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Stratigraphy, geochemistry and origin of Silurian black graptolitic shales of the Carnic Alps (Austria)

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With 10 Text-Figures and 3 Tables

Carnic Alps
Graptolite Shales
Black Shales
Geochemistry
Trace elements
Environmental hazards
Lower Palaeozoic
Silurian

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Contents

Stratigraphie, Geochemie und Ablagerungsbedingungen der Graptolithenschiefer des Silurs der Karnischen Alpen (Österreich)

Zusammenfassung

In den Graptolithenschiefern des Silurs der Karnischen Alpen deutet die Verteilung von Haupt- und Spurenelementen wechselnde Ablagerungsbedingungen an. Während der transgressiven Tendenz und zunehmenden Vertiefung am Beginn des Silurs (Llandovery) wurden hauptsächlich chemisch "reife" Kieselschiefer mit im allgemeinen hohen Zirkoniumwerten in einem normal-marinen Milieu abgelagert. Im Verlaufe des Wenlocks änderte sich aber der Charakter der Sedimentation und weniger reife kalkige Schiefer und Kalke begannen das Sedimentationsgeschehen zu dominieren. Am Ende des transgressiven Zyklus im Obersilur (Ludlow-Pridoli) wurden erneut chemisch reife Kieselschiefer gebildet. Sulfidische Graptolithenschiefer kamen hauptsächlich in euxinischen Becken mit niedrigem O_2-Gehalt zur Ablagerung, die lebensfeindliche Bedingungen unter Bildung von H_2S wiederspiegeln. Diese Entwicklung kann als metallführende Schwarzschieferfazies klassifiziert werden und kann insbesondere in Gebieten, in denen Karbonate fehlen, ernste Umweltprobleme verursachen.

Abstract

The distribution of major and trace elements in Silurian graptolitic shales of the Carnic Alps suggests important changes of depositional environment. With the beginning of the Silurian transgression and progressing subsidence, mostly chemically mature "siliceous" shales with generally higher Zr values were deposited in normal marine environment. The character of sedimentation has rapidly changed during Wenlock when chemically less mature calcareous shales together with carbonates dominated. The termination of basinal subsidence in Upper Silurian (Ludlow-Pridoli), has resulted in the deposition of chemically well mature graptolitic shales. Sulphidic graptolitic shales were mostly deposited in restricted marine environment (low O_2 concentrations) with local periods of inhospitable bottom conditions (little or no O_2 was present and H_2S may have been continually or intermittently present). These facies can be classified as metalliferous black shales and represent a potential environmental hazard especially in areas where carbonate lithology is missing.

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1. Introduction

One of important topics of a newly approved International Geological Correlation Programme – IGCP 429 "Organics in Major Environmental Issues" (1998–2002) is the study of *environmental* aspects of *metalliferous black shales* which widely crop out in many regions of the world. These, usually organic matter – sulphur-metal – rich rocks can cause, by the release of toxic metals, acids, and radioactive gas, serious environmental harm as documented by many authors from various places worldwide (PAŠAVA et al., 1993; PAŠAVA et al., 1995; LOUKOLA-RUSKEENIEMI et al., 1998; CHON et al., 1998, and others.). The area of the Carnic Alps belongs to one of the classical regions of occurrences of Silurian black graptolitic shales. After previous lithological and paleontological studies (JAEGER, 1975; JAEGER et al., 1975; FLÜGEL et al., 1977, SCHÖNLAUB, 1979, 1985; JAEGER & SCHÖNLAUB, 1980; SCHÖNLAUB & KREUTZER, 1994; WENZEL, 1997), this paper provides the first geochemical data on the Silurian black graptolitic shales and compares them with similar facies of the Prague Basin (Czech Republic), Northeast Bavaria (Germany) and Armorican Massif (France).

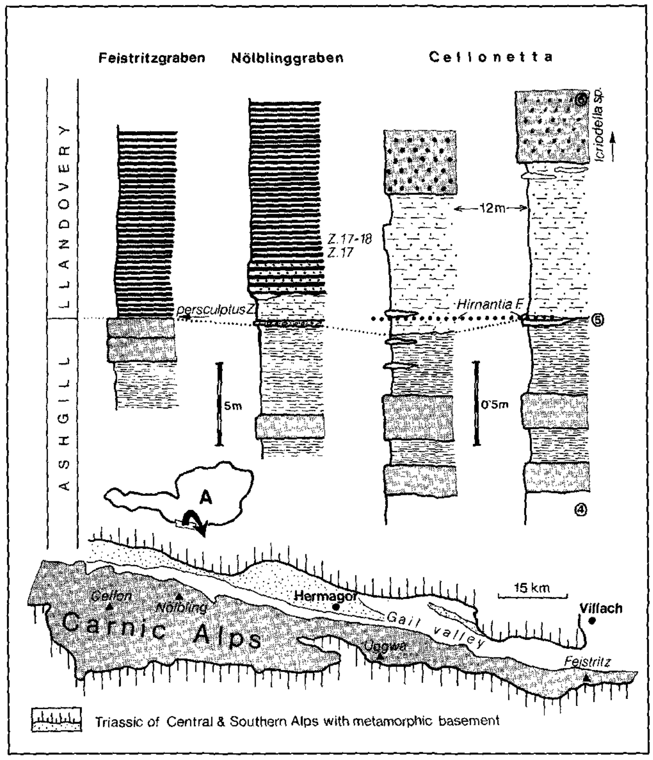

Fig. 1:
Ordovician/Silurian boundary sections in the Carnic Alps and the western Karawanken Alps. Note difference in scale (*shade: limestone*; bold lines: graptolite shale; thin lines: claystones; dots and lines: silstones; bold dots: PLÖCKEN Fm.). From SCHÖNLAUB, 1980 (modified).

