MINERALOGIA POLONICA
Vol. 7, No 2 — 1976

*Barbara KWIECIŃSKA *, Włodzimierz PARACHONIAK **

THERMAL INVESTIGATIONS OF GRAPHITIC SUBSTANCES FROM METAMORPHIC ROCKS

UKD 552.571:552.4:543.226:552.16

Abstract. Differential thermal analysis was applied to determine the nature of alterations taking place within various forms of elemental carbon dispersed in metamorphic rocks. The results thus obtained were used to trace the course of the transformation process of disordered phases occurring in the final carbonification stage (meta-anthracite, semi-graphite or natural coke) into the ordered ones (graphites). Moreover, detailed studies of exothermal effects of products of regional and thermal metamorphism were used in order to estimate the metamorphic facies of graphite bearing rocks. The temperature ranges of maxima of exothermal effects depend on the metamorphic grade of the host rocks, corresponding to 380—740°C for thermal (contact) metamorphism, 500—640°C for greenschists, 640—800°C for amphibolite facies, and above 800°C for granulitic ones.

INTRODUCTION

The thermal properties of coals, carbonaceous matter, coalified and graphitized phytoclasts, and natural graphites have frequently been published by numerous authors. DTA curves of various coals, their lithotypes, and macerals were described by Van Krevelen (1961), Schultze (1974), Swaine (1968) and others. In the case of bituminous coals, the thermal effects are mainly endothermic, except the reaction between 440 and 550°C, which is probably connected with the condensation of aromatic structures. Systematic work on the thermal behaviour of graphitic substances differing in metamorphic grade has been done by Mackles *et al.* (1953), Hamilton *et al.* (1970), Diessel and Offler (1973, 1975), Bliuman *et al.* (1974), and Łobzową (1975). The results of these studies, though not controversial, are not always reproducible and are difficult to compare. The discrepancies, however, in the data are mainly due to the differences be-

* Academy of Mining and Metallurgy, Institute of Geology and Mineral Deposits, Cracow, Al. Mickiewicza 30

tween the types of thermographic techniques used (vacuum and conventional DTA).

Apart from real thermal effects characteristic of the materials examined, there often occur apparent maxima resulting from anisotropic properties of graphitic substances or other features. In Diessel and Offler's opinion (1973) exothermal reactions caused by the burning of the carbonaceous matter or oxidation of the graphite are sometimes preceded by small endothermal effects. Besides, possible changes of thermal effects can be caused by mineral inclusions occurring in primary samples. These inclusions, if present in sufficient amounts, can catalyse thermal reactions proceeding in graphite (Materials, 1971).

EXPERIMENTAL

Carbon and graphite bearing samples examined by the present authors represent the following geochemical environments and different continents:

a. coal beds subjected to contact (thermal) metamorphism,

b. metamorphic rocks from various regional metamorphic facies (greenschist, amphibolite, granulite),

c. natural graphite deposits.

Samples for differential thermal analyses were prepared by applying the same procedure to avoid perceptible influences of particle (crystal) size. The specimens were ground using a dry agate mortar until a grain size below 0.5 mm was obtained. Samples weighting 400 mg were placed in platinum crucibles. Aluminium oxide was used as a thermally inert substance. Its thermal study was carried out using a Hungarian derivatograph in an air atmosphere within the temperature range 20 — 1000°C. The heating rate was 10 — 12°C per minute and the subsequent analytical conditions were: DTA — 1/15, DTG — 1/30, and TG — 100. The results are shown in figs. 1 and 2.

As follows from the DTA curves obtained, there appear distinct exothermal effects in the range between 380° and 860°C. These effects are due to the burning process of graphitic substances which at a given temperature does not proceed simultaneously in the whole sample. The resistance to oxidation was not identical in all specimens. It should be emphasized that the graphitic matter dispersed in regionally metamorphosed rocks was not extracted from the rock. The present authors wanted to find whether even a small amount of graphitic substance (a few per cent), disseminated in the rock would give a visible exothermic reaction. The exothermic peaks originating from pyrite, quartz and others were, of course, neglected.

