

THE DISTRIBUTION OF SULPHUR IN UPPER CRETACEOUS BROWN COALS FROM AJKA (CENTRAL TRANSDANUBIA, HUNGARY)

L. PÁPAY*

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

ABSTRACT

In this study 25 brown coal samples have been examined from Ajka (Jókai mine). The total sulphur content of the studied Upper Cretaceous brown coals is highly variable abundances range from 2.1% to 9.7%, mean 5.1%. The dominant sulphur forms found in the samples were pyritic and organic sulphur. The sulphur content of the brown coals is generally less than 0.3%, the mean ~0.15%.

However, there is a difference between the distribution of sulphur in the lower and upper coal beds of the mine. The brown coal samples taken from the 1st bed can be characterized by extremely high total sulphur values (mean 7.5%), where the pyritic sulphur is dominating giving 65% of the total sulphur content. In the 3rd, 4th, 5th and 6th coal beds of the lower coal series the prevalence of organic sulphur ($\geq 70\%$), an average of ~20% pyritic sulphur and a minimal sulphate sulphur content can be traced. These latter distributions of the sulphur content are very similar to the values experienced during the earlier analyses of the average sulphur content of Transdanubian brown coals, the sequence is organic sulphur > pyritic sulphur > sulphate sulphur. The wide range of the total sulphur content within the individual coal beds – save the 6th one – refers to their heterogenous nature. The inorganic contents of the coal measures are also different, the average ash content of the samples taken from the coal beds showed an upward increase.

The high sulphur content of the coals of Jókai mine can be explained by the fact that they were deposited in a brackish or marine-influenced environment. The really high pyrite content of the 1st bed might be explained by the presence of interbedding clayish inorganic layers within the coal beds, while the high organic sulphur content of the lower coal series may reflect the influence of the carbonate rocks giving the bottom of seams and the low concentration of available reactive iron during peat formation and diagenesis.

INTRODUCTION

It is generally known that sulphur present in the coal is usually as inorganic and organic sulphur compounds. The inorganic sulphur content is originated mainly from iron sulphides (pyrite or marcasite; other sulphides are frequently found in very small quantities e. g. arsenic, copper, lead, zinc sulphides). The presence of sulphates (mainly of calcium and iron) is generally unimportant except in case of highly weathered or oxidized coal samples (weathering of pyrite may generate iron sulphates). Although elemental sulphur sometimes occurs in some coals. The sulphur content is conventionally given in total sulphur values and the so-called forms of sulphur that are pyritic, sulphate and organic sulphur, with the assumption that pyritic sulphur embodies all the metallic sulphides as well.

The first step in the overall process of sedimentary pyrite formation is the bacterial reduction of sulphate, under anoxic conditions. The amount of pyrite formed in a sediment

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

depends on three factors: sufficient dissolved sulphate, concentration of organic matter and reactive iron minerals. Pyrite forms during shallow burial, via the reaction of detrital iron minerals with H_2S . The H_2S is produced by the reduction of interstitial dissolved sulphate by bacteria using sedimentary organic matter as reducing agent and energy source. The initial product of this reaction is not pyrite but rather a series of metastable iron monosulphides which during early diagenesis transform to pyrite by reaction with polysulphide ions (BERNER 1972, 1981, 1984). However, the last reaction step is very complicated process. According to a part of the study pyrite single crystals could be formed rapidly and directly by the reaction of iron monosulphide with polysulphide ions (RICKARD 1975), but direct pyrite formation was not observed in case of reactions of Fe(II) and Fe(III) solutions with polysulphide (LUTHER III 1991). On the other hand a number of laboratory studies have demonstrated that pyrite can be synthesized rapidly from inorganic solution under suitable conditions (HOWARTH 1979) or DROBNER et al. (1990) reported the formation of pyrite under fastidiously anaerobic conditions in the aqueous system of FeS and H_2S .