General geology

In Austria, Silurian strata are irregularly distributed. They can form isolated units in the Alpine nappe system and are also exposed along the northern margin of the southern Alps to the south of the Periadriatic Line in the Carnic and Karavanken Alps (see SCHÖNLAUB & HEINISCH, 1993). Silurian deposits range from shallow-water carbonates to graptolitic shales. The thicknesses are regionally similar and generally do not exceed about 60 m. The main differences across the Periadriatic Line concern the distribution of fossils, facies patterns, rates of subsidence, supply material, amount of volcanism, and the spatial and temporal relationship of climatically sensitive rocks (SCHÖNLAUB, 1993).

The stratigraphic record of the southern Alps includes Ordovician to Middle Triassic strata. In the Carnic Alps, the widespread terminal Ordovician glacial event has been recognized as being responsible for a sedimentary gap in the basal Silurian. During the Silurian, a considerable variety of lithologies developed. Due to extensional tectonics and different rates of subsidence, the facies pattern changed significantly during the Devonian. This is documented by more than 1200 m of shallow-water Devonian limestones which are time equivalent to some 100 m of condensed nodular limestones. Limestone sedimentation was then more uniform and continued through Framennian and earliest Carboniferous, when emergence and karstification occurred near the end of the Tournaisian. The final collapse of the Variscan basin started in the Visean and resulted in the deposition of more than 1000 m of flysch deposits that indicate an active margin at the northern part of the southern Alps.

Silurian in the Carnic Alps

In the Carnic Alps, the Silurian transgression started in the earliest Llandovery (i.e. in the *Akidograptus acuminatus* Zone). Due to the unconformity between the Ordovician and Silurian in the Carnic and Karavanken Alps, a locally varying hiatus, corresponding to several Llandovery and Wenlock conodont zones is present. At a few places, even basal Lochko-vian strata may disconformably rest upon Upper Ordovician limestones (SCHÖNLAUB, 1971, 1988). Location and stratigraphy across the Silurian graptolitic black shales is given on Fig. 1.

Silurian lithofacies are subdivided into four major facies that reflect different depths and energy conditions (WENZEL, 1997). A moderately deep marine environment is represented by the PLÖCKEN Facies, which includes an upward sequence of the pelagic Kok Formation, the Cardiola Formation, and the Alticola-Megaerella Limestones. The classical sec-tion is the 60 m thick Cellonetta profile which is well known for the Silurian conodont zonation established by WALLISER (1964).

The Wolayer Facies represents an apparently shallower environment. It is characterized by fossiliferous limestones with abundant orthoconic nautiloids, trilobites, bivalves, small brachiopods, gastropods, crinoids, and a few corals. Due to a hiatus at the base, this facies is represented by only 10–15 m of variegated limestone. The classical sections are located in the Lake Wolayer region of the central Carnic Alps (von GAERTNER, 1931).

The stagnant water graptolite facies is named Bischofalm Facies. It is represented by 60–80 m black siliceous shales, black cherty beds, and clay-rich alum shales which contain abundant graptolites. This graptolite distribution has been clearly outlined by the comprehensive work of H. JAEGER (JAEGER, 1975; FLÜGEL et al., 1977; JAEGER and SCHÖNLAUB, 1980, 1994; SCHÖNLAUB, 1985). According to JAEGER (1975), the Bischofalm Facies can be subdivided into three units, the lower, middle and upper Bischofalm Shales.

The Findenig Facies represents an intermediate facies between the shallow water and stagnant basinal environment. It comprises interbedded black graptolite shales, marls and blackish limestone beds. At its base, a quartzose sandstone may locally occur (JAEGER & SCHÖNLAUB, 1980).

Those four Silurian lithofacies reflect different rates of subsidence. From the Llandovery to the beginning of the Ludlow, the sedimentation suggests a steadily subsidizing basin and a transgressional regime. This subsidence decreased and perhaps stopped during the Pridoli and led to rather balanced conditions with uniform limestone deposition. Simultaneously, the black graptolitic shales of the middle Bischofalm Facies were replaced by greenish shales and grayish shales of the middle Bischofalm Shale. At the base of the Devonian in the Bischofalm Facies, the deep-water graptolitic environment reappeared and persisted until the end of the Lochkovian Age.

Lithologically, the graptolite-bearing rocks form a monotonous sequence of interbedded radiolarian-bearing cherts and alum shales. The cherts dominate the Llandovery and Wenlock while the shales prevail in the upper part of the succession. The intermediate green and gray shales contain only few graptolites in thin layers.

