokop Limestone, NW margin of the quarry near St. Prokop at Praha-Hlubočepy (sampling station 3), sampled by Prokop 1991; C + P.
24. Lower Devonian, Pragian, Dvorce-Prokop Limestone, "Červený lom" quarry near Praha-Klukovice, sampled by Hanuš 1930; C.
25. Lower Devonian, Pragian, base of the Dvorce-Prokop Limestone (directly above the boundary with the Loděnice Limestone), "Červený lom" quarry near Praha-Klukovice, sampled by Růžička 1949; P.
26. Lower Devonian, Pragian, Dvorce-Prokop Limestone, quarry "V Dvorcích" at Praha-Podolí, sampled by Kříž and Marek 1963; C + P.
27. Lower Devonian, Pragian, Dvorce-Prokop Limestone, topmost part of the eastern wall of the quarry near St. Prokop at Praha-Hlubočepy (sampling station B4), sampled by Prokop 1993; C + P.
28. Lower Devonian, Pragian, Dvorce-Prokop Limestone, NW margin of the quarry near St. Prokop at Praha-Hlubočepy (sampling station 4), sampled by Prokop 1993; C + P.
29. Lower Devonian, Pragian, Dvorce-Prokop Limestone, quarry "U kantiny" near Praha-Řeporyje, about 1 m below the base of the Zlíchov Limestone, sampled by Prokop 1991; C + P.
30. Lower Devonian, Zlíchovian, upper part of the Zlíchov Limestone, so-called "Chapel Coral Horizon", "U kapličky" quarry at Praha-Zlíchov, sampled by Hanuš 1923; C + P.
31. Lower Devonian, Zlíchovian, upper part of the Zlíchov Limestone, so-called "Chapel Coral Horizon", "U kapličky" quarry at Praha-Zlíchov, sampled by Prokop 1993; C + P.
32. Lower Devonian, Dalejan, Třebotov Limestone, "Prastav" quarry near the railway at Praha-Holyně, sampled by Prantl 1932; C + P.
33. Lower Devonian, Dalejan, Třebotov Limestone, quarry "U jezírka" at Praha-Hlubočepy, sampled by Prantl 1932; C + P.
34. Lower Devonian, Dalejan, Třebotov Limestone, "Prastav" quarry at Praha-Holyně, sampled by Marek 1964; C + P.
35. Lower Devonian, Dalejan, Třebotov Limestone,

- "Prastav" quarry near the volley-ball ground at Praha-Holyně, sampled by Prokop 1991; C + P.
36. Lower Devonian, Dalejan, uppermost part of the Třebotov Limestone, section at Praha-Barrandov (sampling station b), 4.5 m below the base of the Choteč Limestone, sampled by Horný 1992; C + P.
 37. Lower Devonian, Dalejan, uppermost part of the Třebotov Limestone, section at Praha-Barrandov at the roadcut below the bridge, 5-10 cm below the base of the Choteč Limestone, sampled by Horný 1992; C + P.
 38. Middle Devonian, Eifelian, basal part of the Choteč Limestone (boundary layer + 20 cm), highway roadcut at Praha-Barrandov, sampled by Horný 1992; C + P.
 39. Middle Devonian, Eifelian, basal portion of the Choteč Limestone (about 150 to 170 above the base), highway roadcut at Praha-Barrandov, sampled by Horný 1992; C + P.
 40. Middle Devonian, Eifelian, Eiffel Mountains in F.R.G., derived from the "white-beds" at Nollenbach, sampled by Prokop 1990; C + P.

Methods

The samples were pulverized and mineralized with mineral acids, 0.5 g of each sample was diluted in 5 ml of HCl (1+1) in platinum crucibles. After the reaction each sample was evaporated to dryness. Then 10 ml of HCl (1+1) were added and sample again evaporated. Cooled sample with 5 ml of HCl and 10 ml of water was filtered to a 100-ml volumetric flask. The filter in the platinum crucible was heated on a hotplate to dryness and then the crucible has been placed in the furnace and gradually heated for 1000 °C (2 hours). After cooling in the dessicator the crucible's weight was determined and the residue dissolved in 5 ml HF and 3 droplets of H₂SO₄ (1+1) on the hotplate. The temperature was increased to 250 °C to evaporate sulphates and after heating in the furnace the crucible has been cooled in the dessicator. The silica contents were computed from the weights of crucibles differences.

The residue in the platinum crucible was diluted in 5-ml saturated H₃BO₃ and solution has been evaporated to dryness; then it was dissolved in 5-ml HCl and 5 ml of water and the solution added to the volumetric flask.

The chemical contents of Cu, Mn, Fe, Zn, Al were determined in the main solution. For the determination of Na, K, and Li, exactly 10 ml of the main solution was pipetted to a 50-ml volumetric flask and 5 ml of caesium reagent solution (2 g CsCl₂/100 ml H₂O) have been added. For the determination of Al, Ca, Mg, and Sr, exactly 10 ml of the main solution was pipetted to a 50-ml volumetric flask and 5 ml of K reagent solution (8 g KCl/250 ml HCl/ in a 1-l volumetric flask), and 5 ml of La reagent solution (23.45 g La₂O₃, 100 g 8-Hydroxyquinoline in 20 ml HCl (1+1) in 1-l volumetric flask) were added. Contents of the elements were determined by AAS-AES techniques. (AAS 1N, Carl Zeiss Jena) The instrumentation was used as suggested by the manufacturers.

The electron microprobe Camebax (developed by the firm Cameca, and operated at 15 kV; the ratio of counts taken for a 10 second period) was used to examine some crinoid ossicles (scyphocrinitid calyx and brachial plates from the so-called "lobolith hillside" near Řeporyje and unidentified calyx plate from the so-called "Chapel Coral Horizon" at Praha-Zlíchov) for the distribution of the main and several trace elements.

General characteristics of echinodermal stereom

The subepidermal endoskeleton of echinoderms is secreted by lime-depositing cells of mesenchyme (Ubaghs 1967) and each skeletal element is initiated intracellularly as a primordial granule which is rapidly transformed into a trifid spicule while other lime-secreting cells begin to participate in the work and the trifid enlarges and bifurcates. The bifurcations fuse at the points of contact and a very small young fenestrated plate is formed. From repeated branchings and fusions a complicated three-dimensional calcareous network is formed - an adult echinodermal skeletal element. It is well-known that such an element is composed of two distinct interlocked networks: stereom (partly discontinuous because of building separate skeletal ossicles) and stroma (continuous throughout the body wall). The hard stereom is formed of spongy or reticulated mineral substance (mineralized mass of calcareous tissue itself) the pores and small canals of which are filled up with soft stroma - organic matter (mesodermic tissue) during the animal's life (the latter may occupy as much as 60 % of the volume of a particular skeletal element). This is easily demonstrated by decalcifying a skeletal piece of a living echinoderm: the decalcification produces an organic residue pierced by holes that correspond to the hard calcareous stereom removed by the acid (Ubaghs 1967, p. S12). The stroma is permeable to nutritive fluids and, therefore, serves for nutrition of the skeletal elements, repairs or restores them when damaged or lost. After Ubaghs (1967, p. S14) the network structure varies in different parts of an individual as well as from one species to another, and the lime-secreting cells produce the skeletal elements partly by peripheral excretion but also have the power of resorbing and redepositing of calcium carbonate (the intimate relation between stroma and stereom can explain how the skeletal elements enlarge during ontogenetic development).

After the original study of Clarke - Wheeler (1922) the echinodermal skeleton is composed of 71 to 95 % calcium carbonate with a moderate content of magnesium carbonate in ionic substitution (3 to 15 %). The proportion of MgCO₃ in echinodermal skeletons is at least partially temperature-dependent (i.e., the more magnesian populations of echinoderms are those from the warm seas). In echinodermal skeletons there are also reported (Clarke - Wheeler 1922) small amounts of phosphate, calcium sulphate, salts, alumina and iron, and traces of strontium, barium, copper, zinc, manganese, cobalt, nickel, cadmium,

and some other elements. The first chemical analysis of a crinoid skeleton (*Metacrinus rotundus* from Japan with "11.72 per cent of magnesium carbonate") was published by H. W. Nichols in 1906. This result attracted attention of the famous zoologist and crinoid specialist, Austin H. Clark and at his request two other analyses were made (Clark 1911) which suggested that crinoids might be really "highly magnesian". The most important analyses were made at his request on 22 specimens of recent crinoids (Clarke - Wheeler 1914). The analyses of the latter authors point to an important result - "relation between temperature (i.e. both the latitude and the depth must be taken in account) and the magnesia content of crinoids". The crinoids from the relatively shallow depths in the Tropics are highest in their magnesian content but those from the Arctic and Antarctic regions are lowest. After A. H. Clark (in Clarke - Wheeler 1914, p. 36) there exists further general relation - between temperature and "compactness" of the crinoid skeleton (crinoids from warm regions have the most compact skeletons) which is also to some extent dependent upon the size of the particular species. In other words, structure, size and chemical composition of crinoid skeletons are correlated with the temperature of seawater. For example, in the genus *Heliometra* we find one of the largest but of the least compact skeletons, moreover bearing the lowest magnesian content among all species examined by Clarke - Wheeler (1914).

Although the recent skeletal ossicles of Echinodermata are typically high-Mg calcite, fossil echinodermal ele-

ments are mostly low-Mg calcite. Weber (1969) made hundreds of analyses of this high-Mg calcite on recent echinodermal skeletal elements (echinoids, ophiuroids, crinoids, holothuroids, asteroids) and has shown that the content of Mg^{2+} varies within different skeletal elements of the same specimen (especially in echinoids, e.g., the difference in Mg content between coronal plates and teeth) and even within a single skeletal element.

Interestingly, the fossil crinoid ossicles are uniformly low-Mg calcite regardless their stratigraphical position or regional geological condition (Clarke - Wheeler 1914, analyses of the material supplied by Frank Springer). If we assume that this low-Mg calcite was originally high-Mg, then the Mg^{2+} must have been lost either by calcitization or by incongruent dissolution (Chilingar 1962). However, the slow rate of lattice diffusion makes the latter hard to justify. The transformation of high-Mg calcite to low-Mg calcite may be a process of diagenetic calcitization during which the calcite is completely repopulated with oxygen and carbon isotopes in equilibrium with the pore water. In general, the fact that this change happens early in diagenesis may reflect the greater solubility of higher-magnesian calcites. The true nature of the change of high-magnesian calcites during diagenesis may be decipherable through examination of their isotopic history. After Bathurst (1971, p. 50) a skeleton altered by incongruent dissolution will keep the primary CO_3^{2-} anion groups that were originally associated with Ca^{2+} ions, whereas that altered by total congruent dissolution and precipitation will acquire a totally new complement of CO_3^{2-} groups with new values of ^{18}O and ^{13}C . In fact, the diagenetic alteration almost always results in ^{18}O depletion of carbonates (see also the chapter on isotopes!).

