

Impact of the heterogeneity of the sandy facies of Opalinus Clay on the retention of Cs, Co and Eu

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M.Sc. Florian Markus Steegborn

1. Referent: Prof. Dr. Horst Geckeis

2. Referent: Priv.-Doz. Dr. Frank Heberling

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Zusammenfassung

Tiefliegende geologische Formationen haben sich als Hauptkandidat auf der Suche nach einem geeigneten Standort für ein Endlager für hochradioaktiven Abfall zur effektiven Isolierung der hochradioaktiven Materialien von der Biosphäre herausgestellt. Unter diesen Formationen wurde der Opalinuston (OPA) als Wirtsgestein für ein Endlager des radioaktiven Abfalls der Schweiz [1] vorgeschlagen, welcher auch in Deutschland in Frage kommt [2]. Der OPA kann in eine Vielzahl von Fazies unterteilt werden, die durch ihre unterschiedliche Mineral- und Fossilzusammensetzungen gekennzeichnet sind [3]. Die sandige Fazies des OPA ist durch einen vergleichsweise hohen Anteil an Quarz und Carbonaten gekennzeichnet und weist eine ausgeprägte Heterogenität im Milli- bis Dezimeterbereich auf. Diese Heterogenität ist eine Gemeinsamkeit mit norddeutschen Tongesteinsformationen aus der Unterkreide und dem Jura und könnte das Migrationsverhalten von Radionukliden und weitere geochemische Eigenschaften entscheidend beeinflussen. In dieser Studie werden daher umfangreiche Analysen an mehreren Bohrkernen der sandigen Fazies durchgeführt, um den Einfluss der Heterogenität auf die mineralogische Zusammensetzung und weitere geochemische Parameter zu untersuchen. Um diese Heterogenität zu quantifizieren und sie in Modellen und Sicherheitsanalysen berücksichtigen zu können, wird ein repräsentatives Elementarvolumen (REV) für die untersuchten Parameter abgeschätzt. Dabei ist das untere REV definiert als das kleinste Probenvolumen, ab welchem die Datenstreuung eine zuvor aufgestellte Grenze unterschreitet und eine Probe daher als repräsentativ und homogen im Hinblick auf den untersuchten Parameter und die untersuchte Skala angenommen werden kann [4]. Das obere REV ist das größte Probenvolumen, welches nur die untersuchte Skala umschließt und nicht benachbarte Domänen miteinbezieht [5]. Diese beiden Volumina sind wichtige Parameter, um experimentelle Daten zu modellieren. Hierbei gibt das untere REV das minimale Probenvolumen an, welches experimentelle Proben umfassen müssen um als repräsentativ angesehen werden zu können und das obere REV das maximale Probenvolumen an, zu welchem diese Daten jeweils hochskaliert werden können.

Gemäß der aktuellen Klassifizierung der OPA Fazies nach Lauper et al. (2021) [6] konnten die untersuchten Bohrkernabschnitte den Subfazies SF2 und SF3 zugeordnet werden, zu welchen sie eine ausgeprägte visuelle und mineralogische Übereinstimmung aufweisen. Mit unterschiedlichen Methoden konnte eine repräsentative elementare Bohrkernlänge (REL) von $\approx 30\text{--}140\text{ cm}$ und $\approx 10\text{--}100\text{ cm}$ für SF2 und SF3 aufgestellt werden. Unter Anbetracht der Auflösung der zugrundeliegenden Bestimmung sind diese Längen vergleichbar mit Literaturdaten [6].

Eine Untersuchung zur Abhängigkeit der Datenstreuung der mineralogischen Zusammensetzung vom Probenvolumen zeigt das zu erwartende Verhalten, dass kleinere Proben spezifischer sind und eine größere Bandbreite an Werten annehmen. Am Beispiel des Illitgehalts zeigt sich bei abnehmendem Probenvolumen von 2000 cm^3 auf 1 cm^3 eine Vergrößerung der Streuung von $\pm 0,75\text{ Gew\%}$ auf $\pm 8,0\text{ Gew\%}$. Als minimales REV für die Mineralogie kann ein Volumen von mindestens 85 cm^3 vorgeschlagen werden, ab welchem die mineralogische Zusammensetzung mit der zugeordneten Subfazies übereinstimmt. Es wurden Andeutungen gefunden, dass ein Volumen von $\leq 2000\text{ cm}^3$ größer als das obere REV sein könnte und sich damit über mehrere Subfazies erstrecken würde. Parallel zur Schichtung des Tongesteins zeigt sich eine ausgeprägte Homogenität auf einer Länge von bis zu 20 m . Innerhalb dieser Reichweite schwankt die mineralogische Zusammensetzung weniger als die analytische Unsicherheit der Bestimmungsmethode. Eine Probe mit einer Dicke von 2 cm (Volumen von 85 cm^3) kann daher als repräsentativ für weite laterale Distanzen in diesem vergleichsweise heterogenen Tongestein angesehen werden.

Neben der Auswirkung der Heterogenität auf die mineralogische Komposition des Tongesteins, untersucht diese Studie die Auswirkung auf das Sorptionsverhalten gegenüber Caesium (Cs-137), Cobalt (Co-60) und Europium (Eu-152). Diese Nuklide wurden beispielhaft als ein Spaltprodukt, Aktivierungsprodukt und Homolog dreiwertiger Actinide ausgesucht, um das Verhalten von ein-, zwei- und dreiwertigen Kationen zu untersuchen. In Batch-Sorptionsexperimenten werden Verteilungskoeffizienten ($\log_{10}(R_d)$ -Werte in $\log_{10}(\text{L/kg})$) im Bereich von $2,3\text{--}3,1$ für Caesium, von $1,8\text{--}2,9$ für Cobalt und von $4,3\text{--}5,5$ für Europium bestimmt. Diese Bandbreite stimmt gut mit vorhandenen Daten für die tonige Fazies überein. Bei der Untersuchung der Abhängigkeit der Sorptionsdatenstreuung vom Probenvolumen zeigt sich im Gegensatz zur Mineralogie nur eine sehr geringe Variation der Adsorption von Caesium und Cobalt über alle untersuchten Volumina. Im Vergleich zur durchschnittlichen Verteilung wird eine Streuung der $\log(R_d)$ -Werte von weniger als $\pm 0,3$

log-Einheiten beobachtet. Eine Probe mit einem Volumen von nur 8 cm³ kann daher als repräsentativ für die ganze zugrundeliegende sandige Fazies angesehen werden, sogar über die Subfazies-Klassifizierung hinweg [6]. Ein leicht größeres REV von 27 cm³ wird für die Adsorption von Europium vorgeschlagen, was durch die generell sehr starke Sorption von trivalenten Kationen an OPA bedingt ist.

Die Rückhaltefähigkeit der tonigen Fazies des OPA und anderer Tongesteine lässt sich sehr gut durch Modellrechnungen reproduzieren [7, 8]. Im sogenannten „bottom-up approach“ werden die Sorptionseigenschaften alleinig wenigen Tonmineralen zugeschrieben, um experimentell gewonnene Daten zu simulieren. Um zu überprüfen, ob sich die zugrundeliegenden Annahmen des Modells auch auf die sandige Fazies mit einem geringeren Tonmineralanteil übertragen lassen, wurden geochemische Modelle mit dem Modellierungscode PhreeqC aufgesetzt.

Versionen des „Generalized Cesium“ (GCs)- und des „two-site protolysis non-electrostatic surface complexation and cation exchange“-Sorptionsmodells (2SPNE SC/CE), die von Bradbury und Baeyens [8-10] eingeführt wurden, liefern eine vom Illitgehalt abhängige Einschätzung des Sorptionsverhaltens für alle drei untersuchten Kationen. Diese Modellrechnungen beschreiben das Sorptionsverhalten von Caesium gut und weichen nur leicht vom beobachteten Sorptionsverhalten von Cobalt ab. Für die Europium-Sorption unterschätzt das Modell die experimentell bestimmten Sorptionskoeffizienten. Modell- und Laborergebnisse stimmen jedoch darin überein, dass mehr als 99,5 % des Europiums adsorbiert. Die Unterschiede können daher auch durch experimentelle- und Datenunsicherheiten verursacht worden sein.

Zeitaufgelöste Laserfluoreszenzspektroskopie (TRLFS) mit Curium wurde durchgeführt, um die für die Sorption dreiwertiger Kationen relevanten Mineralphasen und Spezies zu überprüfen. Die Ergebnisse deuten auf die Bildung ternärer Oberflächen-Carbonat-Sorptionsspezies auf den reinen Tonmineralen und Calcit hin, charakterisiert durch eine verlängerte Fluoreszenzlebensdauer und einer bathochromen Verschiebung des Spektrums. Die Sorption an natürlichem OPA findet überwiegend an Illit statt. Anzeichen einer gleichzeitigen Sorption an anderen Tonmineralen und Calcit werden aber ebenfalls beobachtet. Die Untersuchung an einem dem natürlichem OPA nachgebildeten Gemisch aus Mineralen zeigt dasselbe Verhalten, aber mit einem stärkeren Einfluss des Calcits, was sich durch eine stärkere Ausprägung von Einbauspezies zeigt. Dies ist erklärbar durch den Einsatz von synthetischem Calciumcarbonat als Ersatz für natürlich gealterten und äquilibrierten Calcit. Durch eine

Verlängerung der Sorptionszeit von einem Tag auf dreißig Tage wird eine ausgeprägtere Sorption auf fast allen untersuchten Mineralphasen beobachtet.

Um die Auswirkung der Heterogenität auf einer intakten OPA-Oberfläche mikroskopisch zu untersuchen, wurde diese mit einem Elektronenmikroskop analysiert. Anschließend wurden Autoradiographie-Experimente mit den drei zuvor genannten Kationen durchgeführt. Hier zeigt sich die starke Tonmineralabhängigkeit in der Caesiumsorption, wobei bedingt durch experimentelle Schwierigkeiten bei der Sorption von Cobalt und Europium keine eindeutige Zuordnung zu Mineralphasen möglich war.

Die vorliegende Doktorarbeit wurde im Rahmen des Verbundprojekts iCross durchgeführt, unter Förderung durch das Bundesministerium für Bildung und Forschung (02NUK 053 C), sowie durch die Helmholtz-Gemeinschaft (SO-093).

Abstract

In the selection process for a disposal site of high-level radioactive waste, deep geological formations have emerged as the most promising candidates for an effective long-term isolation of highly active radionuclides from the biosphere. Of these formations, Opalinus Clay (OPA) has been proposed as the host rock for a nuclear waste repository in Switzerland [1] and is also in discussion for a German repository [2]. OPA may be subdivided into different facies, distinguished by variations in mineral and fossil composition [3]. Of these, the sandy facies is characterized by comparatively higher quartz and carbonate contents and displays a more pronounced heterogeneity at the milli- to decimeter-scale. This heterogeneity is a similarity to the Lower Cretaceous and Jurassic clay rocks from Northern Germany and might play a crucial role in influencing the radionuclide migration potential and other geochemical properties. Therefore, extensive analyses of multiple cores of sandy facies OPA have been performed in this study to gather information on the impact of the heterogeneity on the mineral composition and other important geochemical characteristics. For a concise and quantitative display of this heterogeneity and to be able to take it into account in modeling approaches and safety analyses, a representative elementary volume (REV) is estimated for the investigated properties. The lower REV is defined as the smallest sample volume, from which the data scattering falls below a previously established limit. A sample with such a volume can therefore be considered representative and homogeneous with regard to the parameter and scale under investigation [4]. The upper REV is the largest sample volume that encloses only the investigated scale and does not include neighboring domains [5]. Both of these volumes are important parameters for modeling experimental data, since they indicate the minimum volume experimental samples need to encompass in order to be considered representative and the maximum volume to which these representative data can be upscaled at a time.

According to the most recent classification of OPA facies by Lauper *et al.* (2021) [6], segments of the investigated cores are assigned to the subfacies SF2 and SF3, to which they display a pronounced visual and mineralogical concordance. Utilizing two different methods, a representative elementary core length (REL) of $\approx 30\text{--}140$ cm and $\approx 10\text{--}100$ cm has been postulated for SF2 and SF3, respectively, depending on the properties taken into account during the determination. Taking into account the resolution of the underlying determination method, these lengths are comparable to literature data [6]. An investigation on the dependence of the data scattering of the mineralogical composition on the sample volume shows the expected behavior that smaller samples are more specific and assume a wider range of values. On the

example of the illite content, reducing the sample volume from 2000 cm³ to 1 cm³ induces an increase in data scattering from ± 0.75 wt% to ± 8.0 wt%. A volume of at least 85 cm³ is proposed as the minimum REV, above which the mineral composition corresponds to the assigned subfacies'. Indications have been found that a volume of ≤ 2000 cm³ could be larger than the maximum REV for the mineralogy, encompassing more than a single subfacies. Parallel to the bedding, a pronounced homogeneity over a length of up to 20 m is observed. Within this range, the mineral composition of the main components varies less than the analytical uncertainty of the determination method. A sample with a thickness of only 2 cm (volume of 85 cm³) can therefore be regarded representative for wide lateral distances in this comparatively heterogeneous clay rock.

Besides the impact of the heterogeneity on the geological characteristics of the clay rock, this study also explores the impact on the retention behavior towards cesium (Cs-137), cobalt (Co-60) and europium (Eu-152). These nuclides are selected to represent a fission product, an activation product and a homologue to the trivalent actinides to study the behavior of mono-, di-, and trivalent cations. In batch sorption experiments, distribution coefficients ($\log_{10}(R_d)$ -values in $\log_{10}(\text{L/kg})$) are determined in the range of 2.3–3.1 for cesium, from 1.8–2.9 for cobalt and from 4.3–5.5 for europium. These ranges compare well with existing data on the shaly facies. In contrast to the mineralogy, the investigation on the dependence of the sorption data scattering on the sample volume shows only a very small variation in the adsorption of cesium and cobalt across all investigated volumes. Compared to the average distribution coefficient, a scattering of the $\log(R_d)$ -values of less than ± 0.3 log units is observed. A sample with a volume as small as 8 cm³ can be considered representative for its originating sandy facies, even across multiple subfacies [6]. A slightly larger REV of 27 cm³ is proposed for the adsorption of europium, which is caused by the generally very strong sorption of trivalent cations on OPA.

The retention capability of shaly facies OPA and other clay rocks is successfully reproduceable through modeling calculations [7, 8]. In the so-called “bottom-up” approach, the sorption properties are assigned solely to a few specific clay minerals in order to simulate experimentally obtained data. To investigate, if the underlying assumptions of this model are transferable to the sandy facies with a lower clay mineral content, geochemical adsorption models with the modeling code PhreeqC are set up. Versions of the “generalized cesium” (GCs) and the „two-site protolysis non-electrostatic surface complexation and cation exchange“ (2SPNE SC/CE) sorption model, introduced by Bradbury and Baeyens [8-10], provide an illite content-

dependent estimate of the sorption behavior for all three investigated cations. These model calculations describe the sorption behavior of cesium well and deviate only slightly from the experimentally determined sorption behavior of cobalt. For the adsorption of europium, the model underestimates the experimentally determined sorption coefficients. Still, both model and laboratory data agree, that more than 99.5 % adsorbs. The differences may therefore also have been caused by experimental and data uncertainties.

Time-resolved laser fluorescence spectroscopy (TRLFS) with curium is performed, to verify the mineral phases and sorption species relevant for the sorption of trivalent cations. The results indicate the formation of ternary surface carbonate sorption species on the pure clay minerals and calcite, characterized by a prolonged fluorescence lifetime and a bathochromic shift of the spectrum. The sorption on natural OPA occurs predominantly on illite. However, signs of other clay minerals and calcite partaking in the sorption process are also observed. The investigation on a mixture of minerals imitating natural OPA shows the same behavior, but with a stronger influence of calcite, which is shown by a stronger expression of incorporation species. This may be explained by the usage of synthetic calcium carbonate as a substitute for naturally aged and equilibrated calcite. By extending the sorption time from one to thirty days, a more pronounced sorption is observed on most investigated mineral phases.

To investigate small-scale effects of heterogeneity microscopically, electron microscopy and autoradiography experiments on intact OPA rock surfaces are carried out with all three previously mentioned cations. Here, the strong clay mineral dependence of the cesium sorption is evident, whereby no clear connection to certain mineral phases has been possible for cobalt and europium, due to experimental difficulties caused by clay rock swelling.

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List of Abbreviations

OPA	Opalinus Clay
REV	Representative elementary volume
SF	Subfacies
REL	Representative elementary core length
GCs	Generalized cesium
2SPNE SC/CE	Two site protolysis non-electrostatic surface complexation and cation exchange
TRLFS	Time-resolved laser-induced fluorescence spectroscopy
LILW	Low to intermediate level waste
HLW	High level waste
BGE	Bundesgesellschaft für Endlagerung
DGR	Deep geological repository
NAGRA	Nationale Genossenschaft für die Lagerung radioaktiver Abfälle
WIPP	Waste isolation pilot plant
REA	Representative elementary area
MIP	Mercury intrusion porosimetry
SEM-EDX	Scanning electron microscope - energy dispersive X-ray spectroscopy
ARIMA	Auto-regressive integrated moving average
URL	Underground rock laboratory
CEC	Cation exchange capacity
PZC	Point of zero charge
BET	Brunauer-Emmett-Teller
HSAB	Hard and soft acids and bases
SIT	Specific ion interaction theory
XRD	X-ray diffraction
EDZ	Excavation damaged zone
COD	Crystallography open database
XRF	X-ray fluorescence spectroscopy
LOI	Loss on ignition
ICP-MS	Inductively coupled plasma - mass spectrometry
DSC	Differential scanning calorimetry
TGA	Thermogravimetric analysis
XPS	X-ray photoelectron spectroscopy
ISC	Intersystem crossing
TC	Total carbon
TIC	Total inorganic carbon
TOC	Total organic carbon
ICP-OES	Inductively coupled plasma - optical emission spectroscopy
IC	Ion chromatography
HDPE	High-density polyethylene
PP	Polypropylene
ISC	Intersystem crossing
LDPE	Low-density polyethylene
FWHM	Full width at half maximum
EXAFS	Extended X-ray absorption fine structure
FI	Fluorescence intensity
DLU	Digital light unit

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1. Introduction

Since the beginning of the nuclear age worldwide, the question of the disposal of produced radioactive waste arose. The exceptional properties of radioactive materials are predominantly used in electricity generation, scientific research, and medical applications. The accompanied production of waste materials in varying compositions and volumes cannot be prevented and must therefore be dealt with. The spectrum of radioactive waste encompasses small amounts of laboratory waste, to the large-scale debris produced during the decommissioning of nuclear facilities, to spent nuclear fuel. In the context of Germany's radioactive waste program, these materials are systematically classified into two categories: low-to-intermediate-level waste (LILW) and high-level waste (HLW). With the revision of the Atomic Energy Act (§7 Abs. 1a AtG), Germany decided to phase-out of nuclear energy production by April 2024 and to target the year 2050 for the disposal of HLW. However, according to recently revised schedule plans this could also be postponed. The total waste volume produced by that time is approximated to $\approx 500,000\text{--}600,000\text{ m}^3$ of LILW and about $\approx 27,000\text{ m}^3$ of HLW according to the Bundesgesellschaft für Endlagerung (BGE), the German nuclear waste management organization [11]. The large variation in the amount of LILW is caused by the uncertainty on the amount of contaminated rock salt necessary to be retrieved from the shaft Asse [12]. Though making up only $\approx 5\%$ of the total volume, the HLW constitutes to $\geq 99\%$ of the total activity of the waste [13]. It comprises spent nuclear fuel as well as vitrified waste from reprocessing and it is generating heat, due to the overall high activity. The current international consensus on how to deal with the amounting waste is the confinement in deep geological repositories (DGRs). This is currently considered the safest option for the exclusion of the HLW from the biosphere for up to one million years [14], which is the timeframe required by the German site selection act (§1 Teil 1 StandAG). Various types of geological formations are under investigation for a DGR, each with its own advantages and disadvantages. In general, a DGR is composed of a multi-barrier system, comprising three components [15]. The waste matrix and container act as the technical barrier, providing a certain resistance against radionuclide release and consequently water access to the waste form. The second barrier is the geotechnical barrier, consisting of backfill material adapted to the host rock and repository conditions. Bentonites are often discussed in this context, due to their high retention capability to minimize the release of radionuclides into the biosphere and their pronounced ability to inhibit water access to the waste container. On the other hand, mechanical stability properties also need to be considered. The third barrier is the geological formation, consisting of the chosen host rock.

Figure 1 shows a repository concept from NAGRA (Swiss waste management organization) for the proposed system in OPA [16, 17]. In their concept, the beforementioned bentonite will be used as a backfill material as the geotechnical barrier.

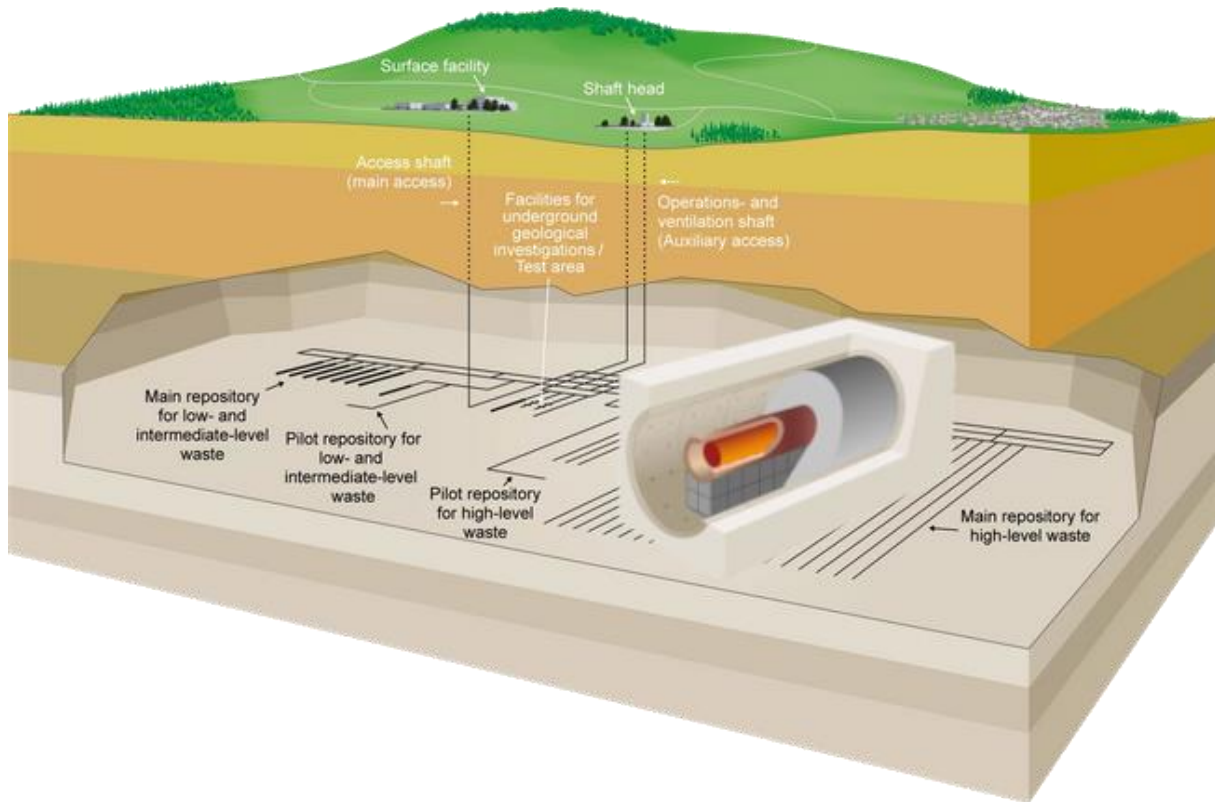


Figure 1: Final repository concept of NAGRA for a nuclear waste repository in Opalinus Clay, adapted from [16, 17].

Crystalline rocks like granite are mechanically stable and heat-resistant, but it is hard to ensure tectonic stress not leading to fracture formation during one million years in such a rock formation. This could lead to the generation of migration pathways for intruding groundwater, making the definite exclusion for a period of one million years difficult. Finland and Sweden both chose this host rock for their final repository, featuring a copper-lined cast iron container, with bentonite as a backfill material to ensure safe enclosure [18]. A big advantage of salt formations is their good thermal conductivity, allowing a tight packaging of the HLW. They are impermeable to water and gases, but have a low radionuclide retention capability in case of water inflow through other pathways. Salt rocks are the chosen formation for a LILW repository in Germany (Morsleben) [19] and in the United States of America with the waste isolation pilot plant (WIPP) in New Mexico [20]. Clay rock formations have low hydraulic permeability, a swelling capacity leading to self-sealing properties of potential fractures and exceptional retention capabilities. In case of radionuclide release from the containers, these are all very beneficial properties, especially in the electrochemically reducing conditions anticipated after

1. Introduction

sealing and oxygen consumption [21]. However, the mechanical stability of clay mineral rich formations is often limited due to the high plasticity, complicating the construction of a DGR. Nonetheless, clay rock is the chosen host rock formation in Switzerland (OPA, Nördlich Lägern) and it is thoroughly investigated in France [22] (Callovo-Oxfordian and Bure Clay) and Belgium [23] (Boom Clay). The German federal company for radioactive waste disposal (BGE) showed in their “Zwischenbericht Teilgebiete” (2020) all areas potentially fit to host a final nuclear waste repository in Germany [24], in accordance with the site selection act (§13–27 Teil 3 StandAG). This report proposed the clay rock areas shown in Figure 2 [25] as being in principle suitable. In southern Germany, these potential host rock formations consist primarily of OPA and the Bavarian Molasses, while the rock formations in the North consist of Jurassic, Tertiary and Lower Cretaceous clay rocks. These are characterized by saline groundwaters with ionic strengths up to 5 mol/L [26], as well as by a pronounced heterogeneity [27, 28]. OPA is composed of different facies, ranging from the relatively homogeneous clay-rich shaly facies to the more mechanically stable but comparatively more heterogeneous and less clay mineral containing sandy facies [29, 30]. The heterogeneous composition of the sandy facies bears some analogy to the Lower Cretaceous Clay formations in northern Germany. Of the geochemical properties defining the suitability of a host rock, one of the main criteria (“Abwägungskriterium”) are the sorption properties towards extruding radionuclides, at which clay rock formations excel. But, besides geochemical conditions, quite a number of other criteria and indicators have to be considered.

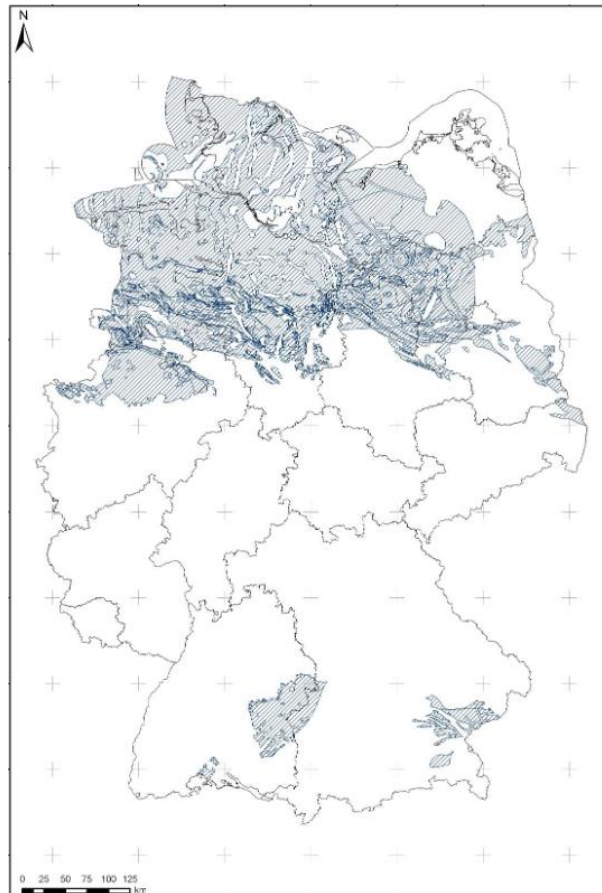


Figure 2: Map of Germany with the areas potentially suitable for a final repository in a clay rock formation highlighted in blue, taken from the “Zwischenbericht Teilgebiete” of the BGE [24].

For a profound safety analysis of a potential repository, the composition of the waste is of utmost importance. An parameter often referred to for this assessment is the long-term radiotoxicity of the waste, which is displayed against the time after emplacement in Figure 3 [31]. The contribution of fission products with a short half-life (e.g. Sr-90) rapidly decreases after the first decades and reaches radiotoxicity levels below natural occurring uranium after less a thousand years. Long-lived plutonium isotopes (Pu-239) and minor actinides with a long half-life (e.g. Am-243) are much more relevant on the timescale of a HLW repository [31].

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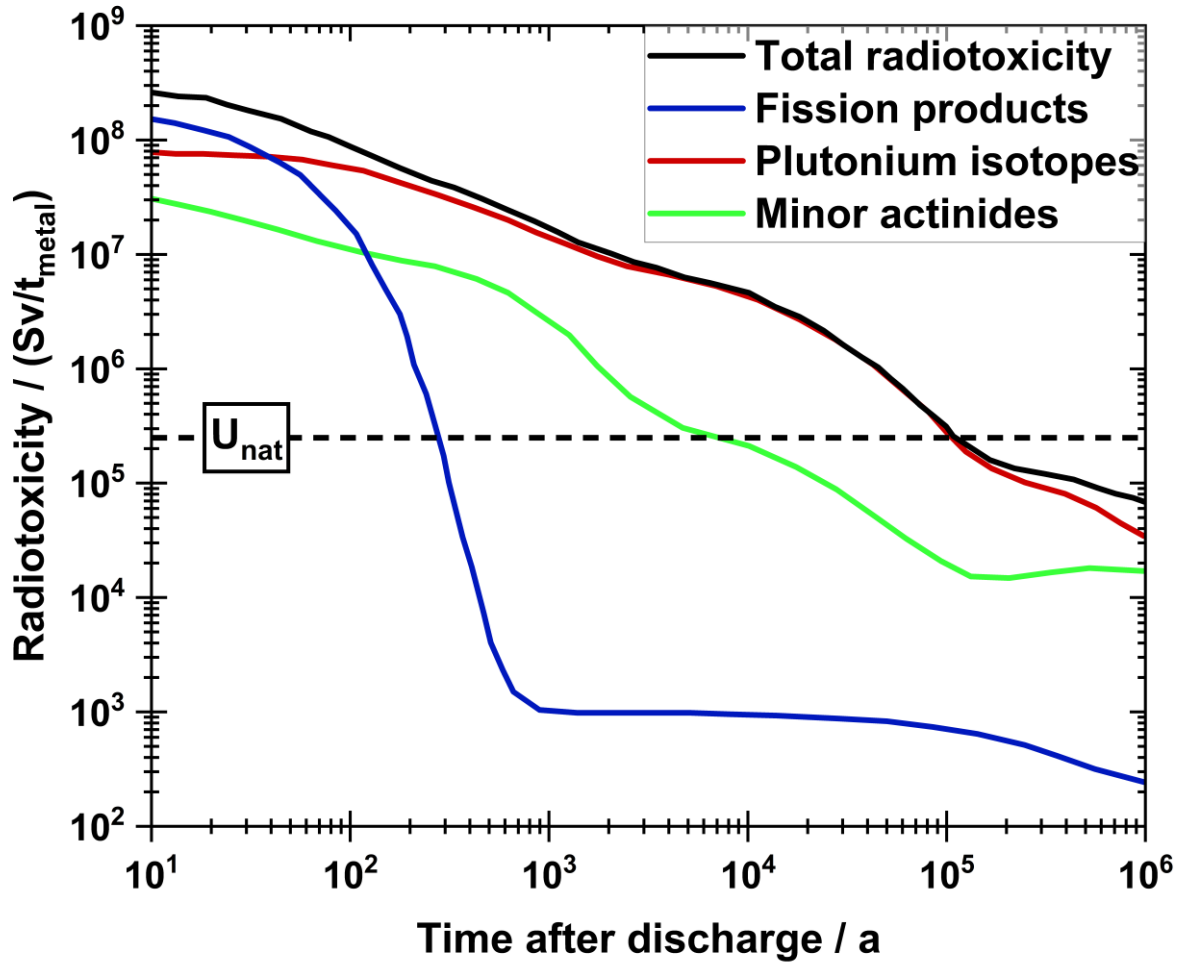


Figure 3: Time dependent radiotoxicity of spent nuclear fuel with the unit of dose (Sv) per mass of metal (t). U_{nat} added for reference of natural occurring uranium as a dashed line. Adopted from Geckeis et al. (2010) [31].

Besides these main contributors to the overall radiotoxicity, other long-lived fission- and activation products need to be considered, due to their comparably high solubility and mobility in the geo- and biosphere. I-129 and Cl-36 are the two main examples for long-lived and very mobile radionuclides. A wide spectrum of hazardous elements needs to be investigated under a multitude of relevant geochemical conditions to accurately assess repository safety. In this study, the radionuclides Cs-137, Co-60 and Eu-152 are investigated. These are not relevant in the risk assessment for a repository, due to their short half-lives, but act as surrogates for other more relevant radionuclides.

Batch sorption experiments are a comparatively easy way to obtain information on the retention capacity of the investigated material. Often a single sorption related parameter, like pH or sorptive concentration, is varied to assess its impact. Numerous sorption experiments have been conducted on shaly facies OPA [32-38] and its mineral constituents [39, 40]. These experiments concluded the radionuclide sorption on OPA to be reasonably well described by only taking the

clay minerals illite and montmorillonite into account. With the so called “bottom-up” approach experimental sorption data on the shaly facies OPA has been reproduced by establishing a geochemical model, estimating the retention behavior based on surface complexation and adsorption parameters on illite and montmorillonite. These modeling approaches are based on a limited number of variables and successfully reproduce experimentally determined radionuclide sorption on natural clay rock. Such models exist for a large set of adsorbing cations [7-10, 41, 42] on different clay rock formations and single clay minerals. In these approaches, a relatively homogeneous composition and a high clay mineral content are assumed, which is the case for the shaly facies OPA. For clay rocks bearing a more pronounced heterogeneity and lower clay mineral content in general, these approaches must not necessarily be true.

Spectroscopic investigations of the sorption mechanism allow an in-depth analysis of the processes taking place at the mineral-water interface. Multiple actinides, including the trivalent americium, curium, berkelium and californium show fluorescence in aqueous solutions [43]. This can be used to obtain information on the chemical environment of the investigated cation. For this purpose, many studies have been performed using time-resolved laser-induced fluorescence spectroscopy (TRLFS). Often spectra are recorded as a function of a single parameter (e.g., pH or ionic strength) to investigate variations in sorption species [39, 44-54]. For a precise understanding of the sorption mechanism in natural systems, the underlying experiment should be as close to the natural conditions as possible. Studies investigating the sorption onto clay rocks and its constituents under conditions present in a proposed repository are still scarce, especially studies taking possible carbonate complexation into account in combination with other ions present in natural pore waters.

The relatively high heterogeneity of some clay rocks, especially of the sandy facies OPA might play a crucial role in affecting the retention behavior towards radionuclides. The laminar bedding with concretions on the decimeter-scale likely influence the mineralogical composition and possibly other properties to a degree, that they need to be considered in a profound safety assessment. A possible center point in the evaluation of the heterogeneity is the representative elementary volume (REV). It refers to the minimum volume of a medium that is large enough to encompass a representative sample of the mediums’ macroscopic properties and characteristics [5, 55]. It is therefore suitable to quantitatively describe the heterogeneity of the sandy facies. It has to be noted, that each investigated parameter is described by a separate REV and the examined scale also needs to be taken into account [56, 57]. For the correct upscaling in geochemical transport models, especially concerning the porosity [29, 55], the REV is an

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important parameter. The representative elementary area (REA) is the two-dimensional counterpart to the REV. It is often analyzed in microscopic studies [58-60], but macroscopic imaging of intact clay rock surfaces of drill cores is also relevant [6]. The REV is important for a correct up-scaling of laboratory results to the repository-scale and ensure comparability of obtained data, especially in heterogeneous rocks. The lower REV offers the smallest volume needed to be processed experimentally to obtain representative data. The upper REV is defined as the maximum volume, which can still be considered representative and homogeneous, not exceeding the investigated scale. The upper REV is thereby important to simplify the procedure of modeling a large-scaled system. Due to the layered sediment structure of clay rocks, representativeness is anisotropic and shows differences depending on investigations perpendicular or parallel to the bedding [6, 61]. The investigated direction relative to the bedding also impacts diffusion experiments on a laboratory-scale [62] and in-situ [63] and therefore also needs to be considered.

With this premise, the following questions are addressed in this thesis:

What impact does the intrinsic heterogeneity have on the mineralogical composition of the sandy facies OPA? How large is a possible REV parallel and perpendicular to the bedding?

Does the heterogeneity impact the retention behavior towards cesium (Cs-137), cobalt (Co-60) and europium (Eu-152) in the same way? Does this impact change when comparing crushed powder and intact clay rock material?

Are established geochemical models for the sorption on illite and clay rocks also applicable to sandy facies OPA? Which mineral phases are taking part in the sorption process and to what extent? What are the dominant sorption species?

This study therefore aims to investigate the possible impact of the comparatively lower clay mineral content and more pronounced heterogeneity of sandy facies OPA on the radionuclide sorption. The pathway of choice is the conduction of batch sorption studies, geochemical modeling and spectroscopic investigations to obtain a profound understanding. Due to the lack of comparative sorption studies on the sandy facies OPA, a modeling approach also presents an adequate way to explore sorption behaviors and -mechanisms within this distinct geological context. To access the crucial REV, a volume dependent analysis is performed to investigate the effect of reducing sample volume on geochemical properties, as well an investigation of samples taken parallel to the bedding to confirm the anisotropy of the heterogeneity.

2. State of Knowledge

2.1 Clay

2.1.1 Clay Minerals

Besides the namesake clay minerals, clay rocks are usually mainly composed of silica, carbonates and feldspars [64]. Clay minerals are characterized by their small particle size of $<2\text{ }\mu\text{m}$ in contrast to the other minerals often with a size $>20\text{ }\mu\text{m}$ [64]. They can be formed in different ways, either from preexisting minerals by exchanging ions through dissolution, from hydrothermal processes or from chemical weathering [65]. Feldspars are often the parent minerals in these chemical weathering processes [66]. The formal chemical reaction for the formation of kaolinite by weathering is presented in Equation 1.

Clay minerals are layered aluminosilicates, made up of two different sheet types. The tetrahedral silica layers (T) are built from SiO_4 tetrahedra, interconnected at the corner oxygen atoms. The octahedral alumina/magnesium hydroxide layers (O) are composed of the basic building block $\text{Al}_2(\text{O},\text{OH})_6$ or $\text{Mg}_3(\text{O},\text{OH})_6$ [67]. These are connected with one another through shared oxygen edges and hydroxyl groups. If two of the three octahedral voids in this oxygen lattice are filled with trivalent cations like Al^{3+} , they are termed dioctahedral, whereas if all octahedral voids are filled with divalent cations like Mg^{2+} they are termed trioctahedral [67]. The general layered structure is shown in Figure 4 for the example of montmorillonite [68].

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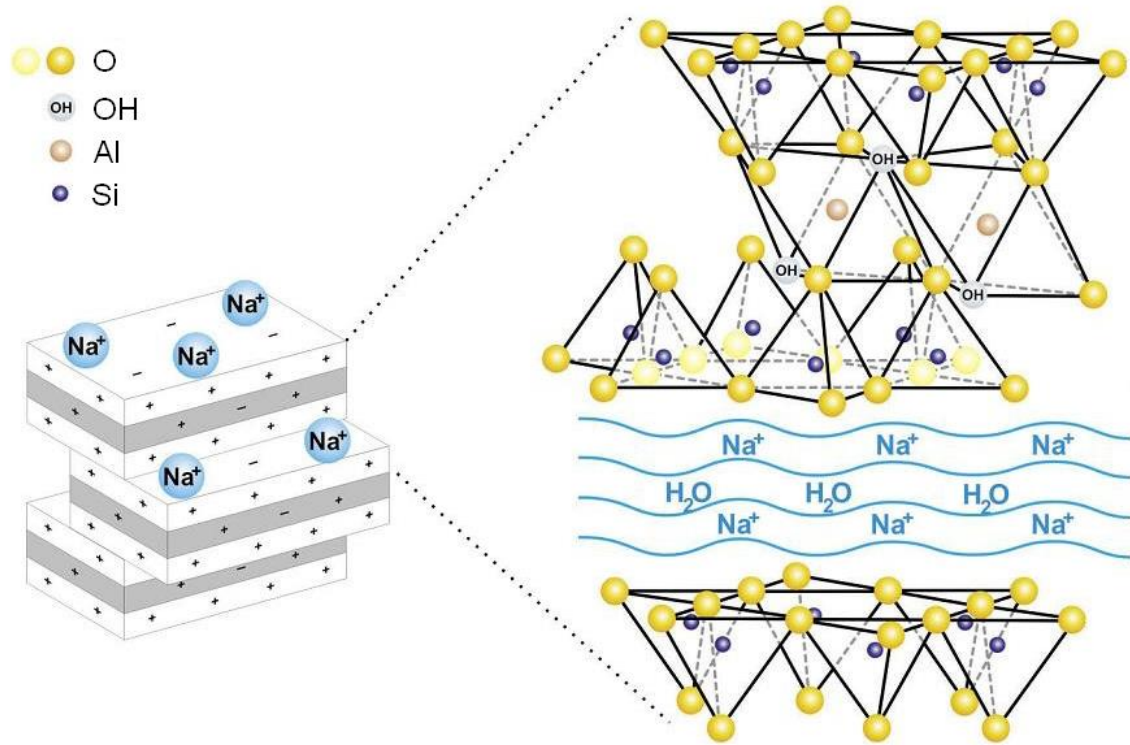
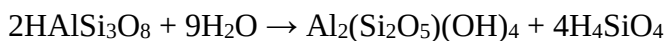
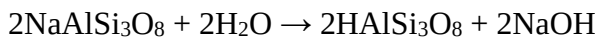


Figure 4: Schematic representation of a dioctahedral three-layer 2:1 montmorillonite type clay mineral with Na-exchanged interlayers. Taken from Harabasz et al. (2013) [68].

Some of the core elements in this structure can be replaced with ones of lower charge in these layers (Si^{4+} by Al^{3+} in the T layer and Al^{3+} by Fe^{2+} or Mg^{2+} in the O layer), resulting in a permanent negative layer charge [69]. This effect is called isomorphic substitution. Clay mineral particles consist of a stack of multiple layers, where the number of stacked layers can be as low as ten in the case of illite or up to several hundred in the case of kaolinite [67]. The space between these stacked formations is called the interlayer space, which can be occupied by water molecules and (often) hydrated cations. These cations compensate the negative layer charge. The possibility of water integration in these interlayers is the main reason for the swelling capability of clay rocks. The layers themselves are connected in different ways, which is the differentiating factor for clay minerals. The most basic agglomerate is the combination of one tetrahedral and one octahedral layer, forming a TO 1:1 clay mineral. In this case, the layers are interconnected via shared apical oxygen atoms. The most common mineral belonging to this group is kaolinite with the chemical formula $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$. It can be formed by the weathering of feldspars through the reaction [70]:



Equation 1

The negative charge on the basal plane of 1:1 clay minerals is comparatively very weak, caused by a less pronounced isomorphic substitution. Therefore, they exhibit an almost net neutral charge towards outside ions in the interlayer basal planes [71] and consequently have a low cation exchange capacity (see Chapter 2.2).

The layers can also form a three-layer sandwich structure in the form of TOT, known as 2:1 type clay minerals. Contrary to the 1:1 clay minerals, these exhibit a pronounced negative charge on the basal planes, which is compensated by cationic intercalation in the interlayers. They are classified based on this negative surface charge. With a negative charge of 0.2–0.6 mol_c/mol, they are assigned to the smectite group [72]. A common member of this group is montmorillonite, whose interlayers are typically filled with hydrated sodium and calcium ions, while still allowing further intercalation of water molecules. Montmorillonites are also the main reason for the swelling capacity of clay rocks.

With a negative charge of 0.6–0.9 mol_c/mol, the next group of 2:1 clay minerals is called the vermiculite-illite group [72]. A typical constituent is illite, with largely potassium connected interlayers. This connection causes the illite layers to be denser packed and strongly reduces its swelling capability. High potassium concentrations as well as elevated temperatures can cause smectites to collapse in a process called illitization [73], causing them to partly lose their swelling properties and transform into illite. Another possible layer arrangement is the 2:1:1 type, where an additional O sheet is sandwiched between two TOT layers forming a TOT-O-TOT construct. A typical constituent of this group is chlorite [72]. Some of clay minerals can also form mixed layer structures, most prominently illite/smectite mixed layers. These exhibit properties intermediate to both clay minerals in proportion to their respective abundance.

2.1.2 Clay Rocks

Clay rocks have a rich geological history that spans vast timescales. The formation of these fine-grained sedimentary rocks commences with the weathering of pre-existing rock formations, encompassing igneous and sedimentary parent rocks [74]. This includes granites, basalts, shales and mudstones. In this initial phase, a multitude of physical, chemical and biological processes are occurring, which collectively disintegrate the parent rocks into progressively smaller particles [74]. Physical processes in this context include frost action, abrasion and exfoliation, while chemical processes encompass reactions with water and

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atmospheric gases like carbon dioxide. The latter are also combinable with biological processes, like mosses releasing acids, further disintegrating the parent rock material. Subsequently, the liberated sediment particles are transported via various pathways such as water or wind, with the distance depending on the prevailing geological environment [75]. These movements cease at local geological minima, like river deltas, floodplains or marine settings, where water flow is particularly slow [76]. Then, through sedimentation the initial phase of actual clay rock formation starts. The continuous accumulation of small-sized particles (like clay minerals, but also organic material) in these depositional settings results in the buildup of sedimentary layers, creating the foundation from which clay rock sequences will eventually emerge [75]. A very general depiction of this process is shown in Figure 5 [77].

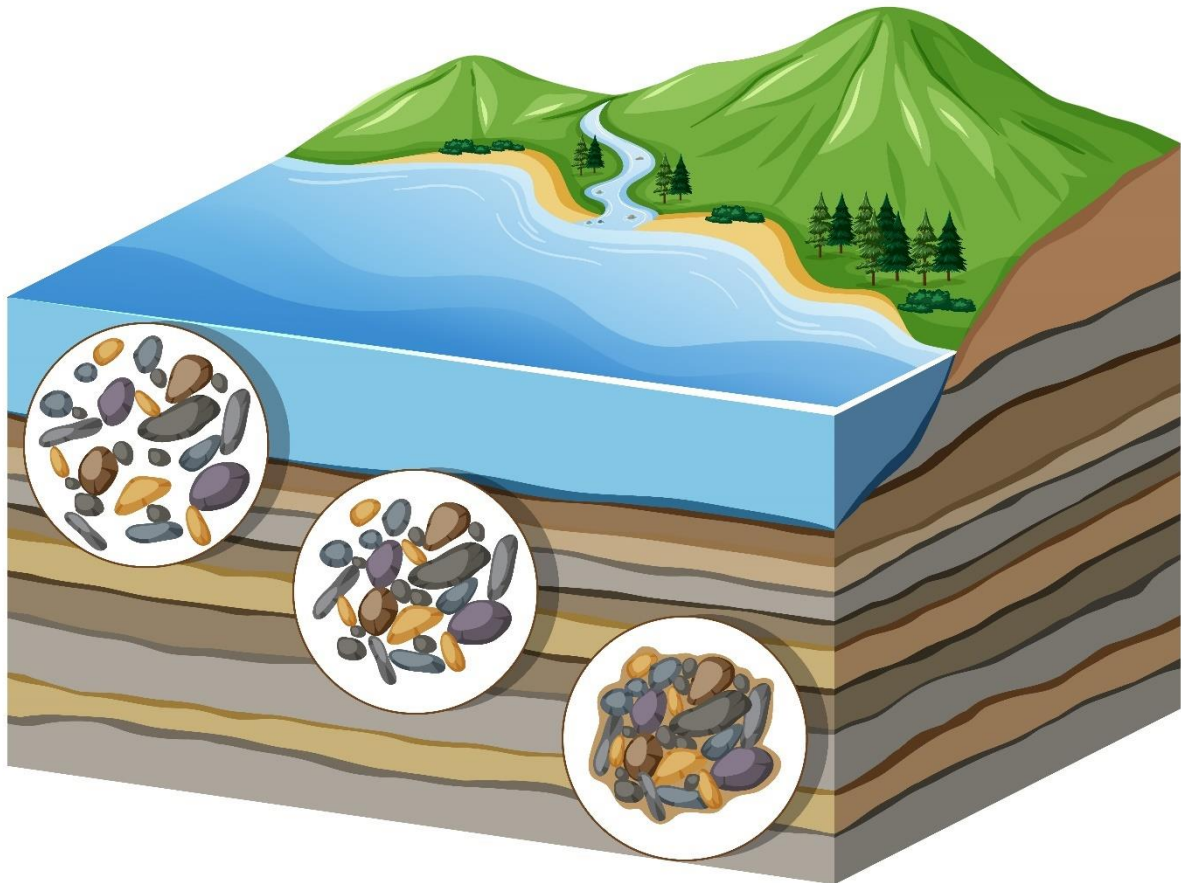


Figure 5: Depiction of the sedimentation and compaction process in prehistoric seas to form clay rock layers, taken from [77].

