

VARIETIES OF SULPHUR IN LOW-RANK HUNGARIAN COALS

L. PÁPAY¹

¹Department of Mineralogy, Geochemistry and Petrography, Attila József University

ABSTRACT

In this paper altogether 17 brown coal and lignite samples have been studied from different parts of Hungary. Both low-rank coals were deposited under freshwater conditions. Most of the samples are characterised by relatively low amounts of total sulphur content.

The total sulphur content in Oligocene brown coals from Vértessomló is the least average value (0.8%) among Hungarian brown coals. The sequence of distribution of sulphur among the different bond forms in them is the same as in other samples of different Transdanubian brown coal mines: organic sulphur > pyritic sulphur > sulphate sulphur.

The lignite samples from Bükkábrány are characterised by relatively low amount (average: 1.3%) of total sulphur content. The moisture in lignite samples is fairly abundant, averagely 40.5%. The comparison of the Pliocene lignite of Bükkábrány with other Hungarian brown coals, according to their average total sulphur content on dry, ash-free basis (2.9%) indicated that they belong to the coal moderately rich in sulphur. In lignites at Bükkábrány organic sulphur and sulphate content dominate usually, and pyrite is minor. The relatively high sulphate concentration of lignites indicate that these samples are weathered or oxidized.

INTRODUCTION

The sulphur in coal is commonly classified into inorganic and organic sulphur. The inorganic sulphur occurs mostly as iron disulphides, FeS_2 , with a small amount occurring as sulphates, mainly in the form of iron and calcium sulphates, barium sulphates are rarely observed in coal. The presence of iron sulphates is generally an indication of coal weathering.

The organic sulphur compounds present in coal have been categorized according to their sulphur functional groups: thiol or mercaptan (R-SH), sulphide or thio-ether (R-S-R'), disulphide (R-S-S-R'), and aromatic systems containing the thiophene ring, γ -thiopyrone systems, where R and R' designate alkyl or aryl groups (GIVEN and WYSS, 1961). Thiol and disulphide are likely secondary products because they are thermally rather unstable and would not survive the coalification process (TSAI, 1982).

Pyrite is a common and widespread authigenic mineral in sedimentary rocks. Most insight on pyrite formation were derived from laboratory studies (BERNER, 1964, 1969; SWEENEY and KAPLAN, 1973; RICKARD, 1975; MUROWCHICK and BARNES, 1986; DROBNER et al., 1990; LUTHER, 1991; and others) or studies on brackish or marine environments (HOWARTH, 1979; BERNER, 1984; CANFIELD, 1989, PERRY et al., 1993; and others). Based on field observations and experimental studies, it is generally accepted that the iron disulphides form either (1) via replacement of FeS precursor or (2) via FeS_2 nucleation. In many cases the first product is iron monosulphide phase and subsequent reaction of this phase with elemental

¹ H-6701 Szeged, P.O. Box 651, Hungary

sulphur or sulphur equivalent (depend on pH polysulphides, thiosulphate SCHOONEN and BARNES, 1991) will produce finally pyrite. But in various sediments, especially in salt marshes (HOWARTH, 1979; LORD and CHURCH, 1983; GIBLIN and HOWARTH, 1984; KOSTKA and LUTHER, 1995) and in freshwater lakes (DAVISON et al., 1985) in peat (ALTSCHULER et al., 1983) in shale (CARSTENS, 1985) pyrite precipitates directly without any monosulphide intermediates. In the same sediment-porewater systems, many components (é.g.: elemental sulphur, iron monosulphides, pyrite, dissolved polysulphides, ferrous ion, hydrogen sulphide) can coexist, thereby obscuring the mechanism(s) by which pyrite is produced (LORD and CHURCH, 1983). Studies on distribution of sulphur in freshwater sediments revealed that organic sulphur forms are dominant (NRIAGU and SOON, 1985), in some freshwater lakes, however, inorganic S forms predominate (WHITE et al., 1989) and in lakes subjected to significant anthropogenic atmospheric S inputs (CARIGNAN and TESSIER, 1988). The formation mechanism of pyrite in freshwater systems is thought to be similar to that in marine sediments (SCHOONEN and BARNES, 1991).

