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STRUCTURAL ORDERING OF CARBONACEOUS MATTER IN PENNINIC TERRANES

A. DEMÉNY*

Dept. of Petrology and Geochemistry, L. Eötvös University

ABSTRACT

This paper presents a study of relations between graphitization processes and metamorphic conditions in the easternmost windows of the Alpine Penninic system (Eastern Austria, Western Hungary). Samples for comparison were collected from the Tauern Window, too. From XRD investigations it can be concluded that strong shearing could result in development of graphite in greenschist facies conditions. The mobility of metamorphic fluids also plays a determining role in graphitization.

KEYWORDS: Penninic units, graphitization, XRD study.

INTRODUCTION

This paper will deal with the Easternmost outcrops of the Alpine Penninic unit. These areas lie on or near the Hungarian—Austrian border as indicated in *Fig. 1.* As the major part of the unit is on the Austrian side the whole system will be called "Burgenland Penninic".

Several geologists have mapped the distribution of different rock types, amongst them were BANDAT (1928, 1932), FÖLDVÁRY *et al.* (1948) and KISHÁZY and IVANCSICS (1976, 1984). A recent summary can be found in the work of KOLLER and PAHR (1980). According to them this Penninic terrane consists mainly of metapsammites-pelites, metacarbonates and metamagmatic rocks. KUBOVICS (1983) and KOLLER (1985) have dealt with the latter ones and showed a possible ophiolitic origin.

The age of the sediments has been determined by SCHÖNLAUB (1973) who described Mid-Cretaceous sponge spiculae in some metacarbonate rocks.

Three metamorphic events have affected the sequence: an oceanic hydrothermal, a subduction-related HP/LT type and a young Alpine influence (LELKES—FELVÁRY, 1982; KOLLER, 1985). In the metasediments only the latest effect can be observed which is characterized by about 350 °C in the northern and 430 °C in the southern part of the area. These temperature data have been obtained from evaluation of mineral parageneses (KOLLER, 1985) and from preliminary fluid inclusion studies (DEMÉNY, unpublished results). The pressure had a maximum of 0.3 GPa during this late event.

At least two deformation phases can be determined (KISHÁZY and IVANCSICS, 1984) that created two imbrications with different fold axes (HERRMANN and PAHR, 1988).

*Present address: Lab. for Geochem. Res., Hung. Acad. Sci., Budapest, Budaörsi út 45.

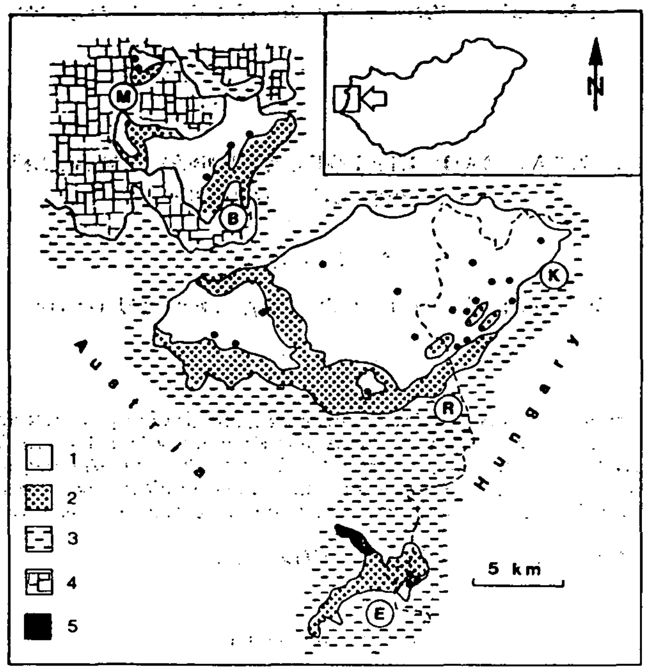

Fig. 1. Geological sketch map of the easternmost. Penninic windows, with sample localities. 1. Penninic metasediments, 2. Penninic metamagmatites, 3. Tertiary sediments, 4. lower eastalpine nappes, 5. upper eastalpine nappes (after KOLLER, 1985). M: Möltern, B: Bernstein, R: Rechnitz, K: Kőszeg, E: Eisenberg

Some samples were collected for comparison from the Tauern Window *(Fig. 2)* following the guide-book written by MATURA and SUMMESBERGER (1980). According to them the metamorphic temperatures were between 450 and 550 °C, while the pressure was around 0.4—0.6 GPa in the study area *(Fig. 2)*.