In the fresh-water amount of sulphate less than in sea-water, during burial sulphate supply become difficult too, therefore in these circumstances pyrite forms not only via reduction of sulphate. According to ALTSCHULTER et al. (1983) the pyrite formation in organic-rich sediment is commonly linked to H_2S formed within the organic tissues and suggests that the sulphid may derive largely from organic sulphur.

In the sediments, H_2S formed from microbial reduction of sulphate initially reacts with available iron to form iron sulphid minerals and more gradually with organic matter to form organosulphur compounds (TUTTLE and GOLDBERGER 1993). The organic sulphur compounds found in coals have been categorized according to functionality: thiols, sulphides, thiophenes, thiopyrones (GIVEN and WYSS 1961; ATTAR 1979). In their experiments CASAGRANDE et al. (1979) demonstrated that not only $H_2^{35}S$ is incorporated in peat as organic sulphur, but elemental sulphur as well (CASAGRANDE and NG 1979). Hydrogen sulphide is an important intermediate for pyrite and organic sulphur formation in peats (CASAGRANDE 1987).

The H_2S produced by bacterial sulphate reduction exhausts not only in reactions mentioned above, but a part of the H_2S escapes from the sulphate reduction zone as well. In a study on recent bioturbated sediments BERNER and WESTRICH (1985) found that only <10–75% of the reduced sulphur remains in the sediments. They have concluded that the main mechanism of loss of reduced sulphur are oxidation “by O_2 mixed into the sediments by the benthos and, to a lesser extent, via enhanced H_2S transport resulting from benthic irrigation”. Therefore we may support that the mechanisms enumerated by BERNER and WESTRICH (1985) did not operate in sediments where bioturbation is absent. Thus these sediments have lost no more than 25% (and probably much less) of the reduced sulphur produced in them (VETŐ and HETÉNYI 1991).

There is an almost universal tendency for the sulphur content of seams in close proximity to marine bands to be abnormally high (WANDLESS 1955; WILLIAMS and KEITH, 1963; REIDENOUER et al. 1967 and others). The high sulphur content is due to the increased availability of sulphate ions in sea-water and by the activity of anaerobic bacteria. Coals, which were deposited in calcium-rich swamps, show similar properties to marine-influenced coals. Calcareous basements, or influx of calcium-rich waters from surrounding swamp areas, reduce the acidity of the peat to a much greater degree than does sea-water (SZÁDECZKY-KARDOSS 1952; STACH et al. 1982).

CECIL et al. (1979) concluded that low ash and low sulphur coals were deposited as fresh-water peats which were underlain and overlain by fresh-water clastic sediments in which limestones were absent. Where limestones are present in fresh-water sedimentary sequences the coals are of intermediate ash yield and sulphur content. High ash and high sulphur coals are associated with brackish or marine sediments.

GEOLOGICAL SETTING

The Upper Cretaceous brown coal mine (Jókai) in the Transdanubian Central Range is situated at the NW edge of the S Bakony Mountains, SE from the town of Ajka in the middle of the Ajka Basin (*Fig. 1.*).

In the NW foreland of the S Bakony Mountains the Senonian coal-bearing series can be found along a 20–25 kilometres long line. The Upper Triassic Norian dolomite complex (“Hauptdolomit”) forms the bottom of this coal-bearing series. Besides these the Kössen beds (Rhaetian) are represented by distinctive forms of limestones, dolomites, marls and clay marls and respectively the rocks of another Upper Triassic Rhaetian deposit the Dachstein Limestone (“Dachsteinkalk”) (KOZMA 1991). The classical term of Ajka Coal Formation covers a unit which consists of an alternation of coal-bearing argillaceous and calcareous rocks deposited in lacustrine and, later, salt water swamps which developed parallel with the marine transgression in the Senonian (HAAS et al. 1977). The series of the Ajka Coal Formation is composed of a multiple cyclical succession of coal, grey clay marl, marl, sandstone and limestone layers. In the lower strata of the formation the presence of an abundant molluscs indicate freshwater facies while in the upper strata it shows an increasing tendency in salinity with cyclical changes (HAAS and EDELÉNYI 1979).

