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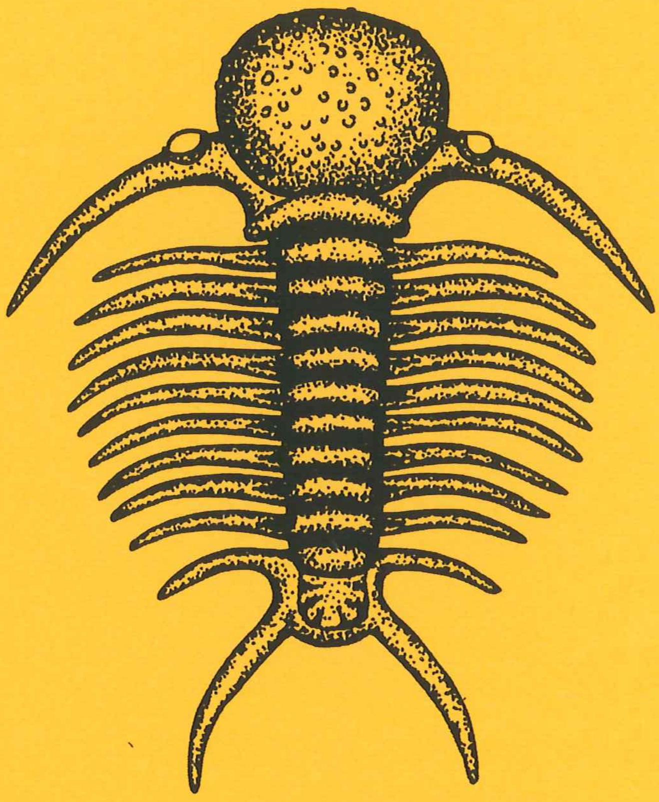

High-resolution methods for study of carbonate rock: a tool for correlating the sedimentary record

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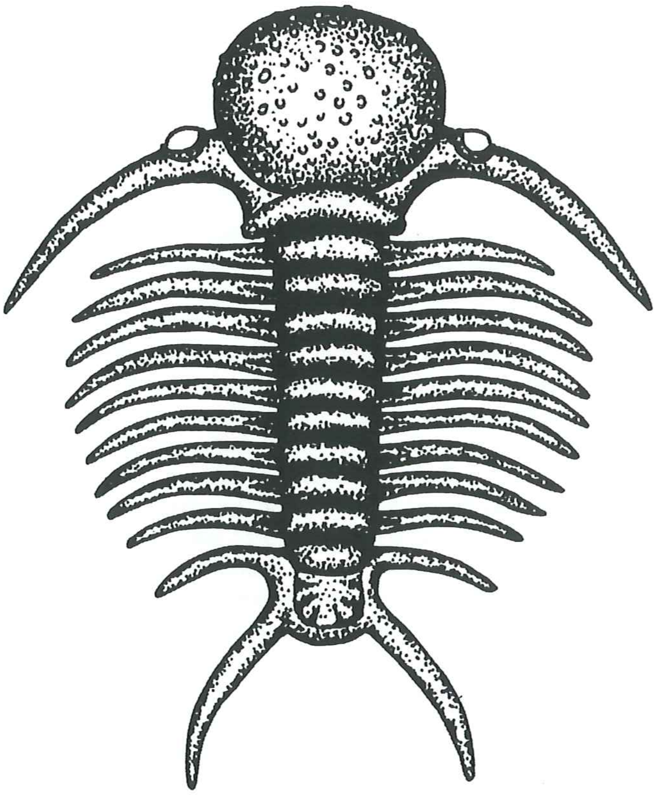

High-resolution methods for study of carbonate rock: a tool for correlating the sedimentary record

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MARTIN STOCKFORS

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Abstract: Geophysical and geochemical methods such as investigation of calcium carbonate content, organic carbon content, magnetic susceptibility and grey scale image analysis may be utilised as correlation tools of sedimentary carbonate rocks. Low carbonate content indicates high terrestrial input into a basin and is associated with clay horizons containing high amounts of organic carbon and also high magnetic susceptibility. Grey scale image analysis shows darker colour in clastic and organic rich marlstone and clay strata, and lighter colour in limestone and carbonate rich coquinas. To use the obtained data as correlation tools the graphs showing the raw data were converted into trend curves showing the general variations in calcium carbonate content, organic carbon content, magnetic susceptibility and grey scale to detect e.g. sedimentary cycles. The grey scale trend curve shows that sequences containing claystone in conjunction with coquinas, despite its dark colour, will expose a lighter colour than limestone/marlstone. The high accuracy the grey scale image analysis shows in a high-resolution record, will be reduced in proportion to what extent the trend is set to in the graph. To compare the grey scale image analysis with the calcium carbonate content, organic carbon content, magnetic susceptibility, the trend has to be calculated on a proportionately high amount of closely sampled data. This result in concealed variations in grey scale and less conformity with the trend graphs from the other methods, calculated on less data. The study shows that grey scale image analysis may be difficult to use where colour variations are great and frequent i.e. especially where coquinas and claystone co-exists.

Keywords: Method study, carbonate content, organic carbon content, magnetic susceptibility, grey scale image analysis, Slite Beds, Gotland, Sweden.

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This high-resolution study of a carbonate succession focuses on the possibility to use geochemical and geophysical methods as correlation tools and to detect cyclical events in the sedimentary record. The content of calcium carbonate and clay minerals are thought to play a major role on the colour variations of the rock (Giraud *et al.* 1997). Four geochemical and geophysical methods have been used besides the sedimentological logging of the investigated core. These include the variations in 1) calcium carbonate content, 2) organic substances, 3) magnetic susceptibility and 4) grey scale properties.

The island of Gotland (Fig. 1) is situated in the Baltic Sea east of the Swedish mainland within the Baltic Shield. Silurian carbonate-rich shallow-marine strata formed the bedrock during the Wenlockian close to latitude 20°S (Torsvik *et al.* 1992). At that time the Baltic Shield was surrounded and transgressed by warm tropical waters (Wilde *et al.* 1991), hence creating a shallow pericratonic sea in the Baltic basin (Kaljo *et al.* 1991), which today constitutes the Baltic Sea. Carbonate environments were established on an extensive platform, sloping slightly towards southeast (Riding 1981). It has been suggested that parts of Gotland were developed as a carbonate ramp setting (e.g. Frykman 1989; Jacobsson 1997). The succession is, according to Riding & Watts (1991), dominated by three shallow-water limestone wedges separated by two deeper water shale-mudstone dominated wedges. In Estonia a similar pattern is found (Bassett *et al.* 1989). This pattern was probably influenced by the early Caledonian orogeny (Frykman 1989; Torsvik *et al.* 1992). The collision between the Laurentian continent and the Baltic continent, led to a simulta-