RESULTS

Correlation analysis of thermal curves for samples representing three different geochemical environments (a, b, and c) lead to the following conclusions.

a. Examination of the products of contact (thermal) metamorphism (Fig. 1, Tab. 1) shows gradual displacement of the maxima of exothermal effects in the range from 380°C to 640°C concordant with structural evolution toward graphite. This phenomenon is best observed in the range 540°—640°C. Moreover, the change of form, shape, and width of peaks on thermal curves is noted, confirming a slow and gradual transformation of the structure of carbonaceous matter. Considering graphitization as a kinetic process, i.e. depending on time, we have to interpret the observed extention of the temperature range of burning of coal as the result of structural ordering of graphite. It is obvious that more time and energy is needed for thermal destruction of a more perfect structure. This phenomenon reflects an increasing perfection of crystallinity of carbonaceous material in metamorphic rocks.

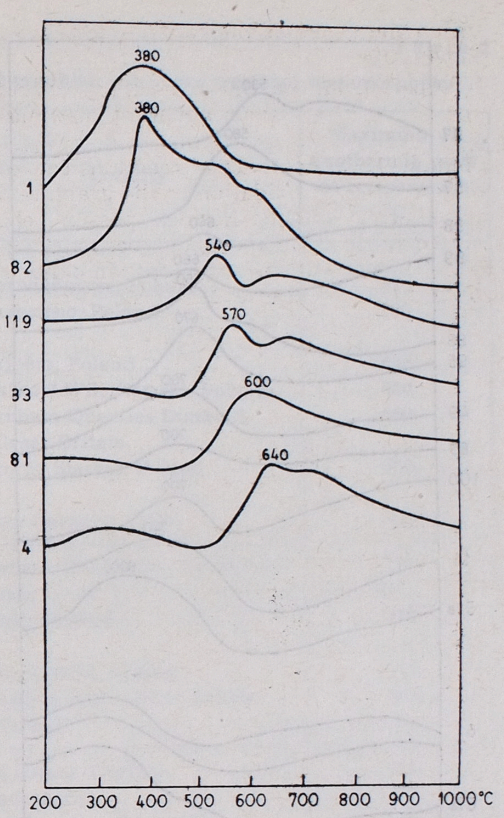

Fig. 1. DTA curves for products of contact (thermal) metamorphism. (Sample references in Table 1)

Table 1

Products of contact (thermal) metamorphism

No	Sample	Locality	Maximum of exothermic peak at temperature °C
1	semi-graphite	Czywczyn, USSR	380
82	meta-anthracite	Dunbartonshire, Great Britain	380
119	natural coke	Wałbrzych, Poland	540
83	semi-graphite	Hurlford, Great Britain	570
81	semi-graphite	Craigman-Pit, Great Britain	600
4	graphite	Pinerolo, Italy	640

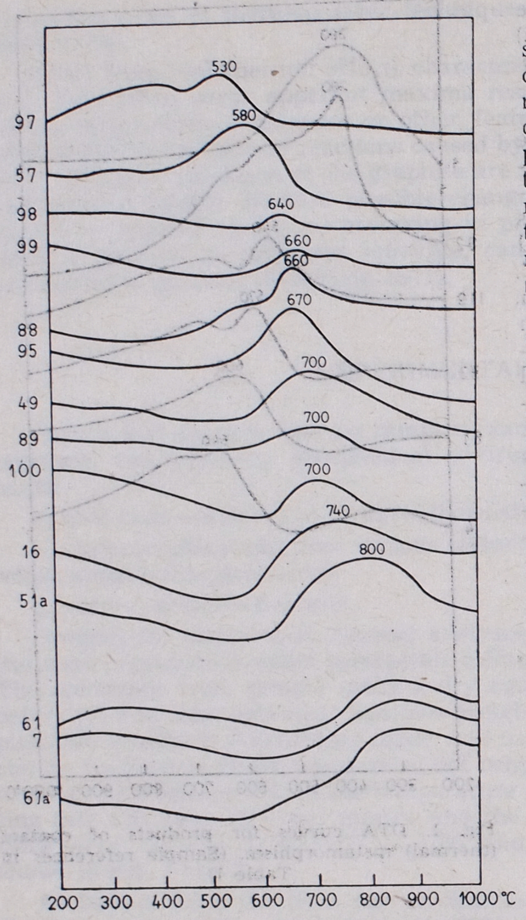

Fig. 2. DTA curves for graphitic substances from regionally metamorphosed rocks. (Sample references in Table 2)

b. Inspection of graphitic substances dispersed in rocks of different regional metamorphic facies confirmed the observed phenomenon of displacement of temperature of the exothermic (combustion) reaction occurring in graphites with increasing metamorphic grade. The observed maxima of exothermal effects for samples shown in table 2, representing individual facies, correspond to temperatures intermediate between those reported by Diessel and Offler (1973, 1975) and by Bliuman *et al.* (1974) and Łobzowa (1975). These maxima for graphite-bearing rocks of different metamorphic facies are as follows:

1) greenschist facies: 500 — 640°C,
2) amphibolite facies: 640 — 800°C,
3) granulite facies: above 800°C (Fig. 2).