Recent studies of S transformations in anoxic sediments have shown that the thiosulphate and sulphite are mainly the products of sulphide oxidation, and not sulphate reduction (FOSSING and JORGENSEN, 1990; ELSGAARD and JORGENSEN, 1992; THAMDRUP et al., 1994). In addition, the hydrogen sulphide (and/or polysulphides) as well as elemental sulphur are important intermediates for pyrite and organic sulphur. Numerous investigators have reported the early diagenetic sulphur enrichments of macromolecular sedimentary organic matter (CASAGRANDE et al., 1979; CASAGRANDE and NG 1979; FRANCOIS 1987; SINNINGHE DAMSTÉ et al., 1989; TUTTLE and GOLDBABER 1993; and others).

The purpose of the present paper is to determine the distribution of sulphur among the different bond forms in low-rank Hungarian coals deposited under freshwater conditions. The primary problem in utilization of coal is the necessity to minimize environmental pollution, therefore it is important to know the distribution of sulphur in this available energy source.

GEOLOGICAL SETTING

In Hungary the brown coal and lignite seams generally occur in the marginal areas of the deep basins and in intramontane lagoons. From Oligocene to Lower Miocene series for the Transdanubian Central Mountains and their NW foreland, the formation of continental-epicontinental terrigenous beds are characteristic (KORPÁS, 1981). At the beginning of Oligocene in the area of Vértessomló there was denudation -this erosional vacuity represents a short time interval- thereafter continental freshwater sediments deposited, in that sequence from 0.2 to 2.4 m thick brown coal bed can be found (GERBER, 1987; GIDAI, 1986), see *Fig. 1*.

In the Upper Pannonian (Pliocene) beds there are considerable lignite seams at the southern foreland of the Cserhát-Mátra and Bükk Mountains. This lignite region is the largest continuous coal area in Hungary (*Fig. 1*). The Mátra-Bükkalja sequence in the exposed Upper Pannonian (Pliocene) deposits are composed in 50 to 80 per cent fine to medium grain sands, less silt, clay and 2 to 15 m thick lignite seams consisting of several beds (RADÓCZ et al., 1987). The structure of the Pannonian lignite-bearing series is layered (so-called "layer cake structure"). The Bükkábrány lignite sequence is composed of varying thick lignite, argillaceous lignite and clay benches [CSILLING, 1965].

