Note

Marine transgressional events in the gigantic freshwater lake Songliao: paleontological and geochemical evidence

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Abstract

The fossil remains of euryhaline organisms in the Mesozoic-Cenozoic, non-marine sedimentary records of eastern China may have resulted from either marine transgressions or inland hypersaline lacustrine environments. Paleontological and organic geochemical results of this study have provided new evidence for marine transgressional events in the gigantic freshwater lake Songliao during the late Cretaceous. Crown Copyright © 2000 Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

The issue of marine transgression in the non-marine sedimentary records of Mesozoic-Cenozoic age from eastern China remains controversial. Westward transgression was proposed to have occurred in large areas of the Cathaysian system, a series of Mesozoic-Cenozoic sedimentary basins bounded by the Zijingguan and Tan-Lu faults (Fig. 1). Based on microfossil evidence obtained from Bohai Bay, and other basins in the Cathaysian system for example, four episodes of transgression were postulated to have occurred from late Cretaceous to Tertiary (Qiu et al., 1994). An alternative to a marine transgression is that fossils of certain euryhaline organisms may have lived in an inland saline lake (Sun, 1995). Evidence for the latter hypothesis comes from the paleontological work on the Quaternary sediments of the Caidam, undisputedly an inland salt lake in northwestern China, where the Foraminifera (Elphidium sp.) and Ostracoda (Europris inflata) were found to co-exist. The resolution of this question has significant implications for the assessment of petroleum resources in China, as the deposition of many non-marine, organic-rich petroleum source rocks in eastern China may have been closely associated with marine transgressions or saline lakes. We present the results of an integrated paleontological and organic geochemical study of the organic-rich, Cretaceous black shales taken from the Songliao basin, northeastern China. Identification of a number of macro, micro and molecular fossils (biomarkers) that are potentially source specific provides evidence for the Cretaceous marine transgressional events in a gigantic, ancient freshwater lake.

2. Samples and analytical methods

The Songliao basin is the largest sedimentary basin in the Cathaysian system and the largest oil-producing province in China. It is a Mesozoic-Cenozoic intracratonic basin developed as the result of the initial rifting of the Eurasian Continent during the late Jurassic (Fig. 1). The stratigraphic column between the top of the Jurassic and the Lower Cretaceous (Fig. 2) consists of two minor sedimentary cycles characterized by infilling with
limited sediments and the initiation of fault depression and downwarping associated with tectonic movement. The Upper Cretaceous Qingshankou, Yaojia and Nenjiang formations, the major petroleum source beds in the basin, were formed during the main period of basin subsidence and development. These sediments were deposited mostly in a gigantic freshwater lake covering an area of 90,000–100,000 sq. km (Fig. 1), with occasional brackish water environments being developed.

The Cretaceous paleontological database of the Daqing Petroleum Bureau indicates that fossils of euryhaline organisms observed from the Songliao basin occur mainly in Section 1 of the Qingshankou Fm. (K2qn1) and Sections 1 and 2 of the Nenjiang Fm. (K2n1–2). These are the most prolific source rock units in the basin, and are also used as regional stratigraphic correlation markers basinwide. Over 200 potential source rocks from the Qingshankou and Nenjiang formations were previously sampled by local researchers for geochemical screening. Samples used in this study included those from the K2qn1(80), K2qn2–3 (19) and K2n1–2 (50) sections. Wherever possible, samples were taken either from similar locations as those used for paleontological studies (e.g. Gao et al., 1994) or from stratigraphically equivalent positions in adjacent wells. After detailed paleontological descriptions, molecular geochemical analyses were carried out on 20 organic-rich source rocks with TOC > 2% that contain euryhaline fossil remains, including 13 and 7 from the K2n1–2 and K2qn1 sections. Five samples with 1–2% TOC from the K2qn2–3 sections were also analyzed for comparison. Analytical conditions are defined elsewhere (Li et al., 1999). Briefly, all of the rock samples were initially screened by Rock-Eval/TOC, then extracted with chloroform (Soxhlet, 24 h). Saturated and aromatic hydrocarbon fractions, obtained from the rock extracts by column chromatography, were analyzed by gas chromatography (GC), gas chromatography–mass spectrometry (GC/MS) and gas chromatography–mass spectrometry-mass spectrometry (GC/MS/MS) using a VG 70 SQ high resolution hybrid magnetic-quadrupole instrument. For GC/MS analyses of the saturates, both full scan and multiple ion monitoring modes were used. For GC/MS/MS, the following transitions were monitored: m/z 370+14n→191 (n=0–3) for C27–C30 hopanes; m/z 358+14n→217, n=0–4 for C26–C30 desmethylsteranes; m/z 414→231, 98 for C30 methylsteranes (including dinosteranes), and m/z 428→231 for 4,22,23,24-tetramethylcholestanol.