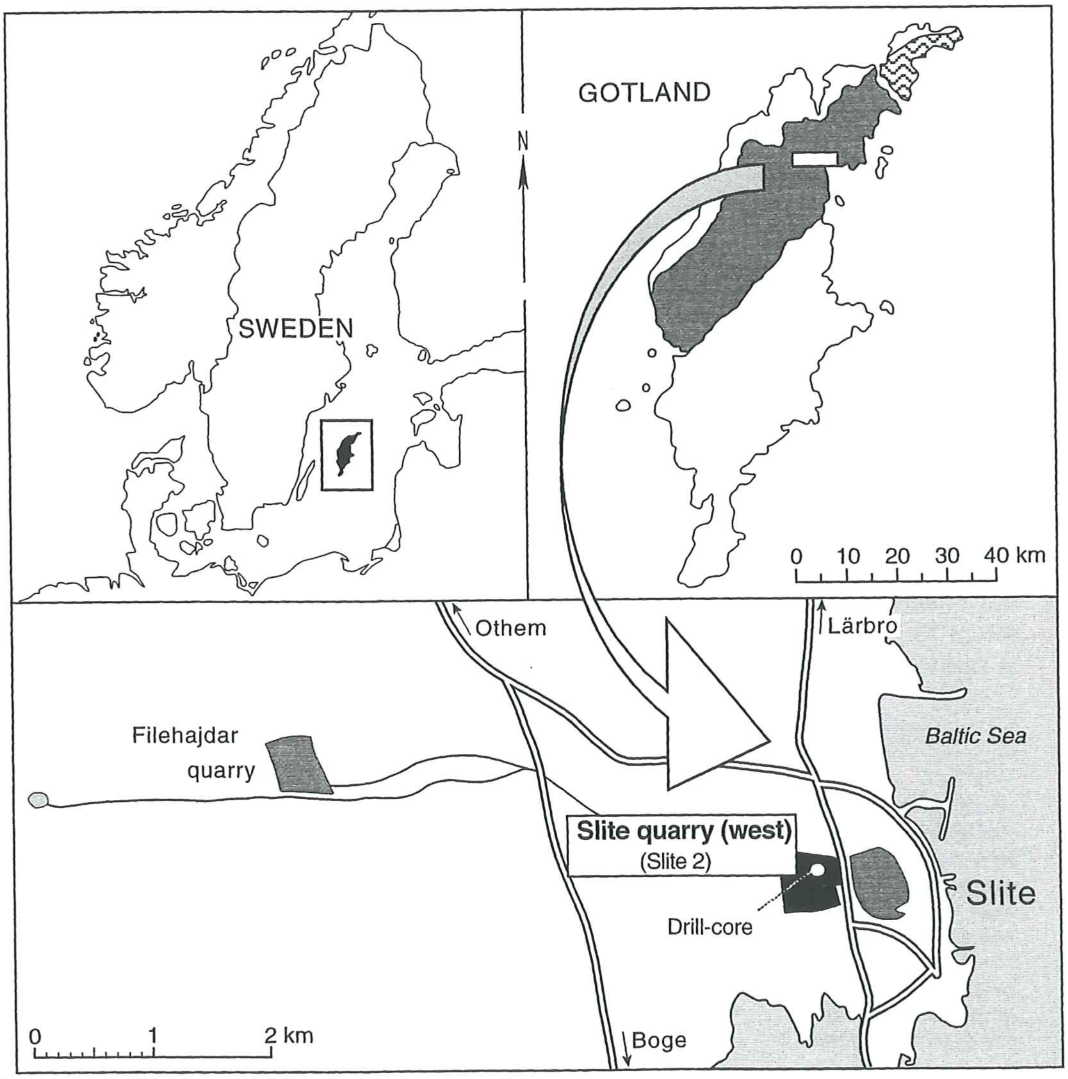

Fig. 1. A) Gotland in the Baltic Sea east of the Swedish coast. B) Shadowed area shows the occurrence of the Slite Beds. C) The Slite quarry and the site of the studied drill core. (Modified after Jacobsson 1997).

neous rising northwest margin and subsiding southeast margin of the Baltic continent. The rising landmasses led to a more intense terrigenous input into the Baltic Basin from northwest (Kaljo *et al.* 1991).

The studied area is located in the Slite quarry (Fig. 1) at co-ordinates 6402552 1678035 (CJ 6855 9904), c. 600 metres NNW of Slite church. The area is covered by the topographical map 66D Slite (7J Fårösund SO & NO) and the geological map Aa 169 Slite (Jeppsson 1997 *in press*). The Slite quarry is described by Shaikh *et al.* (1990). The Slite Beds have been studied by e.g. Laufeld *et al.* (1978), Bergman (1979, 1980 & 1984), Sundquist (1982), Kano (1991) and Jacobsson (1997).

Material and methods

The drill core

The studied material comprises the basal part of a 36 m long drill core with a diameter of 60 mm, from the Slite quarry on Gotland (Fig. 1), where the investigation concentrates on the lowermost eight metres to create a high-resolution record of the succession. The core penetrates the Silurian Slite Beds, which are at least 90 m thick (Jeppsson *et al.* 1994), extending from Fårö in northeast to Klintehamn in southwest (Fig. 1). The studied part of the core is assigned to the Slite *f* unit (Fig. 2) whilst the remaining part is assigned to Slite *g* unit (Hede 1960; Jeppsson pers. comm. 1997). In the Filehajdar quarry, approximately 5 km from the Slite quarry (Fig. 1), the Slite *f* unit was deposited on the middle ramp (Fig. 3) between normal wave base and storm wave base (Jacobsson 1997). The core extends from 0 m to 36.06 m, which is approximately 26 m to 62 m below sea level (Jeppsson pers. comm. 1997). The interval between 28.18 m to 36.06 has been logged because it is continuos with no missing parts in the succession (Fig. 4). The drill core was cut into two longitudinal halves. One half was used for logging and photographing and the other half for sampling.

Sedimentological and digital log

The sedimentological log is based on three lithofacies, where 1) claystone, 2) limestone/marlstone and 3) coquinas are distinguished and logged in relation to the different grain sizes (Fig. 4). In addition a complementary digital log was constructed (Fig. 4). Nodule type, size and amount of trace fossils have been given number codes.

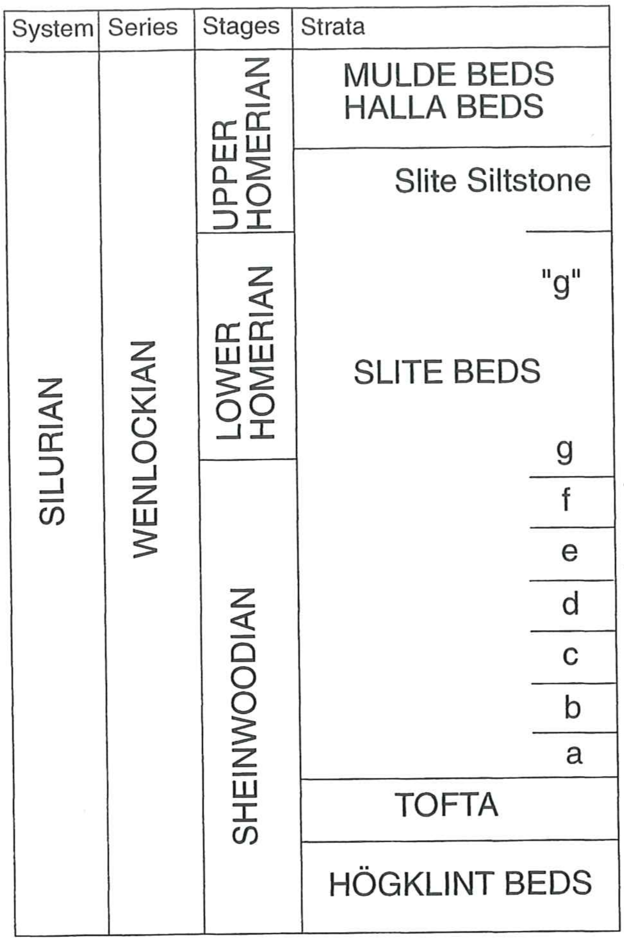

Fig. 2. Stratigraphy of the Slite Beds. The studied core represents parts of unit *f* in the Slite Beds. (Modified after Jeppsson *et al.* 1994).

