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Gypsum-calcite rosettes in sediments from the Congo deep-sea fan

Marge africaine
Delta sous-marin Congo
Rosette calcite
Origine structure salifère
African margin
Congo deep sea fan
Calcite rosette
Deep-sea salt layer

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ABSTRACT

The occurrence of "rose"-like aggregates with diameters of a few centimetres in a core of dark brown siliceous mud of the Congo deep-sea fan (depth of 4 070 m) is reported. The rosettes are well preserved. They have the crystalline outlines of gypsum but are made of calcite (97%) with traces of quartz and clay minerals. In addition to the preserved specimens, fragments of rosettes occur at various levels in the sedimentary column. The core was taken on a levee of the submarine canyon and the depositional environment is thus compatible with down-slope sedimentation. Discussion concerning the origin of the rosettes takes into account regional morphology and structure, sedimentary cover and the isotopic composition of calcite from the rosettes. The most probable origin of the gypsum which was epigenized is the cap-rock of a salt dome. From seismic records, salt domes are seen to affect the lower continental margin, where they form sharp diapiric-structures, and the Congo submarine canyon cut through these structures. These rosettes of salt-dome origin may be the first direct evidence of the presence of deep salt layers off the African coast.

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RÉSUMÉ

Rosettes de calcite épigénétique dans les sédiments du delta sous-marin du Congo

Au cours de la campagne Walda réalisée avec le NO « Jean Charcot », une grande carotte (1 860 cm) a été prélevée au voisinage du cours sous-marin du Congo par 4 070 m de profondeur et à 450 km de la côte. Dans cette carotte, trois agrégats à contours cristallins rappelant des « roses des sables » ont été trouvés à des niveaux différents, ainsi que quelques fragments disséminés dans le sédiment. La forme cristalline rappelle celle du gypse, mais l'analyse chimique montre qu'il s'agit de la calcite quasi pure avec un peu de halite. Le sédiment encaissant de ces « roses » a été étudié et comparé à d'autres carottes prélevées dans le cours profond du Congo. Pour expliquer l'origine de ces rosettes, on apporte des arguments structuraux (sismique), sédimentaires et des résultats d'analyse isotopique : ^{13}C et ^{18}O. Ces données sont discutées. L'hypothèse la plus vraisemblable est que ces rosettes étaient constituées initialement de gypse et proviennent d'un *cap rock* de structure salifère. Une recristallisation en calcite (calcite stœchiométrique) se serait effectuée en milieu pratiquement fermé (sans influence marine) en présence de matière organique fournie par le continent pendant le dernier épisode glaciaire. Des structures diapiriques sont mises en évidence sur les profils sismiques et particulièrement sur la partie profonde de la marge continentale. L'activité érosive des courants de turbidité dans le canyon sous-marin du Congo aurait entaillé ces domes de sel jusqu'au *cap-rock*

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de gypse. Ces rosettes seraient la première évidence directe de la présence de niveaux évaporitiques profonds au large de la côte africaine. —

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INTRODUCTION

During Cruise Walda with RV "Jean Charcot" in July 1971, an 1 860 cm-long core (KW 22) was taken at a depth of 4 070 m on the submarine delta of the Congo River (Fig. 1). X-ray radiography immediately after the coring operation revealed, at three levels in the core (475, 625 and 885 cm), the presence of "rose"-like objects a few centimetres in diameter (Fig. 2). The split core confirmed the occurrence of roughly spherical indurated concretions (3 to 6 cm diameter), composed of numerous pseudocrystals and with the general shape of a small rose (rosette) (Fig. 3). The crystalline contours are sufficiently well preserved to permit identification of monoclinic prisms reminiscent of gypsum. However, the reaction with HCl was strong and suggests the presence of carbonate. The individual pseudocrystals are composed of aggregates of poorly cemented, greyish to reddish grains a few millimetres in diameter, making the roses highly porous and friable. In addition to the complete specimens, fragments of rosettes are visible at various levels in the upper 1 200 cm of the core, scattered throughout the sediment and well-preserved.

