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Carbon isotope stratigraphy of the Liesberg Beds Member (Oxfordian, Swiss Jura) using echinoids and crinoids

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Key words: Isotope stratigraphy, Oxfordian, Swiss Jura, Echinoids, Crinoids

ABSTRACT

The Liesberg Beds form the transition between the lower Oxfordian dark coloured marls (Renggeri Member and the Terrain à Chailles Member) and the middle Oxfordian reefal limestones (St-Ursanne Formation). Both lithofacies and biofacies are diverse and evolve rapidly up-section. Stable isotope studies of whole-rock samples are therefore excluded. In search for a convenient isotopic marker, we measured carbon isotope compositions of several fossil groups and chose crinoid stems of *Millericrinus* spp and echinoid spines of *Paracidaris* spp because of their abundance throughout the section and the small variations of $\delta^{13}C$ within one fossil and between fossils from the same stratigraphic level.

The $\delta^{13}C$ values of echinoderms largely reflect earliest diagenetic conditions at the seawatersediment interface. The porous stereome structure secreted of high Mg-calcite by echinoderms has a high reactive surface/volume ratio, which triggers the precipitation of very early syntaxial cements.

In the four studied sections reproducible carbon isotope shifts were observed both for *Millericrinus* spp stems and *Paracidaris* spp spines. A negative $\delta^{13}C$ shift of 1–1.5‰ was observed near the base of the section, just above the transition from Terrain à Chailles Member, where the first corals occur. In the middle and upper part of the four sections, characterised by a stepwise increase of corals and the macrofossils, a positive $\delta^{13}C$ shift of about 2‰ was observed.

Despite the highly variable lithologic composition of the Liesberg Beds Member, carbon isotope shifts seem to be consistent and warrant an interpretation as an original signal, controlled by the isotopic composition of dissolved carbonic acid in seawater.

We explain the heavy $\delta^{13}C$ values ($\approx$ 2–2.3‰) in the lower Liesberg Beds as a transition from an oxygen-limited environment (Terrain à Chailles Member) to the Liesberg Beds Member. The lowest $\delta^{13}C$ values ($\approx$ 1–1.5‰) correspond to a large input of dissolved nutrients to the platform under oxidizing conditions. The ensuing positive shift (between 2.5 and 3.5‰), however, seems to correspond to a general trend of opening up of the platform and connection to open marine waters. Positive $\delta^{13}C$ values in the upper Liesberg Beds is interpreted as a result of important accelareted extraction of organic carbon from the ocean reservoir, that occurred possibly during periods of warm and humid climate.

RESUME

Les Couches de Liesberg forment la transition entre les marnes sombres de l'Oxfordien inférieur (Membre de Renggeri et Membre du Terrain à Chailles) et les calcaires récifaux de l'Oxfordien moyen (Formation de St-Ursanne). Les lithofaciès et biofaciès sont très variés et évoluent rapidement tout au long de la section. Les analyses isotopiques sur roche totale sont donc exclues. Afin de choisir un marqueur isotopique, nous avons

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effectué des analyses sur différents groupes de fossiles. Nous avons choisi les tiges du crinoides *Millericrinus* spp et les radioles de l'échinoide *Paracidaris* spp, en raison de leur abondance au travers de la section et des faibles variations du $\delta^{13}C$, d'une part à l'intérieur d'un même spécimen et d'autre part entre différents spécimens d'un même niveau stratigraphique.

Les valeurs mesurées sur les échinodermes reflètent largement les conditions de diagenèse précoce à l'interface eau de mer-sédiment. Les échinodermes sécrètent un stéréome (structure poreuse) constitué de calcite magnésienne dont le rapport surface/volume très réactif est favorable à la précipitation d'un ciment syntaxiale très précoce.

Dans les quatre sections étudiées, on observe des pics des isotopes du carbone reproductibles entre les tiges de *Millericrinus* spp et les radioles de *Paracidaris* spp. Un pic négatif du $\delta^{13}C$ de 1–1.5‰ est observé à proximité de la base de la section, juste au-dessus de la transition du Membre du Terrain à Chailles, où les premiers coraux apparaissent. Dans les parties moyenne et supérieure des quatres sections, caractérisées par une augmentation de la quantité de coraux et de macrofossiles, on observe un pic positif du $\delta^{13}C$ d'une valeur de 2‰.

Malgré la diversité de la composition lithologique du Membre des Couches de Liesberg, les pics des isotopes du carbone semblent être cohérents et permettent d'interpréter le signal isotopique comme étant originel, celui-ci étant contrôlé par la composition isotopique de l'acide carbonique dissout dans l'eau de mer.

Nous expliquons les valeurs lourdes du $\delta^{13}C$ ($\approx$ 2–2.3‰) à la base des Couches de Liesberg comme la résultante d'un état de transition d'un environnement peu oxygéné (le Membre du Terrain à Chailles) aux Couches de Liesberg. Les valeurs du $\delta^{13}C$ les plus basses ($\approx$ 1–1.5‰) correspondent à un fort apport de nutriments sur la plate-forme où règnaient des conditions oxydantes. Le pic positif suivant du $\delta^{13}C$ entre 2.5 et 3.5‰ dans la partie supérieure des Couches de Liesberg correspond à la tendance générale à l'ouverture de la plateforme et à une connection avec les eaux marines du large. Ainsi le pic de la parties supérieure des couches de Liesberg peuvent résulter d'un enfouissent important du carbone organique, ce qui se produit durant les périodes de climat chaud et humide.

Introduction

Oxygen isotope ratios of precipitated carbonate vary widely as a function of the temperature of formation whereas carbon isotope ratios more likely preserve information on the isotopic composition of the precipitating environment. Carbon isotope stratigraphy of carbonates has been used to document shifts in global carbon reservoirs (e.g. Scholle & Arthur 1980; de Boer 1986; Magaritz 1991; Weissert & Lini 1991). A tendency towards isotopically heavier precipitates has been interpreted as the result of important withdrawal of light organic carbon from the atmosphere and hydrosphere (e.g. Malkowski et al. 1989). Previous work has been based on both whole rock (Scholle & Arthur 1980; Magaritz 1991; Weissert & Lini 1991) and isolated fossils (e.g. Popp et al. 1986; Malkowski et al. 1989). Important variations in isotopic ratios have been reported both between different taxa and between different parts of the same specimen (e.g. Weber 1968; Weber & Raup 1966a, b). These variations are thought to be a result of metabolic fractionation (vital effects). In this paper we report isotopic measurements carried out on various macrofossils extracted from marls and limestones.

The Liesberg Beds Member crops out in the central Jura mountains (Fig. 1). It is considered a member of the Mont-Terri Formation. Lithologically, the Liesberg Beds form the transition between the lower Oxfordian marls ("Oxfordian" of classical authors) and the middle Oxfordian reefs represented in the platform by "Rauracien". From a chronostratigraphic point of view the Liesberg Beds Member is located within the Transversarium Ammonite Chron (Gygi 1986).

The construction of a new highway tunnel has provided the opportunity to compare fresh subsurface samples to surface samples exposed to acid rain. This tunnel crosses limestones and marls of the Liesberg Beds Member.

