On-site FTIR analysis for accurate mineralogical screening of cuttings and core: a case study of the Boom Clay.

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Abstract. In Belgium, Boom Clay is considered as one of the potential host rocks for deep disposal of high-level, long-lived radioactive waste. Its mineralogy is very well-known from X-ray diffraction interpretations, but this technique is too time consuming to be suitable for guiding site characterization processes and requests a laboratory environment. Therefore, a complementary technique has been developed to derive an accurate mineralogy that can be deployed on-site The technique is based on a Fourier Transform InfraRed spectroscopy (FTIR) measurement followed by an automated conversion of the FTIR spectrum to mineralogy obtained from a pre-calibrated mineral model. As FTIR devices have become common, robust,and portable - measurements only take seconds and are available at relatively low cost. Moreover, the sample preparation is limited compared to the labour intensive XRD. The FTIR method allows for a quasi-continuous mineralogical, clay mineralogical, and organic matter characterization of the Boom Clay and surrounding formations. Whereas previous studies were limited to a few dozen discrete datapoints spread over the on average 100m thick formation, the current extensive dataset with over 1300 datapoints provides the first full stratigraphic framework in terms of basic characterization. The mineralogical data furthermore allow detailed correlations with the variability in natural gamma-ray and resistivity phases Previous predictions of the major detrital compounds (clay minerals versus quartz, feldspars) based on these core logging data, suffer from the significant enrichments in pyrite, organic matter and carbonate minerals being characteristic for numerous stratigraphic key horizons. The FTIR mineralogy, in contrast, accurately quantifies these additional mineral groups within minutes and does thus allow to identify with greater certainty these key horizons while also providing a better understanding of the sedimentary process, insight into thevariability of a formation, and can benefit optimal drilling device properties and identification of the key horizons during drilling.

1 Introduction

Many present-day societal challenges, such as the extraction and storage of resources or the disposal of waste, find their solution in the use or exploitation of the Earth's subsurface. This requires an adequate characterization of the properties and prevailing conditions, as well as insight into the processes that could affect them. Disposal of long-lived and high-level radioactive waste is one of these challenges that takes benefit of the confining properties of an adequate host rocks and the isolating conditions of a deep and stable geological environment. Throughout the different iterative stages of development and realization of a disposal system, its feasibility and environmental and radiological safety (during operation and on the long term) is to be demonstrated and this demands an accurate and detailed characterization of a potential or selected site, before, during and possibly after its execution.

Seismic surveys, well loggings, laboratory testing on cores and monitoring in piezometers are important sources of information. In order to get a maximum of useful data from a minimum investment, these techniques must be deployed in a smart and flexible way. A key parameter in guiding such a characterization campaign is the whole rock mineralogy, as a proxy for the lithology. Being able to determine the mineralogy immediately on site could allow (1) recognizing stratigraphic boundaries and key horizons while drilling and excavating, (2) finetuning the drilling parameters to optimize core recovery and sample quality and (3) subsampling the cores in an informed way in order to obtain, for each parameter to be documented by lab tests, a sample set representative for the whole range of lithological variability or at least containing the most penalizing lithologies.

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2 On-site mineralogical characterization techniques

2.1 Inversion from logging data

Geophysical and geochemical well logs or core loggings partly cover these needs and are non-destructive and continuous. If well calibrated, some log data provide a reasonable prediction of the mineralogy, grain-size or organic matter and are therefore an indispensable source of information [1,2]. However, the sample support of such data is usually different form that of classical mineralogy data, which makes comparison questionable, or inversely, inferring mineralogy from logging data is not applicable on any type of sample or is not sufficiently accurate to become the standard technique in a characterization program. It is moreover sometimes difficult to position a sample exactly on a well log, which is a problem for calibration, but also for later comparison. Regarding the accuracy, compositional data derived from geophysical data has its limitations as well. Indeed, although many components composing the lithology correlate or anti-correlate, lithologic composition can rarely be predicted from one geophysical variable only and larger set of geophysical variables would be required to more accurately determine the bulk composition. As a result, a gap remains between the very large source of mineralogy data that can be derived from well-log data on the one hand and the less numerous, but very reliable direct measurements via another technique on samples on the other hand.

