**Zeitschrift:** Schweizerische mineralogische und petrographische Mitteilungen = Bulletin suisse de minéralogie et pétrographie

**Band:** 82 (2002)

**Heft:** 2: Diagenesis and Low-Grade Metamorphism

**Artikel:** Transmission electron microscopy study of carbonaceous material in a metamorphic profile from diagenesis to amphibolite facies (Bündnerschiefer, Eastern Switzerland)

**Autor:** Ferreiro Mählmann, Rafael / Petrova, Tatjana V. / Pironon, Jacques

**DOI:** https://doi.org/10.5169/seals-62364

# Transmission electron microscopy study of carbonaceous material in a metamorphic profile from diagenesis to amphibolite facies (Bündnerschiefer, Eastern Switzerland)

by *Rafael Ferreiro Mählmann*[1*], *Tatjana V. Petrova*[1], *Jacques Pironon*[2], *Willem B. Stern*[1], *Jaâfar Ghanbaja*[3], *Jean Dubessy*[2] and *Martin Frey*[1] *(deceased)*

**Abstract**

Transmission electron microscopy has been applied to carbonaceous material in twelve metaclastic samples collected from the north Penninic Bündnerschiefer of eastern Switzerland. Metamorphic grade ranges from high diagenesis to the lower amphibolite facies. Microtextures in organic remnants show a progressive evolution with increasing metamorphic grade in the following sequence: amorphous material → initial onions → onions filled with amorphous material → onions with thick rims → onions with a void core → polygonal onions → broken onions → graphite flakes. Broken onions found inside the transition between polygonal onions and graphite flakes are interpreted to be structurally altered onions, torn apart by deformation, hence then do not represent a regular step in the evolution of organic matter to graphite. The nanometric structure of carbonaceous material is very sensitive to variations in metamorphic grade and strain. Graphite flakes are supposed to represent either an end-member of this sequence or to originate from a carbonaceous material source different from that of the onions; flakes also occur as a detrital fraction in nearly all samples. The widespread heterogeneity of the carbonaceous material explains the commonly found variability of various analytical data. We show that strain has a catalytic effect on pre-graphitization and graphite formation in our samples. Strain is an important factor controlling the microstructural ordering, while temperature has a major effect, and pressure is probably insignificant in this respect.

*Keywords:* Carbonaceous material, carbon onion structures, graphitization, metamorphic grade, metamorphic textures, TEM.

## 1. Introduction

In many metasedimentary rocks, carbonaceous material is an ubiquitous constituent. Its elemental composition and structure change systematically with increasing metamorphic grade in a transformation referred as graphitization. Because its study gives insights on the understanding of metamorphic processes, carbonaceous material has widely been studied by various analytical techniques; a recent overview is given by Petrova et al. (2002). Carbonaceous material studied in the present paper by transmission electron microscopy has been characterized previously Petrova et al. (2002) applying optical microscopy, X-ray diffraction, combustion and thermal analysis.

In contrast to mineral transformations during diagenesis and metamorphism, graphitization of carbonaceous material is an irreversible process (Diessel et al., 1978; Itaya, 1981; Pesquera and Velasco, 1988) and, hence, may be considered as a useful indicator of the maximum metamorphic grade reached. Despite a number of studies from low and high grade metamorphic areas little is known about development of the graphitization progress in a natural context. Synthetic graphitization of carbon was studied in some detail, in particular the qualitative influence of temperature, pressure, time and degree of deformation (oriented pressure, shear strain), but has not been quantitatively constrained so far (see e.g. Landis, 1971; Diessel et al., 1978; Bonijoly et al., 1982,

[1] Institute of Mineralogy and Petrography, Bernoullistrasse 30, CH-4056 Basel, Switzerland.
[*] Present address: Institut für Angewandte Geowissenschaften, TU Darmstadt, Schnittspahnstrasse 9, D-64287 Darmstadt, Germany. <Rafael.Ferreiro-Maehlmann@unibas.ch>
[2] UMR G2R-CREGU, BP23, 54500 Vandœuvre-les-Nancy, France.
[3] Service Commun d'Analyses, V, BP 239, 54506 Vandœuvre-les-Nancy, France.

BUSTIN et al., 1995; YUI et al., 1996). Graphitization is mainly a micro-structural evolution progress described or empirically deduced by optical microscopy, X-ray diffraction, combustion and thermal analysis.

Transmission electron microscopy (TEM) is one of the most effective methods to study the structure and morphology of carbonaceous material and to detect heterogeneities at different levels of organization in its carbon (graphitization). Previous TEM studies of carbonaceous material have discovered so-called "onion"-structures (OBERLIN et al., 1974). The phenomenon of synthetically produced carbon "onions" is familiar, and this term is used in physical and chemical organic research studies (UGARTE, 1995). The onions are carbon structures formed by benzene-ring chains with triperiodic (3D) morphology of a round diameter and a cylindrical or beaker shaped onion like form. However, examples from natural samples are scarce, and little is known about the mechanism of "onion" generation. OBERLIN et al. (1974) refers to "carbon-blacks" and BUSECK and HUANG (1985) describe structures that "resemble those of an onion" which "characterize the poorly crystalline graphite".

The first aim of this study is to describe various structures of carbonaceous material and to trace their evolution using samples along a well defined Bündnerschiefer metamorphic profile in the Central Alps (Fig. 2, PETROVA et al., 2002: Table 1). Results are compared with carbonaceous material analysis from terrains with a high-temperature, low-pressure metamorphic field-gradient (e.g. BUSECK and HUANG, 1985; YUI et al., 1996) and a low-temperature, high-pressure metamorphic field-gradient (e.g. DIESSEL et al., 1978; ITAYA, 1981).

The second aim of this study is to present the first comparison between the degree of carbonaceous material organization (graphitization) and the gradual changes of the coalification process (maturation) from diagenesis to low amphibolite facies, including low-grade blueschist facies conditions.

## 2. Terminology

In the literature (e.g. OKUYAMA-KUSUNOSE and ITAYA, 1987; WADA et al., 1994; DALLA TORRE et al., 1996, 1997), the distinction between terms used in optical reflected light microscopy studies and microstructural electron microscopy studies is mostly not clear. Therefore, terms such as graphite may have different meanings. We refer to "graphite" ("true graphite", "real graphite", "pure graphite") as a triperiodic mineral structure and "graphitization" as a process of structural ordering. In reflected light microscopy the term "optical graphite" is defined by an organic particle with a high reflectance (> 10%) and high anisotropy (bireflectance), as proposed by DIESSEL and OFFLER (1975), combined with the occurrence of internal submicroscopic granular (semicrystalline) areas or microscopic, nematoblastic and fiber-like forms ("Graphitische Strukturen", RAMDOHR, 1928). Optical graphite is mostly composed of different mixtures of disordered and ordered organic material types, but can also be formed exclusively by triperiodic ordered carbonaceous material (graphite). In TEM studies this mixture is called "transitional material" (e.g. OKUYAMA-KUSUNOSE and ITAYA, 1987).

"Coalification" is a process defined by an increase in organic matter reflectance (vitrinite reflectance) and is basically the result of compaction, combined with the thermal release of volatiles. In optical microscopy we refer to "transitional material", rather than "transitional matter" (DIESSEL and OFFLER, 1975) as a coalification step where coaly material occurs with the first indications of optical graphite formation. The latter causes reflection histograms with one population with anthracite/meta-anthracite stage values (DIN classification, STACH et al., 1982) and a second one of the semi-graphite/graphite stage (DIESSEL et al., 1978).

"Pre-graphitization" effects are characterized in optical microscopy by the formation of light spots <1.0 μm in homogeneous vitrinite, an abnormally high bireflectance similar to that of optical graphite, but a relative low VR of 6.0 to 8.0 % $R_{max}$. Bituminite shows pores, vesicles and also light spots (FERREIRO MÄHLMANN, 2001). With increasing metamorphic grade a helicitic, undulating extinction (fibroblastic structure showing Brewster cross) under polarized light (SCHNEIDERHÖHN and RAMDOHR, 1931) indicates the initial formation of graphite spherulites (STACH et al., 1982).

## 3. The graphitization process

Graphitization is a complex process of structural ordering of carbonaceous material influenced by the nature of the precursor material, and mainly by temperature, time and shear strain, but also by pressure and catalytic or alteration effects of the matrix minerals (TEICHMÜLLER, 1987). DALLA TORRE et al. (1997) recognized a water fugacity effect on the graphitization process, but oxygen fugacity has no influence (ERNST and FERREIRO MÄHLMANN, 2002). Natural carbonaceous material studied by X-ray diffraction, reflected light microscopy, transmission and scanning electron microscopy show a significant degree of heterogeneity from poorly to well-ordered carbonaceous material (BUSECK and HUANG, 1985). Poorly ordered material may be present even in medium to high-grade metasediments (LARGE et al., 1994) and is also recognized in Bündnerschiefer at amphibolite facies conditions (PETROVA et al., 2002).

In metamorphic rocks different types of carbonaceous material evolve along different paths. FRANKLIN (1951) distinguished "graphitizing" and "non-graphitizing" carbon materials largely based on the structure and composition of their organic precursors. If these are aliphatic, they must be aromatized first before polymerizing into graphite-like molecules. If the precursors are aromatic, the basic hexagonal benzene-ring structure that characterizes graphite already exists, and the formation of a triperiodic (3D) graphite structure is facilitated.

Graphitization may be either a continuous (GREW, 1974; ITAYA, 1981) or discontinuous process (OKUYAMA-KUSUNOSE and ITAYA, 1987). OKUYAMA-KUSUNOSE and ITAYA (1987) suggested that graphitization proceeds through two discontinuous stages: first, optically anisotropic domains develop within formerly isotropic coal phytoclasts, forming "transitional material"; secondly, ordered graphite crystallizes at the expense of pre-existing coal material. These authors ascribed the variation in crystallographic parameters of the bulk carbonaceous material to the variation in modal abundance of three types of carbonaceous material, i.e. coaly, transitional material, and graphite.

In most areas of the Alps studied by FERREIRO MÄHLMANN (1994), the optical characteristics during the first two stages of OKUYAMA-KUSUNOSE and ITAYA (1987) change gradually. The increase of coalification continues up to the semi-graphite stage (DIN classification) and is then suddenly enhanced (in most cases) between a maximum vitrinite reflectance ($R_{max}$) of 8 and 10.0%. This limits the method of vitrinite reflectance studies (FERREIRO MÄHLMANN, 1995, 2001) with the occurrence of optical graphite. At the so called "graphite jump" (FERREIRO MÄHLMANN, 1994; PETROVA et al., 2002), graphitization is thought to be discontinuous due to structural changes from a two-dimensional aromatic plane structure to a three dimensional crystal-like structure (TEICHMÜLLER, 1987; DEMENY, 1989). Transmission electron microscopy promises further insight into the reason of the optical properties observed at low greenschist facies, as in the Bündnerschiefer profile (PETROVA et al., 2002).

## 4. Geological setting

North Penninic Bündnerschiefer are metamorphosed shaly-calcareous marine to terrigenous sediments, partly very rich in organic matter. In the flysch formations clay- and organic matter-rich siltstones are frequently intercalated in the sandstone sequences. Bündnerschiefer originated in an oceanic deep-water facies and the flysch formations in a shallower oceanic facies. The main mass of the Bündnerschiefer is of Cretaceous age (STEINMANN, 1994), and the flysch sediments are of Late Cretaceous to Eocene age and also considered as being of North Penninic origin.

Based on regional geological studies, the North Penninic Bündnerschiefer are subdivided into different units (Fig. 1). Between the different tectonic Bündnerschiefer units of the Prättigau flysch and the Grava nappe, formed during the Tertiary, no important metamorphic discontinuity has been documented in the regional Late Oligocene metamorphic pattern (WEH et al., 1996). The continuous increase of vitrinite reflectance and decrease of illite crystallinity values from N to S and ENE to WSW indicate a low temperature/low pressure and post-nappe tectonic metamorphism (PETROVA et al., 2002). In the Central Alps, the chloritoid-in isograd mapped by FREY and WIELAND (1975) cross-cuts all nappe boundaries of the Helvetic and Penninic tectonic domains. RAHN et al. (2002) showed that the time of chloritoid formation during the Oligocene in both domains is heterochronous. Different metamorphic patterns have been mapped (FERREIRO MÄHLMANN et al., 1992; FREY and FERREIRO MÄHLMANN, 1999) along both sides of the Penninic front (Fig. 2). A small metamorphic hiatus between the Tomül and the Grava nappes and along the Chur-Andeer zone (Fig. 2) has been suggested by WEH et al. (1996) and PETROVA et al. (2002), based on temperature sensitive analytical methods (vitrinite reflectance, maximum combustion temperature of carbonaceous material). Mineralogical studies of metapelites and marbles by TEUTSCH (1982) revealed that in the southern Misox zone Bündnerschiefer amphibolite facies was reached.

