

## **Identification of early Llandovery (Silurian) anoxic palaeo-depressions at the western margin of the Murzuq Basin (southwest Libya), based on gamma-ray spectrometry in surface exposures**

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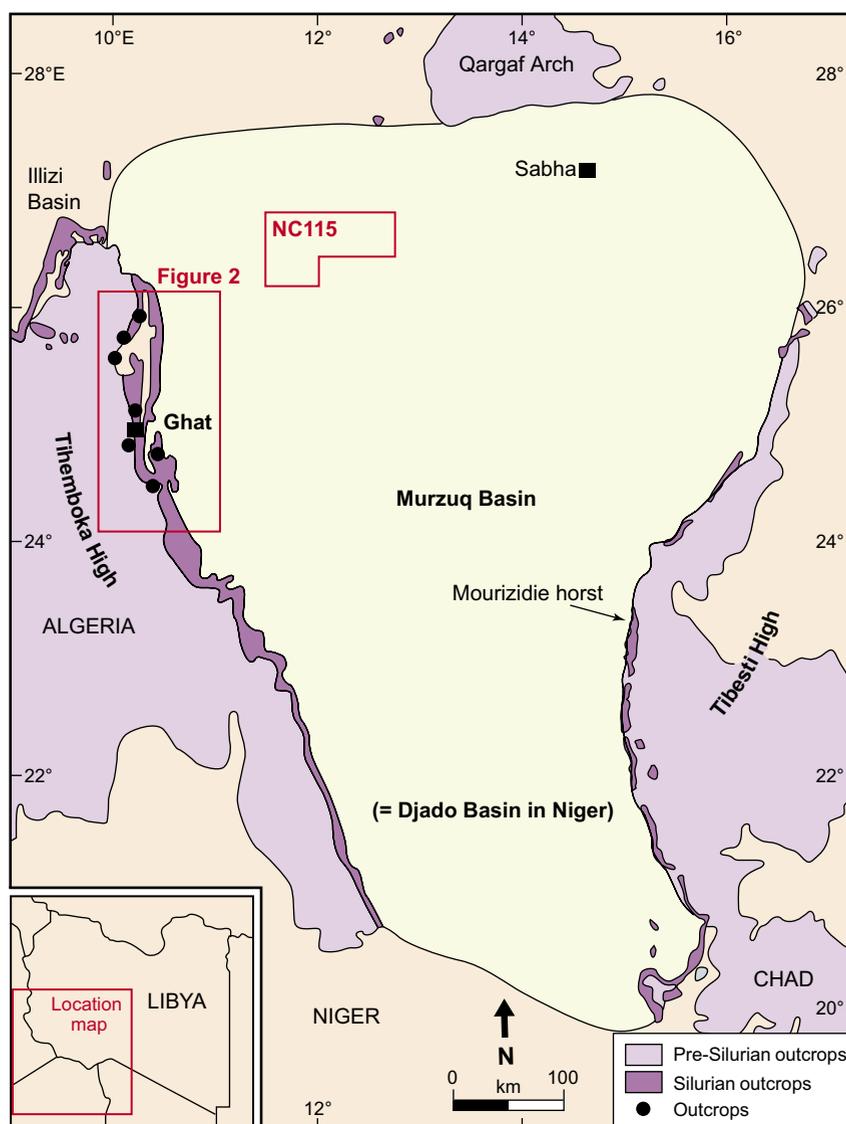
### **ABSTRACT**

Following the melting of the Gondwanan icecap and the resulting postglacial sea-level rise, organic-rich shales were deposited in shelfal palaeo-depressions across North Africa and Arabia during the latest Ordovician to earliest Silurian. The unit is absent on palaeohighs that were flooded only later when the anoxic event had already ended. The regional distribution of the Silurian black shale is now well-known for the subsurface of the central parts of the Murzuq Basin, in Libya, where many exploration wells have been drilled and where the shale represents the main hydrocarbon source rock. On well logs, the Silurian black shale is easily recognisable due to increased uranium concentrations and, therefore, elevated gamma-ray values. The uranium in the shales "precipitated" under oxygen-reduced conditions and generally a linear relationship between uranium and organic content is developed. The distribution of the Silurian organic-rich shales in the outcrop belts surrounding the Murzuq Basin has been long unknown because Saharan surface weathering has commonly destroyed the organic matter and black colour of the shales, making it complicated to identify the previously organic-rich unit in the field. In an attempt to distinguish (previously) organic-rich from organically lean shales at outcrop, seven sections that straddle the Ordovician-Silurian boundary were measured by portable gamma-ray spectrometer along the outcrops of the western margin of the Murzuq Basin.

It was found that the uranium content of the shales remained largely unaltered by the weathering processes and could therefore be used as a valid proxy parameter to distinguish between pre-weathering organically rich and lean shales. It is now possible to identify and map-out the thickness and approximate organic richness of the black shale using measurement of uranium radiation. Five of the newly measured sections are characterised by uranium-enriched intervals, representing areas of earliest Silurian palaeo-depressions. Major uranium peaks are absent in the spectral gamma-ray curves of two other sections, which are interpreted to mark earliest Silurian palaeo-highs. The new data on the distribution of Silurian black shales from the outcrop belt was integrated with subsurface data from the Murzuq Basin. The resulting map of the distribution of black shales may help with predictions of the occurrence of this unit in less well-explored areas of the basin. Graptolite biostratigraphic data suggests that the anoxic event centred on the middle Rhuddanian, with more oxygenated conditions and onset of deposition of organically leaner shales having commenced sometime during the late Rhuddanian. The presence of anoxic palaeo-depressions during the earliest Silurian within the Ghat outcrop belt indicates that the Tihemboka High at the western margin of the Murzuq Basin could not have been a positive structure during this time.

### **INTRODUCTION**

Following the Late Ordovician glaciation of Gondwana, a major sea-level rise occurred during the latest Ordovician and early Silurian, which led to the deposition of a shale-dominated unit in many parts of North Africa and Arabia. The initial transgression was associated with a pronounced anoxic event resulting in the formation of organic-rich "hot" shales in the deepest parts of palaeo-depressions across the North Gondwanan shelf. The distribution of these black shales is now well-



**Figure 1:** Location map of the Murzuq Basin showing the NC115 Concession and the study area in the Ghat outcrop belt on the western margin of the basin.

known for the subsurface of areas that have been intensely explored for hydrocarbons, such as parts of the western Libyan Ghadames and Murzuq basins (Lüning et al., 2003a; Lüning et al., 2000) (Figure 1). Information on the regional distribution of this unit is required by the petroleum industry, as this organic-rich shale represents an important source rock for rich oil reserves in many North African and Arabian basins, including the western Libyan basins.

However, currently little is known about the occurrence of this lower Silurian organic-rich shale in the less-explored parts of the northern Gondwanan Palaeozoic basins where only a few wells have been drilled. In some basins, such as the south-eastern Libyan Kufra Basin and the southern Saudi Arabian Rub' Al-Khali Basin, it is unknown whether the Silurian source rock has been deposited at all, which affects the overall petroleum prospectivity of these basins.

Here we present spectral gamma-ray data from the interval straddling the Ordovician-Silurian boundary in seven field sections in the Ghat outcrop belt at the western margin of the Murzuq Basin (Figures 1 to 3). Usually, the hot shale – and hence its regional distribution – cannot be identified and mapped in outcrop sections because the typical black colour has been altered to red/green/grey tones due to oxidation under desert weathering conditions (Lüning et al., 2003b). The organic matter

is often completely destroyed. Using the hot shale's typical enrichment in uranium it is now possible to identify the Silurian "hot shale" at outcrop and map its lateral distribution along the western margin of the Murzuq Basin based on the uranium curves of the seven sections studied.