The composite thickness of the graptolite-bearing Silurian to Lochkovian sequence ranges from 50 to 100 m. It is, thus, an extremely condensed sequence due to a very low but nevertheless continuous rate of deposition. This conclusion is supported by the very complete graptolite zonal succession. The environmental conditions were anoxic or strongly dysaerobic except of a short interval when the middle Bischofalm Shale was deposited. Due to the intensive Variscan and Alpine tectonic activities, longer undisturbed sections are very rare. By far the best exposed and least disturbed section is the main section of Hauptprofil. This tectonic block is almost 20 m thick and covers the interval from the *Pristiograptus ludensis* Zone of the Wenlock to the Lower Devonian *Monograptus hercynicus* Zone. The Silurian-Devonian boundary sits in a homogeneous black shale and there was no physical break at this boundary (JAEGER in FLÜGEL et al., 1977). A distinct change in facies from green and gray shales to black shales was preceeded by the faunal change at the boundary by one graptolite zone. There is no evidence that *Monograptus transgrediensis* and *Monograptus uniformis* overlap. Finally, the middle Bischofalm Shales occupy the same stratigraphic position as the non-graptolitic Ockerkalk of Thuringia and, presumably also of Sardinia (JAEGER, 1976).

The intermediate facies between the shallow-water and basinal settings is best developed at the Oberbuchach section some 10 km east of Kötschach-Mauthen (JAEGER & SCHÖNLAUB, 1980). This facies is termed the "Findenig Facies". The Silurian represents a mixed argillaceous-calcareous lithology referred to the Nölbling Formation. An almost 50 m thick sequence of Llandovery to Ludlow age is underlain by the Upper Ordovician Uggwa Limestone and the 10 m thick siliciclastic PLÖCKEN Formation of Hirnantian age (Ordovician). This later formation is overlain by interbedded laminated pyritic sandstones, black bedded cherts and black shales with a graptolite fauna of the *Coronograptus gregarius* Zone and *Demirastrites triangulatus* Subzone of early Aeronian age (= early middle Llandovery).

The second horizon of graphitic sandstones occurs in the upper Llandovery. Its age is inferred from diagnostic conodonts of the *Pteroshpatodus celloni* Zone in limestones overlying this siliciclastic interval. These limestones are followed by an alternating sequence of dark argillaceous limestones, black graptolitic shales and cherts that range through the Wenlock to the Ludlow. Conodonts are associated with index graptolites of latest Llandovery to Wenlock age, in this interval. In the overlying shales, graptolites occur at several levels, and include the *Monograptus riccartonensis* Zone in the Sheinwoodian and range up to the *Neodiversograptus nilssoni* Zone at the base of the Gorstian. The Wenlock-Ludlow boundary may thus be placed some 40 m above the base of the graptolite-bearing sequence.

At the Oberbuchach section, fossils other than graptolites and conodonts are very rare. Conodonts are dominated by simple tooth-shaped cones belonging to the genera *Dapsilodus* and *Decoriconus*. Ramiform elements only occur in the lower portion of the section (SCHÖNLAUB, 1980). Strata corresponding to the remaining part of the Ludlow and Pridoli Series are up to 20 m thick. This interval consists of lithologically distinct gray and almost unfossiliferous sulphidic limestones with a very characteristic weathered surface which may have originated through chemical weathering of pyritic concretions.

2. Sample Description and Methods

Altogether 19 samples of Silurian graptolitic shales were taken by the authors from Plöckenpass (classical locality of Upper Ordovician and Silurian – up to Upper Wenlock-Lower Ludlow graptolitic shales and carbonates – XI/6-uppermost Llandovery graptolitic black shale – Kok Formation), Oberbuchach (classical locality of graptolitic shales with intercalations of carbonates and carbonaceous black shales – XII/1-Llandovery – thinly bedded graptolitic shale in between quartzite, a. 1 m above sandstone; XII/2-top part of the graptolitic shale, a. 20 cm below upper quartzite; XII/4-graptolitic shale between #88 and #90 of numbered section; XII/5-graptolitic shale, a. 2m below #91; XII/8 – chert, a. 2m above #92; XII/9-alum shale?, a. 5m below #93; XII/10-graptolitic shale, a. 3m below #93; XII/12-graptolitic shale, weathered with abundant limonite and sulphates, a. 20 cm below carbonate layer of #94; XII/13-graptolitic shale, between #95 and #96 [#96=Wenlock/Ludlow-boundary]; XII/14-graptolitic shale, a. 1m above Wenlock-Ludlow boundary; XII/17-typical graptolitic shale without carbonates – Eß aerated horizon; XII/18-graptolitic shale, a. 5m below Eß horizon), Nölblinggraben (XIII/1-graptolitic shale of the Upper Ludlow – zone #19; XIII/2-graptolitic shale, a. 4m above zone #19; XIII/3-graptolitic shale, a. 5 cm thick layer in bituminous limestone, uppermost Ludlow-lowermost Pridoli; XIII/4-graptolitic shale, middle Llandovery), and Zollnersee sections (XIV/1-graptolitic shale in the hangingwall of the Eß ventilated horizon; XIV/2-graptol-itic shale, Pridoli, *Monograptus transgrediensis* Zone).

Rocks were powdered and analyzed in laboratories of the Czech Geological Survey in Prague. Major oxides were determined using classical wet chemistry (Sixta, Šikl, Mikšovský, Černochová, Císarová and Janovská – analysts). The trace elements (Sn, Zn, As, U, Nb, Cu, Mo, Rb, Y, Ni, Zr, Cr, Pb, Sr and V),were measured on a Philips TW 1404 instrument by the X-ray fluorescence method. The PGE were determined by the flameless AAS after collection of PGE into Ni-button (Rubeška analyst).