Greenschist facies metamorphism overprinted Late Eocene to Early Oligocene low temperature/high pressure metamorphism in the area to the west and south of Chur (OBERHÄNSLI et al., 1995). In Fig. 2, to the west of Chur, relics of blueschist facies complicate the metamorphic pattern (FREY et al., 1999). To the west and south of Thusis most blueschist facies minerals broke down due to the greenschist facies overprint (OBERHÄNSLI et al., 1995). Thus, only the last Late Oligocene metamorphic pattern is shown in this area (Fig. 2).

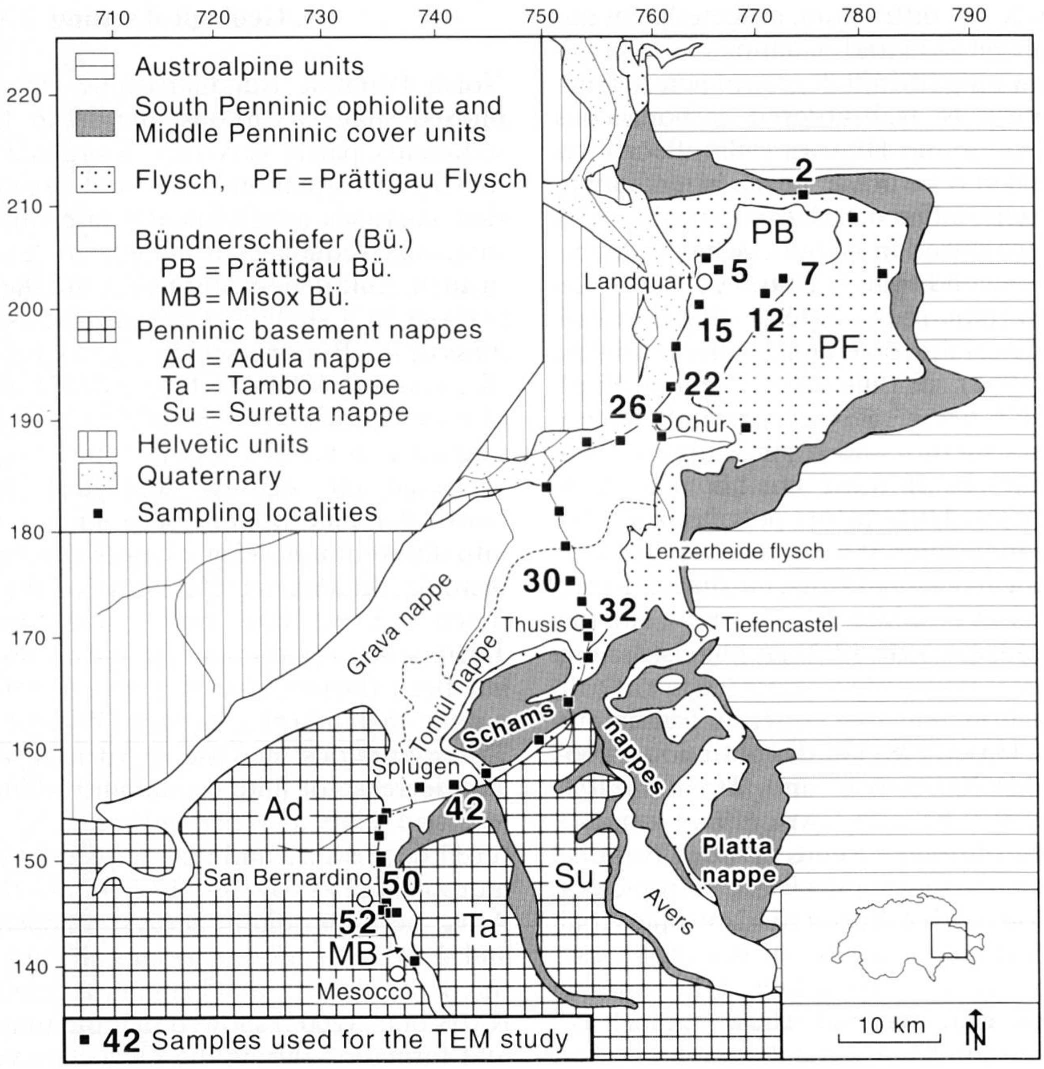


*Fig. 1* Schematic geological map of the North Penninic Bündnerschiefer (eastern Switzerland, see inset in Fig. 1). Numbers refer to sample list (Table 1). Squares: sampling points along the NE–SW metamorphic profile.

An important metamorphic inversion in the older metamorphic pattern at the Middle Penninic front (Fig. 2) is suggested by PETROVA et al. (2002). Greenschist facies metamorphic grade, but without high-pressure relics, was reported by BAUDIN and MARQUER (1993) and FERREIRO MÄHLMANN (1996) from the Middle Penninic nappes. The second Late Oligocene greenschist metamorphic pattern at the Middle Penninic front is also, but less disturbed by post-metamorphic thrusting and normal faulting (FERREIRO MÄHLMANN, 1995; FREY and FERREIRO MÄHLMANN, 1999).

On the basis of a general increase of maximum metamorphic temperatures from high diagenesis to low amphibolite facies (with only local and restricted discontinuities in metamorphic grade) a sample set from the Bündnerschiefer was used to study the evolution of organic matter. The metamorphic profile studied (Fig. 1) extends from east of Landquart (northern Prättigau-Flysch) to Mesocco. Along this profile, grade of Tertiary metamorphism increases from high diagenesis at 220–250 °C and 2.0–3.0 kbar (FERREIRO MÄHLMANN, 1994) to amphibolite facies at 500–550 °C and 6.0 kbar (FREY and FERREIRO MÄHLMANN, 1999). In the middle section, some relics of high pressure-low temperature metamorphism were found, increasing in grade from 350 °C, 7 kbar at Chur to 400 °C, 14 kbar (OBERHÄNSLI et al., 1995, FREY et al., 1999) at the west of Thusis. The high diagenesis, anchizone and epizone division is based on illite-crystallinity values (FREY, 1987). The high epizone is equivalent to the low greenschist facies (FERREIRO MÄHLMANN, 1996), but not the low epizone. Therefore, the low epizone is shown in Fig. 2 with an own label (see also Fig. 5).

The North Penninic units underwent shortening and a first metamorphism during the closure of the North Penninic oceanic realm since the Paleocene. For a more detailed introduction to the tectonic-metamorphic evolution see OBER-

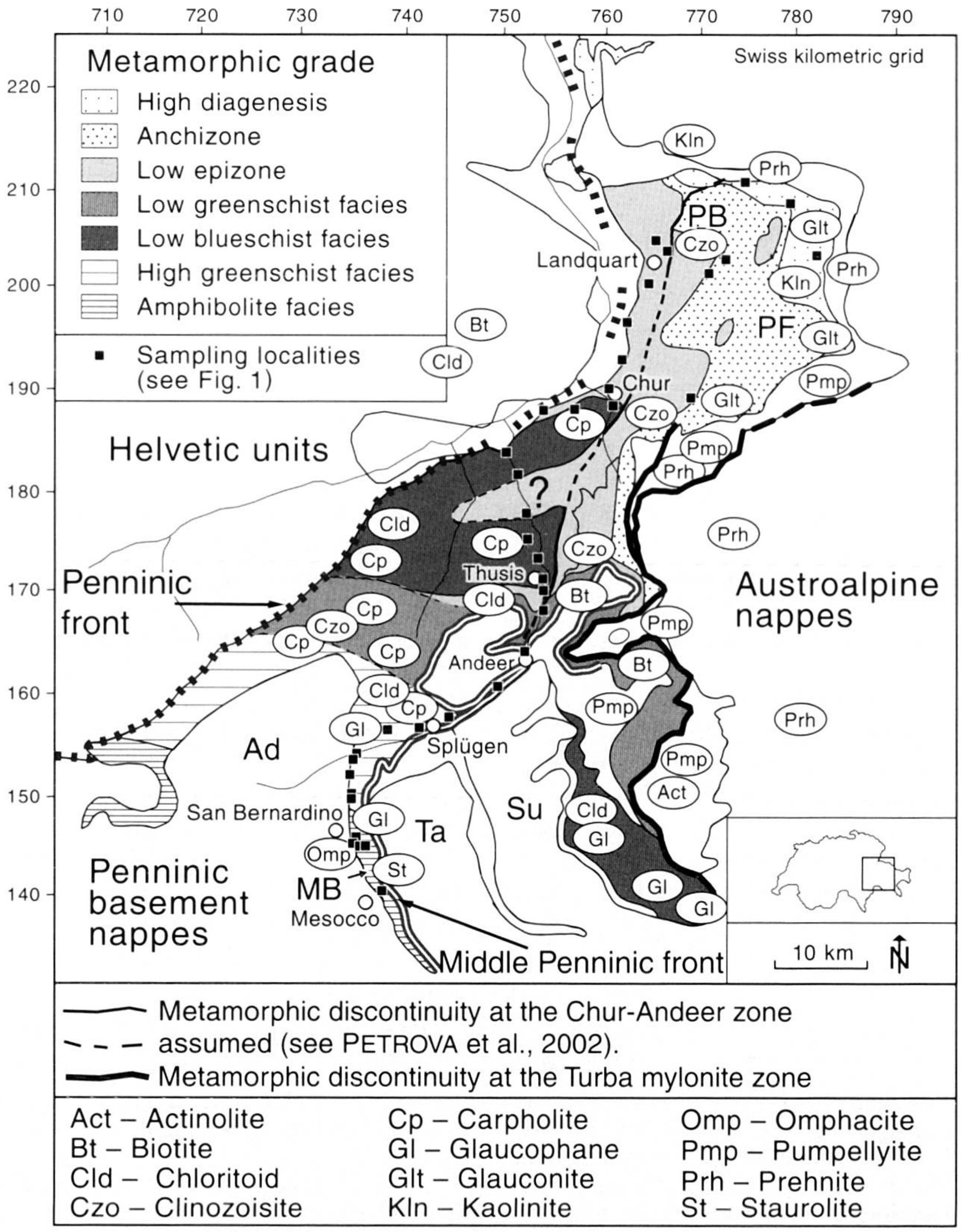


*Fig. 2* Metamorphic sketch map compiled from FREY et al. (1999), FREY and FERREIRO MÄHLMANN (1999), WEH et al. (1996), OBERHÄNSLI et al. (1995), and PETROVA et al. (2002).

HÄNSLI et al. (1995), AGARD et al. (2001) and also RAHN et al. (2002). Metasediments reached low blueschist facies during subduction, and only the upper low-grade metamorphic parts of the accreted units are preserved in eastern Switzerland. The HP-LT event is thought to be contemporaneous with eclogite formation in the Adula nappe (OBERHÄNSLI et al., 1995) during the Paleocene to Eocene deformation event (FROITZHEIM et al., 1996). The second Oligocene LT-LP metamorphism is attributed to a continent-continent collision, when the Penninic units were thrust onto Helvetic units (FREY and FERREIRO MÄHLMANN, 1999).

The studied cross-section is also characterized by a deformation gradient from brittle (with local variations in strain) to plain ductile deformation (WEH, 1998). In the southern area, major ductile shear zones are frequent.

### 5. Type of organic matter and sampling

In the high diagenesis and anchizone organic matter is diffuse and the type of carbon precursor was a kerogen type II, mostly a bituminite rich oil-prone kerogen. Alginite is frequently found and the minor vitrinite and major inertinite (STACH,

1982) composition shows a broad variation. During the tectonic-metamorphic history and with increasing metamorphic grade, carbonaceous material was segregated from the mineral matrix and occurs accumulated in pressure solution joints and foliation in the epizone, and as mm thick bands in the upper greenschist to amphibolite facies. Carbonaceous material strictly follows the rock foliation from microscopic to mesoscopic scale.