MINERALOGY AND CHEMISTRY OF THE ROSETTES

X-ray diffraction study of one of the rosettes (from the 625 cm level) shows it to be composed of Mg-free calcite ($97 \pm 6\%$) with small quantities of halite ($1.3 \pm 0.1\%$) probably due to the evaporation of interstitial sea water, and traces of quartz and clay minerals.

Scanning micro-photographs of the calcite reveal two different types of morphology, the most common of which is "sheaf"-like and the other is rhombohedral. Because it was observed only on the surface of the rosette, the rhombohedral form could be of a secondary origin.

Chemical analyses of major and trace elements give the following results:

Table
Major elements (weight per cent).
Éléments majeurs (pourcentages pondéraux).

	KW 22 475 cm	KW 22 625 cm	KW 22 885 cm	MED gypsum rosette
SiO_2	0.24	1.2	2.08	4.88
Al_2O_3	0.45	0.4	1.15	1.39
Fe_2O_3	0.06	0.1	0.22	0.34
MgO	0.33	0.77	0.55	0.69
CaO	53.34	52.5	50.83	31.17
Na_2O	–	0.14	–	–
K_2O	0.02	0.22	0.06	0.25
TiO_2	0.06	0.04	0.03	0.06
P_2O_5	0.31	–	0.33	0.20
Ignition loss 110°	0.45	0.46	–	17.51
Ignition loss 1 000°	44.42	44.83	44.07	3.59
Total	99.63	–	99.32	60.08

Trace elements (ppm) (level 625 cm): Sr = 1837, B = 78, Mn = 60, Cu = 44, Ba = 36, Cr = 8, Pb = 7, Zn = 5, Ni = 5.

Stable isotopes analyses and radiometric age

Carbon and oxygen isotope measurements give the following values.

Figure 1

Bathymetric chart of Congo submarine canyon showing depths in uncorrected fathoms (after Heezen et al., 1964). *Small solid circles are positions of cores described in the Heezen* et al., *publication. Core KW 22 (large solid circle) is located at 06°38'3 S and 08°17'7 E. P 31 and P 32 are tracks of seismic profiles discussed in text (and see Fig. 4). Dotted area is the lower limit of geographic extension of salt layer on continental margin (Pautot* et al., 1973).

Carte bathymétrique du canyon du Congo (d'après Heezen *et al.*, 1964). Les sondages sont reportés en brasses avec une équivalence de 800 brasses par seconde. Les cercles noirs représentent la position des carottes décrites dans la publication de Heezen *et al.*, P 31 et P 32 sont les profils de sismique réalisés par le Cnexo/Cob durant la campagne Walda. La zone en pointillés correspond à la limite vers le large de l'extension des faciès salifères (Pautot *et al.*, 1973).