3. Results and Discussion

Geochemistry of major elements

Chemical composition of shales is a significant indicator of their origin. The Al_2O_3/Na_2O and Na_2O/K_2O ratios reflect the degree of maturity of the silty-clayey sediments. In chemically mature sediments the value of the Al_2O_3/Na_2O ratio exceeds 15 while in immature sediments the value of this ratio is lower than 15 (KUKAL, 1985). Conversely, the value of Na_2O/K_2O ratio decreases with an increasing chemical maturity. SiO_2/Al_2O_3 ratio basically indicates the contents of siliciclastic material and a contingent admixture of authigenic quartz. Geochemistry of the Silurian graptolitic shales from the Carnic Alps compared to other classical Silurian regions is given in Table 1.

Graptolitic shales of Llandovery with the values of Al_2O_3/Na_2O ranging from 8 to 46 (avg. 21.4), and the values Na_2O/K_2O varying between 0.1 and 0.4 (avg. 0.25), indicate relatively mature sediments. In general, lower degree of maturity show the Wenlockian graptolitic shales (Al_2O_3/Na_2O = 9–28, avg. 18.5; Na_2O/K_2O = 0.1–0.5, avg. 0.25). Similarly as Llandoverian shales, the Ludlow-Pridolian graptolitic facies exhibit a higher chemical maturity (Al_2O_3/Na_2O = 8–48, avg. 27; Na_2O/K_2O = 0.08–0.57, avg. 0.24). This also can be documented on the distribution of Zr which, in general, indicates terrigenous input.

The average SiO_2 content in graptolitic shales firstly decreases from Llandovery to Wenlock to reach approximately the same level of concentration in the Ludlow-Pridoli graptolitic shales. Similar trend is followed up by $C_{org.}$ and Cr. The average value of $C_{org.}$ is 2.65 wt.% in the Llandoverian black shales and with the deepening of the basin it generally increases to 3.61 wt.% in the Wenlockian shales. Ludlow-Pridoli graptolitic shales have the average $C_{org.}$ lower than Wenlockian facies – 2.83 wt.%, possibly indicating termination of basinal subsidence and a period of carbonate deposition. The highest $C_{org.}$ – 7.5 wt.% was found in the Wenlockian shale from the Oberbuchach locality. The average content of total sulphur in the Carnic Alps Silurian graptolitic shales varies from 1.07 wt.% (Llandovery), through 1.69 wt.% (Wenlock) to 1.29 wt.% in Ludlow-Pridolian shales. The highest total sulfur content of 5.42 wt.% was found in the Wenlockian sulphidic black shale from the Oberbuchach locality which also bear the highest $C_{org.}$ = 7.5 wt.% and anomalous Zn, Cu and As concentrations.

The highest average CaO, MgO, MnO and P_2O_5 values have been found in the Wenlockian graptolitic shales. The Wenlockian and Ludlow-Pridolian shales have a similar distribution of Zr which generally decreases with increasing CaO content. The anomalous MnO = 3.18 wt.% was detected in chemically immature Wenlockian shale at Oberbuchach, which together with low $C_{org.}$, $S_{tot.}$, S/C (0.23), DOP (0.04) and V/Cr (1.8) values but relatively high Al, K, Na and Zr contents support that this shale has originated under more aerated conditions (part of the Eß aerated horizon).

Table 1.
Average chemical composition of Silurian graptolitic shales of the Carnic Alps compared to other graptolitic shales

