Trace element contents of carbonate sediments from the Mazagan escarpment off central Morocco (CYAMAZ, 1982)

Geochemistry
Strontium
Trace elements
Chemiostratigraphy
Carbonates

Géochimie
Strontium
Éléments traces
Chimiostratigraphie
Carbonates

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ABSTRACT

Trace element analysis (Mg, Sr, Na, K, Mn, Fe, Ni, Cr, and Zn) of CYAMAZ carbonates shows that a geochemical characterization of platform and post-platform sediments is possible. Platform sediments geochemical study leads to precise the paleoenvironment and shows that late oceanic diagenesis (which take place after subsidence of the platform) does not alter trace element contents of rocks. An attempt of geochemical dating (chemostratigraphy) of post-platform sediments is made.

Oceanol. Acta, **1984.** Submersible Cyana studies of the Mazagan Escarpment (Moroccan continental margin), CYAMAZ cruise 1982, 1982, 153-159.

RÉSUMÉ

Teneurs en éléments traces des sédiments carbonatés de l'escarpement de Mazagan au large du Maroc (campagne CYAMAZ, 1982)

L'analyse des éléments traces (Mg, Sr, Na, K, Mn, Fe, Ni, Cr, Zn) de la fraction carbonatée de 48 échantillons prélevés lors de la campagne CYAMAZ montre la possibilité de caractériser géochimiquement les sédiments de plateforme et les sédiments post-plateforme. L'étude des sédiments de plateforme permet de préciser les conditions du paléoenvironnement et indique que la diagenèse tardive océanique (postérieure à la subsidence de la plateforme) n'a que peu d'influence sur la géochimie des sédiments de celle-ci. L'analyse géochimique des sédiments post-plateforme permet une approche chimiostratigraphique de ceux-ci, qui conduit à préciser l'âge du début de la subsidence de la plateforme.

Oceanol. Acta, **1984.** Études par le submersible Cyana de l'escarpement de Mazagan (marge continentale marocaine), campagne CYAMAZ 1982, 153-159.

INTRODUCTION AND METHODS

Abundances of Ca, Mg, Sr, Na, K, Mn, Fe, Ni, Cr, Zn relative to the carbonate fraction were measured in 48 samples collected on the Mazagan Escarpment during the CYAMAZ campaign (1982). The age of samples ranges from Late Jurassic to Quaternary.

After crushing and washing in distilled water to eliminate pollution by sea water, the rocks were dissolved in acetic acid. Trace element analysis was carried out by atomic absorption, according to the method described by Renard and Blanc (1971 ; 1972) and Renard (1984). Due to the presence of dolomite, some samples had to be discarded. The results are summarized in the Table. To compensate for any possible pollution caused by flushing out of the insoluble residue (*i.e.*, interlayer cations in clay minerals), all results are normalized to a 100 % $CaCO_3$ sediment on the graph *i.e.* :

$$[Sr]_{100} = \frac{[Sr]_{ppm} \times CaCO_3\ \%}{100}.$$

Table

Trace element contents of acetic acid soluble fraction of CYAMAZ sediments.

Teneur en éléments traces de la fraction carbonatée (fraction soluble à l'acide acétique) des sédiments prélevés au cours de la campagne CYAMAZ.