### 3. Results and discussion

As summarized in Fig. 2, paleontological evidence for a dominantly freshwater to slightly brackish lacustrine setting of Lake Songliao during the late Cretaceous is overwhelming. It includes the abundant fossil remains of land, amphibious and freshwater animals and low chloride concentrations (0.014–0.035%) in the Upper Cretaceous black shales (Cui and Gao, 1993). The K2qn2–3 sections, for example, include fauna of the Ostracoda (Cypriidea dekhoiinensis, C. adumbrata, C. fuyuensis, C. panda, Trianglicypris symmetrica, Sunliavia tumida), Conchostraca (Nemestheria qingshankouensis, Cratostracus merus, Dictyestheria elongata, Jilinestheria, Ellipsograpta). Also present are bivalves (Nakamuranaia cf. Chinshanensis, Martinsonella Paucisulata, Plicatounio (P.).equiplicatus, Trigonioides kodairai), Gastropoda (Brotopias shuangchegengensis), fish (Manchurichthys sp.), and vertebrates (Chilinosaurus qingshankouensis, Paraligotor sungaricus, Trachodon, Chelonia indet.). Microalgae identified from these strata include cysts of the Chara (Aclistochata songliaoensis, Mesocha, Maedlerisphaera binxianensis, Obtouchara, Amblyochara) and Dinophyceae (Granodiscus, Filisphaeridium). These fossils, particularly those of the Pediastrum and Scenedesmus.
genera, indicate dominantly neutral-alkaline, freshwater columns for the Upper Cretaceous lake, with a maximum salinity of perhaps less than 1% and a pH of ~8.3 (Li et al., 1982).

On the other hand, the K2qn1 and K2n1–2 sections display fossil records that are not typical of freshwater lacustrine sediments. The 10–30 m black shales and oil shales present at the base of the K2qn1 section contain abundant fauna of the Ostracoda (Cypridea dekoihinnensis, C. subtuberculisperga, Trianglicypris torsuosus, T. Trinoderis, T. torsuosus var. nota) and Conchostraca (Nemestheria lineata, Dictyestheria prima). The abundant algal cysts identified from these shales are dominated by euryhaline Dinophyceae of the Dinogymnium, Kio- kiansus and Impletosphaeridium genera. The two other black shale/oil shale units are at the base of the K2n1 and K2n2 sections respectively, each with a total thickness of 5–20 m. In addition to abundant Ostracoda and Conchostraca fossils, these units also contain specimens typically found in littoral zones with enhanced salinity. These include fish (Hama macrostoma, Jilingchthys rapax, Sungarichthys longicepsalus), Gastropoda (Gyraulus jili- jinensis, Lioplex sungariana, Valvata sinensis), and bivalves (Brachidontes, Musculus, Fulpioides, Striarca and Mytilus) (Cui and Gao, 1993). The identification of shark dens and marine dinophyceae in these strata (Fig. 2) would suggest conditions with a strong marine influence.

Microscopic examination reveals that the highly laminated oil shales and black shales in the K2qn1 and K2n1–2 sections are enriched in carbonate, interlayered with thin siderite lenses and abundant dispersed pyrite. These shales are generally enriched in organic matter, with 2 to over 10% TOC. Organic petrography, Rock-Eval pyrolysis and elemental analysis of kerogen isolates...
were conducted on these shales. The results indicate that
the kerogens in these samples belong to either Type I or
Type II organic matter, with the $\delta^{13}C$ values measured
on the kerogen isolates ranging from $-30$ to $-35\%$ and
$-25$ to $-30\%$ for the K$_{2}$n$_{1}$ and K$_{2}$n$_{1-2}$ samples,
respectively. A number of biomarker features support
deposition of these sediments under conditions of
enhanced salinity / stratified water columns. These
include low pristane/phytane ratios (mostly < 1.0) and
the presence of $\beta$-carotane and gammacerane in the
saturate fractions of the black shale extracts (Fig. 3).
Gammacerane, first identified in the bitumen of the
Green River shale, is often present in samples from
hypersaline marine and nonmarine depositional envir-
onments (e.g. Peters and Moldovan, 1993). It is thought
to derive from the tetrahydroxymanol that is widely
distributed in marine sediments, in freshwater, in marine
bacterial ciliates and in photosynthetic sulphur bacteria,
either by dehydration and hydrogenation (Ten Haven et
al., 1989), or by sulphurisation and early C-S cleavage
(Sinninghe Damsté et al., 1995). Similar processes may
also be responsible for the formation of $\beta$-carotane from
its algal precursors (Adam et al., 1993). One of the
important compositional features of the aromatic hydro-
carbons of these black shale extracts is the n-alkyl-
benzenes and aryl isoprenoid hydrocarbons, present in
concentrations similar to that of the alkynaphthalenes
and alkylphenathrenes. Aryl isoprenoids are believed to
derive from aromatic carotenoids such as isorenieratene
found in green photosynthetic bacteria. As gammacerane,
$\beta$-carotane and aryl isoprenoids are often present in
hypersaline environments, they were previously sug-
gested as indicators of hypersalinity. Evidence that has
emerged from more recent work (Requejo et al., 1992;
Sinninghe Damsté et al., 1995) however, demonstrates
that these compounds are not necessarily restricted to