The Ajka brown coal measures approximately 120 m thick vertically with a 130 coal benches, with the help of the well identifiable unproductive interbeddings can be divided into a lower and upper coal series.

The lower coal series has a 14–25 m vertical thickness and contains most of the coal beds. The 2nd, 3rd, 4th, 5th and 6th coal beds are divided by slightly different interbeddings in the mine. These unproductive interbeddings are 0.3–2.0 metres thick vertically. Between the coal beds and in the beds themselves the appearance of light brown calcareous marls, carbonaceous marls can be observed.

The upper coal series is divided from the lower one by one a 1–20 metres thick light grey clay marl interbedding. In the coal series only one workable seam can be found which is called the 1st or Amber Coal Bed. It was named after the fossilized resins of Cretaceous pine forests, though as it turned out later on practically amber might be found in any of the seams. The amber was given the name of Ajkait after the town of Ajka. Above the 1st bed the previously mentioned light grey clay marl layers occur again in 5 to 20 metres thickness. The geological literature give the name 0 (zero) bed to the 4–5 metres thick carbonaceous clay, argillaceous coal and marl mollusc bearing layers above the 1st coal bed thus indicating that the discovery of this seam took place after the accepted numbering of the coal beds of the series (KOZMA 1991).

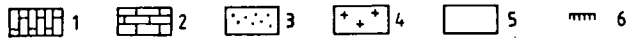
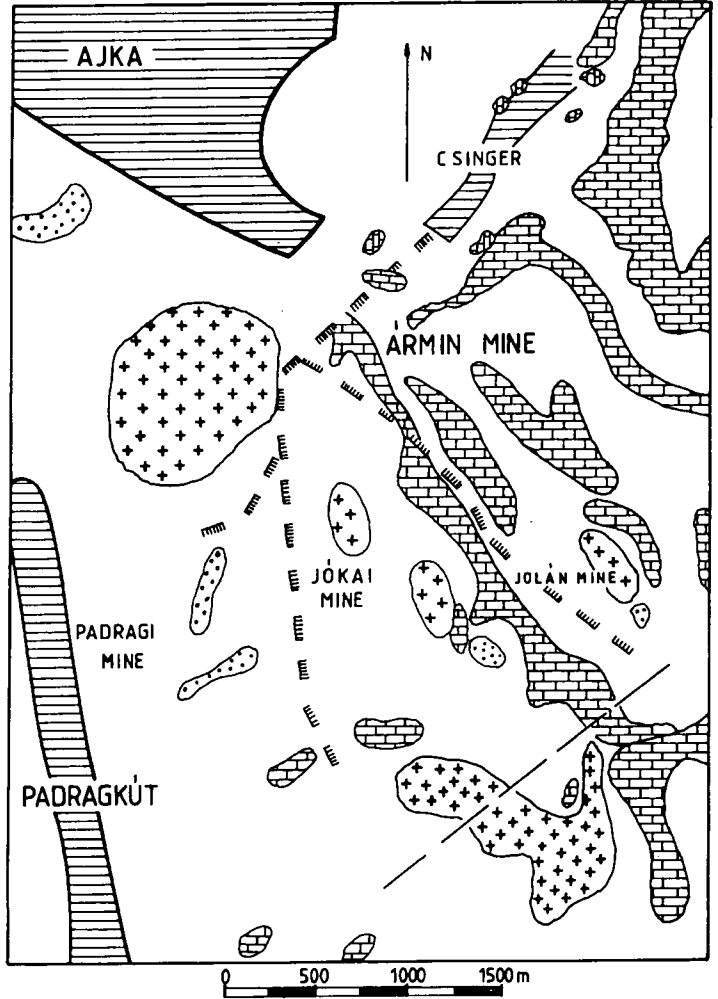
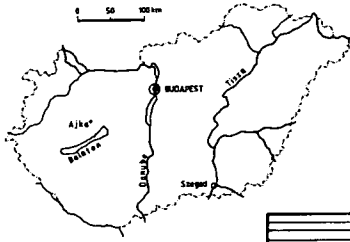


Fig. 1. Geological sketch map of the Ajka Basin (after KLESPITZ, 1971)

Legend: 1 = Upper Cretaceous limestone, 2 = Eocene limestone, 3 = Miocene pebbles, 4 = Pliocene basalt, 5 = Pleistocene, holocene deposits, 6 = Fault, 7 = The boundary of the erosion coal bed.