2.2 Mudlogging and portable XRF

Currently, common direct techniques for in situ characterization are mudlogging and elemental characterization by X-ray Fluorescence (XRF). Mudlogging provides rapid lithological information but this information often comes with a lag as visual inspection of cuttings is less sensitive to subtle changes in composition. Furthermore, mudlogging suffers from an important deal of subjectivity between different experts. XRF is also deployed as an on-site technique as certain elements are used as chemical tracers for stratigraphy but also to infer the mineralogical composition. The main issue with such an inversion, however, is its complexity. Even with a high level of expertise, it is often impossible to correctly predict feldspars and individual clay species or allocate individual atoms such as Fe to the correct minerals (Fe-oxides, siderite, chlorite, Fe in other layer silicates,…). Additionally, these techniques, as along with well log interpretations require time and skilled expertise on-site to interpret all while being prone to a high level of subjectivity whereas the compositional information is often required as soon as possible during drilling highlighting the fact that XRF data in itself is often not an on-site solution..

2.3 X-ray diffraction

Mineralogy derived from X-ray diffraction (XRD) patterns is the most direct and accurate method to achieve analyses on samples. It relies on the interaction of X-rays with the crystallographic lattice of mineral phases of which the distance between lattice planes and site occupancy produces a set of diffraction peaks unique for each mineral phase. . High quality results however, especially in fine-grained sediments with a lot of clay minerals, require a lengthy procedure at laboratory conditions and a high level of expertise from the analyst, increasing its cost. XRD is therefore not suitable for very dense sampling campaigns nor for obtaining instantaneous, on site data, and thus to meet the on-site needs formulated above. Furthermore, X-ray diffraction does not allow a reliable characterization of organic matter.

2.4 FTIR

The aim of this project was therefore to develop a technique that is fast and cost-efficient, applicable on-site that can be applied on any type of sample of the desired representative volume, resulting in a reliable mineralogy. Therefore, an automated software High Speed Mineralogical Quantification (HSMQ) based on fast Fourier Transform InfraRed spectroscopy (FTIR) was developed to acquire very quick and cheap mineralogical analyses, applicable on very small sub-samples of various origin (cuttings, core, trims, scale,…) and of which the result can be compared to results obtained by XRD-analyses.

FTIR characterizes compounds not by their crystal lattice parameters as does XRD, but by identifying characteristic intramolecular vibrations in chemical bonds. Each of these vibrations occur at a different frequency that is unique for every chemical bond and phase. As these frequencies match those of Mid InfraRed (MIR) light with wavenumbers between 400 cm-1 and 4000cm-1, phases can absorb the MIR light which excites the molecular vibrations. A detector is then able to detect which frequencies were absorbed, hence leading to a chemical bond fingerprint of samples.

However, as chemical bonds are not singularly characteristic for individual minerals and spectral peak interferences are common, direct mineral characterization is too complex and calibration with the more accurate XRD method is imperative.

We (the authors, on behalf of Qmineral) have leveraged our established XRD turnaround network to build an FTIR-HSMQ model that is XRD-calibrated. Although Qmineral is a commercial entity, all software algorithms and calibration data presented here have been peer-reviewed and validated under blind, round-robin conditions, ensuring a proven very high data quality [3].

With the use of these very high quality calibration XRD data, this has allowed to identify and quantify an extensive list of minerals within the FTIR-HSMQ models.The most important minerals in the models entail, but are not limited to, quartz, K-feldspar, plagioclase, calcite, dolomite, Fe-dolomite, siderite, pyroxene, amphibole, muscovite, smectite, illite and illite/smectite, kaolinite, chlorite, glauconite, pyrite, barite, gypsum, anhydrite, jarosite, halite and forsterite. Additionally, also Total Organic Content (TOC) was incorporated as an output parameter in HSMQ which provides an estimate of the organic matter present in samples.

The technique developed and presented in this paper does not replace the lithologs shot in a well or on cores during a drilling campaign, nor the high-quality XRD-mineralogy that can be performed on (post-mortem) samples in the lab. Instead it intends to bridge the gap between them, in order to valorize the geophysical data by allowing a more qualitative and quantitative interpretation of the logs and allowing the laboratory data to be extrapolated by using the continuous signal acquired during logging.

