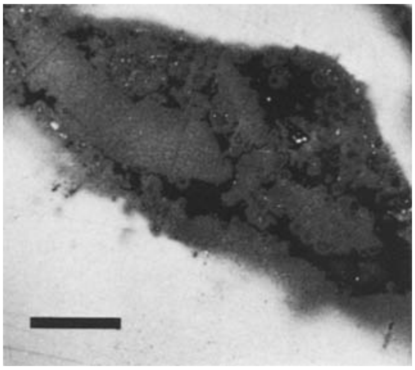

Fig. 2. Photomicrograph, polished section. Vesicular carburan oxide (grey) on vitrinite (light), associated with calcite (dark). Bar 20 µm

is called "carburan oxide" to characterize the submicroscopic intermixture of uranium oxide in vitrinite substance. Microscopical investigations of ore-bearing coal samples show mineralizations of galena, sphalerite, carburan oxide, and minor pyrite and marcasite in the microfissures of the cataclastic vitrinites. These mineral phases were precipitated in the sequence pyrite – marcasite – sphalerite I – galena – carburan oxide – sphalerite II, before a filling of the fissures with calcite (dominating) and/or quartz (subordinate) took place. Carburan oxide mainly occurs at the margins of the crushed vitrinite grains, typically forming impregnation microrims. The vesicular appearance (Fig. 2) suggests gaseous products arising from the chemical reaction of low-temperature hydrothermal uraniferous solutions with vitrinite, yielding carburan oxide as a precipitate mainly by reduction of U(VI) to U(IV). As shown by the brittled shapes of the vitrinite, the coal was consolidated to a great extend prior to cataclasis. Since mylonitization was a necessary precondition for the migration of uraniferous solutions, the carburan oxide mineralizations as well as the sulfide assemblage in the Stockheim coal are significantly epigenetic.

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1. Davidson, C.F., Bowie, S.H.U.: Geol. Surv. G. B. Bull. *3*, 1 (1951)
2. Ramdohr, P.: Die Erzmineralien und ihre Verwachsungen, p. 1277. Berlin: Akademie 1975
3. Breger, I.A., Deul, M.: Int. Conf. Peaceful Uses Atomic Energy, Proc. *6*, 418 (1956)
4. Szalay, A.: Geochim. Cosmochim. Acta *28*, 1605 (1964)
5. Halbach, P., et al.: Chem. Geol. *29*, 117 (1980)
6. Herrmann, R.: Geologie 7, 133 (1958)
7. Halbach, P., et al.: Arbeitsbericht zum DFG-Forschungsvorhaben Ha 563/22-2, p. 79, Clausthal-Zellerfeld 1982

Organic Matter in Surface Sediments of Lake Constance

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More than 50 surface sediment samples of Lake Constance from upper part (0–5 cm), were taken by means of a bottom sampler. The freeze-dried sediments were extracted in a Soxhlet apparatus with dichloromethane. The organic content of sediments was characterized by ultimate analysis of organic carbon and nitrogen. The extracts were directly applied to a silica HPLC column for separation of the alkane/alkene fraction, aromatics and hetero-compounds.

The amount of organic carbon varies between 0.8 and 4.5% (Table 1). A rough classification of the sediments into silty sands, clayey silts and silty clays according to the data in [1] does not show any relationship between the contents of total carbon, inorganic and organic carbon, and nitrogen. It can be concluded from this, that – with the exception of the sandy parts of the littoral zone – the organic matter is distributed in the sediment rather independently of grain size. This could be due to the hydrodynamic conditions that furthermore lead to bad sorting of the lake sediments [1].

Quantitative distribution patterns are characterized by regional particularities. The organic carbon content depends on the allochthonous input of the affluxes. The Rhine river delta with its big sedimentation rates and the broad cone of the Schussen river cause lower amounts of organic carbon by dilution. Interrelation with respect to nitrogen are less clear, but a distinct correlation between nitrogen and organic carbon is recognized.