## GEOLOGICAL FRAMEWORK

### Structural Development

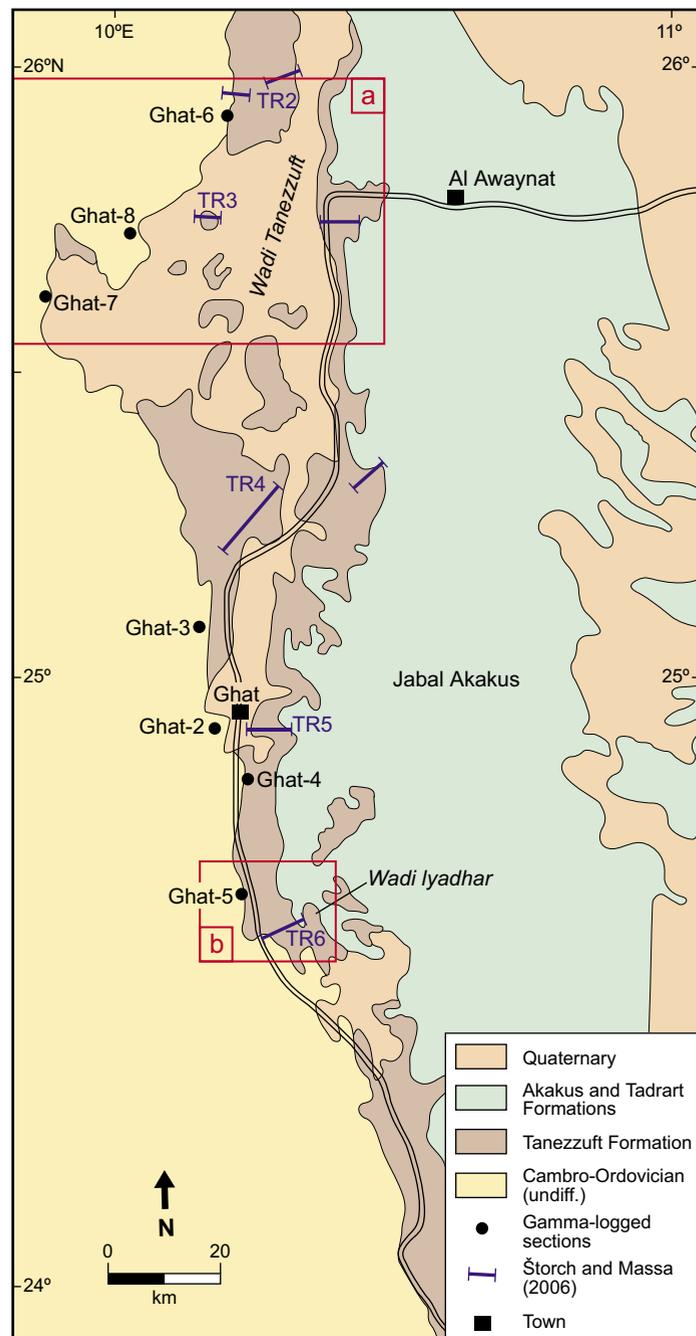
The Murzuq Basin is a Palaeozoic sag basin filled in by Cambrian to Cretaceous continental to shelfal sandstones, siltstones and shales (Figure 1). Following the late Neoproterozoic Pan African Orogeny, Libya entered a tectonically quieter phase in the Cambrian. Intraplate processes dominated during the Cambrian to mid Silurian, including local transpressional/transensional movements as evidenced on seismic from the subsurface of the Murzuq Basin (Davidson et al., 2000). A major intraplate uplift phase affected the central parts of the Murzuq Basin during the late Silurian and Early Devonian (the misleadingly termed "Caledonian" tectonic phase) resulting locally in erosion that cut deeply into the Silurian Tanezzuft shales (Davidson et al., 2000).

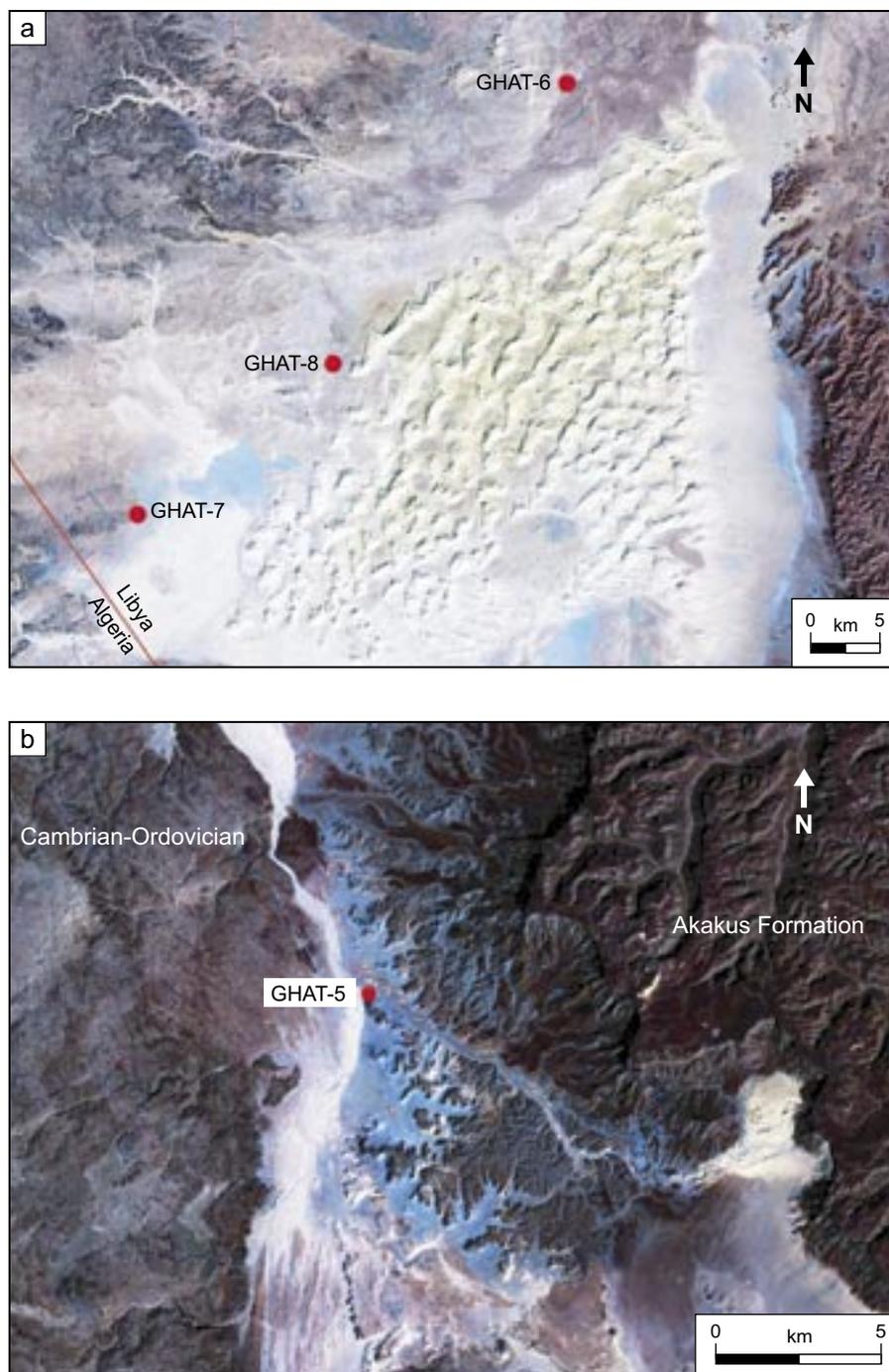
Uplift of the basin flanks, including the Lower Palaeozoic outcrops at Ghat (Figure 1), commenced during the Early Devonian, with a major part of the activity believed to have occurred in the Cretaceous ("Austrian") to Tertiary ("Alpine") tectonic phases. Notably, the beginning of margin uplift in the Murzuq Basin postdates deposition of the early Silurian shales studied in south-western Libya.

### Lithostratigraphy and Facies Development

The shale-dominated unit deposited during the postglacial sea-level rise is termed "Tanezzuft Formation" in Libya (Figure 4), and genetically extends east- and westwards across northern Gondwana from Morocco to Oman (Lüning et al., 2000). Locally, the basal few metres to 30 m of this unit are organically rich and referred to as "hot shale" in the oil-exploration terminology due to increased gamma-

**Figure 2: Geological map of the Ghat study area and locations of measured sections. Also shown are the locations of sections studied by D. Massa in the late 1950s. Basemap modified after Štorch and Massa (2006). Boxed areas mark locations of satellite images shown in Figures 3a and b.**





**Figure 3:** Satellite image of sections Ghat-5 to 8 in the northern and southern parts of the study area (see Figure 2 for location map). The Silurian Tanezzuft Shale in the Ghat outcrop belt is part of an eastward-dipping Palaeozoic unit and forms a valley that lies between harder Cambrian-Ordovician sandstones to the west and Silurian sandstones (Akakus Formation) to the east. Satellite images courtesy Nasa Applied Sciences Directorate (<https://zulu.ssc.nasa.gov/mrsid/>).

ray response caused by uranium (Figure 4). In the Murzuq Basin, the Tanezzuft Shale becomes up to 500 m thick with the vast majority being organically lean. Shale sedimentation was ended by a NW-directed progradation of coastal sandstones that overlie the hemipelagic pelites (Bellini and Massa, 1980).

In the Ghat study area, the Tanezzuft shales are underlain by glacial to periglacial sandstones of the Ashgillian Mamuniyat Formation, or where absent due to pre-Tanezzuft erosion, by shales and siltstones of the Caradocian to Ashgillian Melez Shuqran Formation that was also affected by periglacial processes (Fello, 2001; Fello and Turner, 2004) (Figure 4).