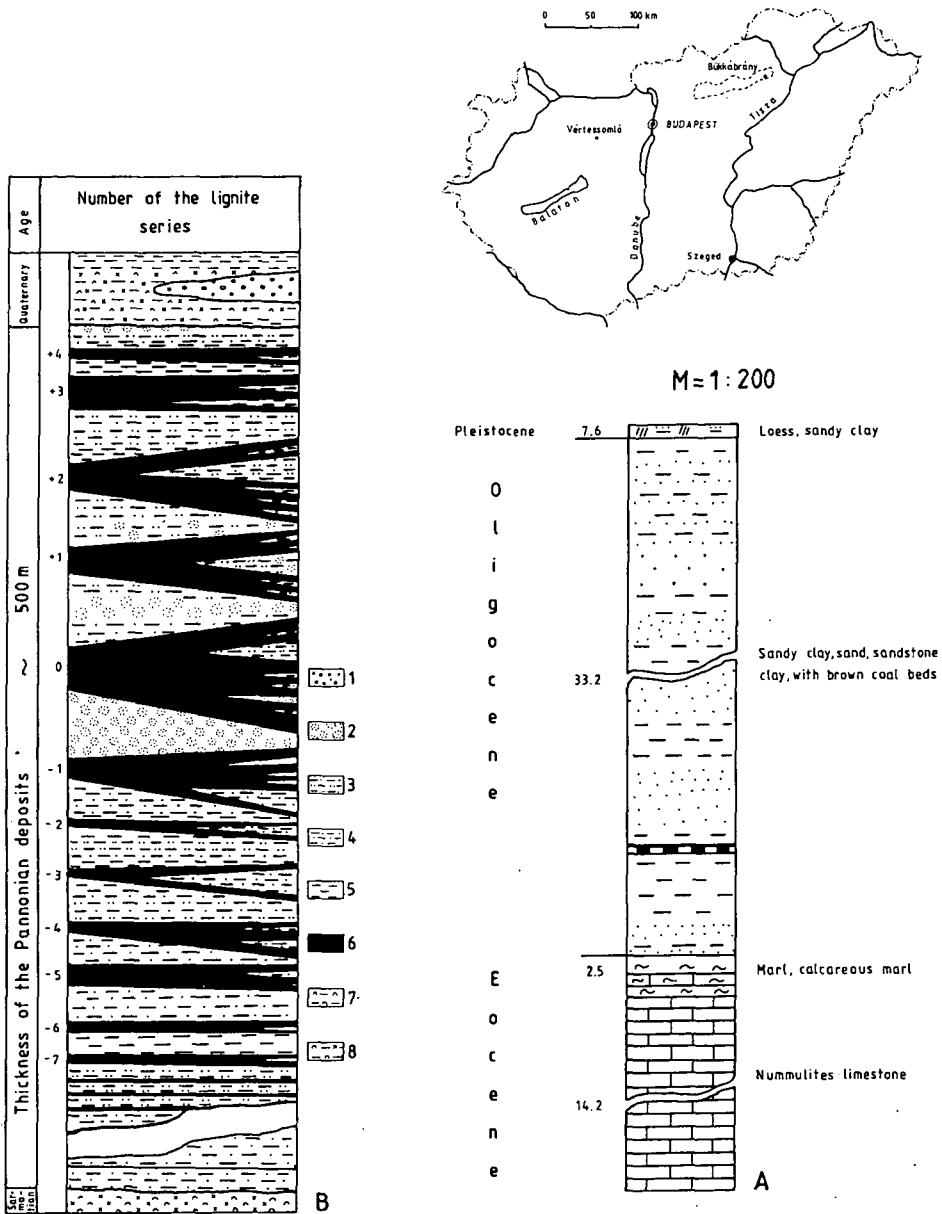


Fig. 1. Location map of the studied area and geological sections to them:
 A) detail of the geological section at Vertessomló (after GERBER, 1987);
 B) ideal geological section at Bükksík (after CSILLING, 1965)
 Legend: 1 = Pebble, 2 = Sand, 3 = Clayey sand, 4 = Sandy clay, 5 = Clay,
 6 = Lignite, 7 = Rhyolite tuff, 8 = Tuffaceous clay.

Faunal and paleogeographic evidence indicate, that in the early Late Miocene the Pannonian Lake/Sea -an inland sea- was finally disconnected from its neighbouring basins and gradually evolved into a large brackish to freshwater lake [JÁMBOR 1980, 1987; KÁZMÉR 1990; MÜLLER and MAGYAR 1992]. The salinity of the Pannonian Lake might have been 14-16‰ when Pannonian sediments started to deposit (BARTHA, 1971). In his study, KORIM (1966) deals in details with the connate waters of the Hungarian Neogene. He found that the Lower Pannonian connate waters immediately above the marl are oligohaline (the total solids content does not attain 10.000 mg/l), the upper horizon in the Lower Pannonian and the Upper Pannonian (Pontian) waters are fresh waters (max. salinity 700 mg/l).