The yield of extracts range between 240 ppm (Rhine delta) and 2600 ppm (near Iznang). Often a much higher content of elemental sulphur is extractable. Normally, the extractable organic matter is better bound in fine-grained sediments of the central part with the deepest location "Tiefer Schweb" (253 m) with 400–800 ppm, but extremely high extraction yields are found in the sediments of "Untersee" (2600 ppm), and the polluted parts of "Überlinger See" (1300 ppm) and "Rorschach" creek (1450 ppm). Coarse-grained sediments near polluted affluxes (e.g. Schussen) show similar extractability as non-polluted slope regions (400–500 ppm).

The dry sediments normally yield 100–200 ppm of the alkane/alkene fraction but some parts show increased values up to 540 ppm (e.g. near Iznang). The amount of alkanes and alkenes in relation to the total extract varies between 6 and 38% and is much higher than in recent terrestrial sediments [2].

All gas chromatograms of the alkane/alkene fraction are very similar with a distinct predominance of odd-numbered higher n-alkanes (n-C_{23} to n-C_{31}) of allochthonous terrestrial input that are overlain by respective 1-alkenes. Appearance of these unsaturates together with the n-C_{17}-alkane suggests their origin in recent aquatic organisms (algae). Influence of the terrestrial plant matter can be recognized in the affluxes of Rhine, Schussen, Argen, and Stockacher Aach by an increase of n-C_{25}- to n-C_{31}-alkanes.

In all samples the polycyclic aromatic hydrocarbons (PAH) have a relatively similar distribution pattern [3]. Major components are phenanthrene, fluoranthene, pyrene, benzo[*a*]fluorene, benzo[*b*]fluorene, benz[*a*]anthracene, chrysene/triphenylene, benzofluoranthenes, benzo[*e*]pyrene, perylene, indeno-(1,2,3-*cd*)-pyrene and benzo[*ghi*]-perylene. The concentrations of them are considerably and are listed in Table 1. Samples from "Rorschach" creek show the highest concentrations.

Table 1. Measured concentration ranges of different components related to dry sediment samples of Lake Constance

Location	No. of samples	Organic carbon [%]	Nitrogen [%]	Extract [ppm]	Alkanes alkenes [ppm]	Polycyc. aromatics [ppm]	Phthalates [ppm]	Cholesterol [ppm]	Coprostanol [ppm]	Cholestanol [ppm]
Central part	5	2.2–3.0	0.2–0.3	400– 800	100–190	4.2– 4.3	0.0–0.3	0.6– 1.5	0.4– 3.3	0.3– 2.0
"Tiefer Schweb"	8	1.0–3.1	0.3–0.4	200– 800	80–210	1.1– 3.4	0.8–1.0	0.5– 7.9	0.7– 4.3	0.9–10.0
Lakesides	10	1.0–2.5	0.2–0.4	100– 600	40–170	1.1– 4.9	0.0–0.2	0.7– 4.5	0.2– 2.5	0.3– 1.5
Affluxes	14	2.0–4.5	0.3–0.4	100– 1000	60–220	1.1– 3.1	0.1–1.1	0.5– 8.0	0.5– 4.9	0.5– 5.0
Rhine delta	4	0.8	0.15	240– 300	35– 50	0.1– 0.3	0.0	0.0– 0.1	0.0– 0.1	0.0– 0.1
Bregenz creek	4	1.0–1.6	0.2	100– 600	70–125	0.5– 0.8	0.0–0.6	0.2– 2.2	0.2– 0.6	0.1– 2.0
Rorschach creek	3	1.7–2.2	0.2–0.3	200–14500	230–260	2.3–11.4	0.1–5.4	1.0–18.6	0.5–23.9	0.5– 5.5
"Untersee"	3	2.7–3.5	0.3–0.5	1300– 2600	30–540	0.8– 5.3	0.1–1.1	0.3–14.5	1.9– 4.9	0.7– 2.7
"Überlinger See"	4	2.9–3.1	0.4	1200– 2000	120–370	3.1– 5.5	0.0–0.1	0.3– 4.2	0.2– 8.7	0.2– 5.1

The PAHs may have been transported by aeolic particles and affluxes into sediments. In comparison with profile analyses in literature, no definite assignment for emmission sources of PAHs can be stated. But there is evidence for the fact that they derive from multiple sources by pyrolytic processes with incomplete combustion for the most part [4], and not only from coal combustion [5]. There are also found small portions of methylized products especially on the basis structure of chrysene, pyrene and fluoranthene. However, there is no definite proof of pollution by lubricating oil [6], since higher homologues cannot be detected.