SAMPLES AND ANALYTICAL METHODS

25 brown coal samples have been examined from Ajka (Jókai Mine) (Table 1). First the samples were ground to grain size $d \leq 0.2$ mm.

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

The determination of calcite and dolomite by gasometry is based on the fact that calcite dissolves rapidly and perfectly in 1:1 HCl at room temperature, but dolomite dissolved after some time and very slowly. At the same time both calcite and dolomite dissolves after 5 minutes boiling (HETÉNYI and VARSÁNYI 1975). $1 \text{ cm}^3 \text{ CO}_2 = 0.1976 \text{ g CO}_2$; $C_{\text{carb}} = 0.2729 \times \text{CO}_2$.

The determination of the total sulphur was carried out with Eschka procedure. The Eschka method consist of thoroughly mixing the powered coal sample with Eschka mixture (two parts calcined MgO and one part anhydrous Na_2CO_3) and then ashing the mixture in muffle furnace at 800 °C. The ashed coal is leached with hot water and filtered, and sulphate precipitated with BaCl_2 was determined by gravimetric analysis as barium sulphate. This method is most accurate for coal samples containing no more than 6 or 7% sulphur (TSAI 1982).

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 buddled through a cadmium acetate solution and the sulphur content of disulphide was determined by iodometry.

The sulphate sulphur was determined by extraction of the powered 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.

RESULT AND DISCUSSION

Examining the data published in Hungarian geological reports concerning the Ajka mine (Table 2) it can be concluded that primarily we have to deal with records of the total sulphur content of the Hungarian coals. It can be plainly seen mainly in case of the more data found in the reports (FEJÉR et al. 1989) as well that there are extreme variations in the quantities of the total sulphur content in the brown coal samples of the Jókai mine. Our measurements proved these extreme variations too. The results of experiments are summarized in Table 3.

The total sulphur content of Upper Cretaceous brown coals from Ajka is highly variable abundances range from 2.1% to 9.7%, mean 5.1%. Pyritic and organic sulphur are dominant sulphur forms in them. The sulphur content of brown coals is generally less than 0.3%, with a mean of $\sim 0.15\%$. Besides the general features of the coal measures we have to take in to consideration the fact that the development of the individual coal beds might be different within the whole system along with the distribution of sulphur content; thus the data concerning the individual coal beds give us more accurate information about the mine. The distribution of sulphur is different in the 1st bed and the 3rd, 4th, 5th and 6th beds of the lower coal series. The brown coal samples taken from the 1st bed can be characterized by extremely high total sulphur values (mean 7.5%!), where the pyritic

TABLE I

Markings connected with the brown coal samples from Ajka (Jókai Mine)