Much less definite is the correlation between the initial and final temperature of exothermal effects and the metamorphic grade of the samples examined. It is only observed that, in general, the initial temperatures increase with the higher metamorphic grade of the host rock.

c. All the examined graphite samples from Sri Lanka and Madagascar, deposits display constant values of maxima of exothermal effect (850 — 860°C), irrespective of their different genetic relations (Fig. 2, samples *61*, *7*, *61a*). It is supposed that in these graphites the process of ideal three-dimensional ordering of crystallites was accomplished. Internal transformation of disordered phases into crystallographically perfect ones was completed earler. This opinion results from X-ray study (Kwiecińska 1974).

CONCLUSIONS

In general, from all thermographic studies it was found that predominant exothermic peaks, in graphitic substances from different grade con-

Metamorphic rocks with dispersed graphitic substance (regional metamorphism)

Facies	No	Sample	Locality	Maximum of exothermic peak at temperature °C
Greenschist	*97*	carbonate	Czerwieńczyce, Poland	530
	57	marble (dark variety)	Przeworno, Poland	580
	98	phyllite	Wojbórz, Poland	640
	99	quartzitic schist	Pustków Wilczkowski, Poland	660
	88	graphitic slate	Dirnham Quarries Dunkeld, Great Britain	660
	95	graphitic quartzite	Stronie Śląskie, Poland	670
	49	gneiss minuti	Gran Paradiso, Italy	700
Amphibolite	*89*	graphitic schist	Portsoy, Banffshire, Great Britain	700
	100	graphitic-sericite schist	Mloty, Poland	700
	16	graphite ore	Witostowice, Poland	740
	51a	quartzitic-sericite schist	Wzgórze Buk, Lower Silesia, Poland	800
Granulite	*61*	graphite	Sri Lanka (Ceylon)	850
	7	graphite	Madagascar	860
	61a	graphite	Bogala mine (Sri Lanka)	860

tact and regional metamorphic rocks, move towards higher temperatures with increasing metamorphic grade of the host rocks. No measurable differences in thermal effects were noted for the pure graphites, regardless of the source.

In our opinion, the DTA method, because of ease of application can be used as a simple criterion for assessing even small amounts (a few per cent) of organic substance dispersed in metamorphic rocks. The quantitative interpretation of thermal curves, however, seems to be a very difficult problem.

REFERENCES

[BLIUMAN B. A., DIAKONOW Ju. S., KRASAWINA T. N., PAWŁOW M. G.] БЛЮМАН Б. А., ДЬЯКОНОВ Ю. С., КРАСАВИНА Т. Н., ПАВЛОВ М. Г., 1974: Использование термо- и рентгенографических характеристик графита для определения уровня и типа метаморфизма. *Зап. Всес. Минерал. Общества* Вып. I, ч. CIII.

DIESSEL C. F. K., OFFLER R., 1973: The relationship between graphite rank and metamorphic grade in the Mount Lofty Ranges, South Australia. *Search*, vol. 4, No 11—12.

DIESSEL C. F. K., OFFLER R., 1975: Change in physical properties of coalified and

graphitized phytoclasts with grade of metamorphism. *N. Jb. Miner. Mh.* H. 1, 11—26.
HAMILTON L. H., RAMSDEN A. R., STEPHENS J. E., 1970: Fossiliferous graphite from Undercliff, New South Wales. *Journal of the Geolog. Soc. of Australia*, vol. 17, pt. 1.
KWIECIŃSKA B., 1974: Wyniki badań rentgenostrukturalnych substancji grafitowych. *Spraw. z pos. Kom. Nauk Mineralogicznych PAN*, Kraków.
[ŁOBZOWA P. W.] ЛОБЗОВА П. В., 1975: Графит и щелочные породы района ботогольского массива. Изд. Наука. Москва.
MACKLES L., HEINDL R. A., MONG L. E., 1953: Chemical analysis, surface area and thermal reactions of natural graphite and refractoriness of the ashes. *Journal of the American Ceramic Soc.* vol. 136, nr 8.
Materials and Technology, 1971: Encyclopedia, vol. II.
SCHULTZE D., 1974: Termiczna analiza różnicowa. Warszawa PWN.
SWAINE D. J., 1968: The identification and estimation of carbonaceous materials by DTA. Proc. of the 2nd Intern. Conference on Thermal Analysis.
VAN KREVELEN D. W., 1961: Coal. Elsevier Publishing Co. Amsterdam—London New York—Princeton.