The fraction of heterocompounds has a very complex composition, and besides diethylhexylphthalate, also contains plant alcohols, carboxylic acids and sterols. Plant alcohols, mainly comprising the range from C_{22} to C_{26}, are thought to be derived from respective plant waxes as hydrolysis products. The corresponding waxy C_{22}- to C_{28}-carboxylic acids and the saturated and unsaturated C_{14}- to C_{18}-fatty acids are also identifiable.

Besides genuine sterols, like cholesterol, campesterol and sitosterol, the respective 5α-H- and 5β-H-hydrogenated products occur too. If early diagenetic, biogeochemical changes are thought to be observable on sterols, two processes must be differentiated. External cellular reduction that, for example, leads to 5α-H-stanols, and intracellular biologic processes leading to 5β-H-stanols. Some microorganisms (e.g. Enterobacteriaceae) are able to hydrogenate cholesterol into coprostanol (5β-H) [7, 8]. Therefore, coprostanol is considered as indicator for fecal matter as it is formed by microbial reduction of cholesterol in the intestinal tract. It can be observed that the coprostanol content normally ranges below that of cholestanol. An exception to this are sediment samples of "Rorschach" creek. In case that there is no important 5β-reduction in non-polluted sediments, it must be stated that among the analyzed Lake Constance sediments only samples taken near "Güttingen" can be considered as insignificantly polluted by sewage. An earlier examination of sediment samples from "Konstanzer Trichter" [9], revealing high contents of coprostanol, also lead to the conclusion that pollution by fecal matter occurs.

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1. Müller, G.: Naturwissenschaften *53*, 237 (1966)
2. Erdmann, W., et al.: Leitfaden zur Unterscheidung von biogenen und mineralölbürtigen Kohlenwasserstoffen. DGMK-Forschungsbericht 150, Hamburg 1977
3. Giger, W., et al.: Art und Herkunft der Kohlenwasserstoffe in Sedimenten des Bodensees. DGMK-Forschungsbericht 294, Hamburg 1982
4. Giger, W., et al.: Erdöl, Kohle, Erdgas, Petrochem. *34*, 451 (1981)
5. Müller, G., Grimmer, G., Böhnke, H.: Naturwissenschaften *64*, 427 (1977)
6. Grimmer, G., Böhnke, H.: Chromatographica *9*, 30 (1976)
7. Bjorkhem, J., Gustafsson, J.A.: Eur. J. Biochem. *21*, 428 (1971)
8. Eyssen, H.J., et al.: ibid. *36*, 411 (1973)
9. Müller, G., Kanazawa, A., Teshina, S.: Naturwissenschaften *60*, 520 (1979)

Lösliche mehrkernige Polysulfido-Metall-Cluster bzw. -Komplexe und erzbildende Lösungen

Über die Isolierung der neuartigen Cluster $[Cu_4S_{13}]^{2-}$ und $[Cu_4S_{14}]^{2-}$ aus einer Polysulfid-Lösung

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Vor längerer Zeit erschien in dieser Zeitschrift ein Aufsatz über einige Ansichten zur Chemie erzbildender Lösungen [1], in dem zum Ausdruck gebracht wurde, daß – wegen der geringen Löslichkeit von Metallsulfiden – der Transport der Bestandteile von Erzlagerstätten nicht umfassend geklärt sei. Dies gilt noch heute („the dilemma of transporting metals together with sulfur" [2]). Es wird angenommen, daß zahlreiche sulfidische Erzminerale hydrothermal aus postmagmatischen Fluida entstanden sind [3].