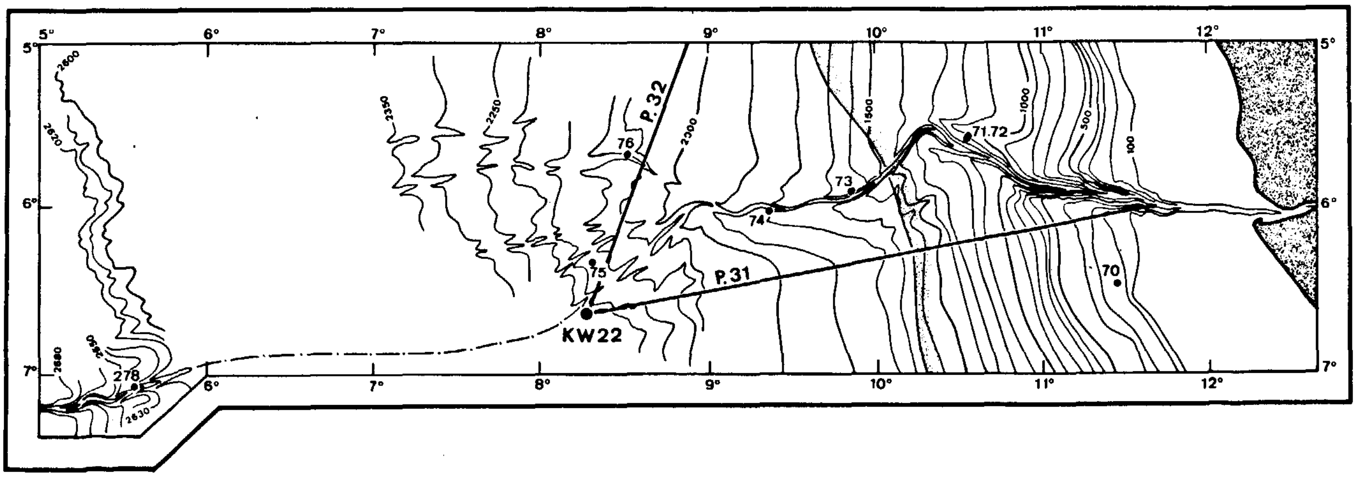
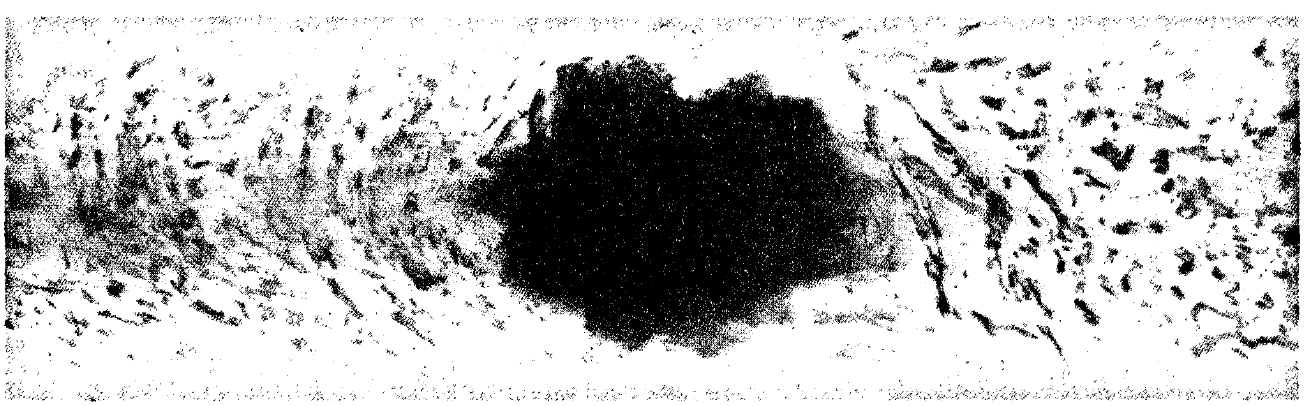


Figure 2

X-ray radiography of the core KW 22 showing rosette at level 625 cm with same diameter as the piston core barrel (about 5 cm).

Radiographie de la carotte Walda KW 22 montrant une rosette au niveau 625 cm qui a un diamètre voisin de la carotte (environ 5 cm).



Level (cm)	δ^{18}O/PDB	δ^{13}C/PDB	^{14}C Age BP
475 m	+ 2.93	− 25.25	–
625 m	+ 1.70 + 1.67	− 21.09 − 21.01	18 650 ± 400
890 m	+ 1.72 + 1.77	− 13.07 − 12.79	–

DEPOSITIONAL ENVIRONMENT OF THE SEDIMENTS

The sediment accompanying the rosettes in the core is a siliceous mud with a high pyrite content. From 0-1 000 cm, the sediment is dark brown with olive green intercalations, wood fragments and well preserved organic material. Numerous hydrotroilite spots and H_2S bubbles provide further evidence of reducing conditions. Apart from a few well-defined silt laminations, there is no grain sorting. The deeper part of the core (1 000-1 860 cm) is darker, and unlaminated silts occur near its base. They are no indications of secondary reworking at or near the levels where the rosettes occur.