Samples are listed in Table 1. The mineral content of all lithologies was described previously by PETROVA et al. (2002). The only variable component is the calcite-dolomite ratio and the total carbonate content. 12 representative samples out of 55 samples of PETROVA et al. (2002) were chosen for the TEM study.

## 6. Analytical technique

### 6.1. SAMPLE PREPARATION

20–30 mg of each sample were placed in a platinum crucible to remove carbonate phases by HCl (38%). The mixture was periodically stirred during 3–5 hours and heated to 40–50 °C in order to accelerate the destruction of quartz and sheet silicates with HCl and $HNO_3$. The solution was filtered carefully with distilled water and placed in HF (48%). Each acid treatment, followed by careful filtration, was repeated at least 3 times to completely remove quartz and sheet silicates. The residue was composed of concentrated organic matter and refractory minerals such as rutile, tourmaline, zircon, pyrite, garnet, and pyrrhotite.

### 6.2. TEM METHODOLOGY

A total of 12 carbon samples (Table 1), evenly distributed along the metamorphic profile, was studied from nano- to micrometer scale. Several TEM images were taken from each sample to check the heterogeneity of carbonaceous material and to get a better resolution on the carbon microtexture.

TEM studies were carried out at the Laboratoire commun d'analyses (University H. Poincaré, Nancy, France) using a Philips CM20 TEM operating at 200 kV. Selected area electron diffraction patterns (SAED) and TEM images were recorded for each sample. A SAED aperture, of 500 nm in diameter was used, hence the SAED patterns of several images together correspond to mixtures of all types of carbonaceous materials found in one sample. Diffraction patterns (Fig. 3) vary with crystallite size. For graphite crystals bigger than 500 nm, separate diffraction spots are observed. When the area contains small particles

*Table 1* Sample characteristics.

| Sample | Geological unit | Organic material (OM) structure | OM d, Å | Rock type | Metamorphic grade /facies |
|---|---|---|---|---|---|
| Sample 2 | Prättigau Flysch | amorphous | – | Calcareous phyllite | high diagenesis |
| Sample 5 | Prättigau Bündnerschiefer | amorphous initial onions | – | Calcareous phyllite | low epizone |
| Sample 7 | Prättigau Bündnerschiefer | amorphous | 3.57 | Calcareous phyllite | anchizone |
| Sample 12 | Prättigau Bündnerschiefer | initial onions | 3.45 | Calcschist | high anchizone |
| Sample 15 | Prättigau Bündnerschiefer | onions | 3.33 | Calcschist | epizone |
| Sample 22 | Prättigau Bündnerschiefer | onions | – | Schistose limestone | low epizone |
| Sample 26 | Grava nappe | onions with thick rims | 3.33 | Schist | low greenschist high epizone |
| Sample 30 | Tomül nappe | onions with thick rims | 3.32 | Phyllite | low greenschist high epizone |
| Sample 32 | Prättigau Flysch s.l. Lenzerheide-Tomül Flysch | broken onions | 3.37* | Calcschist | greenschist |
| Sample 42 | Misox Bündnerschiefer | broken onions | 3.42* | Calcschist | greenschist |
| Sample 50 | Misox Bündnerschiefer | graphite flakes broken onions | – | Siliceous marble | low amphibolite |
| Sample 52 | Misox Bündnerschiefer | graphite flakes | 3.35 | Garnet-mica schist | low amphibolite |

* d-values strongly affected by heterogeneity in carbonaceous material and tectonic deformation of microstructures.

(crystallites) of random orientation, the diffraction patterns consist of discontinuous rings with spots. For very small particles, the rings become continuous and do not show white spots. The radii of the rings are inversely proportional to the corresponding d hkl values expressed in Å (d hkl: interplanar spacing of lattice planes (hkl)).

A suspension of residual carbonaceous material in ethanol was placed in an ultrasonic bath for 5 minutes and then deposited on a holy carbon film copper grid. During such treatment, the ethanol may partly dissolve organic material. For example, the secondary migra-bituminite found in sample 32 (Petrova et al., 2002) is no longer present as amorphous carbon in the final mount (Fig. 4j). On the photomicrographs, shadows of the carbon hollows are frequently superimposed onto the images of the samples (Fig. 4).

## 7. Results

### 7.1. MICROSTRUCTURES AND CARBON ORDERING

Several microstructures of carbonaceous material are distinguished in the Bündnerschiefer, which replace each other with increasing metamorphic grade: a) amorphous carbon, b) initial onions, c) carbon onions, d) onions with thickening rims, e) polygonal onions, f) broken or torn onions, and g) graphite flakes.

#### *7.1.1. Amorphous carbon*

The lowest grade (high diagenesis) examined in the profile was in sample 2 (Table 1, Figs. 1 and 2). For the youngest Bündnerschiefer (Late Cretaceous), anchizonal grade was found for sample 7, and low epizonal grade was determined for samples 5. For all three samples the electron diffraction pattern shows a broad and blurred 002 ring with a hazy outline (e.g. samples 2, Fig. 3A).

The SAED patterns correspond to a turbostratic carbonaceous material with a biperiodic order structure, with only a broad 002 ring well visible. The hk0 reflection is only a fine blurred ring with a large radius (Fig. 3B), indicating that the domains are very small and not oriented (not lying on their basal plane). It is not possible to determine the degree of order from the SAED patterns alone. Because: (1) The diffraction pattern of the carbonaceous material indicates a high grade of disorder, and (2) the radii of the hkl reflections depend on the orientation of the carbonaceous material relative to the electron beam.

TEM micrographs (Fig. 4a) display amorphous carbon with parts showing an "orange skin" like structure (a kind of porosity on wrinkled particles with a semi-rounded surface) or a structureless mass. In the samples of lowest metamorphic grade with a vaguely rounded cloudy surface (Fig. 4a) of the amorphous carbon, no other structure has been detected.

#### *7.1.2. Initial onions*

Samples from the Early Cretaceous Prättigau Bündnerschiefer reached high anchizonal to low epizonal grade (samples 12 and 15). With advancing graphitization at these grades (upper limit of the sub-greenschist facies), the previously amorphous carbonaceous material starts to rearrange into curved layered semicircle-like forms. The initial stage of this onion development is visible in Fig. 4b and also present in sample 15. The SAED pattern shows a broad 002 ring with the smaller hk0 radius showing an increase in domain dimensions (Fig. 3C).

These onions develop a thin layered rim, which is evidently composed of more highly ordered carbonaceous material visible in nearby parallel lattice fringes. This implies that the formation of the onions during graphitization starts from their surface, once the spherical particle reaches a size of 1000–2000 Å. The structure is not empty at this stage, its inner part being filled partly with amorphous material. Fig. 4b shows a relative well-ordered initial onion.

At low magnification, TEM images of the sample from higher metamorphic grade (Fig. 4c, sample 15) demonstrate that some of the curved structures remain interconnected by poorly oriented "chain-like" structures (Fig. 4k). Small areas with parallel lattice fringes (<100 Å) and section structures (~1000 Å) represent less organized carbonaceous material of aromatic bands in-between curved, better ordered segments of the carbonaceous material.

#### *7.1.3. Carbon onions filled with amorphous material*

In the epizone onions with poor structural ordering are the common form of carbon. Different stages of onion development were found in the Bündnerschiefer from the Prättigau (samples 15 and 22), Grava (sample 26) and Tomül nappes (sample 30). In the high epizone (low greenschist facies) of the metamorphic Bündnerschiefer profile distinct carbon structures are formed, with a triperiodic (3D) morphology of a round cross section and a cylindrical or flat-bottom beaker shaped (onion) like form, the center still filled with amorphous material.

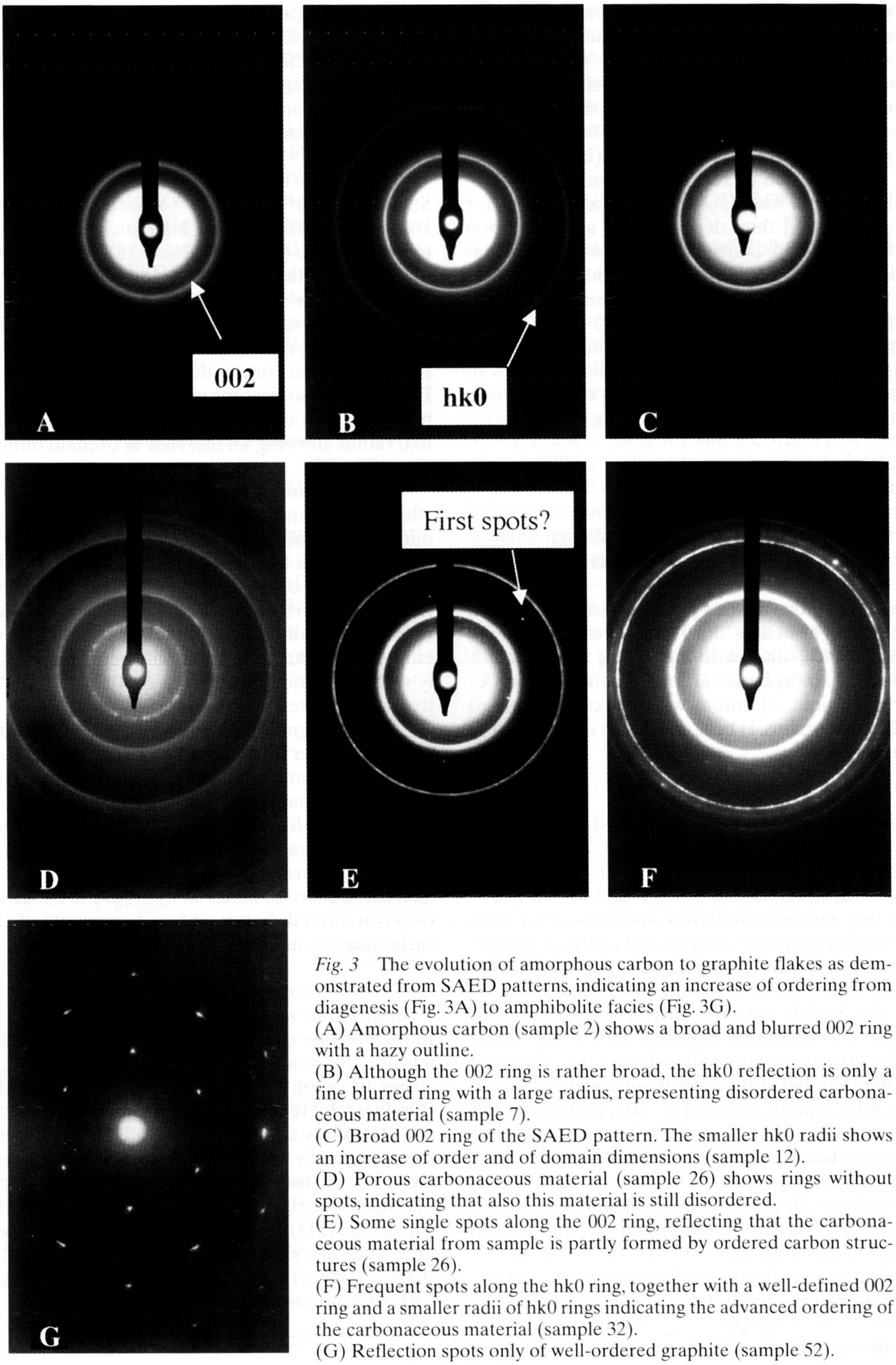


*Fig. 3* The evolution of amorphous carbon to graphite flakes as demonstrated from SAED patterns, indicating an increase of ordering from diagenesis (Fig. 3A) to amphibolite facies (Fig. 3G).
(A) Amorphous carbon (sample 2) shows a broad and blurred 002 ring with a hazy outline.
(B) Although the 002 ring is rather broad, the hk0 reflection is only a fine blurred ring with a large radius, representing disordered carbonaceous material (sample 7).
(C) Broad 002 ring of the SAED pattern. The smaller hk0 radii shows an increase of order and of domain dimensions (sample 12).
(D) Porous carbonaceous material (sample 26) shows rings without spots, indicating that also this material is still disordered.
(E) Some single spots along the 002 ring, reflecting that the carbonaceous material from sample is partly formed by ordered carbon structures (sample 26).
(F) Frequent spots along the hk0 ring, together with a well-defined 002 ring and a smaller radii of hk0 rings indicating the advanced ordering of the carbonaceous material (sample 32).
(G) Reflection spots only of well-ordered graphite (sample 52).