Sample No.	Symbol	Sampling	Features of the coal samples
1	J/I/1	1 st coal bed; coal drawing (37/1)	Slightly stratified durain coal
2	J/I/2	1 st coal bed; coal drawing (37/1)	Durain coal with vitrain lenticles
3	J/I/3	1 st coal bed; coal drawing (37/1)	Durain coal with vitrain lenticles; similar to J/I/2
4	J/III/4	3 rd coal bed; coal drawing (52/6)	Unstratified durain coal with vitrain lenticles
5	J/III/5	3 rd coal bed; coal drawing (52/6)	Unstratified vitrain lenticles coal with brown precipitated resin
6	J/III/6	3 rd coal bed; coal drawing (52/6)	Slightly stratified coal with vitrain streaks and fragments of gastropods
7	J/III/7	3 rd coal bed; air way of coal preparation (38/IV)	Unstratified durain coal
8	J/III/8	3 rd coal bed; haulage drift of coal preparation (38/IV)	Durain coal with fragments of molluscs
9	J/III/9	3 rd coal bed; air way of coal preparation (38/IV)	Unstratified durain coal
10	J/IV/10	4 th coal bed; coal drawing (52/6)	Unstratified durain coal
11	J/IV/11	4 th coal bed; coal drawing (52/6)	Unstratified durain coal
12	J/IV/12	4 th coal bed; coal drawing (52/6)	Unstratified vitrain coal with millimetre sized gypsum
13	J/IV/13	4 th coal bed; haulage drift of coal preparation (38/IV)	Vitrain coal with fragments of molluscs
14	J/IV/14	4 th coal bed; haulage drift of coal preparation (38/IV)	Durain coal
15	J/IV/15	4 th coal bed; haulage drift of coal preparation (38/IV)	Vitrain coal with fragments of molluscs
16	J/IV/16	4 th coal bed; air way of coal preparation (38/IV)	Vitrain coal
17	J/IV/17	4 th coal bed; air way of coal preparation (38/IV)	Vitrain coal with fragments of molluscs
18	J/V/18	5 th coal bed; coal drawing (52/6)	Slightly stratified durain coal
19	J/V/19	5 th coal bed; coal drawing (52/6)	Slightly stratified vitrain lenticles coal
20	J/V/20	5 th coal bed; coal drawing (52/6)	Unstratified durain coal with vitrain lenticles
21	J/V/21	5 th coal bed; 38/IV air way of coal preparation	Durain coal
22	J/V/22	5 th coal bed; air way of coal preparation (38/IV)	Vitrain lenticles coal with fragments of molluscs
23	J/VI/23	6 th coal bed; coal drawing (52/6)	Hard, vitrain and durain streaks coal
24	J/VI/24	6 th coal bed; coal drawing (52/6)	Crumbly, clarain earth coal
25	J/VI/25	6 th coal bed; coal drawing (52/6)	Moderately hard, durain coal with fragments of molluscs

TABLE 2

The total sulphur content and distribution of sulphur in brown coal from Ajka
on the basis of published data

Station of sampling	Number of samples	S _t ^a wt% (mean)	S _p ^a wt% (mean)	S _{sz} ^a wt% (mean)	S _{org} ^a wt% (mean)
Ajka ¹	6	4.30–5.58 ^{1a} (4.98) 6.9 ^{1b}			
Ajka ²	3	2.88–3.98 (3.52)			
Ajka ³	8	3.4–4.5 (4.0)	0.7–1.3 (1.0)	0.2–0.5 (0.3)	1.6–3.3 (2.7)
Jókai mine ⁴	37	1.57–9.34 (3.39)			

S_t^a, S_p^a, S_{sz}^a, S_{org}^a: total, pyritic (+sulphide), sulphate, organic (by difference) sulphur content in air dried sample.

¹ VITÁLIS I. (1939): Occurrence of coals in Hungary; ^{1a} after GRITNER, 1906; ^{1b} after VARGA J. and NYÜL Gy., 1937.

² SZÁDECZKY-KARDOSS E. (1952): Coal Petrology.

³ MR. KOVATSITS M., WOLF GY. (1980): Sulphur survey of the Hungarian commercial coals.

⁴ FEJÉR L., OSWALD GY., SZÉLES L. (1989): The method and results of the sulphur content survey of the Hungarian coals.

