J. Serb. Chem. Soc. *69* (7) 555–561 (2004) UDC 551.351/.352(489)
JSCS – 3182 *Original scientific paper*

Cretaceous-Tertiary boundary deposits in Denmark: A diachroneity

PAVLE I. PREMOVIĆ*

Laboratory for Geochemistry, Cosmochemistry and Astrochemistry, University of Niš, P. O. Box 91, 18000 Niš, Serbia and Montenegro, (e-mail: asteroid_2000_2000@yahoo.com)

(Received 8 January 2004)

Abstract: The lateral distribution of predominantly terrestrial kerogen or humics enriched with copper(II) porphyrins (Cu-P) across the Danish marine basin implies that the alleged Cretaceous-Tertiary (KT) boundary deposits in western Denmark (at the Nye Kløv/Dania locations) were probably formed by erosion/emplacement of the boundary clay (Fiskeler) in eastern Denmark by marine currents, as originally proposed by Hulteberg.[1,2]

Keywords: diachroneity, kerogen, copper(II) porphyrins, Cretaceous-Tertiary, Fiskeler, boundary clay.

LITHOLOGY AND THE FLUVIATILE SEDIMENTATION MODEL OF FISKELER

Alvarez *et al.*[3] have reported an anomalously high concentration of Ir in the KT boundary deposit Fiskeler (Fishclay) at Stevns Klint, Denmark. The authors proposed that this enhanced Ir concentration was produced by the impact of a late Cretaceous chondritic asteroid. Fiskeler is a thin grey-to-black marl which forms the boundary at Stevns Klint, eastern Denmark (Fig. 1). Small marine basins occur here between the Cretaceous white chalk and the overlying calcareous Tertiary formation. The lithology of Fiskeler (FK) has been described by Christensen *et al.*[4] The authors differentiated four distinct layers within this boundary: the bottom layer II (Maastrichtian grey marl: 1–2 cm thick), the middle layers III (block marl: *ca.* 2 cm thick) and IV (grey to black marl: 3–5 cm thick) and the top layer V (light-grey marl: 5–7 cm thick). Layer II is underlain by Maastrichtian chalk (I) and layer V is overlain by Danian cerithium limestone (VI). Palynological studies of FK by Hulteberg[1,2] indicate that layer II was deposited under normal marine conditions and that the basal part of layer III was deposited in a milieu strongly effected by an influx of freshwater; whereas the top of layer III, and the layers IV/V were accumulated under a predominant marine indluence. He suggested that a local Maastrichtian freshwater agent, a river (hereinafter referred to as the FK river) close to the FK Basin, was the source for the detritus (including humics) of the boundary.

* Corresponding author. Fax: +391-18-533-014

A plausible (so-called fluviatile) explanation for the succession of the FK depositional conditions was offered by Hulteberg.[2] According to this author, at some time during the deposition of FK an abrupt increase of the outflow of the FK river occurred, resulting in the formation of the basal unit of layer III. A subsequent decrease in the river outflow resulted in the formation of the top of layer III (and afterward the layers IV and V). The cerithium limestone (layer VI which overlies FK) definitely indicates a return to normal marine sedimentation conditions similar to those of I and II. The chalk I is separated from the upper limestone VI by some < 20 cm of FK (II–V), suggesting that a relatively short period of time (geologically speaking) elapsed between the end of the Maastrichtian chalk-forming stage and the initiation of the Danian limestone deposition.