*7.1.4. Onions with thickening rims*

In the epizone, the maximum onion size increases to 1400–1500 Å (mean 1000 Å), hollow forms replace the amorphous carbon fillings and, hence, microporous structures (<500 Å), develop in the carbonaceous material (Fig. 4d, sample 26). SAED patterns of the porous carbonaceous material show 002- and hk0-rings without spots (Fig. 3D).

With progressive graphitization the onion rims grow thicker (Fig. 4e, as in sample 30). Growth occurs on the outer part of the onions (Fig. 4f), though less ordered (but not amorphous) carbon structures are still evident in the inner part (Fig. 4l).

TEM images demonstrate narrow 002 rings with the first occurrence of a few isolated spots. The spots usually indicate well-crystallized graphite. In the same sample, onions merge to form complex morphologies seen in TEM images (Fig. 4f). From this specific area of the sample, the SAED pattern shows some single spots along the 002 ring (Fig. 3E).

Spots in SAED pattern might also indicate a detrital population, but this should be detectable in the micrograph as well developed graphite flakes, which is not the case. In the samples between Landquart and Chur (samples 5 to 26), Petrova et al. (2002) found the detrital graphite content to be low or not detectable (<10 vol% of the organic matter).

*7.1.5. Polygonal onions*

In several TEM images of sample 26 and 30 carbonaceous materials reorient themselves to form larger and larger continuous aromatic layers. With increasing diameter (>2000 Å) their curvature flattens. With further graphitization, a circular geometry is replaced by a polygonal habitus (Figs. 4g and 4m). The maximum diameter reach a size of 3500 Å. Some initial forms of this poglygonization are recognized also in less metamorphosed carbonaceous material (Fig. 4e). Different stages of the polygonization are recognized. Onions with a thick rim display high polygonization and onions with a relative thin rim retain a curved shape.

*7.1.6. Broken or torn onions*

In the Lenzerheide-Tomül Flysch (Prättigau Flysch s.l.) two Tertiary deformation events have been linked with greenschist facies metamorphism (Weh, 1989). Also in our study (see Petrova et al., 2002) no blueschist minerals were found in the first and second deformation . With further ordering of the carbonaceous material during greenschist facies the onions break down along the edges formed during the polygonal onion stage of their development (Fig. 4h, sample 42). SAED patterns show frequent spots together with a well defined 002 ring and small radii of hk0 rings indicating the advanced ordering of the carbonaceous material (Fig. 3F). In sample 32, the breakdown of the onions to shell-like particles occurs as they reach a size of 3000–4000 Å.

In the northern Misox zone Bündnerschiefer (high greenschist facies) a very strong increase of the second Tertiary foliation and deformation is observed near the Middle Penninic front (Fig. 2). In sample 42, like in sample 32 (Fig. 1), broken onions are the predominant microstructure of the carbonaceous material.

*7.1.7. Graphite flakes*

In sample 50 from the low amphibolite facies, broken onion particles (Fig. 4i) coexist with graphite flakes of well-ordered carbonaceous material (Fig. 4j). In the TEM images of the carbonaceous material different stages of curvature and flattening are found. Flat broken particles (1000 to 2500 Å) show a thick layer stack of ordered carbon material and nearly reach the size of the graphite flakes (2000 to 5000 Å). Curved or polygonal broken particles mostly have smaller diameters. In sample 52 of low amphibolite facies but slightly higher metamorphic grade than sample 50, the polygonal and broken onion microstructures are replaced by an increasing content of graphite flakes. Due to the flattening of the onion walls combined with rupture of these walls along edges, the formation of graphite lamellae is indicated.

The flakes of graphite (from 2000 to 10000 Å) from sample 52 are not strictly homogeneous in their texture (Fig. 4j). The carbonaceous material is still not well-ordered and may contain patches (<500–1000 Å) of less-ordered material (Fig. 4n). The magnification used and the orientation of the carbonaceous material relative to the electron beam do not allow a clear visualization of the internal structure. SAED patterns show reflection spots of well-ordered graphite only (Fig. 3G).

## 7.2. HETEROGENEITY IN CARBONACEOUS MATERIAL

Heterogeneity in metasediments of low metamorphic grade is a natural consequence of the organic matter sedimentary cycle. Materials from sedimentary environments are commonly complex mixtures of aliphatic and aromatic compounds, and this causes a heterogeneous graphitization process (Franklin, 1951).

Heterogeneity in natural carbonaceous material has been widely described. Similar to our Bündnerschiefer study (see also Jäger and Streckeisen, 1958), Landis (1971) observed two

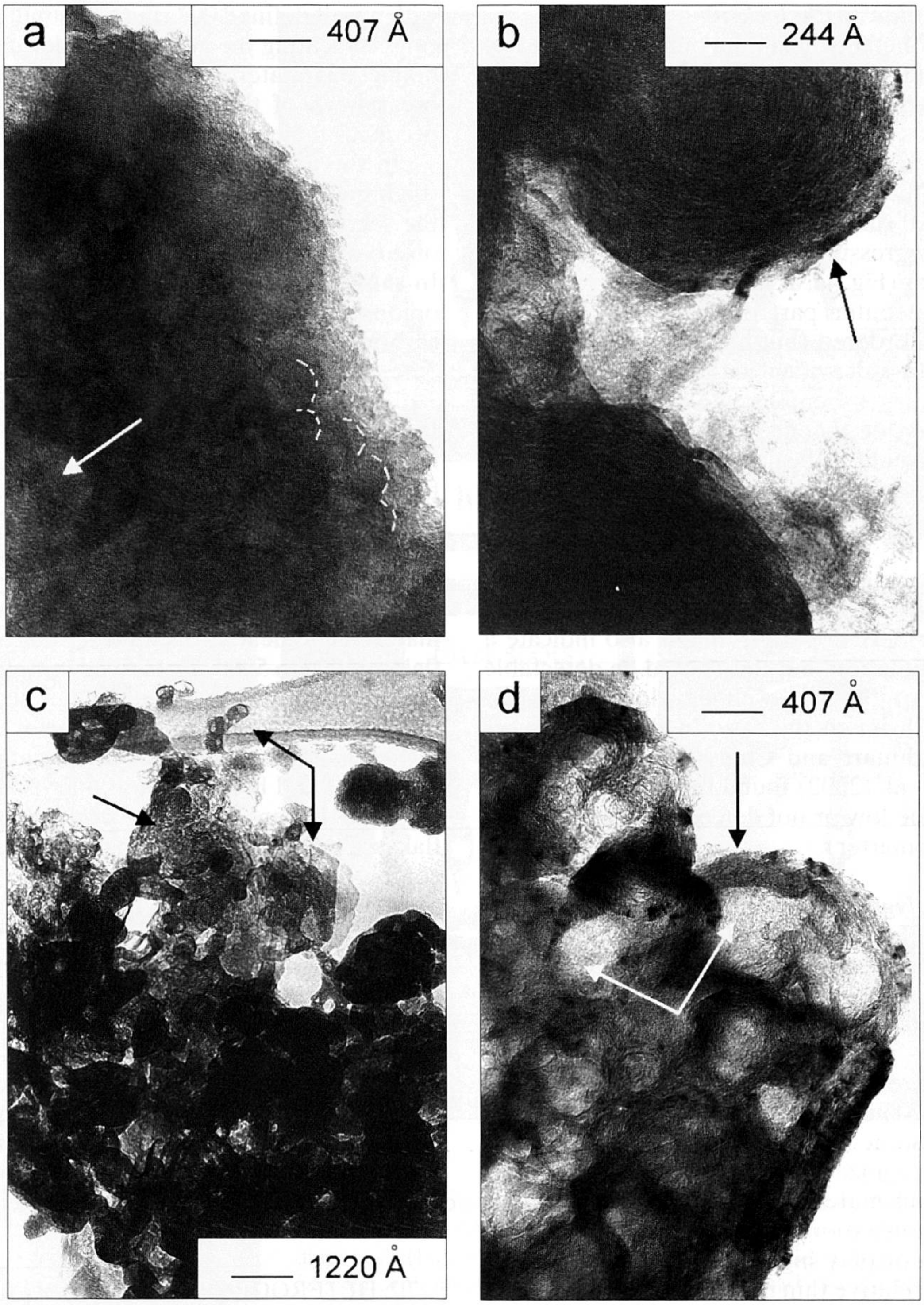


*Fig. 4* The structural graphitization progress from diagenesis (Fig. 4a) to amphibolite facies (Fig. 4j).
(a) Structure-less mass of amorphous carbon is indicated with a white arrow. At the border of the TEM image, the orange skin-like structure is well developed (sample 5).
(b) Initial stage of the onion development. Arrow indicates to a thin layered rim, which is obviously composed of higher ordered carbonaceous material visible in the almost parallel lattice fringes. In-between the two initial onions amorphous material remains (sample 12).
(c) Arrow on the right side point to areas with curved structures that are interconnected through not oriented chain-like structures. A chain structure is shown in a magnification in Fig. 4k (sample 13). The left arrow points to amorphous material.
(d) Onions with amorphous carbon fillings. The black arrow indicates the well-ordered and thick rims and the white arrows less ordered onion fillings, partly also amorphous carbon material (sample 26).

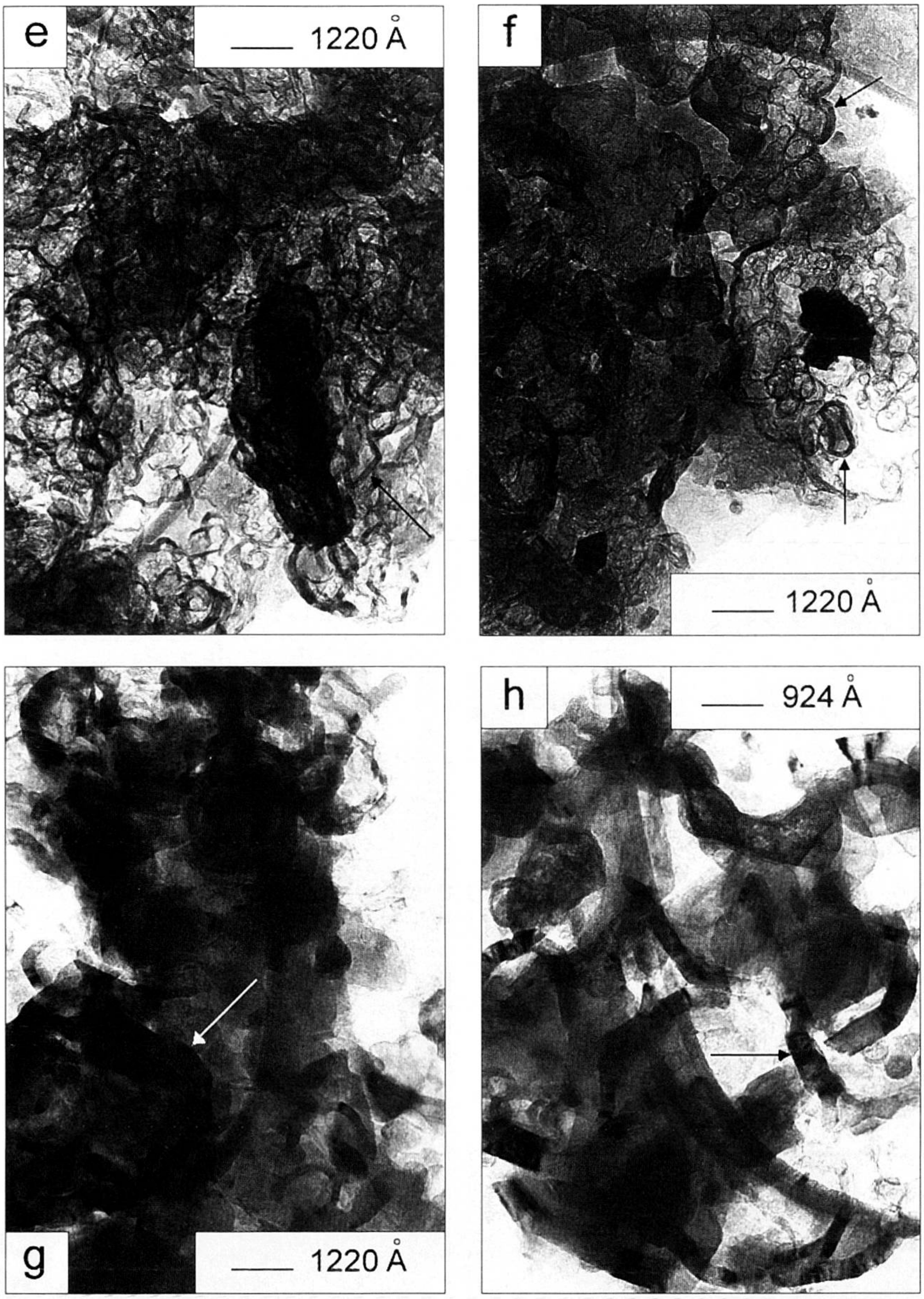


*Fig. 4* (cont.)
(e) Onion with thickened rims. The arrow points to a first development of polygonal structures (sample 26).
(f) The arrow points to a onion, which merges forming complex morphologies. The upper arrow shows the onion enlarged in Fig. 4l (sample 26).
(g) Onions with a thick rim reach a high polygonization step and onions with a relative thin rim still have a curved shape. The arrow indicates a very large polygonal onion (sample 32).
(h) Onions start to break down along the edges (sample 42). The arrow points to a flattened torn particle.

distinct peaks in X-ray diffractograms which were related to the fully ordered and the slightly disordered graphite. WANG (1989) reported distinctive X-ray diffraction patterns from low to medium grade metamorphic samples, with a sharp peak for the (002) reflection of graphite and a weak, broad peak on the lower 2Θ side for poorly crystallized carbonaceous material. The same is indicated for Bündnerschiefer of sub-greenschist to greenschist facies grade (PETROVA et al., 2002).