sulphur is dominating giving 65% of the total sulphur content. In the 3rd, 4th, 5th and 6th coal beds of the lower coal series the prevalence of organic sulphur (≥70%), an average of ~20% pyritic sulphur and a minimal sulphate sulphur content can be traced. These latter distributions of the sulphur content are very similar to the values experienced during the earlier analyses of the average sulphur content of Transdanubian brown coals, the sequence is organic sulphur > pyritic sulphur > sulphate sulphur (PÁPAY 1993). The wide range of the total sulphur content within the individual coal beds – save the 6th one – refers to their heterogeneous nature. The inorganic contents of the coal measures are also different, the average ash content of the samples taken from the coal beds showed an upward increase. The high sulphur content of the coals of Jókai mine can be explained by their deposition in a brackish or marine-influenced environment. The really high pyrite content of the 1st bed might be explained by the presence of interbedding clayish inorganic layers within the coal beds. As it is known, in the argillaceous rocks the amount of reactive iron is plenty 6.5% (Fe₂O₃+FeO), but at the same time in carbonates the iron content is only 0.5% or lower (WOYTKEVITSH et al. 1977). The quantity of available ferrous ion is an important factor for pyrite formation. At the same time the high organic sulphur content of the lower coal series may reflect the influence of the carbonate rocks giving the bottom of seams and the low concentration of available reactive iron during peat formation and diagenesis.

ACKNOWLEDGEMENT

This work has been supported by the Hungarian Scientific Research Fund (OTKA) grant No. T 007445.

Distribution of sulphur in brown coal samples at Ajka (Jókai Mine) in addition to data of the moisture, ash, total, inorganic, organic carbon content

Symbol	W ^a %	A ^d %	C _t %	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.)
J/I/1	7.6	32.7	41.3	0.2	41.1	4.5	1.9	0.1	2.5	7.5	3.2	0.1	4.2
J/I/2	7.0	26.2	44.5	0.2	44.3	8.4	5.8	0.2	2.8	13.2	8.7	0.3	4.2
J/I/3	6.2	40.1	31.3	0.2	31.2	9.7	7.0	0.7	2.3	18.6	13.0	1.3	4.3
J/III/4	9.1	10.4	60.6	0.1	60.5	7.9	2.3	0.1	5.5	9.8	2.9	0.1	6.8
J/III/5	9.0	12.6	64.8	0.6	64.2	5.3	0.3	<0.1	~4.9	6.8	0.4	~0.1	~6.3
J/III/6	8.6	13.9	60.6	0.6	60.0	4.8	0.3	<0.1	~4.4	6.2	0.4	~0.1	~5.7
J/III/7	7.6	15.8	56.0	0.1	55.9	6.3	1.6	0.1	4.6	8.2	2.1	0.1	6.0
J/III/8	6.1	32.9	43.1	3.9	39.2	3.9	0.7	<0.1	~3.1	6.4	1.2	~0.1	~5.1
J/III/9	7.8	20.4	53.5	0.1	53.4	5.7	2.4	0.1	3.2	7.9	3.3	0.1	4.5
J/IV/10	7.8	14.3	58.9	0.2	58.7	5.5	1.1	0.1	4.3	7.0	1.4	0.1	5.5
J/IV/11	8.2	11.1	63.7	0.1	63.6	5.5	0.8	0.2	4.5	6.8	1.0	0.2	5.6
J/IV/12	8.0	13.0	59.6	0.6	59.0	6.3	0.5	0.3	5.5	8.0	0.6	0.4	7.0
J/IV/13	5.1	38.8	34.1	4.0	30.1	3.2	0.4	<0.1	~2.7	5.7	0.7	~0.2	~4.8
J/IV/14	8.5	13.1	53.8	0.2	53.6	6.3	1.3	0.2	4.8	8.0	1.7	0.3	6.1
J/IV/15	4.3	41.4	32.2	5.5	26.7	2.1	0.4	<0.1	~1.6	3.9	0.7	~0.2	~3.0
J/IV/16	6.0	48.6	28.5	0.1	28.4	4.8	2.9	0.2	1.7	10.6	6.4	0.4	3.7
J/IV/17	5.3	38.1	40.3	4.2	36.1	3.2	0.6	<0.1	~2.5	5.7	1.1	~0.2	~4.4
J/V/18	8.0	11.7	63.7	0.2	63.5	3.6	0.7	0.1	2.8	4.5	0.9	0.1	3.5
J/V/19	8.2	23.8	54.0	0.7	53.3	3.7	1.0	0.1	2.6	5.4	1.5	0.1	3.8
J/V/20	8.2	13.9	58.9	0.2	58.7	5.2	1.2	0.1	3.9	6.6	1.5	0.1	5.0
J/V/21	7.7	25.3	46.7	0.1	46.6	6.3	3.2	0.3	2.8	9.4	4.8	0.4	4.2
J/V/22	6.7	25.7	50.0	2.4	47.6	4.6	0.8	<0.1	~3.7	6.8	1.2	~0.1	~5.5
J/V/23	9.5	11.5	58.1	0.2	57.9	4.0	1.1	0.1	2.8	5.1	1.4	0.1	3.6
J/VI/24	9.3	8.9	63.7	0.2	63.5	3.1	0.3	0.1	2.7	3.8	0.4	0.1	3.3
J/VI/25	9.7	13.3	58.5	0.4	58.1	3.6	0.2	0.2	3.2	4.7	0.3	0.3	4.1