Sample	Mn	Fe	$CaCo_3$ %	Sr	Mg	Na	K	Ca	Ni	Cr	Zn
84.5	359.	192.	37.49	164	8 108	3 982.	1 105.	358 754	58.	7.	59.
85.1	31.	30.	98.16	174	4 909	192.	39.	384 968	14.	5.	11.
85.4	53.	70.	92.95	142	4 169	476.	152.	376 132	5.	6.	10.
85.5	44.	49.	98.16	161	4 407	180.	30.	386 041	11.	4.	15.
85.7	51.	75.	88.65	189	4 050	1 659.	366.	389 418	21.	5.	30.
86.2	15.	52.	97.84	307	4 252	500.	52.	397 357	9.	0.	29.
86.6	185.	55.	91.47	289	5 540	1 311.	233.	390 147	18.	1.	32.
86.7	124.	43.	74.89	141	6 639	900.	870.	375 103	31.	4.	37.
87.1	19.	53.	98.43	157	4 909	1 566.	40.	389 635	26.	4.	34.
87.2	66.	103.	86.13	112	2 872	432.	212.	387 303	19.	7.	7.
87.3	81.	41.	85.44	129	4 968	519.	204.	376 369	14.	3.	29.
87.4	27.	53.	94.67	131	3 991	845.	138.	387 528	8.	2.	71.
87.6	23.	50.	98.12	166	4 311	222.	31.	391 930	18.	6.	12.
87.8	23.	44.	97.82	106	3 382	284.	47.	379 293	13.	2.	8.
87.9	559.	81.	23.81	277	7 756	5 454.	2 727.	321 150	163.	15.	137.
88.1	31.	328.	97.70	104	4 713	352.	70.	374 049	20.	1.	52.
88.4	10.	65.	98.02	129	3 978	510.	30.	372 914	14.	4.	8.
88.5	20.	64.	96.14	121	4 602	374.	73.	346 014	14.	1.	30.
88.8	113.	147.	74.74	652	5 954	7 428.	1 423.	509 753	0.	0.	261.
88.9	84.	31.	95.67	245	5 497	484.	91.	384 427	18.	2.	26.
89.1	46.	62.	94.79	115	5 668	393.	112.	370 433	11.	1.	30.
89.3	56.	45.	79.78	134	5 469	901.	433.	343 953	60.	3.	17.
89.4	91.	38.	96.44	140	4 040	1 072.	87.	377 580	11.	0.	22.
91.2	13.	28.	98.80	125	3 922	364.	23.	376 495	17.	4.	11.
91.3	32.	48.	98.69	139	4 663	325.	26.	368 091	21.	4.	7.
91.8	653.	42.	20.06	261	9 126	7 677.	3 422.	308 302	284.	12	62.
92.1	921.	33 612.	81.63	203	100 933	2 793.	593.	218 624	18.	4.	23.
92.2	201.	253.	13.69	872	10 803	10 693.	3 175.	297 518	175.	44.	90.
92.4	113.	18.	80.32	422	11 067	1 359.	133.	350 209	31.	8.	44.
92.5	58.	46.	86.08	378	13 146	1 892.	163.	331 970	27.	10.	28.
94.2	14.	32.	98.31	129	4 618	303.	31.	378 572	7.	0.	15.
94.3	17.	55.	99.55	147	4 790	351.	29.	382 240	7.	3.	6.
94.4	12.	29.	97.40	128	4 173	1 204.	46.	369 267	10.	0.	21.
94.9	34.	16.	95.94	103	4 425	900.	122.	371 898	14.	0.	53.
95.4	1 142.	709.	7.80	563	34 633	41 688.	28 989.	171 755	132.	8.	241.
95.6	40.	52.	95.56	115	3 681	466.	60.	375 667	12.	0.	19.
95.7	22.	45.	96.70	134	4 581	1 307.	57.	375 476	7.	0.	11.
96.1	8.	33.	96.81	146	4 317	523.	36.	389 576	9.	4.	8.
96.5	185.	40.	14.71	710	6 113	10 393.	2 649.	276 864	143.	20.	93.
96.7	15.	52.	97.36	141	4 373	588.	33.	377 031	10.	0.	17.
96.9	13.	16.	98.70	160	4 999	242.	26.	387 018	4.	3.	6.
96.11	43.	52.	82.87	364	4 872	907.	182.	374 783	112.	10.	18.
98.1	19.	49.	97.56	154	4 449	356.	41.	395 484	14.	3.	8.
98.4	50.	69.	95.09	122	4 578	1 777.	114.	384 672	15.	2.	17.
98.5	15.	48.	98.81	168	5 539	424.	34.	378 789	7.	2.	8.
100.1	123.	1 083.	66.12	862	7 257	1 658.	479.	368 376	265.	18.	21.
100.4	112.	101.	71.83	612	6 659	1 934.	327.	372 026	138.	11.	16.
100.11	216.	104.	86.04	274	5 191	732.	257.	370 818	15.	9.	10.

GEOCHEMICAL CHARACTERIZATION OF PLATFORM AND POST-PLATFORM SEDIMENTS

Strontium-magnesium

The strontium *vs.* magnesium correlation graph (Fig. 1) shows geochemical differences between neritic and pelagic facies. For neritic facies samples, there is a positive relationship between strontium and magnesium contents ; for pelagic facies samples, the relation is negative.