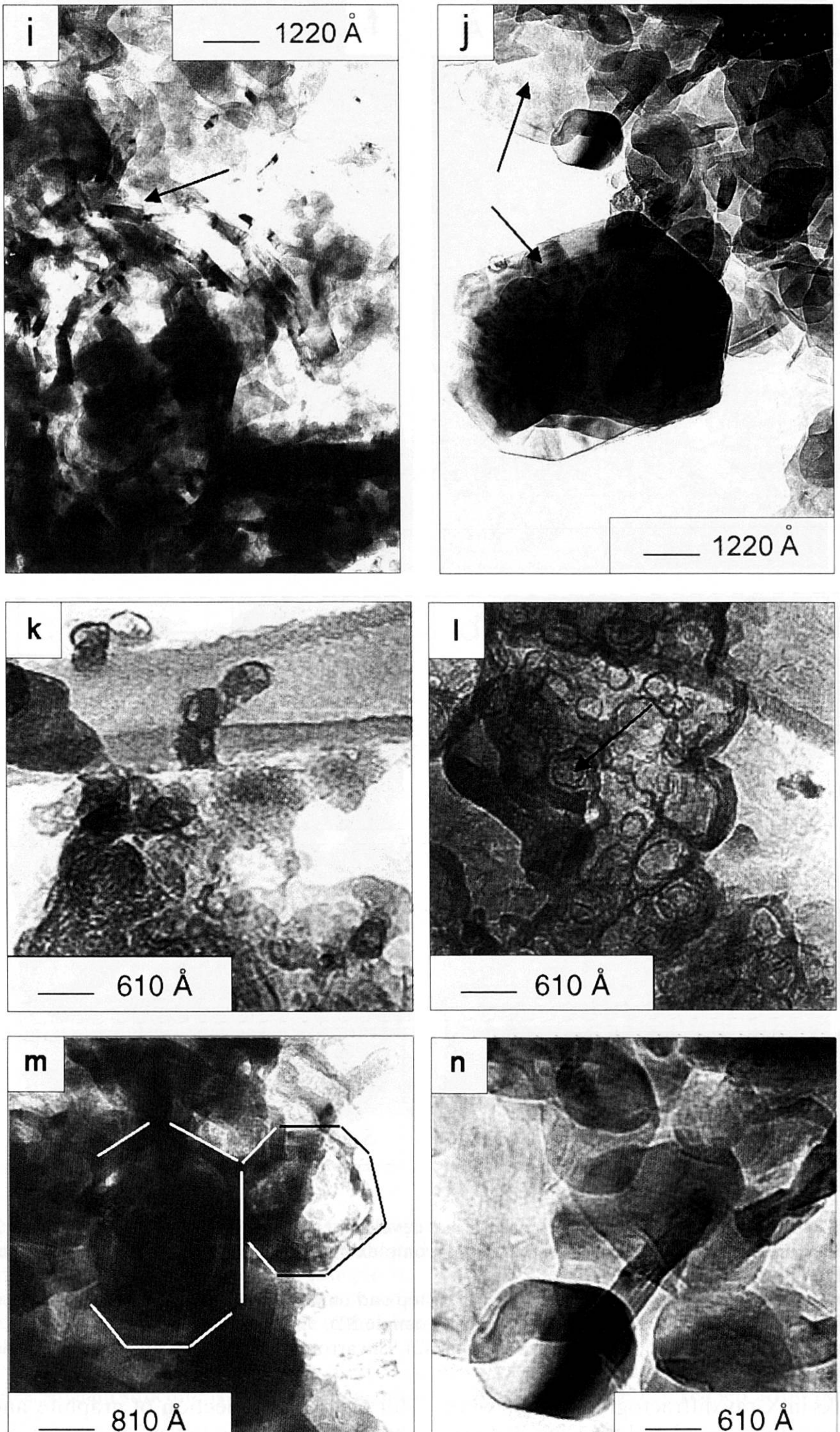


*Fig. 4* (cont.)

In the present study, d (002)-values of graphite obtained by electron diffraction (Table 1) decrease significantly from sample 2 (3.57Å) to sample 22 (3.32Å) at the beginning of the metamorphic profile, but then remain almost constant up to the highest grade studied. Previous XRD studies of the same carbonaceous material samples failed to produce a convincing trend of d-values decrease (PETROVA et al., 2002). This is due in part to the measurement of bulk samples composed of different macerals, as recorded by optical microscopy, with a complex mixture of different textures recorded by TEM micrography, but mainly due to the different resolution of the two methods. Nevertheless, the low significance of the trends reflects the heterogeneity of carbonaceous material.

Using optical microscopy, DIESSEL et al. (1978) described the coexistence of coalified and graphitized particles (transitional matter) at constant metamorphic grade. The same was shown by PETROVA et al. (2002) for the low greenschist facies part of the metamorphic profile studied.

In the same way as shown for Bündnerschiefer samples by PETROVA et al. (2000), also scanning electron microscopy by WINTSCH et al. (1981) and transmission electron microscopy by BUSECK and HUANG (1985) demonstrated heterogeneous organic material. Most samples contain carbonaceous material of different habitus and shape.

Detailed studies by KRIBEK et al. (1994) and LARGE et al. (1994) show that an important problem in the study of metamorphic evolution of organic matter is to deal with its strong heterogeneity in organic matter composition, structure, and microstructure. Heterogeneity in composition was confirmed for the Bündnerschiefer profile by PETROVA et al. (2002). In the present study, microstructure heterogeneity is demonstrated. In the Bündnerschiefer profile, onions with thickened rims coexist in abundance with initial onions. Broken onions have been observed together with graphite flakes (Fig. 4j). The combination of these microstructures in one sample may explain the composite (002) reflections of graphite on X-ray diffractograms and the wide ranges of values obtained in the TGA-DTA analysis and combustion studies of the carbonaceous material (PETROVA et al., 2002). It may also explain the coexistence of different habitus from carbonaceous material (PETROVA et al., 2000).

Comparing TEM and Raman spectroscopy, BUSECK and HUANG (1985) and WOPENKA and PASTERIS (1993) have noticed a heterogeneity in the type of carbonaceous material precursor as the cause for different graphitization degrees in one sample. The occurrence of disordered and poorly ordered graphite in metamorphic rocks is also due to a mixture of coaly material, poorly ordered graphite, natural coke, and graphitized bitumen (KRIBEK et al., 1994), which underwent graphitization at different rates (FRANKLIN, 1951). Optical and chemical analysis of organic matter in the Bündnerschiefer revealed a relative homogeneous overall composition (PETROVA et al., 2002). The precursor material chemistry should therefore only have a minor control on the graphitization process. Nevertheless, the observed heterogeneity complicates the discussion of the results.

## 8. Discussion

### 8.1. STRUCTURAL EVOLUTION OF CARBONACEOUS MATERIAL

The results presented are part of a comprehensive study on natural graphitization along a metamorphic section, combining TEM analysis with temperature sensitive methods such as vitrinite and bituminite reflectance measurements (FERREIRO MÄHLMANN, 1994; PETROVA et al., 2002), combustion analysis, thermo-gravimetric, and differential thermal analysis (PETROVA et al., 2002), all based on detailed maceral analysis. Previous studies on natural graphitization define the grade of metamorphism by index minerals and a gradual metamorphic increase cannot be ascertained. For the present samples, the metamorphic condition is exceptionally well known. The sample preparation used may have removed hydrogen-rich secondary bituminite (migra-bituminite), but this does not affect the macerals of the huminite-vitrinite

←*Fig. 4* (cont.)
(i) Broken onion particles coexist with graphite flakes of well-ordered carbonaceous material (sample 50). Some particles have a very well ordered layer structure (arrow).
(j) The flakes of graphite are not strictly homogenous in their texture. The upper rim of the hexagonal graphite flake is well ordered and shows the typical graphite layers (sample 52). The upper arrow points to highly disordered material.
(k) Chain-like structures interconnecting the onions (see Fig. 4c).
(l) Onions with less ordered carbon present in the inner parts (see Fig. 4f).
(m) Onions obtain a polygonal geometry (enlarged area from the sample 32, but not shown in Fig. 4g).
(n) Graphite material with patches of disordered material. Enlarged area from Fig. 4j.

group and high mature primary bituminite (RAGOT, 1977), hence we are confident to have documented the evolution of primary organic matter.

As an initial approach, microstructural changes were correlated with metamorphic zones defined by vitrinite-bituminite reflectance and illite-crystallinity (FERREIRO MÄHLMANN et al., 1992; WEH et al., 1996). As proposed by GREW (1974), a continuous evolution of the carbon microstructures is postulated. Despite of the heterogeneity found, the trend in the overall microstructural changes with increasing metamorphic grade demonstrates a gradual progress of carbon material ordering. Along the metamorphic profile, this is derived from the overlapping range of a specific microstructure occurrence between its initial and last appearances (Fig. 5).

The textural development in carbonaceous material involves several stages from amorphous material → initial onions → onions filled with amorphous material → onions with thick rims → onions with a void core → polygonal onions → broken onions and finally to graphite flakes.

In the high diagenetic zone the amorphous carbonaceous material from organic matter is the most abundant carbon material in the micrography. Amorphous carbon is formed by short and misoriented aromatic groups of benzene-rings with aliphatic bonds (MARSH, 1989). According to the high diagenetic grade (220 to 250 °C, 2.0 to 3.0 kbar), determined for the lowest metamorphic sample, the aliphatic chains should be mostly transformed, and the primary C-H-O-aliphatic-aromatic composition of the organic matter should be strongly homogenized (TEICHMÜLLER, 1987). Therefore, low-ordered carbon structures should be formed by basic hexagonal, benzene-ring chains (FRANKLIN, 1951) and most volatiles should have degassed (TEICHMÜLLER, 1987).