Cu-P AND THE III HUMICS

If the fluviatile interpretation of Hulteberg is accepted as a reasonable working hypotheses, it follows that one of the very first (impact-induced) traumatic effects in the FK area was perhaps a huge superacid rainstorm. Indeed, D'Hondt *et al.*[5] estimated that a rainout of *ca.* 10^{16} moles of H_2SO_4 created in the atmosphere by the impact of a late Cretaceous asteroid would reduce the pH of (unbuffered) freshwater to below 3. (Very recently, Lyons and Ahrens[6] estimated that *ca.* 1×10^{17} equivalents of strong acid were deposited on the continents during the KT event). This storm was probably caused by sudden impact-related atmospheric[7,8] and climatic anomalies.[9] The rainstorm dramatically increased the acidified runoffs (the flash flooding of the FK soil) of the surface waters (streams, creeks and the FK river), carrying terrestrial plant debris (including humics), inorganic detritus and freshwater algae into the FK Basin.[1,2] This resulted first in the deposition of the basal part of III. Simultaneously, settling of the impact fallout also occurred as high amounts of Ir and soot emerge simultaneously in this sublayer. Geochemical analyses show that the carbonate-free fractions of III/IV contain relatively high contents (up to 6 %) of kerogen[10–12] enriched with Ir/soot[10,11,13] and that the corresponding fractions of the underlying II/overlying V beds contain insignificant amounts (≤ 0.1 %) of this organic insoluble material. Furthermore, the kerogen content of FK increased abruptly with the deposition of the basal part of III and declined gradually towards the deposition of the top of III and across layer IV. These circumstances are consistent with the sedimentation model presented by Hulteberg.[2]

Premović *et al.*[12] also reported that kerogen isolated from the units III/IV contains anomalously high levels (up to 1000 ppm) of Cu. Their geochemical analysis indicates that Cu in this kerogen is predominantly (> 90 %) in the Cu^{2+}-porphyrin form (4000 ppm, determined by ESR). In addition, geochemical evidence presented by these authors indicate that Cu-P of the III/IV kerogen were not formed *in situ* (*i.e.*, within FK) but that they are strictly detrital in character, *i.e.*, they were transported from the nearby (oxic) FK soil to the FK sedimentary site.

Experimental studies and observations on modern and ancient soils imply that the FK soil solution in which Cu-P were formed was not a normal soil solution. It was probably very rich in Cu^{2+} and humic porphyrins and had a lower-than-normal pH. Specifically, the accumulation of the humic Cu-P in an oxic soil solution requires that those chemical factors governing their formation be exactly right; the content of either Cu^{2+} or free humic porphyrins could not be low.

My preferred hypothesis is that the terrestrial humics (as a direct precursor of kerogen) of the FK soil were formed by the rapid deposition of decaying land green flora, as a result of local extinction events, including superacid rainfall/wildfires. In addition, the post-impact atmospheric photosynthesis was very likely interrupted for, at least, several months by dust/aerosols.[3] These suggest that a probable source for the free porphyrin structures within the FK soil humics was chlorophylls of plant vestiges. Thus, it is reasonable to suggest that the basal unit of III, which is highly enriched with both Ir and kerogen with Cu-P/soot, may echo the first geochemical effects of the asteroid impact on the FK soil ecosystem.

According to several studies,[14–16] Cu^{2+} chelation by porphyrins is exceedingly rapid (half-lives $< 1\ s^{-1}$) and the rate of Cu^{2+} incorporation into porphyrins is nearly independent of the nature of the porphyrins themselves. Given that Cu^{2+} is available as such in H_2O – O_2 – CO_2 systems (*e.g.*, the FK oxic soil water) essentially only at pH < 5[12] and Eh > 0.1,[17] it can only be surmised that Cu^{2+} chelation by the humic free porphyrins could only have occurred in the (oxic) FK soil solution under acidic (pH < 5) conditions prior to entering the FK sedimentation site.