This contradictory behaviour (Renard, 1979 ; 1984) seems to be due to :

a) a differential incorporation (biochemical fractionation) of Sr and Mg in the test of neritic and pelagic organisms ;

b) different physico-chemical conditions of diagenesis in the two realms. On continental shelves interstitial waters are impoverished both in Sr and Mg with regard to sea water by mixing with continental waters.

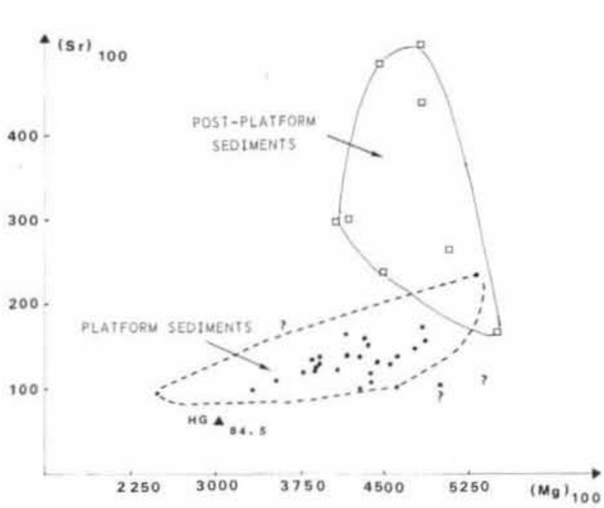

Figure 1

Strontium-magnesium relationship in the CYAMAZ sediments. HG = hard-ground.

Corrélation strontium-magnésium pour l'ensemble des sédiments analysés lors de la campagne CYAMAZ (1982). HG = hard-ground.

In oceanic sediments, interstitial waters, which only result from the diagenetic evolution of sea water, are enriched in Sr and impoverished in Mg with regard to ambient sea water ;

c) contrasting geochemical behaviour of Sr and Mg in the oceanic hydrothermal system.

In the present case, the geochemical distinction of the two types of sediments is complicated because platform and non-platform sediments are not of the same age. As Sr/Ca and Mg/Ca ratios of sea water changed during the last 140 Ma (Renard, 1984), it is difficult to distinguish geochemical evolution linked to facies variation from that linked to age variation. However, in our sample series, the first samples showing geochemical evidences of pelagic sedimentation are 96-11 (Central Mazagan Escarpment) and 100-4 (El Jadida Canyon) which correspond to Valanginian-Aptian biostratigraphic age. We shall try later to determine the age of post-platform sediments by geochemical methods.

Manganese-iron

On the correlation graph of these elements (Fig. 2), neritic samples and pelagic samples are located in two different areas. For these two facies, there is a positive relationship between Mn and Fe, but platform sediments present about the same content in Mn and Fe whereas post-platform sediments are enriched in Mn.

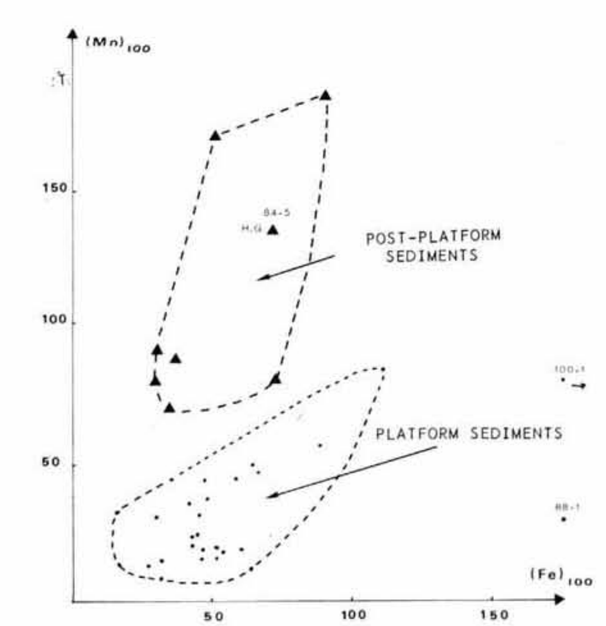

Figure 2

Manganese-iron relationship in the CYAMAZ sediments.

Corrélation manganèse-fer pour l'ensemble des sédiments analysés lors de la campagne CYAMAZ (1982). HG = hard-ground.