SAMPLES AND ANALYTICAL METHODS

Altogether 17 brown coal and lignite samples have been examined from Vértessomló and Bükkábrány. We had collected and put the samples into double plastic bags; within a few days crushed to $\approx 200\mu\text{m}$ size in a ball agate mill, then their moisture and ash contents were determined immediately.

The total carbon content was measured at 1000 °C under intense oxygen flow by combusting in a Carmhograph-8 (Wösthoff) equipment.

The carbon dioxide content of samples was determined by gasvolumetric method.

The determination of the total sulphur content was carried out with Eschka procedure. The total sulphur content was converted into BaSO_4 and weighed gravimetrically.

The sulphur content of disulphide in coal samples was reduced by nascent hydrogen to hydrogen sulphide in the presence of Cr(II)-ions. The hydrogen sulphide originated from reduction was bubbled through a cadmium acetate solution and the sulphur content of disulphide was determined by iodometry.

The sulphate sulphur was determined by extraction of the powdered coal samples with hydrochloric acid followed by precipitation with barium chloride and weighing as barium sulphate.

In every case the organic sulphur was determined by the difference between the total sulphur and inorganic sulphur.

RESULTS AND DISCUSSION

The data of Hungarian brown coal and lignite (from the 1st bed) samples studied are summarized in Table 1.

The total sulphur content in the samples from Vértessomló is the least average value (0.8%) among Hungarian brown coals that have been examined previously (PÁPAY 1993, 1996). In these coals organic sulphur dominates, pyrite is in small quantity and sulphate content is negligible (sulphate S approx. zero). The sequence of the distribution of sulphur among the different bond forms in Oligocene brown coal is the same as in other samples of different Transdanubian brown coal mines: organic sulphur > pyritic sulphur > sulphate sulphur. Though, sulphur dioxide emission is minimum during burning of brown coal at Vértessomló, it is regrettable that total quantity relatively small.

Most of the lignite samples are characterised by relatively low amount (average: 1.3%) of total sulphur content. This value is similar to results (mean: 1.7%) of the prospecting boreholes at Bükkábrány. However, FEJÉR et al. (1989) in their review published only total sulphur data. It must be noted that the moisture in lignite samples is fairly abundant, averagely 40.5%. The comparison of the Pliocene lignite of Bükkábrány with other Hungarian brown coals, according to their average total sulphur content on dry, ash-free basis (2.9%) indicated that they belong to the coal moderately rich in sulphur. In lignites at Bükkábrány organic sulphur and sulphate content dominate usually, and pyrite is minor. The relatively high sulphate concentration of lignites indicate that these samples are weathered or oxidized. The samples were collected from open-pit mine. A part of the pyrite transformed and might transform into iron sulphate. The lignites at Bükkábrány are utilized in the power station near the mine.

TABLE I.

Distribution of sulphur in brown coal at Vértesszló (OI) and lignite samples at Bükkábrány (Bkk) in addition to data of the moisture, ash, total, inorganic, organic carbon content