3 The Boom Clay Formation as a case study

With the aim of using the FTIR technique to derive the mineralogy and fine-tune it, it has been chosen to start from a geological deposit that is already very-well characterized from a mineralogical point of view but nevertheless has a complex mineralogical composition. The Boom Clay is studied in detail for more than 45 years in the framework of potential geological disposal of radioactive waste, in Belgium. Boom Clay and adjacent lithologies, on which this study will concentrate, is known from the field (quarries for brick industry in outcrop area) and from boreholes (subcrop occurrence area), mostly drilled in the framework of possible radioactive waste disposal, i.e. where Boom Clay occurs at a depth of a few hundreds of meters depth and has a reasonable thickness of about 100 m.

Research on the mineralogical composition of this clay formation has been a process of continuous improvement over all these years and has allowed to perfect mineralogical analyses based on the XRD-technique on such fine-grained sediments. The authors have gathered a large database of mineralogical data of which the corresponding samples are still available for FTIR-analyses, and new samples can easily be taken.

The Boom Clay mineralogy and clay mineralogy is very well known. The detrital compounds are mainly quartz, feldspars and clay minerals which are intimately linked to grain-size distribution and are well controlled, i.e. mineralogy of narrow size fractions is stable over large stratigraphic thickness. On the bulk, however, carbonates, pyrite and organic matter are independent variables, having a diluting effect on absolute amount of detrital compounds in the bulk. Carbonates also occur highly concentrated in septarian concretions which are present as stratigraphic key horizons in the Boom Clay (so-called "S"-horizons) that allow for regional lateral correlations [4]. In this study, the FTIR-model was developed to be able to accurately determine the solid matter composition of a clayey sediment having these peculiarities. For the stratigraphic position and lithostratigraphic subdivision of the Boom Clay Formation, the reader is referred to the designated review papers [5, 6].

4 Materials

This study presents three case studies where FTIR-HSMQ was deployed on different material types in order to demonstrate the potential and versatility of the technique. The first is a high-resolution outcrop study (N=269 with 7cm sample spacing) in the Rumst quarry (Belgium) to compare the results with the known microstratigraphy and evaluate the accuracy of FTIR-HSMQ with the reference XRD. Secondly, a high-resolution study on borehole core samples (N=689 with on average 20cm sampling spacing) of the Essen-1 borehole (Belgium) was applied to compare with the known microstratigraphy and the geophysical well logging. Core samples were sampled as 2cm diameter plugs obtained by hand drilling. Finally, FTIR-HSMQ was also applied on borehole cutting shoe samples (N=315, 1m spaced) and cuttings (N=67) of the Mol-2D borehole (Belgium) to compare the results with the geophysical well logs. Two 1m-long cores were also sampled every 4cm, in order to compare the mineralogical data with the variability observed in the core logging data (see Fig. 1 far right). Whereas the first two case studies mainly focus on the Boom Clay Formation and the surrounding formations, the characterization of the Mol-2D borehole crosscuts nearly the entire Cenozoïc stratigraphy of Northern Belgium.

For testing, all different types of samples were used and tests were performed in the lab and directly during dedicated sampling session at the EURIDICE core library, in Mol (Belgium), in order to simulate on site sample handing and mineralogy determination.

The quarry samples are from the Wienerberger clay pit in Rumst (51°05'38"N 4°24'52"E) and give access to the central part of the Boom Clay Formation (Terhagen Member, Putte Member, between the S30 and S60 septarian horizons).

Boreholes samples originate from the Essen-1 borehole (51°27'27"N 4°27'53"E) drilled in 2006 and the ON-Mol-2D borehole (51°14'54"N 5°11'55"E) drilled in 2014. The Essen borehole was cored between 145 and 302 m below drilling table (m bdt), comprising the targeted Boom Clay between 153 and 281m bdt. The borehole reached a total depth of 505 m (destructive drilling). After coring and a first campaign of sampling in 2006, longitudinal slices were taken from the cores and these were sampled in the framework of this study. There are no samples available from the destructive parts of the

Essen-1 borehole. The ON-Mol-2D borehole was cored in the interval 308-448 m bdt, containing the Boom Clay Formation (313 – 418 m bdt), in the interval the 475-483 m bdt and in the interval 499-625 m bdt. The ON-Mol2D borehole reached a total depth of 648 m bdt. Almost all core shoe samples were preserved and systematically sampled in the framework of this study. Cuttings, collected during the destructive parts of the drilling, were preserved as well and exploratory sampled in the framework of this study. Both the Essen-1 and the ON-Mol2D borehole were extensively logged during the drilling campaigns.

