行政院國家科學委員會補助專題研究計畫成果報告

※※※※※※※※※※※※※※※※※※※※※※※※※※※※※※※※※※

※ 陸棚泥與砂中之脂質 ※

※※※※※※※※※※※※※※※※※※※※※※※※※※※※※※※※※※

計畫類別：一般型研究計畫(個別型)
計畫編號：NSC 89-2611-M-002-044
執行期限：89 年 8 月 1 日至 90 年 7 月 31 日
計畫主持人：鄭偉力

(本成果報告應繳交之附件：無)

執行單位：國立台灣大學海洋研究所

中 華 民 國 90 年 10 月 12 日

行政院國家科學委員會專題研究計畫成果報告

計畫編號：NSC 89-2611-M-002-044
執行期限：89 年 8 月 1 日至 90 年 7 月 31 日
主持人：鄭偉力　　國立台灣大學海洋研究所

一、中文摘要

本計畫分析東海中、外陸棚六個表層沈積物中泥質與砂質部份之脂肪族烴類、脂肪醇與固醇的組成。結果顯示：脂肪族烴類組成在砂質部份中分布簡單並以正烷類為主，而在泥質部份中則相當複雜以正烷類與支鏈烷類為主。正烷類碳優指數在砂質部份之平均值為 1.60，在泥質部份之平均值為 2.38；暗示泥質部份較年青或新鮮而砂質部份較年老或受到降解。正脂肪醇與固醇在泥質與砂質部份中之分布相似，而且砂質部份皆檢測到葉綠素醇；此外，泥質與砂質部份之高等植物烷類(HPA)指數很相近，指示砂質部份並非全然為殘餘沈積物，即是含有部份近代沈積物。

關鍵詞：脂質、砂、泥、殘餘沈積物、現代沈積物

Abstract

In this project, six surface sediment samples from the mid- and outer shelf of the East China Sea have been analyzed for their lipid composition in the mud and sand fractions. Results indicate that the composition of aliphatic hydrocarbons in the sand fractions is relatively simple with *n*-alkanes predominant and that the composition of the mud fractions is rather complicated with *n*-alkanes and branched-chain alkanes predominant. Carbon preference index (CPI) values of C_{25}-C_{33} *n*-alkanes average 1.60 for the sand fractions and 2.38 for the mud fractions, suggesting that the sand fractions are relatively older and much degraded and the mud fractions are relatively younger and less degraded. There is a high similarity in the *n*-alkanol and sterol distributions for the mud and sand fractions. Further, phytol has been detected in all sand fractions. Higher plant alkane (HPA) indices for sand and mud fractions are quite close, indicating that the sand fractions are not all relict sediment but palimpest sediment instead.

Keywords: lipids, sand, mud, relict sediment, modern sediment

二、緣由與目的

The sediment discharged from the

Changjiang is confined to the coastal zones of the East China Sea and ultimately transported south and southwestward by the Changjiang Coastal Water (Milliman et al., 1985); offshore transport has been prevented by tidal currents and by the northward movement of the Taiwan Warm Water (Milliman et al., 1989). On the continental shelf of the southern part of the East China Sea where discharge of river sediments is fairly small, relict sediments form a broad continuous deposit, and so far in the coastal zones of China no coastal depositional body is known to have formed from sediments derived directly from the continental shelf (Li et al., 1991). This is supported by geophysical analysis of high-resolution (<1m) GeoPulse seismic reflection and Chirp sonar data, which reveals the presence of a thin (1- to 5-m-thick) sediment veneer over a highly reflective transgressive surface (Bartek and Wellner, 1995). Especially, the outer portion of the East China Sea shelf is mainly composed of relict sediments; they may be the result of sand deposition on ancient beaches formed when the sea stood at a lower level than its does today. After sea level rose, the sands in these areas were not removed or slightly buried by later sediment accumulation. These relict shelf sediments are totally different from those ancient sediments buried at depth, but are on the surface of the sea bottom in the oxic environment. From the analyses of phytol, *n*-alkanes, *n*-alkanols and sterols in these sediments, it is concluded that most sediments are not really relict, but palimpsest instead (Jeng, 1999). Further, during sample work-up of the surface sediments from the outer East China Sea shelf, a distinct size difference was noticed. These sediments exhibit a discontinuity in particle size, that is, sand and mud fractions are clearly separated although sand is the dominant component. This suggests that the sand fraction is relict sediment and the mud fraction modern sediment, which was deposited from the water column and/or through sediment transport. The relict sediments presumably contain residual lipids from the last glaciation and are expected to be quite different from modern sediments in terms of lipid composition. In contrast to heavy metals, lipid molecules have a unique character of degradation, which allows us to compare relict sediment with modern sediment.