The weight of built-up overburden exerts pressure on the accumulating layers, resulting in compaction. This compaction process causes water and air to be squeezed from the spaces between sediment particles, packing the sediment ever tighter and denser [75]. A critical subsequent step in the formation of clay rocks involves concretion. Minerals previously dissolved within pore spaces precipitate from solution and act as natural adhesives to bind the

sediment particles together. The specific mineral composition of this cement can vary, depending to local geological conditions. Common cementing minerals include silica, calcite, and iron oxides. Through lithification at elevated temperature and pressure, these adhered mineral composites solidify further into a compact clay rock. Due to the different origins, weathering and sedimentation conditions, no two clay rocks are equal in composition [75]. Following this diagenesis, tectonic processes (e.g., plate con- or divergences) can alter the sedimentary stratification of clay rocks, sometimes surfacing them and exposing them to the biosphere. Besides OPA, which will be discussed separately in Chapter 2.1.3, important clay rock formations in central Europe are the Callovo-Oxfordian formation [22], primarily located in northeastern France and the Boom Clay [23], located in northeast Belgium but also extending over Northern Germany. In Germany, the Lower Cretaceous Clay in the North near Hannover is also of interest as a possibly suitable host rock formation for a highly radioactive waste disposal site [24]. Its sedimentation happened in the lower cretaceous period, roughly 145–100 million years ago during the Mesozoic, in a shallow sea in the Lower Saxony Basin [78]. Other German clay rock formations possibly of interest in the scope of HLW nuclear waste disposal are the Tertiary clay rocks present in Northern Germany (similar to Boom Clay) and the Bavarian Molasses, both displayed in Figure 2 [24].

Clays in general are in discussion as a host rock due to their multitude of favorable properties. Not only are they proposed as the potential host rock formation, but are also used in various HLW repository concepts as a geo-technical barrier in the form of bentonite [15]. Bentonites are mainly composed of montmorillonite and exhibit a pronounced swelling capacity when contacted with water, due to the large amount smectite type clay minerals contained. After water ingress, which has to be assumed in a repository concept proposed to last for up to one million years, this leads to an effective sealing of artificially or naturally induced fractures. A very low hydraulic conductivity makes water transport almost impossible in clay rocks, due to the low permeability of the layered structure in combination with the particle size of clay minerals causing a very small pore size [79]. Another promising characteristic is the high sorption affinity towards actinides and other fission products. Specifically, the cation retention is very dominant, due to the permanently negatively charged surfaces of clay minerals, allowing the intercalation into interlayers and the abundance of hydroxylic binding sites on the clay mineral edges [64].

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2.1.2.1 Heterogeneity in Clay Rocks

An intrinsic heterogeneity is observed in clay rocks, due to the laminar sedimentary structure. This variation is visible at the microscopic scale with an electron microscope [56], at the cm- to dm-scale by eye [6] and up to the facies overarching lithostratigraphic scale [79]. These variations impact the mineral composition locally significantly [6] and also have a strong impact on other properties like diffusivity [29]. To investigate and quantify this heterogeneity, different approaches have been taken. On the most basic level, clay rocks from different origins and lithologies are simply compared to one another for different characteristics, like diffusion- and sorption distribution coefficients or geochemical parameters [80, 81]. Heterogeneity is hereby simply defined as a stronger observable data scattering. The observable properties can then be used in computer supported modeling, to replicate experimental data and extend it to scales not suitable for laboratory investigations. For example, in the study of Hennig *et al.* (2021) [82] the diffusion of uranium through different facies of OPA is simulated for up to one million years, a timescale unreachable in experiments. They simulated the differences of the facies by varying the clay mineral contents and pore water compositions. With this approach, they found pH and the carbonate and calcite contents of the pore water, governed by the carbonate minerals content, to be the dominant factors for uranium migration.

A more generalized approach to define homo- and heterogeneity is the postulation of a representative elementary volume (REV) or area (REA). This concept has been used in various studies [83, 84], but often referred to is the definition of Bachmat and Bear (1987 and 1988) [4, 5], defining the REV as the volume below which strong fluctuations due to the inhomogeneity of the investigated parameter are observed (Figure 6, left). In their study, porosity has been the parameter under investigation. Reducing the volume to the smallest scale leads to one of two extremes, either the investigated volume is a pore, in which case 100 % porosity is observed or it is not a pore and 0 % porosity is the conclusion. These extremes are indicated by the

increasing fluctuations towards the microscopic domain caused by the heterogeneity on the left of Figure 6.

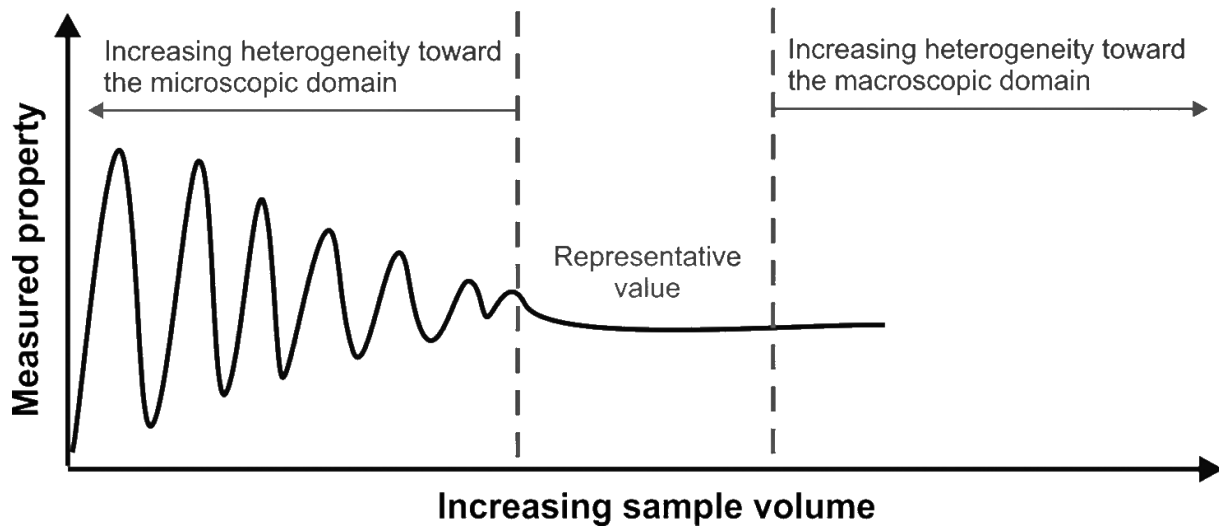


Figure 6: Concept of the definition of a REV in regards to the scale/domain investigated. Taken from Abutaha et al. (2021) [57], adapted from Bear (1972) [4].

The same behavior can be observed for any investigated parameter, when decreasing the sample volume to the extreme (mineral composition, diffusivity [55, 57]). To define a representative value, limits need to be established for homo- and heterogeneity. Samples showing data scattering below these limits can then be considered representative. These limits should be adjusted to the parameter, scale and effect investigated. When increasing the volume further, different effects may be observed. In a theoretical infinite homogeneous system, with increasing volume the observed fluctuations would decay down to the analytical uncertainty of their determination. In reality, increasing the volume can lead to breaching of the investigated scale. Different neighboring phases may then be included in the investigated sample, causing a different type of observable heterogeneity. The average composition remains constant when decreasing the volume, while increasing it beyond the representative domain causes a drift. This leads to the conclusion, that a REV should encompass a lower and an upper boundary. Furthermore, it has to be noted that the REV is strongly dependent on the investigated parameter.

An approach to investigate the REA for the two-dimensional microstructures of OPA is made in the study of Houben et al. (2014) [56], where it is investigated with mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM). Their limit for representativeness is an acceptable variation of less than 10 surf% in an ever increasing area observed. They concluded the side length of a REA square for the mineral composition to range between 111–

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250 μm , and between 82–203 μm for the porosity, depending on the clay rock layer investigated. Since this has been a microscopic investigation, they also highlighted this data not to be suited for upscaling purposes beyond the mm-scale.

In the study of Abutaha et al. (2021) [57], the REV of a clay rock is investigated via X-ray computed tomography. From X-ray density measurements, the mineralogy is derived. Since multiple close layers of the same drill core are investigated, data independence of the single layers is not ensured. To overcome this issue, statistical process control in the form of an ARIMA (auto-regressive integrated moving average) model is used. From this model, an upper and lower limit can be obtained which indicates if a process is “under control”, meaning data independency is ensured. The volume from which on onward the system can be deemed under control has been their criteria for a REV. These volumes range between 0.7–13.1 cm^3 , depending on the layer and composition investigated. They observed a volume normalized REV for the mineralogy of $6.7 \pm 4.4 \text{ cm}^3$. To verify their results, a Monte Carlo simulation of the investigatory procedure is performed. This confirmed the REVs, predicting on average $8.3 \pm 5.5 \text{ cm}^3$. In both of these studies, the mineralogy of OPA has been investigated, but different scales, techniques and limits cause vast differences in the obtained REVs.

In the study of Yuan et al. (2022) [55], a different approach to the REV is chosen. Instead of real clay rock, synthetic microstructures are computed. These digital rocks are composed of two phases, a general clay mineral and a non-clay mineral component. Only the clay mineral phase is responsible for the porosity and diffusivity, the two parameters of interest in that study. From the obtained REA of these microstructures, a REV can be obtained by proper upscaling. With a limit of 10 % deviation from the average composition, a square length of $\approx 330 \mu\text{m}$ is postulated for the REA. Through upscaling, the REV for the porosity is concluded to $2.2 \cdot 10^{-3} \text{ mm}^3$ and for diffusivity to $6.4 \cdot 10^{-2} \text{ mm}^3$. To validate these computed data, through-diffusion experiments with intact clay rock have been performed. In contrast, with a maximum sample volume of 7 cm^3 , the relative deviation in the experiment is still 23 %. Accepting a deviation of 40 % in this upscaling approach leads to a reduction of the REV to $\approx 1 \text{ cm}^3$.

On a larger scale, the optical appreciation of whole drill cores and bore holes is also a common practice to obtain information on the composition and identify heterogeneity [79, 85]. Though this is often a more subjective interpretation, recent advances in computer assisted recognition tools offer a more unbiased approach [6].

A uniform assessment of a REV especially in regards to a heterogeneous clay rock and limits of homo- and heterogeneity are therefore still up to discussion. The dependency on the scale and system investigated need to be taken into account. However, the main parameter influencing the REV is the investigated property, as in the studies mentioned above, REAs on the μm -scale up to REVs on the cm-scale are proposed for different investigated properties.

2.1.3 Opalinus Clay (OPA)

OPA is a sedimentary clay rock formation present in central Europe at the border of Switzerland with Germany. It has been deposited during the Early Jurassic period, specifically during the Toarcian stage, approximately 180–170 million years ago. It has been formed in a shallow epicontinental sea in a prehistoric basin [86], of which a depiction is shown in Figure 7 with some current landmarks [87].

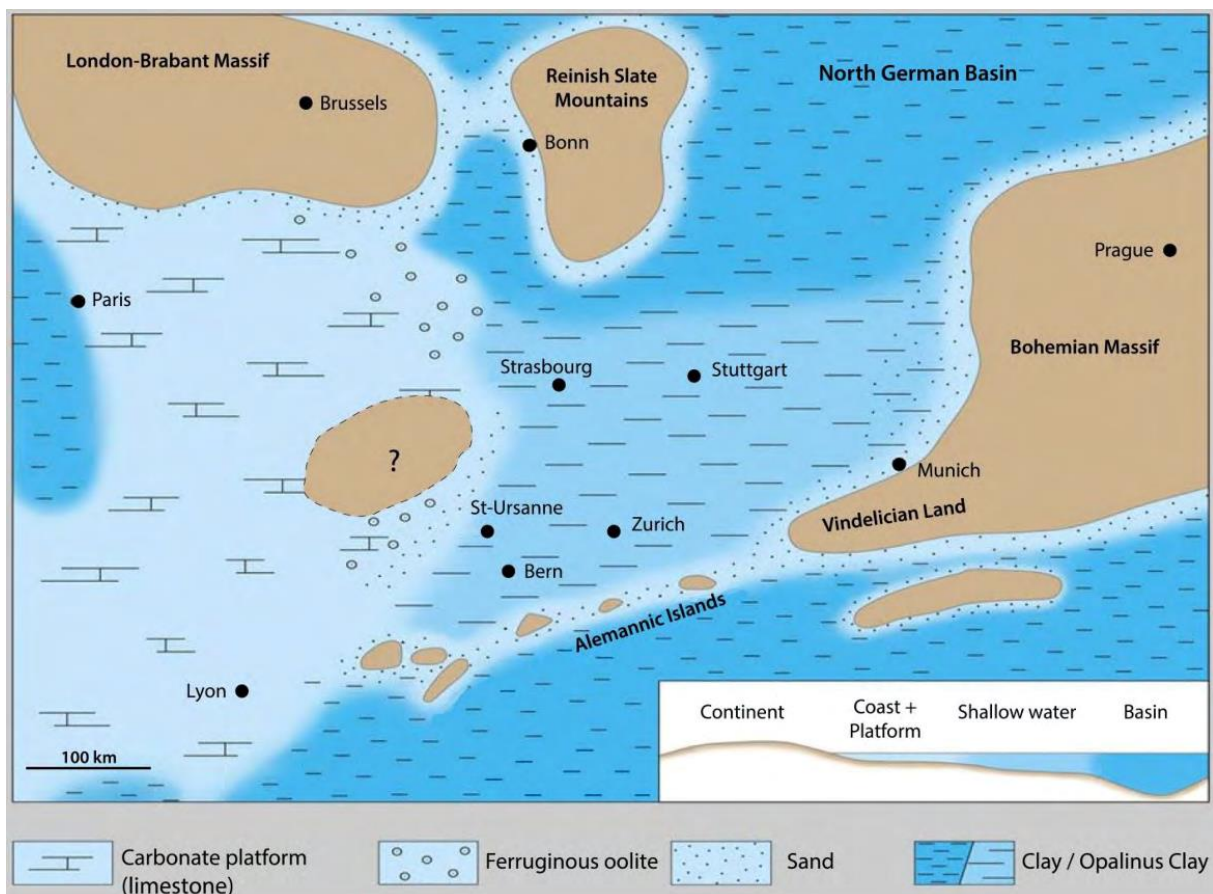


Figure 7: Prehistoric basin of OPA origin during the Jurassic in central Europe with some current landmarks for reference, adapted from [87].

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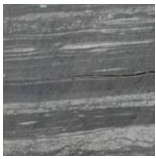
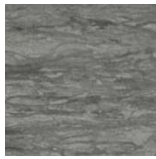
OPA is named after the ammonite “*Leioceras Opalinum*”, which is very abundant throughout the clay rock formation. Due to tectonic movements, it has an overburden of only around 300 m in Northern Switzerland, dives down to several kilometers towards the alps [88], but even surfaces in some areas in Germany [89]. During the sedimentation period and the diagenesis, five distinct facies formed, of which the two shaly and two sandy facies are most relevant in the scope of a host rock for a nuclear waste repository [3]. These facies vary in their mineralogical composition as well as their fossil constituents and other geochemical parameters like water content. The shaly facies is characterized by a relatively homogeneous composition by geological standards, with a comparatively high clay mineral content [79]. In contrast, the sandy facies shows a more pronounced heterogeneity with concretions and clasts on the milli- to decimeter-scale. This is accompanied with a lower clay mineral content, balanced by higher quartz and carbonates contents [29, 90]. These three mineral groups and feldspars are the cornerstones of OPA mineralogy. A mineralogical comparison of the composition of the facies is shown in Table 1, to display the extent of the variations [86]. Here, the general higher clay mineral content of the shaly facies compared to the sandy facies is concealed by the in general large observed ranges. Though the organic carbon constitutes to up to 1.5 wt% of the total inventory, it is tightly bound to mineral particles and only a small portion is dissolvable [91].

Table 1: Mineralogical composition of the main facies of OPA from the Mont Terri underground rock laboratory (URL) according to Pearson et al. (2003) [86].

Mineral / wt%	Shaly facies	Carbonate-rich sandy facies	Sandy facies
Quartz	6–24	27–31	16–32
Calcite	5–28	36–42	7–17
Siderite	1–4	1.1–2.4	1.1–3
Dolomite	0.2–2	2.1–3.3	0.3–2
Kaolinite	15–33	8–13	13–35
Illite	16–40	6–9	15–35
Illite-Smectite	5–20	3–6	5–20
Chlorite	4–20	2.2–4	4.4–15
Feldspars	1.6–5.3	4.1–7.4	3.3–7.2
Organic carbon	0.1–1.5	0.2	0.2–0.5

Recently, a new definition has been established by Lauper *et al.* (2018, 2021) [3, 6], to harmonize the nomenclature of different parts of OPA. They define OPA subfacies, based on visual characteristics and mineralogical composition. In this classification the subfacies types range from SF1–SF5, marking the end-members of the heterogeneity. Intermediate compositions are also reported. Table 2 shows the main characteristics of the subfacies types, together with typical photographs [6].

Table 2: Overview of the key characteristics of OPA subfacies types from Lauper *et al.* (2021) [6].

Subfacies type	SF1	SF2	SF3	SF4	SF5
Appearance					
Texture	Argillaceous fine mudstone	Argillaceous Siliceous fine to medium mudstone	Siliceous medium mudstone	Calcareous Siliceous medium to sandy mudstone	Calcareous limestone
Bedding	Homo- geneous to laminated	Lenticular	Lenticular to wavy	Flaserous to homo- geneous	Homo- geneous
Matrix fraction	>97 %	83–91 %	52–64 %	9–30 %	8–22 %
Mineralogy					
Clay minerals	56–70 %	34–60 %	17–47 %	9–32 %	8–19 %
Quartz	26–33 %	31–46 %	38–52 %	12–23 %	7–17 %
Carbonates	4–11 %	5–24 %	8–35 %	46–69 %	67–84 %

OPA is investigated in an international collaboration in the URL Mont Terri in Switzerland, where in-situ experiments and characterizations as well as drill core retrieval takes place. The shaly facies is deemed most suitable as a potential host rock formation due to the comparatively high homogeneity and clay mineral content. It has been characterized and examined in detail in numerous experiments [79, 86, 92]. The abundance and depth of information about the sandy facies is comparatively low, but still various parameters have been measured and evaluated [56, 79, 90, 93-95].

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The shaly facies OPA is fully water saturated, corresponding to a total of up to 5–9 wt% of the clay rock mass [86], which is classified as low in comparison to other clay rocks [96]. Due to the marine origin of OPA, the natural pore water contains a variety of salts and organic matter introduced during the sedimentation and due to water ingress during diagenesis. Its composition is based on the origin, like prehistoric sea water and is altered by the local mineralogical composition due to dissolution and precipitation processes. For example, the chloride to sulfate ratio of OPA pore water is still the same as in natural sea water [86]. Carbonate containing minerals like calcite usually control the carbonate concentration in the pore water and minerals like celestine strongly determine the amount of strontium found in solution. Various methods can be used to obtain the composition of the pore water, whereby squeezing is the most common. Squeezing with an as low as possible pressure yields a composition most alike the natural [97], which can also be estimated based on the mineral composition. The pore water composition shows a gradient across OPA, which has been discussed in the recent study of Wersin *et al.* (2022) [98]. They show a clear trend of decreasing chloride concentration, when moving from the Staffelegg Formation to the Passwang Formation, two neighboring formations of OPA. This is caused by the contact with an overlying aquifer and demonstrates diffusive transport over millions of years.

Artificial compositions that are often used to mimic the natural pore water are the “Pearson pore water” after Pearson *et al.* (1998) [99] and the „Gimmi pore water“ after Gimmi *et al.* (2014) [63], both composed to resemble pore waters from different parts of the shaly facies. Their respective compositions are shown in Table 3, in comparison to the sea water they originated from [86]. The afore mentioned trend of reduced ion concentration in the pore water when approaching the Passwang formation (closest to the Gimmi pore water origin) is visible.

Table 3: Composition of the pore water as proposed by Pearson et al. (1998) and Gimmi et al. (2014) in comparison to the seawater according to Pearson et al. (2003) [63, 86, 99].

Ionic concentration / (mol/L)	Seawater	Pearson pore water	Gimmi pore water
Na ⁺	$4.7 \cdot 10^{-1}$	$2.4 \cdot 10^{-1}$	$1.5 \cdot 10^{-1}$
Mg ²⁺	$5.4 \cdot 10^{-2}$	$1.7 \cdot 10^{-2}$	$1.1 \cdot 10^{-2}$
K ⁺	$1.0 \cdot 10^{-2}$	$1.6 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$
Ca ²⁺	$1.0 \cdot 10^{-2}$	$2.6 \cdot 10^{-2}$	$8.7 \cdot 10^{-3}$
Sr ²⁺	-	$5.1 \cdot 10^{-4}$	$5.0 \cdot 10^{-4}$
CO ₃ ²⁻	$2.3 \cdot 10^{-3}$	$4.8 \cdot 10^{-4}$	$2.7 \cdot 10^{-3}$
SO ₄ ²⁻	$2.8 \cdot 10^{-2}$	$1.4 \cdot 10^{-2}$	$8.8 \cdot 10^{-3}$
Cl ⁻	$5.5 \cdot 10^{-1}$	$3.0 \cdot 10^{-1}$	$1.7 \cdot 10^{-1}$
Ionic strength	0.7	0.4	0.2
pH	8.1	7.6	7.2

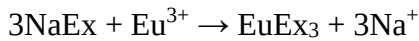
2.2 Sorption on Mineral Surfaces

As mentioned in the previous chapters, one of the main positive aspects of using clay rocks as a host rock formation is the retention capability towards cations, which will effectively sequester radionuclides after water ingress and potential radionuclide release. Migrating cations can be bound to clay minerals via different sorption processes at the solid-liquid interface. The main parameters influencing the sorption behavior of clay minerals are the availability of reactive surface sites and the layer charge, together defining available cation exchange and sorption sites. Generally, the sorption processes can be divided into two categories, electrostatic outer-sphere adsorption in which the hydration shell of the adsorbing cation remains intact and inner-sphere adsorption where the adsorbing ions loose at least part of their hydration shell. Depending on the geochemical conditions, other processes like precipitation and incorporation into the mineral structure can also take place [39].

One of the most important properties of a natural clay rock is its cation exchange capacity (CEC), often measured in cmol_c(+)/kg of rock mass. The concept of the CEC is described by the ability of clay minerals to exchange electrostatically loosely bound cations in the interlayers or basal planes (1) and 2) in Figure 8). These ions compensate the permanent charge deficit of the basal plane of clay minerals, caused by isomorphic substitution (see Chapter 2.1). Since the cation is separated from the bonding partner by at least one water molecule, these electrostatic outer-sphere attachments are usually weak and readily reversible [39]. They therefore show fast ad- and desorption kinetics. This leads to a strong competition between the present cations, with

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the sorption affinity being less element- but rather charge specific. In general, highly charged cations tend to exhibit a stronger affinity and are less likely to be replaced. If competitors have a similar charge, the ionic radius is the next key parameter defining the sorption affinity, with elements having a small ionic radius being preferred [100]. Due to the negative surface charge being permanent, this process is mostly pH independent, though H^+ cations may also compete. The cationic exchange with europium on a sodium saturated clay mineral surface could be expressed by:



Equation 2

Here, Ex stands for a negatively charged exchange site. Besides in the interlayer space, the basal planes of clay minerals can partake in sorption processes more directly. Outer-spherical sorption is more common (2) in Figure 8), though inner-sphere sorption processes (like 3) in Figure 8) can also take place on the basal plane.

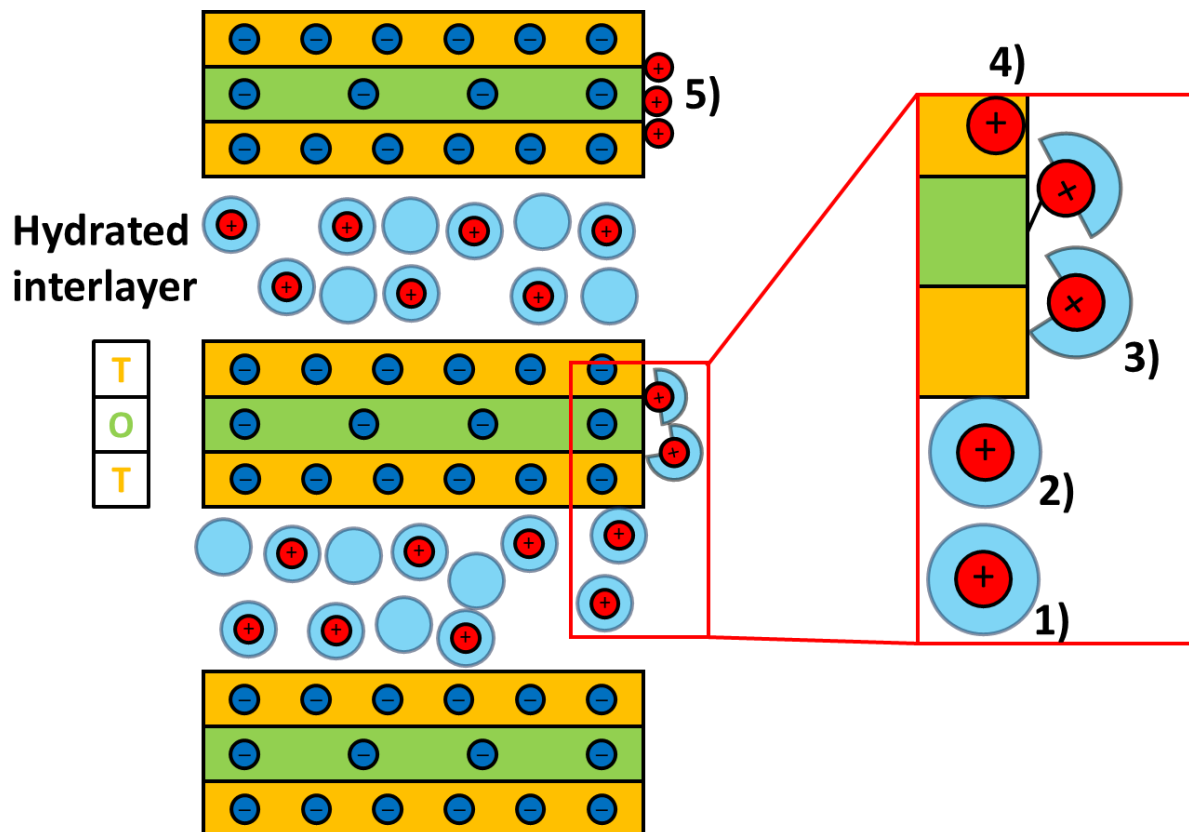
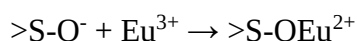
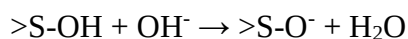


Figure 8: Schematic depiction of the sorption processes on the TOT layers of a clay mineral. 1) exchangeable hydrated cation in the interlayer 2) outer-spherical bound cation on the basal plane 3) inner-sphere sorption complexes 4) incorporated species 5) surface precipitate.

Sorption processes can also take place on the edges of clay minerals (3) in Figure 8). This process is strongly pH dependent, since the hydroxyl edges of the octahedral sheet, consisting of silanol and aluminol groups, can either be protonated or deprotonated. The point of zero charge (PZC) is defined as the pH-value at which the net charge exhibited by the clay mineral is zero. Above the PZC, the deprotonation causes a net negative charge and an elevated sorption of cationic species on these edges occurs. The PZC varies for the different surface hydroxyl groups, being as low as 2.5 for amphoteric silanol groups and as high as 9 for aluminol groups [101]. Therefore, the overall PZC of clay minerals varies depending on their composition.

The amphoteric groups can act as bonding partners to form covalent and ionic bonds with ions present in the liquid phase, whereby highly charged cations predominantly form ionic bonds. In contrast, small ions like Na^+ are more likely to participate in ion exchange processes than chemisorption [102]. In chemisorption, the strongly bound sorption species form inner-sphere surface complexes, with parts of the hydration sphere being removed [103]. The usually stronger nature of this inner-spherical sorption process makes it less easily reversible, resulting in much slower desorption kinetics [104, 105]. Further parameters also affect this process, like the ionic strength or the temperature [106]. A deprotonation and following adsorption reaction of europium could exemplarily be described as displayed in Equation 3.



Equation 3

In this case $>\text{S-OH}$ is a placeholder for a sorption site on the clay mineral edge. Exchange reactions are charge neutral by definition, e.g. trivalent cations occupying three exchange sites with a negative charge of one each, but a positive charge may remain in adsorption process (see Equation 3).

While describing different sorption sites only by their chemical behavior is adequate for the exchange sites, more factors need to be considered for the amphoteric edge sites. The local surface geometry plays an important role in the sorption behavior. On a perfect plane, all sorption sites could be considered equal, but in reality kink and vacancy sites exist on the surface [37]. These show a higher affinity and stronger potential to displace the hydration shell of the aquatic cation in solution. Multiple sorption sites can collectively adsorb one cation and strongly bind it. This can lead to polydentate surface complex structures, like reported for uranyl [107] and europium [108] on ferrihydrite surfaces. A polydentate surface sorption structure is also confirmed by Zhang et al. (2017) [109] for nickel, who have also proposed a similar

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mechanism for the adsorption of divalent cobalt, copper, iron and cadmium. The surface roughness is therefore another parameter, possibly influencing the sorption behavior. Occasionally roughness may influence adsorption even more than the local mineralogy [110]. The total amount of reactive surface sites is also very important for the correct assessment of the sorption behavior. The specific surface area is the total amount of accessible surface area, often determined with the BET-method (see Chapter 3.5). This parameter varies greatly for different clay minerals and is also connected to the CEC, since up to 90 % of the total surface area is located on the inner basal planes of the clay mineral particles [111]. Typical specific surface areas and cation exchange capacities for common clay minerals are displayed in Table 4 [112, 113].

Table 4: Typical specific surface area and cation exchange capacity values for common clay minerals [112, 113].

Clay mineral	Specific surface area / (m²/g)	CEC / (cmol_c(+)/kg)
Kaolinite	5–20	3–15
Illite	80–150	10–40
Smectite	700–800	80–100
Chlorite	70–90	10–40

From this assessment, the conclusion can be drawn that the cationic uptake will be dominated by smectite and illite, but other minerals might still play a role depending on the composition of the investigated material.

Both of the two general sorption processes can become even more complex depending on the composition of the liquid phase, more precisely if complexing agents other than only water are present. The complexation of cations with anionic species causes a net reduction in positive charge, making them in general less accessible for the adsorption on the negatively charged clay mineral surfaces. Ternary surface complexes can also form, causing the hydration shell of adsorbing ions to be further displaced by ligands like hydroxides, carbonates or organic molecules. Figure 9 shows the stepwise surface sorption reaction of trivalent curium on a clay mineral surface with increasing pH [108, 114]. At low pH, the surface hydroxyl groups are still protonated and only outer-sphere attachment is possible. At pH 5.5 in this example, surface complexation as an inner-sphere complex is possible, due to the deprotonation of the amphoteric hydroxyl groups. In an alkaline milieu (pH 8.5) a hydroxide molecule replaces one of the remaining coordinated water molecules. Larger and especially polydentate ligands like carbonates can replace multiple water molecules at once [115].

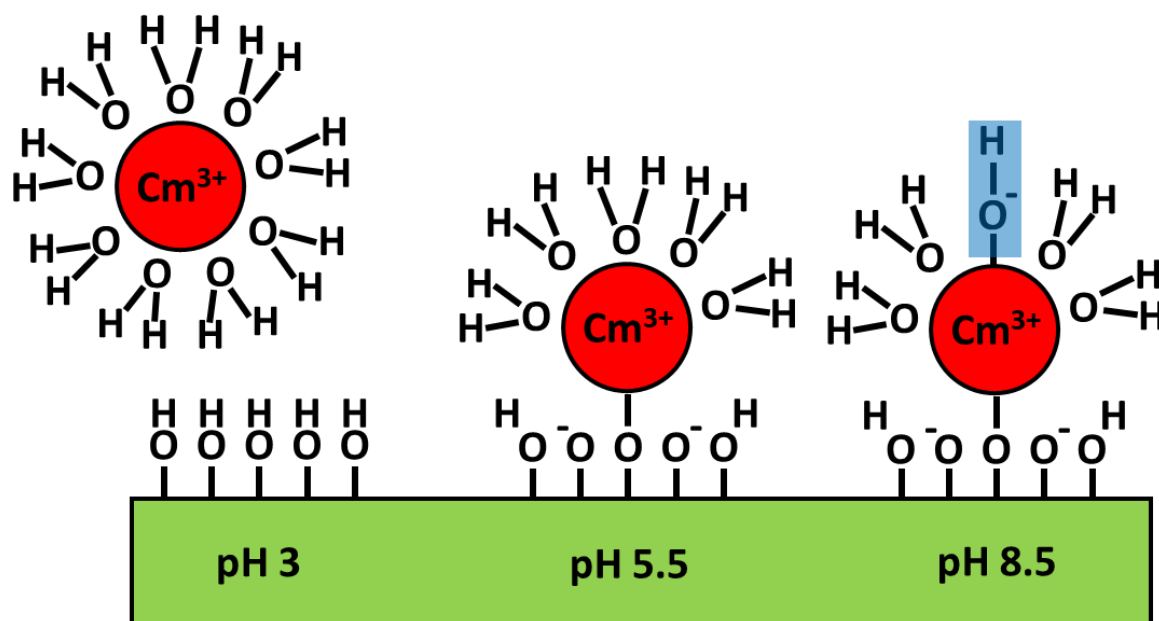


Figure 9: Stepwise surface reaction of curium with a clay mineral surface. From left to right, electrostatic outer-sphere sorption, inner-sphere surface complexation with an amphoteric oxygen, formation of a ternary surface complex with a hydroxyl group displacing a water molecule. Adapted from Geckeis et al. (2015) [108, 114].

At high sorptive concentrations, even more sorption processes can take place. By overextending the maximum solution equilibrium concentration or by changing the chemical environment, precipitates (5) in Figure 8) can form on the sorbent surface. Dissolution and recrystallization processes can lead to incorporation (4) in Figure 8) of the adsorbed ions into the sorbent structure and finally to solid-solution formation. This phenomenon occurs when elements with similar atomic size and charge in solution replace others within the crystal structure [116]. In the clay mineral structure, due to the isomorphic substitution, di-, tri- and tetravalent cations are present in varying sizes, which can therefore also be replaced by other cations present in a contacting solution. This process also takes place during the weathering and formation of clay minerals in general [113]. Clay minerals conditioned under different geochemical environments can show a distinct change in elemental composition, but even vary within one relatively homogeneous clay sample from one particle to another [117].

In natural clay rocks, not only clay minerals are present, but quartz, carbonates and feldspars are also contained in varying amounts. The quartz and feldspar surfaces can undergo a similar deprotonation process as clay minerals with increasing pH [118-120]. The amphoteric oxygen atoms can also act as sorption sites, though with a lower affinity towards heavy metal cations in comparison to clay minerals [121]. Carbonate minerals like calcite contain different surface sorption sites in comparison to the silanol and aluminol groups. The outward facing carbonate groups undergo a comparable deprotonation reaction with increasing pH, though multiple

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oxygen atoms are deprotonated in sequence [122]. In the case of calcite, even calcium hydroxide groups can partake in protonation, deprotonation and sorption reactions [122, 123]. Carbonate containing minerals are also known to frequently undergo solid-solution formation. Multiple cations are reported to be able to be incorporated into the calcite structure [124-127]. Therefore, natural calcites are usually mixed crystals containing varying amounts of impurities, correlated to the composition of the ambient solution. Since natural minerals in a clay rock may be expected to be in equilibrium with the pore solution, due to the long contact times in comparison to laboratory experiments, much slower incorporation kinetics may be expected compared to synthetic calcium carbonate [128].

To quantify experimentally determined sorption data and compare them, a unified quantitative parameter is required. The R_d -value is commonly used for this purpose, the distribution coefficient of the sorption reaction. It allows a valid interpretation of sorption processes at trace concentrations [39] and is defined as described in Equation 4.

$$R_d = \frac{n_{sorb}}{n_{eq}} \cdot \frac{V}{m} = \frac{n_{tot} - n_{eq}}{n_{eq}} \cdot \frac{V}{m} = \frac{q_{eq}}{c_{eq}} \quad \text{Equation 4}$$

n_{sorb} (in mol) is the amount of adsorbed species, while n_{eq} (in mol) describes the amount of the species remaining in solution in equilibrium. V is the volume (in L) of the liquid phase and m (in g) the mass of the solid phase. To easily access the amount of adsorbed species, it can be derived by subtracting the amount left in solution from the total amount (n_{tot} in mol) in the system. This linear correlation between aqueous concentration (c_{eq} in mol/L), and adsorbed concentration (q_{eq} in mol/kg), is equivalent to the description by a Henry isotherm. R_d -value comparison is in general only applicable in absence of effects further complicating the sorption behavior, like surface saturation or interaction between adsorbing species, and only at the specific chemical conditions at which they have been determined.

The same way equilibrium constants (see Chapter 2.3) are used to describe the chemical behavior of reversible reactions and complex formations, they can also be used to describe the affinity of species towards surface sorption. By formulating such surface complexation reactions, the sorption affinity can be put into comparison to aquatic complexation. With these expressions, the simultaneous surface sorption and complexation competition can be described and complicated systems can be modeled by computing such data to predict the behavior on a solid-liquid interface. The abundance of surface sorption sites and their selectivity coefficient can be experimentally determined in titration experiments or estimated to fit underlying experimental data (examples for the selectivity of cesium sorption on illite [129-131]). In these

surface-complexation approaches, the investigated system is thereby often simplified to neglect steric and electrostatic effects on the surface and in the diffuse double layer system. In the “bottom-up” approach, a geochemical model is further simplified to attribute the total sorption behavior to a single clay mineral, often illite or montmorillonite [7]. This approach has been successfully applied in modeling the sorption of various cations on multiple clay rocks and clay minerals [7, 8, 10, 41, 42, 132].

2.3 Complexation

The complexation of ions in solution with organic and inorganic ligands is competing with the sorption interaction with a solid phase. Especially carbonate and carboxylic acids can significantly suppress sorption processes by aqueous complexation [39]. The behavior of these complexes is governed by the principles of coordination chemistry, where often central metal ions coordinate with surrounding ligands to create stable structures. The surrounding solution plays a pivotal role in facilitating the formation and dynamics of these complexes, influencing their thermodynamic and kinetic stability. Very often, the aquatic medium itself functions as a stabilizing agent, as for silver, iron or cobalt ($[\text{Ag}(\text{H}_2\text{O})_4]^+$, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$) [133]. Ligands acting as electron donors to these central metal cations can be classified as Lewis bases [133], though in case of water only as a very weak base.

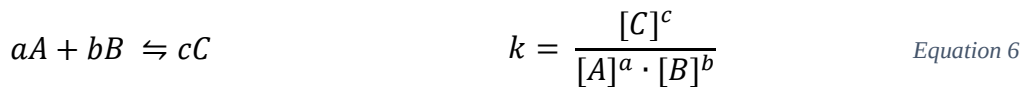
The HSAB (Hard and Soft Acids and Bases) principle is a concept in chemistry that helps predict and explain the formation of chemical bonds and reactions between Lewis acids and bases based on their relative "hardness" or "softness" [134]. It can be used to predict complex formation in aqueous media, though more reliably for inorganic metal complexes in comparison to organic complexes [135]. The main characteristics of a hard acid are a small size and a high charge and thereby electron affinity. Soft acids in contrast show large ionic radii in a comparatively low oxidation state. Hard bases are defined by a high electronegativity with a small size, often small molecules with a central oxygen or nitrogen atom; soft bases show opposite characteristics. In this concept, hard acids match best with hard bases and vice versa. With decreasing “hardness” of the bases, the affinity of the natural occurring inorganic anions towards hard acids is in the order of $\text{CO}_3^{2-} > \text{OH}^- > \text{F}^- > \text{SO}_4^{2-} > \text{Cl}^-$ from strongest to weakest [136]. The amounts of these anions being present in the pore water is dictated by the mineral composition and pore water origin [86]. Under laboratory conditions, when a synthetic pore water is used in an experiment, the amounts of fluoride, sulfate and chloride will likely remain

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constant while in contact with the corresponding clay rock. The concentrations of carbonate and hydroxide, however, will be dependent on pH and carbon dioxide partial pressure, which can vary under experimental conditions. Atmospheric carbon dioxide dissolution is described by the reaction:



This explains carbon dioxide dissolution causing a pH and therefore hydroxide concentration decrease. These parameters being strongly coupled makes speciation predictions without a geochemical model difficult and highlights the necessity of stable conditions. For the assessment of complex systems, complexation constants (k) are used. The magnitude of a complexation constant for a reversible reaction is indicative of the strength of the interaction between the complexing agents. A high complexation constant signifies a strong affinity and stability for the formed complex, while a low constant suggests a weak interaction. For a general reaction, it is defined as shown in Equation 6.



Whereby A and B are the reactants and C is the resulting complex, with a, b and c being the corresponding stoichiometric coefficients [137]. It has to be noted, that this equilibrium constant of the complex is only valid at infinite dilution and is also depends on the temperature. At higher salt concentrations, ion interactions need to be considered to assess the aqueous speciation correctly. The ionic strength (I) of a solution is a central term for calculation of ion interaction parameters, like activity coefficients. It is defined as:

$$I = \frac{1}{2} \sum_i c_i \cdot z_i^2 \quad \text{Equation 7}$$

Here, c_i is the concentration of the respective ion in mol/L and z_i its charge. Under real conditions the activity has to be used in calculations regarding the equilibrium constants instead of the concentration [138]. The Debye-Hückel equation [139] allows the determination of the activity in very dilute systems (up to $5 \cdot 10^{-3}$ mol/L), while the extended Debye-Hückel equation is valid for concentrations up to 0.2 mol/L, by taking the ionic radius of the investigated ions into account. To account for the major influences on the activity in the pore waters used in this study, the specific ion interaction theory (SIT) is used in the geochemical modeling approach. It is a theoretical framework used to describe and predict the activity coefficients of ions in solution, valid at ionic strengths up to 0.5 mol/L [140, 141]. It extends the Debye-Hückel theory

[139], by adding an ionic strength dependent term. The further assumptions made for the assessment of equilibrium constants of complexes are firstly, the background electrolyte concentration is much higher in comparison to the investigated ions. Interaction between the investigated ions themselves can therefore be neglected and only the interaction of ions with the background electrolytes are important. Secondly, uncharged species do not interact, neither attract nor repel. Under these assumptions, the equilibrium constant for complex formation can be described as:

$$\log K' - \Delta z^2 \cdot \frac{A(T) \cdot \sqrt{I_m}}{1 + B(T) \cdot r_i \cdot \sqrt{I_m}} = \log K^0 - \Delta \varepsilon \cdot I_m \quad \text{Equation 8}$$

Here, K' is the conditional equilibrium constant at the ionic strength I_m , Δz is the difference in charge between the investigated products and reactants, r_i the radius of the central ion, K^0 is the thermodynamic equilibrium constant at $I = 0$ mol/L and $\Delta \varepsilon$ is the difference in interaction coefficients. With experimentally determined ε values, equilibrium constants can be assessed.

2.4 Investigated Radionuclides

Cesium-137

A multitude of possible elements and isotopes are present in nuclear waste, stemming from various origins. In spent nuclear fuel, there are three major pathways to form radionuclides. One origin is from the fuel itself, including the transuranium decay products of beforehand activated isotopes. The other two origins are the fission products and direct activation products. When a nucleus undergoes fission, it can split into a wide range of possible combinations of lighter nuclei. In a nuclear reactor, these fission processes are mostly induced by thermal neutrons, originating from prior fissions and slowed down by a moderator. Fission products vary in mass number and atomic number. The fission yield is the probability of formation of a fission product and it depends on the specific nucleus involved and the energy of the incident neutron. Very rarely does a nucleus split evenly, and a so-called “double-humped curve” can be observed when plotting the fission yield of the resulting two main fission products against their mass [142]. This curve is shown for U-235 fission with thermal neutrons in Figure 10.

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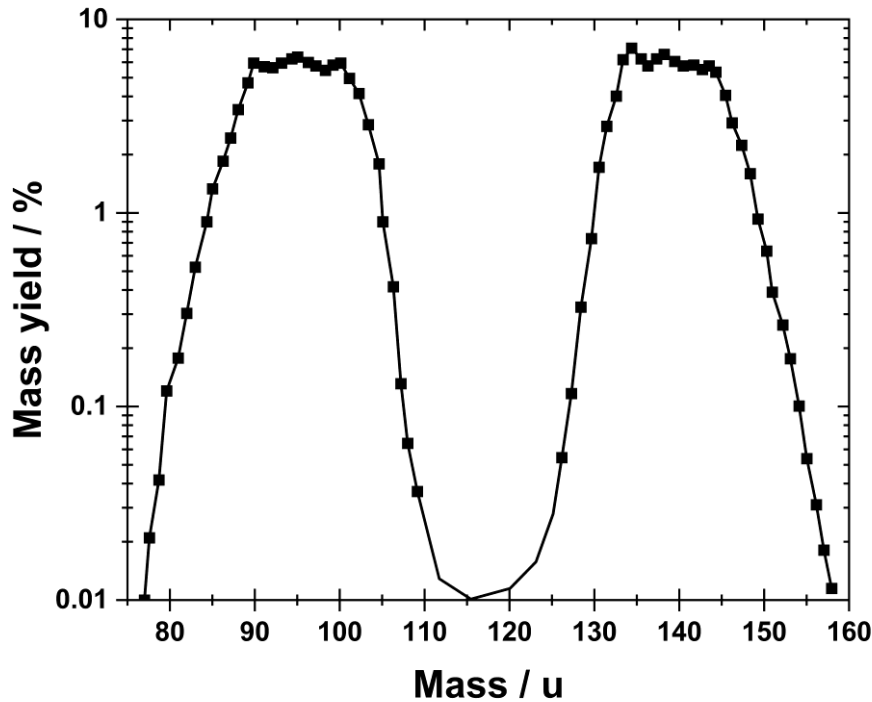


Figure 10: Mass yield from the fission of U-235 in percent on a logarithmic scale plotted against the mass of the fission products, adapted from Krane (1991) [143].

This non-equal distribution can be explained by the concept of “magic numbers”, derived from the nuclear shell theory [142]. This term refers to certain numbers of nucleons (protons or neutrons) that result in a more energetically favorable and therefore more stable core configuration. These numbers are in ascending order 2, 8, 20, 28, 50, 82 and 126 [142]. The isotopes randomly produced in nuclear fission often align with at least one of the magic numbers in their proton or neutron amount, causing the maxima at around ≈ 95 and ≈ 140 u. It has to be noted, that the influence of the magical neutron configuration is much more dominant.

Cs-137 is therefore a nuclide with a high fission yield, since it is composed of the magic number of 82 neutrons. Due to the accidents of Chernobyl and Fukushima in 1986 and 2011, respectively, immense amounts of Cs-137 have been released into the biosphere, where it seriously affected public health [144, 145]. In regards to its relevance for the safety assessment of a repository, it only shows a high contribution to the overall radiotoxicity of HLW in the early years after the emplacement, due to its comparatively low half-life of only ≈ 30 years (see Figure 3). During this timeframe, the waste container will still be intact according to normal development scenarios. The more relevant cesium nuclide for the safety assessment is Cs-135 with a half-life of ≈ 2.3 million years [142]. Cesium compounds tend to be highly soluble in water and this solubility can be of concern as it may potentially lead to the migration through geological formations if it is not properly contained. Cesium exists only as a monovalent cation

under environmental conditions and shows neither redox sensitive behavior, nor does it form a large variety of aqueous complexes [146]. The expected speciation in the pore waters presented in Table 3 is shown in Figure 11 as a pH variation from 3–11.