5 METHODS

FTIR analyses were performed using a Bruker Alpha II Compact FTIR Spectrometer with a Platinum ATR (Attenuated Total Reflectance) module equipped with a monolithic diamond crystal. The procedure involves sample selection, drying, homogenization and fast, short milling , FTIR measurement and automated data interpretation (Fig. 1 and Fig. 2). Core sampling was done by drilling 2cm plugs with a Forstner-type drill bit which resulted in mm-sized grains. After drying (oven-drying, 80°C, if necessary), the samples were homogenized and further crushed for 30s with a Fritsch Pulverisette P23. A second milling step of 30s was repeated for a smaller sample aliquot of about 0.1-0.5g to a size approximately <90µm. After recording of the background conditions (duration 20s), the powder sample is inserted in the FTIR instrument by pressing it firmly against the diamond crystal by the measurement rod after which the measurement is started (duration 20s). The raw data interpretation is performed by the fully automated HSMQ software, to which end the bulk mineralogy,clay speciation, and organic content data are available within minutes.

Reference laboratory XRD measurements for validation were performed on McCrone milled and spray-dried powders, measured on a Bruker D8 diffractometer equipped with Cu-Kα radiation and a LynxEye Xe-T detector. XRD data interpretation is based on an in-house procedure. Qmineral's XRD accuracy has been validated through round robin contests and is better than 0.4% for non-clay minerals and better than 1% for clay mineral phases [3].

Reference laboratory Total Organic Carbon (TOC) measurements were performed by chromatography. Samples used for X-ray diffraction analysis were carefully weighed in a ceramic cup and repeatedly treated with 10M HCl added to remove the anorganic carbon (carbonates) from the samples. Samples were then processed by a Carlo Erba EA1108 Elemental analyzer

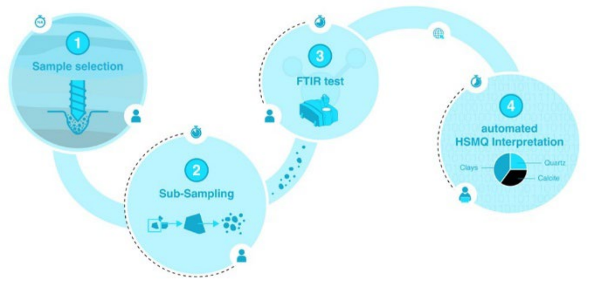

Fig.1 Workflow of the FTIR characterization in four steps. After sampling of cuttings, material is dried and crushed by a small mill in two steps. After measurement of the background (duration 20s), the powder sample is pressed between the measurement rod and the diamond crystal and the measurement is started (duration 20s). The mineralogical, clay mineralogical, and organic content interpretation by the HSMQ software has been fully automatized and is made readily available to the user.

5 Results

The nearly continuous mineralogical data for the Rumst outcrop section, both with FTIR-HSMQ and XRD as a reference are shown in Fig. 3. The comparison of both methods shows an nearly 1:1 correlation for the major mineral groups such as quartz, clays and carbonates. All trends, excursions or outliers observed with XRD are also very well represented in the FTIR data. Quartz absolute deviations are on average around 1.5%, clay minerals vary between 2% and 4% whereas feldspars have absolute deviations of 0.5-0.8% (but are also less abundant). Trace minerals such as pyrite, sulphates, Ti-oxides and apatite provide reliable quantifications down to ca. 1%, which is a good estimation as detection limit for the technique. This confirms the status of FTIR characterization as a fast screening technique. For better detection limits and the highest accuracy, lab-based X-ray diffraction would remain the preferred method.

The FTIR-HSMQ data highlight the presence of the key stratigraphic horizons in the Putte and Terhagen Members of the Boom Clay: the calcitic septarian concretions S30, S40 and S50, the calcitic, sideritic and pyritic S60 horizon and the two successive silt-sand layers ("DB") marked with elevated quartz contents. A clear kaolinite peak seems to indicate the base of the pink ("R") horizon. The data also show the expected inverse relationship between quartz, feldspars and total clays as a result of the sedimentary silt/clay layering typical for Boom Clay. This rhythmic alternation allows to count individual bands between the key horizons which seems to coincide well with the observations known in literature [7, 8]. Apart from the obvious septarian horizons, dispersed calcite occurs only in the lowermost part of the Terhagen Member and these low concentrations are well picked up by the FTIR. TOC-values quantified by FTIR also follows the silt/clay layering with the section between the DB and S40 horizons (interval 7.5-10m) being clearly more organic-rich which matches with observations on the field [4,54].