In this project, six sediment samples were collected from the mid- and outer shelf and separated into sand and mud. These two size fractions were freeze-dried, extracted, isolated, and analyzed for aliphatic hydrocarbons, alkanols and sterols. The purposes of the present proposal (1) to obtain the lipid compositions in the sand and mud fractions in the East China Sea shelf sediments and to compare them, and (2) to assess if the shelf sand is really relict sediment in terms of lipid composition.

三、結果與討論

From the GC chromatograms of aliphatic hydrocarbons, the sand fractions similarly show relatively simple distribution patterns with *n*-alkanes predominant, whereas the mud fractions similarly exhibit rather complicated distribution patterns dominated by *n*-alkanes and branched-chain alkanes. Further, the sand fractions have comparatively low concentrations in aliphatic hydrocarbons, and the mud fractions have relatively high concentrations. This can be attributed to the grain size effect and lipid degradation. With respect to lipid degradation, the shelf sand is presumably deposited in the last glaciation, and the shelf mud is considered modern deposition. A comparison of carbon preference index (CPI, C_{25}-C_{33}) values is given in the following table.

Sample	CPI (C_{25}-C_{33})
493-16S	1.91
493-16M	2.47
493-17S	1.53
493-17M	2.00
493-22S	1.76
493-22M	2.17
551-27S	1.47
551-27M	2.82
551-32S	1.40
551-32M	2.64
551-38S	1.55
551-38M	2.20

It is seen from the above table that generally the sand fractions have lower CPI values than the mud fractions. The grain size effect on CPI for modern sediments is that CPI values decrease as grain sizes decrease (Thompson and Eglinton, 1978; Meyer and Ishiwatari, 1995). However, the present result is the opposite. The reason for this can be attributed to the fact that the shelf sand is derived predominantly from the last glaciation and its lipids are relatively old and much degraded and that the shelf mud is from modern deposition and its lipids are relatively young and less degraded. If these shelf sand fractions are composed entirely of relict sediment, their CPI values are expected to be about 1. However, the CPI values of the sand fractions range from 1.40 to 1.91 with an average of 1.60, indicating a contribution from modern deposition.

The distribution of the alkanol/ sterol fraction for the sand and that of the mud fractions are similar. That is, *n*-alkanols of terrigenous sources--C_{22}, C_{24}, C_{26}, C_{28} and C_{30} (Rieley et al., 1991) dominate over those of marine sources such as zooplankton C_{14}, C_{16}, C_{18} and C_{20} (Boon et al., 1979; Kattner and Krause, 1989). This result can be attributed to *n*-alkanols derived from marine sources being degraded faster than those from terrigenous ones. The alkanol and sterol concentrations of the sand fraction are relatively smaller than those of the mud fractions; this again can be attributed to the grain size effect.

The presence of extractable phytol in the sand fractions points to recent inputs of lipids. Compared to *n*-alkanols, phytol is relatively unstable. For instance, in a sediment core (sedimentation rate 0.33 cm/y) from off southwestern Taiwan, extractable phytol decreases abruptly from 1049 ng/g (0-4 cm) to 375 ng/g (4-8 cm), but bound phytol increases sharply from 43 to 58%. This might suggest that part of the extractable phytol was transformed into the bound form (Jeng *et al.*, 1997). In a field study, Sun *et al.* (1998) demonstrated that solvent-extractable phytol was rapidly converted into highly-bound phytol (in sediment matrix) after deposition. Because of its rapid transformation, the presence of extractable phytol in the sand fractions (range from 6 to 23 ng/g with a mean of 14 ng/g) is an indication of recent inputs of phytol (and other lipids—sterols) to the shelf sediments. In other words, if there were no phytol input from the surroundings to the shelf sediments (i.e. closed system) in the recent past, there would not be any extractable phytol left at present.

Sedimentary *n*-alkanes are more resistant to degradation than *n*-alkanols. Here degradation is defined as the decrease of compound concentration by transformation into other molecules (such as conversion of stenols to stanones to sterenes), decomposition into smaller molecules, or incorporation into high molecular weight components, all of which would remove extractable lipids from the sediment. The higher plant alkane (HPA) index is defined as

$$\mathrm{HPA}=\frac{[\Sigma n-\mathrm{alkanols}]}{[\Sigma n-\mathrm{alkanols}]+[\Sigma n-\mathrm{alkanes}]}$$

and has been used as a degradation signal to estimate the extent of degradation of geolipids (Poynter and Eglinton, 1991; Westerhausen et al., 1993). It is generally considered that the deposition of the sand fractions is much earlier that that of the mud fractions. There will be a substantial difference in HPA values between the sand and mud fractions.