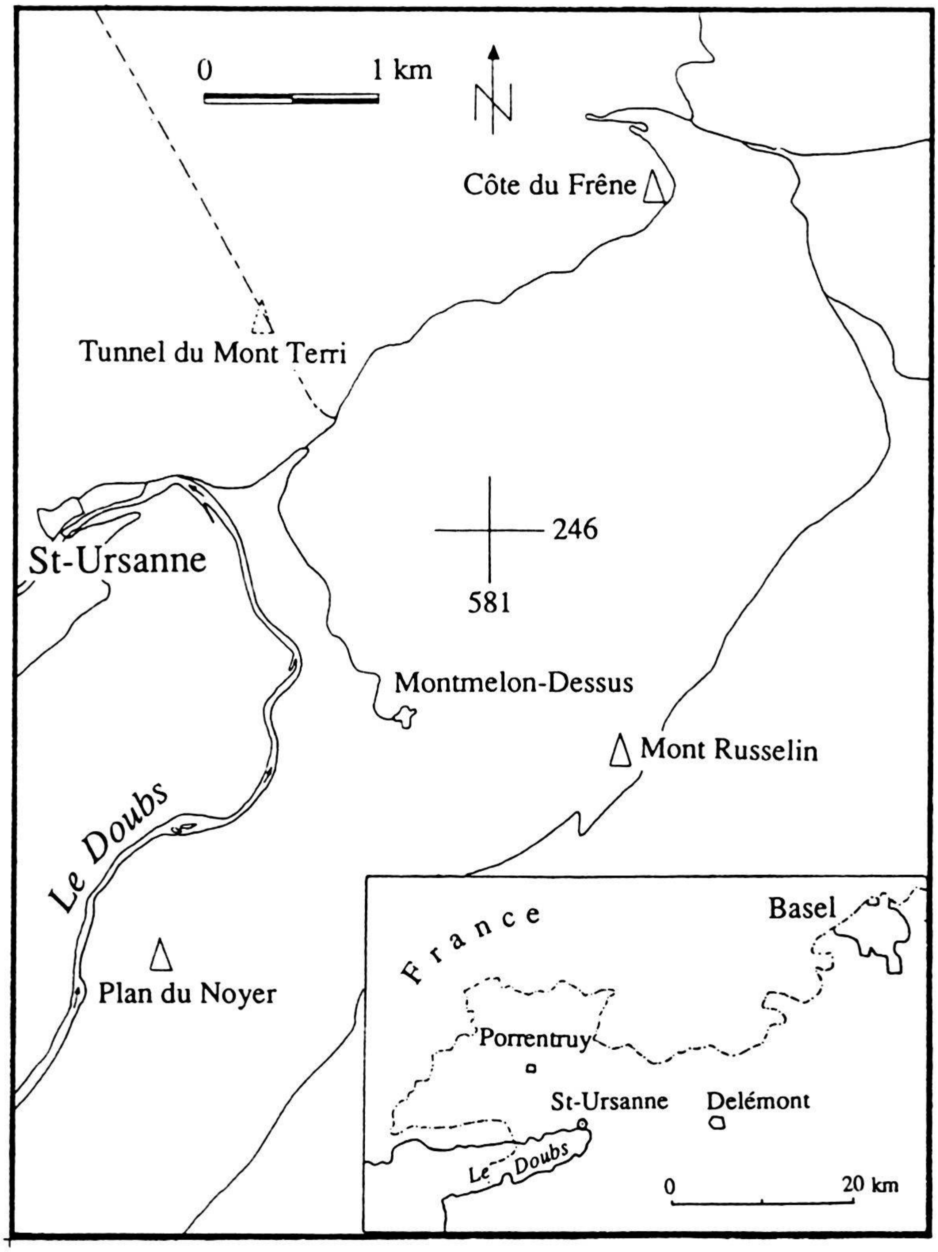


Fig. 1. Location map of isotope stratigraphic profiles (Δ) of the Liesberg Beds near St-Ursanne.

The Liesberg Beds Member is a grey marl with bands of limestone concretions in its lower part. The upper stratigraphic part is composed principally of limestone. The limestone concretions and the limestones are biomicrite and biolithite (Folk 1962). This facies presents a great variety of fossil taxa, principally represented by encrusted hermatypic corals, crinoids, spines of echinids, bivalves, brachiopods, calcisponges, annelids and foraminifers. The maximum thickness of the Liesberg Member is about 24 m (near St-Ursanne, Fig. 2), and laterally disappears towards the SE (Pümpin 1965). The studied sections are situated near St-Ursanne in the canton of Jura (Switzerland) (Fig. 1).

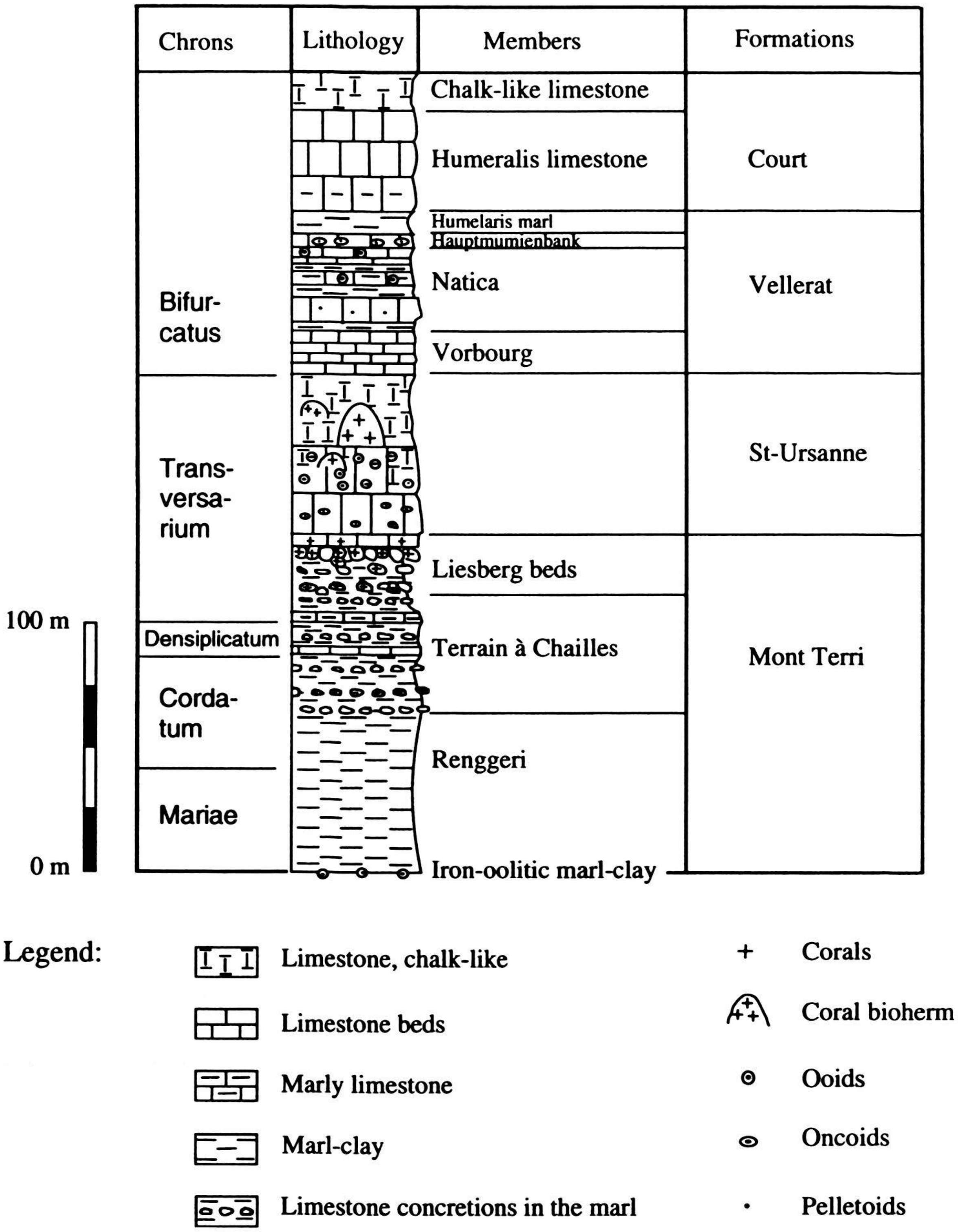


Fig. 2. Synthesis of a stratigraphic profile for the Oxfordian near St-Ursanne.

Methods

Calcite was sampled using a pneumatic drill which splits the crystals along their cleavages. The grains were extracted with tweezers, then checked under the binocular microscope to prevent contamination by the matrix. They were then reduced to powder (about 10 µm) in an agate mortar. Later in the study the samples were drilled with a dental drill. The fine drill bit allows us to drill a hole with a diameter of 1 mm. The powder obtained was checked under the binocular microscope to insure a high purity.

Calcium carbonate was reacted with 100% phosphoric acid at 25 °C under vacuum for 24 hours. This reaction produces CO_2 with an oxygen isotope fractionation of a known value relative to $CaCO_3$ (McCrea 1950). The CO_2 resulting of this reaction was analysed on a Finnigan Mat 251 spectrometer.