The first study on crinoid skeletal crystallography was made by Kirchner (1929). The most important characteristic of echinodermal skeletal elements is that when any individual skeletal plates, spines, spicules, ossicles or teeth are examined in polarized light or by X-ray diffraction, they behave as if they are single crystals of calcite. This phenomenon represents one of the most intriguing puzzles in biomineralization which has been under discussion for more than 65 years (see especially Raup 1959, 1960, 1968; Towe 1967; Donnay - Pawson 1969; Nissen 1963, 1969; O'Neill 1981; Albeck - Aizenberg - Addadi - Weiner 1993). According e.g. to Donnay - Pawson (1969) X-ray diffraction studies confirm that, with few exceptions, each skeletal element of echinoderms is a single crystal of magnesium-rich calcite and that a relation exists between the shape of the element and the crystallographic *a*- and *c*-axes. These exceptions include the teeth of echinoids, and the calcareous ring as well as the anal teeth of holothurians. The tubercles of an echinoid plate begin their growth as parts of the single crystal of the plate; under the mechanical action of the spines that are attached to them, they become partly polycrystalline, as shown by scanning electron microscopy and by X-ray powder diffraction.

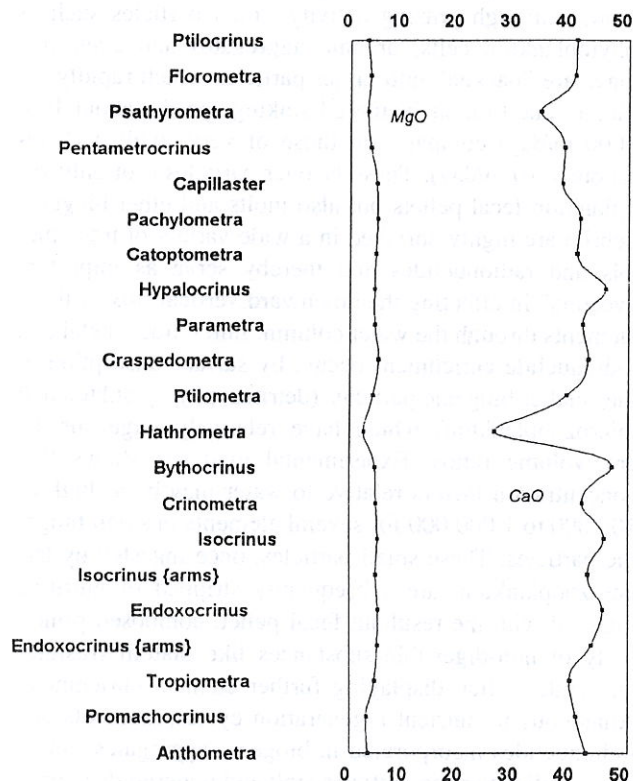


Fig. 1. CaO and MgO content in skeletons of recent crinoids (in % after Clarke - Wheeler 1914)

However, our knowledge of this phenomenon is still uneven and comes largely from the studies on recent echinoids. On the other hand, we have many interesting informations. For example, we know that in spite of their complexity and exceptional structure mentioned above, the recent echinoid teeth also behave optically as if they were constructed of just a few single crystals (Lowenstam - Weiner 1989). The same is true with the morphology of the small triradial spicule mentioned above and formed early in the morphogenesis. The triradial also reflects the crystallography of calcite (each of the radii of this triradial spicule is perfectly aligned with one of the negative directions of the *a* crystallographic axes of the calcite, while with additional growth, the so-called "body rod" forms a right angle and the long axis of the spicule is then perfectly aligned with the calcite *c* crystallographic axis). In the coronal echinoid plates the *c* crystallographic axis is generally either normal to the large surfaces, or nearly tangential to them and parallel to the meridional columns of the ambulacral and interambulacral plates. In both cases, however, the *c* lies in a plane that is radially disposed to the echinoid's symmetry. Some cidarids and arbaciids have *c* normal to the ambulacral plate but tangential to the interambulacral plate. In most echinoids, the symmetry of the apical system is related to the bilateral symmetry of the echinopluteus and not to the adult symmetry. The calcite *c* crystallographic axis tends to be transversely oriented and very rarely it does not lie in the radial plane of the main axis of the echinoid test. In crinoids and blastoids both kinds of orientation are known, i.e. *c* normal to plate or tangential-meridional. There is also a suggestion of a tendency in asteroids and ophiuroids for *c* to have a dorso-ventral alignment. In the crinoid columnal the axis of the axial canal is parallel to the calcite *c* crystallographic axis (see summary in Bathurst 1971). Fossilization does not modify the original orientation of the calcite crystallographic axes unless the mineral was completely dissolved and reprecipitated (Ubaghs 1967). Why? After Bathurst (1971) there seems to be a possibility that the new low-magnesian calcite nucleated epitaxially on pre-existing calcite which in turn preserved the original crystallographic orientation of the stereom. Really, after the fossilization, the stroma generally is replaced by secondary calcite, which invariably is oriented crystallographically with the calcite of the original stereom (Ubaghs 1967).

Biogeochemistry of marine animals

In shallow coastal environments, sediments play a critical role in the biogeochemical cycling of such substances as nutrients and trace metals. By determining the distribution of nutrients and trace metals within sediments, transport processes play a central role in setting the chemical environment there. Because the effects of macrofauna on sediment chemistry are determined by the number, kinds, and sizes of animals, the sediment composition varies in space and time in accordance with the particular benthic community present (Aller 1982). Shallow-water deposit feed-

ers selectively ingest particular grain-size fractions of the sediments and there are interspecific differences in particle size preference. Partitioning of sediments with respect to size may be more likely in the deep sea where macropredation would permit species (deposit feeders) to ingest selectively the more labile components of the sediments. If the deposit feeders in the deep sea partition the sediments with respect to the grain size, then, at least in part, their species diversity may be a function of the sediment particle size distribution. On the other hand, the sediment particle size distribution reflects habitat complexity for the particular benthic community present. For example, in the deep sea, according to Etter - Grassle (1992) the species diversity is a significant positive function of the sediment particle size distribution. Moreover, the insufficiently known effect of biological diversity on the ecosystem biogeochemistry must be strong and both the population biology and ecosystem studies have progressed to the point that the background knowledge and techniques are now in place to begin a rigorous examination of such effects (Vitousek - Hooper 1994). On the other hand, it is very interesting that the seafloor sediment geochemistry closely matches the particle composition of the surface waters. It is because most of the inorganic and organic particles in the surface waters are eaten at least once by small animals and during this process the particles are aggregated into larger, heavier fecal pellets that reach the seafloor in a few or several days and, therefore, the ocean currents do not carry such particles thousands of miles from their source as was originally expected (see e.g. Colgan 1994). In other words, through grazing activity, small particles such as phytoplankton cells, organic aggregates and even fine clays are "packed" into larger particles which rapidly sediment due to their increased sinking speeds (about 100-1000 m/day) compared to those of very small particles (about 1-10 m/day). These heavier particles (not only zooplankton fecal pellets but also molts and other biogenic debris) are highly enriched in a wide variety of trace metals and radionuclides and thereby serve as important "vectors" in effecting the downward vertical flux of these elements through the water column. Initial trace metal and radionuclide enrichment occurs by surface adsorption to the smaller biogenic particles (detritus, phytoplankton and microzooplankton) which have relatively large surface area/volume ratios. Experimental evidence shows that concentration factors relative to water may be as high as 100 000 to 1 000 000 for several elements in small biogenic particles. These small particles, once ingested by larger zooplankton, are subsequently stripped of nutritive material with the resultant fecal pellet, composed principally of non-digestible substances like diatom frustules and chitin, often displaying further element enrichment. Analogous to nutrient regeneration cycles, elements and radionuclides incorporated in biogenic aggregates can be remineralized as the particles sink and undergo decomposition. Laboratory studies have shown that for many elements and radionuclides, half-times for release are on the order of several days which suggests that a substantial

fraction of the element in large, rapidly sinking particles would be transported to great depth. For certain elements and/or under certain conditions, large particles sinking through the water column may scavenge metals and radionuclides onto their surfaces thus increasing their element concentration with depth (Fowler 1989). About 50 years ago, Vinogradov (3 volumes in Russian 1935, 1937, 1944, in English 1953) published his most important work "The Elementary Chemical Composition of Marine Organisms". In the classic period, this was the last major attempt to systematically summarize all that was known about trace metal and metalloid content of marine biota. Most of Vinogradov's data were devoted to levels of C, H, N, O, P, S, Na, K, Mg, and Ca. Unfortunately, the limited information on trace metals was derived from what is now considered insensitive and imprecise analytical methodologies. In the U.S.A., the most pioneering works may be attributed to Heinz Adolf Lowenstam, professor of palaeoecology in Pasadena (from his enormous body of works see e.g. Lowenstam 1954a,b, 1961, 1981, and esp. the most recent and most fascinating book, Lowenstam - Weiner 1989). An interesting summary of the old period, written in Czech, was given by Zýka (1966) in his first volume of the "Olomouc series". During the past three decades, however, newer and more accurate instrumentation, especially atomic absorption spectrophotometry became available to marine scientists. Increasing usage of these techniques by environmentalists, radioecologists and others has caused a disproportionate increase in the technical literature on trace metals, i.e., elements in marine flora and fauna occurring at concentrations less than 100.0 parts per million (i.e., 100.0 mg/kg) on a dry weight basis. The first attempt of the new period to systematically summarize our improved knowledge is the book of Eisler (1981) in which the following elements are emphasized: Al, Sb, As, Ba, Be, Bi, B, Cd, Ce, Cs, Cr, Co, Cu, Ga, Ge, Au, Fe, La, Pb, Li, Mn, Hg, Mo, Ni, Nb, Re, Rh, Rb, Ru, Se, Si, Ag, Tl, Sn, Ti, W, V, Y, Zn, Zr. Unfortunately, data on the elements Na, K, Ca, and Mg, although they were especially abundant, were excluded, as their concentrations in marine organisms were almost always substantially in excess of the 100.0 mg/kg dry weight limit that was set arbitrarily as a trace concentration. According to Eisler (1981), although many echinoderms are prime movers of sediments and detritus in the sea and are very probably extremely important in the cycling of trace metals, little work has been conducted in this subject. And again, the investigations are concentrated predominantly on echinoids and partly on asteroids (see Eisler 1981, p. 427-455 and references therein). Further recent contributions are published in Dallinger - Rainbow (1992). It is also interesting that all around the world (of course, including Barrandian) skeletons of various groups of invertebrates undergo different mineralogical transformation under the same diagenetic conditions. Changes in water chemistry and variations in temperature are often used to explain this phenomenon. However, these parameters are not adequate to justify why, under the same diagenetic conditions, the

skeletons of (for example) sponges and corals do not undergo the same mineralogical transformations (Marin - Gautret 1994). The latter authors point especially to the fact that to interpret this anomaly it is necessary to take into account the peculiar feature of biogenic carbonates produced by the two taxa (in their example sponges and corals), the presence of an organic matrix closely linked to the mineral phase. This matrix, secreted during skeletogenesis, has two presumed functions: binding of calcium ions and orientation of crystal growth. Even after death and burial of the organisms, strong molecular interactions between the organic - mainly proteinaceous - and the inorganic phases will be maintained. The divergent diagenetic trends observed in sponge and coral skeletons could be partially induced by the biochemical differences in the organic matrix. Similarly, in echinoderms, in which the interface between the inorganic crystalline and organic amorphous matter in their skeletal elements appears to be the first example reported in nature of a periodic minimal surface (Donnay - Pawson 1969), it seems possible that the echinodermal diagenetic trend could be induced by biochemical characteristics in their organic matrix.