Smear slides confirm this general megascopic description. The siliceous mud contains a high proportion of clay (up to 60%), organic matter (plants of continental origin), and pyrite (2 to 5%). Diatoms are frequent and are associated with some radiolarians and silicoflagellates. Carbonates are absent and quartz grains are rare. At some levels of the core, pyrite and organic matter are very abundant and the sediment closely resembles deep-sea sapropels, such as those found in the Mediterranean. Diatom spectra suggest a Quaternary age for all the cored sediments.

During the Walda Cruise, sea floor photographs were taken at the site of core KW 22, and reveal soft sediments without bottom-current features, but with numerous animal trails: holes, tumuli and tracks... At a greater depth, in the Congo canyon, Heezen *et al.* (1964) described a similar, generally muddy, current-free bottom with fairly abundant tracks and trails. They describe six piston cores taken during cruise 12 of RV Vema on the Continental Slope and on the Continental Rise in the Canyon (Fig. 1): cores close to the axis of the canyon contain silts and sand beds; cores farther from the axis show mainly hemipelagic silty clays with a few thin silt layers. The closest core (V12-75) to core KW 22 consists of graded silts and sands, with leaves and twigs of dicotyledon land plants.

The six piston cores contain appreciable amounts of pyrite. In many places, pyrite exists as a coating on another mineral; in some places it occurs inside diatom frustules. Gas bubbled profusely from core V12-73 when it was extruded. This core, and cores in the vicinity of the canyon provide evidence of reducing conditions (dark sediment, authigenic pyrite and preservation of organic matter). No rosettes were found in any of the cores described. In core n° 279 (04°56'S and 05°00'E), however, a bed of light-brown crystalline carbonate sand was found. The carbonate is reported to consist of small rhombohedra of calcite (with < 5% aragonite), and the sands contain no organic material.

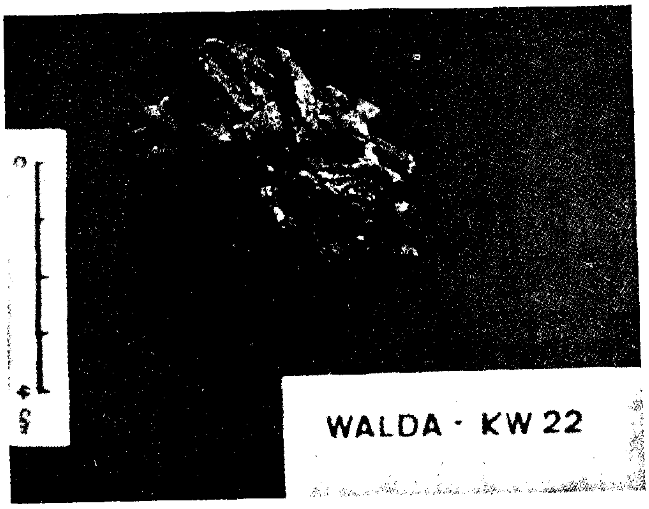
REGIONAL MORPHOLOGY AND STRUCTURE

Profile 31 (Fig. 3) is roughly parallel to the southern side of the Congo Canyon and starts at the shelf break where the upper continental margin deepens progressi-

Figure 3

Photograph of the same rosette (level 625 cm).

Photographie de la même rosette du niveau 625 cm.