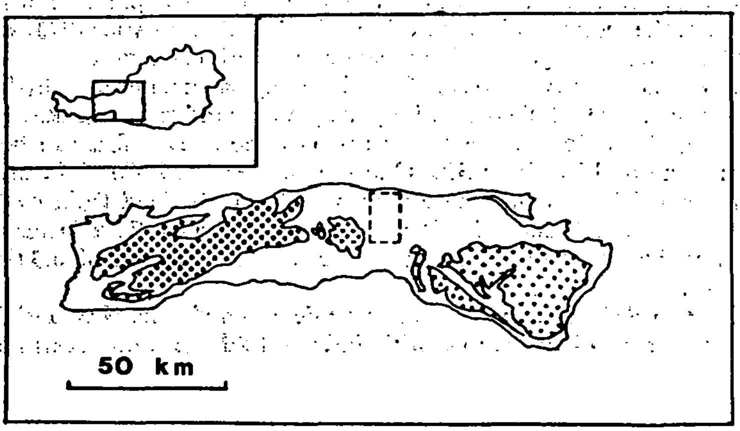

Fig. 2. Geological sketch map of the Tauern Window. Spotted area: Central Gneiss. The study area is indicated by dashed lines. After DROOP (1985)

Here I intend to discuss the relations between graphitization processes and metamorphic influences in these Penninic terranes by means of XRD investigations on the structural ordering of carbonaceous matters.

EXPERIMENTAL AND THEORETICAL APPROACHES OF GRAPHITE FORMATION (A SHORT REVIEW)

Detailed descriptions of graphitization processes appeared in the 60 s, but at first they based mainly on laboratory experiments. During this work several authors proved that the main factor is the temperature, but the pressure, stresses and catalizing materials also play an important role (BRAGG *et al.*, 1964; NODA *et al.*, 1968a, b; MARSH and WARBURTON, 1976).

The bases of X-ray diffraction investigations on graphites of metamorphic rocks were established by FRENCH (1964) and later GRIFFIN (1967) and GREW (1974) made some contributions to the newly recognised problems.

Detailed investigations on the relations between graphitization and metamorphic influences have been made by DIESSEL and OFFLER (1975), DIESSEL *et al.* (1978), and OKUYAMA—KUSONOSE and ITAYA (1987). WINTSCH *et al.* (1981) discussed variable effects of metamorphic fluids, while ITAYA (1981) recognised the dependence of graphitization on the duration of metamorphism. He also managed to determine detrital graphite together with graphitizing carbonaceous matter.

Finally, comparisons between X-ray diffraction results and other methods (TEM, SEM: LANDIS, 1971, BONIJOLY *et al.*, 1982, BÜSECK and HUANG, 1985, illite crystallinity: PESQUERA and VELASCO, 1988) elucidated the processes that can cause development of graphites. The temperature dependence of the structural change of this mineral has been determined by SHENGELIA *et al.* (1977) applying heating experiments.

According to these authors graphitization takes place in three steps: (1) development of hexagonal rings (2) appearance of two dimensional layers (3) formation of three dimensional structure.

During this process volatiles are released creating bubbles and pores in the carbonaceous matter which pores promote development of preferred orientation in case of shear stresses. The next step is the so called "turbostratic structure" in which we have hexagonal layers, but they are random rotated. Further heating can cause partial graphitization forming "transitional material". At even higher temperature (about 500—550 °C) pure graphite will develop.

As it was mentioned before, shear stresses play a great role, but different catalizing materials (SiO_2, FeS_2, Fe, Co, Ni, $CaCO_3$, etc.) can also enhance the graphitization process. In contrast, trapped volatiles inhibit the development of graphite.

The present work is based on the feature that the X-ray diffraction pattern of graphite changes during the structural ordering, namely the 2Θ value and half-height width ($W_{1/2}$) of the d_{002} peak vary with the metamorphic degrees. Previous results have been published in a short abstract form (KUBOVICS *et al.*, 1988).

ANALYTICAL PROCEDURES

As quartz and micas make the investigation of the d_{002} peak of the graphite impossible the graphitic matter had to be separated. Powdered rock samples were treated with hot concentrated HCl and HF at least 5—8 hours long and this procedure was repeated when necessary. After this treatment saturated $AlCl_3$ solution was used with minor amount of HCl to remove the artificial products (GREW, 1974). This stage was followed by washing with destilled water until reaching neutral pH.

Beside graphitic matter, tourmaline, pyrite, zircon and rutile remained in the samples.

The X-ray diffraction patterns were measured with a Siemens D500 type diffractometer using graphite filtered CuK_α emission. Scanning speed was 0.5°/min and chart speed was 1 cm/min. Corrections were made using silicon as internal standard.