Biogeochemistry of Barrandian crinoids

It is clear that in Barrandian crinoids, uptake of trace elements from the dissolved phase occurred probably (like in oxygen) via the tube feet, while from the particulate sources occurred by direct ingesting and assimilating. Crinoids (esp. camerates and inadunates) certainly represented the dominant suspension-feeding organisms in shallow-water environments of the Barrandian seas. In many areas they formed extensive and ecologically very important crinoid "gardens", serving as one of the most effective agents in removal of particulate matter from the water column, and affecting profoundly biodeposition and chemical properties of the carbonate sediments. Thus, they played a role very similar to that reported in recent bivalves, maintaining and controlling phytoplankton biomass of shallow waters at relatively optimal levels (for references see Wang - Fisher 1996).

We have confirmed the above speculation by observations of striking differences between the contents of trace elements in skeletal elements of the pelma (esp. in columnals) and skeletal elements of the crown (esp. in brachials). The differences have turned to be too large that they cannot be caused by analytical errors. They have verified that some parts of the living crinoid body had accumulated certain trace metals. Results of the analyses have demonstrated conclusively that the Barrandian crinoids exhibited biomagnification of certain elements and were very important in the cycling of trace metals in the sea.

Isotopes

Changes in sea level can be reconstructed from the isotopic composition of seawater "locked" in chemically unaltered carbonate skeletons of some invertebrates. Thanks to

Urey (1947) who predicted that equilibrium carbonate-water stable isotopic fractionation during shell formation is temperature dependent, the potential capability of carbonate-secreting invertebrates to record climatic changes is known since the early 1950's (see especially the pioneering works of McCrea, 1950; Epstein - Buchsbaum - Lowenstam - Urey 1951, 1953; Urey - Lowenstam - Epstein - McKinney 1951; Epstein - Lowenstam 1953). At present days, especially foraminifera are used for these analyses (see e.g., Chappell - Shackleton 1986).

Generally, an increase in temperature results in an increase of the light isotope ^{16}O , and, on the other hand, a decrease of temperature results in analogical increase of the heavy isotope ^{18}O , being incorporated into the calcite lattice of both inorganically and organically precipitated carbonates. The evaporated water (water vapour and water of clouds) is enriched in ^{16}O while the remaining ocean water is, therefore, enriched in ^{18}O . Of course, during glacial maxima, the carbonates precipitated in seawater (and the seawater itself, too) have more positive $\delta^{18}\text{O}$ values. Water condensed from the atmospheric vapour is enriched in ^{18}O . Of course, the residual vapour is depleted in ^{18}O . Therefore, subsequent precipitation is consequently lighter than the initial precipitation. The final result is that some Antarctic snow is extremely depleted in ^{18}O relative to tropical rain (Dansgaard 1964). Because ice has a preference for absorbing water enriched in the oxygen isotope ^{16}O , it leaves the lowered ocean enriched in H_2^{18}O . When the ice mass decreases and sea level rises, the oceans are enriched in H_2^{16}O . The $^{18}\text{O}/^{16}\text{O}$ ratio in calcite is therefore strongly dependent on the temperature and isotopic composition of seawater.

Williams - Bé (1979) have discovered also seasonal variations in the $^{18}\text{O}/^{16}\text{O}$ ratio of calcite shells of recent planktonic foraminifera (in the Sargasso Sea off Bermuda) as a direct function of surface water temperature. The oxygen isotope thermometry may be really very important both for recent and fossil carbonates.

For the Lower Devonian time, only a limited number of analyses are known. For instance, partial oxygen-isotope analysis has been performed by Gao (1993), based curiously only on three brachiopod shells coming from the limestones of the Haragan and Bois d'Arc formations, upper Hunton Group in south-central Oklahoma.

Weber (1968) studied fractionation of the stable isotopes of carbon and oxygen in recent echinoderms, particularly asteroids, ophiuroids and crinoids, Weber - Raup (1966) in echinoids. Weber - Raup (1966) reported that although the isotopic compositions of echinoid spines are similar to those of molluscs and foraminifera, echinoid tests and lantern skeletal elements exhibit extremely large $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ variations. Weber (1968) reported that echinoderms really differ from most carbonate-secreting organisms in the isotopic composition of their skeletal calcite. He pointed to a pronounced "vital effect" in echinoderms resulting not only in significant $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ va-

riations at the species and higher taxonomic levels but also for different skeletal elements within a single animal. He also suggested a "primitive" respiratory system in echinoderms, i.e. a respiratory system of very low "efficiency", which provides ample opportunity for the interaction of metabolic CO_2 with HCO_3^- and CO_3^{2-} ions in their coelomic perivisceral fluid. On the other hand, because of relatively normal isotopic composition of ophiuroid skeletal calcite, the latter author inferred for brittlestars the most "efficient" respiratory system among the echinoderms. For the present study the most important Weber's conclusions is that the skeletal calcite of living crinoids is significantly enriched in ^{12}C and moderately enriched in ^{16}O with respect to "inorganic" carbonate precipitated from the same seawater at the same temperature.

The effect of diagenetic temperatures, diagenetic fluids and of the original isotopic composition of carbonates can be complex. For example, the $\delta^{18}\text{O}$ of planktonic shells can be increased because of the influence of colder bottom waters, while higher diagenetic temperatures can decrease the $\delta^{18}\text{O}$ values. On the other hand, with the exception of methanogenic environment, the $\delta^{13}\text{C}$ values generally decrease with diagenesis (Grossman 1994).

Carbon and oxygen isotopic compositions of the samples

The skeletal calcite of the Barrandian fossil crinoids seems to be, in relation to the above mentioned discoveries of Weber (1968), really moderately enriched in ^{16}O but it is not significantly enriched in ^{12}C , even moderately enriched in ^{13}C . Unfortunately, the isotopic composition of all samples is evidently highly influenced by the meteoric environment of the "white beds" which has greatly altered the original isotopic signal. Meteoric environments are commonly known as zones of active carbonate diagenesis because freshwaters are in most cases undersaturated with respect to carbonate building material. Aragonite and high magnesian calcite dissolve rapidly and provide material for newly formed low magnesian calcite. As stated above, meteoric water is depleted in ^{18}O relative to seawater and, therefore, the diagenesis in meteoric environment tends to lower the $\delta^{18}\text{O}$ values of the resulting altered carbonate (Grossman 1994, however, exceptions may also occur - see Meyers - Lohmann 1985). The generally high $\delta^{13}\text{C}$ values in our samples have probably resulted from the same diagenetic effect because of rich occurrence of carbonate minerals in the area of the Barrandian "white beds" (the carbon has been probably derived from the dissolution of less stable carbonate minerals). In the problematical weathered rock sample from the lowermost Dvorce-Prokop Limestone there is probably at least a small input of the carbon derived from the oxidation of organic matter (the value is here below the standard).

In our 40 samples, the stable isotopes of carbon and oxygen have been determined by Ing. F. Buzek (Stable Isotope Laboratories of the Czech Geological Survey,

Praha-Barrandov) on the mass spectrometer Finnigan MAT-251. The values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (in parts per thousand related to PDB or Peedee belemnite) have been established for the rock, and calcareous skeletons of crinoids and brachiopods. The latter have been included because of the fact that at present days the fossil brachiopod shells are frequently used as a relatively faithful record of the chemical and isotopic composition of the ancient ocean water in which they grew, owing to their very stable mineralogy.

The samples under study are briefly listed below (abbrev.: C = skeletal elements of crinoid crowns (esp. brachials), P = skeletal elements of crinoid pelma (esp. columnals), B = brachiopods, R = rock):