Calcium carbonate analysis

Samples were obtained from every fifth centimetre of the core, between 28.20 m and 36.06 m, in total 158 samples. Parts of each rock sample were pulverised and dissolved in hydrochloric acid (HCl) and heated almost to its boiling point, until formation of carbon dioxide (CO_2) ceased. Coarser fractions were removed and ammonium (NH_3) added to the residue. Again the sample was heated to just below boiling point, before H_2O_2 is added. The samples are then cooled and ammonium buffering is added. The samples were heated to 45°C, and Erio-T was also added. An immediate titration with Diamino-tetra-acetic-acid (EDTA) was made. The amount of EDTA necessary for obtaining a colour change is equivalent to a specific amount of calcium carbonate.

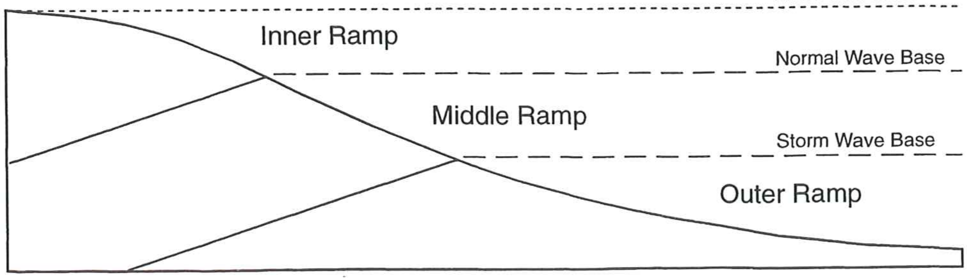

Fig. 3. Slite carbonate ramp. The middle ramp is the zone between the normal wave base and the storm wave base. The studied material from the Slite *f* unit probably originates from the middle ramp. (Modified after Jacobsson 1997).

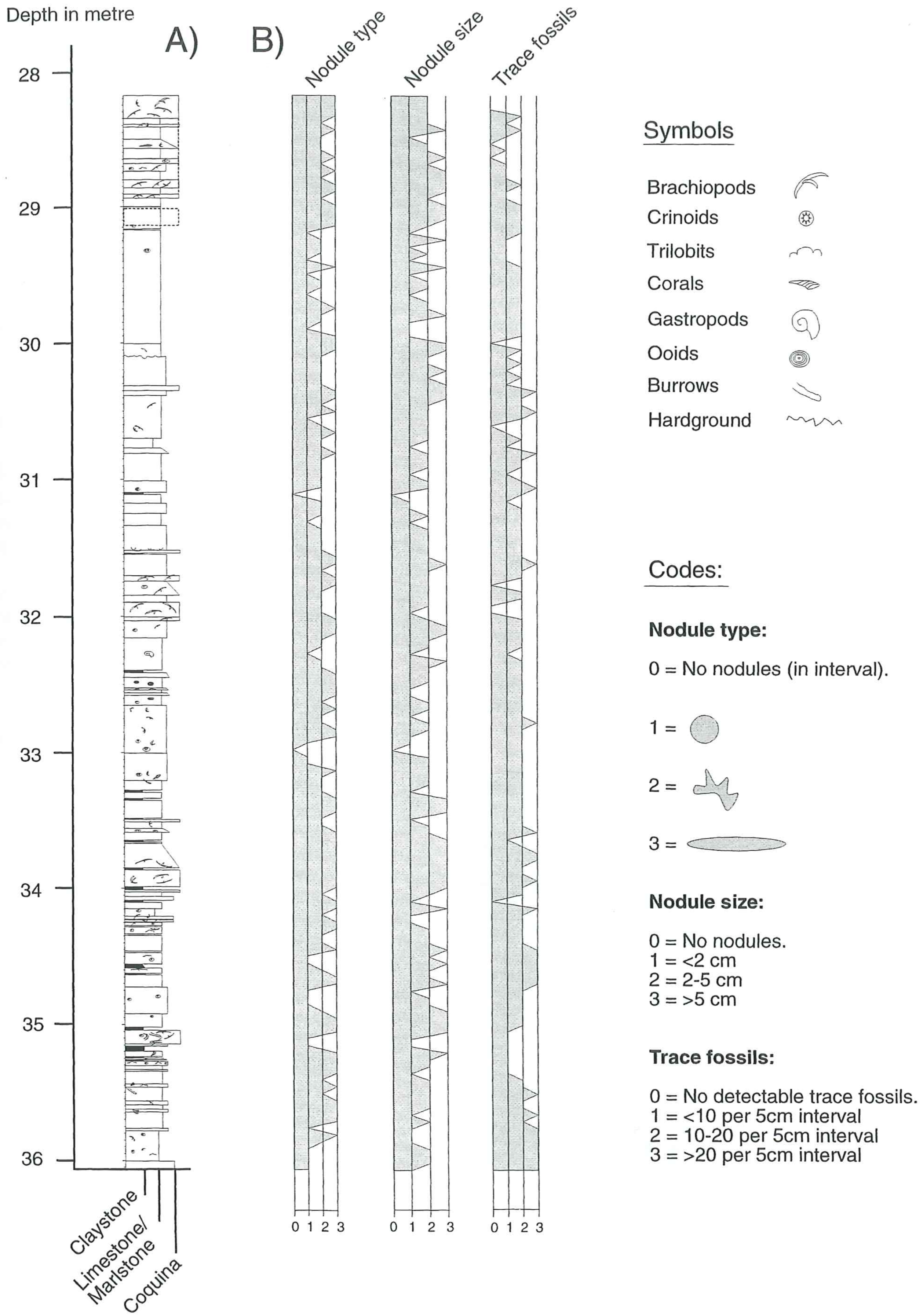

Fig. 4. A) Lithological log of the studied drill core. Interval extending from 28.18m–36.06m below sea level. The log is based on three main lithofacies, claystone, limestone/marlstone and coquinas and show location and kind of the most important and well-preserved fossil groups. B) Digital log based on measurements in intervals of 50mm. *Nodule type*: three different shapes of limestone nodule. *Nodule size*: limestone nodules divided into three sizes. *Trace fossils*: the amount of trace fossils.

Organic carbon content

The organic carbon content was determined by loss on ignition. A fixed volume of each sample was weighed and then heated to 105 ± 2°C for about twelve hours until the sample is dry and the weight is constant. At this stage all water within the sample has evaporated. The completely dry sample is heated to 550°C for two hours. At this temperature the organic carbon will ignite, but little of the carbonate carbon (Fairchild *et al.* 1988). The decrease in weight will give the organic carbon content.

The loss on ignition is often used as a measure of the organic carbon content of a material. Most of the organic matter will be lost during the ignition. Some chemically bound water may also be lost and hereby included in the analysis. The loss of chemically bound water is very low in the present material. Therefore the loss on ignition will reflect the organic carbon content (Fairchild *et al.* 1988).