Symbol	W ^a %	A ^d %	C _i %	C _{carb} %	C _{org} %	S _t ^a %	S _p ^a %	S _{sz} ^a %	S _{org} ^a % (diff.)	S _t ^{daf} %	S _p ^{daf} %	S _{sz} ^{daf} %	S _{org} ^{daf} % (diff.)
OI/1	9.7	13.7	59.4	0.1	59.3	0.8	0.1	0.0*	0.7	1.0	0.1	0.0	0.9
OI/2	9.5	26.7	47.9	0.1	47.8	0.9	0.1	0.0*	0.7	1.6	0.8	0.0	0.9
OI/3	9.5	11.4	58.3	0.1	58.2	1.3	0.6	0.0*	0.7	1.6	0.7	0.0	0.9
OI/4	9.6	32.3	43.2	0.1	43.1	0.3	<0.1	0.0*	0.2	0.5	0.2	0.0	0.3
OI/5	11.1	6.4	60.9	0.2	60.7	0.8	0.2	0.0*	0.6	1.0	0.3	0.0	0.7
Bkk/1	36.5	9.3	27.9	<0.1	~27.8	2.0	0.6	1.0	0.4	3.7	1.1	1.9	0.7
Bkk/2	37.9	8.2	28.9	<0.1	~28.8	1.2	0.3	0.3	0.6	2.2	0.6	0.6	1.0
Bkk/3	30.9	15.0	29.1	<0.1	~29.0	1.3	0.2	0.7	0.4	2.4	0.4	1.3	0.7
Bkk/4	50.3	5.9	31.4	<0.1	~31.3	0.8	0.2	0.2	0.4	1.8	0.5	0.5	0.8
Bkk/5	49.8	5.3	30.8	0.1	30.7	1.2	0.2	0.7	0.3	2.7	0.4	1.6	0.7
Bkk/6	46.6	17.2	23.9	<0.1	~23.8	1.7	1.0	0.3	0.4	4.7	2.8	0.8	1.1
Bkk/7	39.8	17.4	23.1	<0.1	~23.0	1.9	0.2	0.6	1.1	4.5	0.5	1.4	2.6
Bkk/8	41.5	10.4	36.8	<0.1	~36.7	0.7	0.1	<0.1	~0.5	1.4	0.2	~0.2	~1.0
Bkk/9	32.4	16.1	27.8	0.1	27.7	2.3	0.5	0.6	1.2	4.5	1.0	1.2	2.3
Bkk/10	36.7	24.8	30.5	<0.1	~30.5	1.1	0.2	0.3	0.6	2.9	0.5	0.8	1.6
Bkk/11	39.8	12.6	40.6	0.1	40.5	1.3	0.2	0.7	0.4	2.7	0.4	1.5	0.8
Bkk/12	43.8	11.6	24.6	0.1	24.5	0.6	<0.1	<0.1	~0.4	1.3	~0.2	~0.2	~0.9

W^a: analytical moisture wt%; A^d: ash wt %; C_i, C_{carb}, C_{org}: total, carbonate (inorganic), organic carbon content wt%;
S_t^a, S_p^a, S_{sz}^a, S_{org}^a: total, pyritic (+ sulphide), sulphate, organic (by difference) sulphur content in raw sample;
S_t^{daf}, S_p^{daf}, S_{sz}^{daf}, S_{org}^{daf}: total, pyritic (+ sulphide), sulphate, organic (by difference) sulphur content;
dry, ash-free basis

* data to be found under measuring range; <0.05%

As described above, the Oligocene brown coal in the vicinity of Vértessomló and Pliocene lignite of Bükkábrány were deposited as freshwater peats. In general, the common characteristics of freshwater coals are low ash and low total sulphur content. Organic sulphur is a major component of the low-sulphur coals. In freshwater systems, organic S compounds are the most important, because the low concentrations of sulphate, which characterize most freshwater systems limited bacterially-catalyzed reduction of sulphate. Organic sulphur is the dominant sulphur form in freshwater peats (eg. CASAGRANDE et al., 1977, 1980) and sediments (NRIAGU and SOON, 1985; MARNETTE et al., 1993) and in some cases organic S species accounted for 90-99% of total dissolved sulphur in the porewaters (STEIMANN and SHOTYK, 1997).

In low salinity waters, as in freshwater systems, the potential pyrite formation is prevented by both the low availability of sulphate and reducible iron (BERNER et al., 1979). That is the reason why pyrite is not determinant in freshwater coals. Furthermore, in lignites according to weathering or oxidation the pyrite may transform into iron sulphate especially in the period following the opening of mine.

ACKNOWLEDGEMENTS

This work was made possible by the (No. T 023050) Grant of the Hungarian Science Foundation (OTKA).