The FTIR data acquired very small core samples of the Essen-1 borehole (Fig. 4) show a characterization of subsurface core samples and allow a comparison with the natural gamma-ray (GR) and resistivity (RES) logs in order to better understand these log signal in a qualitative and quantitative way. As FTIR-HSMQ allows quantification of the major K-bearing minerals such as K-feldspar, muscovite, illite, llite/Smectite and glauconite, but also of the organic content, the natural gamma-ray curve can be understood in detail. Although there is an obvious difference in resolution between the log data (continuous measure with reported data points approximately 5-10cm spacing) and the FTIR data (approximately 20cm spacing), the quartz and total clay data show the same trends as the gamma-ray data to allow stratigraphic interpretation and thus validate the log signals interpretation, even before the log signals have been interpreted. It allows to identify the most clayey, and thus quartz- and feldspar-poor Putte and Terhagen Members in the central part whereas the Boeretang Member and certainly the lowermost Belsele-Waas Member clearly consist of higher quartz and feldspar contents.

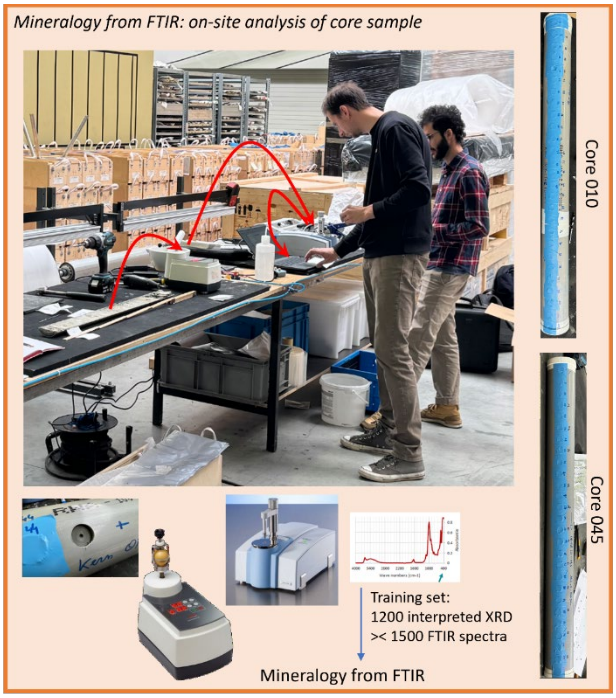

Fig.2 On-site FTIR characterization of core material of the Essen-1 and ON-Mol-2D borehole in the core repository of ESV Euridice in Mol, Belgium. Samples are either drilled using a Forstner drill of 2cm diameter from open, slabbed core (large picture) or from closed core through the pvc tubing (lower left image). Samples are subsequently milled using a small milling device (lowermost image), measured with a Bruker Alpha-II FTIR-ATR (lower central image) and subsequently interpreted by the automated HSMQ software.

The FTIR data also mark important lithological and stratigraphic changes that are not visible on GR/RES such as carbonate data highlighting the positioning of the key horizons (S20, S30, S40, S50, S60), high kaolinite - contents indicating the base of the pink R horizon and high TOC indicates the organic-rich black clay at the base of the Putte Member, which is also marked by a high gamma-ray signal. FTIR also allows to identify glauconitic sand deposits, in the Essen-1 borehole occurring on top of the Boom Clay Formation (Fig. 4), of which the well log signals are often very poorly understood as glauconite occurs as sand-sized pellets composed of clay plates with a K2O-content of approximately 7% but also show low resistivity.

The third presented case study shows FTIR data obtained on 1m-spaced cutting shoe samples from the ON-Mol-2D borehole, augmented with cutting samples in parts which were not cored, which crosscuts several hundreds of meters of Belgian Cenozoïc stratigraphy (Fig. 5). The FTIR mineralogy readily allows to interpret stratigraphy. Glauconite abundance marks Neogene glauconitic sands in the 20-285m interval but is also prominently identified below the Boom Clay Formation (below the Belsele-Waas Member on Fig. 4) and the Boom Clay Formation is readily identified with high clay contents and low quartz + feldspars contents below 341m, in accordance with the high natural gamma-ray and low resistivity values on the logs. Foremost, consistent mineralogical data aid in understanding trends and excursions in the well logging data. Even more, often trends and stratigraphic horizons are even better marked so that certain stratigraphic boundaries, interpreted based on logging signals, could even be challenged. One could for instance argue the upper boundary of the characteristic very clayey Aalbeke unit, not very clear on the well logs, but based on the high total clay contents, the boundary would logically be drawn a few meters lower (Fig. 5). Based on the compositional data, also the boundary between the Mons-en-Pevele and Orchies units could be drawn a few meters higher so that the highest clay contents are still part of the Orchies unit.