(A) GC/MS

(B) GC/MS/MS

Fig. 3. (A) $M/z$ 191, 217 and 231 mass fragmentograms showing the distributions of major biomarker classes in the saturate fractions of the K$_{2}$n$_{1}$ and K$_{2}$n$_{1-2}$ black shale extracts; (b) $M/z$ 414→217, 414→231 and 428→231 transitions showing the complex distributions of C$_{30}$ and C$_{31}$ steranes in the same samples.
hypotheses of enhanced salinity in the K2q1 and K2n1–2 sections must be addressed carefully to ensure that evaporitic sedimentation as for the Qinghai lake (Sun, 1995) is not implied.

Populations of land plant spores and pollen identified in the Upper Cretaceous sediments of the Songliao basin indicate generally warm and wet conditions resembling the modern subtropical zones (Cui and Gao, 1993; Hou et al., unpublished results). Detailed GC/MS/MS analysis was carried out on 25 shale samples in order to verify if the water column stratification, during the deposition of the K2q1 and K2n1–2 sections, was caused by seasonal variation in water volumes of an inland lake, or by an input of marine water into the lake. As shown by a typical example in Fig. 3, biomarker evidence for the marine transgressional events during the deposition of the K2q1 and K2n1–2 sections includes the presence of abundant C30 4-desmethylsteranes (24-n-propylcholestanes) and various C28–C31 4-methylsteranes. This is in contrast to the general absence of the C30 4-desmethylsteranes in the extracts of the K2q2–3 shales. The C30 4-desmethylsteranes are believed to derive diagenetically from 24-n-propylcholesterols present in the marine alga Sarcinochrysidales (Raederstorff and Rohmer, 1984). To the best of our knowledge, these compounds have been reported previously only from marine source rocks and related oils, but not from inland lacustrine or fluvial-swamp source rocks and related oils that lack marine influence (e.g. Moldowan et al., 1985). Therefore, the presence of these compounds (with the ratios of C30 4-desmethylsteranes to C29 regular steranes ranging from 12 to 19%) should be considered as one of the most powerful molecular parameters for identifying marine transgressional events in sedimentary records.

The extracts of the K2q1 and K2n1–2 shales contain complex distributions of C28–C31 4-methylsteranes, with the C29 members in highest relative abundance (Fig. 3). The dinosteranes and C31 4-methylsteranes in the samples taken from the southeastern part of the basin (e.g. Cha-6 well) occur in similar abundance to those of C30 4-methyl-24-ethylcholesterans, but decrease generally toward the northwestern part of the basin. In contrast, these compounds are either absent or in very low abundance in the K2q2–3 shales analyzed in this study. C30 dinosteranes (4,23,24-trimethylcholesterans) are differentiated from their 24-ethyl-counterparts and from C30 4-desmethylsteranes, by monitoring m/z 414→98 ion. GC/MS/MS experiments (Fig. 3) confirm that the dinosteranes are more abundant than their 24-ethyl counterparts in samples with a clear marine influence, whereas the latter compounds dominate the C30 4-methylsteranes in samples more typical of freshwater lacustrine sediments (Hou, unpublished data). It is interesting also to note that the relative abundance of C29 and C31 methylsteranes coincides with that of the dinosteranes. C31 methylsteranes, tentatively assigned as 4,22,23,24-tetramethylcholesterans, were first identified from the late Triassic sediments in England (Thomas et al., 1993). 4-Methylsterols with a 22, 23, 24-trimethyl side chain have not been reported in extant organisms. It is quite possible however, that the C31 4-methylsteranes result from sterols such as 4-methyl gorgostanol by diagenetic cleavage of the strained cyclopropyl ring (Thomas et al., 1993). The proposed sterol precursors are known to occur in unialgal cultures of marine dinoflagellates, e.g. Glenodinium Foliaceum (27% of total sterols; Alam et al., 1979) and Peridinium Foliaceum (14% of total sterols; Withers et al., 1979). They are also in high concentrations in sediments with marine incursion/enhanced salinity (Thomas, 1990). Thus, the presence of abundant C31 4-methylsteranes in the K2q1 and K2n1–2 shales studied here may be taken as further evidence for the marine transgressional events.

In summary, the paleontological and organic geochemical results presented in this study provide new evidence that marine transgressional events occurred periodically in the gigantic freshwater lake Songliao during the late Cretaceous epoch. It was suggested previously, that the Lake Songliao was connected periodically to the East Asiatic Ocean during this period, thus the deposition of the K2q1 and K2n1–2 sections corresponded to the early Cenomanian and late Turonian-early Santonian marine transgressional events respectively (Gao et al., 1994). It should be pointed out that, although the Songliao and other basins in the Cathaysian system (Fig. 1) have been cited extensively as non-marine petrolierous provinces, the most prolific petroleum source rocks in most of these basins appear to be in stratigraphic sections with a significant marine influence.

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