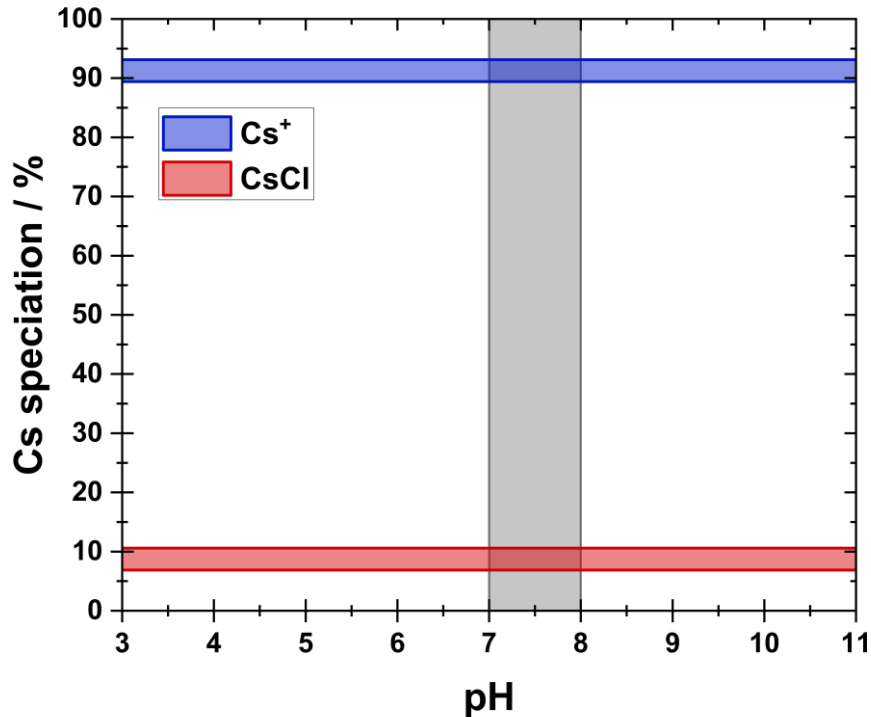


Figure 11: pH dependent speciation of $2 \cdot 10^{-7}$ mol/L cesium in the pore waters from Table 3 ($I = 0.4$ mol/L and 0.2 mol/L; pH 7.6 and 7.2; $[\text{CO}_3^{2-}] = 4.8 \cdot 10^{-4}$ mol/L and $2.7 \cdot 10^{-3}$ mol/L). The speciation is done with the modeling code PhreeqC and the included sit.dat database. The carbonate concentration is fixed as dissolved inorganic carbon. Colored bands show the differences between the two pore waters and the grey region indicates the relevant pH-range in most geological settings.

The speciation of cesium is pH independent and only shows minor deviations in the synthetic pore waters after Pearson and Gimmi from Table 3 [63, 99]. This speciation is expected from the HSAB concept, where Cs^+ is classified as a soft acid and thereby only weakly interacts with hard bases like hydroxide ions. This weak interaction may also lead to a weak retention from the amphoteric hydroxyl groups of clay minerals. The dominant retention mechanism of clay minerals towards cesium is cation exchange, though inner-spheric sorption on the highly affine “frayed edge sites” also has to be taken into account.

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Cobalt-60

Another possible origin of radioactive material in a HLW repository are the activation products. These are isotopes generated as a result of the exposure of (often) stable isotopes to external sources of radiation, usually in the form of neutrons. This can cause inactive material to suddenly become a hazard source and needs to be taken into account when designing a nuclear waste repository. An example for such an activation would be the formation of Cl-36 with a half-life of $\approx 300,000$ years from stable Cl-35 [142].

The main origin of Co-60 in a HLW is its generation as an activation product from cobalt present in alloys like steel. In a $\text{Co-59}(n,\gamma)\text{Co-60}$ reaction, it is produced via neutron capturing, followed by γ -ray emission. This is the same reaction taking place in a nuclear reactor during the production of Co-60, used for technical applications such as sterilization of medical equipment or cancer treatment. Besides the precursor Co-59 being naturally present in the alloy, it is also created through neutron capturing of Fe-58. Though the natural abundance of Fe-58 is only $\approx 0.3\%$ of the total stable iron, the large amounts of steel used in construction still provide a sufficient amount [147]. In a $\text{Fe-58}(n,\gamma)\text{Fe-59}(\beta^-)\text{Co-59}$ reaction, Co-59 is formed rapidly with Fe-59 only having a half-life of 44 days [142]. With a half-life of around 5.3 years, Co-60 transforms via β^- decay into Ni-60, emitting a high-energy electron with high-energy γ -radiation (1.172 MeV and 1.332 MeV). It is not very relevant on the timescale of a nuclear waste repository but can act as a surrogate for other divalent cations like Ni^{2+} , which will be present as Ni-59 (and Ni-63) in a HLW repository and is more relevant due to its half-life of 76,000 years [142]. Co^{2+} is classified as a hard Lewis acid, due to its small ion radius and comparatively high charge, and therefore shows a much broader spectrum of possible complex formations compared to Cs^+ . Co^{2+} shows no redox sensitive behavior under the reducing conditions expected in a HLW repository.

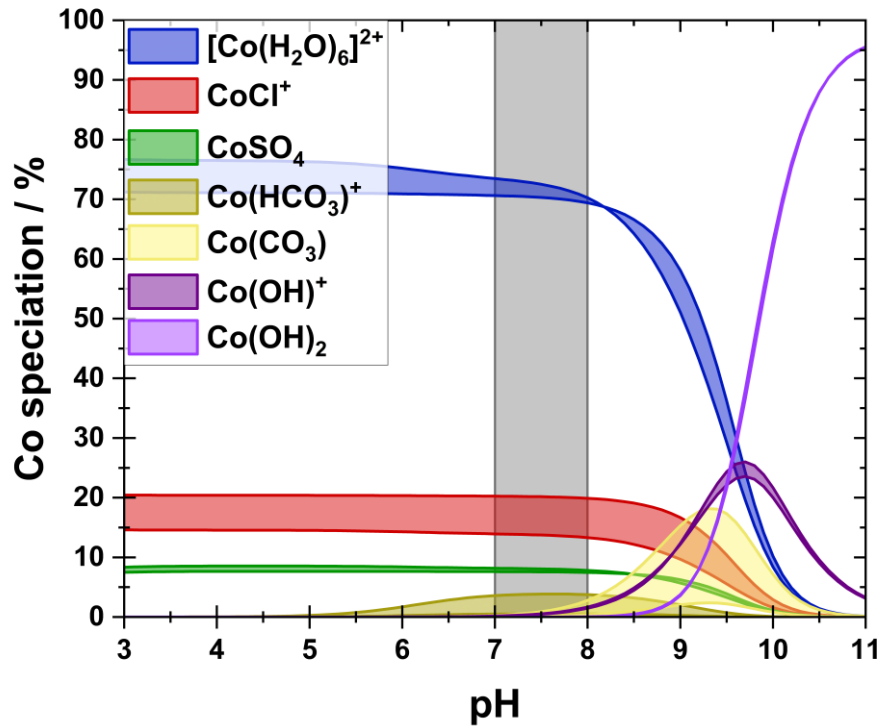


Figure 12: pH dependent speciation of $2 \cdot 10^{-7}$ mol/L cobalt in the pore waters from Table 3 ($I = 0.4$ and 0.2 mol/L; pH 7.6 and 7.2; $[\text{CO}_3^{2-}] = 4.8 \cdot 10^{-4}$ and $2.7 \cdot 10^{-3}$ mol/L). The speciation is done with the modeling code PhreeqC and the included sit.dat database. The carbonate concentration is fixed as dissolved inorganic carbon. Colored bands show the differences between the two pore waters and the grey region indicates the relevant pH-range in most geological settings.

The colored bands in Figure 12 show the influence of the different pore water compositions of Pearson and Gimmi presented in Table 3 [63, 99]. Up to pH 8, almost no change is visible in the speciation. More than 70 % of the total cobalt is present as Co^{2+} aquo-complex, while CoCl^+ is the second most common species. In the circumneutral pH-range highlighted in grey, a small difference in the carbonate complex speciation is observable, caused by the different carbonate concentrations in the respective pore waters. With increasing pH, this difference becomes more dominant. This complexation behavior of cobalt is expected from the HSAB principle and indicates surface sorption with hydroxyl groups to be likely the dominant sorption process in natural clay rocks, due to the strong affinity to form hydroxide complexes. In the circumneutral pH region most likely present in OPA repositories, not much variation in the speciation may be expected. However, changes in the carbonate concentration might alter the speciation more significantly.

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Europium-152

Besides fission and activation products in and around spent nuclear fuel, the fuel itself can also undergo a variety of radiochemical and physical processes. Due to neutron captures and decay chains, a number of transuranium actinides can be produced. The early actinides, especially uranium, neptunium and plutonium, show a great variance with respect to potential oxidation states [142, 148]. As shown in Figure 3, the main contributor to the overall radiotoxicity in spent nuclear fuel are the plutonium isotopes. While its most stable form is tetravalent, under the reducing conditions likely present in a final repository, the trivalent oxidation state also needs to be considered [149, 150]. A recent study of Kaplan *et al.* (2024) [151] on the reduction of pentavalent plutonium in contact with natural OPA via synchrotron micro-spectroscopic techniques revealed the almost quantitative reduction after only 100 μm diffusive transport. This process is governed by the reducing iron minerals pyrite and siderite, as well as the sulfate/pyrite redox couple [86, 98]. Furthermore Pu^{3+} solids are comparatively more soluble and therefore dominate the aquatic speciation [152]. The geochemical behavior of the trivalent plutonium is therefore very relevant for a repository safety case. Starting with americium in the actinide series, the variability in oxidation states narrows down drastically and the trivalent oxidation state dominates. These so-called “heavy actinides” only contribute to a small extent to the overall mass and activity of radioactive waste in a repository. Of these, americium is the strongest contributor to the overall radiotoxicity in the intermediate timeframe (500–10000 years) of a DGR. Both isotopes Am-241 and Am-243 have a significantly long half-life of ≈ 430 years and ≈ 7370 years, respectively. The most relevant oxidation states of all lanthanides and actinides are shown in Table 5 [148].

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Table 5: Primary oxidation states of aquatic lanthanides and actinides according to Runde (2000) [148], most stable state under aquatic conditions highlighted in red.

Lanthanide	+II	+III	+IV	Actinide	+II	+III	+IV	+V	+VI	+VII
Ce		+	+	Th			+			
Pr		+		Pa			+	+		
Nd		+		U		+	+	+	+	
Pm		+		Np		+	+	+	+	+
Sm	+	+		Pu		+	+	+	+	
Eu	+	+		Am		+	+	+	+	
Gd		+		Cm		+				
Tb		+		Bk		+				
DY		+		Cf		+				
Ho		+		Es		+				
Er		+		Fm	+	+				
Tm		+		Md	+	+				
Yb	+	+		No	+	+				
Lu		+		Lr		+				

Due to the oxidation state variance of early actinides, they exhibit a complex chemical behavior. However, the chemical behavior of the trivalent actinides is very similar to the behavior of lanthanides. This is caused by both groups having a similar electronic structure. Besides the preferred half and full occupation of electron orbitals, the general electron configuration can be denoted as $f^n d^0 s^0$ [153] for the ions in aqueous solutions. Through subsequent filling of the inner f-orbitals with increasing proton number, the electron density at the nucleus increases. This results in a decrease in ionic radii and is called the lanthanide- or actinide contraction. It is less pronounced for actinides due to more fully occupied, shielding s- and p-orbitals [153, 154]. The smaller energy difference between the 5f- and 6d orbitals is on reason for the great variance in oxidation states of early actinides [146, 154]. The similar chemical behavior of actinides and lanthanides also includes the interaction with other ions and with mineral surfaces. Therefore, lanthanides are often used as non-radioactive or less toxic and more abundant chemical homologues for the repository relevant trivalent actinides.

2. State of Knowledge

For these reasons, europium is selected as the third element investigated in this study. Though the main motivation to study the isotope Eu-152 is the before mentioned similarity to trivalent actinides, some europium isotopes will also be present in a repository as a minor fission product. Eu-152 shows a complex decay scheme, with a roughly $\approx 70\%$ probability to decay via electron capture to Sm-152 and a $\approx 30\%$ probability to decay via β^- emission to Gd-152 [142]. With a half-life of only 13.5 years, it doesn't contribute to the long-term radiotoxicity of HLW. Trivalent actinides are considered hard Lewis acids, due to their small ion radii with high oxidation state and therefore form a multitude of possible aquatic complexes in pore waters. Europium shows the same behavior, as shown in Figure 13.

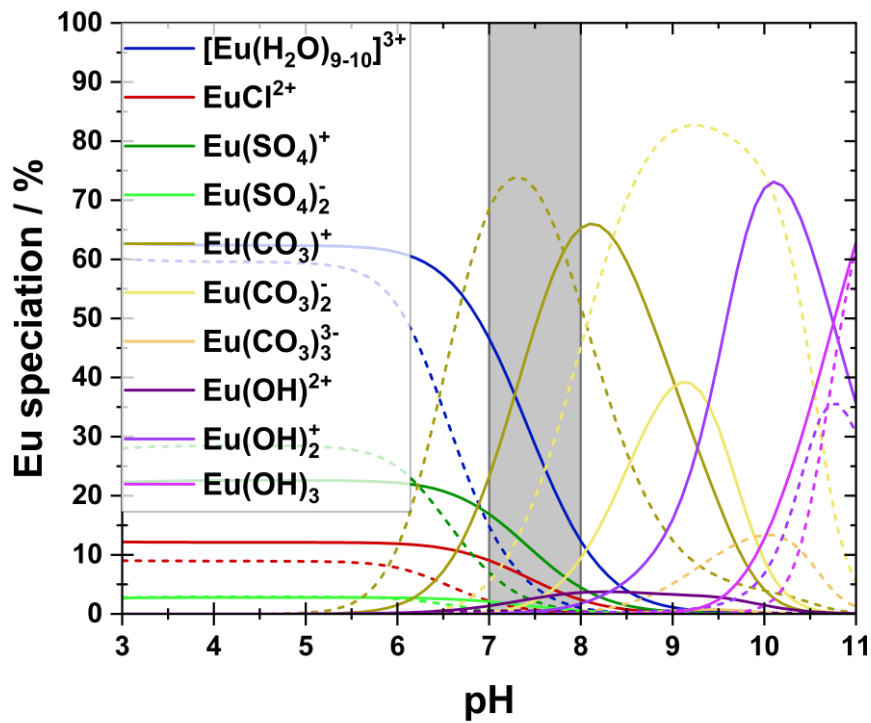


Figure 13: pH dependent speciation of $2 \cdot 10^{-7}$ mol/L europium in the pore waters from Table 3 ($I = 0.4$ and 0.2 mol/L; pH 7.6 and 7.2; $[\text{CO}_3^{2-}] = 4.8 \cdot 10^{-4}$ and $2.7 \cdot 10^{-3}$ mol/L). The speciation is done with the modeling code PhreeqC and the included sit.dat database. The carbonate concentration is fixed as dissolved inorganic carbon phase. Differences in composition between the two pore waters are shown by the intact and dashed lines and the grey region indicates the relevant pH-range in most geological settings.

Due to the more convoluted depiction of the europium speciation, a different graphical approach is chosen in Figure 13. Here the composition in Pearson pore water is shown as an intact line and in the Gimmi pore water as a dashed line [63, 99]. Up to pH 6, the composition is similar to the cobalt system, with the Eu^{3+} aquo complex [155] being the most common species. At circumneutral pH, the carbonate complexes start to dominate and a strong effect of the carbonate concentration in the pore water is observable. At $\text{pH} > 9$, hydroxide complexes become more dominant. The europium speciation, and therefore most likely the speciation of all trivalent lanthanides and actinides, is very sensitive to changes in both pH and carbonate concentration in the expectable water compositions in an OPA repository.

3. Materials and Methods

3.1 Deployed Chemicals

For all experiments as for the cleaning procedures, ultra-pure Milli-Q water is used, purified to exhibit an electrical resistance of 18.2 MΩ with <4 ppm dissolved organic carbon. This is done with a Q-PODTM system from Merck KGaA. An overview of the non-radiating chemicals used in this work can be found in Table 6 below.

Table 6: Chemicals used in this study in alphabetical order.

Name (formula)	Manufacturer
Salts	
Calcium chloride dihydrate (CaCl ₂ ·2H ₂ O)	Merck KGaA
Cesium carbonate (Cs ₂ CO ₃)	Alfa Aesar
Cobalt chloride (CoCl ₂)	Merck KGaA
Europium chloride hexahydrate (EuCl ₃ ·6H ₂ O)	Merck KGaA
Magnesium chloride hexahydrate (MgCl ₂ ·6H ₂ O)	Merck KGaA
Potassium chloride (KCl)	Merck KGaA
Sodium chloride (NaCl)	Merck KGaA
Sodium bicarbonate (NaHCO ₃)	Merck KGaA
Sodium sulfate (Na ₂ SO ₄)	Merck KGaA
Strontium chloride hexahydrate (SrCl ₂ ·6H ₂ O)	Merck KGaA
Acids and bases	
Hydrochloric acid 37 % (HCl)	Merck KGaA
Nitric acid 69 % (HNO ₃)	Carl Roth GmbH
Sodium hydroxide (NaOH)	Merck KGaA

For more precise pH-adjustments, dilutions of the given acids and bases are prepared. For the sorption and spectroscopic experiments, additionally radioactive tracer solutions are utilized. The original solutions, from which the deployed dilutions have been prepared, are listed in Table 7.

Table 7: List of the deployed radioactive standard solutions before dilution, with respective concentrations.

Isotope(s)	Concentration / (MBq/mL)	Background matrix	Manufacturer
Co-60	3.75	0.1 M HCl	Eckert & Ziegler Nuclitec GmbH
Cs-137	0.74	0.1 M HCl	Eckert & Ziegler Nuclitec GmbH
Eu-152	3.7	0.5 M HCl	Eckert & Ziegler Nuclitec GmbH
Cm-243–248	0.01	0.1 M HCl	Inhouse

From these solutions and the salts shown in Table 6, dilutions are prepared (see Table 8). The target activities for these solutions are 100 kBq/mL each for Co-60 and Cs-137 and 200 kBq/mL for Eu-152. This would allow a dilution of a factor of 100 to amount to a specific activity of 1 kBq/mL on case of Co-60 and Cs-137 and 2 kBq/mL in case of Eu-152. Simultaneously, a total concentration of $2 \cdot 10^{-7}$ mol/L of each element would be ensured for all tracers by respective addition of dissolved inactive salts. These activities are chosen to minimize radiation exposure while maintaining a sufficiently well detectable amount. The total concentrations are in the range of investigated literature and avoid low concentration effects, like wall sorption and high concentration effects like surface saturation [156] or precipitation.

Table 8: Stock solutions prepared for the performed experiments. Activities have been determined via γ -spectrometry, concentrations via ICP-OES.

Name	Specific activity / (kBq/mL)	Concentration / (mol/L)
Co	Co-60 63	Co $1.8 \cdot 10^{-5}$
Cs	Cs-137 105	Cs $2.4 \cdot 10^{-5}$
Eu	Eu-152 200	Eu $1.8 \cdot 10^{-5}$

3. Materials and Methods

3.2 Deployed Clay Minerals

The pure mineral phases used for the TRLFS experiments are shown in Table 9. These are chosen to represent the mineral constituents of natural OPA. Their purity has been confirmed via X-ray diffraction (XRD) measurements.

Table 9: Pure mineral phases used in the TRLFS experiments with their composition and origin.

Mineral	Composition	Origin
Quartz	High purity quartz	Inhouse
Calcite	CaCO ₃	Merck KGaA
Illite	Illite du Puy	Inhouse
Kaolinite	KGa-2	Clay Mineral Society
Chlorite	CCa-2	Clay Mineral Society
Muscovite	Mica WG	Normag GmbH
Orthoclase	-	Inhouse

3.3 Natural Clay Rock Samples

In this work, the three drill cores BMB-A7, BDR-D1 and BDR-D2 are investigated. They have been retrieved from the URL Mont Terri, Switzerland and are assigned to the upper and lower sandy facies OPA. The drilling locations are displayed in Figure 14.

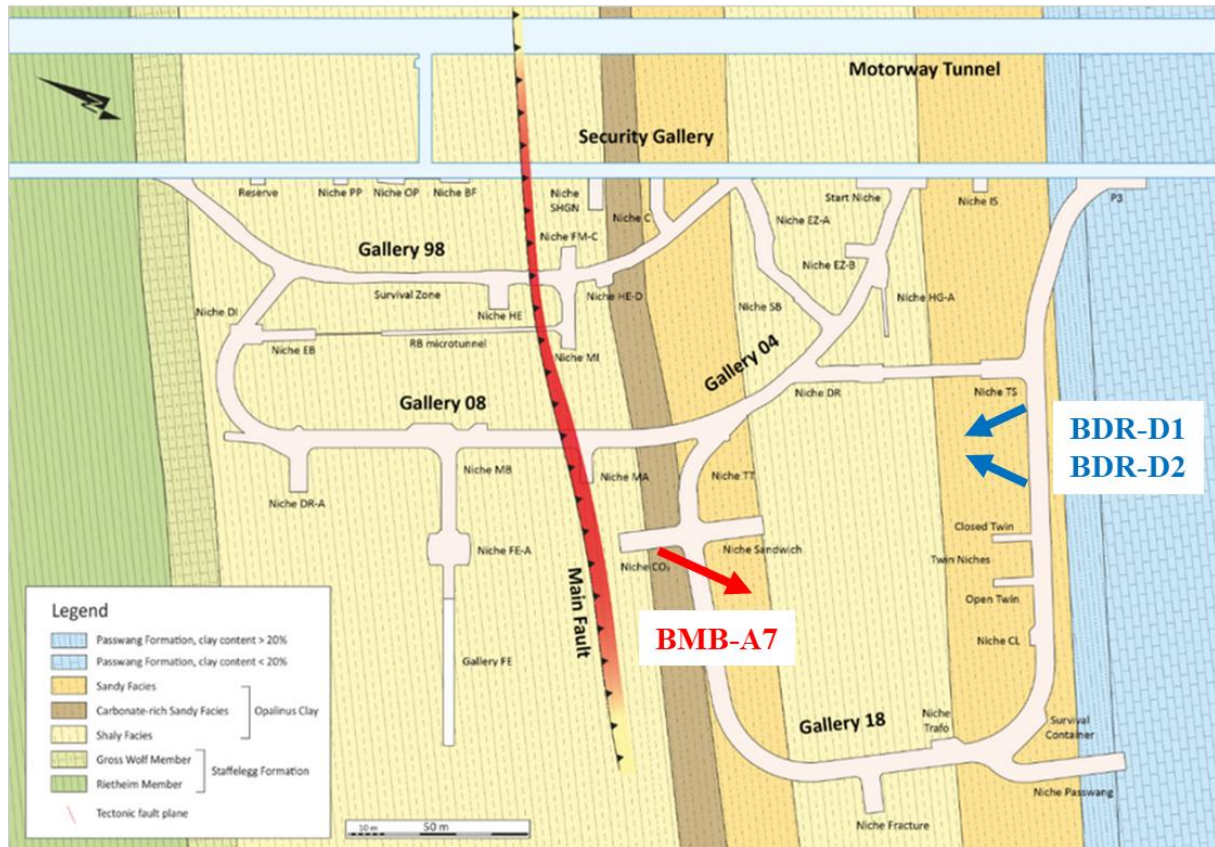


Figure 14: Map of the URL Mont Terri showing the stratigraphy of OPA. Indicated in red the location of the retrieval of core BMB-A7, and in blue the locations of the cores BDR-D1 (top) and BDR-D2 (bottom) [157].

Drill core BMB-A7 originates from the lower sandy facies and has been retrieved under argon countercurrent on the 3rd of July 2018 at an angle of $\approx 45^\circ$ to the bedding. Transportation and storage have been performed under anoxic conditions to prevent possible oxidation of the clay rock components. This has been ensured by sealing the fragments into aluminum composite foil under argon overpressure. Due to the nature of the drilling, packaging and logging process, minor alterations caused by atmospheric oxygen cannot be excluded. Segments from 36.4–36.9 m and 40.0–40.5 m (shown in Figure 15), have been retrieved and transported to the laboratory.

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Figure 15: Core BMB-A7, segment 40.0–40.5 m as a compilation of three separate images.

The cores BDR-D1 and BDR-D2 originate from the upper sandy facies and have been retrieved on the 3rd and 4th of May 2021, respectively. The drilling is part of the DR-D experiment [95]. A segment of both cores presented next to each other as a compilation of a multitude of separate photographs is shown in Figure 16.



Figure 16: Cores BDR-D1 and -D2, segment 5.0–8.0 m laid next to each other at the same well-depth as a compilation of multiple pictures.

The drilling angles are 70° to the bedding and 55° to the floor of the URL, with an angle of 70° towards one another for both cores. For a better understanding of this geometry, Figure 17 shows a schematic drawing of the retrieval. Drilling precisely perpendicular to the bedding may have caused stability issues (so-called diskings of the bedding planes). These drill cores have been drilled, logged and transported under ambient conditions. The whole cores of 3.0–15.5 m well-depth with an inner diameter of 10.25 cm have been retrieved, but only fragments starting in a well-depth of 5.0 m and deeper are subsequently analyzed. This is done to prevent using samples from the EDZ (excavation damaged zone) of the gallery, which could differ from the other fragments due to exposure to unnatural conditions, like vibrations caused by drilling or passing vehicles.

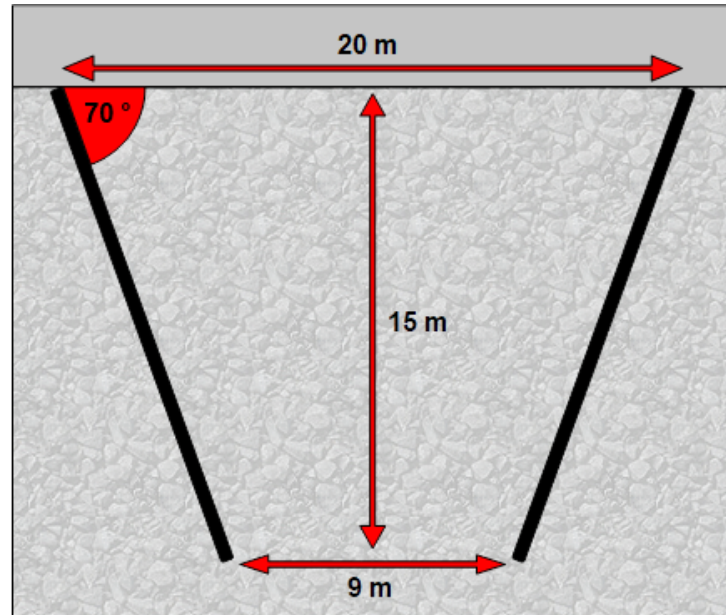


Figure 17: Geometrical arrangement of the drilling of the cores BDR-D1 and -D2 in black. Area in grey on top represents the gallery floor and the area with a stone-like background represents the host rock material.

3.3.1 Sample Preparation

To study the impact of the heterogeneity, for core BMB-A7 a sample volume variation is chosen. The fragment of 36.4–36.9 m serves as a reference bulk with a volume of $\approx 2000 \text{ cm}^3$ and is named BU1. The fragment of 40.0–40.5 m is segmented with a diamond bladed saw in an argon atmospheric glovebox to prevent oxidation. In the region of 40.2–40.5 m, samples are chosen by eye to represent distinct mineralogical compositions. Half of this segment is chosen as a bulk sample of the fragment, with a volume of $\approx 300 \text{ cm}^3$ (BU2). The other half is subdivided into three samples with a volume of $\approx 100 \text{ cm}^3$ each, having distinct visual characteristics. These samples are shown in Figure 18. Due to the perspective of the photograph they seem to be of different size, but the core is cut evenly in two halves. SA is supposed to represent a sand-rich sample, dominated by light grey areas and concretions, SH is supposed to represent a clay rich sample, dominated by the dark clay matrix, and EV represents a mixed sample with an approximately even distribution of the visual characteristics. This sampling procedure has been performed prior to the start of this study by M. Vogt [158].

3. Materials and Methods

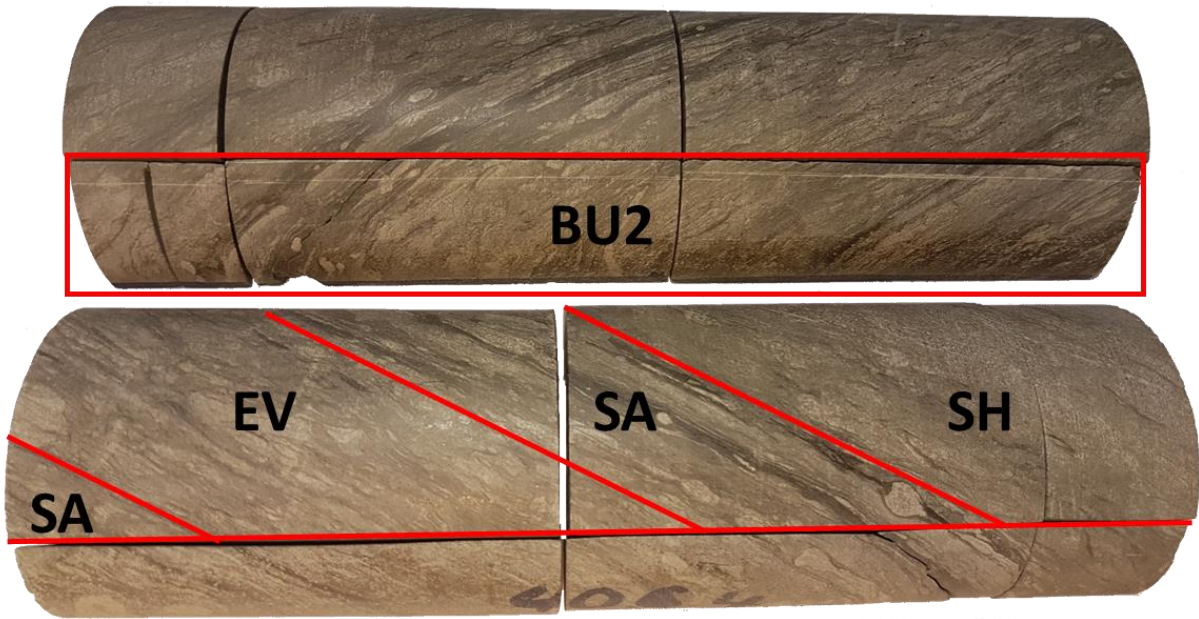


Figure 18: Sampling of core BMB-A7 into the visually chosen samples with distinct characteristics [158]. SH represent the clay-rich “shaly” sample, SA represents the carbonate and sand lenses rich “sandy” sample and EV represents the “evenly-mixed” sample. BU2 is a reference bulk as a combination of the visually chosen samples.

The part of 40.0–40.2 m of core BMB-A7 is cut into even smaller samples. These cubes consist of one 27 cm³ sample, eight 8 cm³ samples and thirty-two 1 cm³ samples. During the sampling process, unfortunately some of the 1 cm³ samples have been lost due to fracturing, reducing the total amount to twenty-one. This sampling procedure has been part of the master thesis of N. Gill and has been performed by her together with the further preparation [159]. Figure 19 shows a schematic drawing of the whole cutting procedure with the resulting blocks. The leftover fragments are gathered and crushed into pieces of <1 mm length. These small pieces are then investigated under a microscope and separated with plastic tweezers into piles. One pile consists of mostly darkish splinters and one of whiteish lenses, while the rest is discarded. The two piles are then labeled as hand-picked clay-rich and sand-rich samples, respectively.

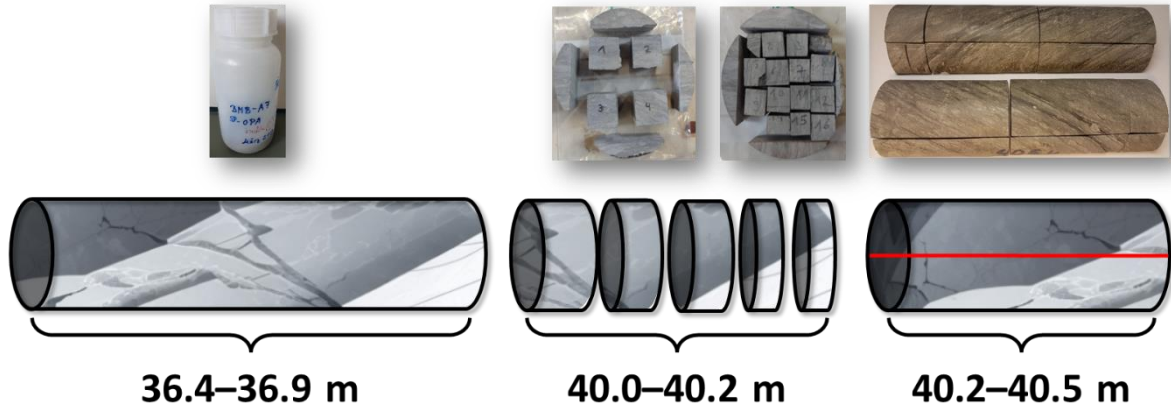


Figure 19: Schematic drawing of the segmentation procedure of core BMB-A7 into the smaller sub-samples.

All samples are ground and sieved to a grain size of less than 100 μm , the samples with a volume of $\geq 100 \text{ cm}^3$ under argon atmosphere, the others at ambient conditions. Afterwards, one half of sample BU2 is taken out of the argon glovebox and stored under ambient conditions to investigate the alteration through atmospheric oxygen. This has had no effect on neither the mineralogy, nor the sorption behavior and consequently won't be mentioned further.

Intact rock surface samples are prepared to gain insight into the impact of the heterogeneity on the microscopic scale. Therefore, a similar set-up to Van Loon et al. (2014 and 2023) [80, 160] is used, who have investigated the in-diffusion into cylindrical small-scale OPA samples. The superglue LOCTITE 401 from *Henkel* is used for impregnation, to prevent intrusion of the epoxide (Epofix from *Struers GmbH*) into the clay rock, prior to the embedding into cylinders with a 1.5 cm diameter. The remnants of glue and epoxy are abraded from the investigated surface by manually polishing with abrasive paper (*Craftomat*) from a coarse grit of 20 up to a smooth grit of 2000. Afterwards, the surface is exposed to a high-pressure air current to remove produced dust. The polishing is done by hand to prevent as much heat exposure as possible, to avoid potential phase alteration at the surface. In the end, a roughly $\approx 3 \text{ cm}^2$ surface surrounded by epoxy resin is produced. Exemplarily, one of these samples is shown in Figure 20. Some of these samples have been prepared by M. Vogt, prior to the start of this study [158].

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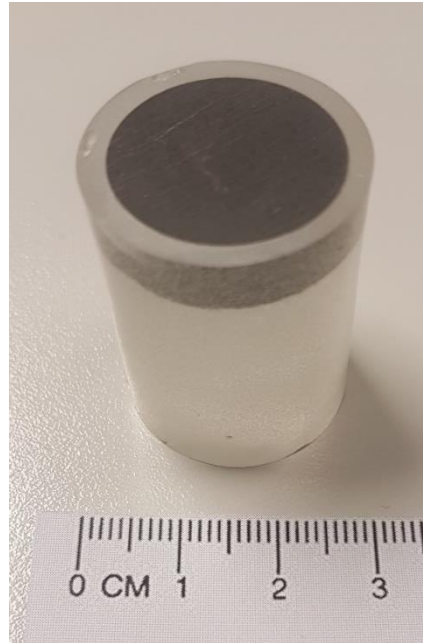


Figure 20: Rock surface sorption sample embedded into epoxy resin during the hardening process with a cm-scale [158].

For the cores BDR-D1 and BDR-D2 a different approach is chosen in comparison to the core BMB-A7. The impact of the heterogeneity is investigated in parallel and perpendicular to the bedding. Both cores are thoroughly polished with an orbital sander using abrasive paper with a grit of 120 all around and then laid out next to one another. A full comparison of the cores is assessed at similar well-depths (Figure 16). After optical categorization (Chapter 3.6.2.1), samples are taken at an interval of 25 cm, at which discs with a thickness of 2 cm are cut out, perpendicular to the drilling vector. These discs are then cut in half, with one half getting polished by hand up to a grit of 2000 for a comparison of both cores. Figure 21 exemplarily shows three of these half discs.

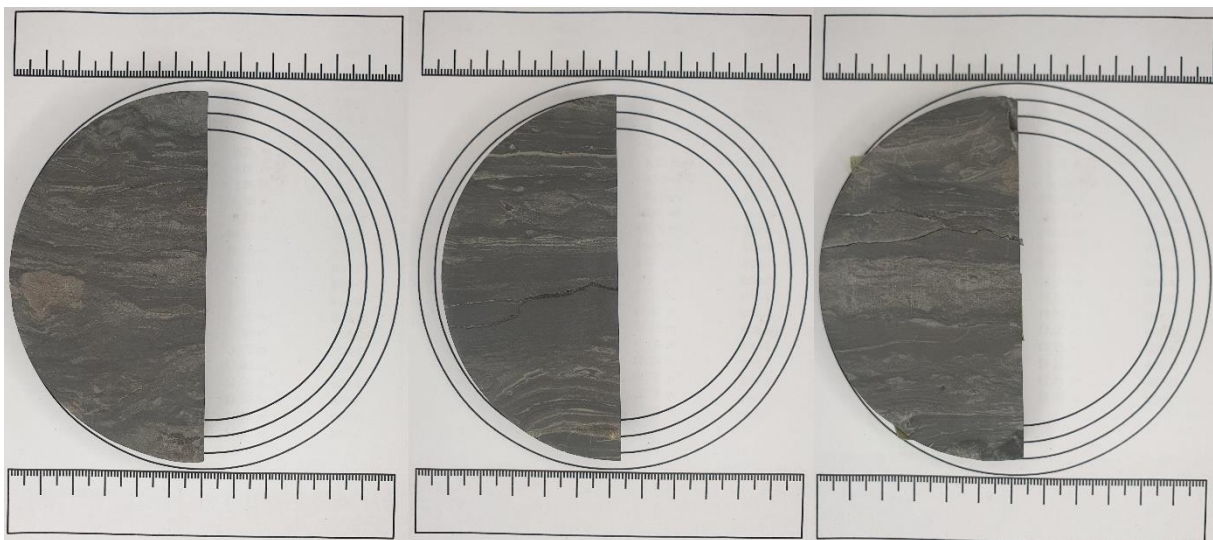


Figure 21: Cutout disks for the optical analysis of core BDR-D1 6.0–6.5 m with a cm-scale.

From the optical analysis, areas of interest are chosen and the respective non-polished halves of the discs are ground and sieved to a grain size of less than 100 μm , as the samples of drill core BMB-A7. This grinding procedure is performed at ambient conditions, resulting in 30 powder samples. They are labeled, firstly, after their respective core and secondly by the respective well-depth, e.g., the sample D1 7.00 m refers to the disk taken from core BDR-D1 at a well-depth of 7.00 m. Note that well-depth means the depth along the drill core as opposed to the real geometrical depth which would have been measured perpendicularly to the gallery floor. Furthermore, it has to be noted that these well-depths should be taken with an uncertainty of ± 10 cm, due to the limited accuracy of the retrieval process, as small parts got lost during the drilling and retrieval.

3.4 Synthetic Pore Waters

Two synthetic OPA pore waters are prepared, one following the composition described in Gimmi et al. (2014) [63], the other is prepared following the recipe proposed by Heberling et al. (2023) [161]. The second recipe is used in the DR-D experiment, situated in the middle of the retrieval locations of the cores BDR-D1 and -D2. Both synthetic pore waters are chosen to match the natural pore water composition at the retrieval locations of the cores in the sandy facies best. Table 10 shows the target compositions of these recipes.

Table 10: Target compositions of the synthetic pore waters used in the batch sorption experiments for the respective drill cores, including the corresponding ionic strength and pH. The recipe for the BMB-A7 pore water follows Gimmi et al. (2014) [63] and the other recipe follows composition used in the DR-D experiment, proposed by Heberling et al. (2023) [161].

Concentration / (mol/L)	BMB-A7 [63]	BDR-D1 and -D2 [161]
Na^+	$1.5 \cdot 10^{-1}$	$8.8 \cdot 10^{-2}$
Mg^{2+}	$1.1 \cdot 10^{-2}$	$8.3 \cdot 10^{-3}$
K^+	$1.4 \cdot 10^{-3}$	$9.0 \cdot 10^{-4}$
Ca^{2+}	$8.7 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$
Sr^{2+}	$5.0 \cdot 10^{-4}$	$4.6 \cdot 10^{-4}$
CO_3^{2-}	$2.7 \cdot 10^{-3}$	$4.3 \cdot 10^{-3}$
SO_4^{2-}	$8.8 \cdot 10^{-3}$	$6.2 \cdot 10^{-3}$
Cl^-	$1.7 \cdot 10^{-1}$	$9.2 \cdot 10^{-2}$
Ionic strength / (mol/L)	0.2	0.12
pH	7.2	7.8

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3.5 Analytical methods

3.5.1 XRD and Rietveld

To gather information on the mineral composition of all prepared powder samples, XRD is performed, using a D8 advance powder diffractometer from *Bruker*. Powder samples are prepared on a silicon waver and measured in an angular range from 2–65 °2 θ in reflection mode with a step size of 0.015 °2 θ and a scan speed of 0.5 s per step, using Cu K α radiation at 1.541 Å.

For quantitative analyses of the recorded diffractograms, Rietveld refinement is used. Firstly, all major components are identified using the program code Diffrac.EVA V5.0 [162] and the crystallographic open database (COD) [163-170]. Next, the CIF-files of the found minerals from the COD are loaded into the program code TOPAS-7 [171] for the Rietveld refinement. To ensure comparability, a single procedure is established during preliminary analyses, to fit for all samples. In this evaluation, the lattice parameters (lengths and angles not defined by the space group) of all crystals are allowed to change by $\pm 3\%$ and a variable underground is implemented as a background correction, both to account for slight deviations in reflex positions. The minimum possible particle size has been identified to be the most critical parameter inducing the biggest changes in the obtained composition. Using the minimal particle size as an unconstrained fitting parameter often results in reflexes broadening until they become indistinguishable from the background, which leads to a severe overestimation of the relative mineral abundance. Therefore, each sample is fit in triplicate with three different lower limits of the adjustable particle size at 30 nm, 100 nm and 200 nm. To obtain the final composition, the average of these three fits is taken and the standard deviation is used as a measure of uncertainty. During this whole procedure, the goodness of the fit, a parameter determining the quality of the fit provided by the TOPAS software, is monitored to maintain adequate quality (<4). To validate the fitting procedure, synthetic mixtures of selected minerals with various compositions are prepared, measured and analyzed. Exemplarily, one fit is displayed in Figure 22.

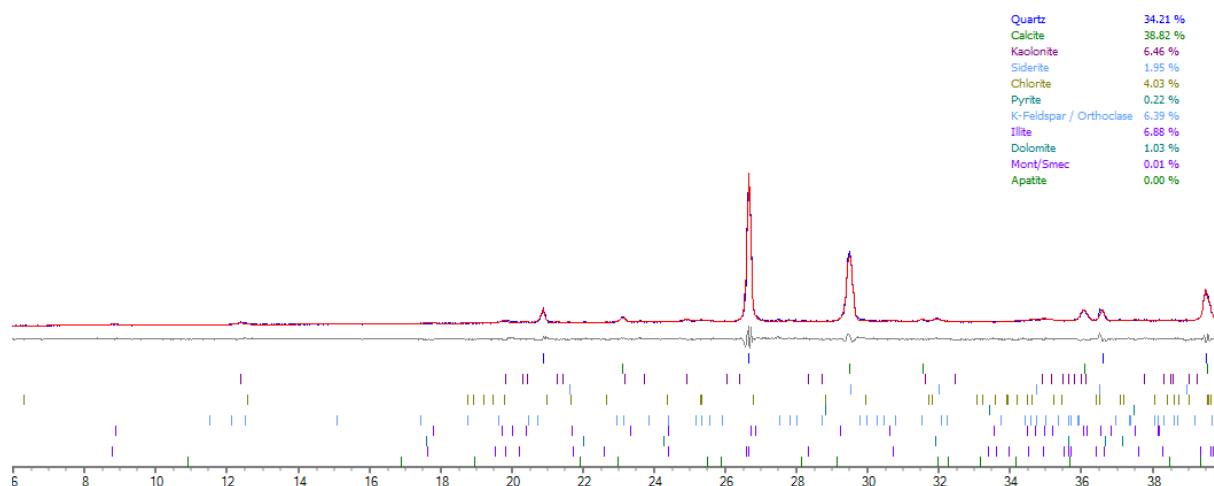


Figure 22: Screenshot from the Rietveld fitting procedure of sample SA, with a minimal particle size of 100 nm and the obtained mineral composition in the top right corner.

3.5.2 SEM-EDX

To compare gathered data of the bulk powder to an intact, polished surface, a mapping procedure is performed with energy dispersive X-ray spectroscopy (SEM-EDX), utilizing a QUANTA 650 FEG scanning electron microscope from *Thermo Scientific*. In SEM-EDX, an electron beam scans the sample surface, exciting and ejecting inner-shell electrons, which leads to the emission characteristic X-rays. The energy of the emitted X-rays reveals the elemental composition, enabling elucidation of the spatial distribution of elements with high sensitivity and resolution. With the obtained elemental mappings, phase analysis is performed to identify different minerals based on their chemical composition. It has to be noted, that this procedure analyses a surface area and the resulting quantitative occurrences at the surface do not necessarily agree perfectly with the bulk mineral abundance in wt%. A strong correlation may still be expected, if a representative area is investigated. A cutout of the sample BU1 and the intact rock surface sorption samples are analyzed with this method.

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3.5.3 XRF

X-ray fluorescence spectroscopy (XRF) is an analytical method yielding similar information as EDX analysis. Instead of bombarding the sample with electrons, the sample is illuminated with an X-ray beam, to produce inner shell electron holes. Subsequently, element specific X-ray emissions are recorded similarly to EDX. The sample preparation is done by pressing a homogeneous powder into a small disk or pellet, followed by smelting of the sample for further homogenization. During the smelting, the pellet loses weight due to phase transformations. This loss on ignition (LOI) is obtained at 1050 °C. Instead of at% at the surface like in the EDX measurement, the average wt% can be obtained by proper calibration. In this study, the XRF powder data of BU1 is obtained following DIN51001 and has been performed externally at the terrachem GmbH (Mannheim) using an S8-Tiger from *Bruker*, calibrated with an array of standard solutions. This task has been commissioned by M. Vogt, prior to the start of this study [158].

μ -XRF combines the specific elemental characterization of the XRF with spatial resolution. A moveable detector allows scanning of the surface and analyzes intact surfaces instead of homogenized powder or smelted samples. Thus, a mapping can be obtained showing the elemental distribution at the surface, similarly to SEM-EDX. Furthermore, phase analysis can also be performed to assign specific surface elemental compositions to certain mineral phases. An S8 Tiger from *Bruker* is also used to analyze the intact rock surface samples by μ -XRF prior to the sorption experiments, but in this case at the INE.

To compare the two methods directly, μ -XRF has the advantage that there is no need for a high-vacuum, which allows faster and easier measurements. However, the electron beam of SEM-EDX can be focused much better, which allows for a much higher spatial resolution. The information depth of both methods is in the micrometer range, though the resolution of the SEM-EDX can be enhanced to several nanometers. Another advantage of μ -XRF is the better sensitivity for light elements.