Barbara KWIECIŃSKA, Włodzimierz PARACHONIAK

BADANIA TERMICZNE SUBSTANCJI GRAFITOWYCH ZE SKAŁ METAMORFICZNYCH

Streszczenie

Posłużono się metodą termicznej analizy różnicowej w celu wykazania obecności substancji organicznej rozproszonej w skałach metamorficznych. Zarejestrowano zmiany występujące w obrębie różnorodnych form pierwiastkowego węgla. Wyniki badań termicznych wykorzystano w celu ujawnienia transformacji faz nieuporządkowanych występujących w końcowym szeregu uwęglenia (meta-antracyt, semi-grafit, koks naturalny) w formy uporządkowane strukturalnie (grafity). Badając produkty przeobrażenia kontaktowego (termicznego) i regionalnego dokonano również próby odczytania facji metamorfizmu skał grafitonośnych, na podstawie analizy maksimów efektów egzotermicznych.

Stwierdzono, że w substancjach grafitowych występujących w różnych strefach metamorfizmu kontaktowego i regionalnego, główne maksima reakcji egzotermicznych przesuwają się w kierunku wyższych temperatur wraz ze wzrostem stopnia metamorfizmu skał macierzystych. Maksima te kształtują się odpowiednio: dla produktów metamorfizmu kontaktowego w zakresie temperatur: 380 — 640°C, dla facji zieleńcowej w 500 — 640°C, dla facji amfibolitowej w 640 — 800°C i dla facji granulitowej w temperaturze powyżej 800°C. W próbkach grafitów naturalnych pochodzących ze złóż Sri Lanka i Madagaskar nie zaobserwowano różnic w efektach termicznych.

OBJAŚNIENIA FIGUR

Fig. 1. Krzywe DTA produktów metamorfizmu kontaktowego (Numeracja próbek zamieszczona w tabeli 1)
Fig. 2. Krzywe DTA substancji grafitowych rozproszonych w skałach metamorficznych (Numeracja próbek zamieszczona w tabeli 2)

Барбара КВЕЦИНЬСКА, Влодзимеж ПАРАХОНЯК

ТЕРМИЧЕСКИЕ ИССЛЕДОВАНИЯ ГРАФИТОВОГО ВЕЩЕСТВА ИЗ МЕТАМОРФИЧЕСКИХ ПОРОД

Резюме

С целью доказания присутствия органического вещества рассеянного в метаморфических породах был использован метод дифференциального термического анализа. Фиксированы изменения выступаемые в пределе в различных формах элементарного угля. Результаты термических исследований использовано для обнаружения трансформации неупорядоченных фаз, встречающихся в конечном ряду углефикации (мета-антрацит, полуграфит, природный кокс) в структурно-упорядоченные формы (графит). Изучая продукты контактного (термического) и регионального изменения, на основании максимумов экзометрических эффектов сделано попытку определить фации метаморфизма графитоносных пород.

Обнаружено, что в графитовом веществе, встречающимся в разных зонах контактного и регионального метаморфизма, главные максимумы экзометрических реакций смещаются в направлении высших температур одновременно с увеличением степени метаморфизма исходных пород. Эти максимумы представляются следующим образом: для продуктов контактного метаморфизма в интервале температур: 380 — 640°C, для фации зеленых сланцев 500 — 640°C, для амфиболитовой фации 640 — 800°C и для гранулитовой фации в температурах свыше 800°C. В образцах природных графитов месторождений Сри Ланка и Мадагаскара расхождения в термических эффектах не наблюдались.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Кривые DTA продуктов контактного метаморфизма (Нумерация образцов указана в табл. 1)
Фиг. 2. Кривые DTA графитового вещества рассеянного в метаморфических горных породах (Нумерация образцов указана в табл. 2)