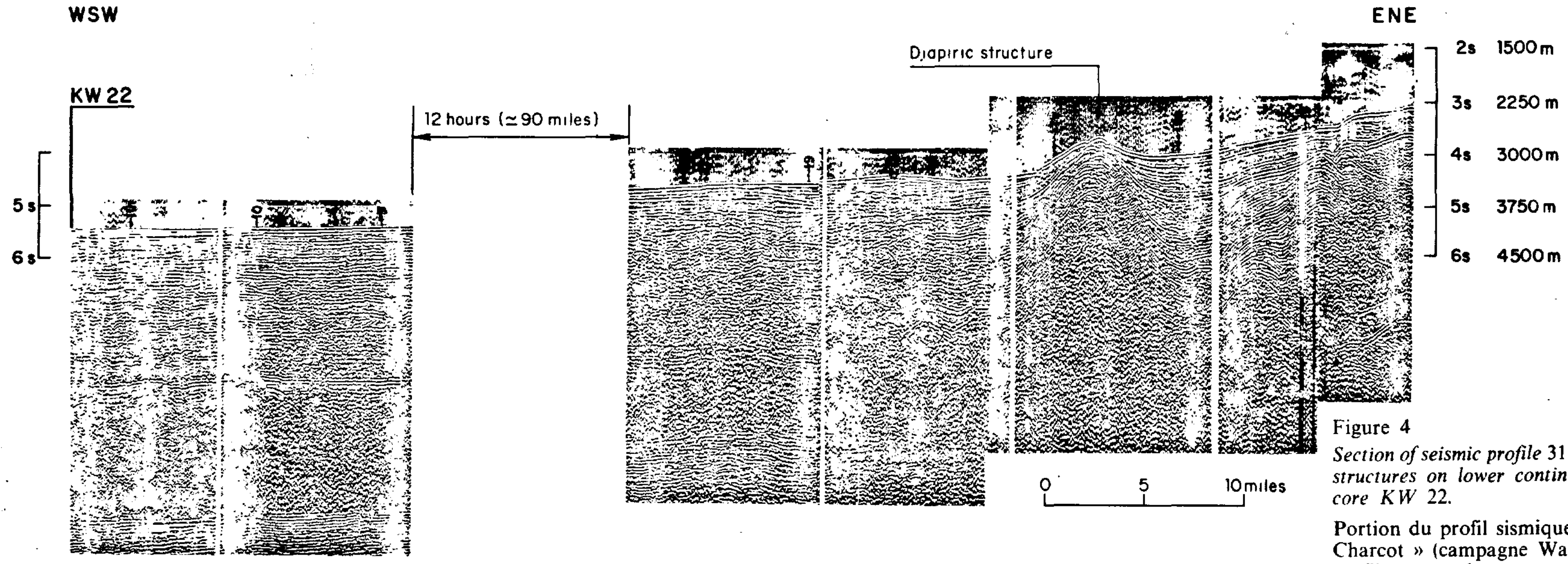
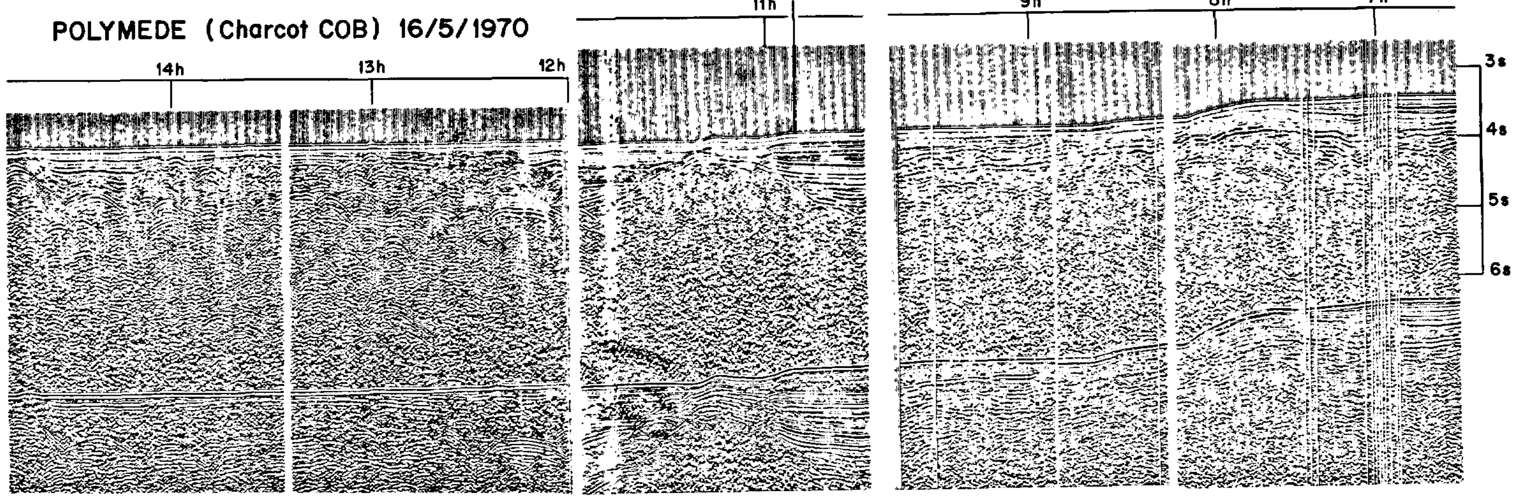