## Material and Methods

Spectral gamma-ray measurements were carried out in seven sections that straddle the Ordovician-Silurian boundary using a portable spectrometer (3" x 3" detector, GRS-2000, GF Instruments, formerly Geofyzika, Brno) with 10–46 measurements per section (Figures 1 and 2). A three-minute measuring interval was selected allowing quantitatively reproducible results (see Lüning et al., 2004, for details concerning measuring duration).

The thickness of the lower Silurian organic-rich shale in exploration wells was measured in well logs based on its characteristically high gamma-ray signature (see Lüning et al., 2000 for details on log characteristics of the Silurian hot shale). In this contribution, we define hot shales as shales with gamma-ray values greater than 150 API corresponding roughly to total organic carbon (TOC) values of greater than 1.0% for oil-window maturities (Lüning et al., 2003b).

The close relationship of uranium and TOC in Type I/II organic-rich strata is based on the fact that in seawater  $U^{6+}$  is carried in solution as uranyl-carbonate complexes that precipitate under oxygen-depletion, reducing conditions during deposition (Postma and ten Veen, 1999; Wignall and Myers, 1988). The authigenic  $U^{4+}$  enrichment in organic-rich shales is independent of the purely detrital potassium and thorium, as evidenced by the general decoupling of the uranium peak versus the potassium and thorium spectral gamma-ray signals in most basal Silurian field sections (Figure 5), and by wireline-log data from the same interval in the subsurface of the Murzuq Basin (Figure 6). Uranium also occurs in the detrital fraction but  $U_{detr}$  concentrations in sediments usually co-vary with those of potassium and thorium (Wignall and Myers, 1988).

## RESULTS

### Lithologies

Colours of the studied shales included red, light to medium grey, and in one case also dark grey (Figure 7c). Black colours, as observed for the Silurian organic-rich shales in the subsurface of the Murzuq Basin, have not been found at outcrop. An exception occurs in a two-metre-deep trench dug by a bulldozer north of Ghat (25°06'30.2" N, 10°08'40.8"E) where less-weathered, black, graptolite-rich shales occur.

In all field sections studied, the shales are strongly weathered, with some of the shales having a very soft, flaky, paper-like character. The shales are interbedded with wavy/rippled siltstone and fine sandstone beds that are mm- to a few cm-thick. Hummocky-cross stratification occurs in some of the coarser units.

### Spectral Gamma-Ray

Spectral gamma-ray data from well H29-NC115 from the Murzuq Basin (Figure 8c) indicate that the high total gamma-ray values of the lower Silurian hot shale are almost entirely due to an increase in uranium, whereas only a moderate to no increase occurs in the potassium and thorium concentrations

	Period	Epoch	Formations
SILURIAN	Upper	Ludlow./Prid	Akakus Formation
		Wenlock	
SILURIAN	Lower	Llandovery	Tanezzuft Formation
			Cold Shale Hot Shale
ORDOVICIAN	Upper	Ashgill	Hirnantian Shale
			Mamuniyat Formation
		Caradoc	Melez Shuqran Formation
	Middle	Llanv./Lland.	Hawaz Formation
	Lower	Arenig	Achebyat "H9" Formation
		Tremadoc	

**Figure 4: Simplified Ordovician-Silurian lithostratigraphy of the Murzuq Basin in southwest Libya (Repsol Oil Operations internal data, modified after Banerjee, 1980).**

## GHAT-5 SECTION

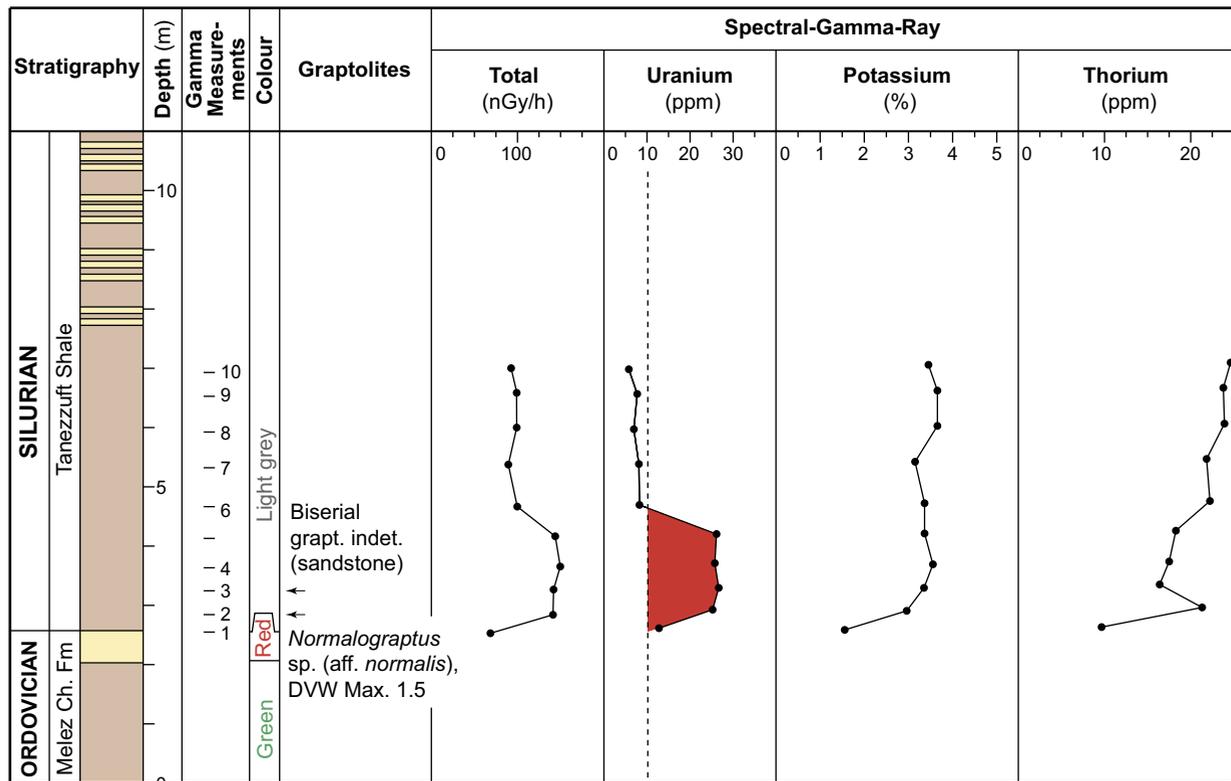


Figure 5: Lithostratigraphy and spectral gamma-ray data for section Ghat-5, located in the southern part of the Ghat outcrop belt in Wadi Iyadhar at the Algerian border. The basal uranium-rich interval is present but only 2 m thick.

compared to the overlying organically lean shales (Figure 6). Total gamma-ray radiation values of 150, 180 and 250 API correspond here to approximately 10, 12 and 15 ppm uranium, respectively.

Similar gamma-ray radiation patterns occur in five of the seven newly measured field sections where the basal Tanezzuft Formation is characterised by elevated total gamma radiation, dominated by uranium, with only small contributions by K and Th (Figures 5, 9 and 10). In the studied Tanezzuft Shale outcrop sections, K concentrations vary between 2.0–4.0%, and Th concentrations between 7–25 ppm. Maximum uranium concentrations, in the basal uranium-enriched part of the Tanezzuft Formation, are around 50 ppm (sections Ghat-2 and Ghat-7), while the shales above the uranium-enriched unit are characterised by uranium values ranging only between 4.5–7 ppm. A cut-off of 10 ppm was chosen to distinguish between the basal uranium-enriched shale unit and the overlying “normal” shales (Figure 10).

A south-to-north cross section of the uranium-enriched basal shales, across the Ghat outcrop belt, shows that uranium-curve shapes, thicknesses and peak-uranium concentrations of the unit vary greatly, partly even within a few tens of kilometres (Figures 2 and 10). Maximum thicknesses of the unit are reached in sections Ghat-3 and Ghat-7 with 12 m (Figures 7b and 7d), whereby uranium values are generally doubled in the latter section compared to the former. The unit reaches intermediate thicknesses in sections Ghat-2, Ghat-8 and Ghat-5 with 7.5 m, 5 m and 2 m, respectively. In all three sections of these the Mamuniyat Formation is absent. The uranium-enriched unit is absent in section Ghat-6 and nearly absent in section Ghat-4 where the uranium concentration exceeded 10 ppm slightly in only one measured horizon (Figures 7a and 10).

The distribution of the lower Silurian hot shale in the Ghat outcrop belt is illustrated in Figure 11a. Generally, the hot shale is present over a wide area with only two documented regions where it is missing.