Reproducibilities of the calculated "c" values were between ±0.013 Å and ±0.002 Å (±0.005 Å on the average). The precisity of the measured $W_{1/2}$ values was ±0.01—0.17 °2Θ (±0.08 °2Θ on the average).

RESULTS

The localities of samples studied in this paper are shown in *Figs. 1* and *2.* Sample numbers (see also Tables 1 and 2) beginning with "A" stand for Austrian localities, while "K" and "Fcs" mean Kőszeg Mts. and Felsőcsatár (Eisenberg—Vashegy window), respectively.

Having measured the X-ray diffraction patterns of these samples, I have calculated the "c" values (Table 1) and plotted them against the metamorphic temperatures *(Fig. 3)*. The temperature data were obtained from interpolation of values mentioned in the Introduction. It is obvious for the first glance that the graphitic matter in the Easternmost Penninic system is generally well developed, but one sample group — at about 400 °C — has higher values than usual in this terrane. As most of the sample points fall in this temperature interval, sampling bias can not be ruled out off-hand. It means that in case of larger number of samples, bigger scatter of results would be expected. On the other hand the areal distribution of sample localities and "c" values

TABLE 1

Lattice parameter values ("C", in Å) of carbonaceous matter in the easternmost Penninic windows and in the Tauern Window

Easternmost Penninic windows

sample	"C"	sample	"C"	sample	"C"
A13	6.72	A18	6.70	A44	6.73
A50	6.73	A51	6.71	A64	6.70
A77	6.69	A80	6.73	A91	6.71
A101	6.71	K12	6.73	K13A	6.74
K16	6.63	K21	6.74	K33	6.74
Fcs—203B	6.73	Fcs—203F	6.70	Kő—6/1	6.77
Kő—6/2	6.76	Bo—8/2	6.74	Fcs—74/96	6.72
B—2	6.74	V15B	6.71	V17B	6.77
V15C3	6.72 and 6.79				

The Tauern Window

sample	"C"	sample	"C"	sample	"C"
A113	6.70	A123	6.72	A125	6.72
HM	6.72				

TABLE 2

Half-height width ($W_{1/2}$, in °2Θ) values of carbonaceous matter in the easternmost Penninic windows and in the Tauern Window

Easternmost Penninic windows

sample	$W_{1/2}$	sample	$W_{1/2}$	sample	$W_{1/2}$
A51	1.0	A54	1.55	A67	1.4
A79	1.3	B10/4K	0.8	B10/4Ab	1.0
V15C3	1.26	Fcs—203B	0.61	Kő—6/1	1.05
Kő—6/2	0.65	Bo—8/2	0.98	K16	0.52
K21	1.07	K29	0.9	K33	0.65

The Tauern Window

sample	$W_{1/2}$	sample	$W_{1/2}$	sample	$W_{1/2}$
A109	0.41	A113	0.58	A116	0.85
A121	0.7	A123	0.45	A125	0.42
HM	0.42				

(Fig. 1 and 5) point to the importance of geological conditions as the main causes of the observed scatter in "c" values. Detailed interpretation of this areal variability is discussed in the next part of the paper.

The comparative samples of the Tauern window provided the general values around 6.70—6.72 Å.

The half-height width values of graphites of the Burgenland Penninic unit range from 0.6 to 1.2 °2Θ, while the samples collected from the Tauern window gave data between 0.4 and 0.85 °2Θ (Table 2). Plotting these $W_{1/2}$ data against the metamorphic temperatures it is apparent that the $W_{1/2}$ values show decreasing tendency with increasing T *(Fig. 4)*. This feature hints at the increasing crystallite-size of the the graphites (KWIECINSKA, 1980).

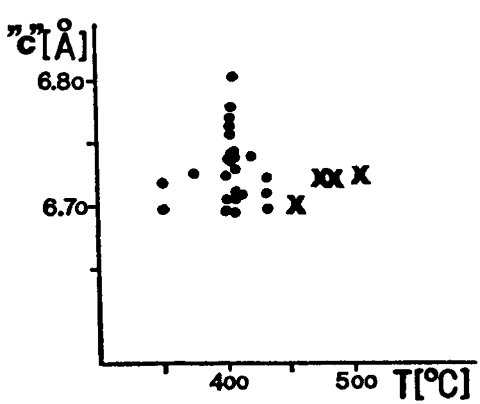

Fig. 3. Lattice parameter dara („C") of graphites versus metamorphic temperatures inferred from results of KOLLER (1985) and MATURA—SUMMESBERGER (1980). o: Burgerland Penninic; x: Tauern Window