Sample	HPA
493-16S	0.64
493-16M	0.63
493-17S	0.57
493-17M	0.55
493-22S	0.66
493-22M	0.71
551-27S	0.61
551-27M	0.69
551-32S	0.66
551-32M	0.69
551-38S	0.64
551-38M	0.66

From the above table, it is important to note that the HPA values of the sand fractions are not very different from those of the mud fractions. Further, the shelf sand fractions are presumably mainly relict sediment and have HPA values range from 0.57 to 0.66 with a mean value of 0.63. However, the sediments from the shelf off northeastern Taiwan are composed mainly of shell fragments and light brown sands, which are primarily remnants of relic beaches of the last glaciation, gave an average HPA value of 0.27 (range from 0.16 to 0.49) (Jeng and Huh, 2001). The present HPA values are clearly much higher than those off northeastern Taiwan, suggesting the sand fractions contain higher proportions of modern deposition. It can be concluded that the ECS shelf sediment is actually palimpest, not relict sediment.

四、計畫成果自評

主持人對本計畫研究成果感到很滿意。

五、參考文獻

Bartek L. R. and Wellner R. W. (1995) Do equilibrium conditions exist during sediment transport studies on continental margins? An example from the East China Sea. *Geo-Mar. Lett.* 15: 23-29.

Boon J. J. and de Leeuw J. W. (1979) The analysis of wax esters, very long mid-chain ketones and sterol ethers isolated from Walvis Bay diatomaceous ooze. *Mar. Chem.* 7: 117-132.

Jeng W. L. (1999) Sedimentary environment of the East China Sea: early diagenesis of lipids. *Workshop for Oceanographic Research Programs 1999* held at Miao-Li, Dec. 7-9, 1999.

Jeng W. L., Huh C. A. and Chen C. L. (1997) Alkanol and sterol degradation in a sediment core from the continental slope off southwestern Taiwan. *Chemsphere* 35: 2515-2523.

Jeng W. L. and Huh C. A. (2001) Comparative study of sterols in shelf and slope sediments off northeastern Taiwan. *Appl. Geochem.* 16: 95-108.

Kattner G. and Krause M. (1989) Seasonal variations of lipids (wax esters, fatty acids and alcohols) in calanoid copepods from the North Sea. *Mar. Chem.* 26: 261-275.

Li C., Chen G., Yao M. and Wang P. (1991) The influences of suspended load on the sedimentation in the coastal zones and continental shelves of China. *Mar. Geol.* 96: 341-352.

Meyers P. A. and Ishiwatari R. (1995) Organic matter accumulation records in lake sediments In: Lerman A, Imboden D. M. and Gat J. R. (Eds.), *Physics and Chemistry of Lakes* pp. 279-328.

Milliman J. D., Shen H. T., Yang Z. S. and Meade R. H. (1985) Transport and deposition of river sediments in the Changjiang estuary and adjacent continental shelf. *Cont. Shelf Res.* 4: 37-45.

Milliman J. D. Qin Y. S. and Park Y. A. (1989) Sediments and sedimentary processes in the Yellow and East China Seas. In: Taira A and Masuda F. (Eds.), *Sedimentary Facies in the Active Plate Margin* pp. 233-249.

Poynter J. and Eglinton G. (1991) The biomarker concept—strengths and weaknesses. *Fresen. J. Anal. Chem.* 339: 725-731.

Rieley G., Collier R. J., Jones D. M. and Eglinton G. (1991) The biogeochemistry of Ellesmere Lake, U.K.—I: Source correlation of leaf wax inputs to the sedimentary lipid record. *Org. Geochem.* 17: 901-912.

Sun M. Y., Wakeham S. G., Aller, R. C. and Lee, C. (1998) Impact of seasonal hypoxia on diagenesis of phytol and its derivatives in Long Island Sound. *Mar. Chem.* 62: 157-173.

Thompson S. and Eglinton G. (1978) The fractionation of a Recent sediment for organic geochemical analysis. *Geochim. Cosmochim. Acta* 42: 199-207.

Westerhausen L., Poynter J., Eglinton G., Erlenkeuser H. and Sarnthein M. (1993) Marine and terrigenous origin of organic matter in modern sediments of the equatorial East Atlantic: the $\delta^{13}C$ and molecular record. *Deep-Sea Res I* 40: 1087-1121.