	PRAGUE BASIN		NORTHEASTERN BAVARIA	ARMORICAN MASSIF		CARNIC ALPS					
	Llandovery	Wenlock	Llandovery--Ludlow	Llandovery	Wenlock	Llandovery		Wenlock			Ludlow--Pridoli
	Clayey mudstones	Calcareous mudstones	Lower graptolitic shales	Clayey shales	Clayey shales	Graptolitic shales	Sulphidic grapt. Ca-shale	Graptolitic shales	Sulphidic grapt.shale	Chert	Graptolitic shales
	n=13	n=4	n=26	n=12	n=13	n=7	n=1	n=7	n=1	n=1	n=6
	Štorch and Pašava (1989)		Dill (1986)	Dabard and Paris (1986)		this work					
SiO_2	73.49	60.84	61.83	47.75	71.79	68.41	14.12	56.89	47.83	89.13	68.68
TiO_2	0.91	0.79	0.59	0.93	0.53	0.45	0.26	0.36	0.48	0.1	0.32
Al_2O_3	9.82	10.1	11.45	15.4	11.28	7.86	6.24	6.72	8.32	1.78	5.21
Fe_2O_3	2.09	2.11	4.24	1.76	0.79	3.5	8.35	3.33	7.93	0.39	0.93
FeO	0.53	1.64	n.d.	n.d.	n.d.	2.22	19.48	1.78	0.46	1.55	1.53
MnO	0.02	0.035	0.02	tr.	tr.	0.11	0.642	0.62	0.26	0.156	0.06
MgO	0.75	1.51	1.49	0.58	0.49	1.06	3.01	1.15	1.48	0.34	0.84
CaO	0.49	7.1	4.31	tr.	0.12	3.1	10.34	9.83	6.8	2.14	7.05
Li_2O	0.003	0.003	n.d.	n.d.	n.d.	0.005	0.005	0.006	0.008	0.002	0.004
Na_2O	1.07	1.28	0.14	0.11	0.15	0.48	0.27	0.45	0.3	0.17	0.2
K_2O	2	2.24	3.46	3.81	2.55	2.06	1.86	1.66	2.16	0.37	1.38
P_2O_5	0.19	0.13	1.61	0.11	0.06	0.5	0.59	0.67	0.38	0.14	0.26
CO_2	0.11	5.1	n-d.	n.d.	n.d.	2.29	19.42	7.24	3.3	1.61	5.34
$C_{org.}$	3.23	2.86	14.13	n.d.	n.d.	2.65	5.41	3.61	7.51	1.2	2.83
$S_{tot.}$	0.22	0.83	3.94	n.d.	n.d.	1.07	4.93	1.69	5.42	0.28	1.29
Rb	59	70	n.d.	207	118	69	60	56	74	12	45
Pb	23	14	46	n.d.	n.d.	53	62	69	216	16	36
Sr	237	179	129	359	132	88	156	250	161	54	164
Y	48	35	n.d.	123	52	44	71	48	45	16	30
U	10	8	42	n.d.	n.d.	10	34	9	7.5	7.5	7.5
Zr	114	109	175	215	113	129	74	83	142	16	58
Sn	7	7	n.d.	n.d.	n.d.	3.5	3.5	3.5	3.5	3.5	3.5
Nb	13	10	n.d.	n.d.	16	8	3.5	7	12	3.5	7
V	n.d.	n.d.	3817	2392	1748	299	251	237	504	71	212
Mo	33	48	137	n.d.	n.d.	11	17	18	14	30	16
Cu	89	112	353	n.d.	n.d.	68	56	137	162	50	66
Ni	77	127	331	n.d.	84	66	203	97	159	47	64
Cr	135	107	589	202	93	235	73	166	390	901	241
Zn	52	258	3144	n.d.	n.d.	59	215	128	269	42	110
As	16	8	130	n.d.	n.d.	31	152	47	174	3.5	15
Au	4.3	3.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

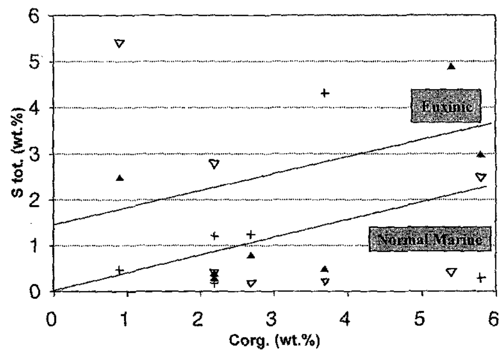

Fig. 2:
$C_{org.}/S_{tot.}$ plot for the Silurian graptolitic shales of the Carnic Alps (Llandovery = filled triangles, Wenlock = open triangles, Ludlow-Pridoli = crosses); reference lines for normal marine and euxinic environment from Berner and Raiswell (1984).

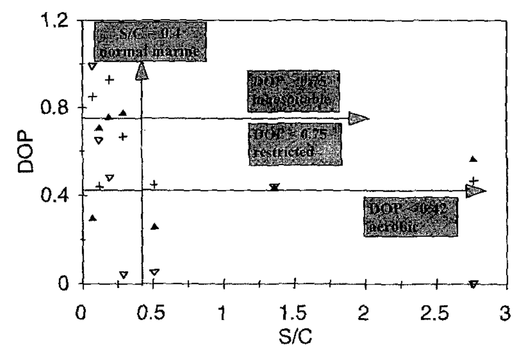

Fig. 3.
S/C versus DOP plot for the Silurian graptolitic shales of the Carnic Alps (Llandovery = filled triangles, Wenlock = open triangles, Ludlow-Pridoli = crosses).

Organic carbon vs. sulphur plots have proved useful in characterizing modern and ancient sedimentary depositional environment. Normal marine environment, with periods of euxinic conditions (anoxic-sulphidic water column) are documented on Fig. 2. Relative to the Holocene "normal marine" sediment line (sediments deposited in oxic environments but with sufficient organic matter to allow pore waters to go anoxic after deposition and with average S/C = 0.4), there are many samples of Austrian graptolitic shales with excess $C_{org.}$ or excess S. In marine environments with anoxic bottom waters, iron-sulphide formation occurs in the water column resulting in excess sedimentary sulphur and a higher S/C ratio in sediments with low $C_{org.}$ contents. The Carnic Alps Silurian graptolitic shales were deposited in normal marine environment with periods of anoxic deposition especially during Llandovery and Wenlock.

Degree of pyritization (DOP), which is the ratio of pyritic Fe (Fepy.) to pyritic Fe + acid-soluble Fe (BERNER, 1984) can be also used for recognizing the degree of bottom-water oxygenation in organic carbon-bearing rocks. In our calculations we have used $Fe_{py.}/Fe_{tot.}$ values because there are no significant concentration of Fe in silicates or other non-suphidizable sites in our samples. RAISWELL et al. (1988) have found that aerobic sediments (deposited in fully oxygenated bottom waters with DOP < 0.42) can be clearly separated from restricted samples (deposited in water with low O_2 concentrations – 0.46 < DOP < 0.80), but the latter have some overlap with the inhospitable bottom category (sediments deposited in environment where little or no O_2 is present, and H_2S may be continually or intermittently present – 0.55 < DOP < 0.93). Our DOP values are summarized in Table 2 and plotted in Fig. 3. The data suggests that the majority of Silurian graptolitic shales in Carnic Alps was deposited under restricted marine conditions with apparent periods of inhospitable bottom conditions (DOP values (0.75). Only few samples indicate more oxygenated conditions.