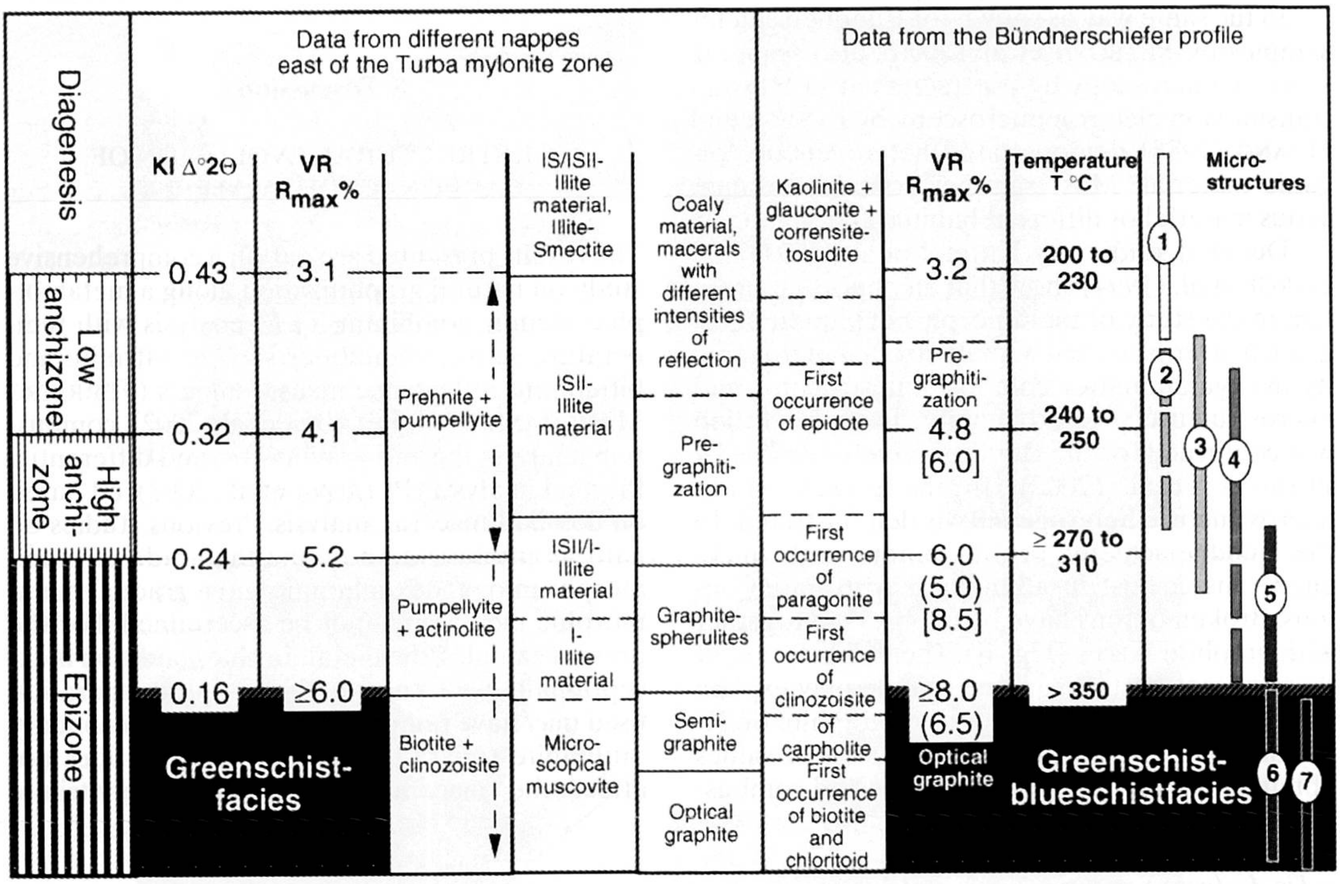


*Fig. 5* Comparison of metamorphic data from east of the "Turba mylonite zone" (NIEVERGELT et al., 1996) and this study. The mineral data, vitrinite reflectance (VR) and temperature estimations are taken from OBERHÄNSLI et al. (1995), FREY and FERREIRO MÄHLMANN (1999), and PETROVA et al. (2002). Data from different nappes east of the Turba mylonite zone are compiled from FERREIRO MÄHLMANN (1996, 2001). I—illite, S—smectite, KI—illite crystallinity shown as Kübler Index. Values in parenthesis give the correlation from the areas of blueschist facies overprint. Values in brackets give the correlation from shear zones. The occurrence of microstructures is shown in the last column: 1—amorphous carbon, 2—initial onions (range not well constrained), 3—different types of carbon onions, 4—onions with thickened rims (lower range limit not well constrained), 5—polygonal onions, 6—broken onions, 7—graphite flakes.

During high diagenesis (sample 2) organic material developed into poorly organized layered stacks of aromatic bands with a vaguely rounded cloudy surface (Fig. 4a), the amounts of which then increase with metamorphism, as shown for samples 5 and 7. "Orange skin" like structures in a structure-less mass were generated from these layered stacks. The curved microstructure demonstrates a very early stage of layered ordering at the transition from diagenesis (sample 2) to anchizone grade (sample 7).

Different evolutionary steps are observed between layered rounded stacks and the formation of initial onions (Figs. 4a–c). Curved, semi-circular microstructures are composed of organized, carbonaceous material embedded in amorphous material. OBERLIN et al. (1974) described similar spherical particles as "carbon-blacks" containing curved sheets of carbon layers. Such particles have been reported for bituminous coals, anthracites, and mature kerogens (OBERLIN et al., 1974). From these structures the initial onions developed in the low anchizone, still coexisting with less ordered and amorphous material.

In the anchizone many initial onions are linked together to form chains. This kind of chains is only present during the development of initial onions from amorphous carbonaceous material. It may be interpreted as a step of ordering following complete loss of aliphatic bonds forming a two-dimensional layered order of aromatic bonds, with many chains still separated by amorphous carbon. The amount of the latter decreases with increasing metamorphic grade. In the low epizone (samples 5, 12 and 22), the first onions appear filled with amorphous carbon; the restricted space in the onion center prevents the restructuring of the carbon bonds. Closed onions initially still filled by amorphous carbonaceous material, but subsequently devoid of filling, evolved during epizonal metamorphism (samples 15, 22, 26 and 30). For nanoscopic carbon a fastening of surface bonds by formation of curved, closed shell-like structures or sheets appears to be the most effective way of minimizing the surface energy (OBRAZTSOVA et al., 1998). Poorly ordered carbonaceous material is composed of tiny aromatic, two-dimensional flat to curved graphitic sheets. The elimination of energetic bonds present at their edges is supposed to be the driving force to induce curvature (OBERLIN et al., 1974; UGARTE, 1995). In the high epizone (low greenschist facies), graphitization proceeds, and the circular and spherical geometry of the onions is replaced by a polygonal one (Fig. 4g), due to successive differentiation of the hexagonal rings. During flattening of the curvature and or prior to polygonization, stacking of aromatic layers radially progresses, sphere by sphere, towards the center of the former onion. The increase in rim thickness during the carbon ordering and onion growth appears to cause polygonal restructuration. Graphitization mainly starts at the pore walls of porous and (initial) onion-like carbon structures (BONIJOLY et al., 1982; BUSECK and HUANG, 1985; LARGE et al., 1994; UGARTE, 1995), from where it expands into those areas with the largest radius of curvature. From the thickened rims and broken fragments of polygonal onions, reordering to graphite flakes probably documents the last step of the structural evolution to graphite. The last step is not very well constrained by this study. In the amphibolite facies, both broken onions and graphite flakes appear together. The flakes transform to large hexagonal particles with increasing metamorphism (Fig. 4j).

## 8.2. THE DEPENDENCE OF TEMPERATURE AND PRESSURE ON GRAPHITIZATION

Temperature is probably the most important factor controlling graphitization: (1) Vitrinite reflectance is mainly dependent on temperature and time (RAGOT, 1977; TEICHMÜLLER, 1987; FERREIRO MÄHLMANN, 2001). The microstructural evolution of carbonaceous material shows a significant correlation with vitrinite reflectance. (2) The north-south trend of increasing vitrinite reflectance and graphitization are both reflecting the low temperature/low pressure pattern of the Oligocene metamorphic event, and correlate with the illite crystallinity (Figs. 2 and 5). (3) In comparison the data from the temperature sensitive combustion analysis (PETROVA et al., 2002) and the present TEM study are well compatible.

A minor pressure influence on organic matter maturation was demonstrated and assigned to the retardation of vitrinite reflectance (DALLA TORRE et al., 1997). We are not able to postulate the same for the graphitization progress. In the metamorphic profile (in the area between Chur and Thusis, Fig. 1), in the section where vitrinite reflectance is partly retarded (PETROVA et al., 2002), the evolution of microstructures shows no significant differences in the ordering progress. Carbonaceous material from samples 22 (epizone), 26 and 30 (both epizone, low blueschist facies) was composed of carbon onions, onions with thickening rims, and polygonal onions. With increasing metamorphism (from sample 22 to 30) only the amount of polygonal onions increased. These observations may indicate that pressure is a minor factor or can be neglected, but a possible retarding influence caused by the Late Eocene to Early Oligocene low blueschist conditions may have been overprinted by the Late Oligocene greenschist event.

### 8.3. STRAIN-INDUCED STRUCTURAL EVOLUTION OF CARBONACEOUS MATERIAL

In the high anchizone and low epizone, mostly in strongly deformed rocks, two-dimensional chains of initial onions are formed instead of isolated onions. Complex morphologies originate from the chain structures of the initial onion stage described above. In the area near samples 5 and 22, intense deformation is evidenced by a penetrative schistosity and the occurrence of mylonites. Intergrowths of onions is abundant and may imply that the shear strain was high preventing the development of single closed onions, so that inter-growth onions did not reach a state where their rims would close. Alternatively, fast graphitization may retard or prevent closure of single onions. The Tertiary metamorphic history (FREY and FERREIRO MÄHLMANN, 1999) does not substantiate the second postulate of a fast and short-lived metamorphism. Graphitization should have evolved during a long time period, from the beginning of the low temperature/high pressure event (Late Eocene) to the end of the second low temperature/low pressure metamorphism (Late Oligocene).

In rocks with high strain, onion chain structures, and initial onions, light spots in the still homogeneous reflecting vitrinite and bituminite were found. These are interpreted as initial forms of pre-graphitization (FERREIRO MÄHLMANN, 2001), e.g. the beginning of a natural coke-like habit (RAMDOHR, 1928). In most cases, the occurrence of pre-graphitization in vitrinite and bituminite of the Bündnerschiefer is closely related to the local strain. With increasing deformation, pre-graphitization effects appear and get more frequent also with increase in metamorphic grade. In bituminite, pre-graphitization is first detected in high anchizonal samples; in the low epizone, vitrinite is also affected (Fig. 5). This corroborates that the chemical composition of the precursor material does influence the rate of the graphitization progress (FRANKLIN, 1951).

The very first pre-graphite structures start to occur close to the transition from the anchizone to the epizone (Fig. 5), i.e. at a temperature between 270 and 310 °C (TEICHMÜLLER, 1987; FERREIRO MÄHLMANN, 1996). Between Chur and Landquart (Fig. 1), the metamorphic grade is more or less uniform (Fig. 2). Studying vitrinite reflectance samples with and without pre-graphitization effects in the organic matter have been detected side by side within two samples. In less deformed rocks of the low epizone, no pre-graphitization effects have been recognized. At the same time, TEM images show the carbon structures mostly to flatten. We propose that flat onions and onion chains may evolve more easily to graphite flakes in the maximum strain direction. The very high degree of optical and structural heterogeneity and the size of broken onions (around 1000 Å smaller than the polygonal onions) in mylonitic rocks at the Middle Penninic front (samples 32 and 42) is also explained as a breakdown due to high strain and deformational overprint.

Along the Bündnerschiefer metamorphic profile, optical graphite occurs at 400 to 450 °C at 5.0 to 6.0 kbar as stated by LANDIS (1971) and DIESSEL et al. (1978). Experimentally synthetic onion-ring structures do not evolve to graphite solely from the effect of heat, even at temperatures as high as 2800 °C. Microstructures are not modified (ROUZAUD and OBERLIN, 1989), and graphite ("real graphite") is not formed at temperatures below 3000 °C, even after a long time of coalification (BONIJOLY ROUSSEL, 1980; BONIJOLY et al., 1982). WADA et al. (1994) made similar observations within contact aureoles at low strain conditions. Graphite occurs at much higher temperatures (>600 °C) than under orogenic metamorphic settings; this is also known for optical graphite (RAGOT, 1977).