3.5.4 Further Analysis

ICP-MS

Inductively coupled plasma mass spectrometry (ICP-MS) is an analytical technique used for the detection and quantification of trace elements and isotopes. Firstly, a liquid sample is converted to an aerosol, then atomized and ionized in an argon plasma torch. The ions produced in the plasma are extracted into a mass spectrometer, which separates and measures the ions based on their mass-to-charge ratio, allowing for precise determination of element concentrations. In this study, the sample BU1 is investigated via ICP-MS, after digestion, following a digestion procedure found in Pearson *et al.* (2003) [86]. A 500 mg powder sample is dissolved in a mixture of 4 mL concentrated hydrofluoric acid and 2 mL aqua regia. This suspension is heated and kept at 90 °C for 24 h and after cooling and addition of 2 mL of concentrated perchloric acid, the liquid is evaporated under an infrared lamp. Finally, the residue is dissolved using 0.1 M nitric acid. This task has been commissioned by M. Vogt, prior to the start of this study [158]. Besides the solid sample, several synthetic pore water samples are investigated via ICP-MS, all in a ThermoICAP-TQ-S from *Thermo Scientific*.

BET

The Brunauer-Emmett-Teller (BET) method is a gas adsorption technique used to determine the specific surface area of powdered or porous materials. It involves the measurement of the amount of gas (often nitrogen) adsorbed on the material's surface at different pressures. The adsorption data is used to plot a BET isotherm and the specific surface area is calculated by fitting the data to a linear equation representing a monolayer gas adsorption. In this study, the samples BU1, BU2, SA, SH, EV and for the smaller samples exemplarily the 27 cm³ sample and two 8 cm³ samples are investigated with the N₂-BET method. The investigation of the small-volume samples has been part of the master thesis of N. Gill [159]. The powder samples are outgassed at 85 °C for 48 h prior to the measurement of the sorption isotherms in an Autosorb 1 automated gas sorption system from *Quantachrome INSTRUMENTS*.

Thermal analysis (DSC/TGA)

Differential scanning calorimetry (DSC) is a quantitative technique that measures the heat flow associated with phase transitions and chemical reactions as a function of temperature. This method enables the determination of thermal properties, such as enthalpy and transition

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temperatures, gathering insight into material composition. Thermogravimetric analysis (TGA) can detect mass changes in a material as a function of temperature. By monitoring weight variations, TGA is adept at identifying decomposition events, oxidation kinetics, and compositional alterations. In this study, DSC and simultaneous TGA is performed in a STA 409 C/CD instrument from *NETZSCH*, heating 20 mg of sample material up to 1300 °C. From the mass loss up to 200 °C, the water content is derived. Further assigned mass losses are discussed in Chapter 4.2. The investigated samples are BU1, the 27 cm³ sample, four 8 cm³ samples and two 1 cm³ samples. The investigation of the small-volume samples has been part of the master thesis of N. Gill [159]. Additionally, three samples from each of the BDR-D1 and -D2 cores are investigated.

XPS

X-ray photoelectron spectroscopy (XPS) allows detection of the elemental composition and chemical states of surface atoms. By irradiating a sample with X-rays, XPS measures the kinetic energy of emitted photoelectrons. This way the elemental composition, oxidation states and chemical bonding states can be derived. In this study, XPS is used on the BU1 powder sample as a comparison to XRF measurements and to shed light on the crucial oxidation states of carbon and iron. The measurement is carried out with a VersaProbe II X-ray photoelectron spectrometer from *ULVAC-PHI*. This task has been commissioned by M. Vogt, prior to the start of this study [158].

Carbon contents

Often, the total organic carbon (TOC) content is determined via a differential method, where the total carbon content is measured via conversion to carbon dioxide through an oxygen current and the total inorganic carbon (TIC) is analyzed as the concentration of carbonates and bicarbonates released as carbon dioxide after acidification and subtracted. In either case, the detection of the carbon dioxide amount produced is conducted in a non-dispersive infrared detector, scanning the reaction chamber for the adsorption of the carbon dioxide specific wavelength. By employing known calibration standards, the desired concentrations can be quantitatively determined. In this study, the carbon contents of BU1, BU2, SH, SA and EV are determined, as well as several samples of synthetic pore water. For this purpose, a multi N/C 2100S instrument from *Analytic Jena GmbH* is employed.

ICP-OES

Inductively coupled plasma with optical emission spectroscopy (ICP-OES) is an analytical technique for elemental analysis. The elemental composition is obtained, based on the characteristic photon emission lines of excited atoms. A high-temperature plasma atomizes and ionizes the sample. Upon relaxation, the excited ions emit photons of characteristic wavelengths, which are dispersed and quantified by a spectrometer. In this study, ICP-OES is used to determine the cation concentrations in various synthetic pore water samples with an Optima DV 8300 from *PerkinElmer*.

IC

Ion chromatography (IC) is a technique used to quantify ions in solution. It focuses on the determination of ionic concentrations by exploiting their different interactions with an ion exchange column. A sample is introduced into a liquid mobile phase, traversing an ion exchange column, resulting in distinct retention times for the containing ions. These separated ions are subsequently detected using conductivity, or other suitable detectors. In this study, IC is used to determine the anion concentrations in several synthetic pore water samples. An ICS 3000 chromatography system from *Thermo Fisher* is used, with an implemented conductivity detector and a Dionex IonPac AS9-HC column as the stationary phase.

γ -Spectrometry

γ -spectrometry is an analytical technique used for the identification and quantification of γ -ray emitting isotopes. It is based on the principle of radioactive material emitting characteristic γ -rays during decay. These γ -rays can be detected and analyzed to determine the presence and concentration of specific radionuclides. It involves the usage of a high-purity germanium detector. When a γ -ray interacts with the detector, it generates an electrical pulse that is subsequently amplified, processed, and analyzed. The resulting energy spectrum represents the intensity of γ -rays detected at different energies, providing a unique fingerprint of the radionuclides present in the sample, allowing the simultaneous determination of several radionuclides at once. By applying appropriate calibration techniques using reference materials, a quantitative determination is possible. Each present radionuclide also casts a broad background at lower energy levels due to the Compton effect (Compton background). A multitude of present γ -ray emitters can cause the Compton background to rise above the

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photoelectron peaks of lower energy emitters to an extent where measuring them becomes impossible. In this study, a HPGe detector from *Mirion* with a resolution of 1.8 keV at 1.33 MeV and 0.875 keV at 122 keV combined with an autosampler from *IMPROMAT* is used to determine the activity and subsequently the concentrations of Cs-137 and Co-60 from the batch sorption experiments simultaneously. The calibration range is 45–1800 keV and calibration is done with a standard multi nuclide solution from *Eckert und Ziegler*. Initially, the simultaneous measurement of all three investigated radionuclides (including Eu-152) has been planned, but due to the high Compton background of Cs-137 and Co-60 and low concentration of Eu-152, this plan has been discarded.

γ -Counting

Similarly to the γ -spectrometer, a γ -counter can be used to quantify the radiation exhibited by a radioactive sample. The fundamental concept is that of a scintillation detector, wherein incident radiation causes the emission of photons. The absorption of a γ -quantum excites an electron and creates highly energetic photo- (and Compton) electrons which lead to ionization within the scintillation crystal, often NaI:Tl. The excited centers of the crystal lattice swiftly transition back to their lower energy levels. During this transition, the excess energy gained during excitation is emitted in the form of photons. The emitted scintillation light is then collected and enhanced by a photosensitive device, such as a photomultiplier tube and subsequently detected by a photodiode. The intensity of the detected light is proportional to the energy deposited by the incident radiation, allowing for the determination of the radiation energy. In this study, a 2480 Automatic Gamma Counter Wizard 2 from *PerkinElmer* is used, with a measurement time of four hours per sample. This setup allows the detection of very low present activities down to <0.5 Bq, rendering it suitable for the detecting remaining Eu-152 in solution after the batch sorption experiments.

3.6 Experimental

All experiments, unless stated otherwise, are performed in an argon glovebox, containing a maximum oxygen concentration of 10 ppm. Special about this glovebox is its additional supply line of carbon dioxide, producing a controlled carbon dioxide atmosphere of 1.0 vol%, to stabilize carbonate containing solutions and mineral phases. The temperature of the glovebox is set to 25 °C and monitored to prevent thermal effects.

3.6.1 pH-Measurement

pH is a crucial parameter when conducting experiments with clay minerals due to the charge dependency of the mineral surfaces as shown in Chapter 2.1 or pH related changes in solution speciation. It is by definition the negative decadic logarithm of the proton activity in a solution:

$$pH = -\log (a(H^+)) \quad \text{Equation 9}$$

At infinite dilution of a solution containing ions, it can be approximated as:

$$pH = -\log (c(H^+)) \quad \text{Equation 10}$$

When determining pH in solutions at ionic strengths higher than 0.1 mol/L, it is necessary to correct the measured pH_{exp} value with so-called A-values. These correct pH_{exp} -values with respect to the diffusion effects occurring at the salt bridge of the electrode. With this empirically obtained parameter, pH is calculated according to:

$$pH_m = pH_{exp} + A \quad \text{Equation 11}$$

These A-values can be calculated by concentration dependent equations for electrolyte solutions. For example, an equation for pure calcium chloride solutions is given in Altmaier et al. (2008) [172] and equations for sodium chloride and magnesium chloride solutions are given in Altmaier et al. (2003) [173]. For mixed solutions, a system of equations has been established from the two references. In case of the proposed porewater compositions, the A-values both amounted to ≈ -0.05 and all measured and reported pH-values have been corrected accordingly.

pH is measured with an ORION 3 STAR pH-meter from *Thermo Scientific* using a BlueLine 16 micro pH-electrode from *Si Analytics*. The calibration is performed at ambient conditions with freshly opened standards buffers (NIST from *Merck KGaA*) at pH 4, 7 and 9. Each measurement is done until no change to pH occurs for one minute. With regards to the accuracy of pH detection, an uncertainty of ± 0.1 units is assumed.

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3.6.2 Characterization

3.6.2.1 Whole rock

Due to the visually small variance in the core BMB-A7, a thorough optical characterization is foregone. For the cores BDR-D1 and -D2 on the other hand, a visual characterization makes sense due to the large amount of material present. At first glance, seven distinct lithological categories can be spotted, which are displayed in Figure 23.



Figure 23: Categories identified on the surfaces of the drill cores BDR-D1 and -D2. From left to right: dark grey clay matrix, turbated light-grey sand/carbonate matrix, light-grey sand/carbonate concretions, light-grey sand/carbonate layers, bituminous lenses (i.e. the small black spot below the middle of the image, embedded in clay matrix), brownish concretions (likely iron-rich (siderite)), fossil-rich layer (containing mussel shell fragments (coquinas) besides brownish concretions).

A rectangular five-by-five grid with a grid cell size of $2 \cdot 2 \text{ cm}^2$ is laid over the whole drill cores, which have been prepared as described in Chapter 3.3.1. For each grid cell, the dominant phase categories from the list shown in Figure 23 are noted and evaluated to obtain an optical categorization of the core. These are then compared to one another and correlated to the mineralogical analyses of the ground powders. This categorization serves as a measure to compare the two drill cores quantitatively. The grid laid on one of the drill cores as an example of this procedure is shown in Figure 24.

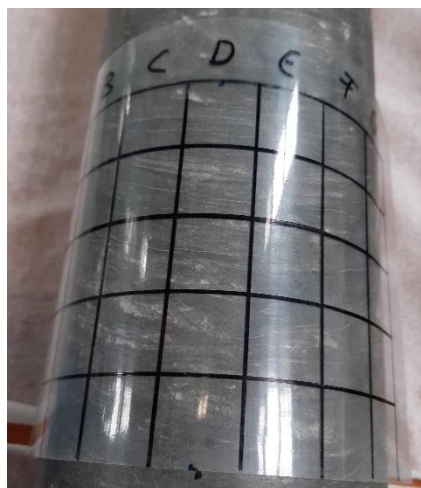


Figure 24: Rectangular five-by-five grid used for the optical categorizations of the cores BDR-D1 and -D2 laid on one of the cores.

This optical analysis can only be considered a rough estimate, due to its subjective interpretation. To counteract a “confirmation bias” such an investigation entails, efforts are made to estimate a degree of uncertainty. Therefore, 1.5 m of a drill core are investigated fivefold in different rotations and the results are compared. This leads to a variation of 9.5 %. An uncertainty of $\pm 10\%$ is therefore assumed for this optical assessments. Besides the comparison of the intact drill core surfaces, the discs cut as described in Chapter 3.3.1 are also compared at the same well-depth of both cores, yielding information on the heterogeneity parallel to the bedding.

3.6.2.2 Clay rock powder

The clay rock powders are manufactured as stated in Chapter 3.3.1 and analyzed as established in Chapter 3.5. Since the CEC is an important characteristic of clay rocks, a determination procedure is established using the Cu-triene method [174]. The Cu-triene solution is prepared by adding 1.46 g (0.01 mol) triethylenetetramine (*Merck KGaA*) to 100 mL of MilliQ-water, then adding 1.6 g (0.01 mol) of dry copper(II) sulfate (*Merck KGaA*) and filling up to one liter of solution with MilliQ-water. This solution is then left untouched for equilibration for one week prior to being used. 100 mg of each clay rock powder sample are put into a 15 mL centrifuge tube (*Sarstedt*, PP) with 10 mL of MilliQ-water and 5 mL of the copper-triene solution and then shaken for two days. Afterwards the samples are centrifuged (*Megafuge 2.R* from *Thermo Scientific*) at 4000 rpm for 30 min and the supernatant is transferred into cuvettes for VIS-Spectroscopy (*Cary 50* from *Varian*). The extinction at a wavelength of 580 nm is measured and compared to a dilution series, which has also been prepared in ratios of 2:1–1:5 with the copper-triene solution and MilliQ-water, respectively. From the change of extinction, caused by the exchange of Cu^{2+} -ions into the clay interlayers, the CEC is determined for each clay sample. The water content of the clay, measured as described in Chapter 3.5.4 from the TGA, is also taken into account. The CEC determination of the small-volume samples has been part of the master thesis of N. Gill [159].

3. Materials and Methods

3.6.2.3 Intact clay rock surface

The intact rock surface samples are prepared as described in Chapter 3.3.1. After polishing, an image of the surface is taken with a VHX-1000 video-microscope from *Keyence*, prior to the surface investigations described in Chapter 3.5. Images are recorded for comparison to the spatial resolved analytical results.

3.6.3 Batch Sorption

Before executing the batch sorption experiments, a pre-equilibration experiment is conducted to investigate the behavior of the clay rock powder in contact with the synthetic pore water. This has been done to justify the usage of the respective synthetic pore water as a substitute for natural pore water and to determine an adequate equilibration time. 500 mg clay rock powder are put in contact with 50 mL of the respective synthetic pore water in a 50 mL tube (PP, *Sarstedt*), leading to the same solid-to-liquid ratio as in the upcoming batch sorption experiments. This is done for the samples BU1 to validate the synthetic pore water for BMB-A7 and for the samples D1 and D2 6.0 m, 10.0 m and 13.0 m to validate the synthetic pore water for the BDR cores. Since the mineralogy of the smaller volume samples has been determined first, the necessity for additional testing of the synthetic pore water compatibility could be deemed unnecessary (see Chapter 4.2). The suspensions are shaken for up to 30 days and sampled in distinct time intervals. The sampling procedure consists of: Taking 5 mL of the shaken suspension, centrifugation at 4000 rpm for 30 min, and subsequent analysis via ICP-OES, IC and TIC/TOC to determine the aqueous ion composition.

After the determination of the optimal equilibration time, batch sorption experiments are conducted. Six samples of 50 mg of each clay rock powder are contacted with 4.95 mL of the respective synthetic pore water in a 15 mL vial (PP, *Sarstedt*) and shaken for 7 days (for clarification on why this time is chosen, see Chapter 4.3). 50 μ L of the CoCs solution (see Chapter 3.1) is added to half of these samples and 50 μ L of the Eu solution (see Chapter 3.1) to the other half, reaching the target solid-to-liquid ratio of 10 g/L. Due to the fact, that cesium and cobalt do not compete for the sorption sites [41], this has been done to reduce the amount of samples and the analytical effort. The samples contain roughly 1 kBq/mL of Co-60 and Cs-137 or 2 kBq/mL of Eu-152, while also maintaining a concentration of $\approx 2 \cdot 10^{-7}$ mol/L of the respective element. pH is measured and readjusted throughout the sorption experiment, if deemed necessary. Procedure blank samples are prepared to which no radioactive tracers are

added and also further clay blank samples, containing no clay powder and only radioactive tracers. For the samples of core BMB-A7, the selected sorption time is seven days, while for the samples of the BDR cores, a slightly different approach has been chosen. To ensure equilibrium sorption, two of the three sorption samples of each clay rock powder are processed after seven days, whilst the third sample is processed after either shorter or longer times (three or ten days). This is done to ensure full sorption and to gather insight on the sorption kinetics. The sampling procedure is centrifugation at 4000 rpm for 30 min, discarding the sediment and decanting the supernatant into a new vial. This procedure should ensure separation of colloidal species down to a particle size of ≈ 50 nm according to the centrifuge geometry. This solution is then acidified with 50 μ L of 1 M HNO_3 to prevent wall sorption. Analysis of the Eu-152 containing samples is done by measuring 1 mL of this solution via γ -counting. The other samples are measured via γ -spectroscopy after diluting 2 mL of the solution with 8 mL of milli-Q water in a 10 mL HDPE vial as required for the standard geometry of the detector. After the experiment, some of the sample vials used during the batch sorption are rinsed with milli-Q water to flush out the contaminated OPA. Then, 5 mL 1.0 M nitric acid is added to desorb possibly adhered radionuclides on the wall of the vial. The resulting solution is then measured in the same way as the experimental samples. All of these wall sorption tests conclude the contribution of wall sorption to be below the detection limit and can therefore be deemed negligible. Similar procedures and findings on the acidic leaching for wall sorption are also reported in literature [175, 176].

To estimate the measurement uncertainties of methods introduced prior to this chapter, a standard deviation of multiple measurements is sufficient. The basic assumption is a student-t-distribution [177] of the deviation with a normal distribution of the values. For the investigated R_d -values, such a simplification is not sufficient, since a lot of parameters influence the calculation. Therefore, a Gaussian error propagation is performed to assess the biggest possible error [178]. Equation 12 shows how errors of the R_d -values are estimated. The respective symbols are used as explained in Chapter 2.2.

$$\Delta R_d = \sqrt{\left(\frac{\partial R_d}{\partial q_{eq}} \cdot \Delta q_{eq}\right)^2 + \left(\frac{\partial R_d}{\partial c_{eq}} \cdot \Delta c_{eq}\right)^2 + \left(\frac{\partial R_d}{\partial V} \cdot \Delta V\right)^2 + \left(\frac{\partial R_d}{\partial m} \cdot \Delta m\right)^2} \quad \text{Equation 12}$$

The conduction of the batch sorption experiments of the 1 cm^3 and single-phase samples has been part of the master thesis of N. Gill [159], while the 27 cm^3 sample and the 8 cm^3 samples have been investigated as part of this thesis.

3. Materials and Methods

3.6.4 Photoluminescence Spectroscopy

Elements can interact with incoming electromagnetic radiation in different ways. One possibility is the absorption of energy through excitation of electrons to unoccupied higher energy levels. Subsequently, possible relaxation pathways include the energy transfer to other atoms or molecules by collision, the energy transfer to vibrational modes of neighboring molecules or the spontaneous emission of electromagnetic radiation [179]. Processes in which the energy is transferred via photon emission are termed photoluminescence, which is an umbrella term for phosphorescence and fluorescence. These are distinguishable by the multiplicity of the excited energy level from which relaxation occurs. In both cases, the initial excitation occurs into an excited singlet state. From there, a non-radiative relaxation to the ground level of the excited state (S_1 in Figure 25) takes place, often through collisions with solvent molecules, accompanied by heat release. This process is known as internal conversion (IC in Figure 25). The relaxation from this excited state to the ground state (S_0 in Figure 25) via photon emission is called fluorescence.

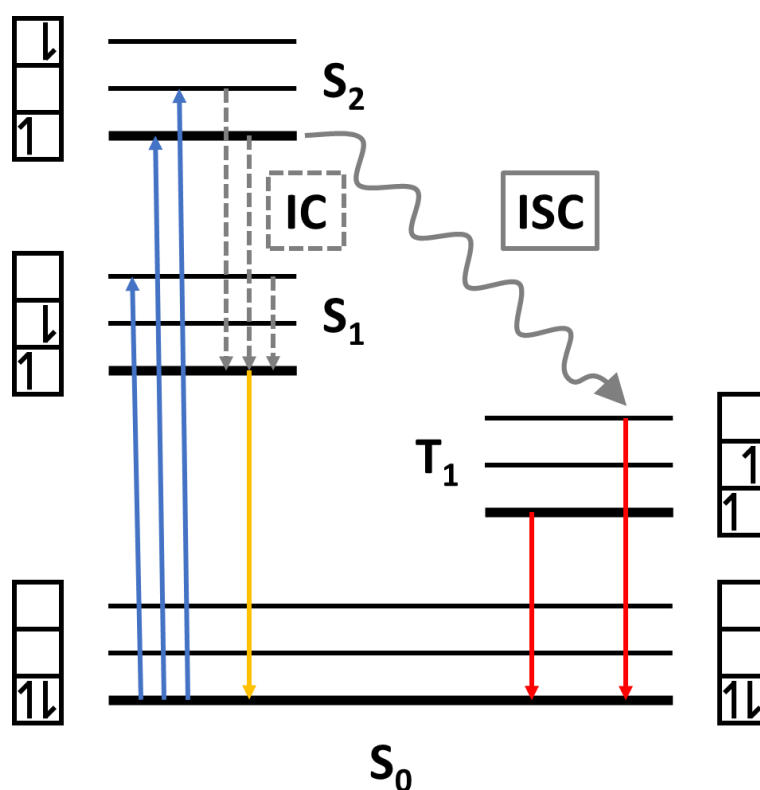


Figure 25: Schematic representation of photoluminescence excitation (blue), fluorescent emission (yellow) and phosphorescent emission (red). Electron orbitals and spins are shown as squares and half-arrows with the positioning reflecting the energy levels schematically.

In phosphorescence, an intersystem crossing (ISC) occurs prior to relaxation. During ISC, the electron transitions from a singlet to a more energetically favorable triplet state T_1 , while changing the spin quantum number and thus, the spin multiplicity from 0 to 1 (see right side of Figure 25). This is formally forbidden, which leads to a significantly lower probability of this relaxation path being taken. After ISC, there is again a possibility of a non-radiative relaxation to the ground level of the T_1 state. The further relaxation to the ground state S_0 is accompanied by photon emission. This transfer is also formally forbidden, since again a change in spin quantum number occurs. Therefore, the depopulation of these triplet states takes longer compared to the fluorescent processes. Described by the ligand field theory, complex formation causes shifts and splits in electron energy level structures to an energetically more favorable situation [180]. The extent of the energy gain depends on the strength of the ligand and complex. Electrons are therefore occupying energetically lower states in complexes, consequently causing a red shift in the wavelength of photons emitted during photoluminescence. Detecting differences in the energy of emitted photons by fluorescence therefore allows drawing conclusions on the bonding situation and chemical environment of the central cation.

As mentioned above, the energy from deexcitation can also be transferred to vibrational states of solvent- or complexing molecules, which is usually a faster process than the fluorescence or phosphorescence pathway of energy transfer. Therefore, differences in the duration of the photoluminescence emissions can be observed [181], depending on the chemical environment of the central cation. The lifetime τ of such a process characterizes the average time-period an electron may remain in its excited state. By measuring the emission intensity at different delay times, an exponential decay can be observed. By fitting the emission-delay profile with Equation 13, the lifetime of a photoluminescence process can be determined.

$$F(t) = A_0 \cdot e^{-\frac{t}{\tau}} \quad \text{Equation 13}$$

$F(t)$ is the function of the emission, A_0 the emission at zero delay, t the delay time and τ the lifetime of the process. By combining the information obtained through measuring the energy shift of the photons emitted during photoluminescence processes and their average lifetime, conclusions can be drawn on the speciation of a complex and its chemical environment [181].

In this study, curium will be used as the central ion for the photoluminescence investigation via TRIFS. It exhibits three prominent absorption bands at 375.5 nm, 381.3 nm, and 396.6 nm. The absorption at 396.6 nm is most intense, exciting into the F state (see Figure 26) [182]. Following nonradiative relaxation, the ground level of the excited state (A state), called ${}^6D'_{7/2}$

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state in case of a coordinated ion, is populated. This state is split fourfold, with mostly the energetically lowest A_1 level being occupied. Figure 26 presents a Jablonski diagram illustrating the ligand field splitting of the ground state Z and A state.

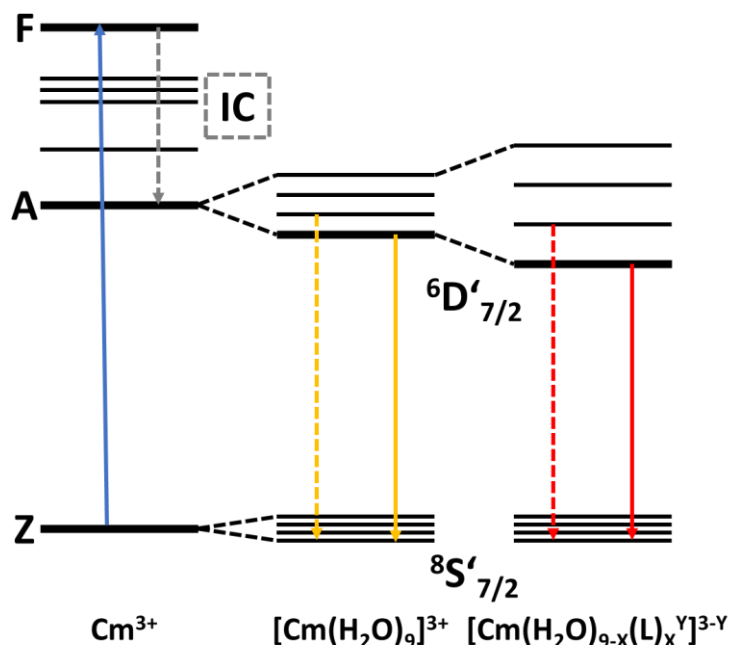


Figure 26: Energy level diagram of trivalent curium, adapted from Beitz et al. (1991) [51]. Excitation in blue, photoluminescence emission of aquatic Cm^{3+} in yellow and of stronger complexed Cm^{3+} in red.

The $^8S'_{7/2}$ ground state (Z state) is likewise split into four levels. Coupling with vibronic transitions of ligand molecules causes the splitting to only show marginal energy differences, leading to these levels being degenerated at room temperature in aqueous solutions [183, 184]. As the emission during relaxation occurs almost exclusively from A_1 to Z state, only one band is observed in the purely aqueous spectrum under acidic conditions, which has its maximum at 593.8 nm (Figure 27). The curium aquo ion is coordinated by eight to nine H_2O molecules in the inner shell [185, 186].

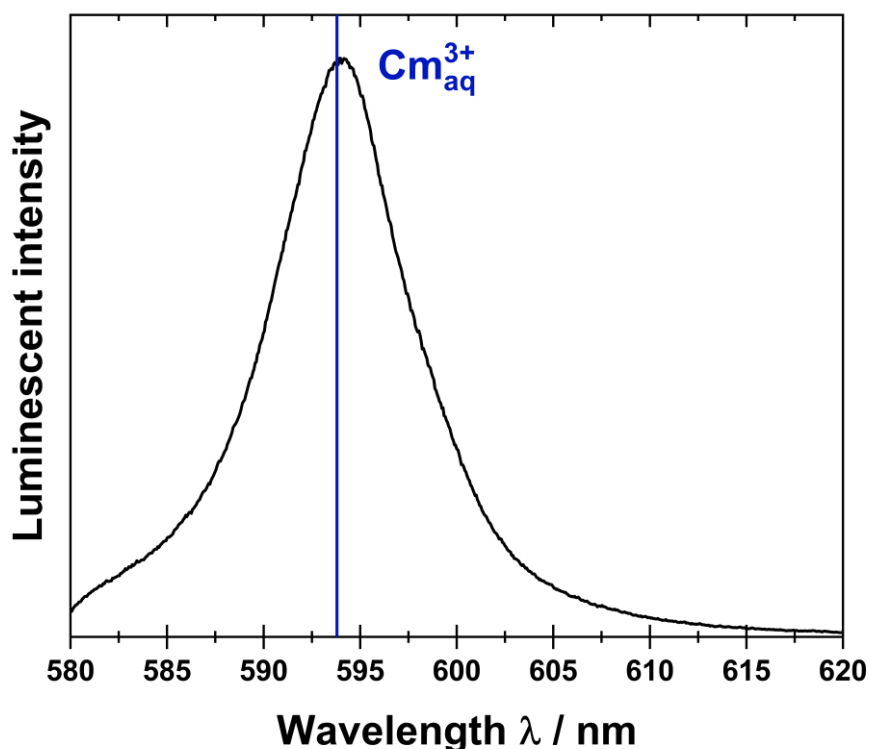


Figure 27: Exemplary TRLFS emission spectrum of trivalent curium at pH 3 in 0.1 M HClO₄.

As explained above, replacing weakly complexing H₂O ligands with stronger complexing agents induces a bathochromic-, or red-shift in the emission band of the Cm³⁺ ion in the spectrum, by moving the A₁ level into an energetically lower state. The stronger the complex partner, the more the energy levels are split. This can also cause the A₂ level (and sometimes even the A₃ level) to be energetically sufficiently more favorably placed to be partly occupied [187]. Since the energy difference from the A₂ to Z transition is still higher than the A₁ to Z transition, emissions at lower wavelengths are observed, hence a very slight shoulder in the emission spectrum of the aquo ion (Figure 27) can be adumbrated. This occurrence happens more frequently at elevated temperatures and is therefore termed “hot band” [186].

Each different chemical environment of Cm³⁺ causes a separate emission spectrum. Coexisting Cm³⁺ complexes therefore complicate an exact evaluation of the spectrum. In case some of the present Cm³⁺ species are known and their separate spectra have been recorded, a peak deconvolution can be performed. Hereby, the single spectra are subtracted from the superposition, in an intensity according to their assumed (or adjusted) abundance and the remaining spectrum is evaluated. With this technique, even in strongly convoluted spectra all present species may be identified.

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With only a single species being present, a monoexponential decay in photoluminescence emission intensity can be observed with increasing delay times. In reality, a consequence of nonradiative relaxation pathways involving ligands causes a significant reduction of the lifetime (quenching). Generally, the lifetime of Cm^{3+} photoluminescence emission is in the millisecond range, but quenching ligands can cause this to be reduced to the 50–100 μs range. The most common quenching ligands are the water molecules coordinating aqueous Cm^{3+} . Vibrational relaxation through collision with water molecules causes the lifetime to be reduced to $68 \pm 2 \mu\text{s}$ [188, 189]. This effect can be seen when Cm^{3+} is investigated in D_2O , the heavier analogue of water. This coordination causes the lifetime of Cm^{3+} to extend to up to 1200 μs , since no water quenching is possible [189].

When multiple species coexist with different lifetimes, the spectrum shifts from one dominating peak to another when the delay time is varied. An example of such a shift is shown in Figure 28, where a waterfall spectrum of curium in contact with calcite is shown. The shoulder at around 593.8 nm seen at low delay times vanishes completely after 600 μs delay, while the peak at 606.2 nm remains and the hint of a shoulder at 615.0 nm emerges.

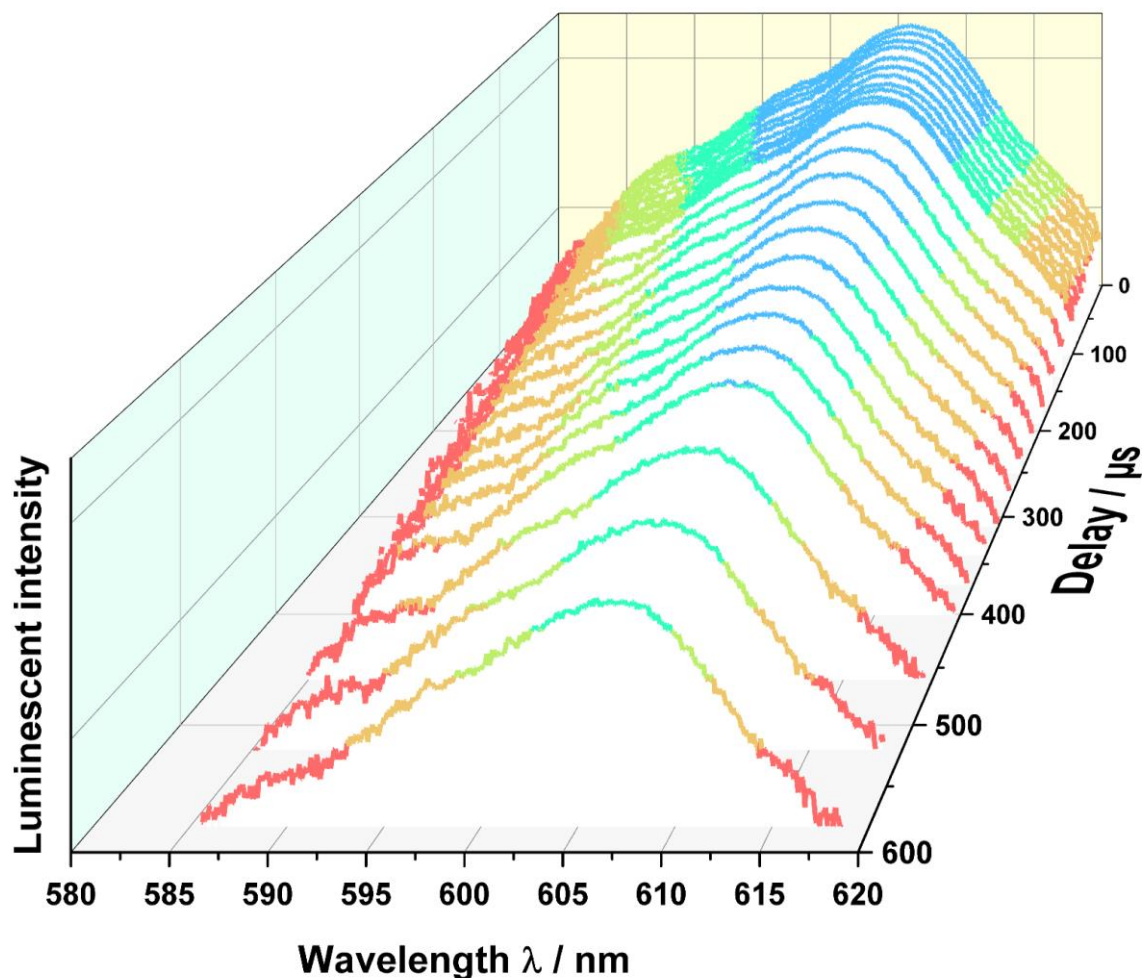


Figure 28: Waterfall emission spectrum with increasing delay time of the recording of trivalent curium [$1 \cdot 10^{-7}$ mol/L] in contact with 0.25 g/L calcite in a synthetic pore water [63] (pH 7.2, $I = 0.2$ mol/L and $[\text{CO}_3^{2-}] = 2.7 \cdot 10^{-3}$ mol/L).

It has to be noted that other effects also alter the lifetime of the emission, besides the removal of water from the inner coordination sphere. If multiple similar coordination environments are present, a fast ligand exchange may occur, causing only the average lifetime to be observable [190]. Knowledge on the composition of a sample is therefore crucial for a correct interpretation. The presence of iron is also known to cause problems when measuring Cm^{3+} due to its quenching behavior [48, 191]. The quenching effect of iron is caused by a nonradiative energy transfer process involving dipole interactions between the excited Cm^{3+} and Fe^{3+} .

Iron ions in solution cause a reduction of the lifetime proportional to the present concentration. The emission is not completely extinguished, because of the distance between iron and curium ions. This process is called dynamic quenching. In contrast, static quenching is caused by more direct contact with the iron ions, for example through sorption processes. In this case, the photoluminescence emission may be completely extinguished.

3. Materials and Methods

In absence of those effects, the number of coordinated H₂O molecules and the lifetime of the Cm³⁺ photoluminescence emission show a linear relationship [192]. Kimura et al. (2001) [193] empirically established it to be:

$$n(H_2O) = 0.65 \cdot k_{obs} - 0.88 \pm 0.5 \quad \text{Equation 14}$$

This equation allows to calculate the number of water molecules in the innermost coordination shell ($n(H_2O)$) based on the decay rate (k_{obs} in ms⁻¹), which is the inverse of the lifetime. This correlation has been adjusted by Stumpf et al. (*pers. comm.*) based on Fernandes et al. (2008) [47]:

$$n(H_2O) = 0.642 \cdot k_{obs} - 0.45 \pm 0.5 \quad \text{Equation 15}$$

This equation is used in this study to estimate the number of water molecules in the inner coordination sphere of Cm³⁺. Besides the investigation of aquatic Cm³⁺ with complexing ligands, TRLFS may also be used to identify sorption species on mineral surfaces and gain insight on sorption mechanisms [49, 194], or even on the incorporation into the mineral structure [195, 196].

In this work, TRLFS is used to verify the assumptions of the geochemical modeling regarding speciation, to identify the mineral phases responsible of the sorption behavior, and to gather insight into the sorption mechanism of trivalent lanthanides and actinides on OPA in carbonate containing synthetic pore waters. Therefore, 2 mL-samples are prepared containing 0.25 g/L of sample material in synthetic pore water, spiked with 10 µL of the Cm³⁺ solution (see Chapter 3.1). This solid-to-liquid ratio has been chosen to have sufficient material for sorption reactions while minimizing the loss of fluorescent light to absorption and scattering on particles. The samples are prepared in glass cuvettes and their pH is adjusted, if necessary, 24 h prior to measurement to reach a steady state. Since the solids tend to sediment during the spectroscopic investigations, the cuvette is stirred to keep the particles in suspensions. The chosen materials are BU1, quartz, orthoclase, calcite, illite, kaolinite and muscovite (see Chapter 3.2). These materials are ground and sieved to a grain size <100 µm prior to the experiment. For calcite, spectroscopy is also performed with unground material, to check whether grinding would affect the reactivity. Additionally, a sample is prepared using the minerals mentioned above in a composition that would resemble the BU1 sample, to compare the sorption behavior of natural OPA with this mixture, termed “synthetic OPA”. These samples are measured once after one day of sorption time and again after 30 days, to check for processes with slow kinetics.

In this work, a Nd:YAG pumped (Continuum Surelite II from *Photonic Solutions* at 10 Hz) dye-laser-system (Exalite 398 Narrow-Scan from *Radiant Dyes Laser*) with an average energy of 45 mW is used. Through frequency tripling, the initial wavelength of 1064 nm of the laser beam is reduced to 355 nm, which allows the dye-laser-system to further vary the emission wavelength to 396.6 nm, specific for the f-f excitation of Cm^{3+} . The detection is done with a Shamrock 303i spectrograph using a 1200 lines/mm grating and an iStar DH720-18F-63 ICCD camera, both from *Andor*, catching the fluorescence emission at an angle of 90° to the laser and magnifying the signal by a factor of 50. The spectra are background corrected and recorded with a central wavelength of 600 nm. The calibration is performed with the luminescence spectrum of a neon-light source at reduced slit width and amplification and verified with a pure $\text{Cm}^{3+}_{\text{aq}}$ solution ($1.0 \cdot 10^{-7}$ M, pH 3). For the single spectra, 1000 accumulations (sum of spectra) with a delay of 1 μs and an exposure time of 1 ms are recorded. For the lifetime investigations, 200 spectra with an exposure time of 2.5 ms are recorded with an increasing delay up to 1 ms. A schematic drawing of the setup is shown in Figure 29, showing most of the equipment mentioned above. The recording and editing of the spectra is done with the system specific software Solis 4.15 from *Andor*. The obtained photoluminescence spectra are then compared to one another and to literature data for the main peak positions and if possible, for their respective fluorescence lifetimes. Additionally, peak deconvolutions are performed to identify the main species in the samples.

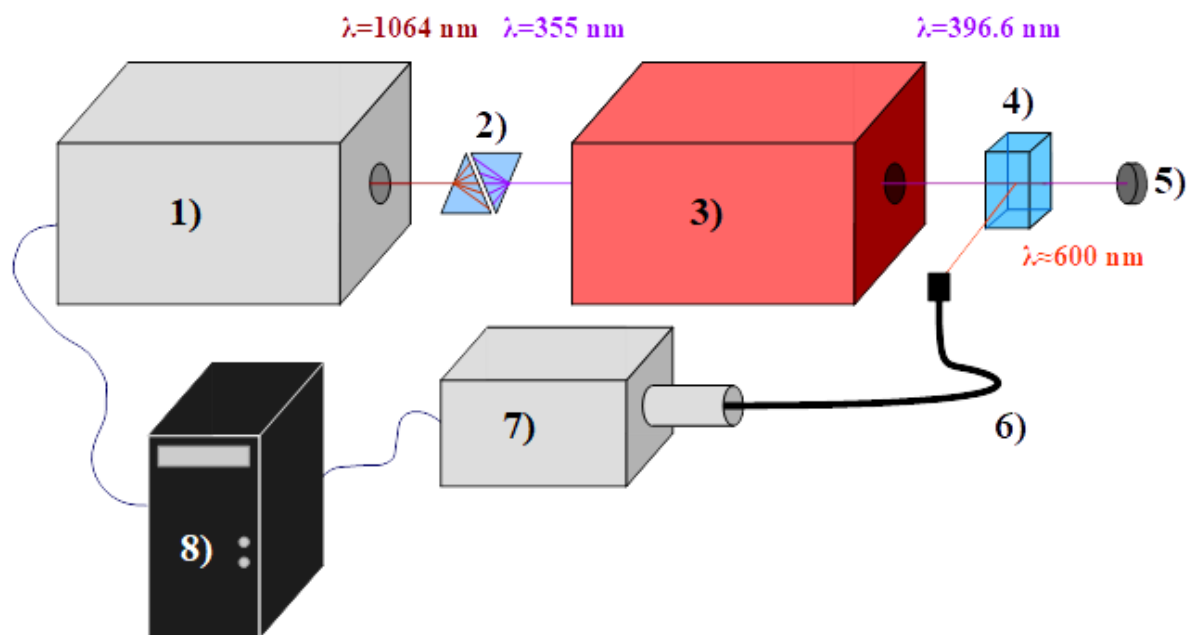


Figure 29: Schematic drawing of the TRLFS setup. 1) Pump laser system 2) frequency tripling device 3) dye-laser-system 4) cuvette with sample 5) beam dump with energy detector 6) fiber optics 7) detection system (spectrometer and camera) 8) computer-aided evaluation.

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3.6.5 Rock Surface Sorption

The in epoxy resin embedded intact clay rock samples are put clay-side down onto a PP net in a PP wide neck bottle, as depicted in Figure 30. With this setup, the clay surface is held in solution while not being in contact with the support, prohibiting its interference with the sorption process.

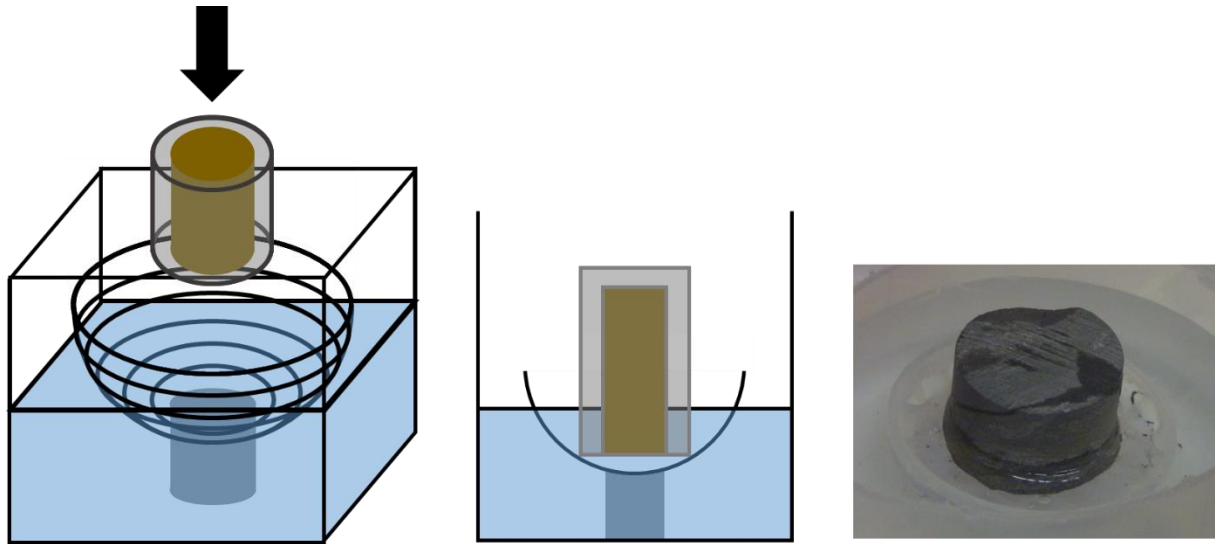


Figure 30: Illustration of the rock surface sorption experiment, schematic drawing on the left, side view in the middle and a picture of the real setup on the right.

The bottle is carefully filled with the solution containing the corresponding synthetic pore water spiked with 10 kBq of Cs-137, Co-60 or Eu-152, respectively. The samples are submerged for 10 minutes only. Due to the swelling properties of the clay rock, longer contact times leads to sample destruction by pressure cracking. This has happened multiple times and different sorption times and setups have been tested. A detailed review of the development of the procedure is given in the Appendix F. In short, a compact setup in a small tube has led to problems with the full submergence of the sample due to the formation of an air film. Insufficient exposure time has been wrongfully interpreted as too low spatial resolution and increasing sample size to address this problem, has led to problems with the swelling capacity of clay rocks.

After the sorption period, the samples are taken out of the solution, rinsed with milli-Q water to avoid precipitation effects during the drying and are then airdried. Next, they are put into a double containment, consisting of two layers of plastic foil (LDPE, $\approx 40 \mu\text{m}$ thickness), and put onto an imaging plate for autoradiographic analysis for 14 days. The imaging plate consists of a BaFBr:Eu²⁺ phosphorous screen [197] and is processed with a Cyclone Plus Phosphor Imager from PerkinElmer. This method yields an activity sensitive spatially resolved map of the rock

surface sample. This map is then evaluated with the program code OptiQuant V5.4. The mappings are correlated with the before mentioned microscopic images and spatially resolved analyses.

3.7 Geochemical Modeling

Geochemical modeling is a computational approach to simulate, estimate and predict the behavior of chemical species in aqueous environments. It comprises the basic thermodynamic principles of chemistry to simulate the interaction between minerals, aqueous components and even gases in complex geochemical environments. The model code PhreeqC (short form of **pH redox equilibrium in C**, whereby C stands for the programming language) is one of the most commonly used programs for this purpose. It encompasses the capability to perform calculations based on the thermodynamic equilibrium such as the geochemical processes of mineral dissolution and precipitation, ion exchange, surface sorption, aqueous complexation and even redox reactions. In this study, the version 3.5.0.14000 of PhreeqC Interactive [198] is used, together with the integrated sit.dat database for the basic thermodynamic data. Firstly, precipitation calculations are performed to assess the preconditions of the planned batch sorption experiments. Therefore, a recurring addition of cesium, cobalt and europium into the composition of the synthetic pore water is calculated and checked for possible precipitates. This calculation includes an exchange with a gaseous carbon dioxide phase as well as a fixed pH, mirroring the conditions present in the batch sorption experiments. Simultaneously, the aqueous speciation of the elements is determined. Also, geochemical modeling is used to estimate the complexation and aqueous speciation of curium in the TRLFS experiments.

Most importantly, the sorption behavior of cesium, cobalt and europium is modeled to mimic the batch sorption experiments and estimate the expecting R_d -values. For this predictive modeling, the so-called “bottom-up” approach is chosen [7]. It assumes the uptake of cations by OPA to be predominantly dependent on the illite content, which allows disregarding other present mineral phases. For these calculations, the composition of the synthetic pore water after seven days of equilibration with OPA (see Chapter 4.3), is chosen as the background electrolyte, with fixed pH. It is equilibrated with a carbon dioxide phase mimicking the partial pressure of the argon glovebox in case of the BMB-A7 calculations mimicking ambient conditions in case of the BDR calculations. Also, a dissolvable calcite phase equal to the average calcite content in the respective sandy facies OPA is introduced into the modeling code. This background

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electrolyte solution also contains ions relevant for the competition for sorption sites, like nickel or rubidium, which is relevant to represent the natural sorption behavior [41]. Due to the insufficient dataset on smectite mixed layers, these are disregarded and simply subsumed to the clay fraction and treated as being illite in the model for the sake of simplicity.