Two samples (88-1 : platform facies and 100-1 : post-platform facies) are iron-rich and do not follow this schematic pattern. At the present time, this iron enrichment with regard to the other samples cannot be explained. This is likely to be an artefact due to fragments of a metalliferous post-sedimentary crust not completely eliminated during sample preparation. For the Sr-Mg as for the Fe-Mn relationship, another sample (84-5) is exceptional. This neritic facies sample, perhaps an outer shelf facies (von Rad, this volume), which corresponds to an oolitic hard-ground, shows very low Sr and Mg contents. The implication is that this diagenetic induration was influenced, at least partially, by continental interstitial water [in the case of sea water interstitial influences, the sample should be Sr-low and Mg-rich with regard to other samples (Renard, 1979 ; Pomerol, 1984)]. Sample 84-5 shows also a Mn enrichment typical of other hard-grounds which explains the location of this neritic facies sample in the post-platform sediment area on the Mn-Fe relationship graph (Fig. 2).

Chromium-nickel

Although the correlation between Cr and Ni contents was not very strong, these two elements distinguish platform and post-platform facies very well (Fig. 3). The characteristics of platform sediments are :

$[Ni]_{100} \leqslant 25$ ppm and $[Cr]_{100} \leqslant 6$ ppm,

and those of post-platform sediments are :

$15 \text{ ppm} \leqslant [Ni]_{100} \leqslant 170 \text{ ppm}$
$6 \text{ ppm} \leqslant [Cr]_{100} \leqslant 15 \text{ ppm}.$

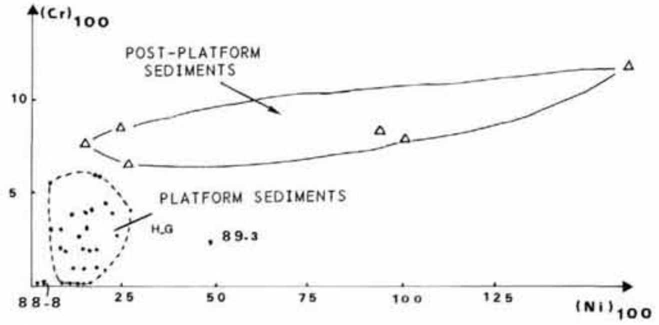

Figure 3

Chromium-nickel relationship in the CYAMAZ sediments.

Corrélation chrome-nickel pour l'ensemble des sédiments analysés lors de la campagne CYAMAZ (1982).

Sample 89-3, which shows post-platform sediment characteristics for Ni content, and platform sediment characteristics for Cr content, is a breccia resulting of a mixing of two facies. Sample 88-8 which has less nickel and chromium is a mixing of different age post-platform sediments but absence of Ni and Cr in this sample is not explainable.

Zinc

Zn contents of post-platform and platform sediments are not significantly different. Samples 87-4, 88-8, 95-4 are enriched in Zn, but this enrichment is not obvious.

PLATFORM SEDIMENT GEOCHEMISTRY AND PALEOGEOGRAPHY

On the whole, geochemical results from CYAMAZ platform sediments are not very different from those obtained from coeval platform sediments sampled in continental outcrops (Jaffrezo, Renard, 1979). This means that oceanic late diagenesis (subsequent to platform subsidence) in the case of CYAMAZ samples or meteoric late diagenesis in the case of continental outcrops, do not play an important role in trace element distribution. The most important part of chemical diagenesis transformation takes place during early and mesodiagenesis under platform conditions.

A previous paper on sediments from a similar facies and age (Jaffrezo, Renard, 1979) has shown that the geochemistry of platform sediments may be a useful paleogeographic tool. For the CYAMAZ sediments, the comparison of geochemical results with microfacies analysis (von Rad *et al.*, this volume) shows that the location of samples on various correlation graphs is linked to the nature of the microfacies (Fig. 4). Statiscally, samples from facies MF1 of von Rad (hemipelagic bioclastic packstone with Calpionellids) have lower Sr and Mg contents than samples from microfacies 2 (fore-slope bioclastic oolitic grainstone) or 3 (columnar stromatolitic peloidal packstone). On the other hand, microfacies 4 and 5 (neritic bioclastic peloidal grainstone and neritic oolitic grainstone) present the highest Mg and Sr contents. Thus, there is a positive gradient of Mg and Sr contents from microfacies 1 to microfacies 5-6 (but there are only a few samples of microfacies 6). If, on the basis of the occurrence of Calpionellids, we take microfacies 1 as the reference for " normal " marine sediments, we may conclude that microfacies 5-6 corresponds to hypersaline environments.