Magnetic susceptibility

This method is used to investigate the variations in the magnetic susceptibility in the drill core. Magnetic susceptibility is a measurement of the ability a material has to respond to a magnetic field and is measured in dimensionless SI-units. Only internal deviations and fluctuations are of importance to detect the variations of the susceptibility, therefore the strength and direction of the susceptibility is excluded.

The Kappabridge KLY2 is designed to measure the magnetic susceptibility of rocks and its anisotropy. This equipment is very accurate and is capable of recording measurements at a high rate. It operates by measuring the changes in inductivity in a rock specimen. The coil is located in an isolated box, which is protecting the sample from surrounding noise during the measurements (Jelínek 1973), thereby obtaining the sensitivity necessary to obtain useful data. This equipment requires samples of a specific size to fit into the coil. These samples have a diameter of 22.5 mm and a height of approximately 30 mm, are taken from the same core level as those used for the examination of calcium carbonate. At first, three measurements of each sample were done to calculate an average value, but due to an excellent accuracy and very few differences between the three measurements it was decided unnecessary to make several measurements on each sample.

Grey-scale image analysis

To accomplish the grey scale image analysis the drill core had to be divided into two halves to obtain a plain surface, suitable for photographing. The plain surface was then treated with glycerol to enhance the contrast in the mudrock and also to obtain first-rate detailed information while photographing. This treatment is only applied on one half of the core, since it might affect the mineralogy of clay minerals. The photographs are then transferred to a Photo CD-ROM, where it was possible to work with the images in Image Tool (for Windows, version 1.28), a programme for analysing images, in grey scale (0-256 grey-levels).

The line profile (graph) obtained in Image Tool was accomplished by choosing a broad line. The line was set to cover half the width of the core, to acquire as much information as possible. Since the rock mainly consists of irregular nodules, it is important to make the line profile broad enough to cover the smallest irregularities and distinguish the general alternations of marlstone and calcium carbonate nodules. In an irregular data source, such as the nodular succession presented here, a single-pixel line would produce more detailed, but yet deceptive information.

When analysing the images in Image Tool, it was noticed that deviating mean grey levels occurred between the images as a result of exposure differences in the photographs. Therefore corrections in the grey scale were made.

Time series smoothing

Raw data that obtains an intensive oscillation in a graph could be difficult to view. The obtained data from the analyses herein, have been subject to time series smoothing, which is a method to treat graph presentations. A calculation of average mean values of the raw data was done to produce a trend curve, which defines the tendencies of the main oscillations in the graph. The trend curves for calcium carbonate content, organic content and magnetic susceptibility are calculated on the mean value of 35 steps, whereas the trend curve for the grey scale analysis is calculated on 350 steps. The smooth trend curves will therefore deviate from the raw data curve.

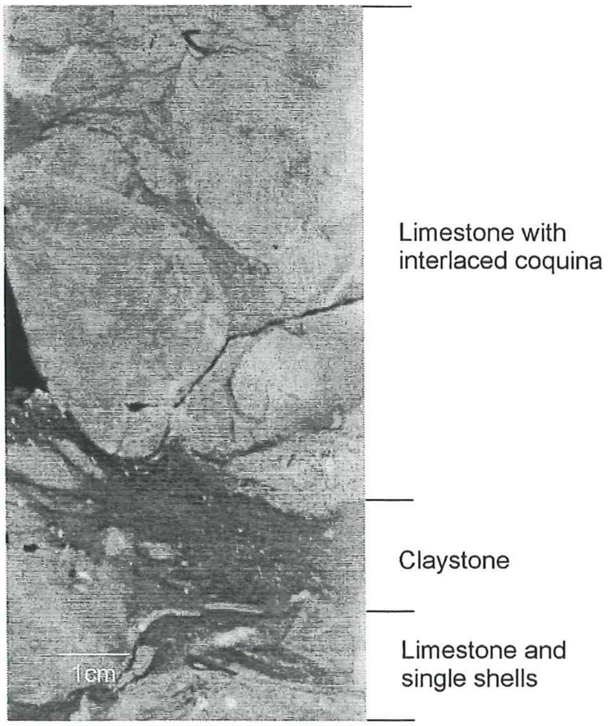

Fig. 5. Coquina interlaced with claystone horizon and limestone nodule. Well-preserved shells and shell fragments are found adjacent to or integrated with the claystone. Calcium carbonate seems to accumulate adjacent to and around the bigger shells.

Results

Lithofacies

Three main lithofacies are distinguished, 1) limestone/marlstone, 2) claystone and 3) coquina. The studied carbonate rock consists mainly of marlstone with interlaced limestone nodules of varying shapes and sizes (Fig. 4). Horizons of claystone are also present in the sequence. The transitions between limestone/marlstone and claystone are commonly gradual and very diffuse. Coquinas, which are shell accumulations mainly consisting of the carbonate shells from the brachiopod *Rhipidium tenuistriatum*, occur frequently and are often associated with claystone horizons (Fig. 5). The coquinas appear mostly as lags, but can also be seen as fining-upward beds with a sharp base. Single shells of *Rhipidium tenuistriatum* can be found sporadically and occur facies-independent (Fig. 6). Three different limestone-nodule shapes and sizes are distinguished (Fig. 4). Trace fossils occur frequently in limestone/marlstone whereas they are rare or absent in claystone and coquinas. The amount and preservation of trace fossils varies in the succession (Fig. 4).

Calcium carbonate content

The raw data (Fig. 7) show high calcium carbonate content where coquinas are found and low in claystone. To illustrate the average fluctuation, the data set will, after time series smoothing show that the carbonate content is generally higher in sequences of limestone/marlstone and lower in sequences of coquina/claystone alternations (Fig. 7). Despite the fact that coquinas consist of calcium carbonate shells, they are often associated with claystone horizons (Fig. 5). Therefore a general decrease in calcium carbonate will occur in these parts. However, coquinas located in limestone/marlstone, will show increasing carbonate content (Fig. 7).

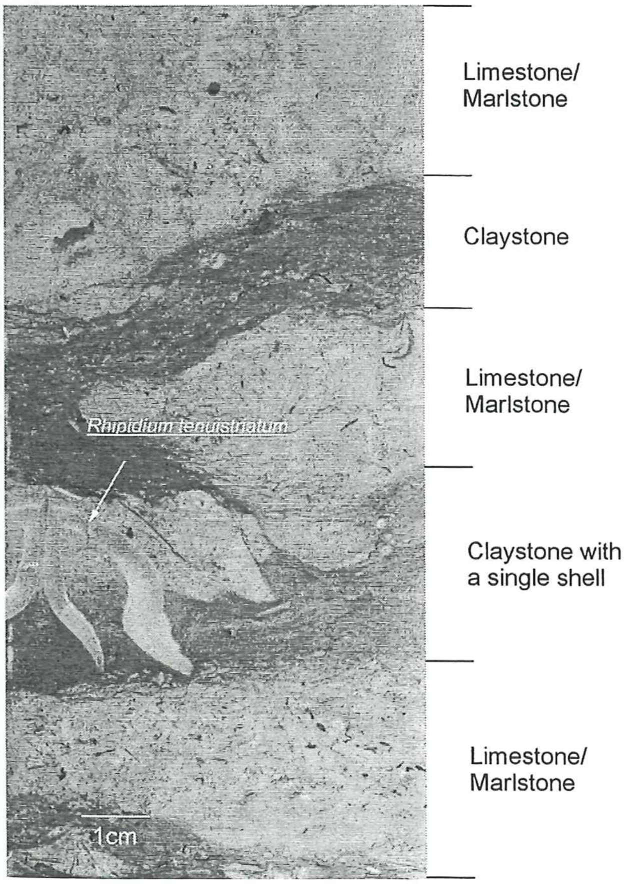

Fig. 6. Single shell of *Rhipidium tenuistriatum* interbedded with limestone nodules and claystone horizons. Note that the limestone and marlstone consists of small fragments of fossils and that the claystone/mudstone also contains shell fragments.