The isotopic composition of oxygen and carbon are conventionally given in parts per thousand in δ-notation relative to the PDB standard:

$$\delta^{13}C = \frac{^{13}C/^{12}C \text{ sample} - ^{13}C/^{12}C \text{ standard}}{^{13}C/^{12}C \text{ standard}} \times 1000$$

and in analogous fashion for $^{18}O/^{16}O$.

Choice of stratigraphic isotopic marker

Numerous stable isotope studies have been made on whole rocks. Such analyses necessarily encompass different diagenetic phases with variable isotopic compositions. In coarse-grained samples, from shallow-water sediment, the variable volumes of different diagenetic phases may create noise that totally masks the original isotopic signal (Popp et al. 1986). The quantity of nannofossils may also influence the isotopic signal (Thierstein & Roth 1991). Lithologic and diagenetic heterogeneities as well as the variation of the quantity of biogenic elements in the Liesberg Member prohibit work on whole rocks if a reproducible original environmental signal is sought. Different parts of a single fossil sometimes may even have different isotopic ratios. As a consequence the choice of a stratigraphic marker is essential. An ideal stratigraphic marker is a fossil or a fossil fragment in equilibrium with the marine environment, or which is equilibrated during the earliest diagenesis. The isotopic information of the potential marker should be preserved during late diagenesis. Moreover, the chosen marker must be widespread in the studied facies.

In the following we review isotopic characteristics and diagenetic behaviour of potentials markers fo the Liesberg Beds Member. The isotopic composition of modern echinoderms at the phylum level varies widely due to vital effects (Weber & Raup 1966a; b; Weber 1968; Land 1989). In other words, metabolism affects both $\delta^{13}C$ and $\delta^{18}O$ values of the secreted carbonate, and a weak correlation between the $\Delta\,\delta^{13}C$ and $\Delta\,\delta^{18}O$ values has been observed (Land 1989).

The class Echinoidea displays a vital effect in the $\delta^{13}C$ value (up to 13 per mil) for the tests and parts of the echinoid lantern, while the isotopic compositions of the spines are similar to those of inorganically precipitated marine carbonate. Variations of the same order may be observed in the different parts of the same skeleton (i.e. in *Goniocidaris* and *Histocidaris*). In comparing the same skeletal parts of one species within the same environment, the variations become fairly small (e.g. $\delta^{13}C$ = 0.14‰, $\delta^{18}O$ = 0.12‰ for the spines of 12 specimens *Arbacia punctulata* and $\delta^{13}C$ = 0.29‰, $\delta^{18}O$ = 0.29‰ for the spines of 12 specimens of *Strongylocentrotus droebachiensis*) (Weber & Raup 1966a, b).

The same species from different localities varies in isotopic composition and this dispersion is interpreted either as intraspecific genetic differences or environment differences. Different species from one locality exhibit different vital effects. However the spines only show a maximum variation of 0.7‰ for $\delta^{13}C$ and $\delta^{18}O$ (Weber & Raub 1966a, b).

The class Echinoidea displays a positive correlation between $\delta^{13}C$ values and temperature whereas $\delta^{18}O$ is positively correlated with this parameter. The spines of Echinoidea generally have an isotopic composition close to that of marine carbonates precipitated in equilibrium. Furthermore, the abundance of spines of the echinoid *Paracidaris* spp in the Liesberg Beds Member assures a good potential marker.

Weber (1968) mentions that crinoids are the class among the echinoderms most depleted in ^{13}C and ^{18}O. For example different species originating from different localities display variations in $\delta^{13}C$ between 0.4 and 3.5‰ and for $\delta^{18}O$ between 0.3 and 1.5‰. However, Weber's data show that species coming from the same locality exhibit variations in $\delta^{13}C$ between 0.06‰ for the *Antedon rosacea* and 1.04‰ for *Comanthus wahlbergi*. These arguments together with the abundance in the Liesberg Beds Member provide optimal condition for an isotopic study.

Many Ophiuroidea display variations of 1 to 2‰ in their skeleton. Their mean isotopic composition is near that of the equilibrium calcium carbonate precipitate from seawater (Weber 1968 p. 49). Unfortunately, Ophiuroidea are rare in the Liesberg Beds Member and only fragments have been observed in thin section. Brachiopods display a small spread in $\delta^{13}C$ and $\delta^{18}O$ at the generic level. Therefore at this level they can be used for the study of secular variations of carbon and oxygen isotope compositions (Veizer et al. 1986; Popp et al. 1986; Malkowski et al. 1989). Unfortunately they are not common in the Liesberg Beds Member. Other groups like the Bivalvia of Liesberg Beds are often recrystallised, suggesting that the initial isotopic information is lost. Corals are either replaced by coarse sparite or are silicified. Thus the initial values are probably lost and this question will not be examined here. Finally in the Liesberg Beds, foraminifera are present at quantities too small to be used.

In summary, echinoid spines and crinoid stems are most likely preserving the isotopic compositions of secreted and earliest diagenetic carbonate. Our measurements were concentrated on these two groups.

Results

In order to validate a paleoenvironmental interpretation of isotopic compositions, we tested the variations within a single fossil (reference) and between different taxa (objects) of the same level. To estimate diagenetic effects, we also measured some void-filling cements.

Isotopic variation in the spines of Echinoidea

The $\delta^{13}C$ values of spines of *Paracidaris* spp are fairly constant (Tab. 1). The standard deviations ar between 0 and 0.15‰. The maximum variation is observed in the spine which

Table 1. $\delta^{13}C_{PDB}$ and $\delta^{18}O_{PDB}$ variations in the spines of *Paracidaris* spp.

Genus Stratigraphic profile	Position in the profile (in m)	Position of the sample in the spine from the base (in mm)	$\delta\ ^{13}C_{PDB}$ (in per mil)	$\delta\ ^{18}O_{PDB}$ (in per mil)
Paracidaris Côte au Frêne	4.30	0.70 1.65 2.45	1.53 1.54 1.54	-3.89 -4.30 -4.11
Paracidaris Côte au Frêne	18.90	0.10 2.65 4.80	2.84 2.74 3.03	-4.25 -4.49 -4.03
Paracidaris Plan du Noyer	1.60	0.65 1.50 2.30	2.13 2.12 2.14	-4.74 -4.65 -4.53
Paracidaris Plan du Noyer	4.32	0.80 1.70 2.80	2.43 2.39 2.44	-4.54 -4.92 -5.46
Paracidaris Plan du Noyer	7.55	Points at the same distance from the base	2.55 2.62 2.64	-4.47 -4.57 -4.60
Paracidaris Mont Russelin	49.20	Points at the same distance from the base	1.77 1.85 1.78 1.81	-5.52 -4.78 -5.03 -4.71

was not previously abraded. Therefore, the outer border must have an isotopic composition different from other parts of the spine. The variations between the $\delta^{13}C$ value and the distance between the base of the spine and the analysed point is not systematic (Tab. 1). $\delta^{18}O$ values are more variable than $\delta^{13}C$ values, $\Delta\ \delta^{18}O$ ranging from 0.1 to 0.46‰. The spine with the largest variation comes from the level 49.20 m of the Mont Russelin cross section. Macroscopically, however this spine appears normal.

Isotopic variations in the Crinoids

The isotopic composition of the crinoid stems of the genus *Millericrinus* spp are presented in table 2. The stems show standard deviations for $\delta^{13}C$ between 0.06 and 0.23‰. The stem with the greatest variations shows recrystallisation textures and as a consequence,

Table 2. $\delta^{13}C_{PDB}$ and $\delta^{18}O_{PDB}$ variations in the *Millericrinus* spp.