Paradoxically, the gradient of Fe and Mn contents is inverse, microfacies 1 samples present higher Mn and Fe contents than microfacies 4-5 samples (Fig. 5).

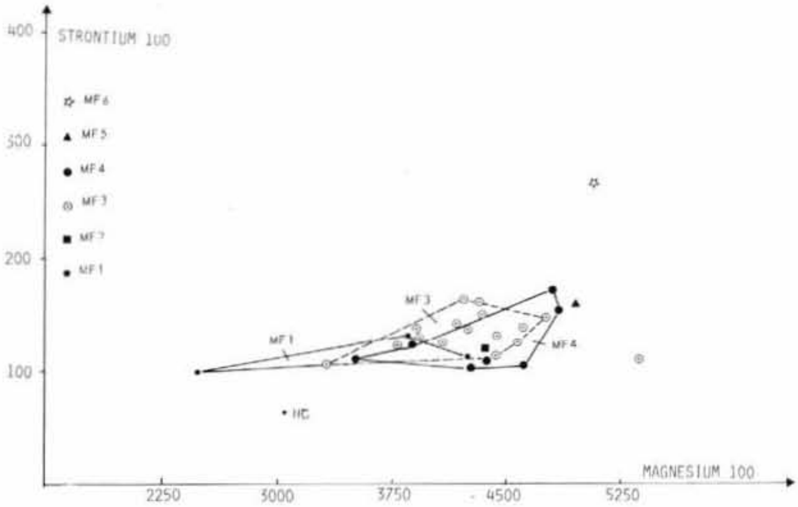

Figure 4

Correlation between Sr-Mg contents and microfacies in the platform sediments. MF1 to MF6 = microfacies types described by von Rad (this volume). HG = hardground.

Relation entre les teneurs en Sr et Mg et les microfaciès dans les sédiments de plate-forme de la campagne CYAMAZ (1982). Les sigles MF1 à MF6 correspondent aux microfaciès décrits par von Rad (1985). HG = hard-ground.

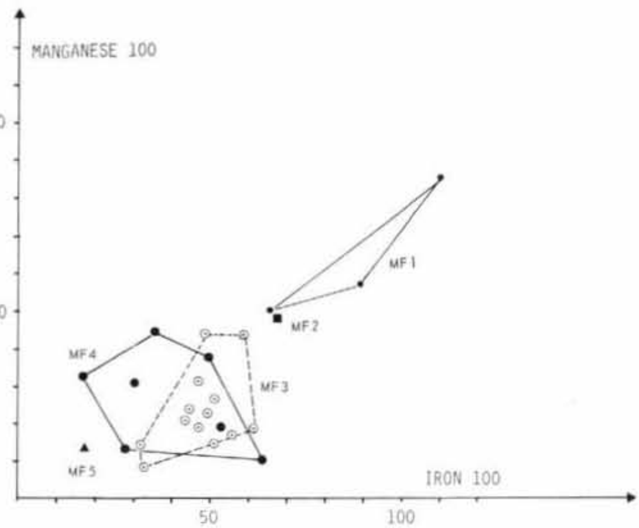

Figure 5

Correlation between Mn-Fe contents and microfacies in the platform sediments.

Relation entre les teneurs en Mn et Fe et les microfaciès dans les sédiments de plate-forme de la campagne CYAMAZ (1982).

Two explanations are possible :

a) the hypersaline environment of microfacies 4-5 is not enough oxidizing to allow the precipitation of Mn and Fe oxides ;

b) the main origin of Fe and Mn is not continental and the more marine microfacies are the more iron-manganese rich.

The occurrence of oolites in microfacies 5 makes the second hypothesis more realistic.

AN ATTEMPT AT GEOCHEMICAL DATING (CHEMOSTRATIGRAPHY) OF POST-PLATFORM SEDIMENTS

General evolution curves of pelagic carbonate Sr and Mg contents have been recently established (Renard, 1984) for the last 140 Ma. These curves are relative to the analysis of 1 520 pelagic carbonate samples obtained from various DSDP sites (116, 305-306, 390A, 391C, 392A, 398D, 400A, 401, 402, 516-516F, 549,