Organic carbon content

The raw data (Fig. 8) shows that organic carbon is low in coquinas and high in claystone. There is however, a general increase in organic carbon content at locations where coquinas and claystone are abundant and co-existing. The same graph also shows a general decrease in organic carbon in limestone/marlstone intervals. Organic carbon content increases where calcium carbonate content decreases and vice versa (Fig. 7).

Magnetic susceptibility

Very stable values of the magnetic susceptibility were measured. Since the samples are well protected from surrounding noise during measurements a highly accurate profile of the variations of the magnetic susceptibility was obtained (Fig. 9). The magnetic susceptibility is high at locations with claystone and low in limestone/marlstone and the susceptibility is on an average high where claystone co-exists with limestone/marlstone (Fig. 9).

Greyscale image analysis

The obtained greyscale curve (Fig. 10) shows that claystone exposes a darker colour than the coquinas and limestone/marlstone. On an average though, after time series smoothing, the greyscale curve shows a lighter colour where claystone and coquinas co-exists. Considerable colour variations can also be seen within the limestone/marlstone alternations where limestone exposes darker colour than marlstone.

Correspondence between the curves

The conformity between the obtained curves is generally good and corresponds to the geological variation in the sequence, whereas the trend curves conceal the details in the original data. Nevertheless these trend curves depict the general fluctuations that are important in correlation studies. Figure 11 displays four trend curves and shows that high organic content and high magnetic susceptibility corresponds to low content of calcium carbonate. The grey scale image curve follows the organic content and magnetic susceptibility, exposing a lighter colour where these show high values, and where calcium carbonate is low.

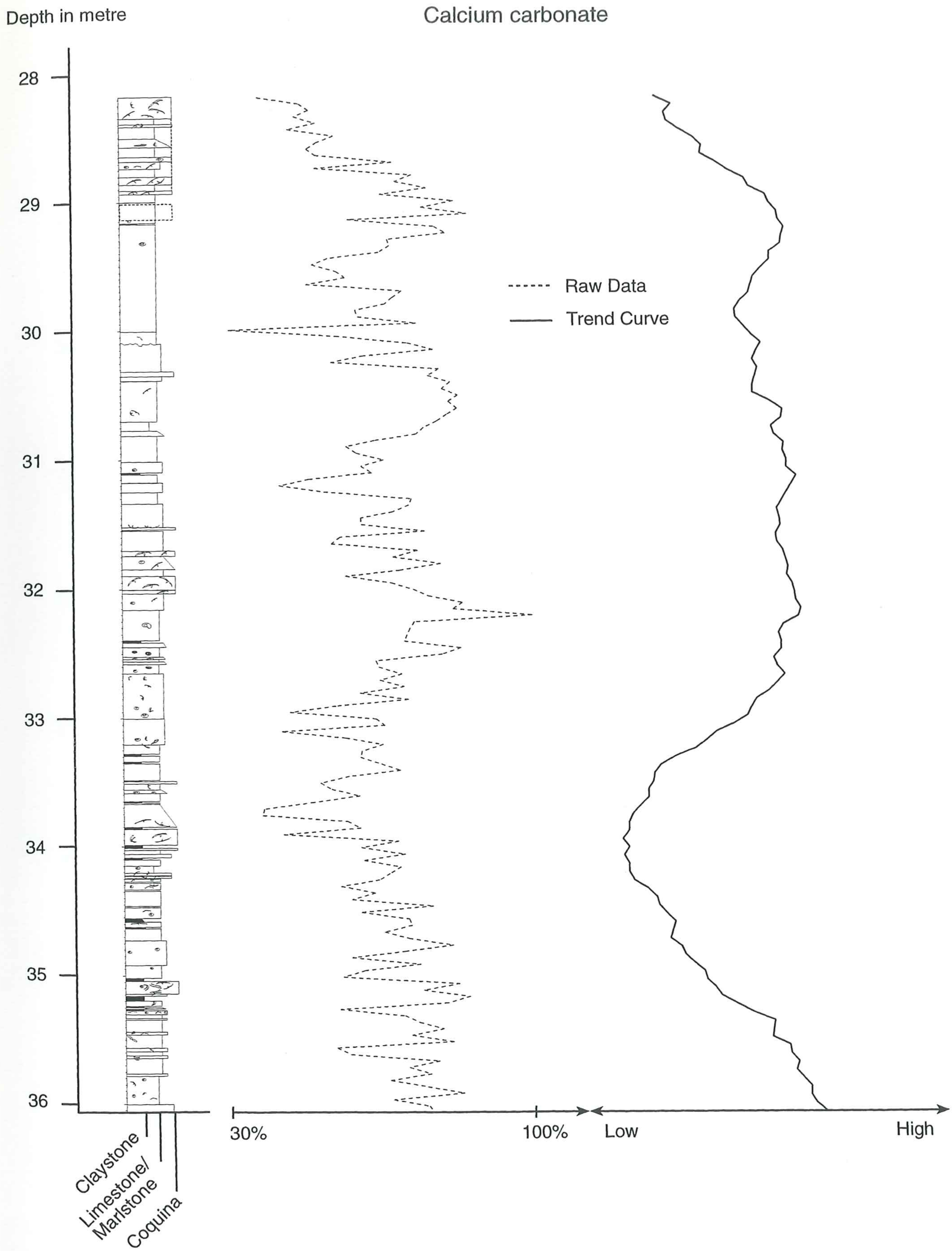

Fig. 7. Calcium carbonate content. Dashed line shows raw data and continuous line shows smoothed data. Positive peaks occur at locations where coquinas are found and on the contrary there are negative peaks at claystone horizons. Note that in the trend curve the calcium carbonate content decreases where coquinas are found, but increases in intervals of limestone/marlstone couplets.