Figure 4
Section of seismic profile 31 (Flexotir system) showing diapiric structures on lower continental margin and position of the core KW 22.

Portion du profil sismique n° 31 réalisé par le NO « Jean Charcot » (campagne Walda) avec le système flexotir. Ce profil montre des structures diapiriques affectant la partie profonde de la marge continentale. La position de la carotte KW 22 est reportée.

Figure 5
Section of seismic profile (Flexotir system) showing a diapiric structure in the Mediterranean Sea, and the position of the drilling site 124, where a gypsum rosette was sampled below 350 m of sediment.

Portion d'un profil sismique réalisé par le NO « Jean Charcot » (campagne Polymède I). Le profil est situé dans le bassin occidental méditerranéen entre les Baléares et la Sardaigne. La position du forage 124 est reportée. Dans ce forage une rosette de gypse a été trouvée sous 350 m de sédiment.



vely. The Continental Rise is relatively flat but shows channels and disturbed areas associated with meanders of the Congo submarine delta or with basement structures.

Core KW 22 is located on a levee south of the Canyon (Fig. 1), and the bathymetric survey conducted by RV "Charcot" further reveals the deltaic nature of the environment. The 3.5 kH records show a transparent layer covering deeper, layered reflectors. Diapiric structures are found from depths of 2 000 m to the foot of continental margin (Fig. 4).

At the location of the core seismic profiles (reflection and refraction) reveal a great thickness of stratified sediments (3 seconds d. t. ~ 3 000 m) covering another sequence of disturbed sediments (1 second d. t.) and a very rough acoustical substratum. This pattern extends for 200 km up to the foot of the continental slope.

On the lower part of the continental slope, diapiric structures (salt domes) disturb the entire sedimentary cover (Pautot *et al.*, 1973). Profile 31 reveals zones of salt undulations (upper continental margin) and zones of salt-injected faults and diapiric structures (lower continental margin), the latter being noticeable to a depth of 3 200 m in this area.

DISCUSSION: ORIGIN OF THE ROSETTES

Although such rosettes have not been described in other cores from this part of the ocean, their large size (approximately the same as the diameter of the core), and their occurrence as preserved specimens or fragments throughout the length of core KW 22, suggest that they could be rather frequent in this area.

As shown by the well-preserved crystalline contours of the aggregates, the rosettes were primarily made of gypsum. Because oceanic water is undersaturated with respect to gypsum, the occurrence of this mineral in bottom sediments can only be due to (i) oxidization of preexisting sulphides, (ii) reworking. Since the environment is clearly reducing, hypothesis (i) may be ruled out. Whatever its primary origin, the gypsum was not authigenic in this sedimentary environment. Because of the vicinity of salt domes on the continental slope we believed that the cap-rock of these domes provided the source of the gypsum.

Cap-rocks have typically three concentric mineralogic zones (Murray, 1968):

- an external carbonate zone;
- a middle transitional zone with gypsum, sulphur or sulphides but in many cases including varied mineralogical suites;
- a lower anhydrite zone.

At site 124 of the leg XIII of the "Glomar Challenger" Mediterranean cruise (Ryan and Hsü, 1973), in the neighbourhood of a diapiric structure (Fig. 5), the drill reached evaporitic series beneath 350 m of plio-pleistocene turbidites and contourites.

A rosette of gypsum very similar to KW 22 (625 cm) was recovered in gypsiferous layers at the boundary of massive anhydrite (Dsdp 13-124-7/1 (10 cm)) (Fig. 6).