Regarding the cesium sorption, a variation of the well-established generalized cesium sorption model (GCs) developed by Bradbury and Baeyens (2000) [8] is set up. This model incorporates three distinct exchange sites for the cesium, which are pH-independent but differ in selectivity and sorption capacity. Their respective capacities are derived as a fraction of the CEC of illite. In their study, the reference illite's CEC amounted to 20 $\text{cmol}_c(+)/\text{kg}$, whereby the planar sites (PLA) make up 79.75 % of the CEC, the type II (TII) sites 20 % and the so-called frayed edge sites (FES) the remaining 0.25 %. The higher selectivity is visible in the exchange reaction of sodium with cesium, where the log k values increase by more than a factor of two when going from PLA to TII and double again when comparing TII to FES (see Table 11).

For the cobalt and europium sorption a similar approach is chosen, namely the 2SPNE SC/CE sorption model (two-site protolysis non-electrostatic surface complexation and cation exchange) to estimate the uptake of the di- and trivalent cations. The basis for this model is found in Bradbury and Baeyens (2009) [9, 10], simplifying the sorption process into the uptake of two sorption and one exchange sites (Ex). The two sorption sites are pH-dependent and labeled by their respective affinity as “strong” ($>S^S$) and “weak”. The impact of the weak sorption sites is negligible under the present low concentrations, so they are cut in the final version of the code. Again, the selectivity and capacity run into opposite directions with the $>S^S$ capacity amounting to 0.2 $\text{cmol}_c(+)/\text{kg}$ illite and Ex to 20 $\text{cmol}_c(+)/\text{kg}$ illite. The equilibrium constants taken from the above-mentioned publications are summarized in Table 11.

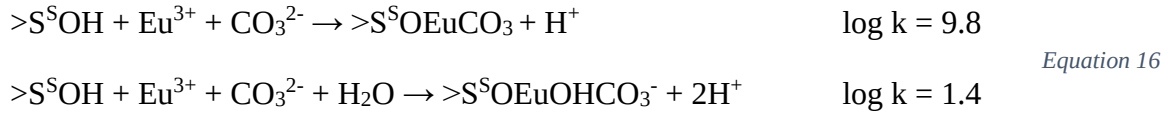
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Table 11: Thermodynamic equilibrium constants implemented for the sorption modeling. *Concentration units chosen to match the setup of the batch sorption experiment.

Cs modeling		log k	Co and Eu modeling		log k
FESNa + Cs ⁺ → FESCs + Na ⁺		7.0	>S ^S OH + H ⁺ → >S ^S OH ₂ ⁺		4.0
FESNa + K ⁺ → FESK + Na ⁺		2.4	>S ^S OH → >S ^S O ⁻ + H ⁺		-6.2
FESNa + Rb ⁺ → FESRb + Na ⁺		4.6			
TIINa + Cs ⁺ → TIICs + Na ⁺		3.6	>S ^S OH + Co ²⁺ → >S ^S OC ⁺ + H ⁺		0.0
TIINa + K ⁺ → TIHK + Na ⁺		2.1	>S ^S OH + Co ²⁺ + H ₂ O →		-7.0
TIINa + Rb ⁺ → TIIRb + Na ⁺		2.6	>S ^S OC ⁺ (OH) + 2H ⁺		
			>S ^S OH + Co ²⁺ + 2H ₂ O →		-16.5
			>S ^S OC ⁺ (OH) ₂ ⁻ + 3H ⁺		
PLANa + Cs ⁺ → PLACs + Na ⁺		1.6			
PLANa + K ⁺ → PLAK + Na ⁺		1.1	>S ^S OH + Eu ³⁺ → >S ^S OEu ²⁺ + H ⁺		1.9
PLANa + Rb ⁺ → PLARb + Na ⁺		1.6	>S ^S OH + Eu ³⁺ + H ₂ O →		-4.7
2PLANa + Ca ²⁺ → PLA ₂ Ca + 2Na ⁺		1.04	>S ^S OEu(OH) ⁺ + 2H ⁺		
2PLANa + Mg ²⁺ → PLA ₂ Mg + Na ⁺		1.04	>S ^S OH + Eu ³⁺ + 2H ₂ O →		-12.7
			>S ^S OEu(OH) ₂ + 3H ⁺		
			>S ^S OH + Eu ³⁺ + 3H ₂ O →		-24.0
			>S ^S OEu(OH) ₃ ⁻ + 4H ⁺		
Site concentration per percentage illite content / (mol/10g)*					
FES	5·10 ⁻⁸		>S ^S OH + Ni ²⁺ → >S ^S ONi ⁺ + H ⁺		0.7
TII	4·10 ⁻⁶		>S ^S OH + Ni ²⁺ + H ₂ O →		-8.2
PLA	1.6·10 ⁻⁵		>S ^S ONi(OH) + 2H ⁺		
>S ^S	2·10 ⁻⁷		>S ^S OH + Ni ²⁺ + 2H ₂ O →		-17.3
Ex	2·10 ⁻⁵		>S ^S ONi(OH) ₂ ⁻ + 3H ⁺		
			2ExNa + Co ²⁺ → Ex ₂ Co + 2Na ⁺		1.3
			3ExNa + Eu ³⁺ → Ex ₃ Eu + 3Na ⁺		1.9
			2ExNa + Ni ²⁺ → Ex ₂ Ni + 2Na ⁺		1.1
			ExNa + K ⁺ → Na ⁺ + KEx		1.1
			2ExNa + Ca ²⁺ → 2Na ⁺ + CaEx ₂		1.04
			2ExNa + Mg ²⁺ → 2Na ⁺ + MgEx ₂		1.04

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In the first iteration of the modeling code, the sorption of europium has been greatly underestimated due to the formation of carbonate complexes in solution, stronger than the sorption species. Since this is contradictory to what is observed in batch sorption experiments, ternary sorption species need to be implemented for europium. Fernandes *et al.* (2008, 2015, 2016) [115, 132, 199] have investigated the europium sorption on illite and montmorillonite in carbonate containing solutions and have found the respective sorption species and constants for illite to be:



In this study, these reactions will be used for the sorption calculation. Sorption is calculated by varying the illite content from 1–30 wt% at a S/L ratio of 10 g/L, like in the batch sorption experiments. The resulting R_d -values are plotted as a band of ± 0.3 log units to roughly estimate the error margins of repeated batch sorption experiments with strongly adsorbing tracers, like stated in Lauber *et al.* (2000) [38] and taken into account by Fernandes *et al.* (2015) [199]. The annotated model code is shown in the Appendix A.

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4.1 Optical Characterization

When obtaining a drill core, the first noticeable thing is its texture on the surface. During the investigation of the polished cores BDR-D1 and -D2, the heterogeneity of the sandy facies is visually striking. Different colored layers and textures, up to multiple centimeters in thickness, are followed by areas which look relatively homogeneous. For a better understanding, a high-resolution photographic stitch of the drill cores is shown in Appendix B. The first noticeable feature is the similarity of both cores' textures at comparable well-depths. When laid next to each other, both cores show the same features and characteristics across the whole twelve-meter length. This includes not only fossil layers or brownish colored concretions, but also extends towards mechanical features like ruptures and cracks. Both cores tend to be weak towards shear forces, to which they have been exposed to during the polishing procedure, at the same positions. A few highlights of these similarities are shown in Figure 31.

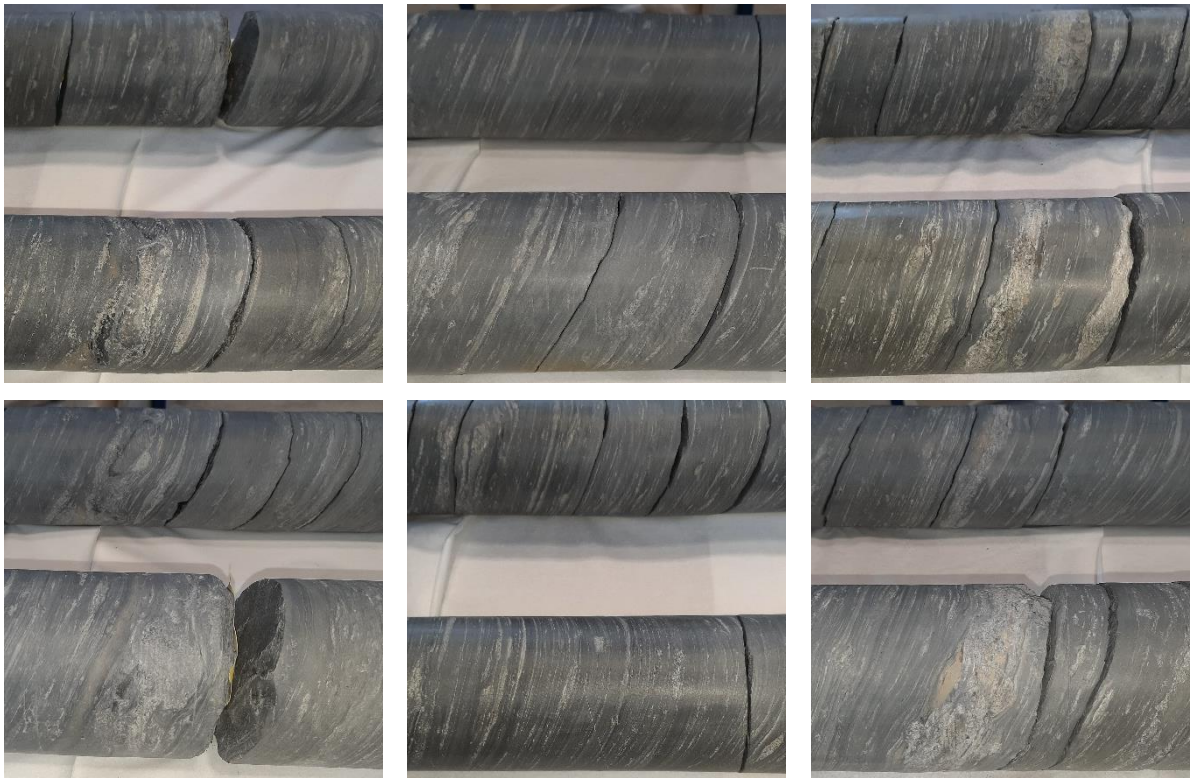


Figure 31: Highlights of the similarities of the cores BDR-D1 and -D2 lying next to one another. Top row showing core BDR-D1 in the front and bottom row BDR-D2 in the front. First column showing a fracture at the same well-depth with some brown layers and signs of bioturbation. Second column showing a large continuous dark area with thin white layers. Third column shows a very prominent layer of fossil shells with brownish concretions.

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To quantify the heterogeneity and the similarities of both cores, an optical logging procedure is performed. This yields a surface abundance of the seven identified categories, shown in Figure 23, against the well-depths of the respective drill core. The results of this analysis are shown in Figure 32, displaying BDR-D1 on the top and -D2 on the bottom, with the total amount of surface coverage of each category summed up to 100 % total. The eye-catching perpendicular heterogeneities from the visual impressions are not reflected well in the logging procedure. Both cores are mostly dominated by the dark-grey clay matrix, which is only superseded by the turbated light-grey sand/carbonate matrix at well-depth 10.0–11.0 m. Across both cores, light-grey sand/carbonate concretions are present, as well as laminated layers of similar color. Brownish concretions are more sparsely scattered but present throughout the whole length. A fossil-rich layer is only found at well-depth ≈ 7.0 –7.3 m. The black dots, categorized as bituminous lenses, feel greasy on touch and can be smeared. They are possibly of organic origin and by far rarest of the categories. Their presence is close to the sensitivity limit of the analysis procedure due to their small surface coverage. Hostettler et al. (2018) [92] have conducted an investigation on the core BDB-1, which is a 250 m long well spanning the whole lithostratigraphy of the Swiss OPA and bounding formations in the Mont Terri URL. In their report, they also show the results of the drilling through the upper sandy facies OPA. Due to the geometry of the drilling procedure, their logging cannot be accurately compared to the logging of this study, but the general observations should be similar. Near the transition from the Passwang Formation to OPA at a depth of 110–135 m of core BDB-1, they have found a composition very similar to what is observed in both BDR cores; a clay-stone matrix including concretionary limestones, sandy argillaceous limestone together with a small fossil-rich layer of coquinas. This suggests the span of these relatively small layers to extent even beyond 100 m. When visiting the drilling location in the URL Mont Terri, some of the brownish features can even be traced to niche 4, the so-called “open twin” to niche 3 in the CD-A experiment [200]. This is a walkable niche, situated south of the retrieval location of core BDR-D2 at a distance of roughly 40 m and can be seen in Figure 14.

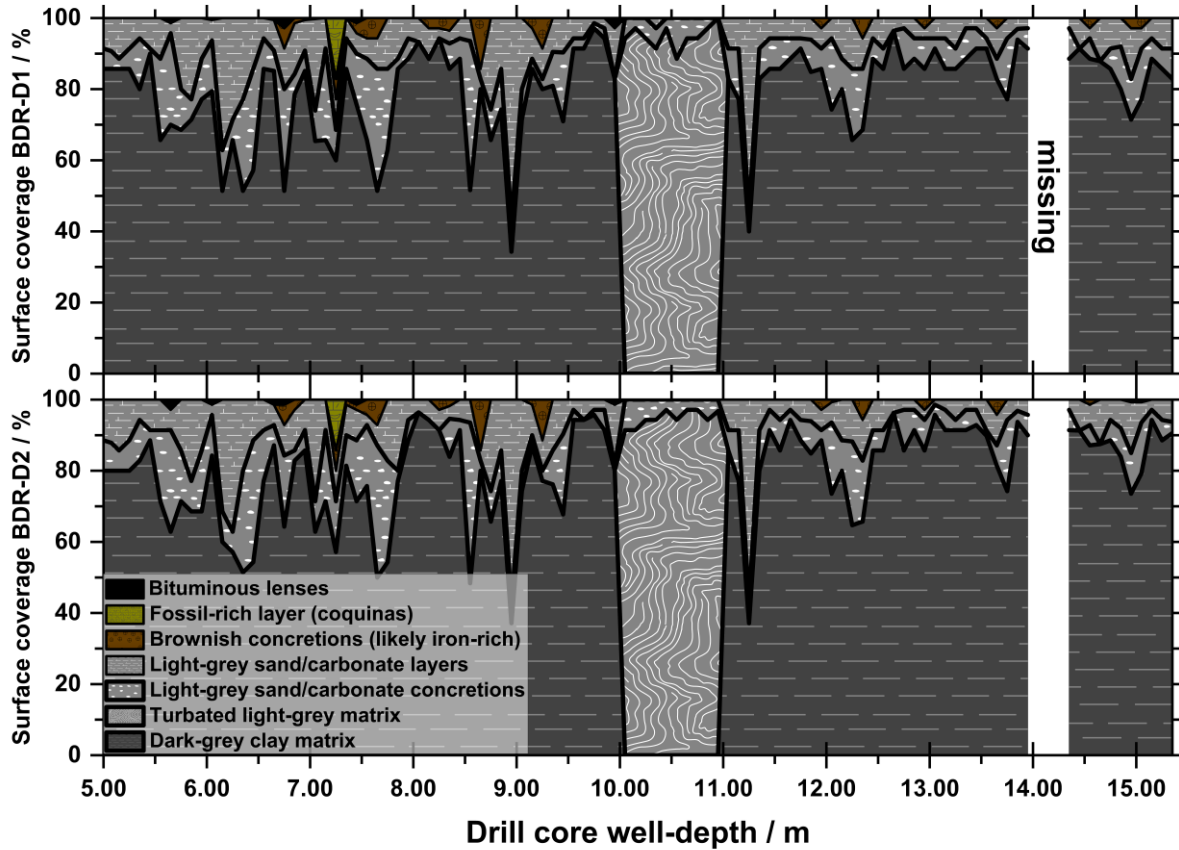


Figure 32: Results of the visual categorization of the drill cores BDR-D1 (top) and -D2 (bottom), with the vertical axis displaying the amount of the respective phase surface coverage in surf% summed up to 100 % in total. The segment from 13.90–14.40 m has been lost during the retrieval process.

In their report, Lauper et al. (2021) [6] have established a uniform characterization model for OPA, subdividing it into the subfacies SF1–5 based on their mineral composition and optical characteristics. Due to the length of the cores in this study, they cannot be assigned to a single subfacies, but segments show distinct characteristics which can be related to this classification. The superficial areas from 5.00–10.00 m and 11.00–15.50 m can be assigned to the SF2, characterized by a fine to medium grained mudstone that is predominantly argillaceous and siliceous. This mudstone displays lenticular bedding, consisting of a dark-gray clay matrix with frequent occurrences of brighter lenses. The brighter lenses are primarily composed of quartz grains and carbonate cements. The biggest visual variation in composition is found in the area from 10.00–11.00 m, which is classified to SF3. The transition here is very abrupt and visually striking. According to Lauper et al. (2021) [6], this subfacies can be considered to be a medium mudstone that exhibits characteristics ranging from siliceous-argillaceous to siliceous-calcareous, and it is marked by a lenticular to wavy bedding, which is previously described as light grey swirly matrix with an abundance of brighter lenses.

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The two most important takeaways from this investigation are firstly, that the proposed visual heterogeneity is fading when examining the cores in 100 cm² segments at a time. This is due to the low and anisotropic surface coverage of some of the phases. Secondly, there is a stunning similarity between the two cores drilled up to 20 m apart from one another. This indicates a robust and precise retrieval operation, but also shows a homogeneous distribution along the bedding of OPA. The deposition and sedimentation processes that have been taking place over extended periods of time have created a large-spanning layered structure. The individual layers extending over hundreds of meters [92, 201, 202] and even kilometers [203], is therefore of no surprise.

The DRD experiment includes logging operations of the bore holes after the retrieval of the cores BDR-D1 and -D2 [95]. This includes an optical scan as well as spectral and neutral γ -logging, quantifying the amount of radioactive potassium (K-40), uranium oxides and thorium oxides via γ -ray detection. Due to the drilling operation, only a heavily damaged surface is visible in the optical scan, with man-made indentations and cracks caused by the retrieval process. Distinct prominent features such as the fossil layer at about 7.0 m well-depth are still visible and the position of some cracks agree with the visual examination of the drill cores. The polishing procedure proves to be necessary to gather reliable information on the surface of the drill cores. The results of the spectral γ -logging could not be correlated to the optical investigation, since they show a steady concentration of radioactive potassium and the results for uranium and thorium from BDR-D1 contradict the logging of -D2 (highs become lows and vice versa). A probable reasoning for this could be the in general low present activity causing only uninterpretable noise to be recorded. The backscattered γ -logging with a Cs-137 source shows an equal distribution across the whole length of both cores. This corresponds to only minor rock density changes across the visually distinct subfacies [95]. Backscattered neutron detection with a Cf-252 source is also performed, which detects the abundance of light weight elements, mainly hydrogen. Increases in intensity can therefore either be interpreted as a higher pore water content or abundance of clay minerals with their outward facing hydroxyl groups. In the range of 10.0–11.50 m, a slight increase can be observed, which is the same region a different subfacies is present [95]. Therefore, in the mineralogical characterization, possible differences may be expected.

To further investigate the optical composition cutout discs are prepared and polished like described in Chapter 3.3.1. The juxtaposition of the discs in similar well-depths is shown in Figure 33. This is also used as a validation of the assignment to the corresponding subfacies based on the visual appearance.

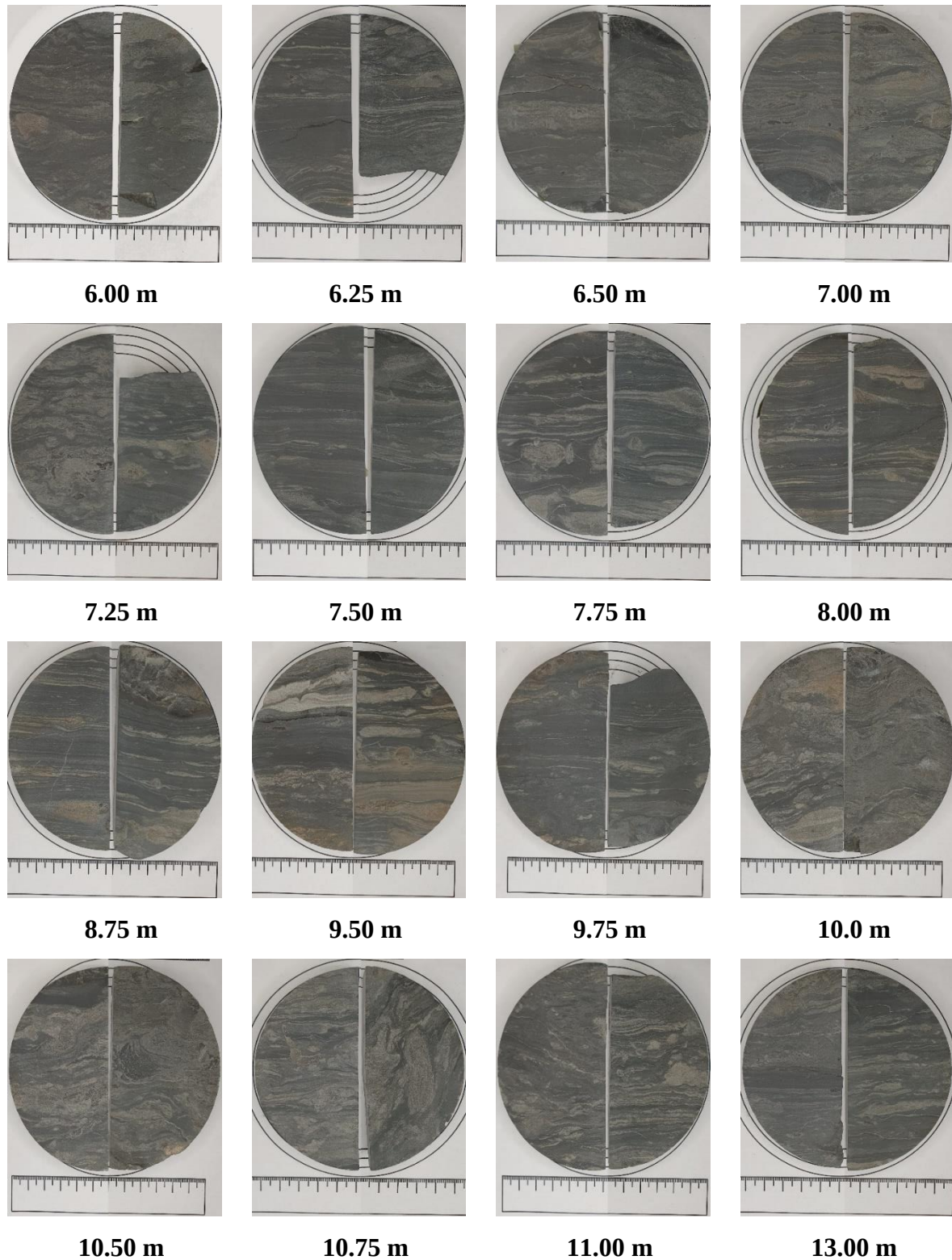


Figure 33: Juxtaposition of the cutout discs of the drill cores BDR-D1 (left) and BDR-D2 (right) at the respective well-depth. A cm-scale is added at the bottom of each picture.

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The appearance of the discs reflects the respective surface composition with the dark-grey clay matrix dominating until a well-depth of 10.0 m, where it is replaced by the turbated light-grey sand/carbonate matrix. The close similarity of the discs cut at the same well-depth from both cores is again visible. This is true for the background matrix as well as the amount and shape of bright and brown layers, especially visible in the bright and brown layers of discs at well-depth 9.50 m and the turbations in the discs from 10.25–11.00 m in Figure 33. The samples at well-depths 7.00 m, 9.75 m and 13.00 m only show a small number of inclusions in a dark grey matrix across both drill cores. This is in accordance with the visual assessment of the drill cores' surface. A very pronounced lateral homogeneity along the bedding stands against a high degree of variation perpendicular to the bedding. During this procedure, the necessity of polishing for an optical investigation showed its importance. Often up to a coarse grit of 200, only light grey areas are visible in a darker matrix. The coloration in brown, shiny dark or even bright-grey only appears in the last steps of the polishing procedure. Unpolished surfaces can therefore likely not be interpreted with sufficient accuracy, based on visual interpretation.

The before established assignment to the subfacies classification holds true and is even more pronounced. The distinct region from 10.00–11.00 m is classified as SF3 and most of the other samples show distinct features indicating them to belong to SF2 according to Lauper et al. (2021) [6].

4.2 Mineralogical Characterization

4.2.1 Characterization of sample BU1 (2000 cm³)

To gather information on the mineral composition, the first approach in this study is to perform XRD analysis. Figure 34 shows the qualitative diffractogram of BU1 with the identified minerals highlighted by the respective reflexes.

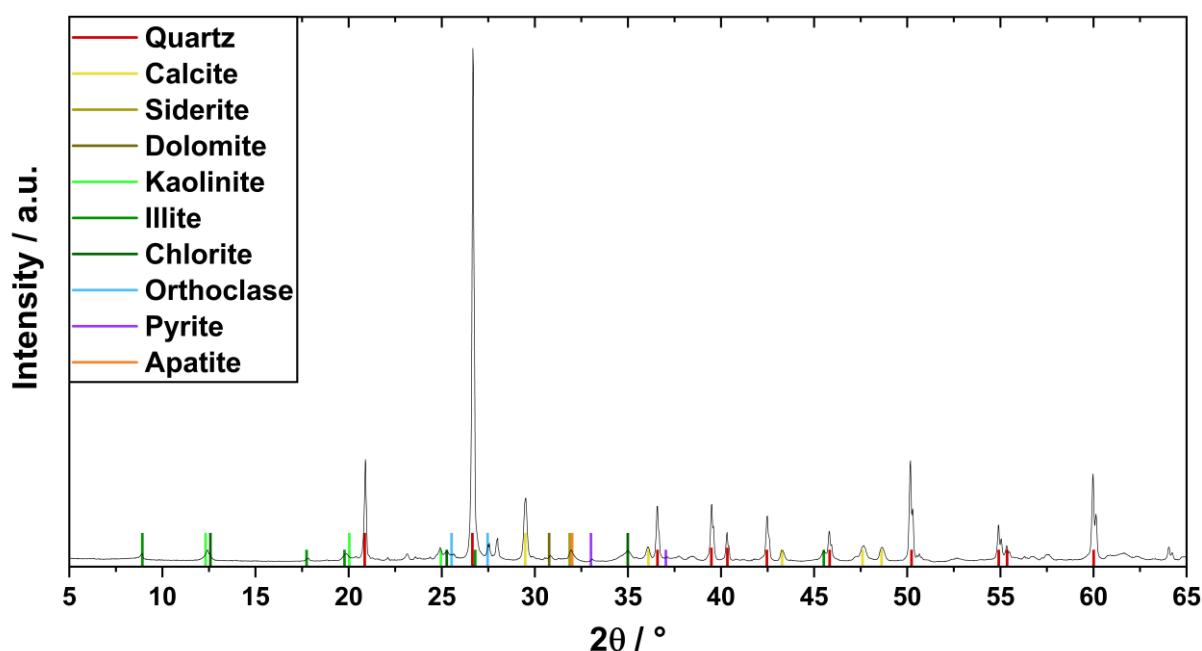


Figure 34: XRD of BU1 with the identified phases highlighted in color, not representative of reflex intensity for clarity reasons.

The diffractogram indicates the presence of the silicate quartz, the carbonates calcite, siderite and dolomite, the feldspar orthoclase, the clay minerals kaolinite, illite and chlorite as well as the sulfide mineral pyrite and the phosphate apatite. This is in agreement with the general common minerals present in OPA [79], besides missing a pure or mixed smectite phase. A possible explanation is the resolution of the obtained diffractogram and the similarity of the reflex positions of smectite and illite. Muscovite is purposefully excluded, since it shares the exact same reflex positions as illite, with the identical space group and unit cell parameters. Albite and other accessory minerals like celestine, rutile or baryte are either absent or not present in measurable amounts. For a quantitative evaluation of the diffractogram, a Rietveld refinement is performed. The composition of BU1 regarding the mineralogy is shown in Table 12, alongside selected literature examples for comparison [86, 90].

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Table 12: Mineral composition of BU1 in comparison to previously examined OPA samples. Uncertainties given as the standard deviation of the three refinements.

Mineral / wt%	BU1 [this study]	Pearson et al. (2003) [86]	Peters et al. (2010) [90]	Jalali et al. (2023) [pers. comm.]
Quartz	47.8 ± 3.0	27.0 ± 1.0	34.7 ± 10.1	25.5–46.1
Calcite	11.1 ± 1.1	14.0 ± 3.0	25.0 ± 18.6	7.3–44.6
Siderite	1.4 ± 0.3	2.5 ± 0.5	0.8 ± 0.9	0.9–1.7
Dolomite	0.9 ± 0.1	2.0 ± 0.0	3.2 ± 4.1	0.4–9.0
Orthoclase	9.7 ± 2.0	4.5 ± 0.5	-	3.3–6.6
Kaolinite	12.3 ± 2.3	13.0 ± 0.0	9.8 ± 5.1	4.0–13.6
Illite (mixed)	10.5 ± 0.8	19.0 ± 2.0 8.0 ± 0.0	8.2 ± 6.2 6.4 ± 4.8	6.0–17.9 2.4–6.4
Chlorite	6.3 ± 0.3	6.5 ± 0.5	2.3 ± 1.5	1.1–3.3
Pyrite	0.1 ± 0.1	3.2 ± 0.0	-	0.5–1.4
Apatite	0.2 ± 0.1	-	-	-

This quantification shows the most dominant mineral phase to be quartz, which the same for Peters et al. (2010) [90] and Pearson et al. (2003) [86], who have investigated multiple samples of sandy facies OPA. The uncertainties for their respective data is given as the standard deviation of their separate measurements and results. A comparison to the data of Jalali et al. (2023), who investigate the link between mineralogy and geomechanical properties of the sandy facies can be drawn, since they investigated a drill core originating very closely to core BMB-A7. In total they analyzed 111 samples on their compressive strength but also their mineralogy, similarly identifying quartz as the most abundant mineral. Nevertheless, the quartz content observed in this study seems to be significantly higher than what is reported in previous studies. The main difference to the literature data however, is the absence of a mixed illite/smectite mineral phase, though no specific sample preparations for swellable clay quantification have been performed. Striking is also the absence of feldspar minerals in the composition found by Peters et al. (2010) [90], as well as the absence of pyrite and apatite, of which all but apatite have been identified by Pearson et al. (2003) [86]. The generally low abundance of these two minerals, making it difficult for them to be detected via XRD, is a sufficient explanation for the absence. The overall clay mineral content of BU1 sums up to $\approx 29.1 \pm 2.2$ wt%, which is in the range of what is reported by Peters et al. (2010) [90] and Jalali et al. (2023), but lower than what Pearson et al. (2003) [86] found with 46.5 ± 2.5 wt%. This can be explained by the different origin of these samples, being retrieved from different parts of the sandy facies and the fact that the higher quartz content needs to be compensated for.

The lower sandy facies, also called lower silty sub-unit according to Mazurek et al. (2020) [203], is generally categorized to be mainly consisting of the subfacies SF3 and SF4, rarely SF2 according to the nomenclature proposed by Lauper et al. (2021) [6]. This classification is consistent with the visual examination of core BMB-A7, as it exhibits characteristics indicative of its affiliation with SF3. In the work of Lauper et al. (2021) [6], the neighboring drill core BMB-A6 is investigated and also assigned to SF3. Mineralogically, they have found the composition of the lower sandy facies to be very similar to what is observed in this study, with a quartz content of around ≈ 50 wt%, a carbonate content of ≈ 10 wt% and a comparatively high clay mineral content of around ≈ 40 wt%. The visual assignment to SF3 is therefore validated by the mineralogical composition.

XRF is performed on homogenized smelted powder pellets, to investigate the elemental composition of BU1. The results of this investigation together with selected literature data for comparison are shown in Table 13 [86, 94]. The proposed uncertainties of this study stem from the standard deviation of five separate measurements.

Table 13: Elemental composition of BU1 as oxides from the XRF measurement in comparison to literature data of sandy facies OPA samples. Uncertainty given as the standard deviation of five measurements.

Oxide / wt%	BU1 [this study]	Pearson et al. (2003) [86]	Kaufhold et al. (2013) [94]
SiO₂	65.21 $\pm$ 1.31	53.30 $\pm$ 2.62	55.10 $\pm$ 5.77
Al₂O₃	9.58 $\pm$ 0.21	14.70 $\pm$ 0.33	8.71 $\pm$ 1.89
CaO	6.87 $\pm$ 0.14	8.43 $\pm$ 1.19	11.70 $\pm$ 4.57
Fe₂O₃	4.38 $\pm$ 0.11	5.19 $\pm$ 0.06	4.24 $\pm$ 0.51
K₂O	1.89 $\pm$ 0.04	2.64 $\pm$ 0.17	1.54 $\pm$ 0.31
MgO	1.25 $\pm$ 0.02	1.66 $\pm$ 0.18	2.11 $\pm$ 0.49
TiO₂	0.64 $\pm$ 0.02	0.95 $\pm$ 0.06	0.62 $\pm$ 0.10
Na₂O	0.41 $\pm$ 0.01	0.71 $\pm$ 0.04	0.38 $\pm$ 0.06
P₂O₅	0.31 $\pm$ 0.01	0.26 $\pm$ 0.01	0.36 $\pm$ 0.05
MnO	0.03 $\pm$ 0.01	0.06 $\pm$ 0.01	0.09 $\pm$ 0.04
LOI	8.89 $\pm$ 0.18	12.91 $\pm$ 0.26	14.20 $\pm$ 3.29

The most abundant elemental oxide in BU1 is silica, which is in accordance to the XRD data showing high amounts of quartz, clay minerals and feldspars [204, 205]. Silica is also the main elemental oxide found in the studies of Pearson et al. (2003) [86] and Kaufhold et al. (2013) [94]. However, the silica content found in this study is higher compared to literature data, which may be caused by the higher quartz content present. Aluminum oxide and calcium oxide being the second and third most common element oxide found via XRF is also in accordance with

4. Results and Discussion

literature data, as well as the contents of the sparse element oxides. The potassium content is of great importance, since in the upcoming batch sorption experiments with cesium, it will be the main competitor for the cation exchange sorption processes [206]. Notably, LOI values are substantially lower compared to previous literature reports. This difference might be explained by a lower water content in comparison, caused by drying of the samples during the transport and storage. The lower clay mineral content present in comparison also leads to less pore water being containable in the clay rock. This can both be validated in the upcoming thermal analysis.

Using the mineral composition derived from the Rietveld refinement and the estimated elemental compositions specific to each mineral phase, an elemental distribution is calculated that closely resembles XRF results. A comparison of these two datasets is presented in Table 14. This approach confirms the XRF data nicely and gives confidence into the robustness of the Rietveld refinement method. The only major differences are a higher calculated aluminum content and a lower iron content, likely related to uncertainties with respect to the clay mineral composition assumed in the calculation procedure. This is especially true for chlorites, for which a more general composition can be denoted as $(\text{Fe,Mg,Al,Zn})_6(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8$ [65].

Table 14: Comparison of the measured XRF data with the calculated elemental oxide composition of the XRD refinement.

Mineral	Elemental composition	Oxide	XRF / wt%	XRD / wt% (calculated)
Quartz	SiO_2	SiO_2	65.2 ± 1.3	65.6 ± 4.1
Calcite	CaCO_3	Al_2O_3	9.58 ± 0.2	11.6 ± 0.73
Siderite	FeCO_3	CaO	6.87 ± 0.14	6.41 ± 0.64
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	Fe_2O_3	4.38 ± 0.1	1.86 ± 0.46
Orthoclase	KAlSi_3O_8	K_2O	1.89 ± 0.04	2.84 ± 0.43
Kaolinite	$\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$	MgO	1.25 ± 0.02	1.90 ± 0.28
Illite	$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$			
Chlorite - Clinocllore	$\text{FeMg}_4\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$			
Pyrite	FeS_2			

To gather more information on the less common elements present in the sandy facies OPA, supplementary to the XRF, ICP-MS after digestion is performed. The digestion procedure is described in Chapter 3.5 and the results are shown in Table 15, together with selected literature data for comparison.

Table 15: Trace elemental composition of BU1 according to XRF and ICP-MS investigation in comparison to literature data of shaly facies OPA. This studies' uncertainties given as the standard deviation from three measurements.

Element / ppm	XRF	Pearson et al. (2003) [86] (shaly facies)
Sr	325 ± 6.5	233 ± 66.6
Ba	305 ± 6.1	233 ± 66.6
Zr	288 ± 5.8	0–44
Zn	69 ± 1.4	72.3 ± 20.3
Rb	68 ± 1.4 80 ± 4 (ICP-MS)	-
Ni	24 ± 0.48	42.3 ± 10.2

	ICP-MS	Lauber et al. (2000) [38] (shaly facies)
Cs	5.6 ± 0.03	5.8 ± 1.2
Co	1.6 ± 0.01	-
Eu	2.2 ± 0.01	1.7 ± 0.3
U	3.0 ± 0.02	-

The elements chosen to be investigated are of interest due to either their presence in accessory minerals (strontium in celestine, barium in baryte and zirconium in zircon) or to their importance in the upcoming batch sorption experiments. Of the investigated elements displayed in Table 15, rubidium acts as competitor for the sorption of cesium, zinc and nickel as competitors for the cobalt sorption [7, 206]. The natural cation inventory of the elements investigated in the batch sorption experiments is also of interest, since it needs to be taken into account in the evaluation. The overall obtained data matches well with literature reports, except the zirconium content, which might be caused by a higher zircon content. Still, the amount found is very low, indicating only trace amounts of this mineral being present.

A thermal analysis is performed with simultaneous DSC and TGA to gather complementary information on the mineral composition and to determine the water content. The resulting thermograph is shown in Figure 35. The obtained values are presented with the analytical uncertainty given as the standard deviation of the triplicate measurement.

4. Results and Discussion

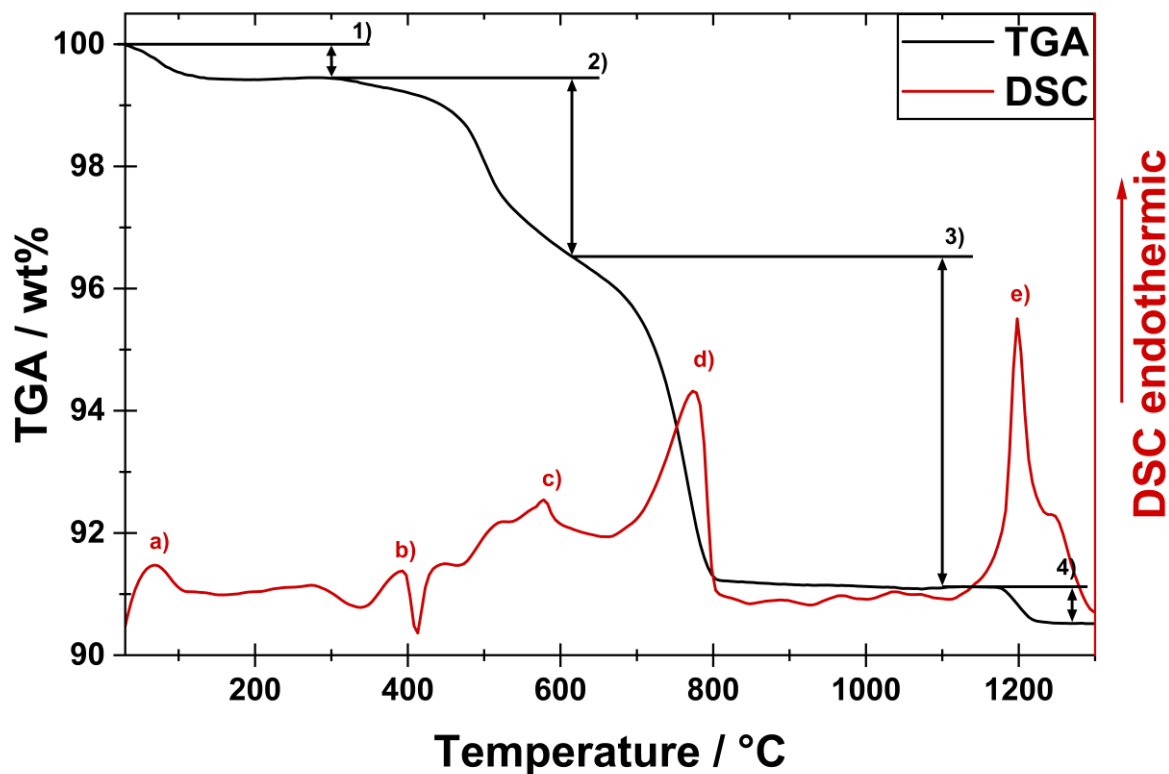


Figure 35: Thermograph of BU1 with the TGA-scale in black and the DSC-scale in red on the right, background corrected and with the endothermic reactions pointing upwards. Mass losses labeled from 1)–4) and DSC peaks from a)–e).

Free water leaves the samples first during the heating procedure, corresponding to a mass loss of 0.54 ± 0.13 wt% at around 80 °C (Figure 35 1) and a)). A thermal analysis of shaly facies OPA by Gaucher *et al.* (2003) [86] shows a similar endothermic peak and mass loss of 3.8 wt% at 100 °C. They have attributed it to the loss of free and absorbed hydration water of the interlayers, therefore this peak is consequently interpreted as such. The difference can be assigned to the higher amount of swellable and therefore water containing clay minerals present in the shaly facies. This is also indicated by the lower temperature of the mass loss in this study. Furthermore, this difference can also be attributed to different degrees of water saturation, since the samples have been stored under different conditions. The before estimated low water content in the sample is therefore confirmed.

The dehydroxylation of clay minerals happens in the temperature range of 450–600 °C [86, 207]. The mass loss at that temperature range found in this study is 3.1 ± 0.42 wt% (Figure 35 2)). The shaly facies sample of Gaucher *et al.* (2003) [86] shows an endothermic peak for this reaction at 520 °C, accompanied by a mass loss of 6.7 wt%. The difference is likely caused again by the different amounts of clay minerals present. The exothermic troughs at 300–450 °C may correspond to the combustion of organic matter (left of b) in Figure 35) [86]. The

endothermic peak in the DSC at ≈ 410 °C (right of b) in Figure 35) may be caused by siderite decomposition to iron oxide and carbon dioxide. The absence of a corresponding mass loss in the TGA is likely due to the low abundance of this accessory mineral. Between the peaks b) and c), a small shoulder can be adumbrated. This process is not accompanied by a weight loss and might be caused by the phase transformation of feldspars [86]. The endothermic peak at ≈ 570 °C (Figure 35 c)) is interpreted to result from the oxidation of pyrite and the phase transformation of quartz from α -quartz to β -quartz, happening at 573 °C [207]. Due to the still continuing dehydroxylation of clay minerals and the small amounts of pyrite present, a specific mass loss could not be assigned to this process.

At about 780 °C, the mass loss of 5.35 ± 0.21 wt% (Figure 35 3) and d)) is caused by the thermal dissociation of carbonates [207]. Attributing this mass loss only to calcite would imply a content of ≈ 12.2 wt%. This is in agreement with the so far investigated mineralogy. For the shaly facies, Gaucher et al. (2003) [86] have found the decarbonation of calcite to occur at ≈ 770 °C and obtained a corresponding mass loss of 7.1 wt%. This implies a calcite content of around 16.6 ± 2.4 wt%, which is also in good agreement with their respective mineralogical characterization.

Sulfates release their free water at low temperatures and are stable up to approximately 1000 °C [208]. At temperatures above 1200 °C (Figure 35 4) and e)), minerals like barite or celestine transform, leading to degassing of sulfur dioxide and causing a mass loss of 0.57 ± 0.05 wt%. The small shoulder to higher temperatures in the DSC in this range is explained by feldspar phase transformations. Since these two processes overlap, no definite estimation on the present sulfates could be made. If the mass loss would be assigned to only barite or celestine, the amounts present would be 1.7 wt% or 1.3 wt%, respectively. The total mass loss in the TGA of 9.5 ± 0.36 wt% corresponds well to the data gathered from XRF measurements, where a LOI of 8.89 ± 0.18 wt% has been determined for heating up to 1050 °C.

Though the planned batch sorption experiments are not going to involve redox sensitive tracers, the oxidative behavior might still be of interest for phase alteration due to atmospheric oxidation, like Fe^{2+} in clay minerals. The respective molecular environment can be derived from the oxidation state of some elements, offering further insight on the chemical composition. XPS offers these kinds of information, which can be compared to the previous analyses. Figure 36 shows the received XPS spectrum of the powder sample. The peaks are labeled with the corresponding element and electron transition. The resulting elemental distribution is shown as a cake diagram.

4. Results and Discussion

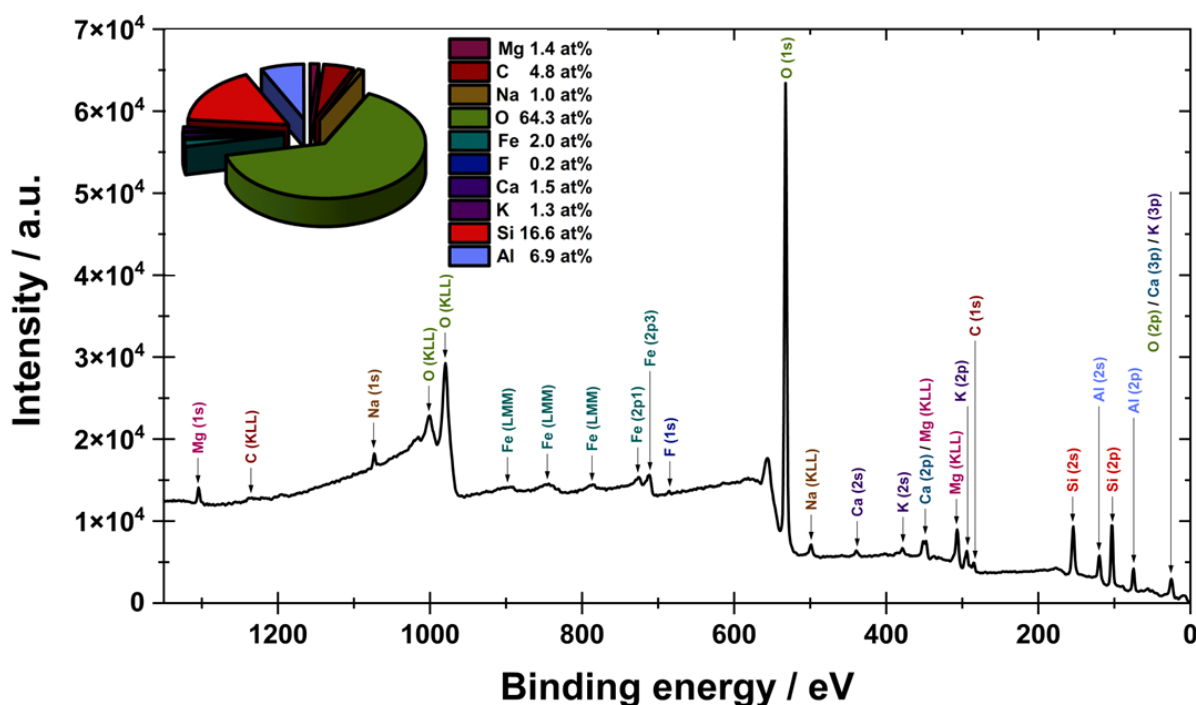


Figure 36: XPS spectrum of the BU1 powder sample with the peaks labeled by the respective element and shell transition. The resulting elemental distribution is shown as a pie diagram in the top left corner, with the composition next to it.

The elemental composition obtained from the XPS is in accordance with previous analyses. Following omnipresent oxygen, silicon is the second most common element. This is expected for the same reasons discussed for the XRF. The abundance of aluminum also follows the previous explanation. The high amount of carbon can originate from carbonates or organic materials, possibly from surface contamination during the preparation. The next most common elements are iron, magnesium, potassium and sodium, the typical clay mineral exchange elements and feldspar constituents. Similar to the calculations performed to compare the XRD and XRF data, the elemental at% distribution can also be transformed into oxide wt%. In this comparison, carbon and oxygen are excluded and the remaining elements are readjusted to 100% in total. This has been done to reflect the conditions of the XRF. The results of this evaluation are shown in Table 16.