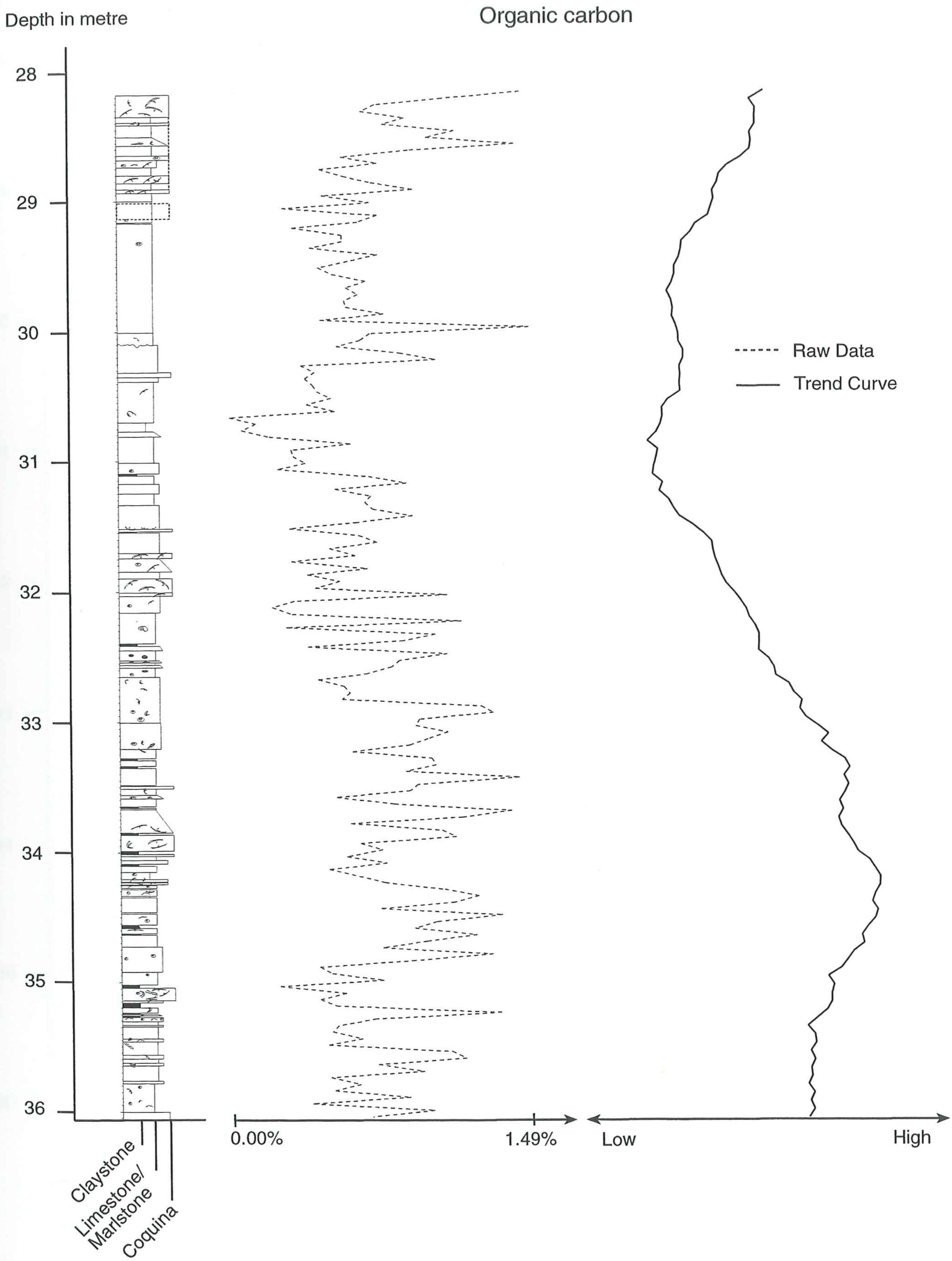

Fig. 8. Organic carbon content. Dashed line shows raw data and continuous line shows the smoothed data. Organic content is high in intervals rich in claystone horizons. The trend curve shows high content despite the apparent coquinas.

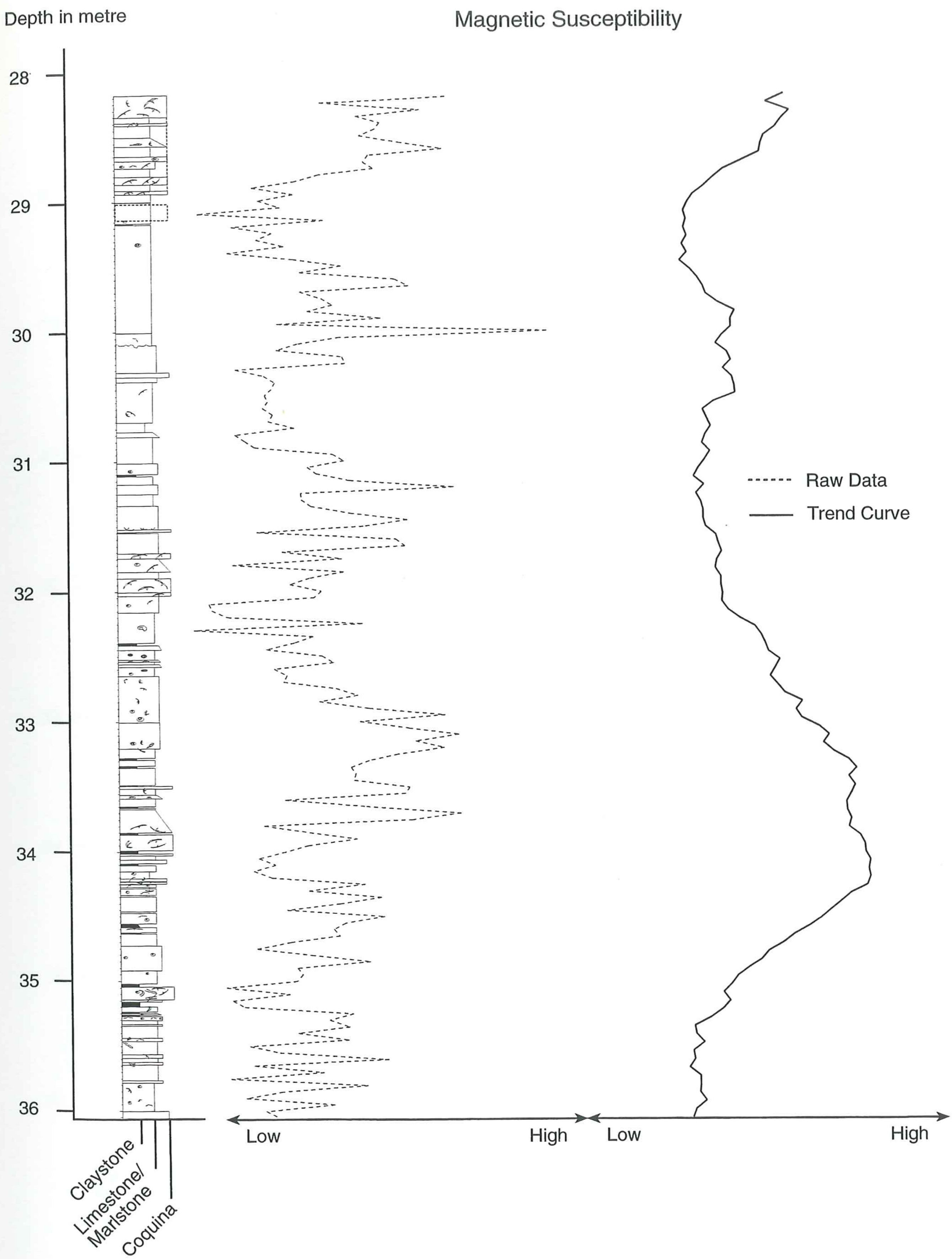

Fig. 9. Magnetic susceptibility. Dashed curve shows raw data and continuous curve shows smoothed data. Note that the magnetic susceptibility is high in intervals of claystone and the trend curve shows high values despite the frequent appearance of coquinas.