Scatter plot of percent total iron ($Fe_{tot.}$) versus percent total sulphur (Fig. 4), shows mostly good correlations with most values plotting near the stoichiometric pyrite line (S = 1.15 Fe), which means that most iron is fixed as pyrite. Only two samples contain excess iron (not fixed as pyrite but in the form Ca-Fe-carbonate and Fe-oxide – weathering product).

Trace elements

The distribution of trace elements in the Silurian graptolitc shales from the Carnic Alps is listed in Table 3.

It is clear, that except of locally deposited carbonate-rich sulphidic shale in the upper Llandovery, the Wenlockian calcareous shales bear the highest average metal concentrations. Similar trend applies for the Wenlockian calcareous facies in the Prague Basin (Bohemia). Table 3 shows the comparison of the distribution of selected trace elements in the Silurian shales from the Carnic Alps with that of the average black shale (VINE and TOURTELOT, 1970), normal and metal-rich black shale (KANE et al., 1990) and the average siliceous and carbonaceous black shale (YUDOVICH and KETRIS, 1997). Compared to all the reference concentrations in various average black shales, the Silurian graptolitic shales from

Table 2.
C-S-Fe contents, S/C ratios, and degree of pyritization (DOP) for the Silurian graptolitic shales (Carnic Alps, Austria)

	CARNIC ALPS											
	Llandovery n=7				Wenlock n=7				Ludlow Pridoli n=6			
	x	$x_{min.}$	$x_{max.}$	2δ	x	$x_{min.}$	$x_{max.}$	2δ	x	$x_{min.}$	$x_{max.}$	2δ
$C_{org.}$ (%)	2.65	0.91	5.82	1.68	3.61	0.91	7.51	2.04	2.83	0.55	5.18	1.67
$S_{tot.}$ (%)	1.08	0.08	2.96	1.16	1.69	0.17	5.42	1.98	1.29	0.19	4.25	1.51
S/C	0.76	0.07	2.76	0.98	0.42	0.11	0.72	0.26	0.66	0.13	2.72	1.01
$Fe_{py.}$ (%)	2.22	0.88	7.67	2.45	1.53	0.001	4.55	1.59	1.53	0.47	3.0	1.02
$Fe_{tot.}$ (%)	5.72	1.26	25.17	8.64	4.86	1.83	9.1	2.84	2.47	0.8	4.73	1.63
DOP	0.55	0.26	0.78	0.22	0.38	0.001	0.99	0.37	0.64	0.44	0.93	0.22
x – mean, $x_{min.}$ – minimum value, $x_{max.}$ – maximum value, 2δ – standard deviation												

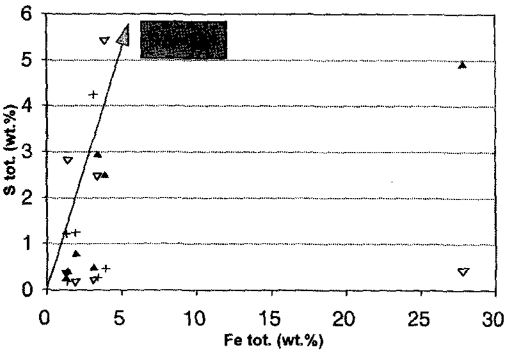

Fig. 4.
$Fe_{tot.}$ vs. $S_{tot.}$ plot for Silurian graptolitic shales of the Carnic Alps (Llandovery = filled triangles, Wenlock = open triangles, Ludlow-Pridoli = crosses).

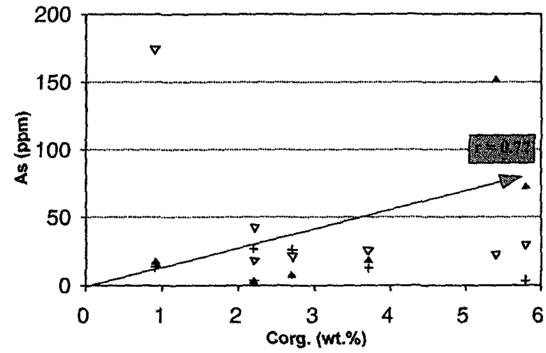

Fig. 5.
$C_{org.}$/As plot for Silurian graptolitic shales of the Carnic Alps (Llandovery = full triangles, Wenlock = open triangles, Ludlow-Pridoli = crosses).

the Carnic Alps are clearly enriched in Cr values. These values seem to increase with increasing Si-contents (higher Cr in "siliceous" Llandoverian facies decreases in carbonate-dominating Wenlockian shales, however, reaching a peak value in the Wenlockian chert and in the Ludlow-Pridolian facies returning to the similar distribution pattern as in the Llandoverian shales). It is also apparent that beside sulphidic graptolitic shales especially Carnic Alps Wenlockian graptolitic shales, which have a number of metals (Cr, Cu, Pb, Zn) comparably high as those in metalliferous black shale (SDO-1 analytical standard of the Devonian black shale – KANE et al. 1990), can be classified as metal-rich facies.