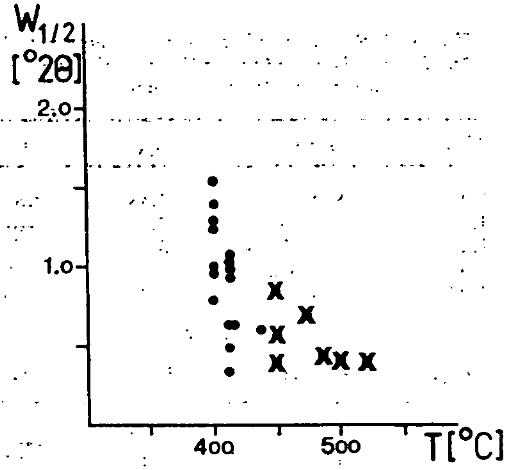

Fig. 4. Plot showing half-height width ($W_{1/2}$) values against metamorphic temperatures for carbonaceous matter of Penninic terranes. Tauern Window: (x), Burgerland windows: (o). The temperature data are the same as in *Fig. 3.*

RELATIONS BETWEEN GRAPHITIZATION AND METAMORPHIC CONDITIONS

Plotting the "c" values on the map of the study area a systematic distribution can be observed *(Fig. 5)*. It is apparent that these data are higher in the Kőszeg Mts. (Western Hungary) than in other parts of the windows. On the other hand, there is no distinct trend from lower to higher metamorphic degrees. This latter observation points to the role of sheart stresses that were effective enough to produce well developed graphite even at 350—400 °C. This feature is not unique, as ÁRKAI *et al.* (1981) have mentioned that shearing can promote graphitization even under very low-grade metamorphic conditions.

There is another factor that can also enhance this effect: the composition of the starting organic matter. DEMÉNY and KREULEN (1989) have described an areal variability having normal marine organic matter in the Möltern and Bernstein windows and detrital carbonaceous material in the Kőszeg—Rechnitz area. It is well known that the former material is much more sensitive to metamorphic influences than the latter one (MCKIRDY—POWEL, 1974). As the metamorphic temperatures were higher in the area of the Kőszeg—Rechnitz window where detrital organic matter is predominant than in the Möltern and Bernstein windows with normal marine material, no surprise that there are graphites with about the same "c" values throughout the whole unit.

The explanation of the high "c" data of the Kőszeg Mts. can be found in the difference in deformations and fluid behaviours. Several samples of this area contain trapped carbonaceous material that structurally poorly developed (DEMÉNY, 1986, KUBOVICS *et al.*, 1988), such as sample V15C3. This observation hints at a locally closed system that prevented the release of volatiles which inhibited the structural ordering of graphites. As it has been pointed out by WINTSCH *et al.* (1981) such trapped fluids can prevent the complete graphitization resulting in lower degree of ordering.

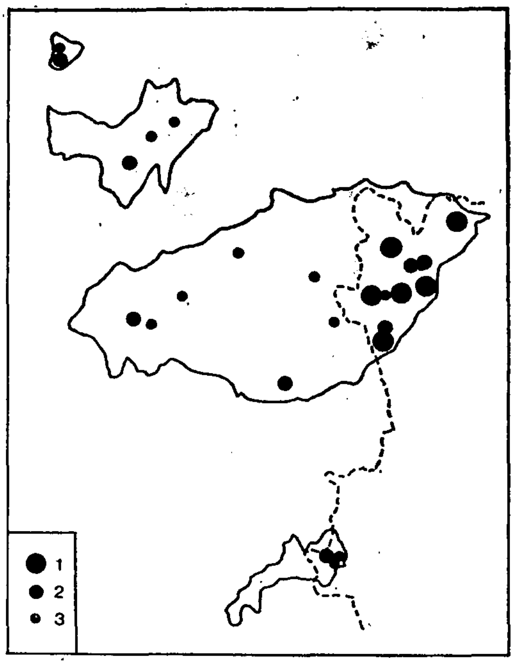

Fig. 5. Areal variability of „C" lattice parameter data in the easternmost Penninic windows. 1. values higher than 6.74 Å, 2. values between 6.74 and 6.71 Å, 3. values lower than 6.71 Å. See *Fig. 1.* for comparison

After these considerations I intended to correlate the "c" data with the graphite geothermometer of SENGELIA *et al.* (1977), but I had difficulties in the interpretation. To solve this problem I have collected the data of several authors mentioned before and plotted them in the diagram given by SHENGELIA *et al. (Fig. 6)*. It is apparent that the experimental curve greatly differs from the others. In my oppinion the reason is that the laboratory conditions of Shengelias'work didn't follow properly the natural processes, hence the graphite "geothermometer" should be reevaluated. The curves for different metamorphic regimes (HP/LT type to LP/HT one) prove that the pressure has a determining role during natural graphitization as has been mentioned before.