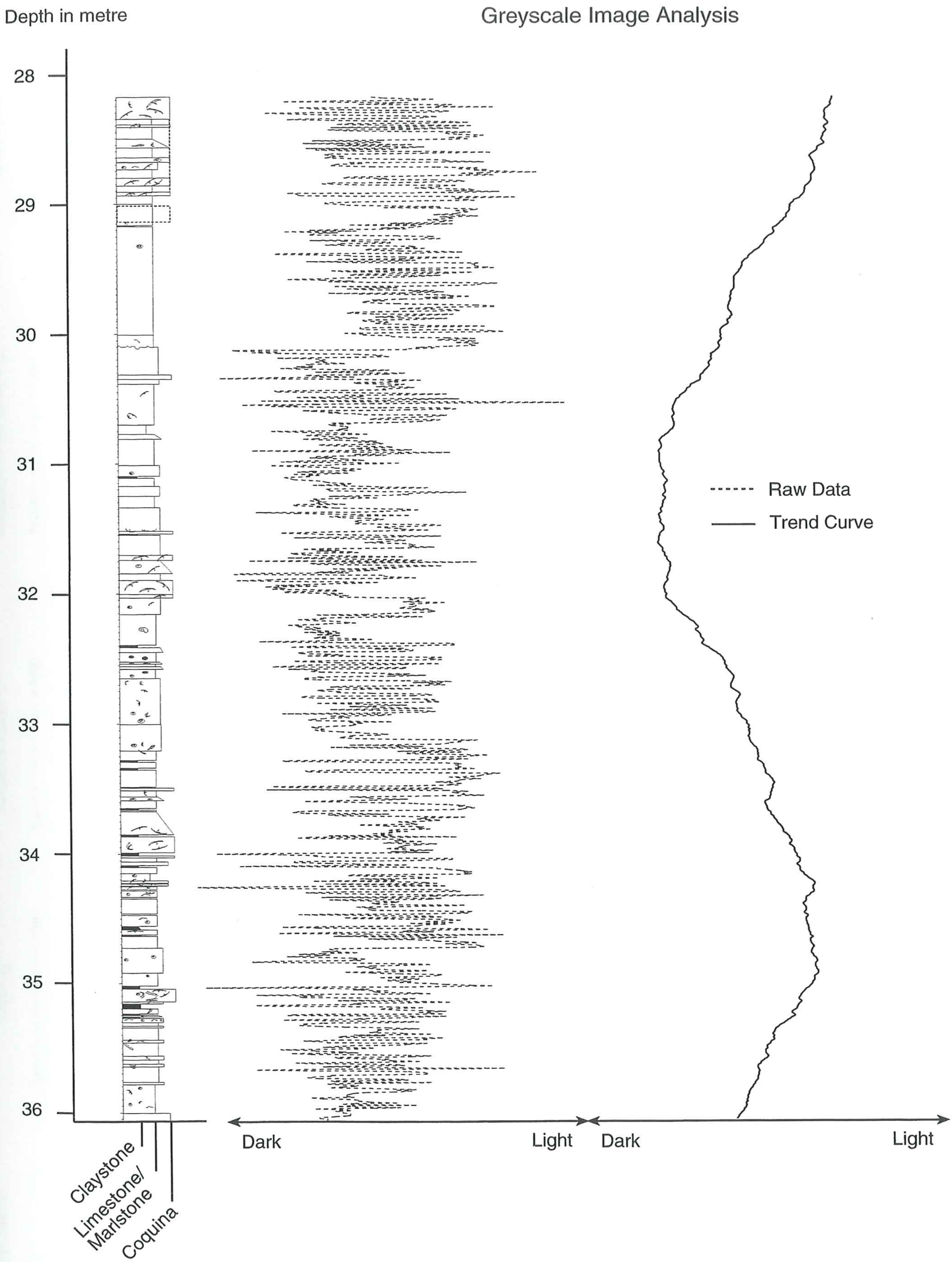

Fig. 10. Grey scale image analysis. Dashed line shows raw data and continuous line shows smoothed data. Note that coquina/claystone alternations show an in average light colour, though it's high clastic content. The limestone/marlstone couplets show a proportionally darker colour.

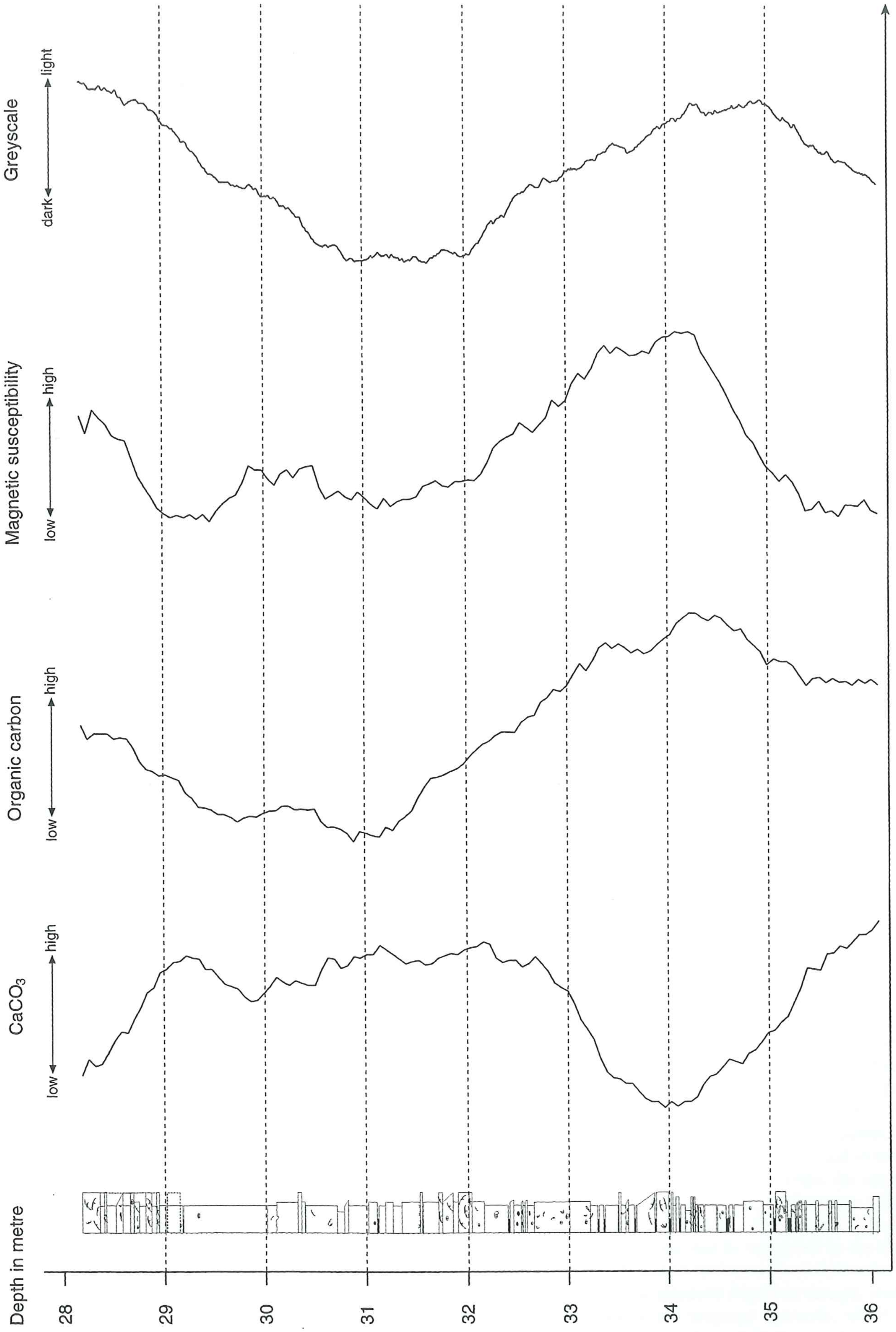

Fig. 11. The calcium carbonate content, organic carbon content, magnetic susceptibility and grey scale curves shown and correlated in comparison to lithological log. Note that the grey scale curve correlates well with magnetic susceptibility and organic content. Where calcium carbonate contentdecreases, grey scale increases and vice versa. The average brightness increases with higher amount of darker clastic material. The lighter coquinas associated with higher clastic input conceal the darker thin claystone after time series smoothing.