Table 16: Comparison of the measured XPS data transformed to oxide wt% with the XRF data and the calculated elemental oxide composition of the XRD refinement.

Oxide / wt%	XPS (calculated)	XRF	XRD (calculated)
SiO₂	64.0 ± 12.8	65.2 ± 1.3	65.7 ± 4.1
Al₂O₃	15.7 ± 3.1	9.58 ± 0.2	11.6 ± 0.73
CaO	6.2 ± 1.2	6.87 ± 0.14	6.41 ± 0.64
Fe₂O₃	2.9 ± 0.6	4.38 ± 0.1	1.86 ± 0.46
K₂O	3.2 ± 0.6	1.89 ± 0.04	2.73 ± 0.43
MgO	8.0 ± 1.6	1.25 ± 0.02	1.90 ± 0.28

Given the rough assumptions made for this transformation and the comparably large uncertainties of the XPS (20 % of the respective value), these values correlate quite nicely. Another goal in the XPS measurement is to gather information on oxidation states. Therefore, the 1s environment of carbon is investigated, showing a split of carbon content into 62 % organic C_xH_y, 11 % CO and the remaining 27 % into carbonates. The differentiation of Fe²⁺ and Fe³⁺ is also attempted, but due to the rather small energy gap between the two, the resolution of the XPS has not been sufficient to quantify these oxidation states. This distribution is resolved via Mössbauer spectroscopy, shown in Appendix G.

To gather more information on the before mentioned ratio of inorganic to organic carbon, TIC and TOC concentrations are determined. They amount to 2.1 ± 0.6 wt% and 0.5 ± 0.2 wt%, respectively. This contradicts the XPS analysis, where the amount of organic carbon is higher than the inorganic carbon. A likely reasoning is the pollution of the surface of the XPS sample with adventitious organic material during the fabrication and transport of the sample. Since the XPS is very surface sensitive, the carbon and oxygen values are sometimes erroneous. The observed TIC and TOC values are in good agreement with the data of Kaufhold et al. (2013) [94], who have reported a TIC of 3.0 ± 1.1 wt% and a TOC of 0.4 ± 0.1 wt% for sandy facies OPA. If the total TIC would be present as calcite, this would assume a content of 16 ± 5 wt%. This is in reasonable agreement with the data gathered so far, considering the rather high uncertainty and the fact that other carbonate phases like siderite or dolomite are disregarded.

Further investigations of BU1 include the determination of the CEC, since this is an important parameter for the sorption capacity towards cations. It amounts to 4.8 ± 0.2 cmol_c(+)/kg, which is in good agreement with the data of Kaufhold et al. (2013) [94], who have found the CEC of their sandy facies OPA samples to range from 1.4–6.5 cmol_c(+)/kg. Kneuker et al. (2023) [93] have investigated the CEC of OPA based on the facies and subfacies categorization and have

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found an average of $3.3 \pm 0.8 \text{ cmol}_c(+)/\text{kg}$ for the lower sandy facies and a CEC range of 2.2–8.5 $\text{cmol}_c(+)/\text{kg}$ for SF3, which is the assigned subfacies for the core BMB-A7. The CEC observed in this study therefore falls in the middle of this assessment. Assuming an average CEC for the contained clay minerals as shown in Table 4, choosing 20 $\text{cmol}_c(+)/\text{kg}$ for illite and chlorite and 8 $\text{cmol}_c(+)/\text{kg}$ for kaolinite, leads to an expected CEC of 4.3 $\text{cmol}_c(+)/\text{kg}$ for the natural BU1. A deviation from the experimental values is expected, due to the rather large ranges given in literature [112, 113].

An additional important parameter for the sorption characteristics is the specific surface area. This value is measured with the BET method and is determined to be $14.4 \pm 1.4 \text{ m}^2/\text{g}$. This is lower than what is described by Gaucher *et al.* (2003) [86], who found the specific surface area of the sandy facies to be $30 \text{ m}^2/\text{g}$. This discrepancy can be explained by different milling and sieving procedure, exposing different amounts of surface area. The different amounts and composition of clay minerals may also contribute to the observed difference. Since the reactive surface is strongly correlated to the adsorption of cations, a possibly lower sorption compared to the shaly facies may be expected.

The data gathered on the powder of BU1 is compared to the intact rock surface investigated via SEM-EDX. Not only does this give information on the spatial distribution of the mineral phases, but also grants the ability to identify and locate even trace minerals with a lower abundance than the detection limit of the XRD. Figure 37 shows the total investigated area of around 10 mm^2 as a backscattered electron image. The brightness correlates with the elemental mass. At a first glance, there are at least four distinct phases visible, a white phase with high mass, a light grey phase, a dark grey phase and a blurry distribution of black spots, possibly pores.

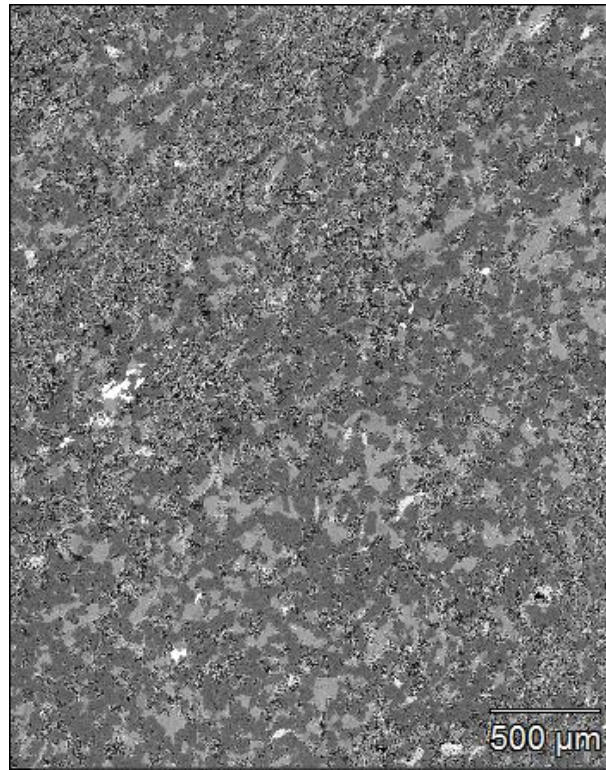


Figure 37: Backscattered electron image from the SEM-EDX investigation as a stitch of six separate analyses. The total area of BU1 investigated amounts to $\approx 10 \text{ mm}^2$.

Due to the large surface area investigated, the total area has been subdivided into six areas of equal size. Each of these sub-areas has been examined separately. Exemplarily, one of the phase analyses performed on all six sub-areas is shown below. The elemental composition of the identified phases is shown in the Appendix C. For conductivity reasons, the surface is covered with carbon prior to the measurement, causing a uniform distribution of carbon on the whole surface. The thereby identified pure carbon phase has been disregarded in the calculation of the surface coverage of the mineral phases. Figure 38 shows the phases identified as quartz and calcite.

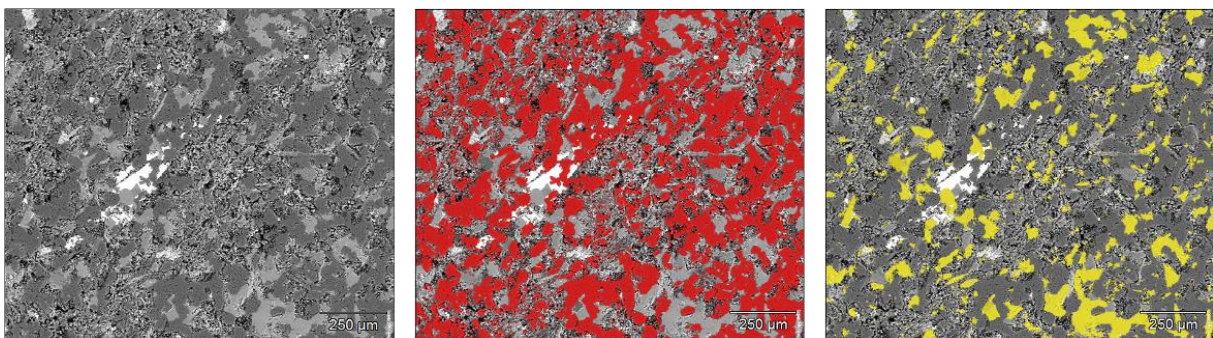


Figure 38: Phase analysis of one of the six sub-areas investigated via SEM-EDX of BU1. On the left the backscattered image, in the middle in red the areas identified as quartz and on the right in yellow the areas identified as calcite.

4. Results and Discussion

The quartz phase encompasses 48 ± 9 surf% in total, whereby the uncertainties are calculated from the standard deviation of the six analyzed sub-areas. Calcite makes up 18 ± 5 surf% as the second most abundant single mineral phase. Due to their similar elemental composition, feldspars and clay minerals could not be distinguished from one another in the phase analysis. Another complicating factor is the surface roughness of the sample, since oblique incidence of the electron beam onto the surface results in blurring and information obtained from different depths.

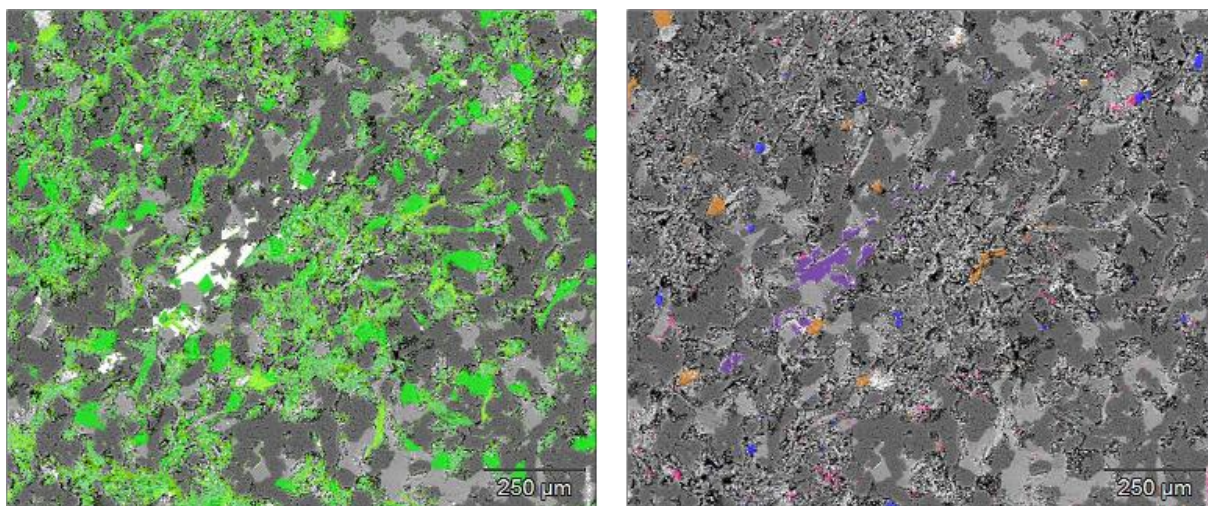


Figure 39: Phase analysis of one of the six sub-areas investigated via SEM-EDX of BU1. On the left in green the areas identified as feldspars and clay minerals, on the right the accessory minerals rutile in blue, pyrite in pink, apatite in orange and celestine in violet.

Figure 39 shows the remaining identified mineral phases, with the feldspar and clay mineral phase on the left and the trace minerals rutile, pyrite, apatite and celestine on the right. The total surface abundance of the feldspar-clay mineral phase amounts to 30 ± 12 surf% and the trace minerals are present with 0.28 ± 0.15 surf%, 0.37 ± 0.16 surf%, 0.53 ± 0.17 surf% and 0.14 ± 0.31 surf%, respectively. The large uncertainty for the celestine surface coverage is caused by it only being present in one of the six investigated sub-areas. In that area, it makes up 0.85 surf%.

These results can now be compared to the data gathered on the powder sample of BU1, although it has to be mentioned that the surf% and wt% do not necessarily translate well into one another and the information depth of the EDX measurement can vary depending on surface conditions.

Table 17: Comparison of the SEM-EDX data to the mineral phases and elemental composition of the previous analyses.

Mineral	EDX / surf%	XRD / wt%	Element	EDX / surf%	XRF / at%
Quartz	48 ± 9	47.8 ± 3.0	Oxygen	65.0 ± 1.0	66.9 ± 4.6
Calcite	18 ± 5	11.1 ± 1.1	Silicon	24.7 ± 0.6	23.1 ± 2.4
Clay minerals and feldspars	30 ± 12	38.8 ± 4.2	Calcium	4.42 ± 0.6	2.4 ± 0.5
Pyrite	0.37 ± 0.16	0.1 ± 0.1	Aluminum	3.11 ± 0.5	4.8 ± 0.5
			Iron	1.02 ± 0.12	0.5 ± 0.1
			Potassium	0.67 ± 0.12	1.2 ± 0.1
			Magnesium	0.58 ± 0.05	1.0 ± 0.1
			Sodium	0.46 ± 0.07	-

The oxide weight percentages of the XRF are converted to match the elemental surf% of the SEM-EDX. The comparison of the EDX data to the XRD data again shows the main components to be present in a very similar ratio. This is also true when comparing the elemental distribution to the XRF data. Although the validity of this comparison of a non-homogenized surface to a powder sample might be limited, the results fit surprisingly well. This is another indication for a robust identification procedure with all analyses showing very similar distribution of elements and mineral phases.

In short, all the characterization methods employed and described above complement each other very well. This reassures that analyses are accurate, more so, when also taking the close resemblance across the board with literature reports into account. This similarity to the literature suggests a surprisingly high degree of homogeneity on the scale of the volume of BU1 ($\approx 2000 \text{ cm}^3$). Otherwise, bigger differences should be observable. This is further true for the multitude of different investigated parameters, each of which should be characterized by a separate REV. A volume of $\approx 2000 \text{ cm}^3$ could therefore be large enough to be representative for the sandy facies. On the other hand, only one sample being investigated bears some degree of debatable statistical relevance.

The similarity of the obtained mineralogy from different methods indicates, that one characterization method may be sufficient when describing the mineral and chemical composition. Therefore, the mineral composition is only assumed by Rietveld refinement after XRD measurement for further samples. Other characterization methods are only used sparsely on samples of great interest or high specificity or to obtain information not obtainable by XRD.

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4.2.2 Characterization of Drill Core BMB-A7

With the gathered knowledge of the characterization methods above, analyses of the further samples of BMB-A7 are performed. The most interesting characteristics are the mineral composition and the CEC. The TIC and TOC values could also be of interest for the planned batch sorption experiments. Table 18 describes the samples and their origins, investigated in this chapter.

Table 18: Summary of the samples described in this chapter with their respective volume, origin and special features. The originating fragments are numbered from 1–3 for readability purposes.

Abbreviation	Sample volume / cm^3	Drill core segment origin (depth) / m	Special features	Color code
BU1	≈ 2000	36.4–36.9 (1)	-	
BU2	≈ 300	40.2–40.5 (2)	Average of SA, SH and EV	
SA	≈ 100	40.2–40.5 (2)	Sand-rich	
SH	≈ 100	40.2–40.5 (2)	Clay-rich	
EV	≈ 100	40.2–40.5 (2)	Evenly mixed	
27 cm^3	27	40.0–40.2 (3)	-	
8 cm^3	8	40.0–40.2 (3)	-	
1 cm^3	1	40.0–40.2 (3)	-	
Single-phase	<0.2	40.0–40.2 (3)	-	

For the comparison of the mineralogy, a ternary diagram is set up with the amount of quartz, carbonates and clay minerals on the axes, normalized to 100 wt% in total. This excludes the amount of feldspars and accessory minerals present, which will be addressed later.

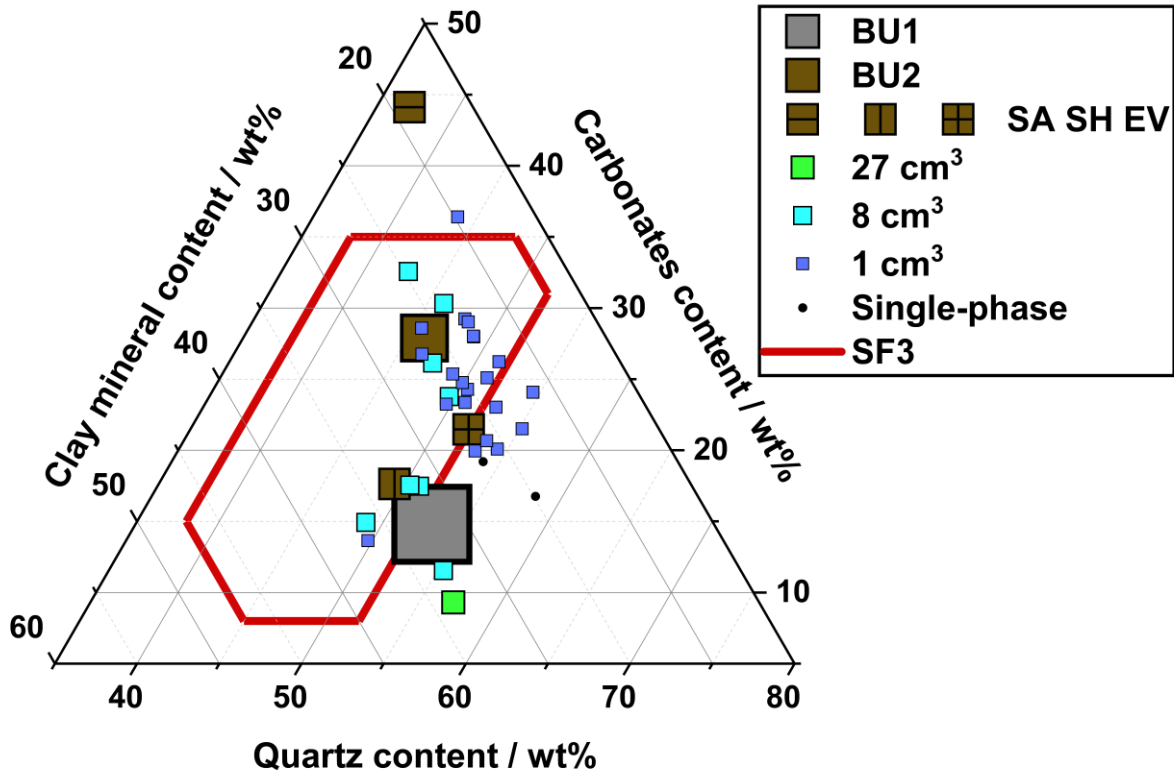


Figure 40: Ternary diagram of the samples of BMB-A7 with the quartz, carbonates and clay mineral contents normalized to 100 wt% total. The volume of the respective samples is reflected somewhat proportionally by the size of the datapoint. Highlighted in red is the average composition of the SF3 from Lauper et al. (2021) [6] as comparison.

Figure 40 shows all the samples of core BMB-A7, with the size of the respective datapoints adapted to the volume of the corresponding samples. Due to the nature of the ternary diagram, uncertainties cannot be displayed easily. The average standard deviation regarding the contents of quartz, carbonates and clay minerals are 3.0 wt%, 2.6 wt% and 4.4 wt%, respectively.

Most of the randomly chosen samples match the classification to SF3 from Lauper et al. (2021) [6] nicely, displayed as a red polygon. Only the small-volume samples show a deviation, when taking the uncertainties of the determination into account. Since SF3 is the subfacies with the highest quartz content, arguments may be made to extend to range of the observed quartz content, since the samples investigated in this study show a distinct visual concordance to SF3. The obtained mineral composition is further in accordance with the data of Peters et al. (2010) [90], who have found the quartz content to range from 21–52 wt%, the calcite content from 6–66 wt% and a clay mineral content from 6–62 wt% for sandy facies OPA. It has to be noted though, that their research is focused on the investigation of samples with a highly specific mineralogy. Therefore, they have not investigated random samples, but those with visually striking features. Finding more pronounced extremes is consequently no surprise.

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The big difference of BU1 to BU2 can be explained by their different origin. Regarding the visual selection of specific samples in this study, the process has been a success for the large-volume samples. SA shows the largest amount of carbonates with the lowest amount of clay minerals. SH in contrast has a comparatively high clay mineral content with low carbonates content. The visual features on which the selection has been based upon are therefore likely carbonates and not sand lenses (quartz), as originally proposed. EV shows a more average composition in comparison and the composition of BU2 fits nicely as the median of the three samples SA, SH and EV. This is also true for the TIC directly following the carbonate contents, where SA has by far the highest content with 4.35 ± 0.4 wt% and SH the lowest with 1.6 ± 0.3 wt%. EV has a more average inorganic carbon content of 1.8 ± 0.4 wt% and BU2 again a median content of 2.8 ± 0.3 wt%.

The investigation of the smaller samples with a volume ≤ 27 cm³ shows an unexpected trend. The expected diversification of mineralogy with reducing sample volume is not as pronounced. The samples are all in rough accordance of either BU1 or BU2, seemingly building the cornerstones of the mineralogy of BMB-A7. However, in general, a high variation in carbonate and clay mineral content are seen within this sample volume. The most plausible explanation for this phenomenon originates in the sampling procedure (see Chapter 3.3.1), visualized in Figure 41.

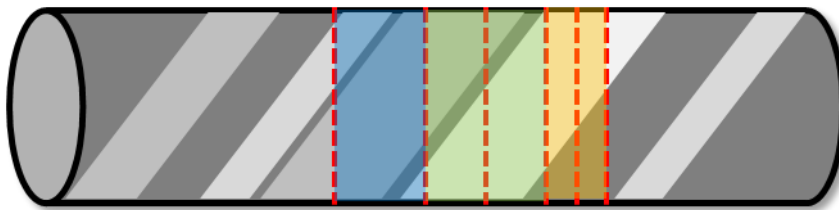


Figure 41: Visualization of the possible issues arising from the sampling procedure of the smaller samples of core BMB-A7. 1 cm³ samples indicated in yellow, 8 cm³ samples in green and the 27 cm³ sample in blue.

The discs have been cut perpendicular to the cores drilling vector, neither in parallel nor perpendicular to the bedding. Assuming a perfectly parallel bedding and a random assortment of bedding laminae, cutting the discs like visualized in Figure 41 would lead to more than half of the 1 cm³ samples (yellow) to be very similar in composition to most of the 8 cm³ samples (green). Furthermore, they both would be rather different to the 27 cm³ sample (blue). A comparable situation as pictured in Figure 41 is likely to have occurred during the volume-dependent sampling, and rendered the basis of the analysis questionable.

Handpicking of individual supposedly single-phase mineral grains did not yield the expected result. Both of these samples consist of a similar amount of clay minerals and the main difference is the quartz content. From the experience of the preparation of the BDR core samples, the true coloring of an OPA contained mineral phase can only be seen after thorough polishing. Some phases previously bright grey became almost black after being polished to a grit size of 4000 with sandpaper. Thus, the selection procedure after crushing OPA into pieces is certainly not a suitable approach, since the coloration could stem from the fragmentation and rather reflect the surface roughness than the mineral content.

A thermal analysis is performed on the 27 cm³ sample and some of the smaller samples. The experiments with these samples took place much later in comparison to the investigation of the large-volume samples. Therefore, possible saturation from atmospheric water or further drying could have happened in the meantime. Furthermore, thermal analysis allows to obtain information on the carbonate content and cross check the XRD results. The obtained contents are shown in Table 19, together with a calcite content assuming all carbonates to be present as calcite and the calcite content derived from XRD.

Table 19: Results of the thermal analysis of the low-volume samples of core BMB-A7, showing the water content and mass loss through carbonate phase transformation in comparison to the XRD data.

Sample	Water content / wt%	Carbonate loss / wt%	Calcite (TGA) / wt%	Calcite (XRD) / wt%
27 cm³	1.17 ± 0.05	5.61 ± 0.22	12.79 ± 0.50	5.0 ± 0.8
8 cm³ - 1	0.77 ± 0.03	8.27 ± 0.32	18.85 ± 0.74	20.2 ± 2.7
8 cm³ - 2	0.94 ± 0.04	5.87 ± 0.23	13.39 ± 0.53	12.9 ± 1.6
8 cm³ - 3	0.54 ± 0.02	10.28 ± 0.40	23.44 ± 0.92	26.2 ± 5.4
8 cm³ - 4	0.61 ± 0.02	8.66 ± 0.34	19.74 ± 0.78	23.5 ± 3.6
1 cm³ - 1	0.88 ± 0.03	8.56 ± 0.33	19.52 ± 0.77	21.2 ± 2.6
1 cm³ - 2	0.80 ± 0.03	11.43 ± 0.45	26.06 ± 1.02	23.4 ± 0.22

The overall water content ranges from 0.5–1.2 wt%, which is similar to what is observed in the sample BU1. Likely no further drying or hydration has taken place and all samples can be assumed to be in equilibrium with ambient conditions. The 27 cm³ sample has one of the highest siderite contents with 3.6 ± 1.1 wt%, which partly explains the discrepancy between the thermal analysis and the XRD results for the calculated calcite content. Overall, the obtained calcite values derived from the TGA match the XRD results nicely.

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The obtained clay mineral and feldspar contents and the CEC are shown in boxplot diagrams, to better visualize data scattering. The boxes themselves cover the median 50 % of the datapoints, with the stopped lines above and below the box covering the respective remaining top and bottom 25 %. The average is indicated with a dot and the median value is indicated by a line within the box. For the samples consisting of a single sample (BU1 and the 27 cm³ sample), the box indicates the uncertainty of the measurement. Figure 42 shows these boxplots of all BMB-A7 samples.

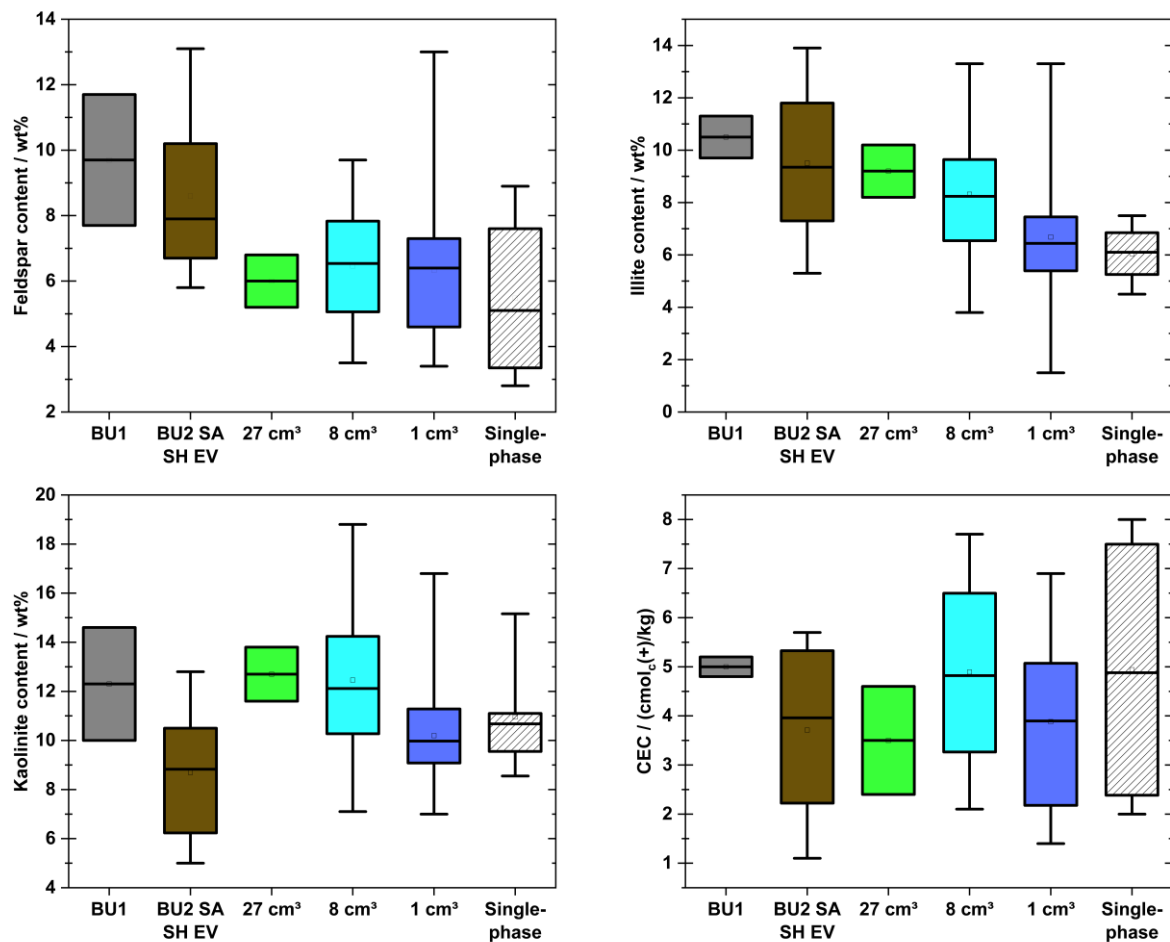


Figure 42: Boxplots of the feldspar, illite, kaolinite contents and the CEC of the samples of core BMB-A7. Sample BU1 indicated in grey, samples BU2, SA SH and EV together in brown, the 27 cm³ sample in green, the 8 cm³ samples in teal, the 1 cm³ samples in blue and the single-phase samples in dashed black.

The brown and dashed boxes need to be taken into account with caution in this assessment, since they consist of a specifically picked mineralogy. In the brown box, the box itself corresponds to the random samples BU2 and EV, while the whiskers indicate the samples SA and SH. Only for the kaolinite content, the 8 cm³ samples show a larger data scattering

compared to the 1 cm³ samples. Aside this mineral content, the trend of larger data scattering with decreasing volume is visible. This is contrary to the before mentioned findings, where sample volume hasn't shown a distinct effect, but a first indication that lowering the sample volume does in fact increase data spread.

The volume dependent average CEC amounts to $4.8 \pm 0.2 \text{ cmol}_c(+)/\text{kg}$ and the observed range is in agreement with the data of Kaufhold et al. (2013) [94] and Kneuker et al. (2023) [93], already discussed before. It has to be noted, that the SH sample shows the highest CEC of the “brown box” (SA, SH and EV in Figure 42) and that the clay-rich single-phase sample shows the higher CEC in the single-phase box. The clay-rich single-phase sample even shows the highest CEC among all investigated samples, which is contrary to the amount of clay minerals in general present. A possible explanation is that an unidentified smectite phase might influence to CEC to a large degree. Due to the high CEC of smectites, even amounts present below the detection limit of the XRD may play a role (see Table 4). The CEC is expected to be dominated by the clay mineral content, but efforts to correlate these two parameters have been unsuccessful in this dataset so far. This is contrary to the results of Kneuker et al. (2018 and 2023) [93, 209], who found a distinct relation of CEC and the amount of clay minerals present.

An investigation on the specific surface area is performed, since it correlates to the amounts of reactive surfaces being present for the batch sorption experiment. Of the high-volume samples, the sample SH has the highest specific surface area with $17.0 \pm 2.0 \text{ m}^2/\text{g}$, followed by EV and BU2 with $15.0 \pm 1.6 \text{ m}^2/\text{g}$ and $14.1 \pm 1.5 \text{ m}^2/\text{g}$, respectively. This is in the same range as the sample BU1 with $14.4 \pm 1.4 \text{ m}^2/\text{g}$. The sample SA has a lower specific surface area of $11.2 \pm 1.1 \text{ m}^2/\text{g}$. Since the sample preparation procedure for all samples has been the same, the differences are likely solely caused by the clay mineral content. This shows a clear correlation with the clay mineral content, who contribute most to the specific surface area. Including the small-volume samples in this correlation, a medium correlation with a Pearson R (correlation coefficient) of 0.82 is determined (see Figure 43).

4. Results and Discussion

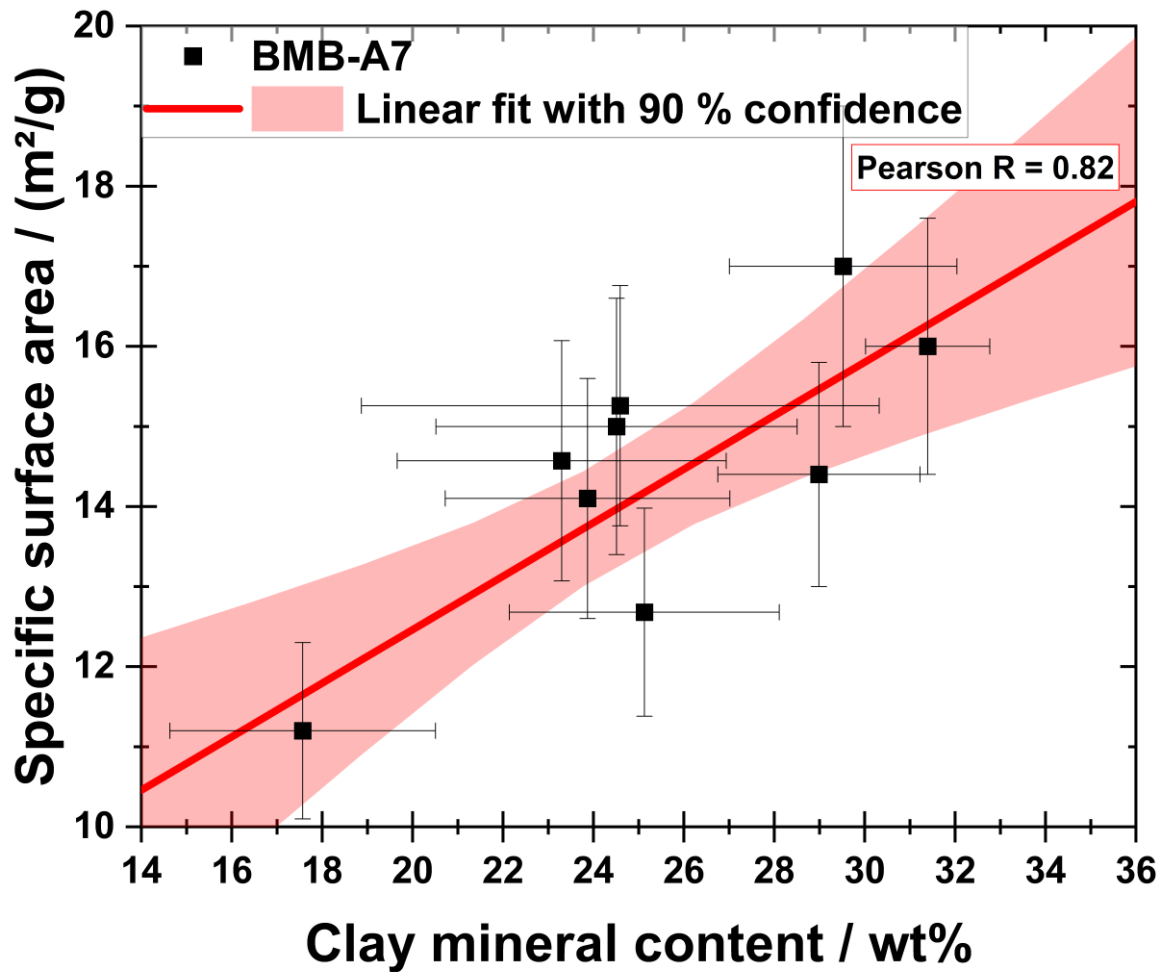


Figure 43: Correlation of the specific surface area of the BMB-A7 samples to their respective clay mineral contents, displayed with a linear fit and a 90 % confidence interval.

To summarize, the mineralogical composition of core BMB-A7 is in general close to that of the previously described sample BU1. Related parameters shift accordingly, e.g., a lower clay mineral content leading to a lower specific surface area. All samples also fall in the expected range of compositions from literature. Visually selected samples like SA and SH show the expected changes in mineralogical composition and related properties, like the BET and CEC. Due to the rather small sampling size, the expected shift to higher specificity with decreasing sample volume could be only partly be verified. The sampling procedure may be the main reason for this controversial finding, since the discs from which specific sized cubes have been cut, largely originate from similar bedding horizons.

4.2.3 Characterization of Drill Cores BDR-D1 and BDR -D2

Of interest for the investigation are the beginning of the core beyond the EDZ (6.00–7.25 m), the part with changed coloration and pattern as seen in Figure 32 (9.25–11.00 m) and a part of the last segment of the obtained core at 13.00 m. The resulting mineralogical composition across both cores is shown in Figure 44.

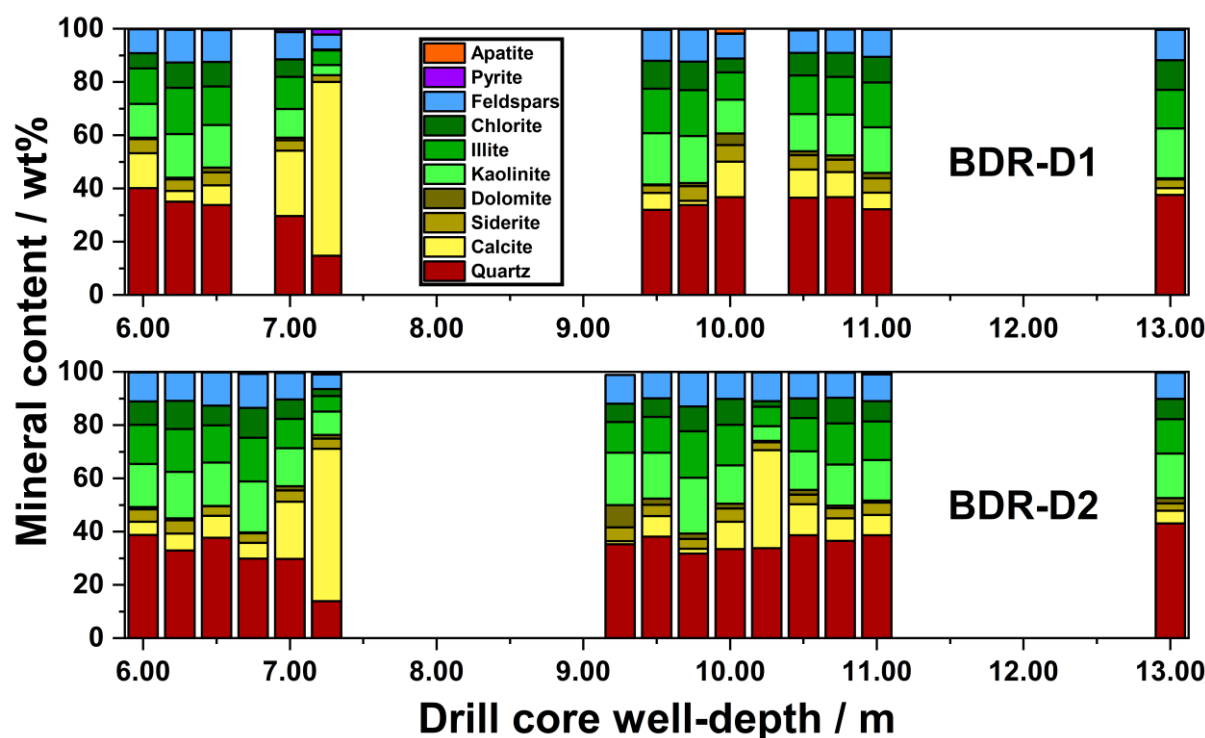


Figure 44: Mineral composition of the cores BDR-D1 (top) and -D2 (bottom) as a bar chart plotted against the well-depth of the respective disc.

Due to unfortunately positioned cracks in the drill cores, partly induced by the polishing or the packaging, transport, storage and unpackaging, some discs could not be retrieved. The disc D2 6.00 m has been taken from the position at 6.10 m for the same reason, but the notation has been kept unchanged.

The first notable feature is the similarity in the composition across the two cores. Both show in- and decreases of the same mineral phases at the same well-depth. From 6.00–6.75 m, both cores show a decrease in quartz content with an increase in clay mineral contents. Starting at 7.00 m well-depth, the calcite content spikes up, outcompeting quartz and the clay minerals and reaching more than 55 wt% in both cores at well-depth 7.25 m. The samples at this well-depth are also the only ones with a notable pyrite content of up to 2.0 ± 0.6 wt%. The obvious reason for the high calcite content are the fossil shells (coquinas) present in these discs. The fossil layer

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carries partly over to the sample at 7.00 m well-depth still having an elevated calcite content. At the next investigated interval, the calcite content starts out very low and then rises from 9.75 m to the maximum at 10.25 m well-depth, reaching a content of ≈ 37 wt%. The clay mineral contents decrease accordingly and the quartz content remains more or less constant. The sample D1 10.00 m is the only sample bearing a notable apatite content with 1.6 ± 1.0 wt%. In this interval, a significant change in coloration of the drill cores has been observed and displayed in Figure 32, but this color change cannot be attributed to a significantly different mineralogical composition.

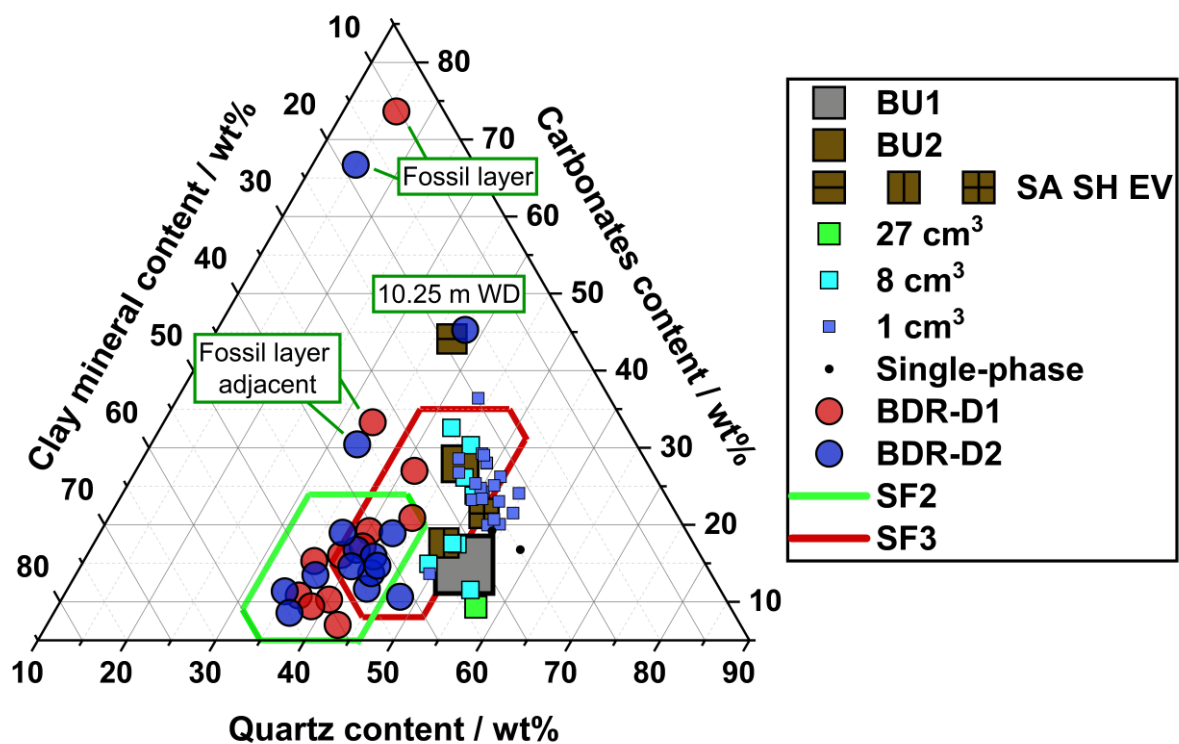


Figure 45: Ternary diagram of the samples of BMB-A7, BDR-D1 and -D2 with the quartz, carbonates and clay mineral contents normalized to 100 wt% total. The volume of the respective samples is reflected somewhat proportionally by the size of the datapoint. Highlighted in green and red are the compositional ranges of the SF2 and SF3 from Lauper et al. (2021) [6] as comparison.

To better assess the mineral classification of the subfacies by Lauper et al. (2021) [6] and compare them to the visual assignments, Figure 45 shows the prior ternary diagram together with the data of the cores BDR-D1 and -D2. The compositional ranges of SF2 and SF3 are highlighted in green and red, respectively. These areas should only be taken as a rough allocation, since visualizing ranges in a ternary diagram can only be done to a certain extent and uncertainties also need to be taken into account. Samples slightly out of bounds can therefore still be considered to belong to a specific subfacies. The areas previously identified as

SF2 fit the described mineralogy quite well, when excluding samples containing the fossil layer. The area of the BDR drill cores classified as SF3 shows only a slightly different composition with on average ≈ 40 wt% quartz, ≈ 21 wt% carbonates and ≈ 39 wt% clay mineral contents. These minor differences, however, are enough to be more in line with the mineralogical ranges of SF3 than with SF2. The large compositional overlap of the two subfacies makes a distinct separation solely on mineralogical data difficult. The optical characterization therefore also needs to be taken into account when trying to differentiate between SF2 and SF3.

To compare the average compositions of the cores BDR-D1 and -D2 with core BMB-A7, the average mineral composition is determined and shown in Table 20.

Table 20: Average composition of both BDR cores and the BMB-A7 samples BU1 and BU2.

Mineral / wt%	BDR-D1	BDR-D2	BMB-A7 BU1	BMB-A7 BU2
Quartz	33.2 ± 2.9	34.1 ± 3.2	47.8 ± 3.0	42.2 ± 2.6
Calcite	13.7 ± 1.7	13.0 ± 1.5	11.1 ± 1.1	22.4 ± 2.7
Siderite	4.5 ± 1.1	4.1 ± 0.9	1.4 ± 0.3	2.4 ± 0.5
Dolomite	1.3 ± 0.6	1.7 ± 0.3	0.9 ± 0.1	0.8 ± 0.2
Kaolinite	14.5 ± 1.3	15.4 ± 2.1	12.3 ± 2.3	8.6 ± 1.4
Illite	13.9 ± 3.9	13.2 ± 3.1	10.5 ± 0.8	9.4 ± 2.3
Chlorite	8.0 ± 3.9	7.7 ± 3.8	6.3 ± 0.3	5.8 ± 0.8
Feldspars	10.1 ± 2.1	10.4 ± 2.1	9.7 ± 2.0	8.2 ± 1.7
Pyrite	0.5 ± 0.4	0.2 ± 0.3	0.1 ± 0.1	0.2 ± 0.2
Apatite	0.2 ± 0.3	0.2 ± 0.2	0.2 ± 0.1	0.1 ± 0.1

Again, the similarities of the cores D1 and D2 are striking, linking to a high homogeneity along the bedding even when comparing whole drill cores. In comparison to the large BMB-A7 samples, they show a lower quartz content and a higher clay mineral content. In comparison to BU2, they also show a lower calcite content, though this is also true when comparing BU1 and BU2. Differences to BMB-A7 can be explained by the different origins, since the cores have been retrieved from different parts of the sandy facies (lower sandy for BMB-A7 and upper sandy for the BDR cores, see Figure 14). Those two lithologies, though stemming from a similar sedimentation environment and showing similar compositions, can still be differentiated by distinct characteristics. Furthermore, the BDR drill cores are much larger and consist of multiple subfacies as already established, while BMB-A7 only consists of SF3. The overall mineral composition of the cores BDR-D1 and -D2 is more in line with the literature reports already discussed [86, 90].

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The water content of some BDR samples is measured via TGA, amounting to 1.0–1.5 wt%. This small variation could not be correlated to specific mineralogical features or to the well-depth.

The CEC of the drill cores BDR-D1 and -D2 ranges from 4–12 $\text{cmol}_c(+)/\text{kg}$, being slightly higher in core BDR-D2. This general range is higher than what has been determined for BMB-A7, which is likely caused by the higher clay mineral content. In comparison to the data of Kaufhold et al. (2013) [94], who have found the CEC to range between 1.4–6.5 $\text{cmol}_c(+)/\text{kg}$, it is also higher. Gaucher et al. (2003) [86] have found the CEC of their respective samples to be 8.5–9 cmol_c/kg with a higher clay mineral content than both BDR cores. A comparison to the data of Kneuker et al. (2023) [93] can also be drawn, with the areas defined as SF2 from this study showing a CEC of 7.3–12.2 $\text{cmol}_c(+)/\text{kg}$ with an average of $9.8 \pm 1.5 \text{ cmol}_c(+)/\text{kg}$. The range for this subfacies obtained by Kneuker et al. (2023) [93] is 4.0–10.5 $\text{cmol}_c(+)/\text{kg}$ with an average of $\approx 7.5 \text{ cmol}_c(+)/\text{kg}$. The difference might be caused by the low amount of samples investigated and therefore be a purely statistical difference. For the SF3, they have found values from 2.1–8.5 $\text{cmol}_c(+)/\text{kg}$ with an average of $\approx 6.0 \text{ cmol}_c(+)/\text{kg}$ compared to this studies' range of 6.0–9.7 $\text{cmol}_c(+)/\text{kg}$ and an average of $8.0 \pm 1.3 \text{ cmol}_c(+)/\text{kg}$. Again, the range is a little higher than what is found in literature, but a similar trend is found with SF2 having a distinctively higher CEC than SF3.