The importance of $C_{org.}$ and S for metal concentration has been stressed by many authors (LEVENTHAL, 1985; DISNARD and SUREAU, 1990; GIZE and PAŠAVA, 1995 and others). Calculation of correlation coefficients suggests mutually close relationship between $C_{org.}$ and S ($r = 0.57$) and thus a significant link between $C_{org.}$ and the group of As ($r = 0.77$), Pb ($r = 0.75$), Ni ($r = 0.60$), and V ($r = 0.69$) on one hand (see Figs. 5, 6 and 7), and a similarly important relationship between S and As ($r = 0.91$), Ni ($r = 0.71$), and Pb ($r = 0.70$) – see Figs. 8, 9, and 10.

Determinations of platinum group elements (Pd and Pt) in selected graptolitic shales has shown that the content of Pd varies from 7 to 30 ppb and Pt from 4 to 54 ppb. The highest Pd concentration was found in the Wenlockian chemically mature sulphidic metal-rich calcareous graptolitic shale from Oberbuchach. Anomalous Pt value (54 ppb) was detected in the uppermost Llandoverian chemically mature sulphidic metal-rich calcareous graptolitic shale from the same locality. Similarly good correlation was found in the Silurian graptolitic shales of the Prague Basin (ŠTORCH and PAŠAVA, 1989).

ROESLER et al. (1971) and others have used a V/Cr ratio as a facies indicator for pelitic sediments deposited under oxygenated conditions (V/Cr < 2), or as sapropelites (V/Cr > 2). The values of this ratio are mostly below 2 in all studied Austrian samples, ranging 0.8–2.5 (avg. 1.3) in Llandoverian, 0.9–2.6 (avg. 1.7) in Wenlockian, and 0.2–2.1 (avg. 1.0) in Ludlow-Pridolian graptolitic black shales. Together with the S/C and DOP values, such a distribution indicates mostly weak oxic sedimentation conditions, possibly with local anoxic periods.

Comparison of chemistry of the Carnic Alps graptolitic shales with that of similarly old graptolitic shales of the Prague Basin, Northeastern Bavaria and Armorican Massif have shown that the Carnic Alps Llandovery sediments are generally very close to those of the Prague Basin. Looking at the distribution of major and trace elements in more detail, there

Table 3.
Average contents of selected trace elements in Silurian graptolitic shales of the Carnic Alps and comparison with their contents in black shales

	Carnic Alps			Average black shale	SDO-1 normal black shale	SDO-1 metalliferous black shale	Average siliceous black shale	Average carbonaceous black shale
Element (ppm)	Llandovery	Wenlock	Ludlow-Pridoli	Vine and Tourtelot (1970)	Kane et al. (1990)		Yudovich and Ketris (1997)	
	average	average	average	average	average	average	median	median
As	31	47	15	n.d.	69	132	30	34
Cr	235	166	241	100	66	132	86	45
Cu	68	137	66	70	60	120	100	55
Mo	11	18	16	10	134	134	29	16
Ni	66	97	64	50	99.5	199	63	41
Pb	53	69	36	20	28	56	17	26
Rb	69	56	45	n.d.	126		47	39
Sr	88	250	164	200	75		140	480
U	10	9	7.5	n.d.	49	49	13	10
V	299	237	212	150	160	320	250	99
Zn	59	128	110	<300	64	128	160	140
Zr	129	83	58	70	n.d.	n.d.	140	74

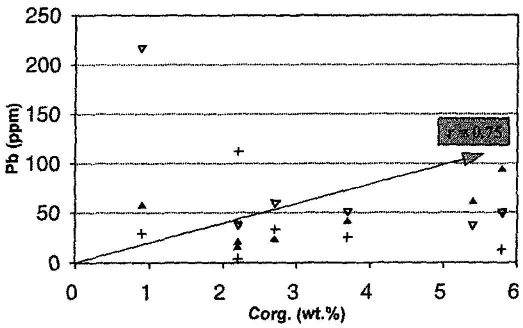

Fig. 6.
$C_{org.}$/Pb plot for Silurian graptolitic shales of the Carnic Alps (Llandovery = full triangles, Wenlock = open triangles, Ludlow-Pridoli = crosses).

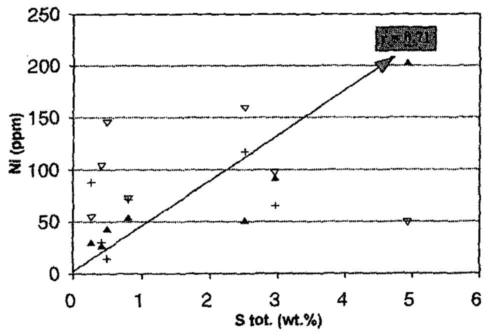

Fig. 9.
$S_{tot.}$/Ni plot for Silurian graptolitic shales of the Carnic Alps (Llandovery = full triangles, Wenlock = open triangles, Ludlow-Pridoli = crosses).

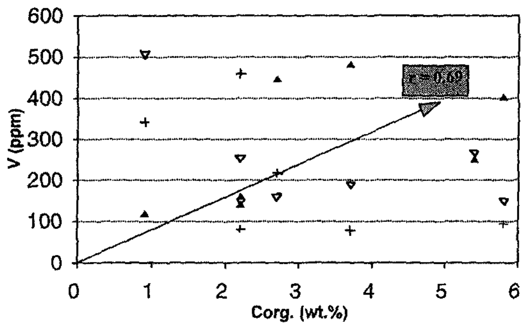

Fig. 7.
$C_{org.}$/V plot for Silurian graptolitic shales of the Carnic Alps (Llandovery = full triangles, Wenlock = open triangles, Ludlow-Pridoli = crosses).