Discussion

Rhythmic sedimentation in the drill core

There are primarily two overriding controls on carbonate sedimentation, geotectonics and climate, which together control another important variable, the relative sea level (Tucker & Wright 1990). These two factors are of fundamental significance for the formation of cyclical sedimentary patterns in carbonate strata. The climate and hence the sea level and sedimentation rates, may in turn be controlled by orbital forcing (variations in Earth's orbit), which is an attractive hypothesis to explain cyclic events in sediments and sedimentary rocks. Sea-level changes are strongly connected to glacial/interglacial periods, since large volumes of water are enclosed in continental ice. Arai *et al.* (1997) suggests that high concentrations of magnetic minerals occur in marine sediment during glacial periods, while interglacial periods are characterised by lower concentrations. Hardie *et al.* (1986) suggested that not only Milankovitch's glacio-eustatic cycles control sea-level oscillations, but also tectonics, since high-frequency sea-level changes do occur during non-glacial periods. Krijgsman *et al.* (1997) studied lithology as well as carbonate and gamma ray records, correlated with rock magnetism and found evidence of cyclicity. Kauffman (1988) used physical, chemical, biological and composite events for making high-resolution event stratigraphy. De Boer & Smith (1994) concluded that orbital forcing affects the production of carbonate and organic matter in marine surface waters and oxidation and dissolution in the deep ocean. Giraud *et al.* (1997) proposed that repeated positive calcium carbonate excursions commonly are linked to the orbital forcing, especially obliquity and/or precession. These two factors alternatively control the cyclic sedimentation and are dominant during different periods. Jacobsson (*pers. comm.* 1997) tested the analysis results in this study, for cyclicity by the use of spectral analysis. He found several cycles matching the ratios between the calculated Milankovitch's orbital parameters (*cf.* Berger *et al.* 1989).

Bioturbation – oxic and anoxic periods

High content of organic carbon is generally associated with anoxic environments and commonly with non-bioturbated sediments. Sediments rich in organic matter and clayminerals normally cause dark sediment colours. In the studied succession the only non-bioturbated beds are the dark claystone horizons that correlate well with high content of organic carbon (Fig. 11).

The limestone/marlstone alternations are well bioturbated and trace fossils appear as burrows and borings both in limestone nodules, which are a product of early diagenesis (Mullins *et al.* 1980), and in the marlstone. The limestone is lighter and contains less organic carbon and has lower magnetic susceptibility than the marlstone. This may indicate a more oxic environment in the limestone than in the marlstone. Despite this, no differentiation between bioturbation in limestone nodules and marlstone can be distinguished. Consequently the amount of trace fossils in the succession does not have to reflect the rate of oxygen during compaction. The absence of trace fossils in the claystone may be due to compaction processes.

Terrigeneous input – clay minerals and magnetism

The clay mineral content shows strong positive correlation with the content of organic matter. Higher contents of clastic and organic substances indicate higher terrigeneous influx and/or lower carbonate sedimentation rates. The presence of organic carbon also implies the relation to anoxic environments. It is possible that carbonates may have dissolved and migrated diagenetically in the sediment (*cf.* Munnecke & Samtleben 1996), especially under influence of dewatering processes and hereby separate the sediment into clay horizons with high organic content and lime nodules.

Most claystone horizons have smooth transitions to limestone/marlstone, but some are distinct without dewatering structures and sharper transitions. Significant for the claystone horizons is that they consist of bentonite (Jacobsson 1997), which is a pyroclastic deposit and hence indicating volcanic origin. According to Batchelor & Jeppsson (1994) these layers may be good chemostratigraphic markers, as each bentonite has a specific chemical composition that makes them unique and important as a correlation tool. The calcium carbonate content is low where the bentonites are found (Fig. 11), because the pyroclastic sedimentation is very high. Iorio *et al.* (1995) found strong connections between remanent magnetism and sedimentary successions and suggests that cyclic lithological and magnetic parameters may be controlled by the Milankovitch's cycles. High magnetic intensities occur in sediments with high carbonate content associated with redox boundaries and lower intensities occur in sediments with low carbonate content (Schwartz *et al.* 1997). This relationship proposes that the intensity of magnetic susceptibility does not simply reflect non-carbonate sedimentation, but other processes may also be of importance.

Coquinas are associated with high terrigeneous input since they are often found together with claystone beds. Both organic content and magnetic susceptibility increases where coquinas are found (Fig. 11), while calcium carbonate decreases. Where coquinas are abundant and thick, they can often be found adjacent or integrated with thinner layers of claystone (Fig. 5). Jacobsson (1997) suggests that coquinas are storm weather deposits. This explains why coquinas are strongly connected to terrigenous matter such as clay and mud. Since the coquinas are rich in calcium carbonate, they will expose a lighter colour in the grey scale analysis. The thin and integrated mudstone and claystone will be concealed by the thicker and also lighter coquinas and hence invisible in the grey scale curve. The terrigeneous claystone though, contains organic substances and magnetic minerals, which proportionally lower the content of calcium carbonate (Fig. 11). Therefore, the grey scale curve will follow the curves for organic carbon and magnetic susceptibility rather than the calcium carbonate curve (Fig. 11). A potential source of inaccuracy is that the assembling of samples every fifth centimetre is compared to the grey scale curve exposing millimetre precision. This way the lack of information in the gaps in between the samples will be represented in the grey scale curve, but not in the rock-sampled curves.

Conclusions

· A very good correspondence between calcium carbonate content, organic carbon content and magnetic susceptibility was obtained.

· High calcium carbonate content is associated with low organic carbon content, low magnetic susceptibility and light colour in grey scale image analysis.

· Low calcium carbonate content is associated with high organic carbon content, high magnetic susceptibility and dark colour in grey scale image analysis.

· Raw-data graphs show accurate variations in calcium carbonate content, organic carbon content and magnetic susceptibility, whereas trend graphs show the mean variations and therefore conceal the frequent small-scale oscillations.

· Grey scale raw-data graph shows high accuracy in colour variations while the trend curve conceals the large and frequent colour variations, which are present in coquinas and claystone sequences. The grey scale trend curves must therefore be utilised as a correlation tool only where coquinas (tempestites) are absent or rare, especially where they co-exist with claystone horizons.

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