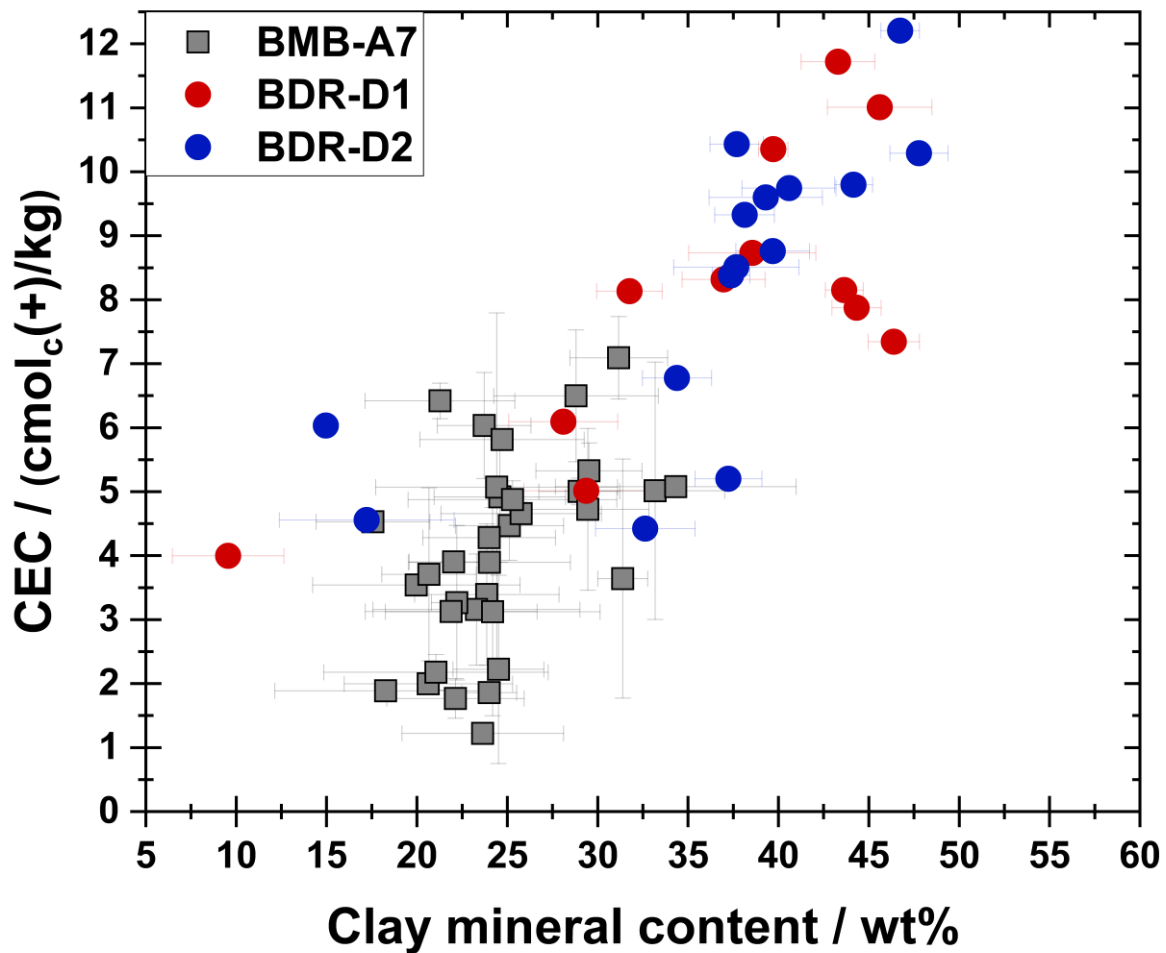


Figure 46: Correlation of the CEC of all samples from the three cores plotted against the respective clay mineral contents.

The assumption of higher clay mineral contents leading to a higher CEC is confirmed by literature [209] and is also true for both cores BDR-D1 and -D2, as shown in Figure 46. The absence of this trend in the data of core BMB-A7 (grey squares) is explained by the low range of observed clay mineral contents and unfortunate scattering. This relationship being validated is crucial for the assembly of a geochemical model.

Overall, a high lateral homogeneity can be seen parallel to the bedding even reaching lengths of 20 m with only very small differences in mineralogy and geochemical properties like the CEC. Perpendicular to the bedding a strong impact of the heterogeneity on the mineral composition is observable. Exemplarily, samples taken only 25 cm apart show a change in calcite content by a factor of five and higher. The full discussion on the impact of the heterogeneity on the mineral composition is shifted to Chapter 4.7.

4.3 Batch Sorption

The investigation on the retention behavior towards cesium, cobalt and europium is performed via batch sorption experiments. Prior to the sorption experiments, the synthetic pore waters need to be investigated on their compatibility with the respective natural clay rock samples. The general recipes and target compositions can be found in Chapter 3.4 [63, 161]. The results of the equilibration experiments are shown in Figure 47 for sample BU1 of drill core BMB-A7 and in Figure 48 for the four samples from the drill cores BDR-D1 and -D2. The change in ion composition and pH over time is shown as full lines with data points and the target compositions are shown as dashed horizontal lines. The analysis methods are described in Chapter 3.5.

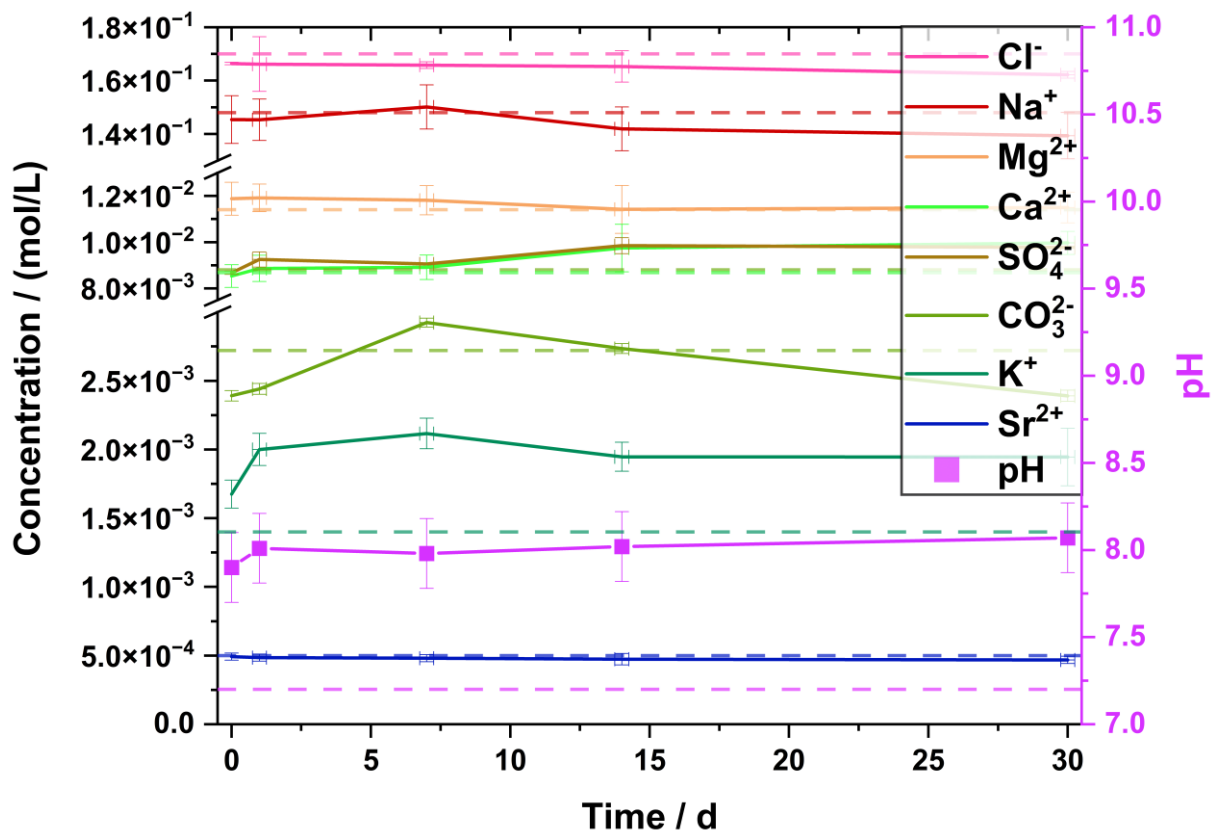


Figure 47: Ion and pH variation over time of the synthetic pore water in contact with 10 g/L of BU1. The dotted lines indicate the target composition [63].

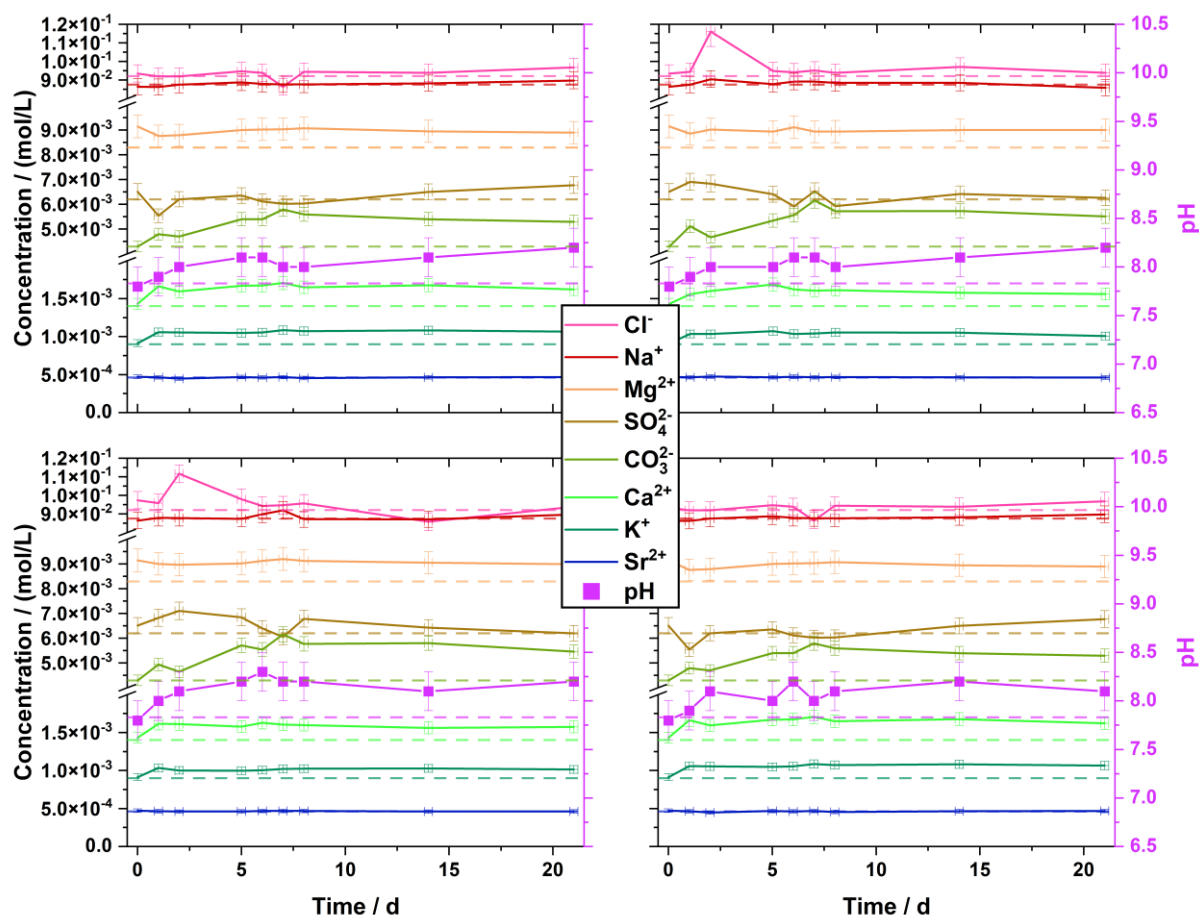


Figure 48: Ion and pH variation with time of synthetic pore water in contact with 10 g/L of clay powders from the drill cores BDR-D1 and -D2. The dotted lines indicate the target composition of the pore water. Top left the equilibration with D1 6.00 m, top right with D2 6.00 m, bottom left with D2 10.0 m and bottom right with D2 13.00 m.

In all equilibration experiments the composition fluctuates slightly in the first seven days, but remains stable afterwards. pH shows the strongest deviation, together with the carbonate content. It has to be noted, that these equilibration experiments have been conducted under ambient conditions, which may cause carbonate degassing and thereby pH increase. Carbonate containing minerals could then dissolve, causing the carbonate content in solution to remain stable or even increase. For the batch sorption experiments pH will be controlled and an elevated carbon dioxide atmosphere will be present to prevent these occurrences (see Chapter 3.6.3). The composition of the synthetic pore water designed for the BDR samples is very similar to the target composition and seems to fit well for all four investigated samples. It can therefore be used across the whole bore core and no adjustments need to be made. For the BMB-A7 pore water, the potassium concentration is slightly higher than originally planned for unknown reasons. This needs to be taken into account in the evaluation of the batch sorption experiments and modeling with cesium, since potassium acts as a strongly competing ion.

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Summarizing, seven days of pre-equilibration prior to the batch sorption experiments seems to be sufficient and will consequently be implemented in the procedure.

Besides the surveillance of the intentionally added ions, further elements are investigated as possible contaminations of the added salts or originating from dissolution of OPA minerals. Of interest here are the elements used in the batch sorption experiments (cesium, cobalt and europium), as well as ions competing for the sorption with these, like rubidium and nickel. Furthermore, the iron, silicon and aluminum contents are investigated to identify possible clay dissolution. The iron content is also important for the TRLFS measurements and in its divalent state, it may also act as a competitor for cobalt sorption [210].

For all equilibrations, the concentrations of these elements have been stable from seven days on onwards. The results are shown in Table 21, on the right showing the maximum contents obtained of the four equilibrations with the BDR samples.

Table 21: Elemental concentrations of the elements dissolved from OPA samples in the equilibration experiments after seven days.

Element / mol/L	BMB-A7	BDR
Cs	$3.7 \cdot 10^{-8} \pm 7.6 \cdot 10^{-10}$	$5.0 \cdot 10^{-9} \pm 4.8 \cdot 10^{-10}$
Co	$1.7 \cdot 10^{-7} \pm 9.5 \cdot 10^{-9}$	$5.2 \cdot 10^{-8} \pm 9.2 \cdot 10^{-10}$
Eu	$5.1 \cdot 10^{-10} \pm 8.2 \cdot 10^{-11}$	$9.6 \cdot 10^{-10} \pm 1.4 \cdot 10^{-10}$
Rb	$4.6 \cdot 10^{-7} \pm 2.8 \cdot 10^{-8}$	$2.5 \cdot 10^{-7} \pm 2.7 \cdot 10^{-9}$
Ni	$5.5 \cdot 10^{-7} \pm 2.4 \cdot 10^{-8}$	$6.6 \cdot 10^{-8} \pm 1.4 \cdot 10^{-9}$
Fe	$2.4 \cdot 10^{-5} \pm 8.1 \cdot 10^{-6}$	$7.3 \cdot 10^{-5} \pm 4.2 \cdot 10^{-6}$
Si	$7.8 \cdot 10^{-5} \pm 3.9 \cdot 10^{-6}$	$1.7 \cdot 10^{-5} \pm 4.9 \cdot 10^{-6}$
Al	$4.1 \cdot 10^{-6} \pm 2.0 \cdot 10^{-7}$	$7.7 \cdot 10^{-5} \pm 1.1 \cdot 10^{-5}$

None of these ions have been detected in the initial porewater, meaning they originate from the dissolution of mineral phases and not from impurities in the chemicals. With the proposed tracer concentration of $2 \cdot 10^{-7}$ mol/L for the batch sorption experiments, the dissolvable cobalt needs to be taken into account for the calculation of the sorption coefficient. The amounts of cesium and europium are low enough to be negligible for the sorption behavior but are considered in the calculations nonetheless. Similarly, the amounts of dissolvable rubidium and nickel are also added into the background electrolyte composition for the modeling procedure in addition to the synthetic pore water composition. The comparatively high amount of iron present in solution might play a role for the TRLFS measurements and the sorption of cobalt [210]. The nickel concentration is in the same range as cobalt, leading to possibly strong competition for

the sorption sites. Clay mineral dissolution might also play a role, due to the amounts of dissolvable silicon and aluminum in both systems, which needs to be kept in mind.

After this preparatory experiment, the batch sorption experiments have been conducted. The results of the cesium batch sorption on the BMB-A7 samples are displayed as boxplots in Figure 49 (left), together with selected literature data as comparison. Furthermore, the sorption coefficients are plotted against the illite content (right).

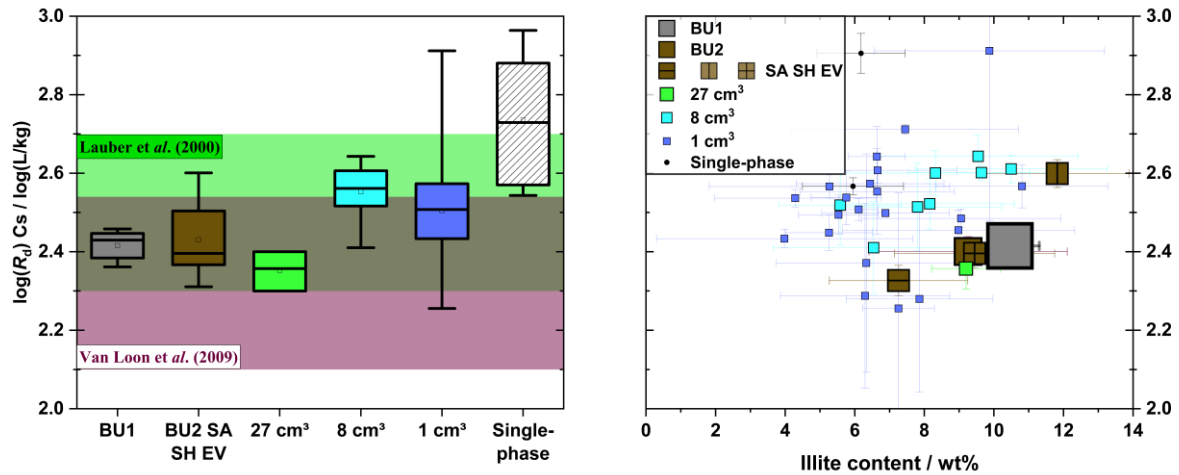


Figure 49: Results of the cesium batch sorption experiments of BMB-A7. On the left, the distribution of the $\log(R_d)$ -values dependent on sample size as boxplots with literature data as comparison [35, 38]. On the right, the $\log(R_d)$ -values plotted against the respective illite contents.

As shown on the left side of Figure 49, the $\log(R_d)$ -values gathered for the batch sorption of cesium ranged from 2.2–2.9 $\log(\text{L/kg})$. The trend of a higher data spread with decreasing sample volume is observable, with the sample BU1 and the 27 cm^3 sample being excluded, since only one sample has been processed. The single-phase samples are also excluded from this discussion, since only two samples have been processed with specifically chosen visual characteristics. Despite the visible trend, the average and median R_d -values do not deviate much, as can be seen by the dots and lines within the boxplots. The average $\log(R_d)$ -values fall into the range of literature reported data. Lauber et al. (2000) [38] (green area) report $\log(R_d)$ -values ranging between 1.4–3.1 $\log(\text{L/kg})$ at pH 7.9 on shaly facies OPA with an illite content of 18–26 wt% and an additional illite/smectite mixed layer of 14–22 wt%. The range is caused by different equilibrium concentrations of cesium used in their experiment. The closest experimental datapoint to this studies concentration amounts to an R_d -value of $\approx 2.5 \pm 0.2$ $\log(\text{L/kg})$, which is shown in Figure 49. The area indicated in violet is the range of $\log(R_d)$ -values obtained by Van Loon et al. (2009) [35], who have performed a concentration dependent

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sorption analysis of the shaly facies (no mineral composition determined), taking the effect of the natural cation inventory of cesium into account. The highlighted area is derived from their respective low concentration experiments, similar to the concentrations present in this study. Van Loon et al. (2009) [35] have also implemented a universal uncertainty of 0.2 log units to their evaluation to cover the fluctuation of the whole dataset. Almost all the cesium sorption data gathered in this study falls into these literature-reported ranges. These findings are unexpected, since the cesium sorption should be highly dependent on the general clay mineral content and specifically on the illite and smectite content present and these are much higher in the shaly facies samples from the literature reports [93]. Illite contents between 2–14 wt% are found for the BMB-A7 samples, while the sample investigated by Lauber et al. (2000) [38] contain more than three times as much. The same is true for the CEC, which should characterize the dominant adsorption process for cesium. In this study, values between 1.5–8 cmol_c(+)/kg have been observed with on average 4.8 ± 0.2 cmol_c(+)/kg, while Lauber et al. (2000) [38] determined 12.1 ± 0.4 cmol_c(+)/kg.

To have a closer look at this finding, the log(*R_d*)-values are plotted against the respective illite content on the right side of Figure 49. The visually selected samples, SH, EV and SA show the expected trend of decreasing sorption towards cesium. From the hand-picked single-phase samples, though almost identical in illite content, the “clay-rich” sample also displays a significantly higher sorption coefficient in comparison. This is similar to what is observed with the CEC, which is expected to be strongly related to cesium sorption. This indicates an unnoticed phase besides the clay minerals determined via XRD to participate in cation exchange and cesium sorption. A possible candidate for this could be organic matter, though both fulvic and humic acids show only very minor impact on the sorption of cesium [211, 212]. Minor amounts of smectite mixed layers being present may lead to such a difference, since these might have been unnoticed in the XRD due to the same reflex positions as illite and still exhibit a significantly higher CEC (Table 4). Biotite is another mineral phase not taken into account, but might be present as an accessory mineral and exhibiting an elevated CEC [212]. This mineral might also have caused the different coloration of the chosen particles for the single-phase samples, but due to the uniform determination procedure with the Rietveld fitting, this would have been unnoticed.

An overall trend indicating a higher illite content to lead to a higher sorption coefficient for the cesium sorption cannot be identified. This is also true when plotting against the kaolinite content or the total clay mineral content (not shown). A probable reasoning for this is the

comparatively small range of investigated illite contents, preventing a higher spread in obtained $\log(R_d)$ -values. In Chapter 4.4, this observation will be addressed with the help of geochemical modeling.

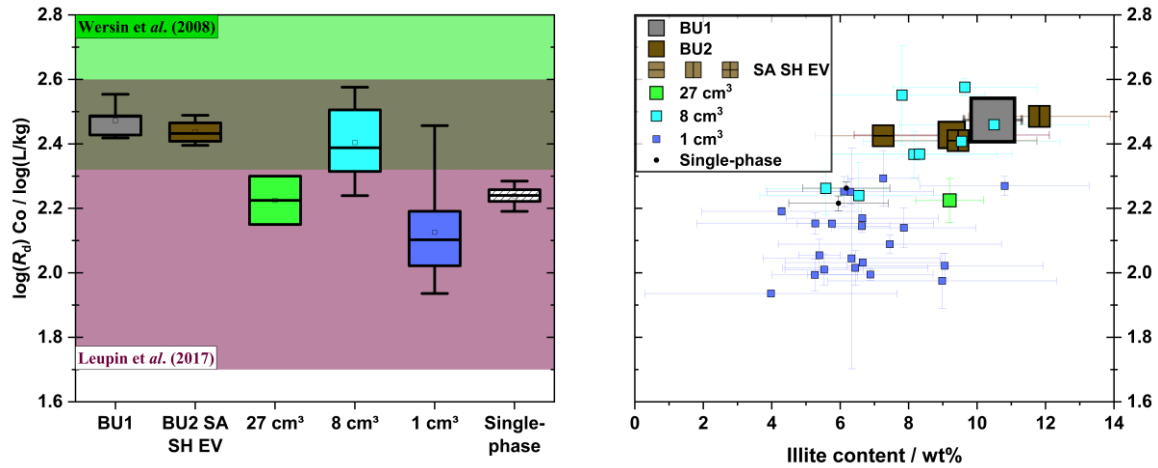


Figure 50: Results of the cobalt batch sorption experiments of BMB-A7. On the left, the distribution of the $\log(R_d)$ -values dependent on sample size as boxplots with literature data as comparison [213, 214]. On the right, the $\log(R_d)$ -values plotted against the respective illite contents.

The results of the cobalt batch sorption experiments are shown similarly to the cesium sorption in Figure 50. The $\log(R_d)$ -values gathered for the sorption of cobalt on BMB-A7 samples range from 1.9–2.6 $\log(\text{L/kg})$. The trend of higher data spread with reduced volume is also clearly visible when only taking the randomly chosen samples into account. However, in contrast to the cesium sorption, the average values deviate quite heavily from one sample volume to another. To verify the integrity of the obtained data, a literature comparison is done. In the study of Wersin *et al.* (2008) [213] (from Leupin *et al.* (2017) [214]) the measured R_d -value for their batch sorption experiment on shaly facies OPA is $2.62 \pm 0.3 \log(\text{L/kg})$. This is slightly higher than in this study, which can be explained by the differences in clay mineral content and pH in the experiment. The slightly elevated pH may lead to stronger adsorption, as it has been observed for both cobalt and nickel as a homologue in the absence of carbonate on illite [9, 215]. In the compilation of Leupin *et al.* (2017) [214] also an in-situ sorption experiment with cobalt as a tracer and the Pearson *et al.* (1998) [99] pore water as the chosen background electrolyte has been conducted. In this experiment, $\log(R_d)$ -values ranging from 1.7–2.6 $\log(\text{L/kg})$ have been observed. These are highlighted in violet in Figure 50 and span exactly the data range observed in this study.

The sorption of cobalt on OPA is also supposed to be highly influenced by the clay mineral content. Similar to the evaluation of the cesium sorption experiment, the $\log(R_d)$ -values are

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plotted against the illite contents of the respective samples on the right side of Figure 50. Again, the visually chosen sample SH and the hand-picked single-phase shaly sample show a higher affinity than their respective sandy counterpart, though to a much smaller degree than what is observed for the cesium sorption. Another similarity is the absence of a clear correlation of sorption coefficient and illite content, but a slight trend may be adumbrated.

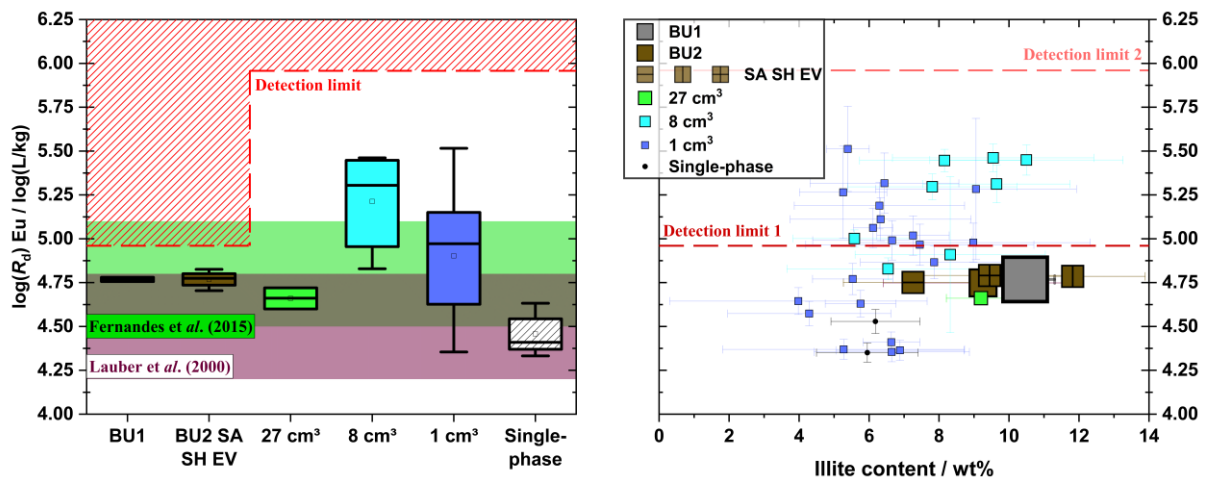


Figure 51: Results of the europium batch sorption experiments of BMB-A7. On the left, the distribution of the $\log(R_d)$ -values dependent on sample size as boxplots with literature data as comparison [38, 199]. On the right, the $\log(R_d)$ -values plotted against the respective illite contents. Detection limit 1 serves for the high-volume samples ($>27 \text{ cm}^3$) and detection limit 2 for the smaller samples.

In Figure 51, the results of the europium batch sorption are shown in the same way as the prior batch sorption experiments. A first notable difference in the graph is the integration of a detection limit. Due to the high affinity of trivalent cations towards mineral surfaces and especially clay minerals, $\geq 99\%$ of all europium remains adsorbed. This leads to very low amounts of detectable substance remaining in solution. The first experiment with BU1 and the high-volume samples ($>27 \text{ cm}^3$) have been conducted with 1 kBq/mL Eu-152, which has led to $\log(R_d)$ -values very close to the detection limit. Since here also the possibility of conducting the experiments as a cocktail has been investigated, the detection method of choice has been a γ -spectrometer (see Chapter 3.5.4). In the batch sorption experiment of the low-volume samples, a γ -counter has been used with a much longer measurement time and 2 kBq/mL Eu-152. This has led to a higher sensitivity and hence higher detection limit.

The $\log(R_d)$ -values range from 4.3–5.5 $\log(\text{L/kg})$, which at first glance looks like a big range but represents a sorption of 99.17–99.95 %. Therefore, the deviation of the $\log(R_d)$ -values does not indicate as much of a difference in sorption behavior as may be expected. The trend of

higher data spread with lower sample volume increases similarly to the cobalt sorption but the very strong adsorption and data close to the detection limit needs to be considered in this interpretation. Again, a literature review is done to compare the obtained data to previous studies. The range found by Lauber *et al.* (2000) [38] is the result of a pH variation from 6.3–8.0 with shaly facies OPA. Most of the sorption coefficients obtained in this study fit within the range of this literature report, though some of the small-volume samples exceed the upper boundary. This is contrary to the differences in pH causing only slightly elevated sorption in this pH-range and also the lower clay mineral content as mentioned for the cesium. However, as mentioned above, the changes in $\log(R_d)$ -values do not reflect a big change in sorption behavior and Lauber *et al.* (2000) [38] even consider an uncertainty of ± 0.3 log units for the strongly adsorbing tracers. In the study of Fernandes *et al.* (2015) [199] the sorption of europium on shaly facies OPA with an 2:1 clay mineral content of 47 wt% is investigated. This is again much higher than what has been found in this study with 2–14 wt% illite content. In their study, they investigated in a synthetic pore water containing carbonates at pH 7.8. Their obtained $\log(R_d)$ -values are slightly higher than those observed by Lauber *et al.* (2000) [38] and fit well to the ranges observed in this study. Plotting the $\log(R_d)$ -values against the illite content does again not yield the expected correlation. The visually specifically chosen samples do not show their characteristic sorption behavior in contrast to the other two investigated cations. The likely reasoning is the overall strong sorption and proximity to the detection limit.

All in all, the decrease in sample volume shows the expected increase in variation in the obtained $\log(R_d)$ -values for all three investigated cations. The range of sorption is comparable to literature data of the shaly facies, in spite of the lower clay mineral contents of the samples. A lack of correlation between the clay mineral content or the illite content and the R_d -values is likely due to the limited range of clay contents investigated.

Next up is the discussion on the batch sorption experiments on the cores BDR-D1 and -D2. The overall experimental procedure has been the same, but a different synthetic pore water and atmosphere have been used, as described in Chapter 3.6.3. The most noticeable differences in the composition for the batch sorption experiments will be pH, which is in comparison increased from 7.24 to 7.8, and the carbonate concentration. In this pH-range, the dependency of the sorption of cobalt and europium on pH in carbonate containing solutions is comparatively weak, so no strong deviations are expected [9, 199, 215]. At the end of this chapter, the sorption time variation mentioned in Chapter 3.6.3 will be discussed.

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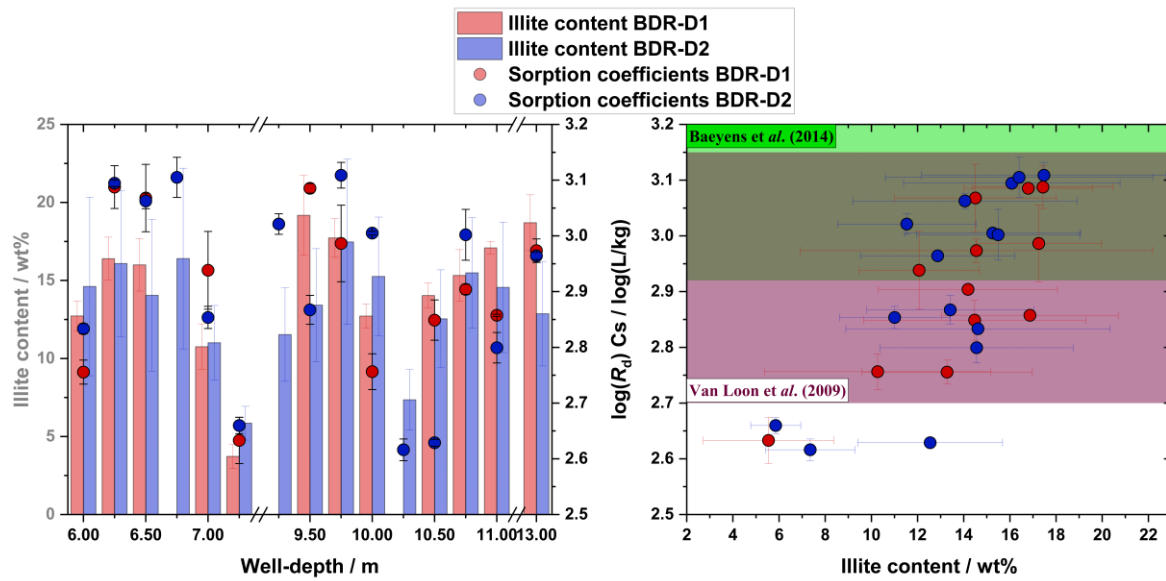


Figure 52: Results of the cesium batch sorption experiments on the drill cores BDR-D1 and -D2. The obtained $\log(R_d)$ -values are shown as circles in red for core BDR-D1 and in blue for core BDR-D2. They are shown as a function of the well-depth together with the respective illite contents on the left and correlated to the illite content on the right, with literature data as comparison [35, 216].

Figure 52 shows the results of the cesium batch sorption experiment on both BDR cores. On the left, the $\log(R_d)$ -values are plotted against the respective well-depth and on the right correlated to the illite content. The overall spread of $\log(R_d)$ -values of both cores is similar, in the range of 2.6–3.1 $\log(\text{L/kg})$. They also have the same average $\log(R_d)$ -value of $2.9 \pm 0.2 \log(\text{L/kg})$. This similarity is expected from the mineralogical composition. When comparing to the data of core BMB-A7, the respective range obtained has been 2.2–2.9 $\log(\text{L/kg})$, which is a bit lower. This difference can be attributed to the amount of clay minerals present in the respective samples, which is higher in the BDR cores on average and also led to a higher CEC.

When comparing the obtained sorption coefficients at similar well-depths, a strong correlation is observed. Both show low, medium and strong sorption at the same well-depths. Furthermore, the $\log(R_d)$ -values correlate to the clay mineral contents of the respective samples and a clear correlation of the cesium sorption to the illite content can be seen for both cores. A comparison to the before mentioned sorption data of Van Loon et al. (2009) [35] is done and shown as a purple range. The leachable cesium content has only been slightly lower from the BDR cores in comparison to the BMB-A7 core, as shown in Table 21. Since Van Loon et al. (2009) [35] have conducted an experiment taking the natural cation inventory into account, the respective $\log(R_d)$ -values for very low additional cesium present are chosen for comparison. These values agree very well with the observed sorption coefficients from this study. A comparison to the

Nagra report of Baeyens *et al.* (2014) [216] shows a similar range of R_d -values (green area). In their study, the sorption on a reference OPA is studied depending on the pore water composition. Since they assume a 2:1 clay mineral content of 33 wt%, which is again higher than what is present in both BDR cores, the lowest sorption coefficient from their study is chosen for comparison. At similar pore water conditions as the BDR cores (high carbonate content and pH of 7.5), $\log(R_d)$ -values of up to of 3.3 $\log(\text{L/kg})$ have been obtained. The higher sorption capacity is expected, since cesium sorption is dominated by the 2:1 layer clay mineral content which is 2–3 times higher in their study. To summarize, the overall observed cesium sorption is in the expected range of literature reports, and the data from both cores show a strong correlation.

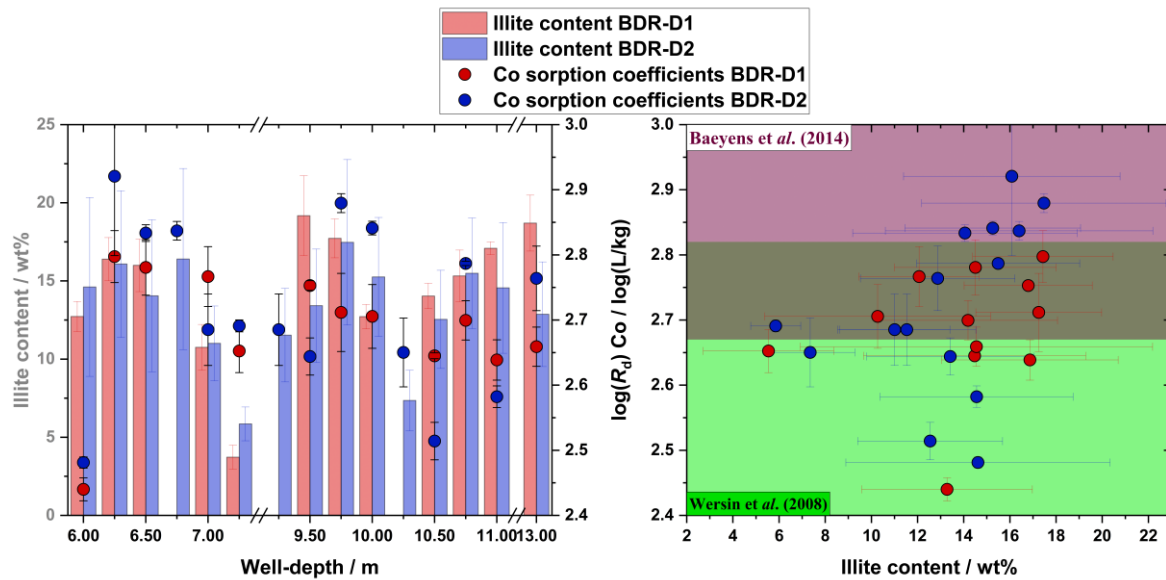


Figure 53: Results of the cobalt batch sorption experiments on the drill cores BDR-D1 and -D2. The obtained $\log(R_d)$ -values are shown as circles in red for core BDR-D1 and in blue for core BDR-D2. They are shown as a function of the well-depth together with the respective illite contents on the left and correlated to the illite content on the right, with literature data as comparison [213, 216].

Figure 53 shows the results of the cobalt batch sorption experiment on the samples of the BDR cores. The data spread of the $\log(R_d)$ -values for the cobalt sorption amounts to ≈ 0.5 log units. Both cores again have the same average sorption coefficient of $2.7 \pm 0.1 \log(\text{L/kg})$. The BMB-A7 core has shown a sorption coefficient for cobalt of 1.8–2.6 $\log(\text{L/kg})$, lower than the $\log(R_d)$ -values gathered for the BDR drill-cores. This can again be explained with reference to the clay mineral content, but also by the lower amount of competing leachable nickel present with similar amounts of iron (though no oxidation state can be specified). When looking at the well-depth profile, a similar pattern to what is observed in the cesium sorption can be seen. Both cores have a very similar sorption capacity for cobalt at comparable well-depths across

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the whole investigated area. The samples from the well-depth of 6.00 m show a lower-than-expected sorption coefficient when compared to the clay content. A correlation of the cobalt sorption with the illite content can be seen on the right side of Figure 53. The trend of increasing amount of illite causing higher R_d -values continues. A comparison of the obtained data can be drawn to the work of Baeyens *et al.* (2014) [216], who have found $\log(R_d)$ -values ranging from 2.7–3.0 $\log(\text{L/kg})$ for their reference OPA with 33 wt% illite/smectite content. These values are derived from a range of synthetic pore water compositions, being highest in a high pH (7.5) and low carbonate content pore water. Most of the obtained data falls into this reported range, with some outliers to lower sorption (6.00 m samples). The data of Wersin *et al.* (2008) [213] is already discussed in the evaluation of the BMB-A7 batch sorption experiment of cobalt and is added again to the graph as a reference. The batch sorption data fits the literature data quite well and is in the expected range. A trend of elevated cobalt sorption with increasing illite content is somewhat visible, though it is unclear whether these are two branches of correlation, or just a few outliers either at low clay content or consisting of a few low sorbing samples.

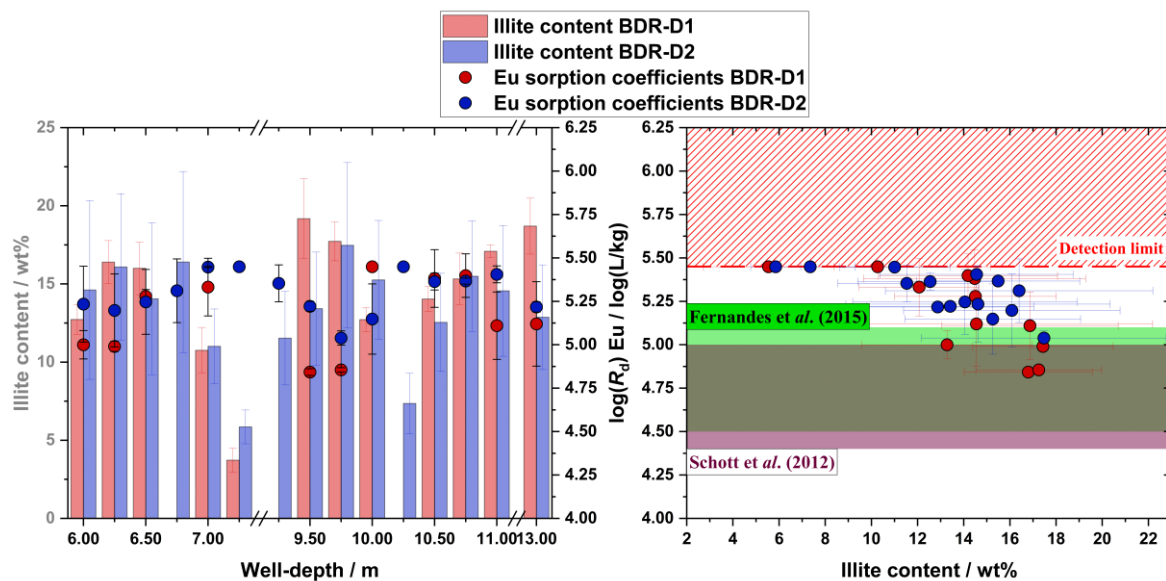


Figure 54: Results of the europium batch sorption experiments on the drill cores BDR-D1 and -D2. The obtained $\log(R_d)$ -values are shown as circles in red for core BDR-D1 and in blue for core BDR-D2. They are shown as a function of the well-depth together with the respective illite contents on the left and correlated to the illite content on the right, with literature data as comparison [199, 217].

The results of the batch sorption experiment with europium as a tracer are shown in Figure 54. The overall sorption coefficients range between 4.9–5.5 $\log(\text{L/kg})$, while all samples above the detection limit are displayed as being at the limit. The detection limit has been redetermined since the measurements of the samples from the BDR drill cores has been conducted much later than those of core BMB-A7. The differences in the limits may be caused by different amounts

of radioactive material being stored close enough to induce an elevated background. For all samples the obtained values correspond to a sorption of $\geq 99.9\%$. The average obtained $\log(R_d)$ -value is $5.2 \pm 0.3 \log(\text{L/kg})$ for both cores. While this average is higher than what is determined for the samples of core BMB-A7, these observed range is in the same order of magnitude. Again, both BDR-D cores show similar $\log(R_d)$ -values at the same well-depth, but this trend is completely disconnected from the illite content, shown on the right of Figure 54. Apparently, even an illite content of 6.0 wt% is sufficient to absorb more than 99.9 % of the added europium. Nonetheless, the obtained values are at least in the vicinity of the data of Schott *et al.* (2012) [217], who performed a temperature dependent batch sorption experiment with shaly facies OPA at pH 7.6. The displayed range is their obtained $\log(R_d)$ -value at 25 °C with an added uncertainty of $\pm 0.3 \log$ units. The data of Fernandes *et al.* (2015) [199] has already been described and also shows a slightly lower sorption in comparison. The strong proximity to the detection limit may also have an impact on the precision and accuracy of the obtained data in this study, which has to be taken into account during these comparisons.

Next up is the investigation of the sorption variation as a function of time. For the cesium sorption on the BDR cores, the reduction of the sorption time to only three days leads to a reduction of the average $\log(R_d)$ -values from $2.9 \pm 0.2 \log(\text{L/kg})$ to $2.8 \pm 0.2 \log(\text{L/kg})$, which is a negligible decrease. Increasing the sorption time to ten days shows no effect, indicating a complete sorption process. For the cobalt sorption, a decrease and increase in sorption time changes the average $\log(R_d)$ -values from $2.7 \pm 0.1 \log(\text{L/kg})$ to $2.5 \pm 0.1 \log(\text{L/kg})$, which is again only a small deviation and within the often referred to uncertainty of $\pm 0.2\text{--}0.3 \log$ units [38, 199]. Increasing the sorption time to ten days increases the average $\log(R_d)$ -values to $2.8 \pm 0.1 \log(\text{L/kg})$. This indicates the sorption process to possibly be not complete, even after 10 days, though the increase is within the uncertainty of the determination. A possible explanation is other processes taking place than pure adsorption to the mineral surfaces. Incorporation into mineral phases via slow recrystallization processes, e.g., into calcite [218] is a possibility. This will be investigated for the trivalent curium in the upcoming TRLFS experiments in Chapter 4.5. For the europium sorption, in- or decreasing the sorption time does not have an effect, which is expected due to the generally very strong sorption.

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To summarize, batch sorption experiments with cesium, cobalt and europium have been performed. Decreasing the sample volume leads to a higher spread of the obtained R_d -values. These sorption coefficients on the core BMB-A7 are within the range of literature data on the shaly facies OPA. For the sorption on the cores BDR-D1 and -D2 also comparable values are obtained. A well-depth dependent comparison of the two cores reveals a high lateral homogeneity along the bedding, with a strong heterogeneity across the bedding. The sorption time of seven days is found to be sufficient for the quantification of cesium and europium sorption, while cobalt might need longer equilibration times.

4.4 Geochemical Modeling

The aquatic speciation is a relevant parameter for the assessment of radionuclide mobility. Complexation with ligands in solution generally decreases sorption affinity, unless ternary surface complexes are formed [219]. In the presence of calcium and carbonate in solution, the uranium complexation in the neutral pH-range leads to a massive decrease in sorption strength [32, 220] on OPA. A similar behavior is observed for the europium sorption in a basic milieu ($\text{pH} > 8$) on montmorillonite [132]. Since pore waters include complexing ions like carbonate, sulfate, chloride and hydroxide, the aqueous speciation of the three investigated cations is relevant for the interpretation of batch sorption data, as already pointed out in Chapter 2. To assess the aquatic complexation in the deployed synthetic pore waters, speciation calculations are performed using PhreeqC. As the background electrolyte composition, the pore water composition after seven days of equilibration is used. Figure 55 shows the results of these calculations for the BMB-A7 experiments in the top row and for the BDR experiments in the bottom row for cesium, cobalt and europium, from left to right.