1. Upper Silurian, Přídolí Formation, uppermost part of the Přídolí Formation, western margin of the so-called "lobolith hillside" near Praha-Řeporyje, beds directly underlying those with the common pisocrinid *Pisocrinus ubaghsi*, sampled by Prokop in 1982; P (epipelagic scyphocrinitids): $\delta^{13}\text{C}_{\text{PDB}}$ 1.2 and $\delta^{18}\text{O}_{\text{PDB}}$ -5.4; C (epipelagic scyphocrinitids): $\delta^{13}\text{C}_{\text{PDB}}$ 1.2 and $\delta^{18}\text{O}_{\text{PDB}}$ -5.6; B (only *Dayia navicula bohémica*): $\delta^{13}\text{C}_{\text{PDB}}$ 1.6 and $\delta^{18}\text{O}_{\text{PDB}}$ -6.1.
2. Lower Devonian, Lochkovian, pink-coloured biostrome Kotýs Limestone, quarry "Černá skála" near Praha-Řeporyje, sampled by Petr 1987; P: $\delta^{13}\text{C}_{\text{PDB}}$ 2.5 and $\delta^{18}\text{O}_{\text{PDB}}$ -4.2; C: $\delta^{13}\text{C}_{\text{PDB}}$ 2.6 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.6.
3. Lower Devonian, Pragian, Koněprusy Limestone (perireefal facies), Plešivec Hill near Koněprusy, sampled by Prokop 1992; P: $\delta^{13}\text{C}_{\text{PDB}}$ 1.8 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.2; C: $\delta^{13}\text{C}_{\text{PDB}}$ 2.4 and $\delta^{18}\text{O}_{\text{PDB}}$ -2.5; R: $\delta^{13}\text{C}_{\text{PDB}}$ 1.5 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.2.
4. Lower Devonian, Pragian, Loděnice Limestone, "Červený lom" quarry near Praha-Klukovice (lowermost 20 cm at the sampling station C), sampled by Horný 1991; P: $\delta^{13}\text{C}_{\text{PDB}}$ 2.6 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.1; C: $\delta^{13}\text{C}_{\text{PDB}}$ 2.4 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.4; B: $\delta^{13}\text{C}_{\text{PDB}}$ 2.8 and $\delta^{18}\text{O}_{\text{PDB}}$ -2.8.
5. Lower Devonian, Pragian, Loděnice Limestone, "Červený lom" quarry near Praha-Klukovice (sampling station D), sampled by Prokop 1991; P: $\delta^{13}\text{C}_{\text{PDB}}$ 2.3 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.1; C: $\delta^{13}\text{C}_{\text{PDB}}$ 2, 3 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.2; B: $\delta^{13}\text{C}_{\text{PDB}}$ 2.3 and $\delta^{18}\text{O}_{\text{PDB}}$ -2.8; R: $\delta^{13}\text{C}_{\text{PDB}}$ 1.6 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.7.
6. Lower Devonian, Pragian, lower part of the Loděnice Limestone, Praha-Smíchov, "Na Konvářce", sampled by Horný 1991; P: $\delta^{13}\text{C}_{\text{PDB}}$ 3.0 and $\delta^{18}\text{O}_{\text{PDB}}$ -4.3; C: $\delta^{13}\text{C}_{\text{PDB}}$ 2.8 and $\delta^{18}\text{O}_{\text{PDB}}$ -4.5; B: $\delta^{13}\text{C}_{\text{PDB}}$ 2.5 and $\delta^{18}\text{O}_{\text{PDB}}$ -4.9; R: $\delta^{13}\text{C}_{\text{PDB}}$ 2.5 and $\delta^{18}\text{O}_{\text{PDB}}$ -5.7.
7. Lower Devonian, Pragian, basal part of the Dvorce-Prokop Limestone (about 1 to 2 m above the boundary with the underlying Loděnice Limestone), "Červený lom" quarry near Praha-Klukovice, sampled by Horný 1991; P: $\delta^{13}\text{C}_{\text{PDB}}$ 2.1 and $\delta^{18}\text{O}_{\text{PDB}}$ -2.9; C: $\delta^{13}\text{C}_{\text{PDB}}$ 2.0 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.2; B: $\delta^{13}\text{C}_{\text{PDB}}$ 2.2 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.2; R: $\delta^{13}\text{C}_{\text{PDB}}$ -1.4 and $\delta^{18}\text{O}_{\text{PDB}}$ -5.1.
8. Lower Devonian, Pragian, Dvorce-Prokop Limestone, north-eastern wall of the quarry at St. Prokop near the road to the former church, sampling station 3/4-4, Praha-Hlubočepy, sampled by Prokop 1993; P: $\delta^{13}\text{C}_{\text{PDB}}$ 1.9 and $\delta^{18}\text{O}_{\text{PDB}}$ -3, 6; C: $\delta^{13}\text{C}_{\text{PDB}}$ 1.7 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.6; B: $\delta^{13}\text{C}_{\text{PDB}}$ 2.1 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.2.
9. Lower Devonian, Pragian, Dvorce-Prokop Limestone, quarry "U kantiny" near Praha-Řeporyje, 90 to 100 cm below the base of the Zlíchov Limestone, sampled by Prokop 1991; P: $\delta^{13}\text{C}_{\text{PDB}}$ 2.2 and $\delta^{18}\text{O}_{\text{PDB}}$ -4.9; C: $\delta^{13}\text{C}_{\text{PDB}}$ 1.8 and $\delta^{18}\text{O}_{\text{PDB}}$ -4.9; B: $\delta^{13}\text{C}_{\text{PDB}}$ 1.6 and $\delta^{18}\text{O}_{\text{PDB}}$ -5.4.
10. Lower Devonian, Dalejan, Třebotov Limestone, quarry "Prastav" at Praha-Holyně, sampled by L. Marek 1964; P: $\delta^{13}\text{C}_{\text{PDB}}$ 0.4 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.9; C: $\delta^{13}\text{C}_{\text{PDB}}$ 1.0 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.1; B: $\delta^{13}\text{C}_{\text{PDB}}$ 1.0 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.4; R: $\delta^{13}\text{C}_{\text{PDB}}$ 1.3 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.6.
11. Lower Devonian, Dalejan, upper part of the Třebotov Limestone, quarry "U jezírka" at Praha-Hlubočepy, uppermost 3.5 m, sampled by Prantl 1932; P: $\delta^{13}\text{C}_{\text{PDB}}$ 1.4 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.4; C: $\delta^{13}\text{C}_{\text{PDB}}$ 1.0 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.6; B: $\delta^{13}\text{C}_{\text{PDB}}$ 1.1 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.7.
12. Middle Devonian, Eifelian, basal part of the Choteč Limestone, the roadcut of the highway at Praha-Barrandov, 150-170 cm above the base of the Choteč Limestone, sampled by Horný 1992; P: $\delta^{13}\text{C}_{\text{PDB}}$ 1.2 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.3; C: $\delta^{13}\text{C}_{\text{PDB}}$ 1.4 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.3; B: $\delta^{13}\text{C}_{\text{PDB}}$ 1.7 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.7; R: $\delta^{13}\text{C}_{\text{PDB}}$ 1.8 and $\delta^{18}\text{O}_{\text{PDB}}$ -3.1.

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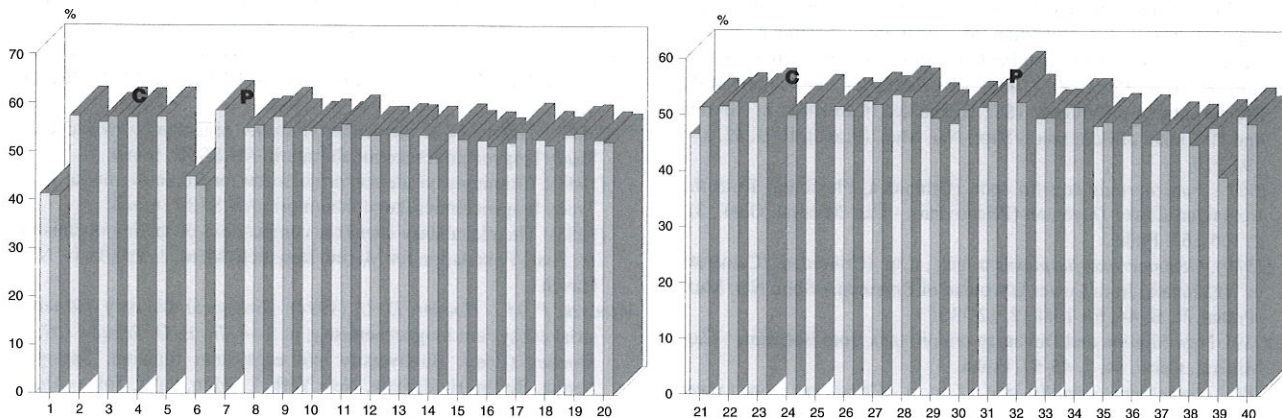
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Chemické složení kosterních elementů krinoidů (Echinodermata) ve zvětralých partiích vápenců českého spodního devonu (Barrandien)

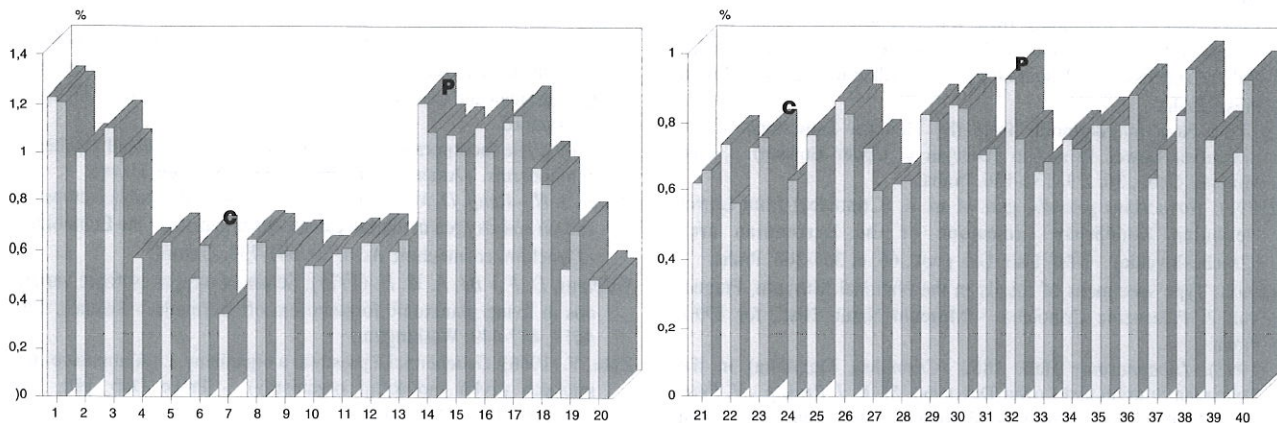
Autoři předkládají předběžnou zprávu o chemickém složení kosterních elementů krinoidů ze spodního devonu Barrandienu a podávají též stručnou interpretaci získaných dat. Celkem bylo pro chemické analýzy proplaveno 40 vzorků z nejrůznějších lokalit v barrandienských "bílých vrstvách" (především spodní devon), a navíc ještě 12 vzorků pro stanovení stabilních izotopů. Výsledky chemických analýz byly v plné shodě s předpokladem, že fosilní krinoidi mají kostru složenou z nízkohořecnatého kalcitu, a to bez ohledu na jejich stratigrafickou příslušnost či regionálně-geologické podmínky. Ve vzorcích byly stanoveny obsahy Fe, Pb, Zn, Cu, Mn, Sr, Li, Na, K, MgO, CaO a Si + organické hmoty. Za použití vzorků získaných dřívějšími autory i během začátku tohoto století na stejných lokalitách bylo provedeno též jednoduché přezkoumání moderní antropogenní kontaminace těžkými kovy. Proti našemu očekávání však nebylo zjištěno progresivní znečištění vzorků ani vzhledem ke stavu za první republiky, ani za Rakouska-Uherska, a to na žádné z lokalit (dokonce byl na některých vzorcích pozorován nepatrný úbytek koncentrace těžkých kovů). U každého vzorku pak proběhlo nezávislé měření chemického složení kosterních elementů koruny krinoidů (především brachiálií) a pelmy krinoidů (především kolumnálií). S překvapením byly zaznamenány značné rozdíly v obsahu stopových prvků, a to takové, že nemohly být v žádném případě způsobeny analytickou chybou při měření. Získali jsme tak potvrzení, že určité části těla krinoidů v sobě koncentrovaly specifické těžké kovy ještě za života. Výsledky analýz jasně prokázaly, že barrandienská krinoidi byli výraznými činiteli v koloběhu těžkých kovů v staropaleozoických mořích. U 12 vzorků bylo pak provedeno 40 měření stabilních izotopů, která se nezávisle soustředila na brachiálie krinoidů, kolumnálie krinoidů, schránky brachiopodů a vzorky hornin. Bohužel, žádné paleotploty prostředí barrandienských moří nebyly stanoveny, neboť se domníváme, že poměrně nízké hodnoty $\delta^{18}\text{O}$ a naopak vysoké hodnoty $\delta^{13}\text{C}$ (vztážené k standardu PDB) ukazují na možnou přeměnu původního izotopického signálu v diagenetickém prostředí přístupném meteorické vodě. Nutno však dodat, že interpretace chemického složení i izotopového obsahu jsou jen předběžné a nelze je proto chápat jako definitivní.