REFERENCES

- ALTSCHULER Z. S., SCHNEPPE M. M., SILBER C. C. and SIMON F. O. (1983): Sulfur diagenesis in Everglades peat and origin of pyrite in coal. - *Science* **221**, 221-227.
- BARTHA F. (1971): A magyarországi pannon biosztratigráfiai vizsgálata. (Biostratigraphic examination of Pannonian sediments in Hungary) In: (GÓCZÁN F., BENKŐ J. (eds.) A magyarországi pannonkori képződmények kutatásai. (Researches of Pannonian formations in Hungary) (in Hungarian). - Akadémiai Kiadó, Budapest, 9-173.
- BERNER R. A. (1964): Iron sulfides formed from aqueous solution at low temperatures and atmospheric pressure. - *J. Geology*, **72**, 293-306.
- BERNER R. A. (1969): The synthesis of framboidal pyrite. - *Econ. Geol.*, **64**, 383-384.
- BERNER R. A. (1981): Authigenic mineral formation resulting from organic matter decomposition in modern sediments. - *Fortschr. Miner.* **59**, 117-135.
- BERNER R. A. (1984): Sedimentary pyrite formation: An update. - *Geochim. Cosmochim. Acta*, **48**, 605-615.
- BERNER R. A., BALDWIN T., HOLDREN Jr. G. R. (1979): Authigenic iron sulfides as paleosalinity indicators. - *J. Sediment. Petrol.* **49**, 1345-1350.
- CANFIELD D. E. (1989): Reactive iron in marine sediments. - *Geochim. Cosmochim. Acta*, **53**, 619-632.
- CARIGNAN R. and TESSIER A. (1988): The co-diagenesis of sulfur and iron in acid lake sediments of southwestern Québec. - *Geochim. Cosmochim. Acta*, **52**, 1179-1188.
- CARSTENS H. (1985): Displacive growth of authigenic pyrite. - *J. Sediment. Petrol.* **56**, 252-257.
- CASAGRANDE D. J., GRONLI K. and SUTTON N. (1980): The distribution of sulphur and organic matter in various fractions of peat: origins of sulfur in coal. - *Geochim. Cosmochim. Acta*, **44**, 25-32.
- CASAGRANDE D. J., IDOWU G., FRIEDMAN A., RICKERT P., SIEFERT K. and SCHLENZ D. (1979): H₂S incorporation in coal precursors: origins of organic sulphur in coal. - *Nature* **282**, 599-600.
- CASAGRANDE D. J. and NG L. (1979): Incorporation of elemental sulphur in coal as organic sulphur. - *Nature* **282**, 598-599.
- CASAGRANDE D. J., SIEFERT K., BERSCHINSKI C. and SUTTON N., (1977): Sulfur in peat-forming systems of the Okefenokee Swamp and Florida Everglades: origins of sulfur in coal. - *Geochim. et Cosmochim. Acta* **41**, 161-167.
- CSILLING L. (1965): A bükkábrányi-emödi pannóniai barnaköszén terület (Pannonian brown coal area in the vicinity of Bükkábrány-Emöd) (in Hungarian). - *Földt. Kut.* **VIII/2**, 8-15.