Terrestrial humics can either solubilize or fix particular trace metals, depending on their state of aggregation. For example, the distinction between fulvic acids, humic acids and humin is based on their aqueous solubility, which is mainly a consequence of their molecular weights. Fulvic acids are soluble in neutral to acidic (pH ≤ 7) milieu and have molecular weights near 1000. Humic acids are soluble only in aqueous alkaline (pH > 7) solution and have molecular weights $>10^4$; and humin (which is very heavy) is insoluble. Thus under the acidic (pH < 5) conditions of the FK soil water, the fulvic acids would be soluble and they would chelate particular trace metals (*e.g.*, Cu^{2+}) to form stable, but soluble complexes. Evidently surface waters would have removed most of these complexes from the FK soil immediately afterwards. Under the same conditions, the FK soil humic acids are insoluble and their presence would have resulted in the fixation of Cu^{2+}. Indeed, high levels of both Cu and Cu-P are only found in humic acids of a wide variety of organic-rich soils: recent soils (including peat-soils)[18–23] and paleosols.[21] Thus, the FK soil humic acids (enriched with traces of Cu^{2+}/Cu-P) can be regarded as the ultimate precursors of the III kerogen with high contents of Cu/Cu-P. These acids had probably functional (carboxyl, porphyrin, *etc.*) groups that were able to chelate Cu^{2+} before it reached the FK deposition site. This can account for the relatively high contents of Cu/Cu-P in the III kerogen.

If the above humic concept is correct, then the relatively high levels (up to 1000 ppm) of Cu in the III kerogen[12] would imply that the top horizon of the FK soil must originally have been extremely enriched in terrestrial Cu and that significant hydromorphic dispersion of Cu, probably, occurred in the vicinity of the FK soil. Cu was most likely mobilized by oxidation of disseminated Cu-sulfides (*e.g.*, chalcopyrites) and transported in solution to the FK topsoil by the acidified surface/ground waters. These waters could highly enhance the concentration of Cu (and other terrestrial trace metals) by severe leaching of the corresponding rock source(s). (Very recently, Frei and Frei[22] carried out a multi-isotopic and trace elements study of FK. Their isotopic Nd, Sr and Pb results implicitly support this rationalization). This would, for certain, facilitate the formation of the humic Cu-P in the FK topsoil

REDEPOSITION OF THE BOUNDARY IN EASTERN DENMARK AND THE KEROGEN Cu-P

A diachroneity between the Nye Kløv boundary and FK based on extinction data of planktic foraminifera was first reported by Hansen *et al.*[23] According to a (speculative) sedimantation model presented by Hulteberg,[2] the boundary deposits in western Denmark (*e.g.*, Nye Kløv) represent erosion and subsequent marine redeposition of the true boundary (FK) in eastern Denmark. In accordance with this model, it appears likely that FK was extensively eroded and then dispersed laterally after the KT boundary event by marine currents, from the marginal zone (close to the FK river delta) to the central parts of the Danish Basin in western Denmark (Fig. 1). Indeed, according to Premović *et al.*,[12,24] the bulk of