Appendix

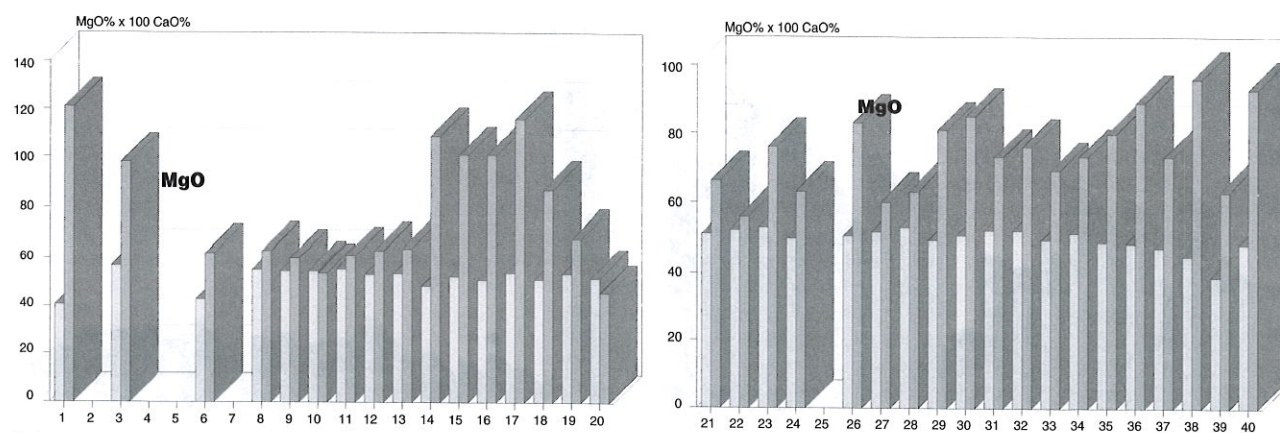
Chemical composition of Barrandian crinoids (for localization of the individual samples see the chapter "Material")



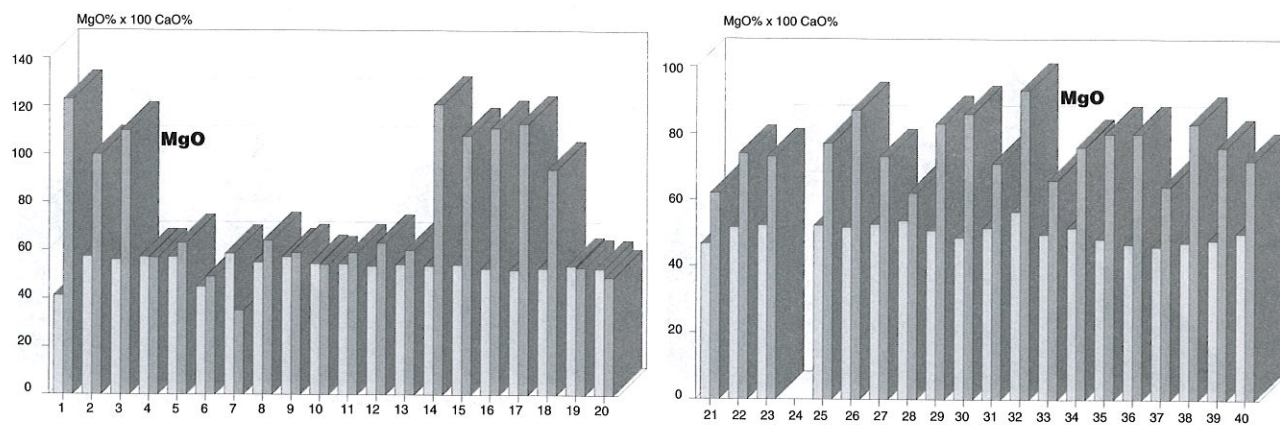
1-2. CaO content in the skeletal elements of crinoids: 1 - samples 1-20; 2 - samples 21-40



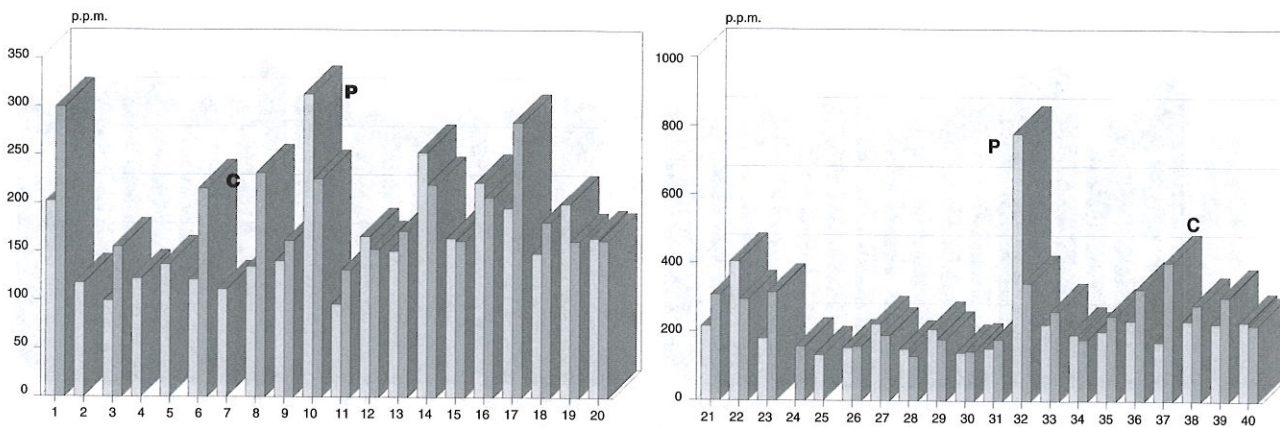
3-4. MgO content in the skeletal elements of crinoids: 3 - samples 1-20; 4 - samples 21-40



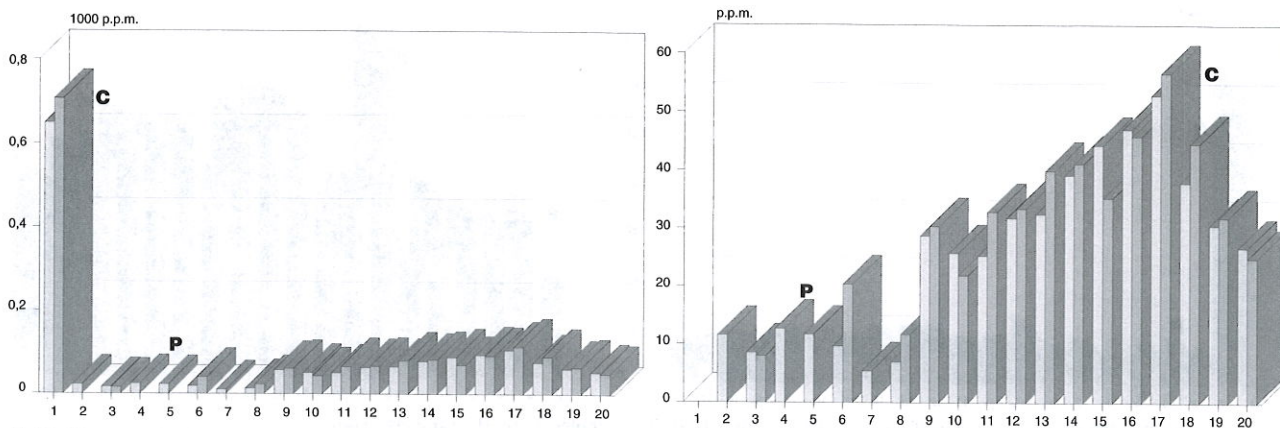
5-6. MgO (x100) and CaO relations in the crinoid crowns: 5 - samples 1, 3, 6, 8-20; 6 - samples 21-24, 26-40



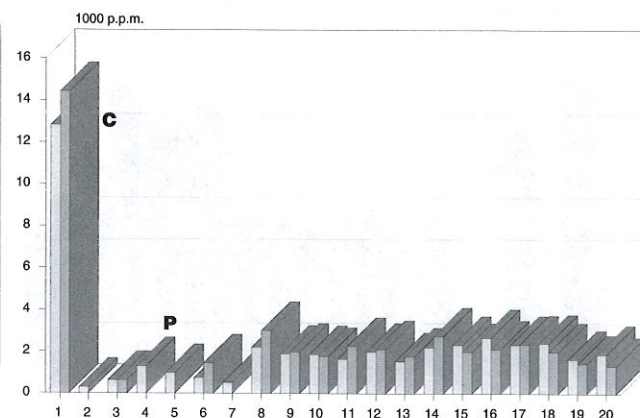
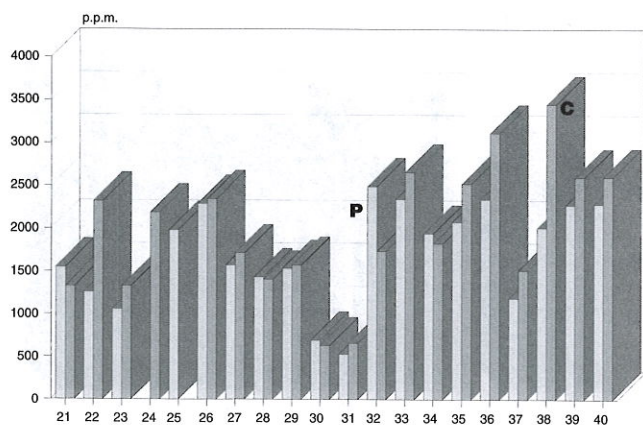
7-8. MgO (x100) and CaO relations in columns (and holdfasts) of crinoids: 7 - samples 1-20; 8 - samples 21-23, 25-40



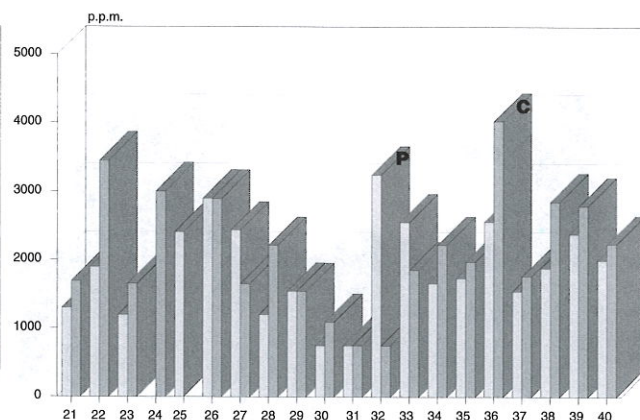
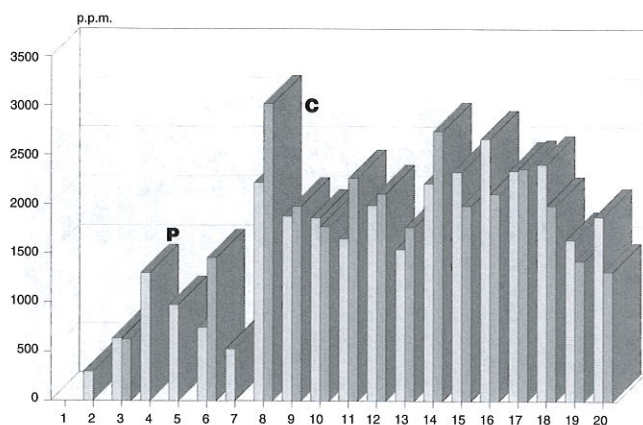
9-10. Na content in the skeletal elements of crinoids: 9 - samples 1-20; 10 - samples 21-40