The submarine Congo Canyon cuts through areas of salt domes on the lower continental margin (Pautot *et al.*, 1970; Pautot *et al.*, 1973; Belmonte *et al.*, 1965) with some sharp changes in direction which are apparently related to major fault systems. Tectonic activity, including diapirism and subsidence as well as erosion by turbidity currents, are the basis of the explanation of the presence of the gypsum rosettes buried in shallow deep sea sediments.

The following questions thus arise: what were the environmental conditions of epigenesis of gypsum into calcite? did the epigenesis take place within bottom sediments at the sampling location or in the cap-rock itself before transportation?

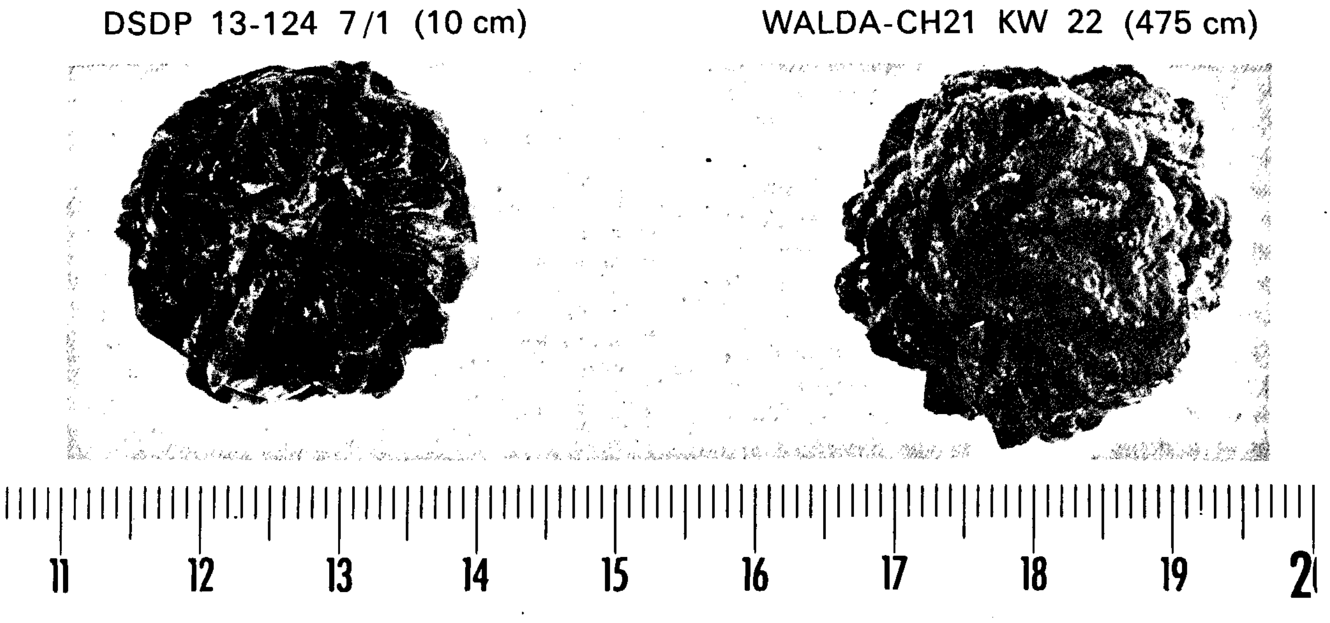
If one excepts the rosettes, the remainder of the sediment is carbonate free. It thus appears that carbonate crystallization is exclusively correlated to the occurrence of preexisting gypsum. The very low isotope content of the carbon indicates that during crystallization of the carbonate the aqueous carbon of the environment was mainly provided by organic decay. This biogenic origin of the CO_2 is strict at 475 cm and dominant at 625 cm.

This suggests that the carbon of calcium was supplied by organic compounds which reduced gypsum. Since all the carbon of the carbonate comes from organic matter, one may propose a reaction of the type:

Figure 6

Comparison of a Congo rosette (Walda-CH 21) and a Mediterranean gypsum rosette (Dsdp 13-124-7/1).