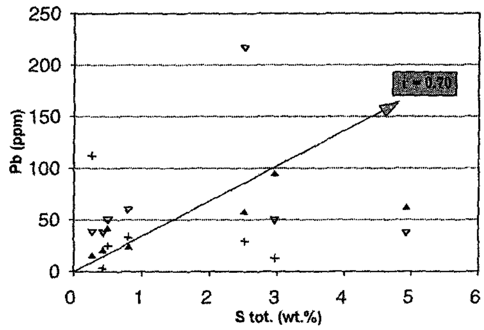

Fig. 10.
$S_{tot.}$/Pb plot for Silurian graptolitic shales of the Carnic Alps (Llandovery = full triangles, Wenlock = open triangles, Ludlow-Pridoli = crosses).

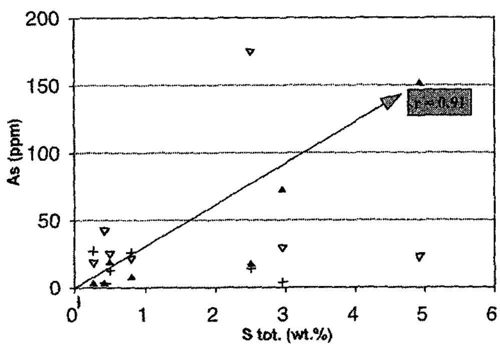

Fig. 8.
$S_{tot.}$/As plot for Silurian graptolitic shales of the Carnic Alps (Llandovery = full triangles, Wenlock = open triangles, Ludlow-Pridoli = crosses).

are, however, some differences (Table 1). The Carnic Alps shales have higher CaO values at similar SiO_2 values and contain lower $C_{org.}$ contents. Strontium concentrations are significantly higher in the Prague Basin Llandovery clayey mudstone while the Carnic Alps facies possess apparently lower Cr values. The Llandoverian black shales of the Ar-morican Massif are strongly depleted in SiO_2 but richer in Al_2O_3, Rb, Sr, Z, Zr and V than those of the Carnic Alps and Prague Basin. The Carnic Alps Wenlockian graptolitic shales have slightly lower SiO_2, TiO_2, Al_2O_3 and significantly lower Na_2O values, however, they are markedly enriched in MnO, CaO, Zn and As when compared with the Wenlockian calcareous mudstone of the Prague Basin. Wenlockian shales of the Armorican Massif are characterized by significantly higher SiO_2 contents but strongly depleted in CaO and P_2O_5 in comparison with similar facies of the Carnic Alps and Prague Basin.

4. Conclusions

The overall geochemical trends are in good agreement with the results of previous sedimentological and paleontological studies that the basin had a steadily subsiding and transgressional regime from the Llandovery to the beginning of Ludlow.

Sudden appearance of Silurian black shales was causally related to a rapid rise of sea-level which followed the ice-cap melting at the end of the late Ordovician glaciation. Both sediments and biota were strongly affected by this event. With the beginning of the Silurian transgression and progressing subsidence in the region of the Carnic Alps, mostly chemically mature "siliceous" shales with generally higher Zr values were deposited in a normal marine environment. Our S/C, DOP and V/Cr values suggest that the majority of the Llandoverian graptolitic shales was deposited under restricted marine conditions with apparent periods of inhospitable bottom conditions (sulphidic metal-rich graptolitic shales were mostly deposited in environment where little or no O_2 was present, and H_2S may have been continuously or intermittently present; DOP values 0.75).

The character of sedimentation rapidly changed during the Wenlock when chemically less mature calcareous shales together with carbonates dominated. Again, our S/C, DOP and V/Cr values suggest changes of depositional environment from normal marine with oxygenated bottom waters (aerobic) to euxinic (inhospitable bottom conditions with mostly sulphidic calcareous graptolitic black shales). The termination of basinal subsidence in Upper Silurian (Ludlow-Pridoli), has resulted in sedimentation of chemically well mature graptolitic shales (± cherts), characterized mostly with higher Si but lower $C_{org.}$ and CaO values.

The changes in the distribution of major elements are also clearly reflected in the distribution of trace elements. Llandoverian, often "siliceous" graptolitic shales are depleted by Sr when compared to Wenlockian calcareous facies (Sr bound in carbonates). The highest average Zr and TiO_2 contents in the Llandoverian graptolitic shales reflect nearby continental source which was most likely not rich in metals. Conversely, the highest average concentration of Pb, Zn, Cu, Ni and As are associated with calcareous graptolitic shales of the Wenlock. These facies can be classified as metalliferous black shales. The distribution of metals in the Upper Silurian graptolitic shales is rather similar to that of the Llan-dovery but more calcareous Ludlow-Pridolian shales bear significantly higher Sr, Zr and Zn contents.

It has been documented that some of the Silurian graptolitic shales in the Carnic Alps are sulphur- and metal-rich and can be classified as metalliferous black shales. These rocks widely crop out in many places throughout the region. It should be noted that these facies could cause a potential environmental harm especially where carbonate lithology is missing.

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