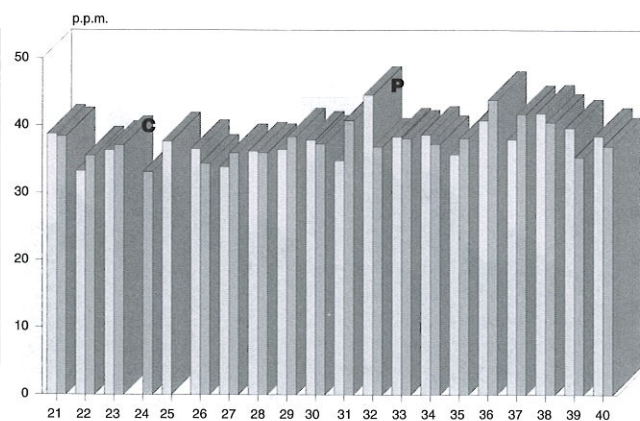
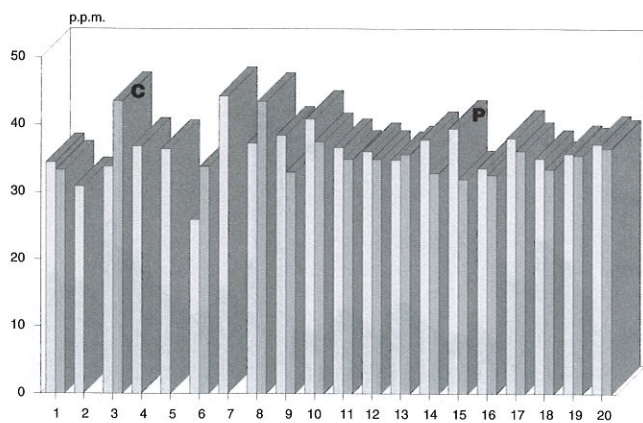
11-13. K content in the skeletal elements of crinoids: 11 - samples 1-20; 12 - samples 2-20; 13 - samples 21-40



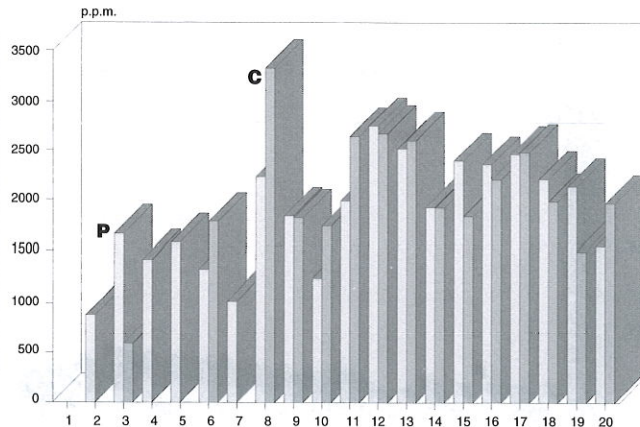
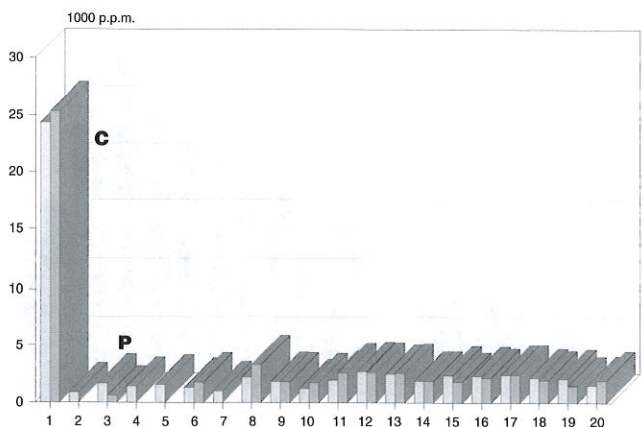
14-16. Al concentrations in the skeletal elements of crinoids: 14 - sam-



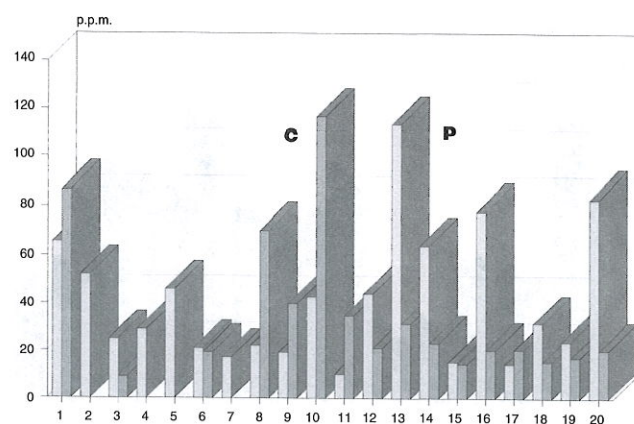
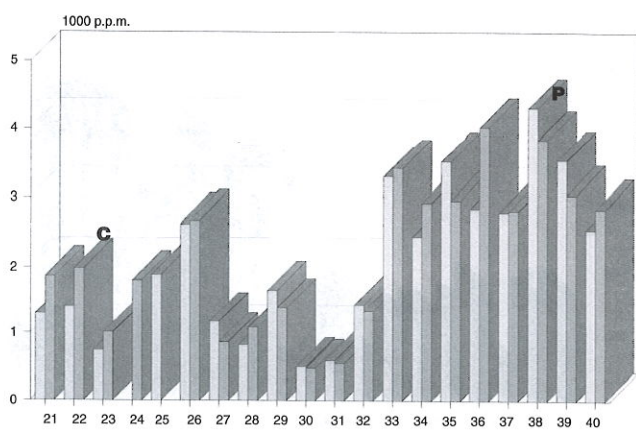
ples 1-20; 15 - samples 2-20; 16 - samples 21-40



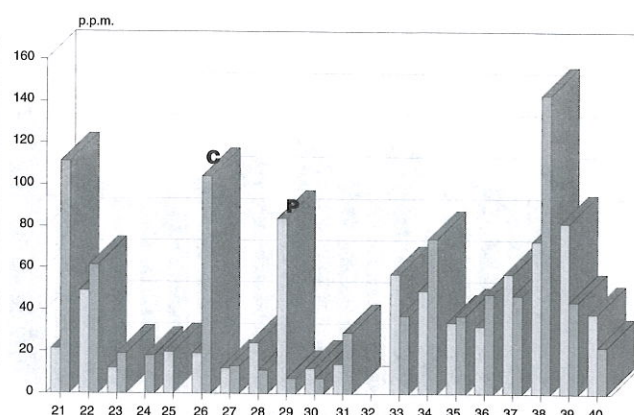
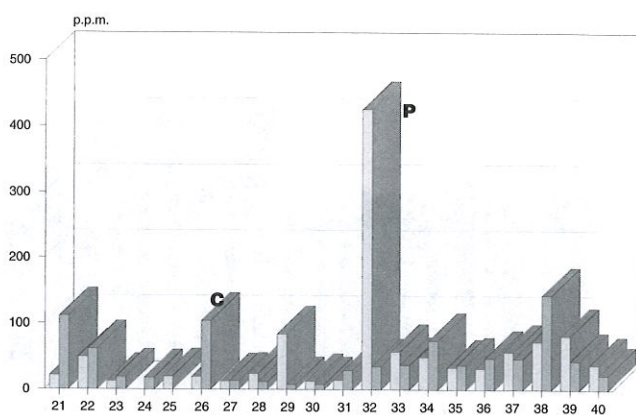
17-18. Li content in the skeletal elements of crinoids: 17 - samples 1-20; 18 - samples 21-40



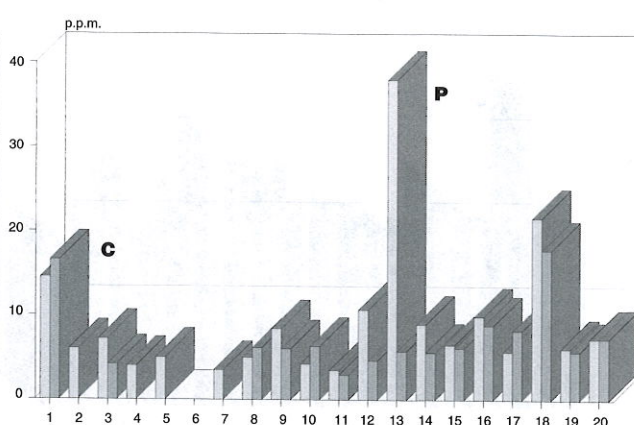
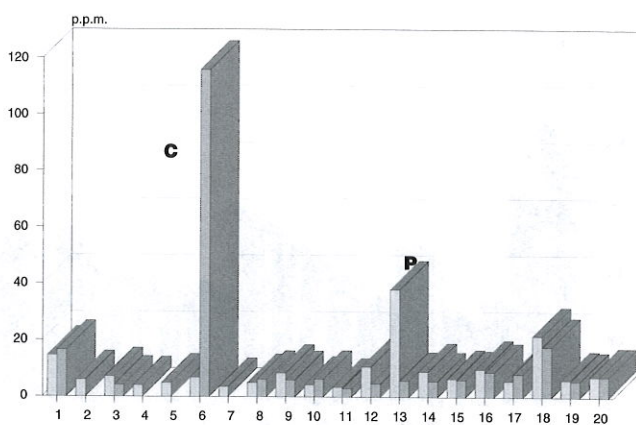
19-21. Fe content in the skeletal elements of crinoids: 19 - samples 1-20; 20 - samples 2-20; 21 - samples 21-40



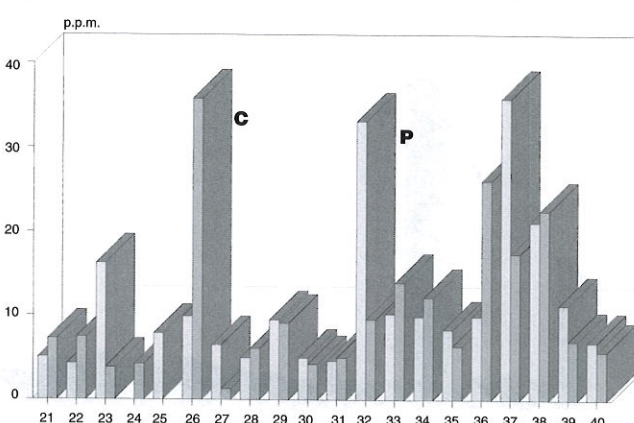
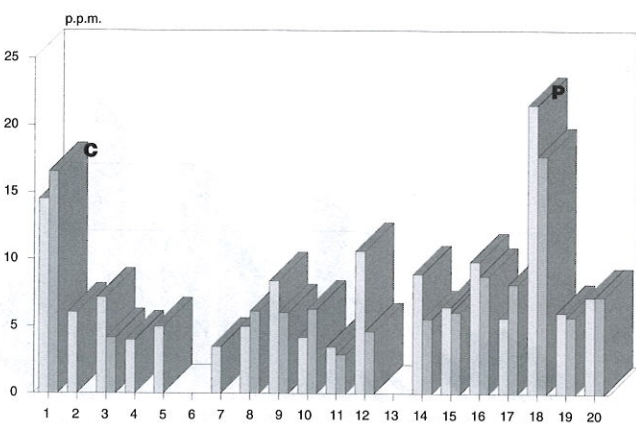
22-24. Zn concentrations in the skeletal elements of crinoids: 22 - sam-