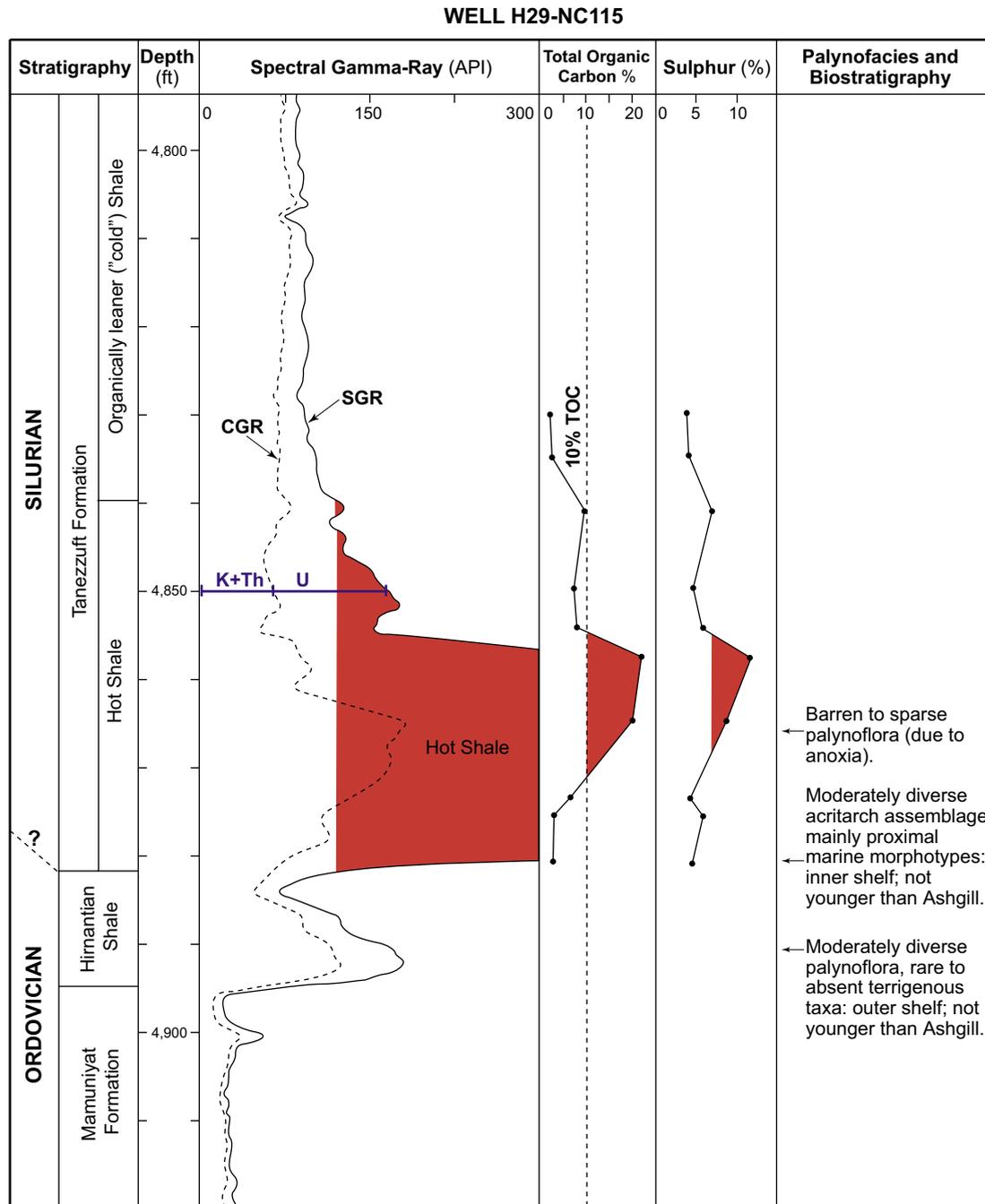


Figure 6: Spectral gamma-ray characteristics of the lower Silurian organic-rich shale in well H29-NC115 (see Figure 8 for location map). The high gamma-ray signal is almost entirely due to enrichment in uranium (note that values >300 API were not recorded). The palynoflora of the hot-shale interval was found to be barren to sparse, contrasting with moderately diverse palynofloras in the underlying Ordovician Hirnantian Shale. Note that core/cutting samples have been depth-shifted 8 ft downwards to correlate with log depth.

### Organic Richness

The organic richness of the hot shale was measured from fresh core and cuttings of well H29-NC115 (Figure 8c) and from weathered outcrop samples of field section Ghat-3 (Figure 9).

#### Subsurface samples

TOC values of the samples from well H29-NC115 range between 2.0 and 22.0% (Figure 6). The highest TOC values coincide with the interval with maximum gamma-ray radiation of greater than 300 API.

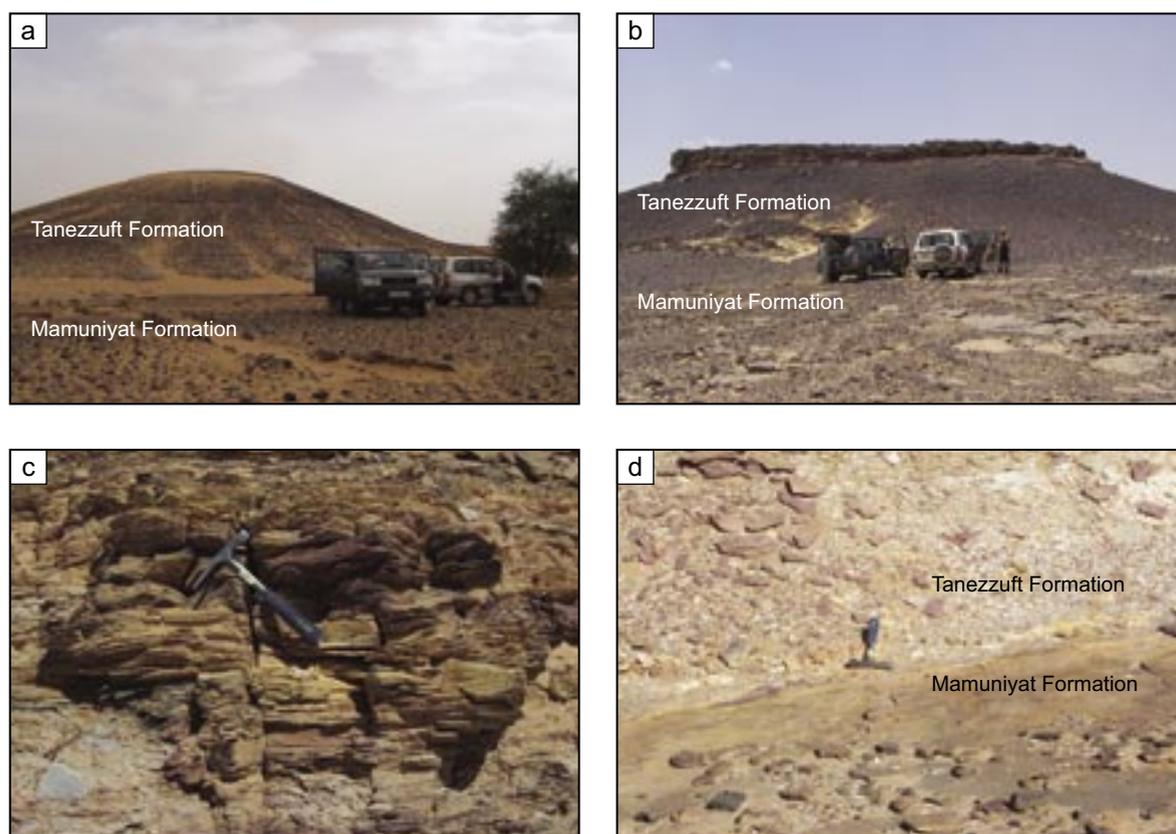
Following an organically very rich three-metre-thick interval with TOC values of 20.0% and more, organic richness generally decreases upwards. A similar decreasing trend is also developed in the gamma-ray curve. Furthermore, the variations occurring in organic richness are also reflected in the sulphur-concentration curve where values vary between 4.0–12.0% (Figure 6).

### ***Weathered outcrop samples***

TOC values of the samples from field section Ghat-3 range between 0.1 and 1.3% (Figure 9). Values higher than 0.5% generally correspond to the uranium-enriched hot shale interval at the base of the Tanezzuft Shale.