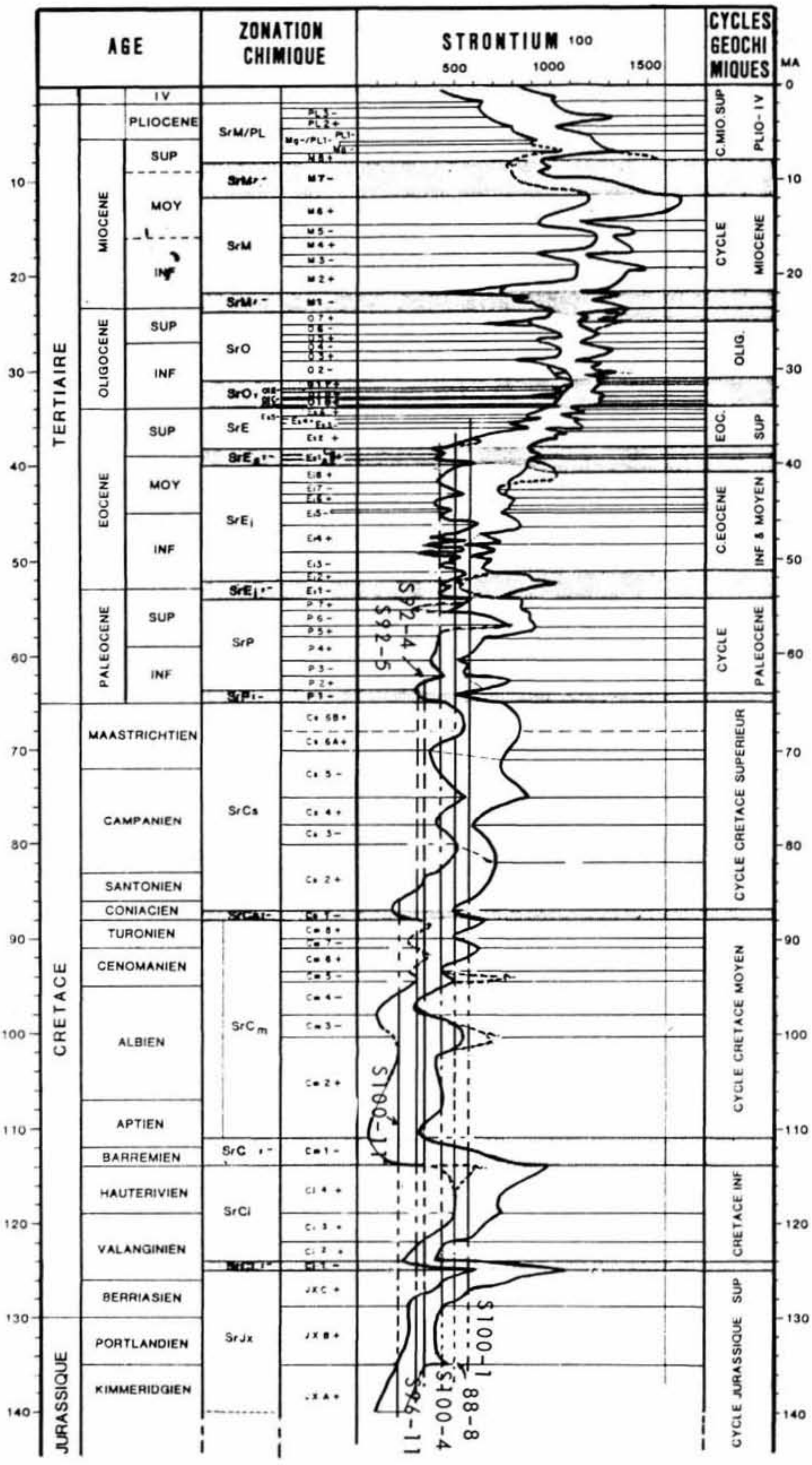

Figure 6

Attempt to date post-platform sediments by their Sr content. General evolution curve of Sr contents from Renard (1984).

Essai de datation des sédiments post-plate-forme de la campagne CYAMAZ (1982) par leurs teneurs en Sr. La courbe d'évolution générale des teneurs en Sr des carbonates pélagiques provient de Renard (1984).