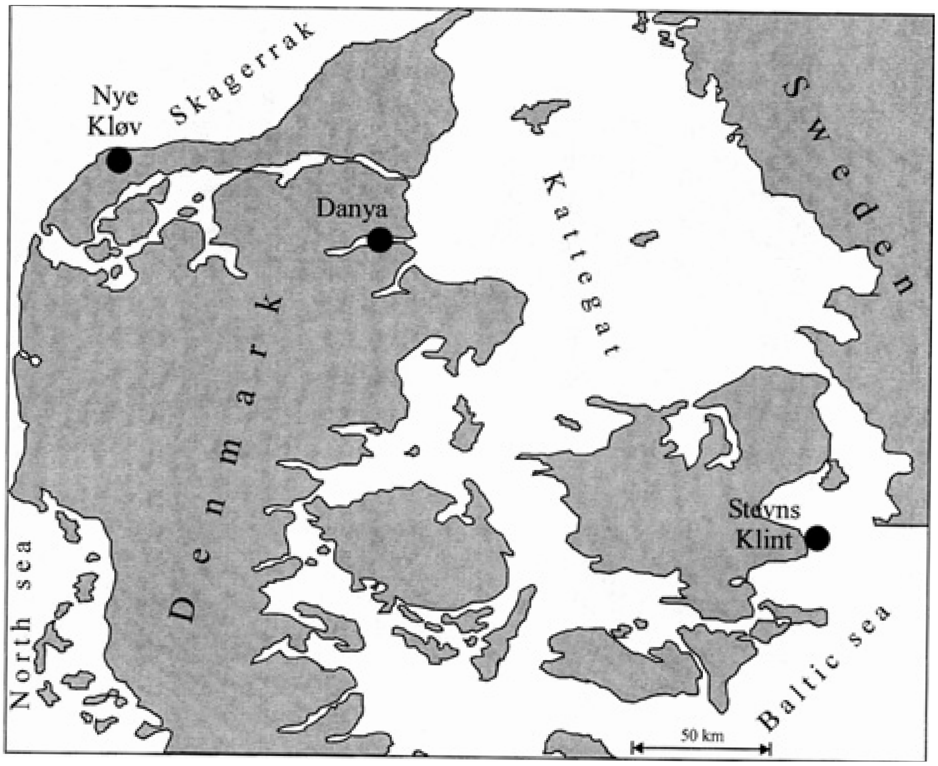

Fig. 1. Location of samples of the Danish boundaries.

the smectite of the boundary deposits at the Nye Kløv/Dania locations are of detrital origin. Hulteberg[1,2] also claims, on the basis of dinoflagellate biostratigraphy, that the deposition of FK took place several hundred thousands years (*i.e.*, 200,000 y. to 1.5 m.y.) earlier than the deposition of the boundary beds in western Denmark (*e.g.*, Nye Kløv). In short, he placed the deposits in western Denmark in the uppermost Danian, not in the KT time, *i.e.*, he questioned whether these beds represent a true KT boundary.

The kerogen and humic Cu-P are rare and atypical for ancient sedimentary rocks of marine origin.[12] According to Baker and Louda,[25] Cu-P were probably derived from enhanced weathering of terrestrial organic accumulations and as such are reliable markers for oxidized terrestrial organic matter, such as kerogen or humics redeposited in a marine environment (*e.g.*, the FK Basin). In all these cases, the humic Cu-P are generally solitary or sporadic occurrences and are found confined to relatively small soil or sedimentary areas. It seems, therefore, implausible that the humics or kerogen (enriched with Cu-P) could be formed simultaneously during the short time (geologically speaking) period of the KT event in both eastern and western Denmark in soils widely separated from each other by *ca.* 320 km (FK-Nye Kløv) and *ca.* 220 km (FK-Dania) (Fig. 1). I suggest, therefore, that the humics or protokerogen (highly enriched with the Cu-P) of eastern Denmark were translocated by marine currents (including the impact-caused storm-generated bottom currents) in the westarn parts of the Danish KT Basin (Fig. 1). This could be an explanation for the lower contents ($<$ 0.1 %) of kerogen (enriched with Cu-P) of the Nye Kløv/Dania rocks compared to FK.[12,24] Obviously, redeposition of the humics (or even protokerogen) occurred soon after the KT boundary event, supporting the diachroneity between FK and the boundary deposits (such as Nye Kløv/Dania) in western Denmark, proposed by Hulteberg.[1,2]

Ni, VANADYL (VO^{2+}) AND Ir OF THE NYE KLØV/DANIA ALLEGED BOUNDARIES

Premović *et al.*[12,24] reported a high level ($\leq$ 300 ppm) of Ni within the biogenic calcite of FK. These results were interpreted by these authors as reflecting an enormous influx of cosmogenic Ni into the FK seawater induced by a late Cretaceous impactor. It is suggested that a global (imact-induced) superacid rainfall and associated toxic metals (including Ni) had decimated any Cretaceous marine calcareous nanoplanktons (coccoliths) in the surface seawater at this distal site. Ni in the biogenic calcite of the Nye Kløv/Dania boundaries was also analyzed. The results indicate that this calcite contains normal background Ni contents ($\leq$ 15 ppm). This suggests that most (if not all) of the biogenic calcite of the Nye Kløv/Dania alleged boundaries is primarily composed of authigenic material locally sourced by calcareous planktic organisms. It is interesting that no sudden mass extinction occurred in these organisms at the boundary at Nye Kløv.[26]