Well-ordered carbon material is formed due to the break-up of the aromatic ordering, the translation of the basal layers (001), and mechanical stacking followed by triperiodic bonding (TEICHMÜLLER and TEICHMÜLLER, 1954; RAGOT, 1977; BONIJOLY ROUSSEL, 1980). Tectonic deformation of the starting material reorders the basic benzene-ring structure sub-parallel to the basal plain (001) and facilitates the formation of a bi-periodic early stage of graphite (layered stacks in the TEM images). The mechanical process causes preferential stacking of poly-aromatic layers (TEICHMÜLLER et al., 1979; ENGLAND and BUSTIN, 1985) first in bituminite (DIESSEL et al., 1978). This accounts for the early increase of ordering and formation of flattened initial onions, onion chains and broken onions. Therefore, strain has a catalytic effect between 300 and 450 °C on graphitization and graphite formation. In nature, pre-graphitization is also strongly controlled by strain. This is indicated by enhanced vitrinite reflectance (FERREIRO MÄHLMANN, 1994, 1995; SCHMIDT et al., 1997), the formation of optical graphite ("true graphite", LANDIS, 1971; TAYLOR, 1971) and or by other features of pre-graphitization (TEICHMÜLLER, 1987; FERREIRO MÄHLMANN, 1996, 2001) and this study. In different samples from the area near Landquart (near sample 15, Fig. 1), only very few small light anisotropic spots in the still optically homogeneous organic matter (vitrinite and bituminite particles) as described by RAMDOHR (1928) are recognized. In the same area, vitrinite develops a strong bireflectance indicating the change from meta-anthracite to optical graphite. Anisotropy in the repartition of stress (BUSTIN et al., 1995) was discussed as a major origin for the heterogeneity within carbonaceous material. Comparing vitrinite reflectance versus mineral facies and illite crystallinity (Fig. 5) and with data from other areas of the Alps, it is remarkable that vitrinite reflectance is strongly enhanced in the Bündnerschiefer. Same results are well constrained in the study from SCHMIDT et al. (1997). Thus, strain is evidently a major factor controlling vitrinite-bituminite reflectance (not to be mistaken for coalification sensu stricto, which is a thermal maturation), and also an important factor controlling graphitization at low-grade metamorphic conditions.

## 8.4. THE DEPENDENCE OF OPTICAL CHANGES ON STRUCTURAL ORDERING

Reflected light microscopy studies on huminite-vitrinite and bituminite show that along the metamorphic Bündnerschiefer section from diagenesis to epizone (low greenschist facies) the first two stages of OKUYAMA-KUSUNOSE and ITAYA (1987) evolve continuously. The evolution from isotropic to anisotropic reflectivity (development of bireflectance) gradually starts at low diagenetic conditions (not studied here, but in a structurally equivalent unit further north, FERREIRO MÄHLMANN, 1994), i.e. the optical characteristics do not change suddenly.

In the Bündnerschiefer metamorphic profile between Landquart and Chur (Fig. 1) the microstructural development of initial onions and semicircular onions with amorphous material fillings correlate with optical observations of pre-graphitization. In this area the increase in optical anisotropy indicates an enhancement in density of the vitrinite, which is also related to pre-graphitization effects (STONE and COOK, 1979; TEICHMÜLLER, 1987). This is much more evident in the area near Chur (Fig. 1), where the formation of onions with thick-rims is observed. In the same area, the maximum temperature of S-type peak combustion reactions (PETROVA et al., 2002) increases from 400 to 600 °C. Compared with the samples from the Prättigau the reaction temperature in thermal analysis is strongly enhanced. In agreement with the TEM investigation, this increase in reaction temperature reflects an increase in ordering of the organic matter and hence in thermal resistance with metamorphic grade. The formation of onions and onions with thick rims and the successive aromatization and carbon ordering are, therefore, seen as the main causes for the increased thermal resistance of organic matter and the occurrence of small light pregraphitization spots in reflected light microscopy. The optically recognized graphite spherulites, related to better ordered carbonaceous material seen in the TEM images, are thought to cause the first occurrence of spots in the SAED pattern.

Along with the formation of onions and polygonal onions, vitrinite reflectance indicates a metamorphic grade of the semi-graphite stage (6.0 to 10.0 % $R_{max}$). At this rank of maturation, most vitrinite and also bituminite particles can still be distinguished optically by their habit and typical bireflectance. However, some particles show optical features of optical graphite. The step of maturation of the semi-graphite stage along the metamorphic profile may correspond to the zone of transitional matter of DIESSEL et al. (1978) and the stage of the "rhombohedral graphite" of KWIECINSKA (1980). It is not easy to classify single organic particles even by TEM studies, as coaly material or graphite. We propose to relate the three optical stages of DIESSEL and OFFLER (1975) and OKUYAMA-KUSUNOSE and ITAYA (1987) to the structural graphitization progress (amorphous carbon, carbon onions, graphite flakes) and the early pre-graphitization to the formation of initial onions. The stages cannot be separated by sharp boundaries (Fig. 5). Features found in a structural study may overlap with observations at the boundary between two optical stages, suggesting yet a continuous process of maturation and graphitization from diagenesis to low greenschist facies.

## 8.5. THE TRANSITION FROM COALY MATERIAL/POLYGONAL ONIONS TO OPTICAL GRAPHITE/GRAPHITE FLAKES

Similar to many metamorphic profiles (FERREIRO MÄHLMANN, 1994), a so-called "jump" to the graphite stage of maturation (TEICHMÜLLER, 1987) is observed within the Bündnerschiefer south of Thusis (Fig. 1), where the maximum vitrinite reflectance increases from 8.0 ± 0.5% to 10 ± 1.0%. At this maturation stage, it is assumed that graphite is ordered to a triperiodic structure and that this change from the two- to three-dimensional carbon bound structure of aromatics is discontinuous (e.g. TEICHMÜLLER, 1987; DEMENY, 1989; PETROVA et al., 2002). Unfortunately, at the transition from the polygonal onions in the epizone (low greenschist facies) to the graphite flakes in the low amphibolite facies, the increase in metamorphic grade in the high greenschist facies is characterized by "metamorphic inversion" (FREY, 1988) across the Middle Penninic front. High deformation rates are typical at such a tectonic discontinuity. In both samples from the Middle Penninic front, broken onions were found (samples 32 and 42). This suggests that the broken onions may not reflect a structural ordering stage in the normal graphitization process, instead deformation may have played a role.

However, owing to the coincidence between tectonic and metamorphic limits in this area, the discussion about the "graphite jump" still remains unsolved for the Bündnerschiefer metamorphic profile. The sudden increase of "vitrinite-graphite" reflectance and bireflectance on one side and on the other side of the combustion reaction temperature (PETROVA et al., 2002) from the Tomül Bündnerschiefer to the Lenzerheide-Tomül flysch is mainly the product of the discontinuous metamorphic pattern.

For the same reason it remains unclear, which temperature is required for the breakdown of onions and the configuration of graphite flakes and at what size the transition occurs between closed surface particles and macroscopic planar graphite (UGARTE, 1995). A change in size is observed between polygonal onions (2000–5000 Å) and graphite flakes (2000–10000 Å) at high greenschist to low amphibolite facies. In the transition zone between greenschist and amphibolite facies, more systematic work is necessary. In addition, areas of high-grade amphibolite facies should be studied to determine the conditions of macroscopic planar graphite formation. Laboratory investigations in physical material sciences on well-ordered graphite demonstrate that, in small volumes, graphitic material often has an almost perfect graphite lattice (BONIJOLY ROUSSEL, 1980). With increasing volume, however, defects, distortions and heteroatoms reduce the regularity, partly producing a very disordered graphite structure. True single crystals of tri-periodic graphite are rare (MARSH, 1989). Graphite with a reflectance >16% (RAMDOHR, 1928) was not found in the metamorphic profile. The relatively low temperature (<600 °C, see WADA et al., 1994) and large size of the flakes may explain that homogeneous graphite is absent in the Bündnerschiefer profile, but optical graphite occurs elsewhere at conditions less than 450 °C (RAGOT, 1977).

## 9. Conclusions

Graphitization of carbonaceous material proceeds in several progressive and continuous steps, each possessing its characteristic microstructures:

1. In the high diagenetic zone, amorphous carbon develops concentric layers and forms initial onions.
2. In the low anchizone, these initial onions develop rims of better ordered carbonaceous material, generating onions with a filling of amorphous carbon material in the high anchizone, and later in the low epizone, with a void core.
3. In the high epizone, under low blueschist and low greenschist facies conditions, the rims of these onions grow thicker, and the onions become polygonal.
4. Polygonal onions start to breakdown after they reach a size between 3000 and 4000 Å. It is postulated that broken onions may be the result of a breakup due to high strain conditions.
5. At the greenschist to amphibolite facies transition, broken onions develop into graphite flakes. It is indicated that under low strain conditions polygonal onions may be precursors of graphite flakes and of planar, hexagonal-holoedric, mineralogical graphite.

The carbonaceous material of the Bündnerschiefer is heterogeneous in microstructure over the whole metamorphic range studied. In all samples, a major part of the carbonaceous material was transformed to a specific microstructural type after reaching a critical metamorphic grade. However, a minor fraction remained less evolved in a metastable stage of graphitization. A pressure effect on graphitization could not be constrained. Graphitization, pre-graphitization and optical graphite formation can be strongly enhanced in highly deformed rocks. It is evident that strain has a catalytic effect and is a major factor in graphite evolution and can locally be more important than temperature.

**Acknowledgements**

This study is part of the PhD. thesis of T.P. who was financially supported by the Swiss National Science Foundation, grant no. 20-56633.99. Vitrinite reflectance and maceral analysis by R.F.M. were supported by the Swiss National Science Foundation, grant no. 21-50642.97. We thank Monika Wolf (RWTH Aachen, D) for copies of the exellent PhD. studies from J.P. Ragot and M. Bonijoly Roussel, giving us essential hints for the correlation of microstructural and optical data on coal. Thankfully we want to mention the high quality of the resin mounted polished sections prepared by Willi Tschudin (Univ. Basel). Drawing of Fig. 1 by Silvio Lauer (Univ. Basel) is gratefully acknowledged. The work benefitted greatly from reviews by Wolfgang Müller (TU Darmstadt, D) and Meinert Rahn (HSK-Villigen, CH), and a very thoughtful revision of the English by Meinert Rahn and Martin Engi. We appreciate very much a carefull editorial handling by Martin Engi (Univ. Bern, CH) and Peter Nievergelt (ETH Zürich, CH), also a last revision by Susanne Th. Schmidt (Univ. Gèneve, CH). With the tragic death of Martin Frey our research group has lost its principal leader and a remarkable teacher. R.F.M. is strongly indebted to Bernard Kübler. He aroused my interest to compare clay mineral and coal petrological methods. I will not forget the long and enthusiastic discussions during the IGCP meeting in Auckland 1991 and the field trip in New Zealand with Bernard Kübler and Martin Frey. Later in Basel I appreciated to work very independantly under the guidance of friendly and taciturn Martin Frey.

## References

AGARD, P., JOLIVET, L. and GOFFÉ, B. (2001): Tectonometamorphic evolution of the schistes lustrés complex: implication for the exhumation of HP and UHP rocks in the western Alps. Bull. Soc. Géol. Fr. 172/5, 617–636.

BAUDIN, T. and MARQUER, D. (1993): Métamorphisme et déformation dans la nappe de Tambo (Alpes centrales suisses): évolution de la substitution phengitique au cours de la déformation alpine. Schweiz. Mineral. Petrogr. Mitt. 73, 285–299.

BONIJOLY ROUSSEL, M. (1980): Evolution des substances carbonées naturelles. Formation de graphite. Unpublished PhD. thesis, Univ. Orléans, 185 pp.

BONIJOLY, M., OBERLIN, M. and OBERLIN, A. (1982): A possible mechanism for natural graphite formation. Int. J. Coal Geol. 1, 283–312.

BUSECK, P.R. and HUANG, B.J. (1985): Conversion of carbonaceous material to graphite during metamorphism. Geochim. Cosmochim. Acta 49, 2003–2016.

BUSTIN, M., ROUZAUD, J.N. and ROSS, J.V. (1995): Natural graphitization of anthracite: experimental considerations. Carbon 33/5, 679–691.

DALLA TORRE, M., DE CAPITANI, C., FREY, M., UNDERWOOD, M.B., MULLIS, J. and COX, R. (1996): Very low-temperature metamorphism of shales from the Diabolo Range, Franciscan Complex, California: New constraints on the exhumation path. Geol. Soc. Am. Bull. 108/5, 578–601.

DALLA TORRE, M., FERREIRO MÄHLMANN, R. and ERNST, W.G. (1997): Experimental study on the pressure dependence of vitrinite maturation. Geochim. Cosmochim. Acta 61/14, 2921–2928.

DEMENY, A. (1989): Structural ordering of carbonaceous matter in penninic terranes. Acta Mineralogica-Petrographica, Szeged 30, 103–113.

DIESSEL, C.F.K. and OFFLER, R. (1975): Change in physical properties of coalified and graphitized phytoclasts with grade of metamorphism. N. Jb. Mineral. Mh. 1975/1, 11–26.

DIESSEL, C.F.K., BROTHERS, R.N. and BLACK, P.M. (1978): Coalification and graphitization in high-pressure schists in New Caledonia. Contrib. Mineral. Petrol. 68, 63–78.