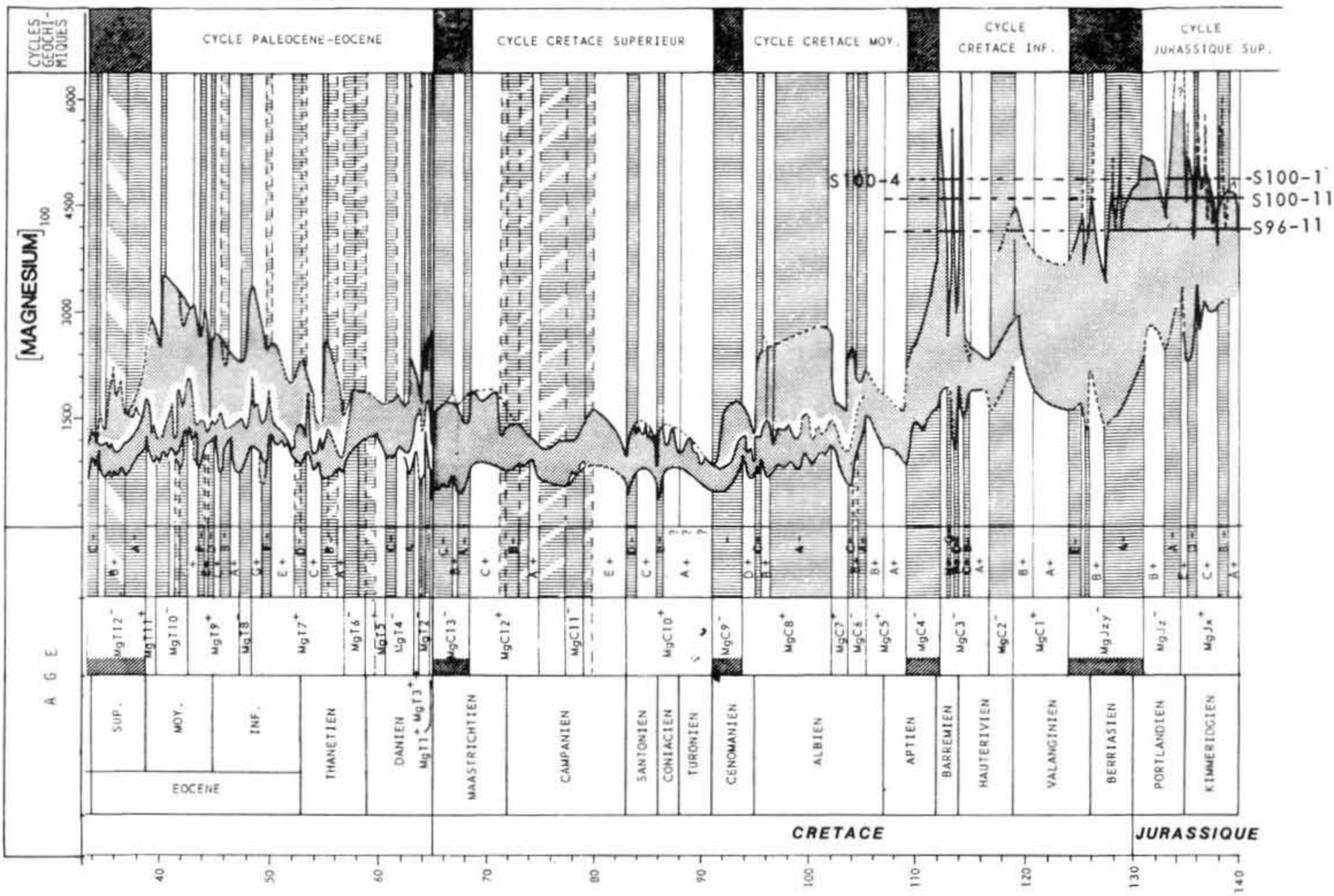

Figure 7

Attempt to date post-platform sediments by their Mg content. General curve of Mg contents from Renard (1984).

Essai de datation des sédiments post-plate-forme de la campagne CYAMAZ (1982) par leurs teneurs en Mg. La courbe d'évolution générale des teneurs en Mg des carbonates pélagiques provient de Renard (1984).

550) and from inshore outcrops (Gubbio : Italy ; Sierra Fontcalent : Spain ; El Kef : Tunisia ; Bidart : France).

These curves make it is feasible to attempt to date post-platform sediments of the CYAMAZ campaign. The age of a sample is given by the intersection of horizontal line corresponding to Sr and Mg content of the sample and the general evolution curve of these elements (Fig. 6 and 7). For one element, many age assignations are possible. Figure 8 gives age estimates obtained from Sr curve, from Mg curve and from biostratigraphic data (this volume). It may be seen that when we use the double calibration of Sr plus Mg (samples 96-4, 100-1, 100-4, 100-11), geochemistry leads not only to age estimates in correlation with biostratigraphic date but also to more restricted age ranges than those found through biostratigraphic methods (in these more or less recrystallized limestones, only a very poorly preserved, sparse nannoplancton flora was determined, *see* Čepek *et al.*, this volume).