W^a: analytical moisture wt %; A^d: ash (air dried sample) wt %; C_t, 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 air dried sample

S_t^{daf}, S_p^{daf}, S_{sz}^{daf}, S_{org}^{daf}: total, pyrite (+sulphide), sulphate, organic (by difference) sulphur content; dry, ash-free basis

REFERENCES

- ATTAR A. (1979): Sulfur groups in coal and their determination. In: Analytical Methods for Coal and Coal Products, Vol. III, 353–357. Academic Press, New York.
- 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.
- BERNER R. A. (1972): Sulfate reduction, pyrite formation, and the oceanic sulfur budget. – in: *The Changing Chemistry of the Oceans*, Eds. Dyrssen D. and Jagner D., Almquist and Wiksell, Stockholm, 347–361.
- 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. and WESTRICH J. T. (1985): Bioturbation and the early diagenesis of carbon and sulfur. – *Am. J. Sci.* **285**, 193–206.
- CASAGRANDE D. J., IDOWU G., FRIEDMAN A., RICKERT P., SIEFERT K. & SCHLENZ D. (1979): H₂S incorporation in coal precursors: origins of organic sulphur in coal. – *Nature* **282**, 599–600.
- CASAGRANDE D. J. & NG L. (1979): Incorporation of elemental sulphur in coal as organic sulphur. – *Nature* **282**, 598–599.
- CASAGRANDE D. J. (1987): Sulphur in peat and coal. – In: Scott A. C. (ed): *Coal and coal-bearing strata: Recent Adv. Geol. Soc. Spec. Publ.* **32**, 87–105.
- CECIL C. B., RENTON J. J., STANTON R. W. & FINKELMAN R. B. (1979): Mineral matter in coals of the central Appalachian Basin. – 9th Internat. Congr. Carbonif. Strat. Geol. Abstr. p. 33, Urbana III.
- DROBNER E., HUBER H., WACHTERSHAUSER G., ROSE D. & STETTER K. O. (1990): Pyrite formation with hydrogen evolution under anaerobic conditions. – *Nature* **346**, 742–744.
- 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.
- GRITTNER A. (1906): Szénelemzések (Coal analyses). Budapest. In: Vitális I. (1939): Magyarország szénelőfordulásai (Occurrence of coals in Hungary) (in Hungarian). Sopron.
- GIVEN P. H. & WYSS W. F. (1961): The chemistry of sulfur in coal. – *British Coal Utilization Research Association Monthly Bulletin*, **25**, 165–179.
- HAAS J., J. EDELÉNYI E., CSÁSZÁR G. (1977): Mezozoós formációk vizsgálata a Dunántúli-középhegységben (Study of mesozoic formations of the Transdanubian Central Mountains in Hungary) (in Hungarian with English abstract). – Annual Report of the Hungarian Geological Institute of 1975, 259–269.
- HAAS J., J. EDELÉNYI E. (1979): A dunántúli-középhegységi felsőkréta üledékciklus ösföldrajzi elemzése (Paleogeographic analysis of the late Cretaceous sedimentary cycle in the Transdanubian Central Mountains, W Hungary) (in Hungarian with English abstract). – Annual Report of the Hungarian Geological Institute of 1977, 217–224.
- HETÉNYI M., VARSÁNYI I. (1975): Rapid determination of calcite and dolomite for routine analysis by gasometry. – *Acta Miner. Petr.*, Szeged **XXII/1**, 165–170.
- HOWARTH R. W. (1979): Pyrite: its rapid formation in a salt marsh and its importance in ecosystem metabolism. – *Science* **203**, 49–51.
- KLESPITZ J. (1971): Az ajkai barnakőszén medence Jókai Bánya területének bányaföldtani viszonyai (Geology of the Jókai brown coal mine in the Ajka Basin (in Hungarian with German abstract). – *Föld. Kut.* **XIV/1–2**, 6–14.
- KOVATSITS M.-NÉ, WOLF GY. (1980): A hazai kereskedelmi széntermékek minőségi katasztere (Sulphur survey of the Hungarian commercial coals) (in Hungarian). Budapest–Tatabánya, KBFI, Magyar Szénbányászati Tröszt.
- KOZMA K. (1991): Az ajkai szénbányászat története. (The history of the coal mining at Ajka) – *Veszprémi Szénbányák, Veszprém*, 29–38.
- LUTHER III G. W. (1991): Pyrite synthesis via polysulfide compounds. – *Geochim. Cosmochim. Acta*, **55**, 2839–2849.
- PÁPAY L. (1993): Distribution of sulphur in Transdanubian (Hungary) and Middle European brown coals. – *Acta Geologica Hungarica*, **36/2**, 241–249.
- REIDENOUER D., WILLIAMS E. G. & DUTCHER R. R. (1967): The relationship between paleotopography and sulfur distribution in some coals of western Pennsylvania. – *Economic Geology*, **63**, 632–649.
- RICKARD D. T. (1975): Kinetics and mechanisms of pyrite formation at low temperature. – *Amer. J. Sci.* **275**, 636–652.
- STACH, E., MACKOWSKY M.-TH., TEICHMÜLLER M., TAYLOR G. H., CHANDRA D., TEICHMÜLLER R. (1982): *Stach's textbook of coal petrology.* – *Gebrüder Borntraeger, Berlin, Stuttgart.*