## **Biostratigraphy**

Graptolites are rather rare in the studied field sections, most probably due to poor preservation as a result of intense weathering. Graptolites were recovered from five sections, however in many cases only a rough generic identification was possible due to the poor preservation (Figure 1). All the collected graptolites yielded early Llandovery (Rhuddanian) ages. Only in a few cases was it possible to interpret the biostratigraphic age on a more precise biozone level. The thick uranium-enriched interval in section Ghat-3 (Figure 9) most probably includes the middle Rhuddanian *tariti-africanus* Zone. In section Ghat-4 where the uranium-enriched unit is nearly absent, the basal shales are dated as late Rhuddanian *fezzanensis* Zone based on the occurrence of *Neodiplograptus fezzanensis*. Early to middle Rhuddanian strata are missing here. The graptolite *Neodiplograptus* aff. *imperfectus* was recovered from the hot shale in well H6-NC115 and indicates an age no younger than early



**Figure 7: Ordovician-Silurian contact exposed in section Ghat-6 (a) and Ghat-7 (b) (see Figure 2 for location map). The vehicles stand on sandstones of the upper Ordovician Mamuniyat Formation, while the hills are formed by the basal part of the Silurian Tanezzuft shales. In section Ghat-7 (b) the exposed shales are capped by a volcanic rock unit. (c) Typical red and green colours of the Silurian hot shale in the Ghat outcrop belt (section Ghat-3). (d) Close-up of the contact between Ordovician Mamuniyat Formation sandstones and Silurian Tanezzuft shales in section Ghat-3.**

Rhuddanian. In the hot-shale core of well H29-NC115 graptolites are not preserved, probably due to tectonic deformation. Some relict pieces of highly reflecting material were observed in the core which may represent the deformed remains of graptolites. In contrast, the hot-shale core of well E1-NC174 contains abundant and well-preserved graptolites that yield a latest Ordovician (*persculptus* Zone) to Rhuddanian age (Lüning et al., 2000; Lüning et al., 2003b).

In general, palynomorphs cannot be recovered from Saharan outcrop samples because weathering has usually completely destroyed the palynomorph fauna. In fresh subsurface samples palynomorphs often offer the only means of biostratigraphic dating because graptolites are destroyed in cutting

samples. Nevertheless, the palynoflora from the Silurian hot shale in core H29-NC115 turned out to be barren (Figure 6). In contrast, a moderately diverse acritarch assemblage was found in the underlying Hirnantian Shale, dominated by mainly proximal morphotypes, indicating inner-shelf conditions (unpublished data, Repsol Oil Operations, Tripoli). Generally, a hiatus of variable duration has been predicted to occur between the Hirnantian Shale and the Tanezzuft hot shale (unpublished data, Repsol Oil Operations, Tripoli).

(a) B Field NC115

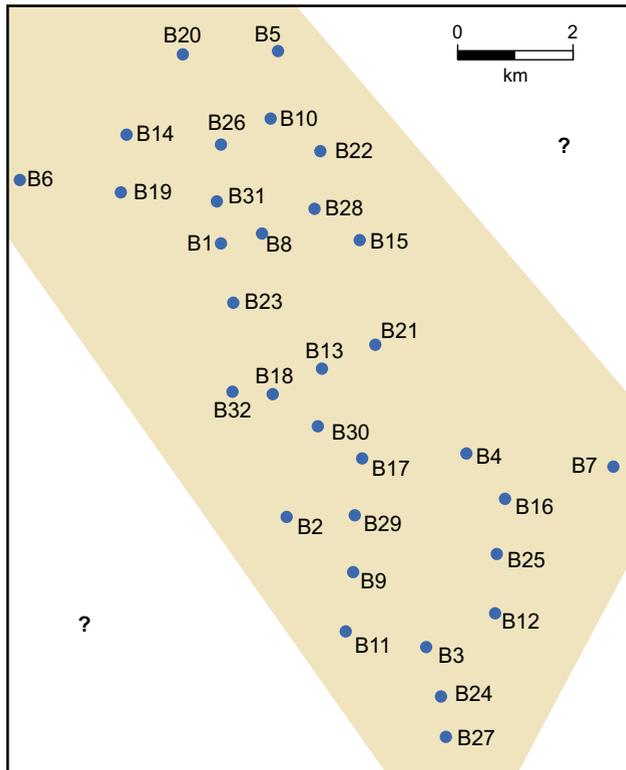
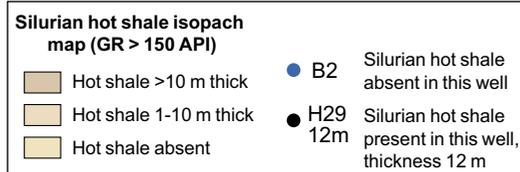
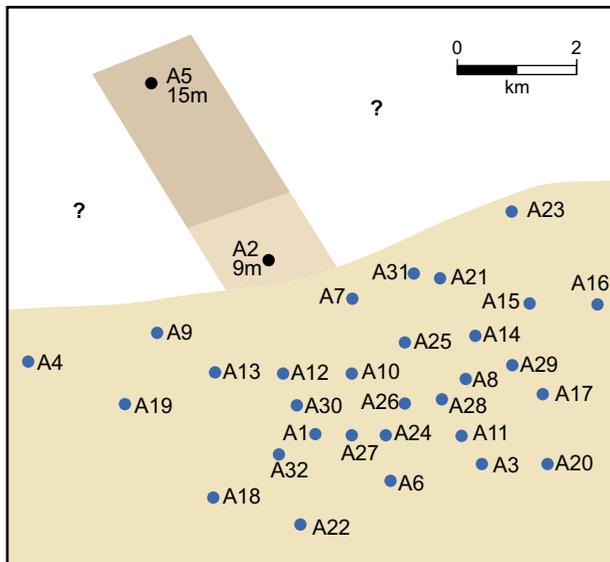


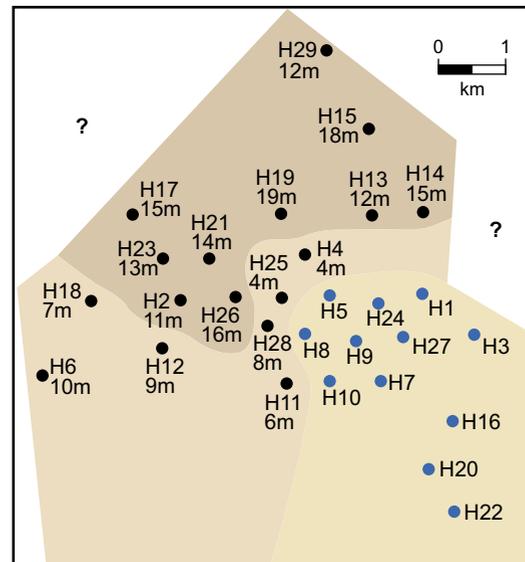
Figure 8: Isopach maps of the lower Silurian hot shale in the B, A and H fields of the Murzuq Basin concession NC115. For location of fields and integration of data into larger scale isopach trends see Figure 12.