On the other hand, when occurrence of dolomite makes the " Mg age zonation " invalid (sample 88-8, 92-4, 92-5), geochemical dating (based only on Sr values) is too imprecise. However, it is now possible using several " chemical markers " (adding carbon isotopic ratio ; Renard, 1984) to attempt a coherent chemostratigraphy of pelagic carbonates from Late Jurassic to Quaternary.

For the CYAMAZ sediments, this chemostratigraphic methods leads, by dating the first non-platform sediments, to a more precise age estimate of the platform subsidence. This ranges from Late Kimmeridgian-Erly Portlandian on Central Mazagan Escarpment (sample 96-11) to Barremian in El Jadida Canyon area (samples 100-1, 100-4, 100-11). According to von Rad *et al.* (synthesis chapter, this volume), the subsidence of the Central Mazagan Escarpment and El Jadida canyon area below " shallow-water depth " was Late Berriasian to Valanginian and certainly before Barremian (based on different evidences).

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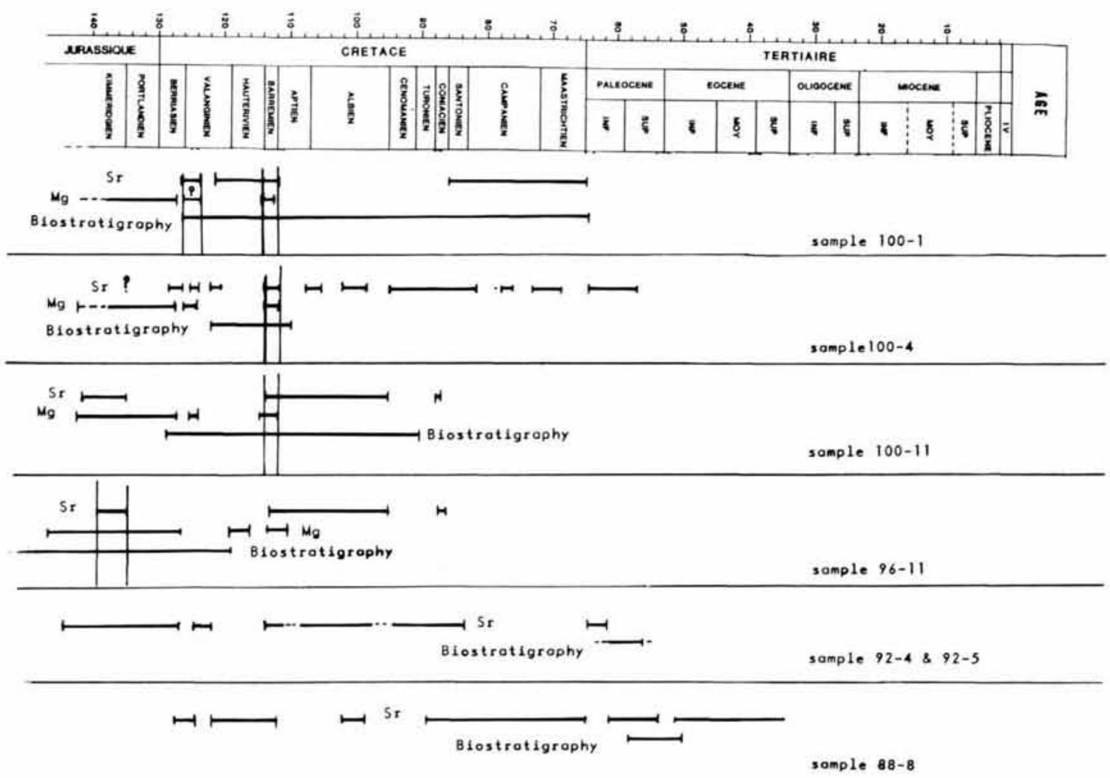

Figure 8

Comparison of age obtained by biostratigraphic and by chemostratigraphic methods for six post-platform samples.

Comparaison entre les âges obtenus par biostratigraphie et par chimiostratigraphie pour six échantillons post-plate-forme.

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