Specific mineralogical excursions can also be linked to stratigraphic boundaries or units which are more difficult to identify using well logging. Similar to the previous presented cases is the elevated organic content at the base of the Putte Member which is also marked by the high gamma-ray in that section (Fig. 4). Another example is the base of the Orchies unit, being marked by a very distinct increase in K-feldspar, which is a very useful new marker for this stratigraphic boundary. Carbonate-bearing units such as the Brussels Formation are also very clearly marked as well as the base of the Lede Formation which appears to be very rich in glauconite. It is clear that the FTIR mineralogy provides a powerful tool to better understand the well logging signals and when combined, allow to draw more reliable stratigraphic boundaries.

6 Conclusion

The data presented show that FTIR-HSMQ is a fast, accurate, reliable and objective tool for quantitative mineralogical, clay mineralogical and organic content measurements that can be performed directly on the field and outcrops or immediately on the wellsite for cuttings or scale analysis when fast decisions are required, even when sampling density is low or drilling goes very fast. As the time for FTIR analysis only takes 6-7 minutes from milling to data reporting, augmented with the time required for washing and drying cuttings, this allows to keep up with analysis on cored drillings (within the order of 0.5-1h/m core) or even with destructive drilling (within the order of 15-20 minutes/3m). All major and crucial minerals and organic matter can be reported and this allows for quick identification of potential wellbore stability issues (swelling clays), an improved stratigraphic interpretation of units (quartz, feldspars, carbonates clay speciation,…), lithological boundaries and key horizons and correlation with the well log data and furthermore already provides a first compositional screening that allows a better informed decision making for detailed subsampling. Additionally, also on slabbed cores or even closed cores FTIR analysis can be very valuable as often specific observations and hypothesis are formulated in the core repository, as these can be directly tested by fast FTIR-HSMQ analysis.

FTIR analyses is a more objective alternative for mudlogging, without the need for a highly skilled operator on site, also leads to faster stratigraphic and even microstratigraphic positioning within formations, identification of key horizons that allow to take faster drilling-technical decisions, deduction of fundamental reservoir properties such as mechanical parameters, sorption, radionuclide transport, hydrological parameters and (thermal) conductivity.

Quantitatively, the technique approaches that of Qmineral's high-quality XRD and provides a much higher detail and level of accuracy than other techniques currently available on the market. The relatively low cost of the technique compared to lab analyses allows for more continuous data collection.

The initial XRD-calibrated FTIR-HSMQ models that were set up are not confined for only the Boom Clay Formation but, as demonstrated in the two borehole case studies, appear to wider applicable within the regional context of sedimentary basins. XRD calibration is therefore not required for each new study and can be used within the same context. Evidently, specific calibration also yields even more accurate mineralogical HSMQ output.