According to Premović *et al.*,[12,24] the abundant smectite in FK was formed in early diagenesis in anoxic conditions and is the major carriers of V and VO^{2+} ions. There are, however, no indications in the form of abundant pyrite (FeS_2) and/or organic matter that anoxic conditions existed during the deposition of the Nye Kløv/Dania alleged boundaries but rather oxic conditions may have prevailed during their accumulation.[24] Indeed, the bioturbated nature of the Nye Kløv boundary strongly supports oxic conditions during its deposition.[9]

The V concentrations of the smectite concentrates of the Nye Kløv/Dania alleged boundaries are relatively high (180–200 ppm) and comparable with those measured (150 ppm) for the corresponding fraction of FK. In constrast, the concentrations of VO^{2+} ions in the smectite concentrates of oxic Ney Kløv (15 ppm)/Dania (35 ppm) alleged boundaries are small compared with the VO^{2+} concentration (150 ppm) in the corresponding fraction of anoxic FK. In general, VO^{2+} ions show highest abundances in anoxic sediments and they are absent in their oxic counterparts. Indeed, in normal (pH *ca.* 8) oxic seawaters, VO^{2+} ions are rapidly oxidized by air O_2 within hours.[12] For this reason, it is suggested that the VO^{2+} ions within the smectites of the Nye Kløv/Dania boundaries are detrital in the sense of having been brought into the KT basin of western Denmark already located in the smectite structures.[24] Accordingly, it is likely that the majority of VO^{2+} ions in the redeposited FK smectite was oxidized by seawater O_2 during its redeposition/settling on the oxic seafloor in western Denmark. If this was the case, very low VO^{2+} abundance should be expected in the Nye Kløv/Dania alleged boundaries.

The Nye Kløv (2 ppb[27]) and Dania (4 ppb[28]) boundaries contain rather low Ir compared with the Ir abundance (*ca.* 55 ppb) of FK.[29] It is likely that the FK material and associated Ir (micrograins) gradually became decoupled during redeposition/settling at the sites in western Denmark.

Certainly, the redeposition of smectite, humics enriched with Cu-P (or protokerogen) and Ir from the original FK site is a vast over-simplification of what is a very complex process. For example, local influences (including local contributions of smectite, humics and kerogen, and Ir), and possible multiple impacts[30] may complicate this interpretation.

Finally, it is an interesting fact that neither Cu-P nor VO^{2+} were detected in the other marine KT boundary deposits at the distal sites Geulhemmerberg (Holland), Furlo/Gubio (Italy), Caravaca/Agosta (Spain) and El Keef (Tunisia) and at the proximal location the ODP Leg 171B (site 1049, drill core 1049 A, section 17X-2, Blake Nose Plateau, NW Atlantic). Thus, Cu-P and VO^{2+} within a boundary section is not a world-wide phenomenon.

Acknowledgments: Funding support from le Ministère français de l'éducation nationale, de'enseignement supérieur et de la recherche to P. I. P. for his stay at LMCP, Université Pierre et Marie Curie (Paris), is gratefully acknowledged. This work was supported in part by the Ministry of Science, Technology and Development (Serbia), Project 1235. Thanks also go to Drs. H. Hansen, H. Schummel and T. Damholt who generously supplied samples of the Danish boundary samples.

ИЗВОД

КРЕДА-ТЕРЦИЈАР ГРАНИЧНИ ДЕПОЗИТИ У ДАНСКОЈ: НЕИСТОВРЕМЕНА СЕДИМЕНТАЦИЈА

ПАВЛЕ И. ПРЕМОВИЋ

Лаборайорија за геохемију, космохемију и асйрохемију, Природно-майемайички факулйей, Универзийей у Нишу, й. йр. 91, 18000 Ниш

Латерална расподела претежно копненог керогена или хумичних материјала обогаћених бакар(II) порфиринима (Cu–P) у данском морском басену показује да су креда-терцијар гранични депозити из западне Данске (на локацијама Nye Kløv и Dania) вероватно настали ерозијом (изазваном морским струјама) налазишта граничне глине (Fiskeler) из источне Данске, као што је првобитно предложио Hulteberg.[1,2]

(Примљено 8. јануара 2004)