ENGLAND, T.D.J. and BUSTIN, R.M. (1985): Effect of thrust faulting on organic maturation in the south-eastern Canadian Cordillera. In: LEYTHÄUSER, D. and RULLKÖTTER, J. (eds): Advances in Organic Geochemistry 10, 609–616.

ERNST, W.G. and FERREIRO MÄHLMANN, R. (2002): Experimental rate study of vitrinite maturation as a function of temperature, time, starting material, aqueous fluid pressure, and oxygen fugacity: Corroboration of prior work. Am. Geophys. Union, Eos. Trans. AGU, 83(19), Spring Meet. Suppl., Abstract V41A-10.

FERREIRO MÄHLMANN, R. (1994): Zur Bestimmung von Diagenesehöhe und beginnender Metamorphose – Temperaturgeschichte und Tektogenese des Austroalpins und Süpenninikums in Vorarlberg und Mittelbünden. PhD. thesis, Frankfurt University. Frankfurter geowiss. Arb., Serie C, 14, 498 pp.

FERREIRO MÄHLMANN, R. (1995): Das Diagenese-Metamorphose-Muster von Vitrinitreflexion und Illit-"Kristallinität" in Mittelbünden und im Oberhalbstein. Teil 1. Bezüge zur Stockwerktektonik. Schweiz. Mineral. Petrogr. Mitt. 75, 85–122.

FERREIRO MÄHLMANN, R. (1996): Das Diagenese-Metamorphose-Muster von Vitrinitreflexion und Illit-"Kristallinität" in Mittelbünden und im Oberhalbstein. Teil 2: Korrelation kohlenpetrographischer und mineralogischer Parameter. Schweiz. Mineral. Petrogr. Mitt. 76, 23–46.

FERREIRO MÄHLMANN, R. (2001): Correlation of very low grade data to calibrate a thermal maturity model in a nappe tectonic setting, a case study from the Alps. Tectonophysics 334, 1–33.

FERREIRO MÄHLMANN, R., PETSCHICK, R., ERDELBROCK, K., KRUMM, H., WOLF, M. and BERNOULLI, D. (1992): Coalification Map of the Pennine-Austroalpine-Boundary (Switzerland, Liechtenstein and Austria). Terra Nova, 4, Abstract Supplement 2: 21, ALCAPA meeting, Graz.

FRANKLIN, R.E. (1951): The structure of graphitic carbons. Acta Crystallogr. 4, 253–261.

FREY, M. (1987): Very low-grade metamorphism of clastic sedimentary rocks. In: FREY, M. (ed.): Low Temperature Metamorphism. Blackie, Glasgow and London, 9–58.

FREY, M. (1988): Discontinuous inverse metamorphic zonation, Glarus Alps, Switzerland: evidence from illite "cristallinity" data. Schweiz. Mineral. Petrogr. Mitt. 68, 171–183.

FREY, M. and WIELAND, B. (1975): Chloritoid in autochthon-parautochthonen Sedimenten des Aarmassives. Schweiz. Mineral. Petrogr. Mitt. 55, 407–418.

FREY, M. and FERREIRO MÄHLMANN, R. (1999): Alpine metamorphism of the Central Alps. Schweiz. Mineral. Petrogr. Mitt. 79/1, spec. issue: The new metamorphic map of the Alps, 135–154.

FREY, M., DESMONS, J. and NEUBAUER, F. (1999): Alpine Metamorphic Map 1:500000. Schweiz. Mineral. Petrogr. Mitt. 79/1, spec. issue: The new metamorphic map of the Alps, 1–4.

FROITZHEIM, N., SCHMID, S.M. and FREY, M. (1996): Mesozoic paleogeography and the timing of eclogite-facies metamorphism in the Alps: a working hypothesis. Eclogae geol. Helv. 89, 81–110.

GREW, E.S. (1974): Carbonaceous material in some metamorphic rocks of New England and other areas. J. Geol. 82, 50–73.

ITAYA, T. (1981): Carbonaceous material in pelitic schists of the Sanbagawa metamorphic belt in central Shikoku, Japan. Lithos 14, 215–224.

JÄGER, E. and STRECKEISEN, A. (1958): Nachweis von Graphit in graphitführenden Schiefern des Simplon-Gebietes (Wallis, Schweiz). Schweiz. Mineral. Petrogr. Mitt. 38/2, 375–386.

KRIBEK, B., HRABAL, J., LANDAIS, P. and HLADIKOVA, J. (1994): The association of poorly ordered graphite, coke and bitumens in greenschist facies rocks of the Ponikla Group, Lugicum, Czech Republic: the result of graphitization of various types of carbonaceous matter. J. Metamorphic Geol. 12, 493–503.

KWIECINSKA, B. (1980): Mineralogy of natural graphite. Prace Mineral. 67, 87 pp.
LANDIS, C.A. (1971): Graphitization of dispersed carbonaceous material in metamorphic rocks. Contrib. Mineral. Petrol. 30, 34–45.
LARGE, D.J., CHRISTY, A.G. and FALLICK, A.E. (1994): Poorly crystalline carbonaceous matter in high grade metasediments: implications for graphitisation and metamorphic fluid compositions. Contrib. Mineral. Petrol. 116, 108–116.
MARSH, H. (1989): Introduction to carbon science. Butterworth, Boston.
NIEVERGELT, P., LINIGER, M., FROITZHEIM, N. and FERREIRO MÄHLMANN, R. (1996): Early to Mid Tertiary crustal extension in the Central Alps: The Turba Mylonite Zone. (Eastern Switzerland). Tectonics 15/2, 329–340.
OBERHÄNSLI, R., GOFFÉ, B. and BOUSQUET, R. (1995): Record of a HP-LT metamorphic evolution in the Valais zone: Geodynamic implications. In: LOMBARDO, B. (ed.): Studies on metamorphic rocks and minerals of the western Alps. Boll. Mus. Reg. Sci. nat. Torino, 13/2, 221–240.
OBERLIN, A., BOULMIER, J.L. and DURAND, B. (1974): Electron microscope investigation of the structure of naturally and artificially metamorphosed kerogen. Geochim. Cosmochim. Acta 38, 647–650.
OBRAZTSOVA, E.D., FUJII, M., HAYASHI, S., KUZNETSOV, V.L., BULENKO, Y.V. and CHUVILIN, A.L. (1998): Raman identification of onion-like carbon. Carbon 36, (5–6), 821–826.
OKUYAMA-KUSUNOSE, Y. and ITAYA, T. (1987) Metamorphism of carbonaceous material in the Tono contact aureole, Kitakami mountains, Japan. J. Metamorphic Geol. 5, 121–139.
PESQUERA, A. and VELASCO, F. (1988): Metamorphism of the Paleozoic Cinco Villas massif (Basque Pyrenees): illite crystallinity and graphitization degree. Mineral. Mag. 52, 615–625.
PETROVA, T.V., RUBOLZ, J., GUGGENHEIM, R., STERN, W.B. and FREY, M. (2000): SEM studies of carbonaceous material in metamorphic rocks of the Bündnerschiefer (Eastern Switzerland). Abstract volume, Brno, July 28, 2000.
PETROVA, T.V., FERREIRO MÄHLMANN, R., STERN, W.B. and FREY, M. (2002): Application of combustion and DTA – TGA analysis to the study of metamorphic organic matter. Schweiz. Mineral. Petrogr. Mitt. 82, 33–53.
RAHN, M.K., STEINMANN, M. and FREY, M. (2002): Chloritoid composition and formation in the eastern Central Alps: a comparison between Penninic and Helvetic occurrences. Schweiz. Mineral. Petrogr. Mitt. 82, 409–426.
RAGOT, J.P. (1977): Contribution à l'étude de l'évolution des substances carbonées dans les formations géologiques. Unpublished PhD thesis, Univ. Toulouse, 150 pp.
RAMDOHR, P. (1928): Mikroskopische Beobachtungen auf Graphiten und Koksen. Arch. Eisenhüttenwesen Dtschld. 25 A, 669–672.
ROUZAUD, J.N. and OBERLIN, A. (1989): Structure, microtexture, and optical properties of anthracene and saccharose-based carbons. Carbon 27, 517–529.
SCHMIDT, D., SCHMIDT, S.Th., MULLIS, J., FERREIRO MÄHLMANN, R., FREY, M., (1997): Very low-grade metamorphism of the Taveyanne formation of western Switzerland. Contrib. Mineral. Petrol. 129, 385–403.
SCHNEIDERHÖHN, H. and RAMDOHR, P. (1931): Lehrbuch der Erzmikroskopie. Teil 1, T 11, edition 1941, Berlin, 714 pp.
STACH, F. (1982): The microscopically recognizable constituents of coal. In: STACH, F., MACKOWSKY, M.TH., TEICHMÜLLER, M., TAYLOR, G.H., CHANDRA, D. and TEICHMÜLLER, R. (eds): Textbook of Coal Petrology. 3rd ed., Bornträger, Stuttgart, p. 87–152.
STEINMANN, M. (1994): Ein Beckenmodel fur das Nordpenninikum der Ostschweiz. Jahrb. Geol. Bundesanstalt Wien 137, 675–721.
STONE, I.J. and COOK, A.C. (1979): The influence of some tectonic structures upon vitrinite reflectance. J. Geol. 87, 497–508.
TAYLOR, G.H. (1971): Carbonaceous matter: a guide to the genesis and history of ores. Soc. Min. Geol. Japan, spec. Issue 3, 283–288.
TEICHMÜLLER, M. (1987): Organic material and very low-grade metamorphism. In: FREY, M. (ed.): Low Temperature Metamorphism. Blackie, Glasgow and London, 114–161.
TEICHMÜLLER, M. and TEICHMÜLLER, R. (1954): Die stoffliche und strukturelle Metamorphose der Kohle. Geol. Rdsch. 42, 265–296.
TEICHMÜLLER, M., TEICHMÜLLER, R. and WEBER, K. (1979): Inkohlung und Illit-Kristallinität – Vergleichende Untersuchungen im Mesozoikum und Paläozoikum von Westfalen. Fortschr. Geol. Rheinland u.Westfalen 27, 201–276.
TEUTSCH, R. (1982): Alpine Metamorphose der Misoxer-Zone (Bündnerschiefer, Metabasite, Granitische Gneise). Unpublished PhD. thesis, Bern University, 172 pp.
UGARTE, D. (1995) Onion-like graphitic particles. Carbon 33(7), 989–993.
WADA, H., TOMITA, T., MATSUURA, K., IUCHI, K., ITO, M. and MORIKIYO, T. (1994): Graphitization of carbonaceous matter during metamorphism with references to carbonate and pelitic rocks of contact and regional metamorphism, Japan. Contrib. Mineral. Petrol. 118, 217–228.
WANG, G.F. (1989): Carbonaceous material in the Ryoke metamorphic rocks, Kinki district, Japan. Lithos 22, 305–316.
WEH, M. (1998): Tektonische Entwicklung der penninischen Sediment-Decken in Graubünden (Prättigau bis Oberhalbstein). Unpublished PhD. thesis, Basel University, 296 pp.
WEH, M., FERREIRO MÄHLMANN, R. and FROITZHEIM, N. (1996): Strukturelle und metamorphe Diskontinuitäten im Penninikum am Westrand der Ostalpen. In: AMANN, G., HANDLER, R., KURZ, W. and STEYRER, H.P. (eds): VI. Symposium Tektonik – Strukturgeologie – Kristallingeologie. Facultas Univ.-Verl., Salzburg, Extendet abstracts, p. 479–482.
WINTSCH, R.P., O'CONNELL, A.F., RANSOM, B.L. and WIECHMANN, M.J. (1981): Evidence for the influence of $CH_4$ on the crystallinity of disseminated carbon in greenschist facies rocks, Rhode Island, USA. Contrib. Miner. Petrol. 77, 207–213.
WOPENKA, B. and PASTERIS, J.D. (1993): Structural characterization of kerogens to granulite-facies graphite: applicability of Raman microprobe spectroscopy. Am. Mineral. 78, 533–557.
YUI, T.F., HUANG, E. and XU, J. (1996): Raman spectrum of carbonaceous material: a possible metamorphic grade indicator for low-grade metamorphic rocks. J. Metamorphic Geol. 14, 115–124.

Manuscript received December 12, 2001; revision accepted July 3, 2002.
Editorial handling: M. Engi