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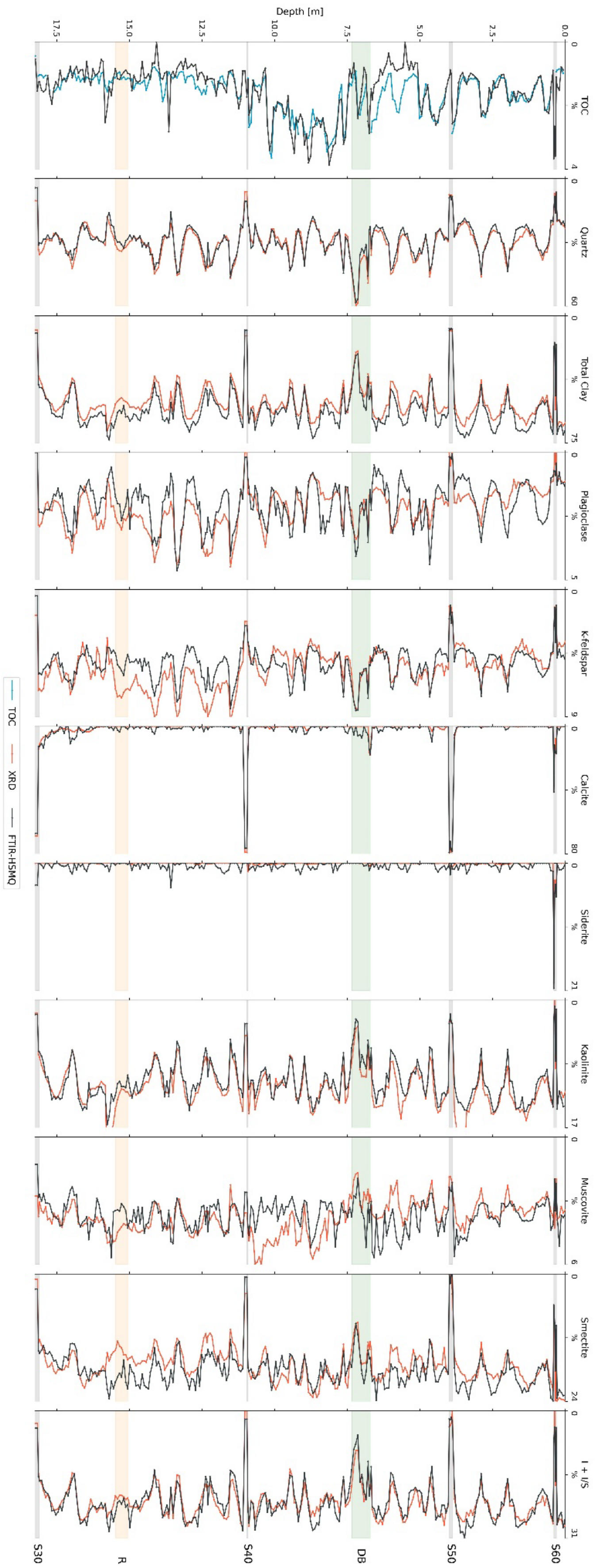

Fig. 3. Mineralogical and clay mineralogical results of the Rumst outcrop and comparison with the known microstratigraphy of the Boom Clay Formation. The curve in black is the FTIR-HSMQ quantification, the curve in red represents the XRD reference data, the curve in blue represents the TOC reference data..