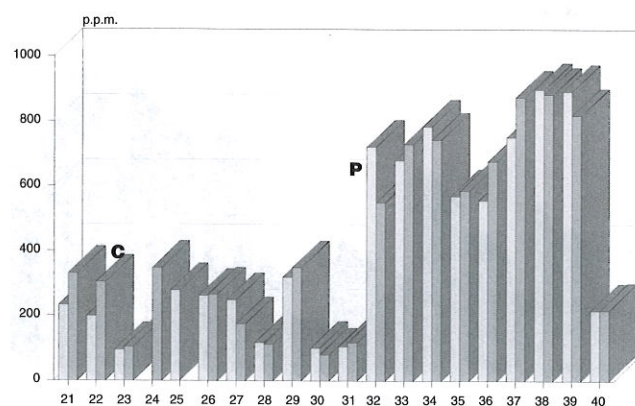
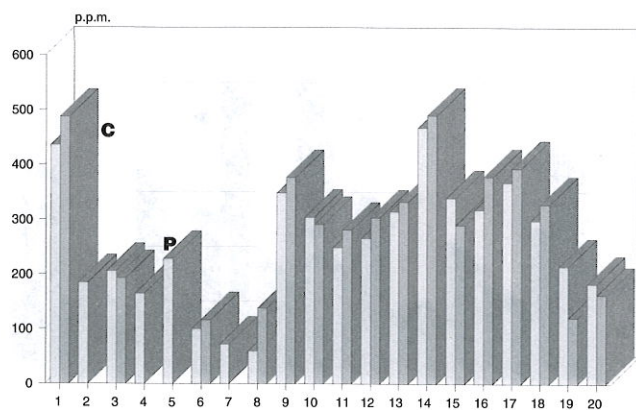
ples 1-20; 23 - samples 21-40; 24 - samples 21-31, 33-40



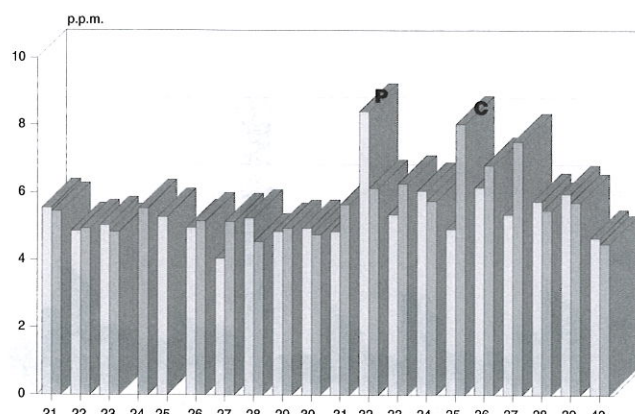
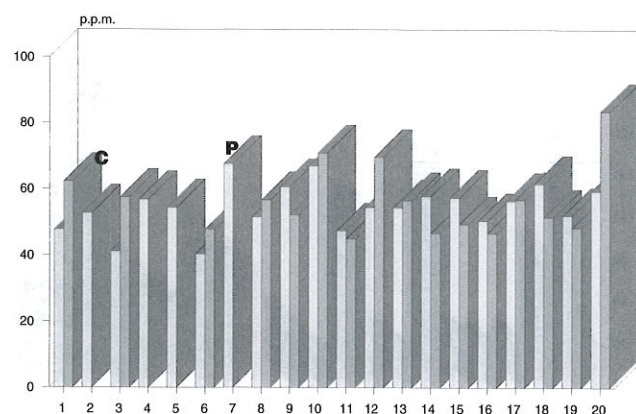
25-26. Cu concentrations in the skeletal elements of crinoids: 25 - samples 1-20; 26 - samples 1-5, 7-20



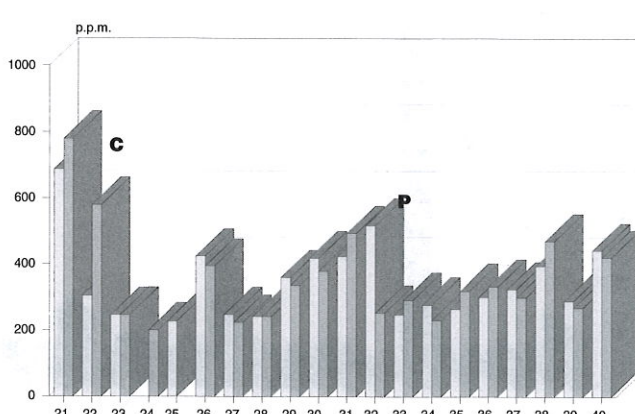
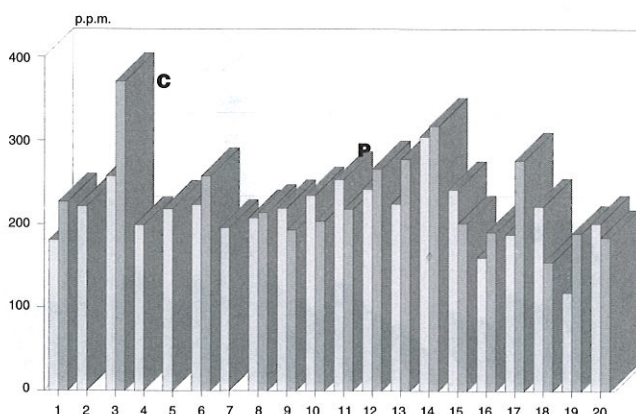
27-28. Cu concentrations in the skeletal elements of crinoids: 27 - samples 1-5, 7-12, 14-20; 28 - samples 21-40



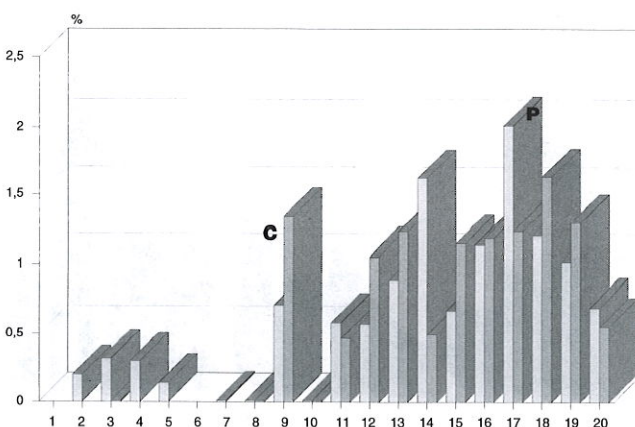
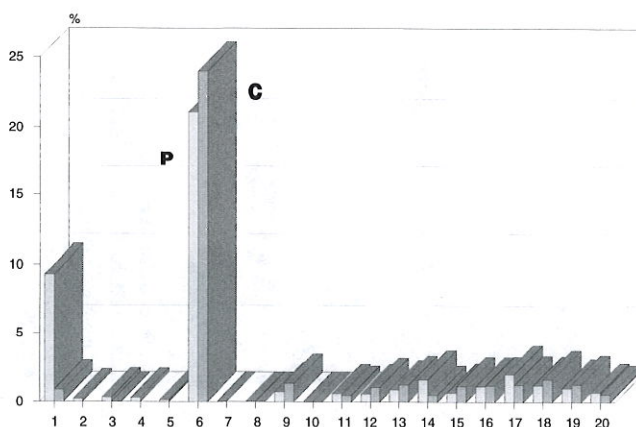
29-30. Mn concentrations in the skeletal elements of crinoids: 29 - samples 1-20; 30 - samples 21-40



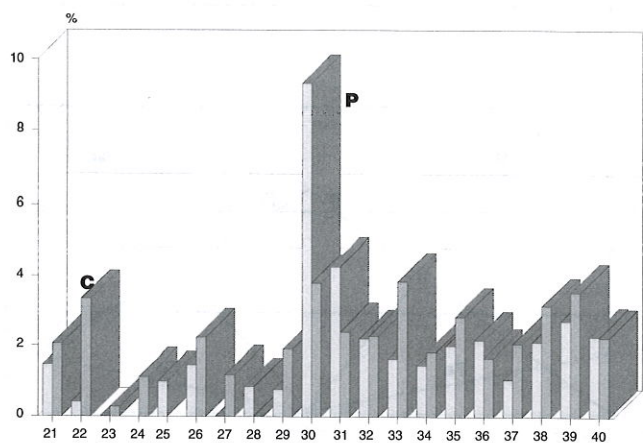
31-32. Pb concentrations in the skeletal elements of crinoids: 31 - samples 1-20; 32 - samples 21-40



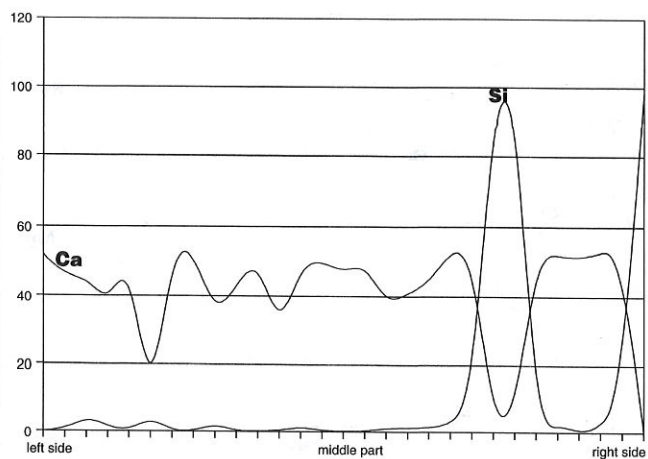
33-34. Sr concentrations in the skeletal elements of crinoids: 33 - samples 1-20; 34 - samples 21-40