(b) A Field NC115



(c) H Field NC115



GHAT-3 SECTION

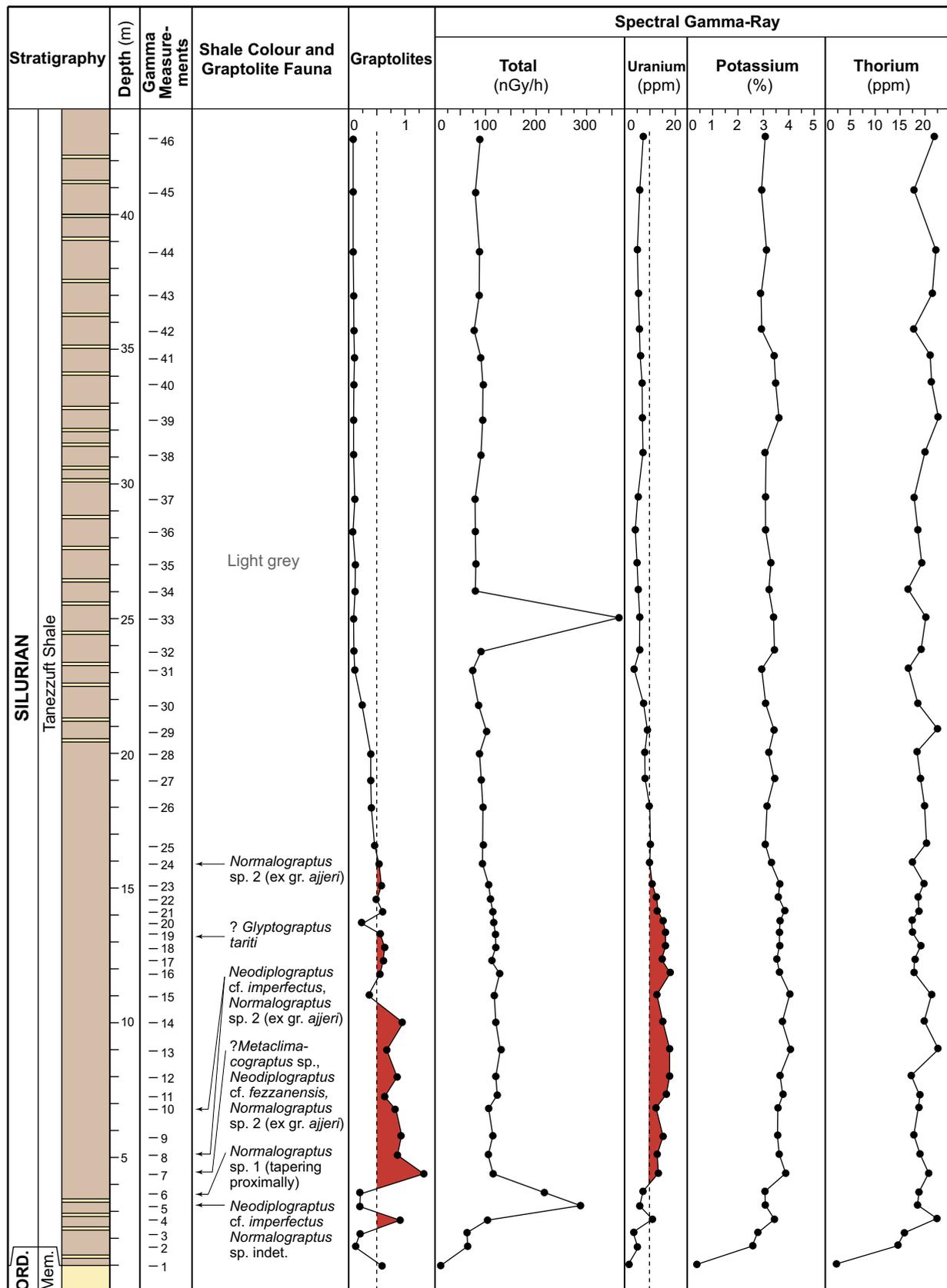


Figure 9: Lithostratigraphy and spectral gamma-ray data for section Ghat-3, located 10 km north of Ghat. The basal part of the Tanezzuft Formation is characterised by a 12-m thick interval enriched in uranium, interpreted here as representing the lower Silurian hot shale. Notably, uranium-values do not exceed 20 ppm, compared to peak values of 50 ppm in sections Ghat-2 and Ghat-7.

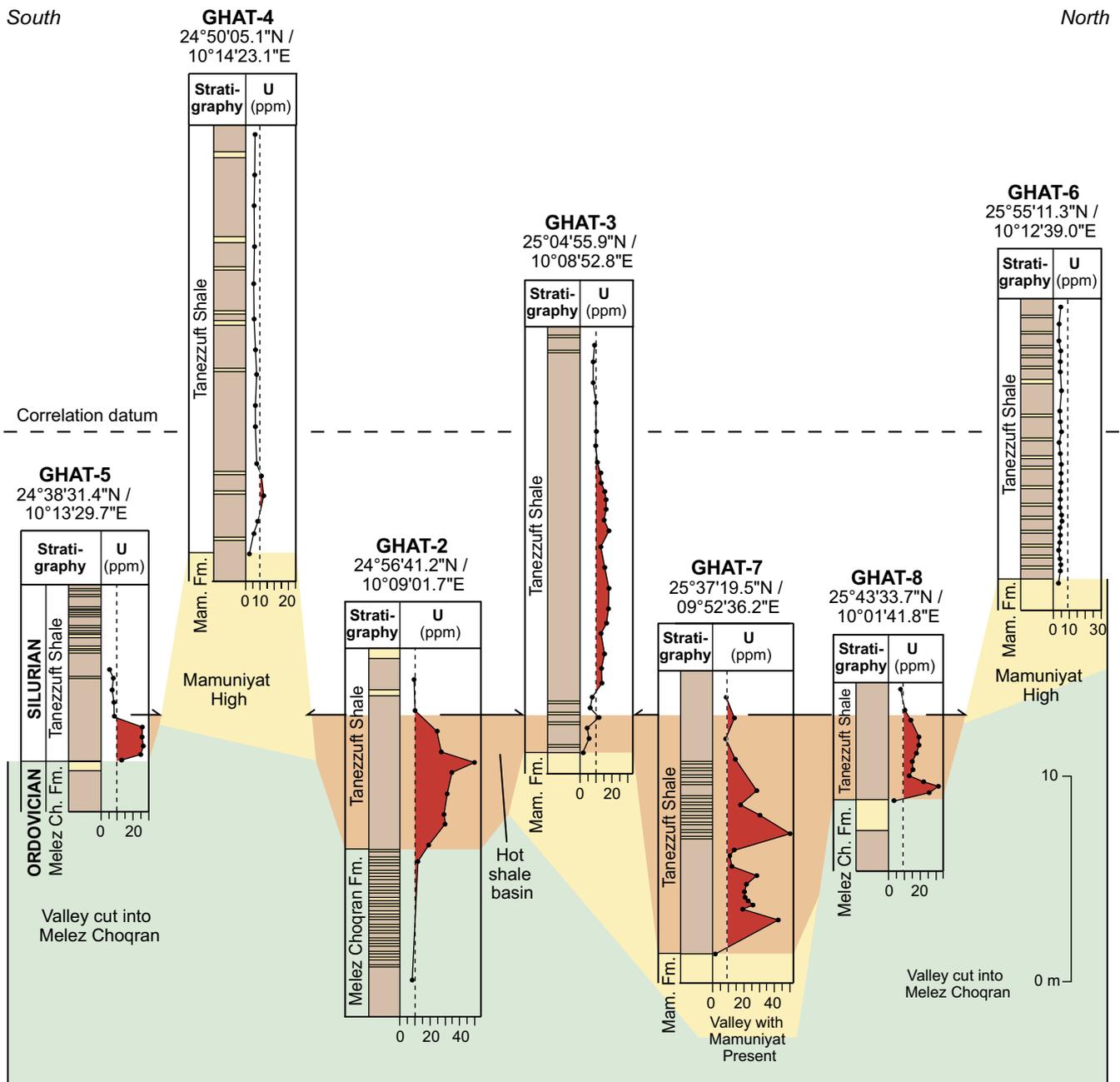


Figure 10: Cross section of the seven basal Silurian shale sections studied (see Figure 2 for location of sections; no horizontal scale implied). Using a cut-off of 10 ppm, the Silurian hot shale appears to be largely absent in two of the sections (Ghat-4 and Ghat-6), while maximum thicknesses of 12–13 m are reached in sections Ghat-3 and Ghat-7. The largest uranium concentrations were measured in sections Ghat-2 and Ghat-7 with values around 50 ppm. Topography interpreted based on lateral pinch-outs of Mamuniyat Formation and hot shale. “Correlation datum” lies in the organically lean, “cold” shale.

### Subsurface Hot Shale Isopach

Hot Shale isopach maps have been constructed for the NC115 concession area in the Murzuq Basin based on the hot shale’s high gamma-ray signature in wireline logs (Figures 8, 11 and 12). The hot shale is absent in the B and M fields of the concession (Figures 8 and 11). In the A field the hot shale is only developed in the northern part, whereas it is more common in the H field where it covers the whole north-western part (Figures 8b and 8c). On a larger scale, the hot shale occurs widely in an EW-trending belt along the northern margin and in the central part of NC115 (Figure 12). The

western part of the concession appears to be devoid of the Silurian hot shale. These isopach data were integrated with existing hot-shale distribution data from other parts from the subsurface of the Murzuq Basin, mainly based on Lüning et al. (2000) (Figure 11a). A central area with abundant hot shales appears to be flanked by areas where this unit has not been deposited. Towards the west, hot shales are again developed in well E1-NC115 (2 m of shales peaking at 220 API). The basal Silurian radioactive zone is also present in wells A1-76 and H1-NC58, although the unit here is very thin (up to 2 m thick) and maximum API values do not exceed 180 and 170, respectively. The gamma-ray values of these “warm shales” are higher than the chosen cut-off of 150 API but are also significantly lower than the values in the anoxic depocentres where natural radiation may partly exceed 600 API. Notably, when correlating a regionally developed silty zone in the lower part of the Tanezzuft Shale from well H1-NC58 across Concession NC58 (Figure 11), it is apparent that the base Tanezzuft Formation is much deeper in other wells, such as F1-NC58 and E1-NC58, which both contain 2–3 m of well developed hot shale (Echikh and Sola, 2000; Meister et al., 1991).

## DISCUSSION

### Timing of Deposition and Biostratigraphy

The hot-shale model by Lüning et al. (2000) suggested that organic-rich strata were deposited in palaeo-depressions during the early to middle Rhuddanian initial transgression. With rising sea level, hot shales began to onlap the margins of these palaeo-depressions. Sometime during the late Rhuddanian, shelfal waters eventually became more oxygenated resulting in a switch to organically lean shales, which initially still lapped onto palaeo-depressions until they were completely infilled and their relief was leveled out.