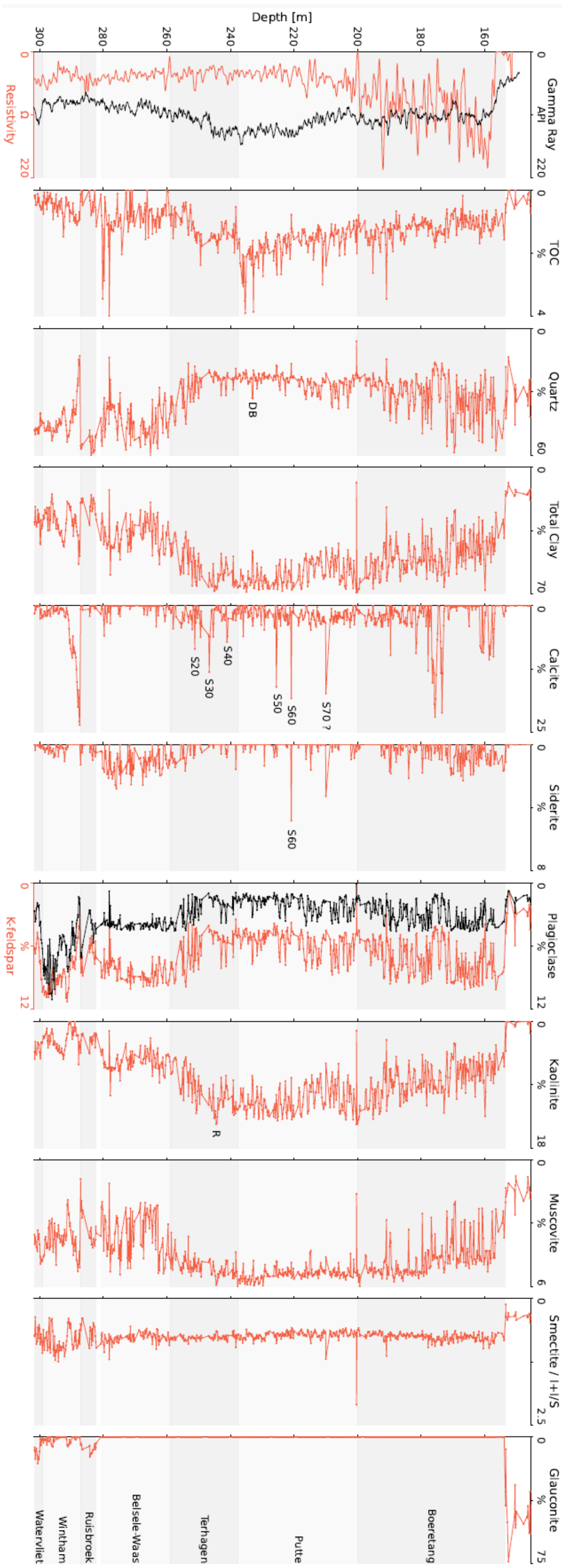

Fig. 4. Mineralogical and clay mineralogical results of the Essen-1 borehole with reference to the natural gamma-ray and resistivity logs and stratigraphic interpretation. Some of the key horizons with in the Boom Clay Formation (Belsele-Waas Member, Terhagen Member, Putte Member, Boeretang Member) have indicated.

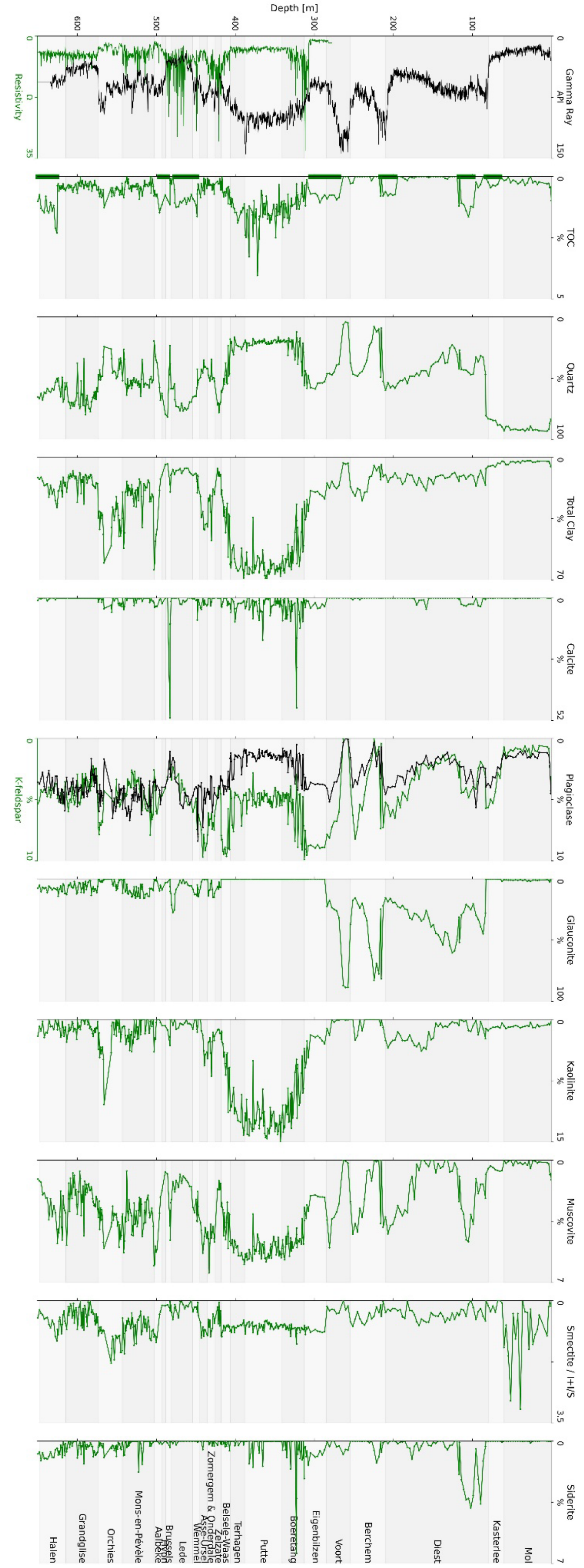

Fig. 5. Mineralogical and clay mineralogical results of the O/N-Mol-2D borehole with reference to the natural gamma-ray and resistivity logs and stratigraphic interpretation. Intervals where cuttings where used for analysis are indicated by green dots on the left of the TOC plot.