Genus Profile	Position in the profile (in m)	Position of the analyse in the crinoid	Delta 13C PDB (in per mil)	Delta 18O PDB (in per mil)
		From the base of the stem (in cm)		
Millericrinus Mont Russelin	48.02	1.35	2.05	-6.87
		2.15	2.24	-1.41
		3.95	2.06	-7.29
		4.80	2.20	-1.37
Millericrinus Mont Russelin	49.53	9.05	2.20	-5.09
		9.10	2.18	-4.90
		14.70	1.74	-4.91
		14.70	1.89	-4.83
Millericrinus Côte au Frêne	24.98	0.05	2.42	-5.53
		0.55	2.66	-5.60
		0.85	2.58	-5.90
		1.20	2.52	-6.03
		1.45	2.58	-5.85
		1.70	2.54	-5.97
		1.90	2.56	-6.06
		2.15	2.60	-5.75
		2.45	2.66	-5.68
		4.05	2.59	-6.49
		5.05	2.65	-6.20
		6.05	2.60	-6.23
		8.45	2.62	-5.74
		11.55	2.66	-6.24
		13.45	2.60	-5.51
		14.40	2.63	-5.96
		16.45	2.68	-5.76
		In the root		
Millericrinus Mont Russelin	48.1	0.45	1.59	-0.73
		3.05	1.78	-4.03
		Distal part of the stem and root		
Millericrinus Mont Russelin	49.08	0.35	2.15	-4.25
		1.05	2.23	-4.40
		0.35	1.81	-4.53
		1.10	2.21	-3.23
		1.40	2.09	-3.53

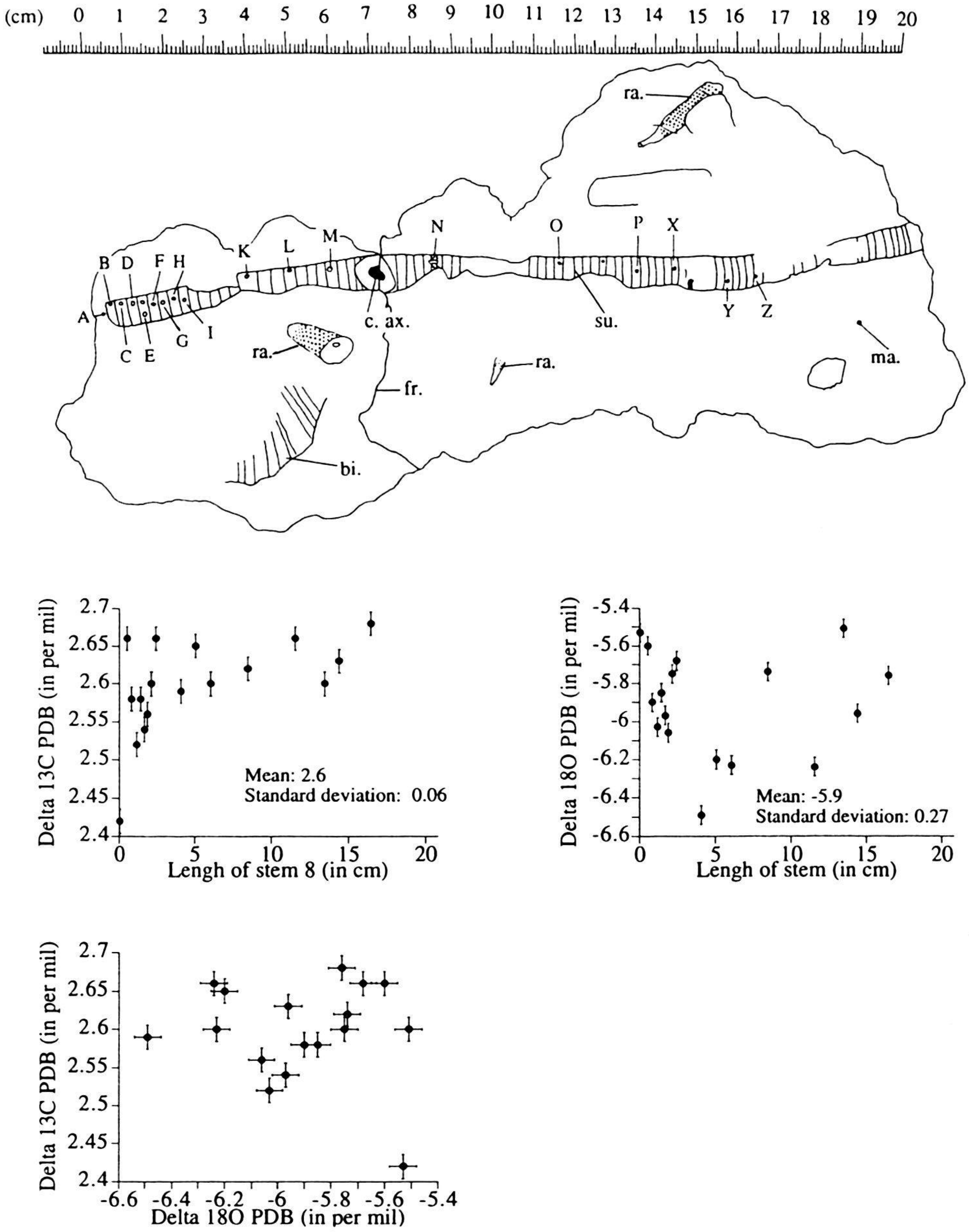


Fig. 3. Stem of *Millericrinus* spp, sample from Côte du Frêne stratigraphic profile, level 24.98 m, scale (in cm). (See also table 2.)

Capital letters indicate point of isotopic analyses; c. ax. axial canal; su. suture; ra. spines of echinoid; bi. Bivalvia; fr. fracture; ma. matrix.

The two upper diagramms show variations $\delta^{13}C_{PDB}$ and $\delta^{18}O_{PDB}$ (in per mil), with error bars, *versus* length of stem.

Lower diagram: no linear correlation between $\delta^{13}C_{PDB}$ and $\delta^{18}O_{PDB}$ is observed.

a heavier isotopic composition. $\delta^{18}O$ values have a standard deviation between 0.11 and 3.29‰. The result of 17 analysis (Fig. 3) shows no correlation for the stem. The crinoid root *Millercrinus* spp has a lighter isotopic composition than the distal part of the stem (difference $\Delta\ \delta^{13}C$ about 0.15‰ and $\Delta\ \delta^{18}O$ about 0.55‰).

Isotopic variations in the same level

In order to test the isotopic variation of the various diagenetic phases, samples with calcite monocrystals and coming from the same level enclosing a maximum thickness of 20 cm were chosen. These monocrystals represent either spines, fragments of crinoids, undetermined remains or burial cements. The results show that in the same level, related taxonomic fossils have closely clustered isotopic values whereas the values of nonidentified grains are dispersed. The analysed calcite cements represent diagenetic fossil infills (i.e. bivalvia and brachiopods). They have a particularly low $\delta^{18}O$ of ≈ –7.5‰. Two $\delta^{13}C$ values, however, are close to those of echinoderms. The results are presented in table 3.

Isotope stratigraphy

Four stratigraphic sections were studied: Côte du Frêne, Mont Russelin, Tunnel du Mont Terri, Plan du Noyer (Fig. 1). In the Côte du Frêne section the stratigraphy is based on two stratigraphic markers (Fig. 4), the *Paracidaris* spines (19 points for 12 specimens) and the *Millericrinus* stems (21 points for 3 specimens). In the Mont Russelin section the stratigraphy is based on the same two isostratigraphic markers (Fig. 5) with the exception of the three uppermost points of the diagram which represent nonidentified spines. For the *Millericrinus*, nine analytical points are from the roots of four specimens. Only two points with a respective stratigraphic position 37.45 m and 40.55 break the trend (Fig. 5 A). These are the two representing the lowermost points of the profile!

In the Mont Terri Tunnel section the stratigraphic marker could generally not be determined with the same precision as for the other cross sections. Two sets of echinoderms are distinguished; the Echinoidea spines and the stems of crinoids. These two sets show a clear upwards increasing trend in $\delta^{13}C$. Only two points from the same specimen of Echinoidea spines with a stratigraphic position at 40.77 m break the trend. The location of the specimen is about 4 m from the base of the Liesberg Beds Member. The same evolution is displayed by crinoid stems, indicating a shift at the base of the section. $\delta^{18}O$ values do not show a trend (Fig. 6: A, B, C, D).