- DAVISON W., LISHMAN J. P. and HILTON J. (1985): Formation of pyrite in freshwater sediments: Implications for C/S ratios. - *Geochim. Cosmochim. Acta*, **49**, 1615-1620.
- DROBNER E., HUBER H., WACHTERSHAUSER G., ROSE D. and STETTER K. O. (1990): Pyrite formation with hydrogen evolution under anaerobic conditions. - *Nature* **346**, 742-744.
- ELSGAARD, L. and JORGENSEN, B. B. (1992): Anoxic transformations of radiolabeled hydrogen sulfide in marine and freshwater systems. - *Geochim. Cosmochim. Acta*, **56**, 2425-2435.
- FEJÉR L., OSWALD Gy., SZÉLES L. (1989) : A magyarországi kőszének kéntartalom-felmérésének módszere és eredménye (The method and results of the sulphur content survey of the Hungarian coals) (in Hungarian). - Központi Földtani Hivatal kiadványa, Budapest.
- FOSSING H. and JORGENSEN B. B. (1990): Oxidation and reduction of radiolabeled inorganic sulfur compounds in an estuarine sediment, Kysing Fjord, Denmark. - *Geochim. Cosmochim. Acta*, **54**, 2731-2742.
- FRANCOIS, R. (1987): A study of sulphur enrichment in the humic fraction of marine sediments during early diagenesis. - *Geochim. Cosmochim. Acta*, **51**, 17-27.
- GERBER P. (1987): Vértessomló környékének földtana a barnakőszén-kutatások tükrében (Geology of the vicinity of Vértessomló in the light of brown coal exploration) (in Hungarian with German, English, Russian abstract). - Földt. Kutatás, **XXX/4**, 45-53.
- GIDAI L. (1986): A Vértessomló-Majkpuszta-Oroszlány környéki oligocén barnakőszén-telepek kutatásának lehetőségei (Possibilities of Oligocene brown coal exploration in the vicinity of Vértessomló-Majkpuszta-Oroszlány) (in Hungarian). - *BKL Bányászat*, **119/2**, 90-98.
- GIBLIN A. E. and HOWARTH R. W. (1984): Porewater evidence for a dynamic sedimentary iron cycle in salt marshes. - *Limnol. Oceanogr.* **29**, 47-63.
- GIVEN P. H. and WYSS W. F. (1961): The chemistry of sulfur in coal. - *British Coal Utilization Research Association Monthly Bulletin*, **25**, 165-179.
- HOWARTH R. W. (1979): Pyrite: its rapid formation in a salt marsh and its importance in ecosystem metabolism. - *Science* **203**, 49-51.
- JÁMBOR Á. (1980): A Dunántúli-középhegység pannóniai képződményei (Pannonian in the Transdanubian Central Mountains) (in Hungarian and in English). - *Ann. Inst. Geol. Publ. Hung. Budapest*, **LXII**, 1-259.
- JÁMBOR Á. (1987): A magyarországi kunsági emeletbeli képződmények földtani jellemzése (Geological Characterisierung der Ablagerungen der Kunság-Stufe in Ungarn) (in Hungarian with German abstract). - *Ann. Inst. Geol. Publ. Hung. Budapest*, **LXIX**, 1-452.
- KÁZMÉR M. (1990): Birth, life and death of the Pannonian Lake. - *Paleogeogr. Paleoclim. Paleocool.*, **79**, 171-188.
- KORIM K. (1966): The connate waters of the Hungarian Neogene. - *Acta Geol. Hung.*, **10**, 407-426.
- KORPÁS L. (1981): A Dunántúli-középhegység oligocén-alsó-miocén képződményei (Oligocene-Lower Miocene formations of the Transdanubian Central Mountains in Hungary) (in Hungarian and in English). - *Ann. Inst. Geol. Publ. Hung. Budapest*, **LIV**, 1-140.
- KOSTKA J. E. and LUTHER G. W. (1995): Seasonal cycling of Fe in saltmarsh sediments. - *Biogeochem.* **29**, 159-181.
- LORD C. J. III and CHURCH T. M. (1983): The geochemistry of salt marshes: Sedimentary ion diffusion, sulfate reduction, and pyritization. - *Geochim. Cosmochim. Acta*, **47**, 1381-1391.
- LUTHER III G. W. (1991): Pyrite synthesis via polysulfide compounds. - *Geochim. Cosmochim. Acta*, **55**, 2839-2849.
- MARNETTE E. C. L., VAN BREEMEN N., HORDIJK K. A. and CAPPENBERG T. E. (1993): Pyrite formation in two freshwater systems in the Netherlands. - *Geochim. Cosmochim. Acta*, **57**, 4165-4177.
- MUROWCHICK J. B. and BARNES H. L. (1986): Marcasite precipitation from hydrothermal solutions. - *Geochim. Cosmochim. Acta*, **50**, 2615-2629.
- MÜLLER, P., I. MAGYAR (1992): Continuous record of the evolution of lacustrine cardiid bivalves in the Late Miocene Pannonian Lake. - *Acta Paleont. Polonica*, **36**, 4, 353-372.
- NRIAGU J. O. and SOON Y. K. (1985): Distribution and isotopic composition of sulfur in lake sediments of northern Ontario. - *Geochim. Cosmochim. Acta*, **49**, 823-834.
- PÁPAY L. (1993): Distribution of sulphur in Transdanubian (Hungary) and Middle European brown coals. - *Acta Geol. Hung.*, **36/2**, 241-249.
- PÁPAY L. (1996): The distribution of sulphur in Upper Cretaceous brown coals from Ajka (Central Transdanubia, Hungary). - *Acta Miner. Petr., Szeged*, **XXXVII**, 89-98.
- PERRY K. A. and PEDERSEN T. F. (1993): Sulphur speciation and pyrite formation in meromictic ex-fjords. - *Geochim. Cosmochim. Acta*, **57**, 4405-4418.
- RADÓCZ Gy., BOHN-HAVAS M. and SZOKOLAI Gy. (1987): Neogene brown coal deposits in Hungary. Proceedings of the VIIIth RCMNS Congress. - *Ann. Inst. Geol. Publ. Hung. Budapest*, **LXX**, 601-608.
- RICKARD D. T. (1975): Kinetics and mechanisms of pyrite formation at low temperature. - *Amer. J. Sci.* **275**, 636-652.