- SZÁDECZKY-KARDOSS, E. (1952): Szénkőzettan (Coal petrology) (in Hungarian). Akadémiai Kiadó, Budapest.
- TSAI S. C. (1982): Fundamentals of coal beneficiation and utilization. Elsevier Scientific Publishing Company, Amsterdam–Oxford–New York, 227.
- 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.
- VARGA J. and NYÚL GY. (1937): A magyar tüzelőszerszár (The Hungarian fuel industry). Technika, Budapest, 1 sz. – In: Vitális I. (1939): Magyarország szénélőfordulásai (Occurrence of coals in Hungary) (in Hungarian). Sopron.
- VETŐ I. & HETÉNYI M. (1991): Fate of organic carbon and reduced sulphur in dysoxic-anoxic Oligocene facies of the Central Paratethys (Carpathian Mountains and Hungary). In: Tyson R. V. and Pearson T. H. (eds.): Modern and Ancient Continental Shelf Anoxia. Geological Society Special Publication No. 58, 449–460.
- VITÁLIS I. (1939): Magyarország szénélőfordulásai (Occurrence of coals in Hungary) (in Hungarian). Sopron.
- ВОУТКЕВИТШ, Г. В., А. Е. МИРШНИКОВ, А. С. ПОВАРЕННИК, В. Г. ПРОХОРОВ (1977): Краткий справочник по геохимии (Brief guide to geochemistry). – Nedra, Moskva 80–83.
- WANDLESS A. M. (1955): The occurrence of sulphur in British coals. – *J. Inst. Fuel*, **28**, 54–62.
- WILLIAMS E. G. & KEITH M. L. (1963): Relationship between sulfur in coals and occurrence of marine roof beds. – *Economic Geology*, **58**, 720–729.

Manuscript received 17 May, 1996