The cross section Plan du Noyer covers only a part of the Liesberg Member. In this section the isotopic evolution is based only on the *Paracidaris* spp spines. The values of $\delta^{13}C$ spread between 2.05‰ and 2.62‰ and between –2.97‰ and –5.46‰ in $\delta^{18}O$ (Fig. 7: A, B).

The same upwards increasing trend of $\delta^{13}C$ relative to the stratigraphic position is shown in three stratigraphic sections with the *Paracidaris* spines and in two sections with the *Millericrinus* spp and only in one cross section with the echinoidea spines and the crinoids. The minimum and maximum value for the $\delta^{13}C$ values of *Paracidaris* spines are 0.64‰ and 3.14‰. However, an unclassified echinoidea spine from the Tunnel of Mont Terri section has a value of 3.32‰. The minimum and maximum value for the $\delta^{13}C$ of *Millericrinus* are 0 and 2.83‰. However, a slightly more positive value of 3.25‰ is found

Table 3. $\delta^{13}C_{PDB}$ and $\delta^{18}O_{PDB}$ variations in the same level.

Stratigraphic profile Positions in the profile (in m)	Samples	Delta 13C PDB (in per mil)	Delta 18O PDB (in per mil)
Tunnel du Mont Terri 61.54	Spine	2.81	-6.09
	Spine	2.74	-5.93
	Spine ?	3.32	-4.63
Tunnel du Mont Terri 59.23	Crinoid ?	2.78	-4.93
	Unindentified debris	2.86	-5.11
	Unindentified debris	2.6	-5.21
	Unindentified debris	3.17	-4.76
	Spine ?	2.74	-6.07
	Unindentified debris	3.21	-5
	Spine	2.96	-5.55
	Spine	2.71	-5.64
	Spine	2.81	-5.73
Tunnel du Mont Terri 56.92	Root of Millericrinidae	3.25	-4.43
	Spine of Paracidaris ?	2.97	-4.88
Tunnel du Mont Terri 53.8	Spine	2.22	-2.28
	Calcite cement	2.24	-7.67
Tunnel du Mont Terri 52.3	Stem of crinoid	1.54	-3.95
	Calcite cement	2.11	-7.31
Tunnel du Mont Terri 51.54	Stem of crinoid	2.3	-2.6
	Unindentified debris	2.71	-2.95
	Calcite cement	2.22	-7.73
Tunnel du Mont Terri 51.77	Stem of Millericrinus	1.81	-4.32
	Spine of Paracidaris	1.5	-5.09
	Stem of Millericrinus	1.51	-1.56
	Axial canal of Millericrinus	1.63	-3.83
Tunnel du Mont Terri 40.77	Stem of crinoid	2.23	-3.28
	Spine	2.17	-4.64
	Spine	2.24	-4.53
Côte du Frêne			
CF 24.92	Spine of Paracidaris	2.66	-5.63
CF 24.98	Stem of Millericrinus (mean)	2.6	-5.9
Mont Russelin			
49.2	Spine of Paracidaris (mean)	1.8	-5.01
49.201	Spine of Paracidaris	1.64	-5.57
49.08	Stem of Millericrinus (mean)	2	-4.93
Mont Russelin	Spine of Paracidaris (mean)	1.81	-5.89
48.21			
48.02	Stem of Millericrinus (mean)	2.14	-4.23

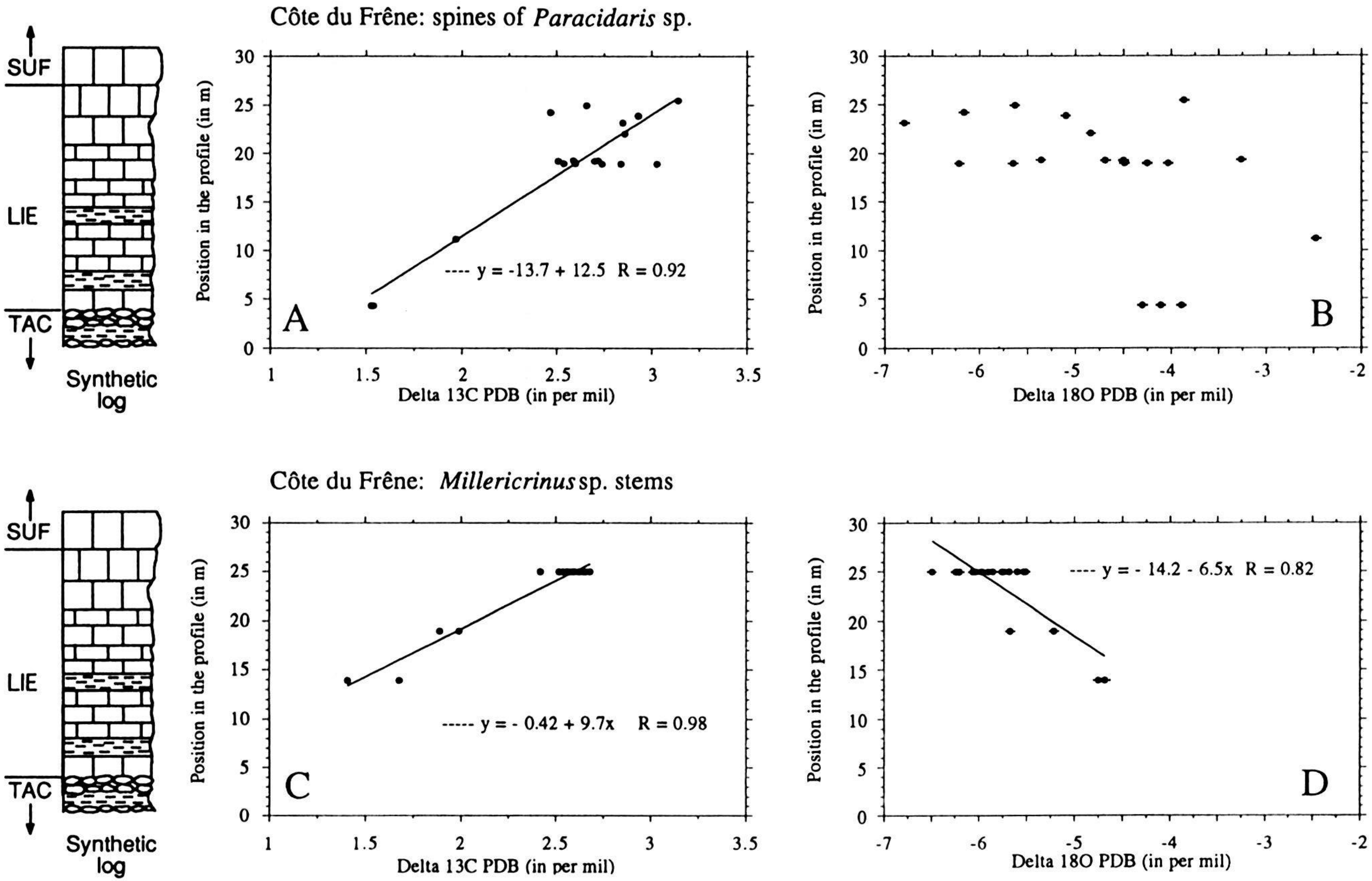
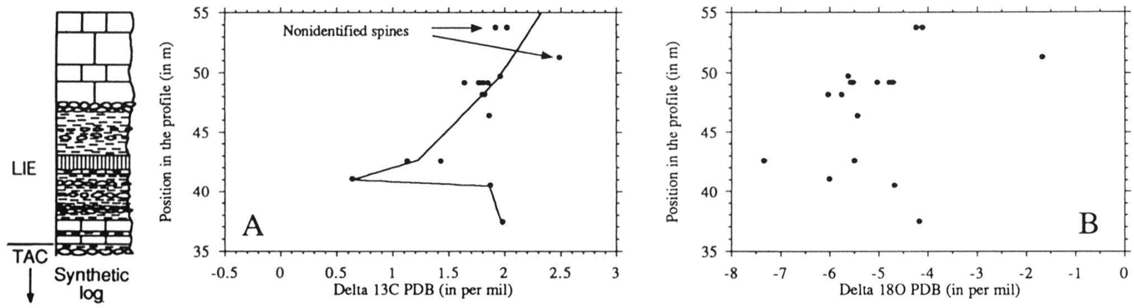


Fig. 4. Isotopic variations in the Côte du Frêne section,
TAC: Terrain à Chailles Member; LIE: Liesberg Beds Member; SUF: St-Ursanne Formation.
A $\delta^{13}C_{PDB}$, B $\delta^{18}O_{PDB}$ for the spines of *Paracidaris* spp *versus* stratigraphic position, 19 points from 12 specimens, C $\delta^{13}C_{PDB}$, D $\delta^{18}O_{PDB}$ for the *Millericrinus* spp stems *versus* stratigraphic position, 21 points from 3 specimens.