REFERENCES

1. S. U. Hulteberg, *J. Micropalaeontol.* **5** (1986) 37
2. S. U. Hulteberg, *J. Micropalaeontol.* **6** (1987) 35
3. L. W. Alvarez, W. Alvarez, F. Asaro, H. V. Michel, *Science* **208** (1980) 1095
4. L. Christensen, S. Fregerslev, A. Simonsen, J. Thiede, *Bull. Geol. Soc. Denmark* **22** (1973) 193
5. S. D'Hondt, M. E. Q. Pilson, H. Sigurdsson, A. K. Hanson, S. Carey, *Geology* **22** (1994) 983
6. J. R. Lyons, T. J. Ahrens, Personal communication (2001)
7. R. G. Prinn, B. Fegley, *Earth Planet. Sci. Lett.* **83** (1987) 1
8. H. Sigurdsson, S. D'Hondt, S. Carey, *Earth Planet. Sci. Lett.* **109** (1992) 543
9. A. A. Ekdale, R. G. Bromley, *J. Sed. Petrol.* **54** (1984) 681
10. B. Schmitz, *Geology* **16** (1988) 1068
11. B. Schmitz, P. Andersson, J. Dahl, *Geochim. Cosmochim. Acta* **52** (1988) 229
12. P. I. Premović, N. D. Nikolić, I. R. Tonsa, M. S. Pavlović, M. P. Premović, D. T. Dulanović, *Earth Planet. Sci. Lett.* **177** (2000) 105
13. F. T. Kyte, Z. Zhou, J. T. Wasson, *Nature* **288** (1980) 651
14. J. G. Erdman, J. W. Walter, W. E. Hanson, *Preprints Division of Petroleum Chemistry, American Chemical Society* **2** (1957) 259
15. G. Cole, D. W. Doll, *J. Am. Chem. Soc.* **105** (1983) 4477
16. P. P. Zelmer, E. H. Mann, *Org. Geochem.* **5** (1983) 43
17. R. M. Garrels, C. L. Christ, *Solutions, Minerals, and Equilibria*, Harper and Row, New York, 1965, p. 450
18. B. A. Goodman, M. V. Cheshire, *J. Soil Sci.* **27** (1976) 337
19. M. V. Cheshire, M. I. Berrow, B. A. Goodman, C. M. Mundie, *Geochim. Cosmochim. Acta* **41** (1977) 1131
20. A. L. Abdul-Halim, J. C. Evans, C. C. Rowlands, J. H. Thomas, *Geochim. Cosmochim. Acta* **45** (1981) 481
21. N. Senesi, G. Calderoni, *Org. Geochem.* **13** (1988) 1145
22. R. Frei, K. M. Frei, *Earth Planet. Sci. Lett.* **6384** (2002) 1
23. H. J. Hansen, R. Gwozdz, J. M. Hansen, R. G. Bromley, K. L. Rasmussen, *Lecture Notes in Earth Sci.* **8** (1986) 382
24. P. I. Premović, N. Z. Pavlović, M. S. Pavlović, N. D. Nikolić, *Geochim. Cosmochim. Acta* **57** (1993) 1433
25. E. W. Baker, J. W. Louda, in *Advances in Organic Geochemistry*, P. A. Schenck, J. W. de Leeuw, G. W. M. Lijmbach, Eds., Pergamon Press, Oxford, 1983, p. 12
26. G. Keller, E. Barrera, B. Schmitz, E. Mattson, *Geol. Soc. Amer. Bull.* **105** (1993) 979
27. W. C. Elliot, J. L. Aronson, H. Jr. Millard, E. Gierlowski-Kordesch, *GSA Bulletin* **101** (1989) 702
28. R. Ganapathy, S. Gartner, M. J. Jiang, *Earth Planet. Sci. Lett.* **54** (1981) 393
29. R. Ganapathy, *Science* **209** (1980) 921
30. G. Keller, W. Stinnesbeck, T. Adatte, D. Stüben, *Earth-Sci. Rev.* **1283** (2002) 1.