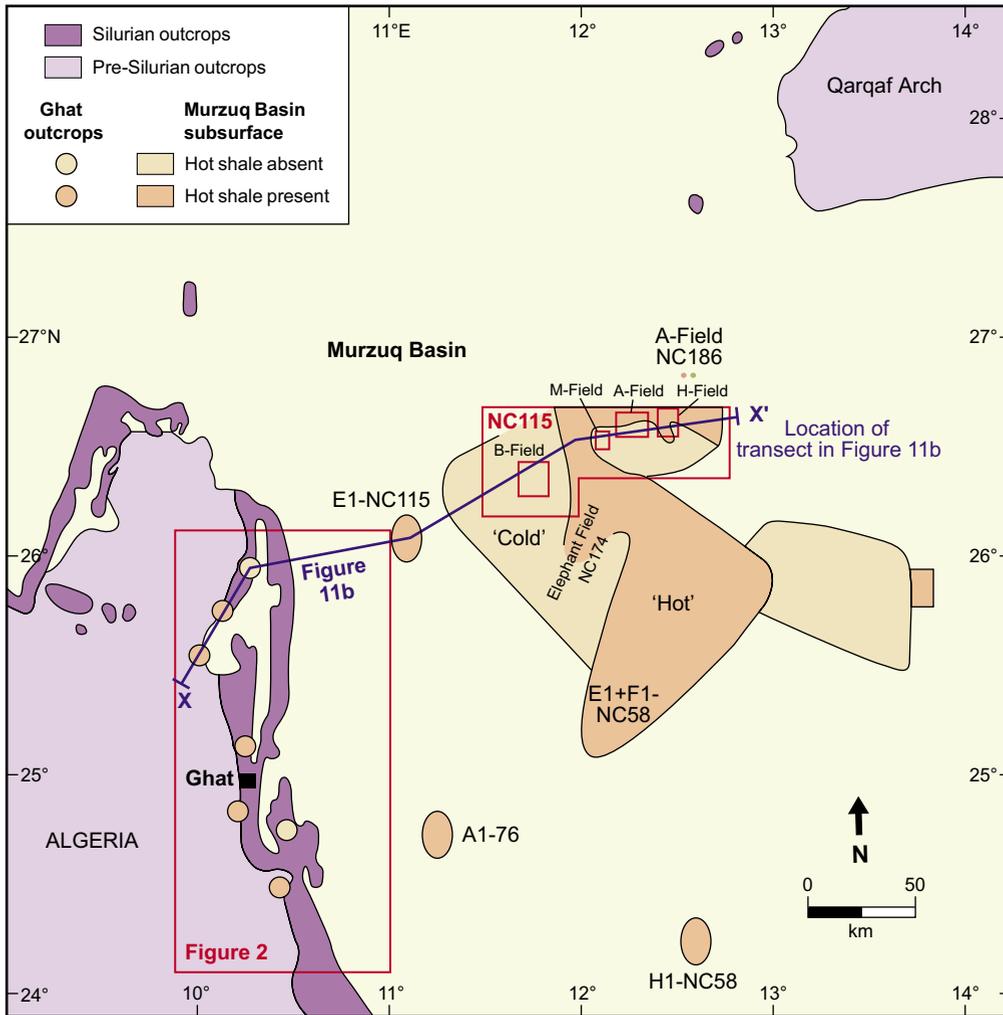
Graptolites, newly recovered and previously described (e.g. Bellini and Massa, 1980; Klitzsch, 1969; Massa and Jaeger, 1971; Protic, 1984; Radulovic, 1984a; Radulovic, 1984b) from the basal Tanezzuft Shale in the studied sections, all yield Rhuddanian ages. The sections, therefore, are suitable in the attempt to unravel the oxygenation and depositional history during the latest Ordovician-Silurian postglacial, initial sea-level rise.

Generally, biostratigraphic resolution in the newly measured sections is poor due to poor graptolite preservation. The Silurian hot shale was dated as Rhuddanian in sections Ghat-3, 5, 7, and 8, which in principal confirms the general age model originally proposed by Lüning et al. (2000) for this organic-rich horizon in the Murzuq Basin. The association of hot-shale deposition in palaeo-depressions during the earliest sea-level rise is also supported by an early Rhuddanian (or older) graptolite age of the hot shale in well H6-NC115 (Figure 8c) (Repsol Oil Operations, Tripoli, internal data).

Additional biostratigraphic data backing up this depositional age model comes from Wadi Iyadhar (our Ghat-5 section), which is characterised by high uranium values of up to 30 ppm (Figure 5). This section was previously also studied by D. Massa and G. R. Collomb (TR6, unpublished data) in the 1950s together with several other Tanezzuft sections in the Ghat area (locations of sections in Figure 2). The graptolites collected then were recently re-studied by Štorch and Massa (2006). They documented that shale deposition also here commenced during the middle Rhuddanian (*tariti-africanus* Zone), matching well with the elevated uranium values measured in the present study. Massa and Jaeger (1971) and Klitzsch (1969, his figure 2) showed that the Rhuddanian here is exceptionally thick (about 125 m), followed by 350 m of Aeronian shales. The great thickness supports the idea of a middle-Rhuddanian anoxic palaeo-depression in the Wadi Iyadhar area.

Palaeo-highs are interpreted for the areas around sections Ghat-4 and Ghat-6 based on the absence of the basal-Tanezzuft uranium peak (Figure 10). For both sections biostratigraphic data exists that supports this interpretation. In section Ghat-4, new graptolite data (see above) indicate a late onset of shale sedimentation during the late Rhuddanian age providing evidence for shale onlap into a high. 20 km south of our section Ghat-6 lies section TR3 of Štorch and Massa (2006) (Figure 2). Based on graptolites, Štorch and Massa (2006) report a Rhuddanian interval that is very thin (around 10 m), with probably only the upper Rhuddanian being present. This provides independent evidence suggesting the presence of a palaeo-high in the Ghat-6/TR3 area.

(a) "Hot Shale" distribution map



(b) Distribution of earliest Silurian palaeo-depressions

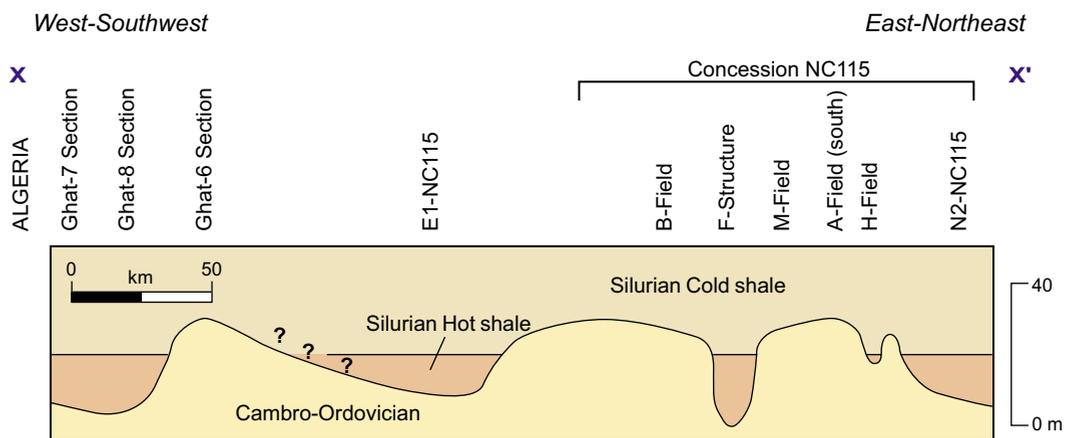


Figure 11: Integration of hot shale distribution data from the subsurface and surface sections. (a) Distribution map of "hot shale"; (b) distribution of earliest Silurian hot shale filling palaeo-depressions along transect X-X' (see location in (a)). Vertical scale exaggerated and conceptual, applies to present-day (compacted) sediment thicknesses. Subsurface data simplified and modified after Lüning et al. (2000). The patchy distribution pattern of lower Silurian "hot shales" in the subsurface is repeated in the surface exposures along the western margin of the Murzuq Basin.

Section Ghat-3 (Figure 9) is interpreted to have been located on the upper slope of an anoxic palaeo-depression. The hot shale is present here and is dated by graptolites as middle Rhuddanian (*tariti-africanus* Zone). Peak uranium values, however, do not exceed 20 ppm, contrasting with 50 ppm in true basinal hot-shale sections such as Ghat-2 and Ghat-7 (Figure 10). In most cases the hot shale sections are underlain by the Melez Chogran Formation, whereas the non-hot shale sections (Ghat-4 and Ghat-6) are underlain by Mamuniyat Formation sandstones. The presence of hot shales therefore appears to correlate with areas where the Mamuniyat Formation was eroded or not deposited (e.g. in glacial palaeovalleys) before deposition of the Tanezzuft Formation (Figure 10). In some cases erosion may have only removed part of the Mamuniyat Formation (e.g. section Ghat-7, Figure 10), so that the hot shale may overly older stratigraphic levels of the Mamuniyat Formation here.