Mont Russelin: spines of *Paracidaris* sp.

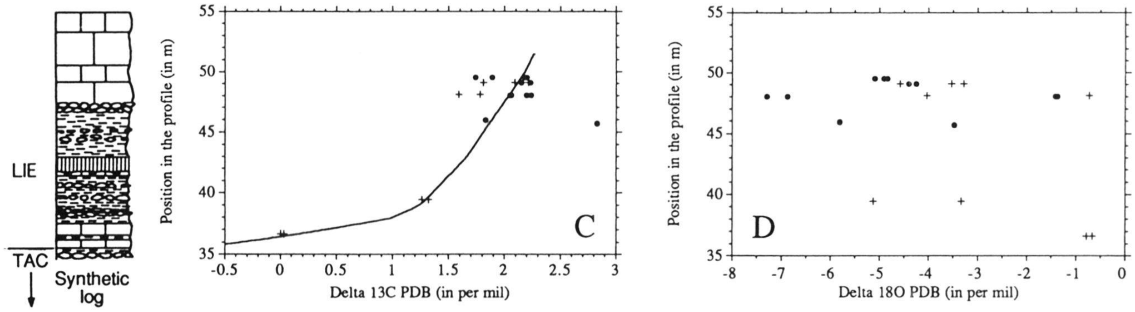

Mont Russelin: *Millericrinus* sp. stems & roots

Fig. 5. Isotopic variations in the Mont Russelin section,
TAC: Terrain à Chailles Member; LIE: Liesberg Beds Member.
A $\delta^{13}C_{PDB}$, B $\delta^{18}O_{PDB}$ for the spines of *Paracidaris* spp (with the exception of the last three uppermost points of the diagram representing nonidentified spines) *versus* stratigraphic position, 17 points from 11 specimens.
C $\delta^{13}C_{PDB}$, D $\delta^{18}O_{PDB}$ for the *Millericrinus* spp stems (with the exception of 9 analytical points represented by + are from the roots of 4 specimens) *versus* stratigraphic position, 21 points from 12 specimens.

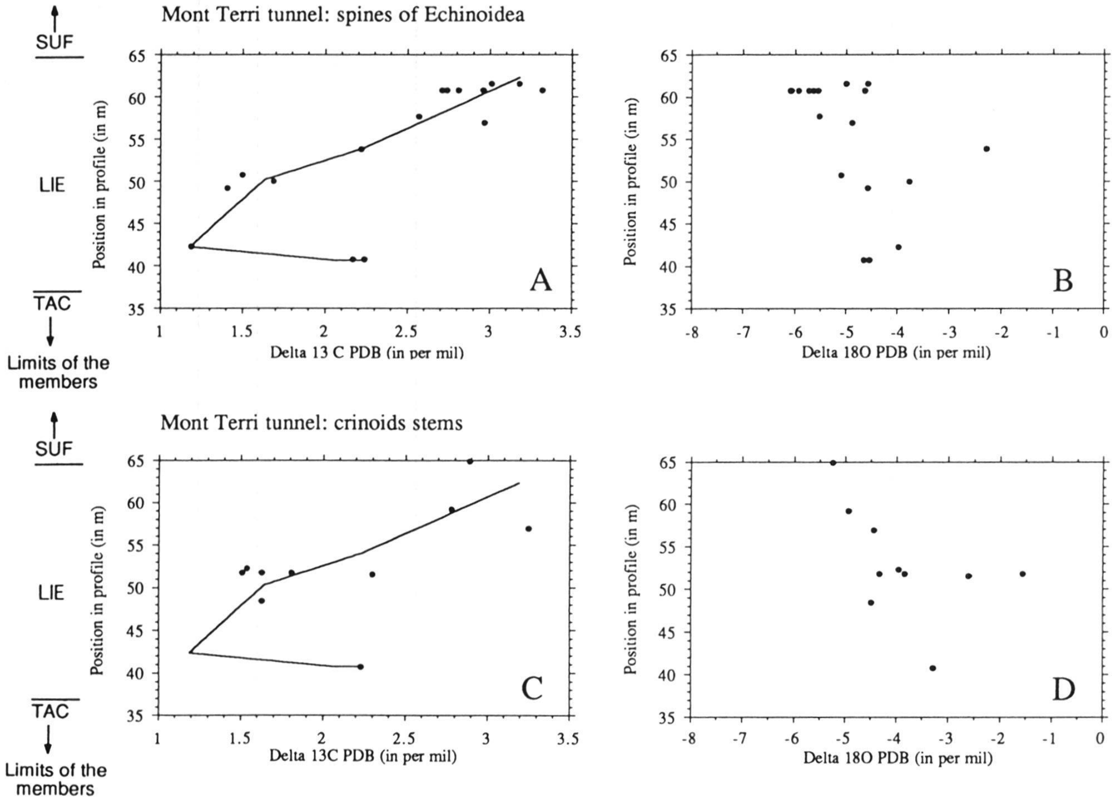


Fig. 6. Isotopic variations in the Mont Terri Tunnel section,
TAC: Terrain à Chailles Member; LIE: Liesberg Beds Member; SUF: St-Ursanne Formation.
A $\delta^{13}C_{PDB}$, B $\delta^{18}O_{PDB}$ for the spines of Echinoidea *versus* stratigraphic position. 18 points from 18 specimens.
C $\delta^{13}C_{PDB}$, D $\delta^{18}O_{PDB}$ for the crinoid stems *versus* stratigraphic position, 10 points from 10 specimens. The curve of C is projected from A.

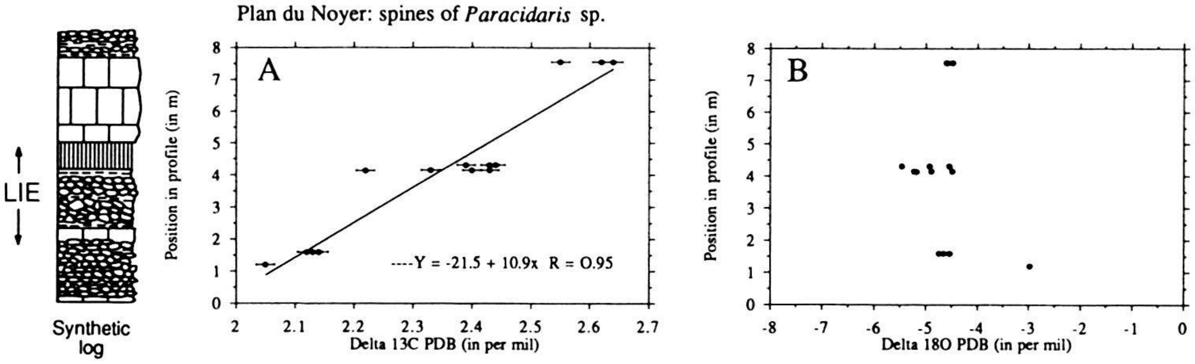


Fig. 7. A $\delta^{13}C_{PDB}$, B $\delta^{18}O_{PDB}$ for the spines of *Paracidaris* spp *versus* stratigraphic position, 14 points from 6 specimens, in Plan du Noyer section.
LIE: Liesberg Beds Member.

for a crinoid of the Millercrinidae family coming from the Mont Terri tunnel. In summary, the $\delta^{18}O$ values do not generally show an isotopic evolution relative to their stratigraphic position.