The results presented in this paper show a relationship with the curves of the high pressure and regional dynamothermal metamorphic terranes *(Fig. 7)* which connection is in a good agreement with the geological facts (see Introduction).

Finally it can be concluded that in the rock sequence studied here the structural ordering of graphites doesn't serve as a good geothermometer, but it can provide valuable information for the metamorphic evolution.

CONCLUSIONS

The "c" values of graphites of the Burgenland Penninic system show a distinct areal distribution which seems to be independent of the increasing metamorphic degrees. It would mean that about 350—400 °C well developed graphite has been

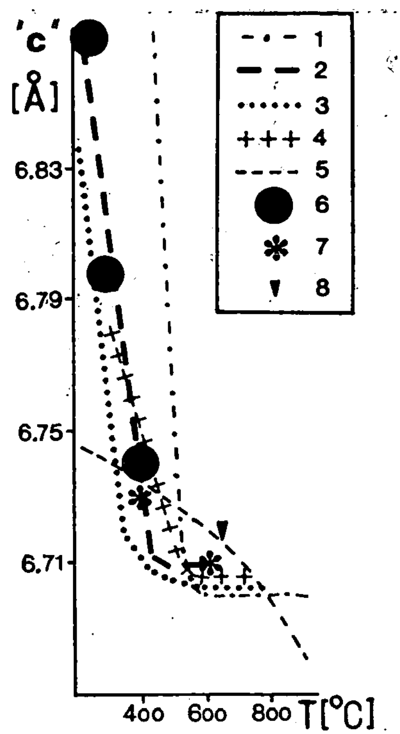

Fig. 6. Lattice parameter data („C") of graphites versus metamorphic temperatures. „C" values are from: 1. OKUYAMA—KUSONOSE and ITAYA (1987), 2. DIESSEL *et al.* (1978), 3. GREW (1974), 4. DIESSEL—OFFLER (1975), 5. SHENGELIA *et al.* (1977), 6. ITAYA (1981), 7. FRANK (1983), 8. KATZ (1987)

formed which can be attributed to the effect of strong deformation and shearing. This process is enhanced by differences in the starting organic compositions as we have more sensitive matter in the areas with lower metamorphic degrees than in the areas of higher temperatures. As a consequence of these compositional differences the same "c" values have been determined in areas with slightly different metamorphic temperatures.

The metamorphic fluids may have also affected the process of graphitization. The poor development of carbonaceous matter in some rocks of the Kőszeg Mts. indicates a locally closed system in which trapped organic compounds prevented the complete ordering.

On the contrary, the $W_{1/2}$ values show good correlation with the metamorphic temperatures that points to increasing crystallite size of graphites regardless of deformation and fluid mobility.

I applied the graphite "geothermometer" to the studied samples on the base of literature data. It has turned out during the interpretation that — at least in this case — this method can provide useful information for the effects of deformation, shearing and fluid behaviours rather than for the metamorphic temperatures.

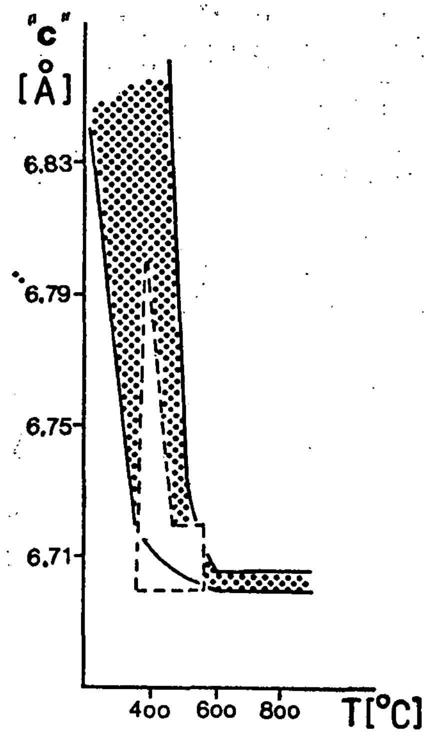

Fig. 7. „C" parameter distributions of literature data and the Penninic carbonaceous matter. Spotted area: data shown in *Fig. 6.* The area indicated by dashed lines consists of the "c" values of Penninic samples

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