### Identification of the Silurian Hot Shale at Outcrop

The study proved that an identification of the Silurian hot shale in surface sections in the Sahara is possible, based on gamma-ray spectrometry. The character of the basal uranium-enrichment corresponds well to patterns observed in wireline logs of exploration wells. Oxidation has altered the original rock colour, palynomorph microflora and largely destroyed any organic carbon. In field section Ghat-3 (Figure 9) the basal, uranium-enriched hot-shale interval still contains some relict organic matter. However, original TOC values are thought to have been significantly higher than the maximum 1.3% preserved here today. The maximum TOC value measured for Silurian organic-rich shales in the Murzuq Basin is 22.0% (well H29-NC115), and matches well with very high gamma-ray values of probably significantly more than 300 API (values of more than 300 API not recorded on the log for this well) (Figure 6).

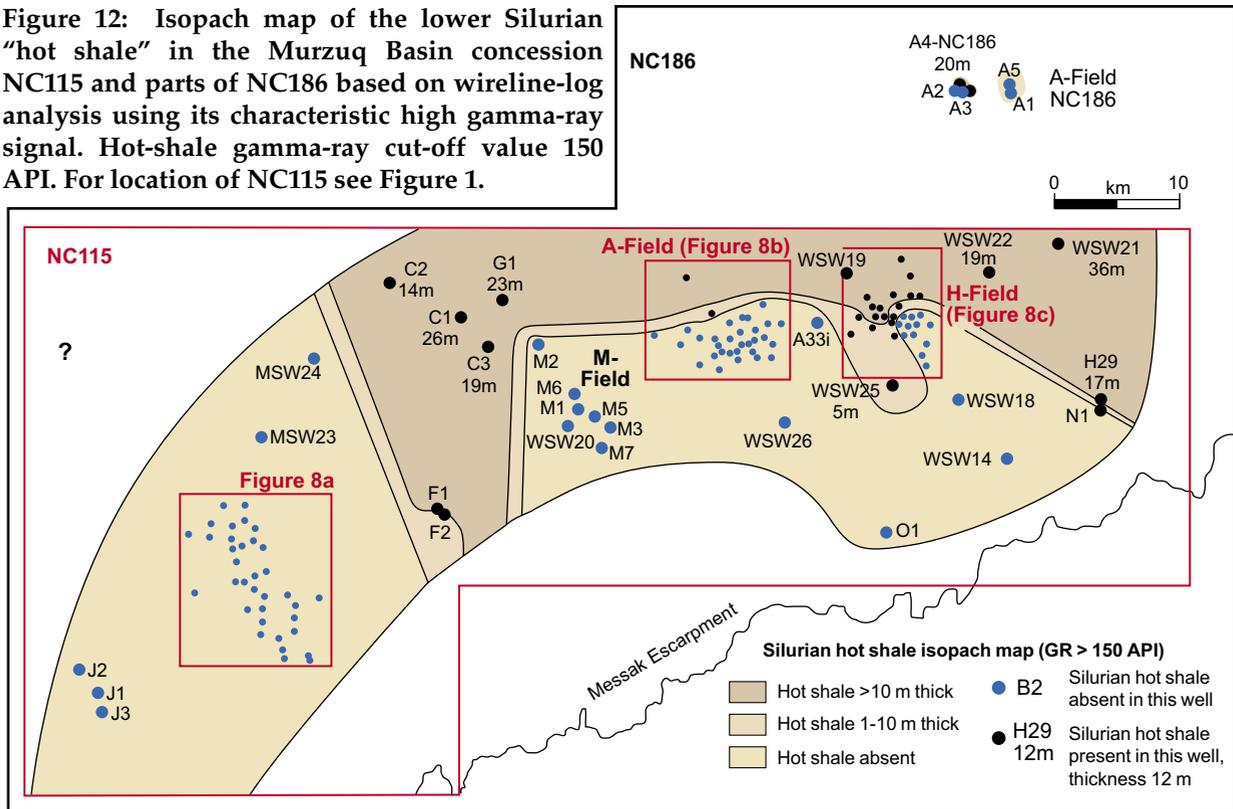
Importantly, the uranium in the field sections does not seem to have been affected much by the weathering processes. The transition from the unsolvable  $U^{4+}$  to the generally solvable  $U^{6+}$  due to oxidation clearly has not led to significant removal of uranium from the basal Silurian shales. The typical shape of the basal Silurian gamma-ray peak in several of the studied sections, resembling that in the data from fresh subsurface samples, suggests that no major uranium remobilization has taken place. One reason for the stability of the uranium concentration in these shales might be the absence of water under the present-day Saharan climatic conditions, which may prevent transport of uranium here (personal communication, S. Petsch, 2003). Studies are currently underway which suggest that the  $U^{6+}$  released from oxidative black-shale weathering might be directly adsorbed/captured by newly forming iron oxides and hydroxides to which it is then loosely bound (Fischer, 2004).

The study demonstrated that analyses of the uranium-concentrations, preferably carried out in the field by portable gamma-ray spectrometer, are a suitable way to identify and subsequently map the Silurian hot shale in Saharan surface exposures.

### Larger-scale Hot Shale Distribution Pattern

For the first time the basal Silurian hot shale was identified at outcrop around the margins of the southern Libyan basins. Hitherto, the presence of hot shales in the Ghat outcrop belt has only been suspected based on biostratigraphic data (Lüning et al., 2000) and pyrite framboids (Lüning et al., 2003b). The strong variability in thickness and uranium concentrations in the seven studied sections, and the overall absence of the hot shale in two of these sections, indicates that the generally patchy distribution pattern of hot shale known from the subsurface is also repeated in the Ghat outcrop belt (Figure 11a). Based on the depositional model in which deposition of the organic-rich shales is inferred to have occurred in earliest Silurian palaeo-depressions (Lüning et al., 2000), a profile was constructed interpreting the palaeo-relief across Concession NC115 south-westwards into the Ghat outcrop belt (Figure 11b). Hot-shale depocentres on this transect are located in the H and A Fields of NC115, around well E1-NC115 and in parts of the Ghat outcrop belt. The hot shale is also present in the southern part of the Murzuq Basin (wells A1-76 and H1-NC58) and in parts of northern Niger, although thickness and maximum organic richness (based on maximum gamma-ray intensity) are markedly reduced here (compared to hot shales further north) because the basin here was not deep enough to allow shale deposition during the main phase of the anoxic event. Shales were deposited here only during the final, waning phase of the oxygen-restricted episode.

Figure 12: Isopach map of the lower Silurian "hot shale" in the Murzuq Basin concession NC115 and parts of NC186 based on wireline-log analysis using its characteristic high gamma-ray signal. Hot-shale gamma-ray cut-off value 150 API. For location of NC115 see Figure 1.



The presence of Silurian hot-shale basins within the Ghat outcrop belt indicates that the Tihemboka High (Figure 1) was not a positive structure during the latest Ordovician to earliest Silurian. It is assumed that the Murzuq Basin, at the time, was part of a wide North African shelf, with a direct connection to the Algerian Illizi Basin (Figure 1) towards the west.

The presence of the Silurian hot shale at the western margin of the Murzuq Basin reduces significantly the source-rock availability risk in the subsurface of the western part of the Murzuq Basin. Nevertheless, a direct and continuous correlation of the hot-shale belts from the subsurface with the surface data is not possible, yet, because only few wells have been drilled along the western margin of the basin.

## CONCLUSIONS

Organic-rich shales were deposited in shelfal palaeo-depressions across North Africa and Arabia during the latest Ordovician to earliest Silurian postglacial transgression. The distribution of the Silurian organic-rich shales in Saharan outcrops is poorly known because surface weathering has commonly destroyed the organic matter and black colour of the shales, making it difficult to identify the previously organic-rich unit in the field. Seven Ordovician-Silurian boundary sections were measured by portable gamma-ray spectrometer along the outcrops of the western margin of the Murzuq Basin. Based on uranium radiation, it was now possible to identify and map the thickness and approximate organic richness of the black shale. The uranium content of the shales appears to have remained largely unaltered by the weathering processes and could therefore be used as a valid proxy parameter to distinguish between pre-weathering organically rich and lean shales.

Five of the newly measured sections are characterised by uranium-enriched intervals, representing areas of earliest Silurian palaeo-depressions. Major uranium peaks were absent in the spectral gamma-ray curves of two other sections which are interpreted to mark earliest Silurian palaeohighs. Graptolite biostratigraphic data suggests that the anoxic event was centred around the middle Rhuddanian, with

more oxygenated conditions and onset of deposition of organically leaner shales having commenced sometime during the late Rhuddanian. The presence of anoxic palaeo-depressions during the earliest Silurian within the Ghat outcrop belt indicates that the Tihemboka High at the western margin of the Murzuq Basin was not a positive structure during this time.

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