Discussion and interpretations

Validity of stratigraphic marker fossils

The modern Echinoidea spines of the Cidaridae family have $\delta^{13}C$ values between –1.05‰ and 1.68‰ and $\delta^{18}O$ values between –2.87‰ and 0.64‰ (Weber & Raup 1966b). These values change with species and environments. If at a given moment in the history of the Liesberg Beds the carbon isotope composition of seawater was near present day values, the values of $\delta^{13}C$ measured on the spines may be comparable, if we assume that diagenesis has not erased the initial signal.

In figure 8 we compare values of $\delta^{18}O$ and $\delta^{13}C$ of the modern spines of the family Cidaridae and the spines of *Paracidaris* of the Liesberg Beds. It shows that modern spines have generally higher $\delta^{18}O$ values, whereas the $\delta^{13}C$ values are similar, with a tendency towards lower $\delta^{13}C$ values.

These isotopic differences may be interpreted as follows:

a. The vital effect is different between different species of the Cidaridae and the *Paracidaris* of the middle Oxfordian.
b. The isotopic composition of the Oxfordian ocean was different from that of the present day ocean (the Oxfordian ocean could have been about 10 °C warmer).
c. Diagenesis modified the δ-values, particularly the isotopic composition of the oxygen. In view of the unrealistic temperature shift implied, the diagenetic effect seems predominant.

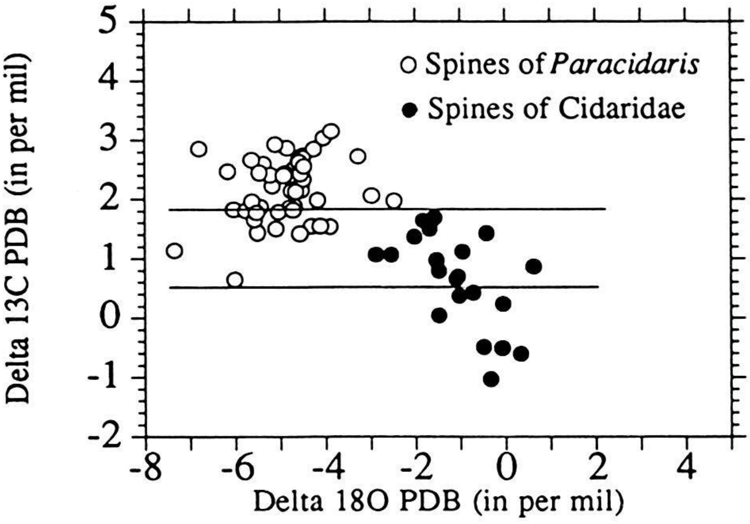


Fig. 8. $\delta^{13}C_{PDB}$ and $\delta^{18}O_{PDB}$ of the actual spines of the family Cidaridae and the spines of the *Paracidaris* spp of the Liesberg Beds.

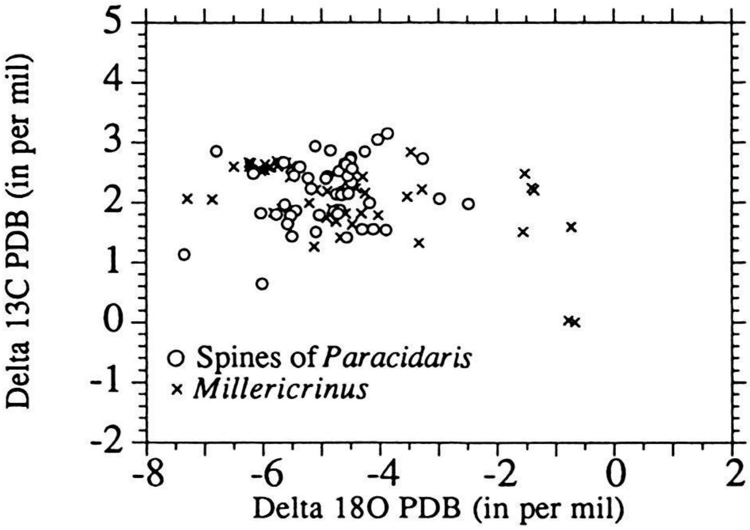


Fig. 9. $\delta^{13}C_{PDB}$ and $\delta^{18}O_{PDB}$ of the spines of *Paracidaris* spp and *Millericrinus* spp stems of the Liesberg Beds.

There are no published isotopic data on modern Millericrinidae. Weber (1968) demonstrated an important variation of the vital effect between the different crinoid orders. Therefore it is not adequate to compare the Millericrinida from the middle Oxfordian with other living orders. Figure 9 displays compiled values of $\delta^{18}O$ and $\delta^{13}C$ for the *Paracidaris* spines and *Millericrinus* stems of the Liesberg Beds. The *Paracidaris* spines field is superimposed on the *Millericrinus* field. An identical vital effect between the two classes can not be considered if the *Millericrinus* have a biological fractionation comparable to that of recent Isocrinidae and Comatulida. However, it may be interpreted as the result of diagenesis. Indeed, actual crinoids are fairly depleted in ^{13}C but generally, are comparable in ^{18}O to calcium carbonate precipitated inorganically. Modern echinoid spines (with the known exception of the orders Holectypoida, Clypeasteroidea, and perhaps Cassiduloida) have an isotopic composition similar to that of inorganically precipitated calcium carbonate (Weber & Raup 1966 a).

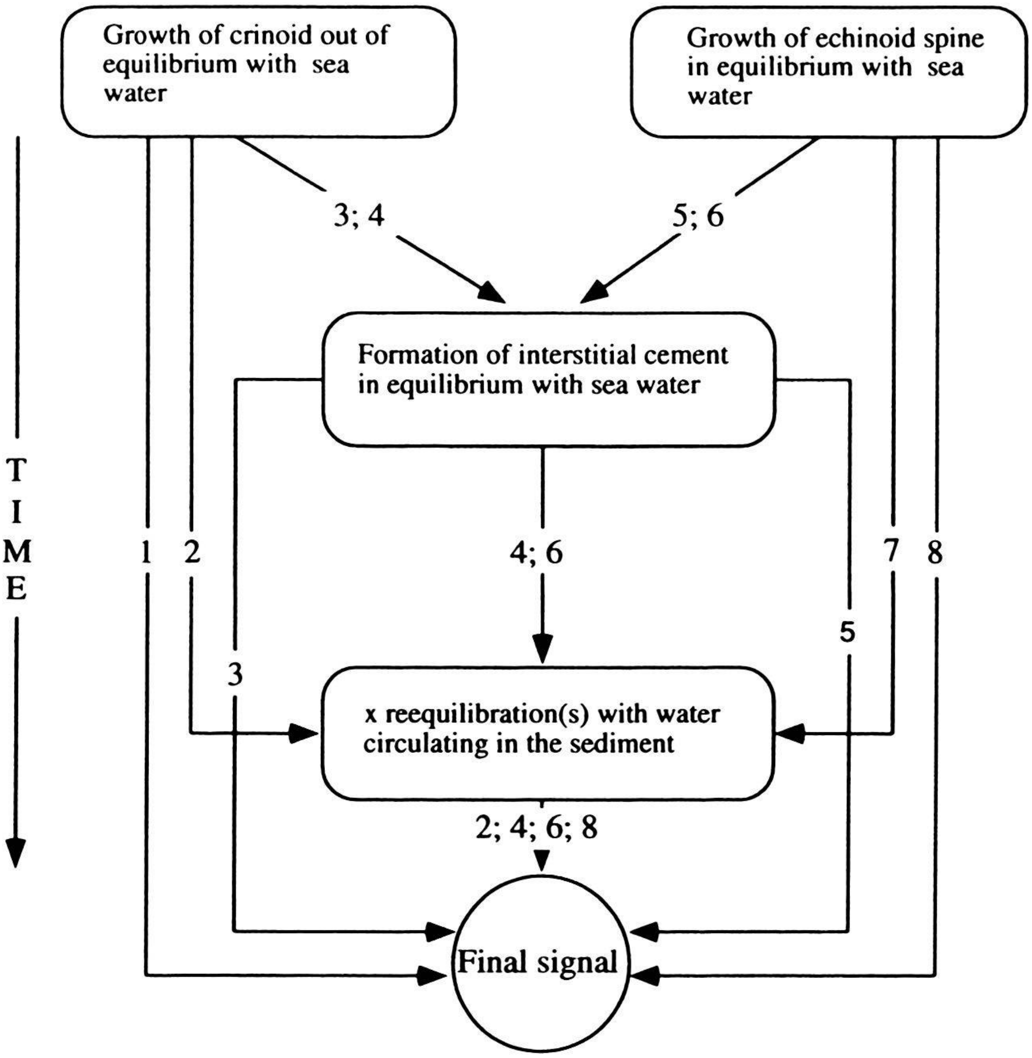


Fig. 10. Theoretical evolutionary paths to arrive to the final isotopic signal.