Comparaison d'une rosette du delta du Congo (Walda-CH 21-KW 22) et d'une rosette de gypse de Méditerranée (Dsdp 13-124-7/1).



$$CaSO_4 + C^{4-} + \cdot H^+ \rightarrow CaCO_3 + H_2O + S^{2-},$$

which represents a fully-closed system in which calcite saturation is continuously maintained.

The $\delta\ ^{13}C$ value of $-25.25^0/_{00}$ is typical of most continental plants (see Deines, 1979).

Because the available mass of the sample at 475 cm was too limited, no ^{14}C measurement was attempted. But at 625 cm the ^{14}C age of $18\,650 \pm 400$ indicates that the reduction process involved Pleistocene organic matter and probably wood as suggested by the numerous plant relicts found in the core. Furthermore this finite age rules out the possibility that fossil fuel could have been involved in the process.

A $\delta\ ^{13}C$ value close to $-13^0/_{00}$ is obtained at 890 cm. Two mechanisms may account for this deviation from pure closed system value. First, the aqueous carbon released by the reduction process ($\delta\ ^{13}C \simeq -25^0/_{00}$) be mixed with an approximately equal amount of aqueous marine carbon ($\delta\ ^{13}C \simeq -1$). The resulting carbonate would have an isotopic content of $-13\ /_{00}$. Another possibility is that the reduction process released more CO_2 than necessary for a stoichiometric precipitation of calcite. For instance:

$$CaSO_4 + 2C \rightarrow 2\,CO_2 + S^{2-} + Ca^{2+}.$$

In the case of CO_2 excess the fractionation which takes place between CO_2 and the solid carbonate is approximately $+13^0/_{00}$ at ocean bottom temperature (Bottinga, 1968). Thus, the calcite is enriched in ^{13}C with respect to CO_2 as soon as CO_2 is in excess with respect to calcium. Whatever the mechanism, mixing or isotopic fractionation, for the observed enrichment at level -890 cm, it means that the system was open when calcite crystallized.

Environmental conditions of crystallization can be deduced from ^{18}O content assuming isotopic equilibrium. In this case the relationship between temperature, $\delta\ ^{18}O$ (carbonate) and $\delta\ ^{18}O$ (water) is (Craig, 1965):

$$t°C = 16.9 - 4.2\,(\delta_{carb} - \delta_{water}) + 0.13\,(\delta_{carb} - \delta_{water})^2.$$

The conditions were probably identical for samples -890 cm and -625 cm, which exhibit similar ^{18}O values (average $\delta\ ^{18}O = +1.72$). With the present-day value of ^{18}O of mean ocean water, i. e. zero, a temperature of 9.4°C may be calculated, which appears too high for ocean water at 4 000 m depth. Furthermore, if account is taken of the glacial age of the sample a positive value must be adopted for ^{18}O content of ocean water (Shackleton, 1977). In that case, the calculated temperature is higher than 9.4°C and incompatible with ocean bottom temperature.

The ^{18}O content of +2.93 found at 475 cm leads to a calculated temperature of 5.1°C in postglacial water which is still probably higher than actual bottom temperature at a depth of 4 000 m. The difference in the calculated temperatures of crystallization could suggest that epigenesis took place at different depths along the continental slope.

It must, however, be noted that the hypothesis of transportation in the form of calcite is difficult to reconcile with the porous and friable texture of the rosettes. Furthermore, the sedimentary environment where they were sampled is compatible with an *in situ* reduction of gypsum. In that case the ^{18}O content of ocean bottom waters would have been lower than present-day average for ocean masses. This would imply a significant local dilution of marine waters by continental suppliers, especially during glacial times.

If however the rosettes were transported in the form of calcite by bottom currents the sedimentation rate calculated on the basis of the ^{14}C age at 625 cm, i. e. $0.34\ m.myr^{-1}$, is a lower limit.

Acknowledgements

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