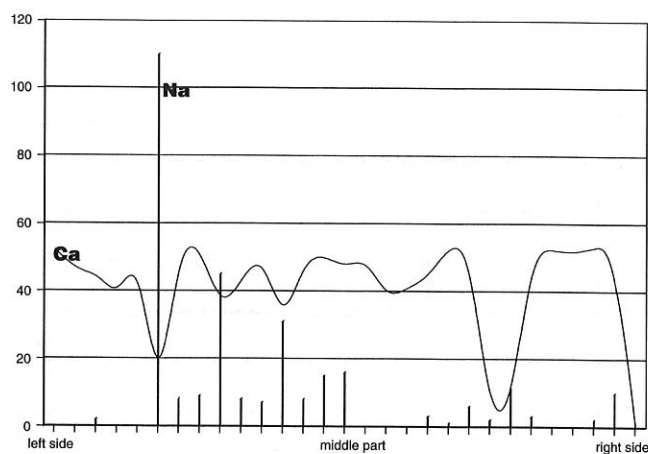
35-37. In HCl insoluble residue (esp. silica and organic matter) in the skeletal elements of crinoids: 35 - samples 1-20; 36 - samples 2-5, 7-20; 37 -



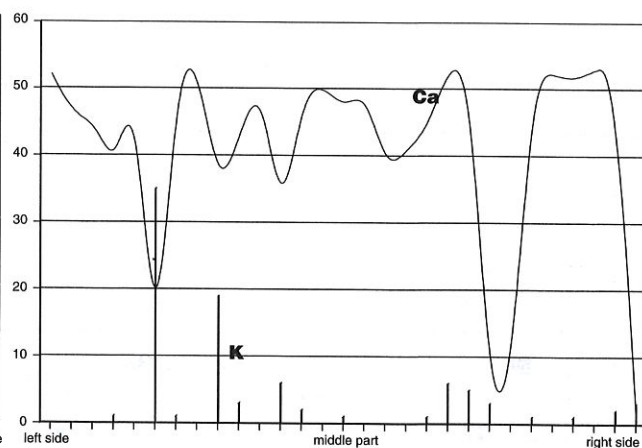
samples 21-40



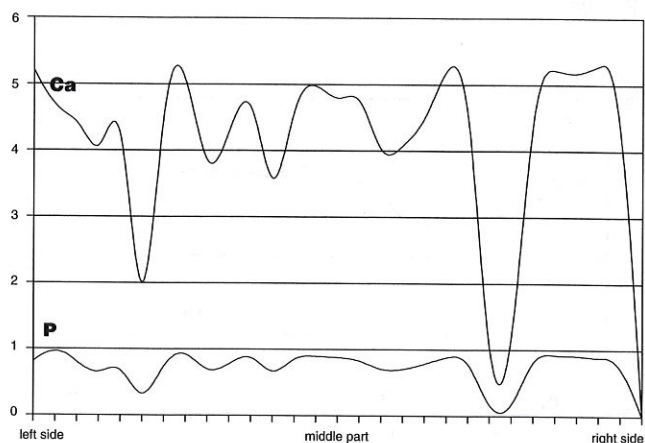
38-39. Microprobe zonal measurements of (38) Si (x1000) and Ca



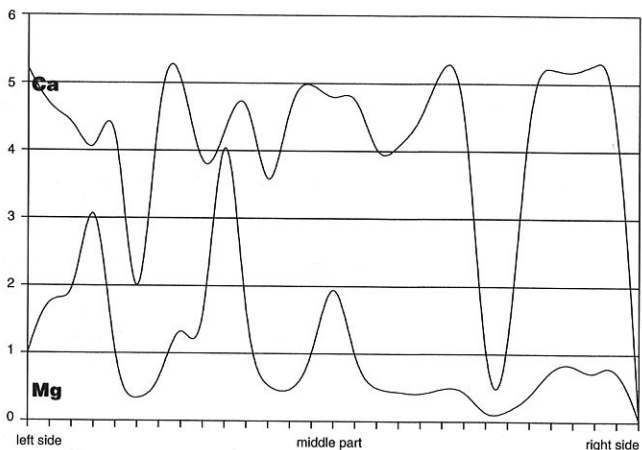
(x100), and (39) Na (x10000) and Ca (x100) contents in a calyx plate of an undetermined crinoid from Chapel Coral Horizon near Kaplička (Praha-Zlíchov)

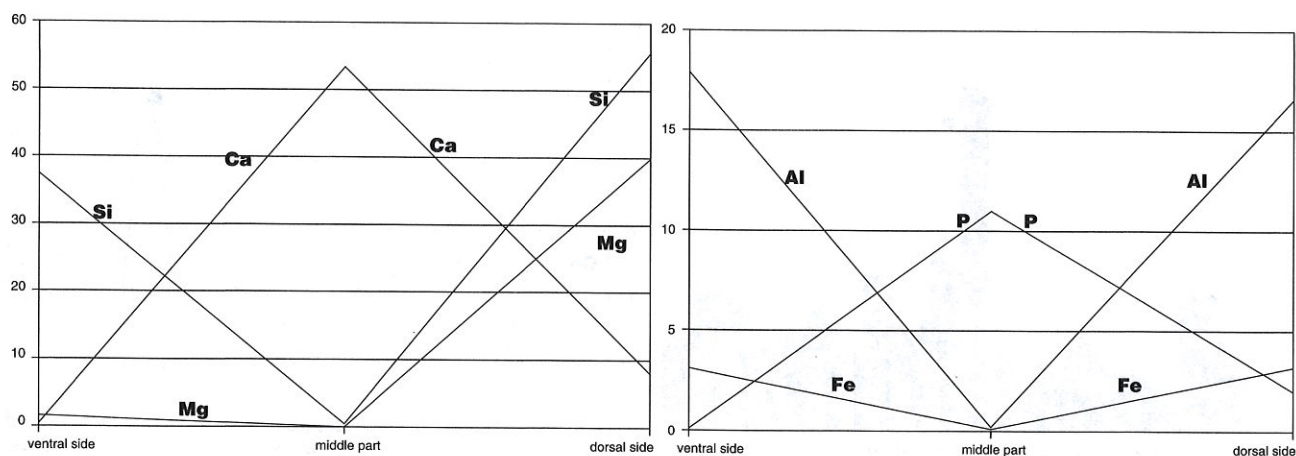


40. Microprobe zonal measurements of K (x10000) and Ca (x100) contents in a calyx plate of an undetermined crinoid from Chapel Coral Horizon near Kaplička (Praha-Zlíchov)

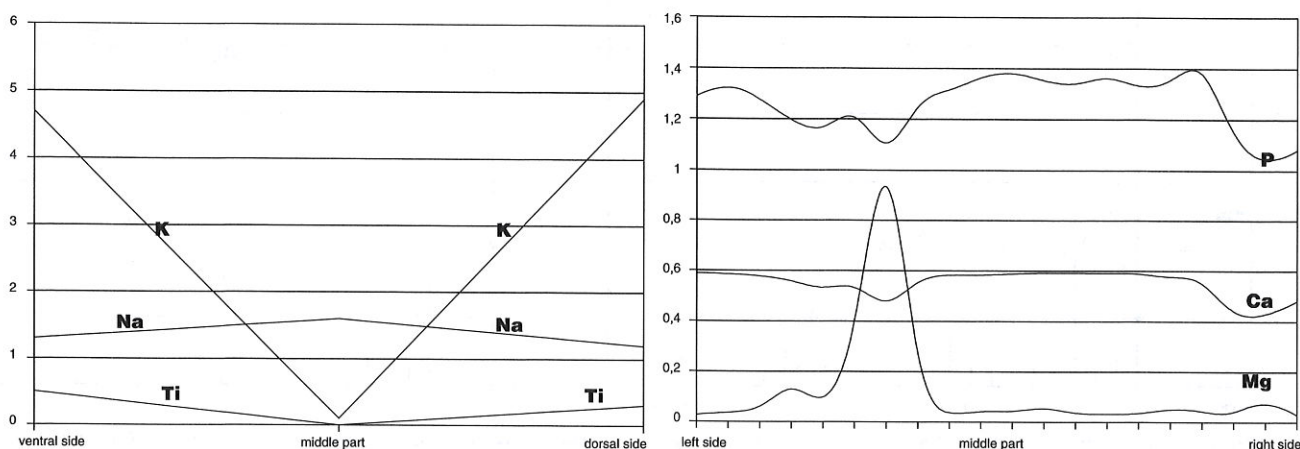


41-42. Microprobe zonal measurements of (41) P (x100) and Ca (x10), and (42) Mg (x1000) and Ca (x100) contents in a calyx plate of an undetermined crinoid from Chapel Coral Horizon near Kaplička (Praha-Zlíchov)



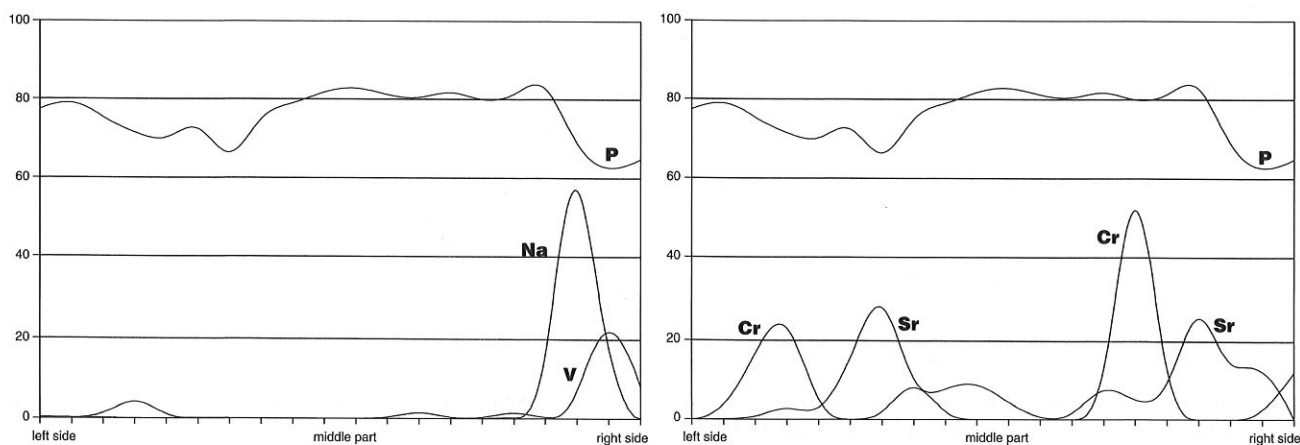


43-44. Microprobe zonal measurements of (43) Ca (x100), Mg (x1000) and Si (x100), and (44) Al (x1000), Fe (x1000) and P (x1000) contents in a brachial plate from the Chapel Coral Horizon (Praha-Zlíchov)



45. Microprobe zonal measurements of Na (x1000), K (x1000) and Ti (x1000) contents in a brachial plate from the Chapel Coral Horizon (Praha-Zlíchov)

46-47. Microprobe zonal measurements of (46) P (x100), Mg (x10) and Ca, and (47) P (x300), Na (x10) and V (x1000) contents in a calyx plate of a scyphocrinitid crinoid from the "lobolith hillside" near Praha-Řeporyje



48. Microprobe zonal measurements of P (x300), Cr (x3000) and Sr (x1000) contents in a calyx plate of a scyphocrinitid crinoid from the "lobolith hillside" near Praha-Řeporyje