Burial and evolution of skeletal calcite

The final isotopic signal can be represented as the result of different evolutions. It must be assumed that there are multiple evolution paths from a starting point through a choice of intermediate steps to a common final signal. Theoretically there are eight different possible paths (Fig. 10):

a. If the spines were in equilibrium during the growth, four paths lead to the final signal (paths No. 5, 6, 7, 8).
b. If the crinoids had a vital effect, four other paths would have been followed (paths No. 1, 2, 3, 4).

In these two cases, the final isotopic values of carbon and oxygen are dependent on the path taken. Crinoids and echinoids secrete skeletal elements with a "spongy" structure (stereome), characterised by an important fine porosity (~ 25 μ) with a high surface energy. This porosity facilitates the precipitation of very early interstitial cement with an isotopic composition in approximative equilibrium with inorganically precipitated calcium carbonate in seawater (paths No. 3, 4, 5, 6).

With increasing temperature of diagenesis, the oxygen isotopes of calcite are more sensitive to change than the carbon isotopes (e.g. Anderson & Arthur 1983). The poor correlation between carbon and oxygen isotope ratios may be explained by a dissolution-reprecipitation of calcite with light pore waters and/or increasing temperature during burial phase (e.g. Dickson & Coleman 1980). These two processes are called reequilibration. If one accepts a mechanism of dissolution-reprecipitation, the preservation of the texture in the echinoids suggests that diagenetic dissolution-reprecipitation phenomena were confined to a micron scale. The stratigraphic marker (echinoid) acts as microenvironment. The isotopic composition of this microenvironment was buffered by the dissolving phase in the microenvironment and was different from that of the bulk water. (For details of the discussion of this mecanism see Veizer 1983.)

We conclude that the $\delta^{13}C$ of the spines of *Paracidaris* spp followed path No. 5 and the $\delta^{13}C$ of the *Millericrinus* spp followed path No. 3. The $\delta^{18}O$ of the spines of *Paracidaris* spp followed path No. 6 and the $\delta^{18}O$ of the *Millericrinus* spp followed path No. 4.

Isotopic variations within the same beds

The analysed calcite cements represent diagenetic fossil infills, which do not luminesce under cathodoluminescence. The analysed calcite cements preceeded a fibrous cement that covered the interior of shells. The calcite cements have low $\delta^{18}O \approx -7.5‰$ (Tab. 3). The difference $\Delta\,\delta^{18}O$ between echinoderms and calcite cements is between 3.4‰ and 5.4‰. The $\delta^{13}C$ values of calcite cements is about 2.2‰.

No dissolution features have been observed in out-crop or in thin-section. Gravitative, meniscus or microstalacitite cements also were not observed in thin-section. If diagenetic low-Mg calcite (= dLMC) replacing the original echinoid were in equilibrium with the bulk pore (aquifer) water, all calcite in the rocks should have a similar isotopic signal (Veizer 1983).

The last calcite cement with the most negative $\delta^{18}O$ value must have precipitated from connate fluids.

Values around –7.5‰ are characteristic of Jurassic burial cements (Hudson 1977, Fig. 1). Same taxa of the same stratigraphic level have similar isotopic values, whereas nonidentified grains have dispersed values.

Positive carbon isotope shift – a global signal

The Liesberg Beds Member is chronologically placed within the Transversarium ammonite chron, which coincides with an eustatic sealevel rise (Gygi 1986). An eustatic rise may be produced during a warm climatic period due to a change in the radiation budget of the Earth (or greenhouse effect) (Lini et al. 1992). Near the base of the Liesberg Beds Member, just above the transition from the Terrain à Chaille Member a negative shift of 1–1.5‰ is recorded. Four sections in the middle and upper part show a positive $\delta^{13}C$ shift of about 2‰.

The negative shift must be explained by the change of the marine environment from the Terrain à Chailles Member (formed by calcareous nodules in marl) to the Liesberg Beds Member. The Terrain à Chailles Member, is characterized by no abundant fauna except in one horizon in the middle part of the Terrain à Chailles Member (Gygi & Persoz 1986). Benthonic fauna generally cover less than 1% of the surface area in thin-section. The calcareous nodules contain organic matter framboid pyrite (~20 micron diameter). The small frequency of benthonic fauna, the presence of organic matter and pyrite are consistent with an oxygen-limited environment. We explain the heavier values of the lowermost points of Mont Russelin and Mont Terri profiles (Fig. 5, 6) as a transition from the Terrain à Chailles Member to the Liesberg Beds Member. When the lowest $\delta^{13}C$ values (≈ 1–1.5‰) are reached, hermatypic corals, crinoids, echinoid, bivalves are already well developed and seem to occupy entirely their ecologic niche. The abundance of these fossils occurred at a time when there was a large input of dissolved nutrients to the platform under oxidizing conditions, resulting in low $\delta^{13}C$ values. The ensuing positive shift, however, corresponds to a general trend of opening up of the platform and a connection to open marine waters (e.g. Ziegler 1988). Moreover Gygi (1986) proposed that the climate at the beginning of the Oxfordian to early Tranversarium Chron was relatively wet and became drier towards the end of the Transversarium Chron. He also proposed an eustatic sealevel rise in the upper part of the Transversarium Chron. We interpret the positive shift as a result of important accelerated extraction of organic carbon from the ocean reservoir, that occurred possibly during periods of warm and humid climate (e.g. Weissert & Lini 1991). The rate of seafloor spreading and volcanism during the Oxfordian is poorly known. Therefore it is not possible to determine whether an increase in the juvenile production of CO_2 occurred. We think that the carbon isotope evolution of the Liesberg Beds most likely reflects a climate change.

Conclusions

The most important result of this study is the introduction of the use of the *Millericrinus* spp crinoids and *Paracidaris* spp spines as isotope-stratigraphic markers. The spines of *Paracidaris* and stems of *Millericrinus* have nearly constant $\delta^{13}C$ values. Morever, when they come from the same level they have similar isotopic compositions, implying that they are good isotopic markers.

The $\delta^{13}C$ values of *Paracidaris* spines from Liesberg Beds overlap somewhat with those of the modern Cidaridae spines, but tend towards higher $\delta^{13}C$ values. The isotopic composition of carbon of the Oxfordian seawater must have been heavier than today.

The important $\delta^{18}O$ shift implies a diagenetic overprint for the oxygen.

The overlapping data fields of spines of *Paracidaris* spp and stems of *Millericrinus* spp demonstrate a common diagenetic evolution that includes precipitation of early cement in their stereome pores in equilibrium with seawater.

No difference was measured between subsurface samples from Mont Terri tunnel and the surface samples exposed to acid rain.

The heavier $\delta^{13}C$ values obtained in samples just above the transition from the Terrain à Chaille Member occurred during the transition away from an oxygen-limited environment with a high burial rate of organic matter. The lowest $\delta^{13}C$ values (≈ 1–1.5‰), which immediately follow stratigraphically, occurred during a high dissolved nutrient input to the platform under oxidizing conditions suggested by the well developed benthonic fauna. The positive $\delta^{13}C$ shift of 2‰ is confirmed by two different stratigraphic isotopic markers in the four studied sections. The positive shift seems to correspond to a general trend of opening up of the platform and connection to open marine waters. The $\delta^{13}C$ shift coincides with an eustatic sea level rise and a climate change proposed by Gygi (1986). The positive $\delta^{13}C$ shift of 2‰ within the Liesberg Beds Member probably reflects a global variation of the carbon cycle related to climate change.

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