- SINNINGHE DAMSTÉ J. S., EGLINTON T. I., DE LEEUW J. W. and SCHENCK P. A. (1989): Organic sulphur in macromolecular sedimentary organic matter: I. Structure and origin of sulphur-containing moieties in kerogen, asphaltenes and coal as revealed by flash pyrolysis. - *Geochim. Cosmochim. Acta*, **53**, 873-889.
- SCHOONEN M. A. A. and BARNES H. L. (1991): Reactions forming pyrite and marcasite from solution: II. Via FeS precursors below 100 °C. - *Geochim. Cosmochim. Acta*, **55**, 1505-1514.
- STEIMANN P. and SHOTYK W. (1997): Chemical composition, pH, and redox state of sulfur and iron in complete vertical porewater profiles from two *Sphagnum* peat bogs, Jura Mountains, Switzerland. - *Geochim. Cosmochim. Acta*, **61**, 1143-1163.
- SWEENEY R. E. and KAPLAN I. R. (1973): Pyrite framboid formation: laboratory synthesis and marine sediments. - *Econ. Geol.*, **68**, 618-634.
- THAMDRUP B., FINSTER K., FOSSING H., WÜRGLER H. J., and JORGENSEN B. B. (1994): Thiosulfate and sulfite distribution in porewater of marine sediments related to manganese, iron, and sulfur geochemistry. - *Geochim. Cosmochim. Acta*, **58**, 67-73.
- TSAI S. C. (1982): Fundamentals of coal beneficiation and utilization. Elsevier Scientific Publishing Company, Amsterdam-Oxford-New York, 222-274.
- TUTTLE M. L. and GOLDHABER M. B. (1993): Sedimentary sulfur geochemistry of the Paleogene Green River Formation, western USA: Implications for interpreting depositional and diagenetic process in saline alkaline lakes. - *Geochim. Cosmochim. Acta*, **57**, 3023-3039.
- WHITE J. R., GUBALA C. P., FRY B., OWEN J. and MITCHELL M. J. (1989): Sediment biogeochemistry of iron and sulfur in an acidic lake. - *Geochim. Cosmochim. Acta*, **53**, 2547-2559.

Manuscript received 10 August, 1997