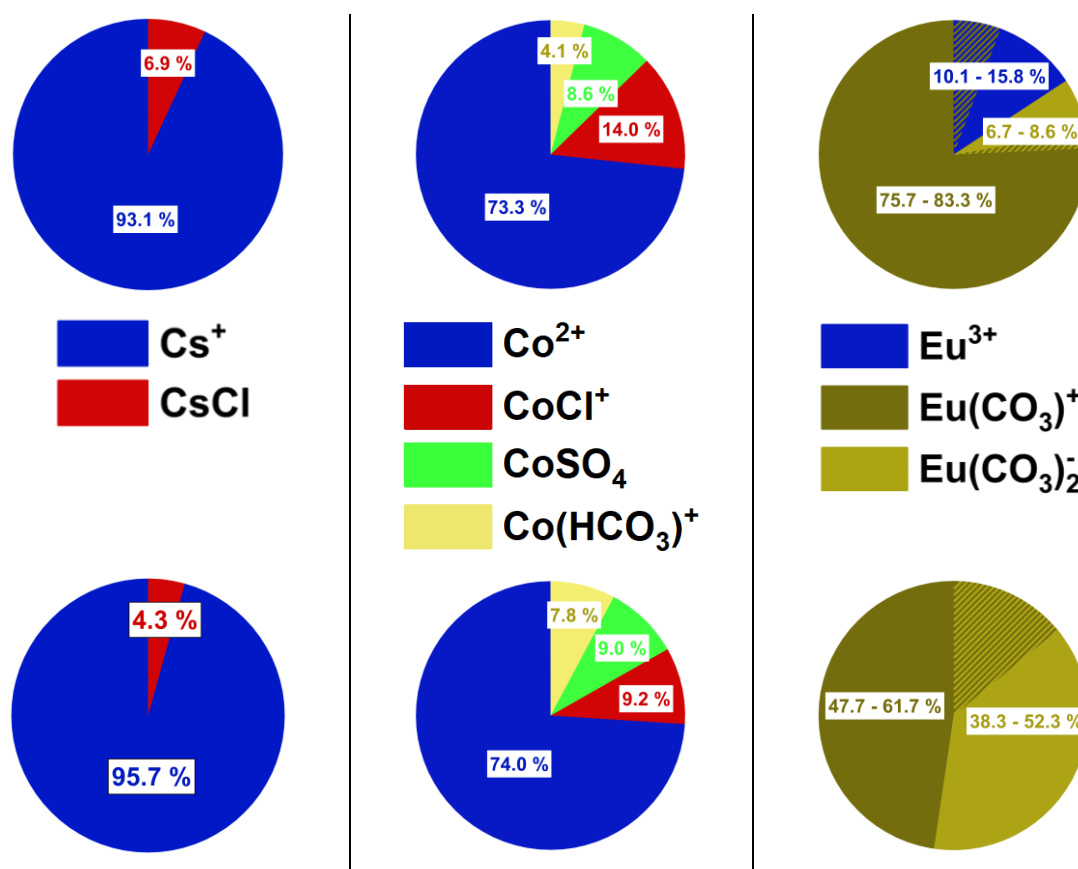


Figure 55: Expected aquatic speciation of cesium, cobalt and europium (from left to right) in the synthetic pore waters of the batch sorption experiments. Top row shows the speciation in the BMB-A7 batch sorption experiments and bottom row the BDR-D1 and -D2 batch sorption experiments. The shaded areas indicate the impact of a pH variation from 7.0–7.5 in the case of the BMB-A7 speciation and from 7.5–8.0 in case of the BDR-D speciation.

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To better estimate the impact of possible pH-variations due to carbonate equilibria and other phase dissolutions, pH is varied in this modeling procedure. For the top row, the variation is done from pH 7.0–7.5 and for the bottom row between 7.5–8.0. As shown in Figure 11 for cesium and Figure 12 for cobalt, their speciation is relatively pH independent in the investigated circumneutral pH-range. For europium, this pH variation causes the ranges displayed shaded in Figure 55, as expected from Figure 13. The speciation in both pore waters is very similar for cesium and cobalt. For europium, pH variations have a much bigger effect and stronger differences are observable.

Since no batch sorption data is present of the three investigated cations on the sandy facies OPA, geochemical modeling can be used to validate the obtained sorption data. The used set of adsorption constants and thermodynamic data is shown in Chapter 3.7 and a detailed input file in Appendix A. For an estimation on the theoretical sorption coefficients, a ± 0.3 log unit band is added around the obtained $\log(R_d)$ -values to account for experimental and modeling uncertainties of the surface complexation data [38, 199]. Firstly, the sorption of cesium is calculated and the results are shown in Figure 56.

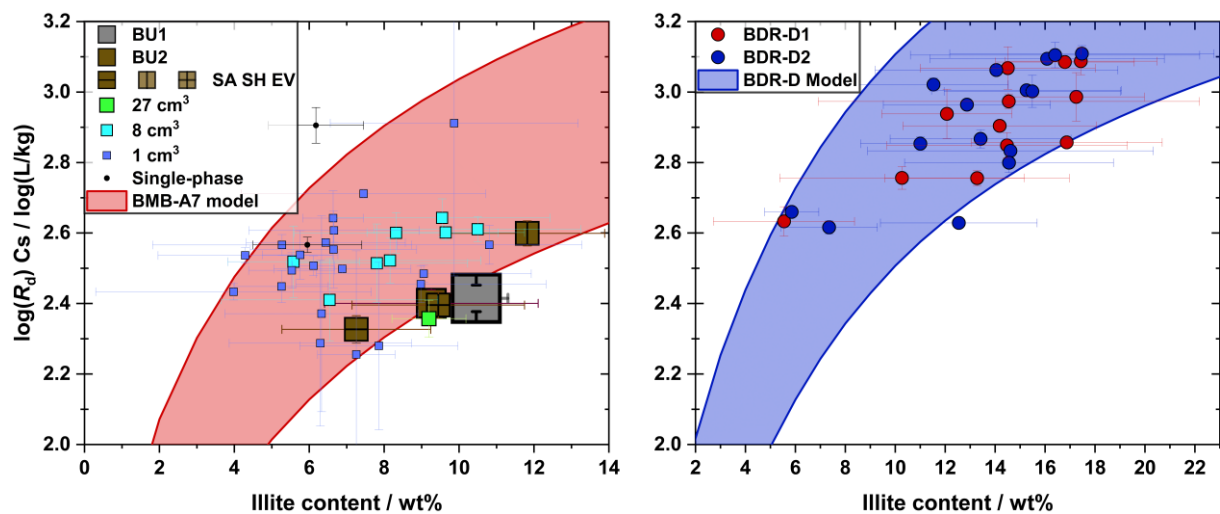


Figure 56: Results of the geochemical modeling of the cesium sorption depending on the illite content under the conditions of the batch sorption experiment on core BMB-A7 (left) and BDR-D1 and -D2 (right), shown in comparison to laboratory results.

On the left, the model for the samples of core BMB-A7 and on the right the model for the samples of the BDR drill cores are shown. While the curve starts out comparatively steep, flattening is observed already at low illite contents (≈ 8 wt% for the BMB-A7 model and ≈ 10 wt% for the BDR model). Only minor differences are observable between the two models. This is expected since the main differences in composition of the synthetic pore waters are pH and carbonate content, both of which do not impact the speciation of cesium (see Figure 11)

and only have a minor impact on the loading of exchange sites. The main parameter influencing cesium uptake is the concentration of the competing potassium, which is also very similar in both synthetic pore waters. With a bandwidth of ± 0.3 log units, almost the entire dataset is covered. The model therefore fits the experimental data very well, especially when the uncertainties of measurements are taken into account. The absent trend in the batch sorption data can now be explained by the low variation in illite content, as well as with the uncertainties in the determination of the illite content. Bradbury and Baeyens (2003) [221] have mentioned, that when switching from modeling illite to natural argillaceous rock systems, an uncertainty of a factor of 2–3 can be assumed for cesium concentrations lower than 10^{-3} mol/L. This would translate to an uncertainty of ± 0.48 log(L/kg), covering the whole dataset.

The models for the cobalt batch sorption are shown in Figure 57 for the BMB-A7 samples on the left and for the BDR samples on the right, together with the experimentally obtained data. A clear impact of the different conditions in the systems is visible, causing a higher adsorption in the BDR model. The impact of ion exchange sites is negligible under the conditions present for both clay rock systems and only the sorption sites influence the uptake (this is also true for the europium sorption). The exchange sites only impact the sorption behavior at very low illite contents (≈ 1 wt%). Of the competing ions, the main influence is exerted by nickel and to a smaller extend by rubidium. The influence of iron is tested by adding the respective thermodynamic data for the adsorption on montmorillonite by Soltermann *et al.* (2014) [210]. Since this impact is negligible, it has been discarded in the final version of the modeling files.

Most of the laboratory obtained data fits well within the modeled bandwidths, especially taking the relative uncertainties into account. The consistency between experimental and calculated data suggests illite (or clay minerals in general) to be indeed the primary sorbents for cobalt. However, some outliers in the BMB-A7 system show a slightly stronger adsorption than expected. A slight correlation of the obtained $\log(R_d)$ -values of the deviating samples with the calcite content is considered. The sample deviating the strongest (SA) has the highest calcite content. This may suggest calcite also playing a subordinate role in the uptake of cobalt. Cobalt fits well into the calcite structure [218, 222], which makes calcite a possible candidate for further uptake by recrystallization. Also, very small deviations from the target pH have a comparatively strong effect. When altering pH from 7.24 to 7.34 (which is the established uncertainty of pH measurement in this study), the outliers are encompassed by the sorption band (not shown). In the BDR system, the same minor correlation with calcite content is observable. The three samples with the lowest illite contents and the most amount of calcite

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contents (36.8–65.2 wt%) show an adsorption near the upper limit of the sorption band. Overall, the model fits the experimental data well and validates illite or clay minerals to be the primary relevant sorption phases.

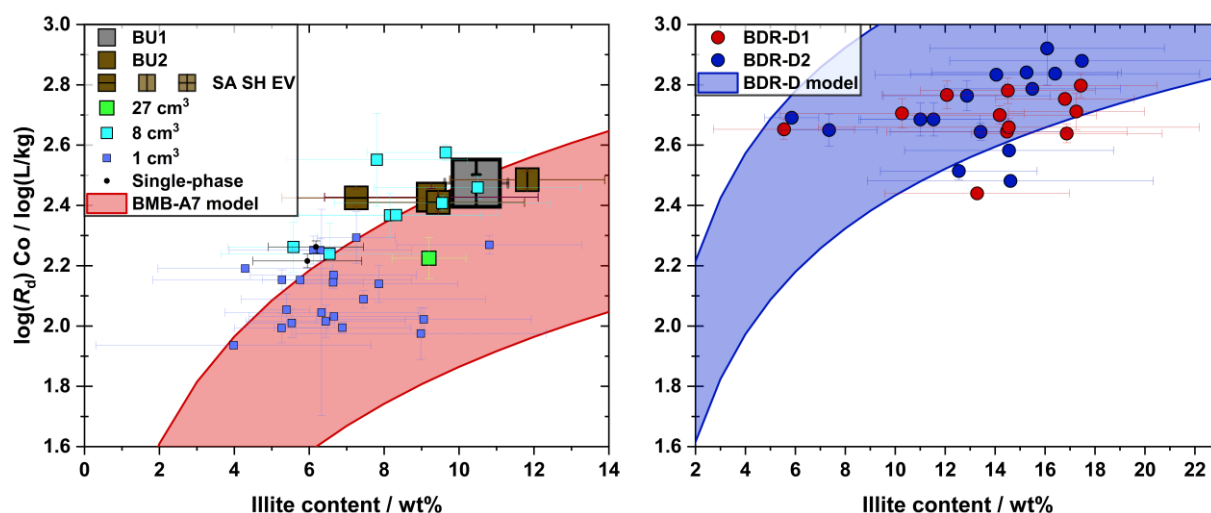


Figure 57: Results of the geochemical modeling of the cobalt sorption depending on the illite content under the conditions of the batch sorption experiment on core BMB-A7 (left) and BDR-D1 and -D2 (right), shown in comparison to laboratory results.

The modeling fits for the batch sorption experiments of europium are shown in Figure 58. The amount of europium adsorbed on OPA exceeds 99.8 %, meaning that seemingly large differences in the obtained $\log(R_d)$ -values should not be overrated. Both models underestimate the obtained $\log(R_d)$ -values from the laboratory experiment by up to one order of magnitude, but both experiment and model agree that a very strong sorption is taking place. Considering the uncertainty in the determination of the laboratory data and their proximity to the detection limit, this is an adequate representation. On the other hand, other clay mineral phases, may need to be considered for europium uptake. Calcite, like already discussed for the cobalt sorption, might also play a role in the europium sorption [123]. To test this hypothesis, laser spectroscopic investigations on curium, as a chemical analogue to the trivalent europium, are performed and discussed in Chapter 4.5.

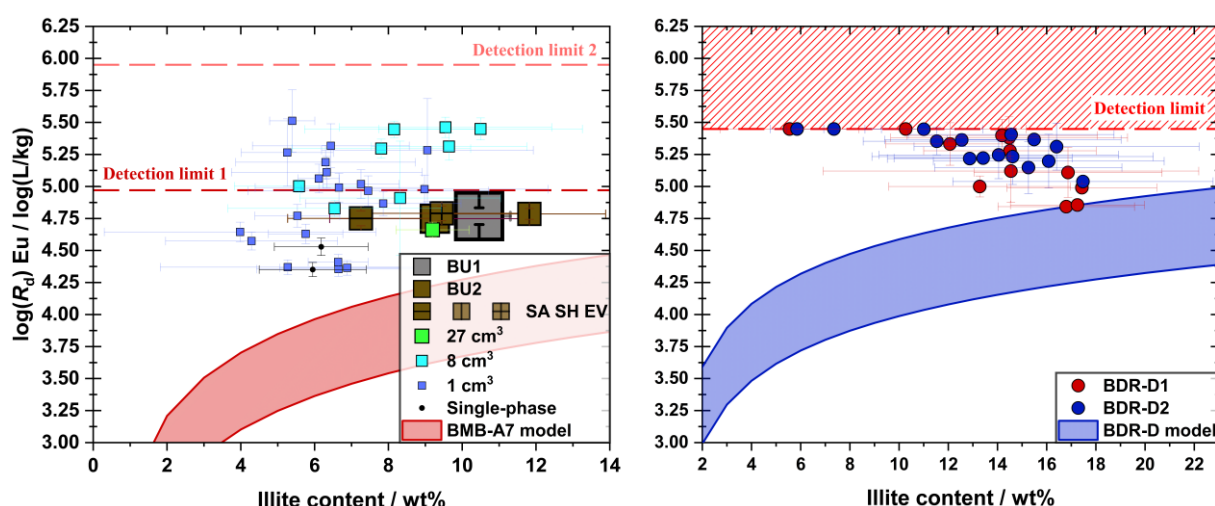


Figure 58: Results of the geochemical modeling of the europium sorption depending on the illite content under the conditions of the batch sorption experiment on core BMB-A7 (left) and BDR-D1 and -D2 (right), shown in comparison to laboratory results. Detection limit 1 serves for the high-volume samples ($>27 \text{ cm}^3$) and detection limit 2 for the small samples.

Besides these assumptions, efforts are made to further investigate the deviation of the modeling fits to the obtained experimental data in the europium modeling. To identify the impact of the inherent pH uncertainty, a slight pH variation is performed. In both systems, increasing pH by 0.1 units leads to marginally higher $\log(R_a)$ -values, but not to the extent of the observed differences. Stronger fluctuations in pH lead to the opposite effect, reducing the sorption taking place. This is similar to what is observed in Fernandes *et al.* (2015) [199], who have also seen a decreasing sorption of europium in a carbonate containing system on illite above pH 7.8.

The next approach has been a variation of the equilibrium constants of the ternary sorption species. This is similar to what has been done by Patel *et al.* (2017) [223], who adjusted the $\log k$ of the ternary carbonate surface complex up to 11.5 to fit their obtained data. An adjustment might even fit better to the experimental data of Fernandes *et al.* (2015) [199], whose model slightly underpredicts their experimentally determined sorption above pH 8. The best fit for the obtained experimental data from this study would be an adjustment of the $\log k$ values for the formation of the $>\text{S}^{\text{S}}\text{OEuCO}_3$ complex from 9.8 to 10.3. This would, however, vastly overcorrect the data obtained by Fernandes *et al.* (2015) [199], especially around pH 8. This approach is therefore not investigated further.

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To summarize, the modeling adds another perspective to the batch sorption data. The results of the geochemical calculations show that experimental sorption data obtained within this thesis are consistent with existing surface complexation data assuming that illite is the primary sorbent phase. This does not exclude that other mineral phases, such as calcite, could also play a role. The general assessment for the cesium speciation to be pH independent, for the cobalt speciation to be slightly pH dependent and for the europium speciation to be highly pH dependent is confirmed by the scoping calculations on the aqueous speciation. The modeling approach of the experimental batch sorption data is a success for cesium and cobalt. For europium, the model underestimates the experimental data. This is an indication that other mineral phases might also need to be considered for a precise sorption assessment, or that the $\log(R_d)$ are afflicted with a stronger than expected uncertainty, due to the proximity to the detection limit.

4.5 Laser Spectroscopy

To shed light onto the assumptions made in the evaluation of the modeling for europium, TRLFS experiments are conducted. The goal here is to gain additional information on the aquatic speciation of trivalent cations in the synthetic pore water composed for sandy facies OPA, as well as to identify the phases relevant for sorption and to enhance the understanding of these processes. Efforts are made to perform peak deconvolutions and lifetime evaluations and compare the obtained results to established literature data. All the plots used for the lifetime evaluation can be found in Appendix D.

A spectroscopic evaluation of curium in a 1 mol/L HClO_4 solution and in the synthetic pore water is done to validate the estimated speciation from the modeling procedure shown in Figure 55. This has suggested a pH dependent mixture of the mono- and dicarbonato complexes with small amounts of the aquatic Cm^{3+} species coordinated with water molecules. Figure 59 shows the results of the spectroscopic investigation of curium in the synthetic pore water.

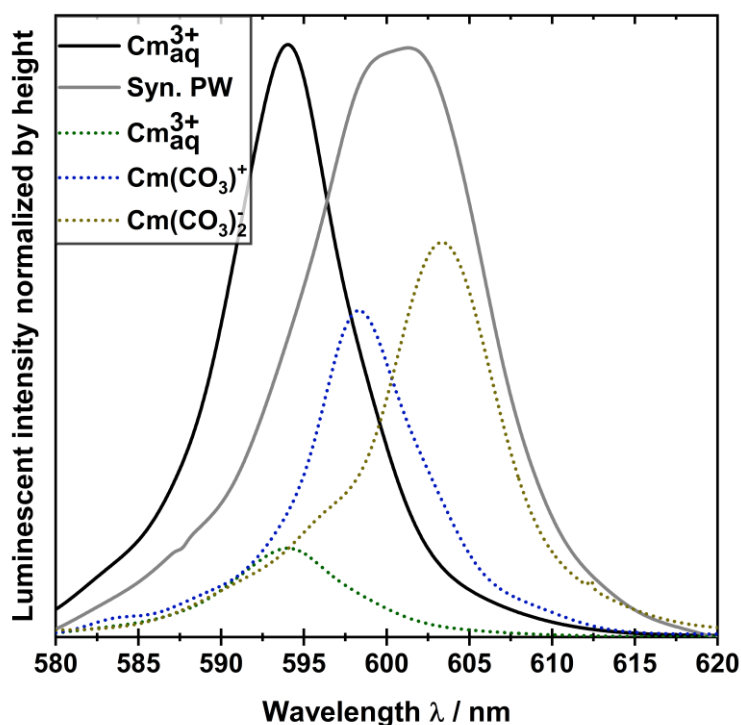


Figure 59: Spectrum of the Cm^{3+} aquo ion under acidic conditions in black as a comparison to the spectrum in synthetic carbonate pore water in grey. A peak deconvolution is shown in dotted lines, with the single spectra taken from Fanghänel et al. (1998) [224].

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The spectrum of the Cm^{3+} aquo ion is shown in black, with the emission maximum at a wavelength of 593.8 nm and exhibiting a lifetime of $67 \pm 1 \mu\text{s}$, which is both expected from literature [186]. Looking at the spectrum emitted in the synthetic pore water, a clear bathochromic shift is visible. The maximum shifts to 601 nm and the peak shape broadens, indicating multiple overlapping species being present. A peak deconvolution is performed, using the single species spectra from Fanghänel et al. (1998) [224] for the mono- and dicarbonato complexes. During the data conversion, their obtained spectra have had to be smoothened to fit to the spectra from this study, but the main features remain unchanged. The porewater spectrum can be roughly estimated to be a mixture of the two carbonate complexes with some minor contribution of the aquo ion. Fanghänel et al. (1998) [224] report the fluorescence lifetime of curium carbonate complexes to decay monoexponentially with around 70–90 μs , depending on pH and carbonate content present. In the work of Kim et al. (1994) [50] these lifetimes have been observed to be $85 \pm 4 \mu\text{s}$ and $105 \pm 5 \mu\text{s}$ for the mono- and dicarbonato complexes, but with the same proposed peak positions of around 598.0 nm and 605.9 nm, respectively. In this study, a monoexponential decay with $\tau = 80 \pm 5 \mu\text{s}$ is observed. The monoexponential decay indicates a very fast ligand exchange, as it has been reported by Fanghänel et al. (1998) [224]. The observed lifetime fits in the middle of the literature reported data for the mono- and dicarbonato complexes and translates into ≈ 6 water molecules still being present in the inner coordination sphere of curium (see Equation 15). Assuming the bidental carbonate complexes each replacing two water molecules from the initial eight to nine, six water molecules left concludes a mixture of one and two complexing anions. The obtained peak deconvolution fits quite well and is also in agreement with the modeling data, suggesting a mixture of the two complexes with small amounts of the Cm^{3+} aquo ion.

In the following, TRLFS spectra are recorded for curium in interaction with OPA and compared to respective spectra of curium sorbed onto individual mineral phases being constituents of natural OPA. Furthermore, the sorption behavior after different sorption times is investigated to identify possible slower processes (e.g., incorporation processes). The first investigated mineral phases are two of the most abundant non-clay constituents of the sandy facies, quartz and orthoclase (as a representative of the feldspars). The spectra after 1 day and after 30 days of sorption on quartz are shown in Figure 60.

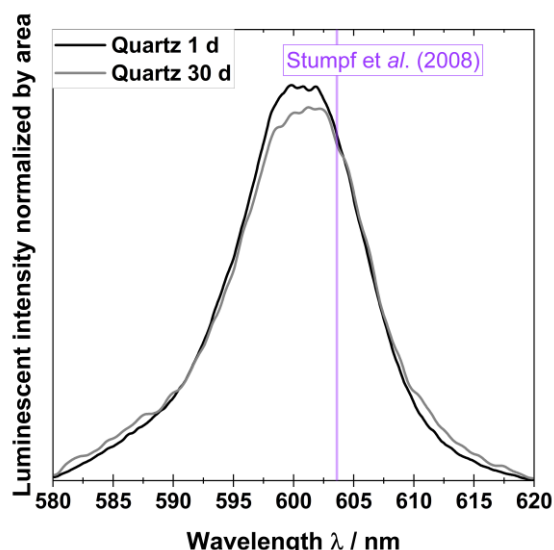


Figure 60: TRLFS spectra of Cm^{3+} in contact with quartz after 1 day (black) and 30 days (grey) of sorption time in the synthetic pore water. Literature reference added in purple as a comparison [225].

Origin	Central λ / nm	Lifetime τ / μs
This study 1 d	601.0	85 ± 5
This study 1 d	≈ 602.5	204 ± 70
This study 30 d	601.5	91 ± 10
This study 30 d	≈ 602.5	252 ± 25
Reference [225]	603.6	123 ± 10

Spectra obtained after 1 day and 30 days of sorption time look very similar. The main peak positions are identical to the peak position of the pore water spectrum. However, the peak shapes seem to differ and look slimmer with a smaller FWHM (full width at half maximum) than what has been previously observed in the pure pore water spectrum. Stumpf et al. (2008) [225] have investigated Cm^{3+} adsorption onto quartz under carbonate free conditions in a sorption edge experiment (pH-variation). In the pH region investigated in the present study, they observed a prevailing surface sorption species with an emission wavelength at 603.6 nm. It can thus be excluded, that the observed species in this study corresponds to this curium-quartz surface complex. A biexponential lifetime decay is observed after both sorption times with none of the lifetimes matching the literature report. The first lower lifetime fits to the aquatic carbonate complexes and the fluorescent shift matches as well. A peak deconvolution is performed by subtracting the obtained synthetic pore water spectrum, revealing no other species being present. A spectrum which may correspond to the second observed lifetime only becomes visible after a delay of $>300 \mu\text{s}$, at which the spectra's quality diminishes greatly through the reduced intensity. The final peak position of the second species can therefore not be determined and is only very roughly estimated. The longer lifetime in comparison to Stumpf et al. (2008) [225] indicates more water molecules being replaced in the inner coordination sphere of curium. According to Equation 15, a lifetime of 200–250 μs suggests ≈ 2 water molecules remaining. This can either be caused by a stronger sorption site in comparison, like a kink or vacancy site, by further complexation of the sorption species or by a very strong complex. In the review of Geckeis et al. (2013) [39], a multitude of sorption investigations of Cm^{3+} onto minerals are listed. The average lifetime of sorption species onto minerals present in OPA is $\approx 110 \mu\text{s}$, rarely

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deviating by more than 15 μ s. This leads to the conclusion that the sorption process displaces four of the eight to nine coordinated water molecules in a carbonate free system. Only having two water molecules left therefore indicates a coordination with non-quenching anions, exchanging two to three more water molecules. This could be caused by complexation with a carbonate ligand and possibly another hydroxyl ligand. The existence of an europium surface sorption species coordinated by carbonates has been postulated by Fernandes *et al.* (2008) [132] on montmorillonite, (2010) on γ -Al₂O₃ and kaolinite [226] and (2015) [199] on illite. In Fernandes *et al.* (2016) [115] they have proven the existence of such a surface complex via TRLFS and EXAFS (extended X-ray absorption fine structure) on montmorillonite. Furthermore, they have tried the formation of $>S^SOEu(CO_3)_2^{2-}$ and $>S^SOEu(CO_3)_3^{4-}$ surface complexes in their models to describe their observed sorption behavior [132]. The postulation of a surface adsorbed carbonate complexed curium species onto quartz does not seem a far stretch. Since Fernandes *et al.* (2016) [115] also did TRLFS investigation, a rough lifetime comparison can also be made. In their study from 2016 [115] they have investigated the curium sorption onto montmorillonite in absence and presence of carbonate. Besides a bathochromic shift from 602.4 nm to 604.6 nm, they have observed an increase in lifetime from $117 \pm 5 \mu$ s to a biexponential progression of $133 \pm 5 \mu$ s and $380 \pm 12 \mu$ s. This increase in lifetime is similar to what is observed in this study on quartz, further hinting at a ternary surface sorption species. On the other hand, possible recrystallization processes cannot be excluded and mineral alteration is a possibility. Though the cuvette has been sealed during the measurement, the preparation of the sample has been performed under ambient conditions. Still, equilibrium with atmospheric carbon dioxide is unlikely. Crystal incorporation would also lead to a redshift and strong increase in lifetime, but is unlikely on quartz. Complexation with dissolved silica is another possibility, which might cause the observed redshift and longer lifetime. An elevated silicon content has already been reported for the equilibration experiment, caused by mineral dissolution (see Table 21). The overall low contribution of the possible sorption species may be explained by the lower exhibited fluorescence intensity (FI), which is significantly lower for sorbed species in comparison to aquatic complexes. Nevertheless, it can be concluded that only very minor amounts (if any) are adsorbed on the quartz surface.

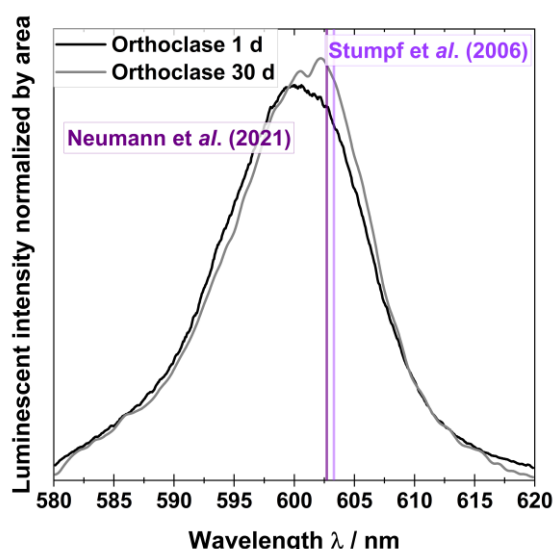


Figure 61: TRLFS spectra of Cm^{3+} in contact with orthoclase after 1 day (black) and 30 days (grey) of sorption time in the synthetic pore water. Literature references added in different shades of purple for comparison [227, 228]

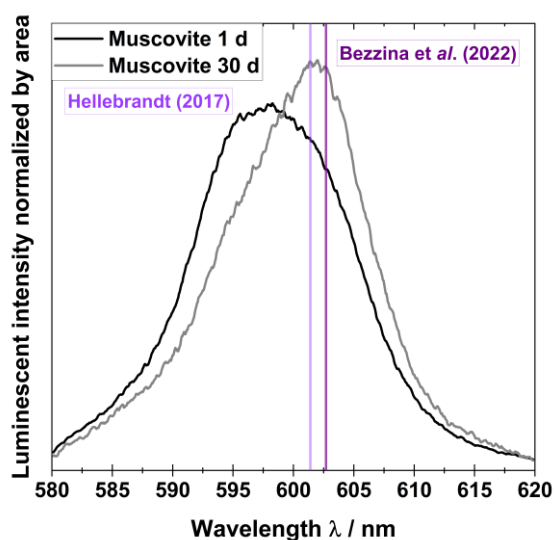
The investigation of the sorption onto orthoclase is shown in Figure 61. After 1 day of sorption time no difference to the pore water spectrum is visible. After 30 days of sorption, a small additional peak with a very slight red shift is observable. Stumpf et al. (2006) [227] and Neumann et al. (2021) [228] investigated the sorption of Cm^{3+} onto orthoclase in a carbonate free system as a sorption edge. They each found a surface sorption species at pH comparable to this study at 603.3 nm and 602.7 nm, respectively. These are a little further shifted than what is observed in this study after 30 days.

A peak deconvolution with the pore water spectrum reveals no other species contributing significantly. The fluorescence decay is biexponential with the first lifetime being similar to the aquatic carbonate complexes. It can therefore be concluded, that most of the detectable curium is present as aquatic carbonate complexes. With increasing delay time, spectra with a maximum at ≈ 604 nm remain, though in poor quality for both sorption samples. The species exhibiting the longer lifetime is slightly more prominent after 30 days of sorption time. The corresponding longer lifetime suggests only one or two water molecules being coordinated in the inner sphere, according to Equation 15. Considering the shift of the peak maximum, this could also indicate ternary surface sorption complexes with carbonate on the orthoclase mineral surface. However, mineral alteration and minor incorporation processes over time cannot be excluded. The small proportion of surface species being seen in the TRLFS spectrum can again be explained by the FI factor. However, again only a very low (if any) amount of curium is observed to be adsorbed.

Origin	Central λ / nm	Lifetime τ / μs
This study 1 d	601.0	94 ± 10
This study 1 d	≈ 604.0	422 ± 30
This study 30 d	602.1	100 ± 20
This study 30 d	≈ 604.0	476 ± 70
Reference [227]	603.3	107 ± 3
Reference [228]	602.7	-

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Muscovite is of special interest since it shares the exact same peak positions as illite in the XRD and the two can therefore not be resolved easily. The amount of muscovite present has been neglected in the XRD analysis of this study, and the low $^{\circ}2\theta$ reflex in the XRD has been fully assigned to illite in the previous chapters. Figure 62 shows the obtained TRLFS spectra of muscovite.



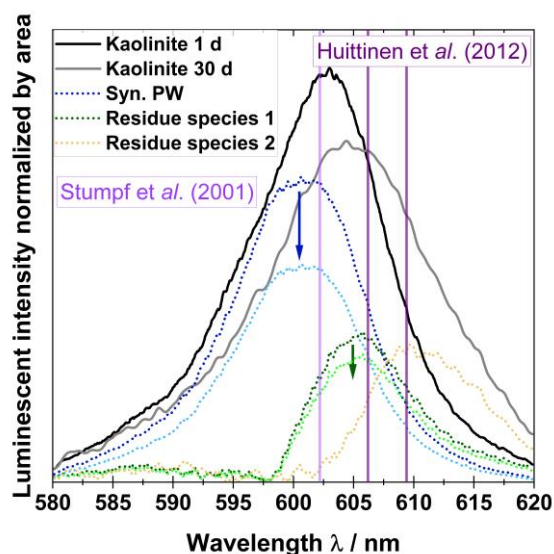
Origin	Central λ / nm	Lifetime τ / μ s
This study 1 d	598.1	102 ± 10
This study 1 d	≈ 604.5	312 ± 35
This study 30 d	601.2	96 ± 10
This study 30 d	≈ 604.5	353 ± 70
Reference [229]	601.4	-
Reference [230]	602.7	-

Figure 62: TRLFS spectrum of Cm^{3+} in contact with muscovite after 1 day (black) and 30 days (grey) of sorption time in the synthetic pore water. Literature references added in different shades of purple as a comparison [229, 230].

After 1 day of sorption time, the spectrum shows a slight hypsochromic shift in comparison to the spectrum derived from the synthetic pore water, with a very minor shoulder to the right at 605.0 nm. After 30 days of sorption time a clear red shift is visible in comparison. Hellebrandt (2017) [229] and Bezzina et al. (2022) have studied curium sorption on muscovite spectroscopically in carbonate free systems. They found multiple pH dependent species, with the ones found under comparable conditions to this study shown for comparison. Both literature reports couldn't identify lifetimes due to the quality of the spectra, caused by the inherent iron content of muscovite.

In contrast, in this study a biexponential lifetime decay can be observed. The relatively short first lifetime in addition to the peak position suggest the aquatic carbonate complexes to be dominant after both sorption times. A peak deconvolution shows no other species present than aquatic carbonate complexes with a small amount of aquo ion; less after 30 days of sorption time. The differences in the spectra can be explained by a different ratio of the aquo ion and the two carbonate complexes. However, literature data shows maximum peak positions at the same region as the mixture of the mono- and dicarbonato complexes. Since no lifetimes have been obtained, the spectrum could contain surface sorbed curium species. The species exhibiting the

longer lifetime is only observable at long delay times of $>350 \mu\text{s}$, at which it is only visible in very poor quality. The emission maximum can be roughly estimated to be at 604–605 nm, but definitely at a longer wavelength than the literature reported species. This species may be assigned to a ternary curium carbonate surface complex, which would explain both the bathochrome shift and the longer lifetime. Mineral alteration and incorporation would likely cause the curium emission to be extinguished, due to the iron content of muscovite. However, the aquatic complexes still dominate the speciation by a large amount.



Origin	Central λ / nm	Lifetime τ / μs
This study 1 d	601.1	94 ± 10
This study 1 d	605.8	282 ± 70
This study 30 d	601.1	100 ± 10
This study 30 d	605.8	339 ± 30
This study 30 d	610.1	-
Reference [49]	603.3	110 ± 7
Reference [231]	606.2	116 ± 13
Reference [231]	609.4	132 ± 5

Figure 63: TRLFS spectrum of Cm^{3+} in contact with kaolinite after 1 day (black) and 30 days (grey) of sorption time in the synthetic pore water. Literature references [49, 231] added in shades of purple as comparison and peak deconvolution in blue for the aquatic carbonate complexes and different shades of green and yellow for all further species. Dark colors indicate the deconvolution after 1 day and bright colors after 30 days of sorption time.

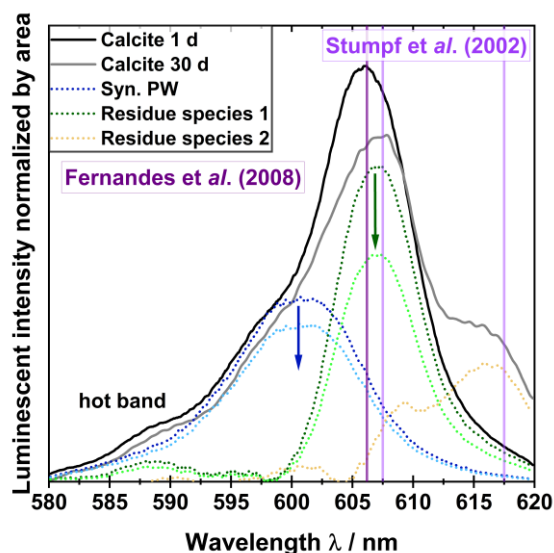
An investigation of kaolinite, which is a natural weathering product of muscovite, might yield similar results to muscovite due to their similar composition. The obtained emission spectra are shown in Figure 63. Compared to the previously investigated minerals, both obtained spectra show a clear bathochromic shift, with the longer sorption time causing a further shift. Also, the FWHM is much broader in comparison.

Stumpf et al. (2001) [49] and Huittinen et al. (2012) [231] have investigated the sorption of curium on kaolinite in a carbonate free system. Of the multiple sorption species they found, only the species highlighted by Stumpf et al. (2001) [49] matches pH in this study. The species shown for reference by Huittinen et al. (2012) [231] have only been observed at $\text{pH} > 9.5$. Fernandes et al. (2010) [226] have already investigated the impact of carbonate on the sorption of curium on kaolinite at $\text{pH} 8.4$. They have found an emission peak shift to $\approx 606 \text{ nm}$ with an increased lifetime of $490 \pm 27 \mu\text{s}$ and attributed it to a ternary carbonate surface sorption

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species. Their displayed emission spectrum still exhibits an above average FWHM, possibly indicating another underlying species being present. The structural iron present in kaolinite makes a precise lifetime assessment of surface adsorbed species difficult, due to static quenching.

A peak deconvolution is performed, again subtracting the aquatic carbonate species to compare the species present in this study to the literature references. The residues are shown in brown and green. After 1 day of sorption time, a single species remains with a longer lifetime. It has to be noted, due to the worsening of the signal-to-noise ratio at elevated delay times, the observed longer lifetimes possibly underestimate the actual lifetimes (see Appendix D). The emission maximum matches what has been observed by Fernandes *et al.* (2010) [226], as does the prolonged lifetime. Therefore, the species 1 (brown) is likely a similar ternary surface sorption species. After 30 days of sorption time, a much broader residue is observed, which is again deconvoluted with species 1. This left the broad green residue of species 2. This species shows an even further bathochromic shift of the emission maximum and an elevated lifetime. From the FWHM, it is likely not a single species but a combination of multiple species. Unfortunately, only a biexponential decay of the lifetime is observable, which cannot be attributed to a single species besides the aquatic carbonate complexes. A possible explanation is the presence of a further complexed surface sorption species with silica, derived from minor mineral dissolution. This is also the explanation for observed species by Huittinen *et al.* (2012) [231] with an emission maximum at ≈ 610 nm. Kaolinite shows a much stronger sorption compared to the previously examined minerals. The aquatic carbonate complexes are still clearly visible due to their higher FI factor. Likely a ternary surface sorption species is observed and an even further red shifted species is visible, which may be an incorporation species or a silica complex.



Origin	Central λ / nm	Lifetime τ / μ s
This study 1 d	601.0	104 ± 25
This study 1 d	607.2	367 ± 30
This study 30 d	601.0	101 ± 30
This study 30 d	607.2	377 ± 30
This study 30 d	≈ 616	1542 ± 100
Reference [196]	607.5	314 ± 6
Reference [196]	618.0	1302 ± 75
Reference [47]	606.2	386 ± 40
Reference [47]	620.3	1874 ± 200

Figure 64: TRLFS spectra of Cm^{3+} in contact with calcite after 1 day (black) and 30 days (grey) of sorption time in the synthetic pore water. Literature references [47, 196] added in shades of purple as comparison and a peak deconvolution in blue for the aquatic carbonate complexes and different shades of green and yellow for all further species. Dark colors indicate the deconvolution after 1 day and bright colors after 30 days of sorption time.

The next investigated mineral is calcite, which is also very abundant in OPA. Figure 64 shows the spectra obtained for Cm^{3+} sorption onto calcium carbonate as a homologue of natural calcite. In the description of the experimental procedure in Chapter 3.6.4, the execution of an experiment with ground and unground calcite has been explained. These yield the exact same results, so the unground calcite is not mentioned further. After 1 day of sorption time, a much stronger bathochromic shift is observable in comparison to the previous minerals. Two shoulders to the lower wavelength area are visible, whereby the lower is most likely a hot band caused by a strong ligand field. After 30 days of sorption time, the main peak position shifts even further with an additional shoulder to the right.

Literature reports show surface adsorbed Cm^{3+} onto calcite only at shifts above 606 nm [47, 196, 232]. In the spectra of Stumpf et al. (2002) [196] and Fernandes et al. (2008) [47], the peak maximum is reported at a similar wavelength as observed in this study and a shoulder at around 601 nm is also visible, though it is not discussed. They have investigated the sorption and incorporation of curium on and into calcite. Schmidt et al. (2008) [232] have investigated the incorporation of Cm^{3+} into a calcite solid-solution, embedding Cm^{3+} into the calcite structure during the precipitation. They have found lifetimes for the species described in this study of 1450 μ s at a wavelength of 616.8 nm, but have also identified a fully incorporated curium species with a bathochromic shift up to 624.24 nm and an even longer lifetime of up to 4608 μ s. The effect of increasing amount of incorporated Cm^{3+} into the calcite structure with

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increasing time is also found in the study of Stumpf *et al.* (2002) [196], who have observed this effect for up to 6 months with a steady increase of the incorporated species.

A peak deconvolution reveals the residue of species 1, likely a surface sorption species with the same peak maximum at ≈ 607 nm and lifetime of ≈ 370 μ s as reported in the literature. In comparison to the sorption species found in the prior investigations on other mineral surfaces, the additional coordination with carbonate seems very likely. This would explain only 1–2 water molecules being left in the inner coordination sphere according to Equation 15. Carbonates are omnipresent in calcite sorption studies due to dissolution processes and are often added to the background electrolyte to stabilize calcite. After 30 days of sorption time, the deconvolution yields a much broader residue. This is again deconvoluted with the residue of species 1, revealing the spectrum of species 2. This spectrum still has traces of species 1 left, hinting at the spectrum of species 1 not being that of a single species, but a superposition of multiple species. Ignoring these traces to the left, the peak maximum can be assigned to ≈ 616 nm. This is in accordance with literature reported data for a curium species incorporated into the calcite structure and also exhibits a similar lifetime. Summarizing for calcite, some amounts of aquatic species are still observable, but to a much smaller extent. Most of the curium is sorbed on the calcite surface, which is in accordance with literature data. After 30 days of sorption time, incorporation into the calcite structure is observable.

Lastly of the single clay minerals, the sorption process onto illite is investigated. The obtained luminescence spectra are shown in Figure 65, together with peak maxima from literature in purple.

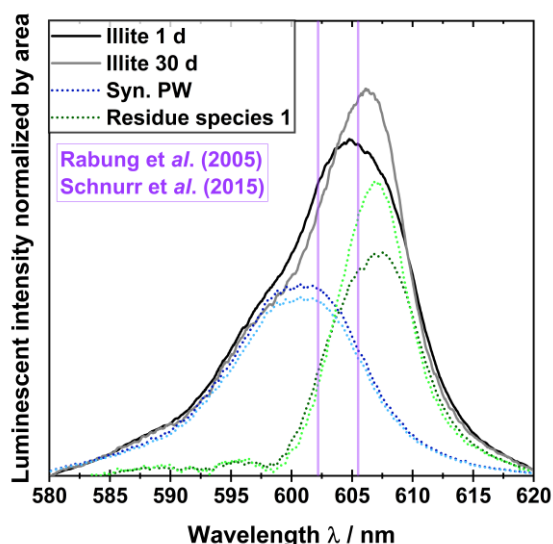


Figure 65: TRLFS spectra of Cm^{3+} in contact with illite after 1 day (black) and 30 days (grey) of sorption time in the synthetic pore water. Literature references [48] added in purple as a comparison and a peak deconvolution in blue for the aquatic carbonate complexes and different shades of green for all further species. Dark colors indicate the deconvolution after 1 day and bright colors after 30 days of sorption time.

The spectra after 1 day and 30 days of sorption time look similar, with a bathochromic shift of the main peak position and a hypsochromic shoulder at around 596 nm. With increasing sorption time, the shift increases. Rabung *et al.* (2005) [48] and Schnurr *et al.* (2015) [44] have investigated the sorption behavior of curium onto Na-illite as sorption edges in a carbonate free system. Of the species they found, only the two with peak maxima shown for reference may be formed under the conditions present in this study. These have both been identified as ternary surface sorption species with one and two complexing hydroxide ions ($>\text{SOCm}(\text{OH})(\text{H}_2\text{O})_4^+$ and $>\text{SOCm}(\text{OH})_2(\text{H}_2\text{O})_3$). Fernandes *et al.* (2016) [115] have investigated the effect of added sodium (bi)carbonate on the sorption of curium on montmorillonite at pH 9. With the addition of carbonate ions to their solution, the observed emission peak maximum shifts from 602.4 nm to 604.6 nm and the lifetime increases from a monoexponential decay of $117 \pm 5 \mu\text{s}$ to a biexponential decay with $133 \pm 5 \mu\text{s}$ and $380 \pm 12 \mu\text{s}$. Since their data is on the sorption on montmorillonite, it can only be compared roughly to the sorption on illite performed in this study.

A peak deconvolution is performed again subtracting the carbonate species mixture found in the synthetic pore water in this study. Large amounts of aquatic species are visible, taking the strong sorption observed in the batch sorption experiment of trivalent europium into account. However, with an estimated $\log(R_d)$ -value of ≈ 5.0 for illite and the reduced S/L ratio of 0.25 g/L, this would amount to $\approx 4\%$ of aquatic species being left in solution. With a roughly tenfold larger FI factor of the aquatic species in comparison to the surface sorbed species, the

Origin	Central λ	Lifetime τ
	/ nm	/ μs
This study 1 d	≈ 601.2	144 ± 20
This study 1 d	≈ 606.9	400 ± 50
This study 30 d	≈ 601.2	146 ± 20
This study 30 d	≈ 606.9	370 ± 40
References [44, 48]	602.3	115 ± 4
References [44, 48]	605.5	115 ± 4

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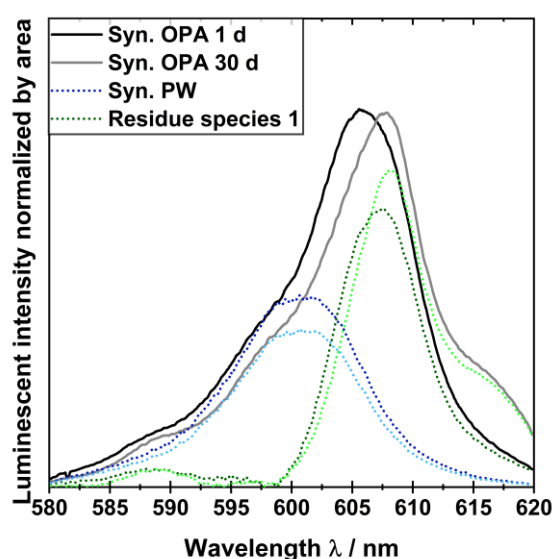
spectrum may reflect this situation. The observed lifetimes however, do not correlate to those of the aquatic carbonate species observed so far, but are also longer than what has been found by the literature references. With a fast ad- and desorption kinetic, the observable lifetime may reflect a mixture of surface sorbed and aquatic species.

The remaining residue reveals a spectrum likely composed of multiple species according to the visible shoulder towards longer wavelengths. The emission maximum of the dominant species 1 can be estimated to ≈ 607 nm and the lifetime to ≈ 370 – 400 μ s. This is a further bathochromic shift and lifetime increase than what is reported by Rabung *et al.* (2005) [48] and Schnurr *et al.* (2015) [44], indicating a stronger displacement of water from the inner coordination sphere. The emission peak shift and increase in lifetime are comparable to the observations from the study of Fernandes *et al.* (2016) [115], who identified this surface adsorbed species as a ternary carbonate complex $>\text{SOCm}(\text{CO}_3)(\text{H}_2\text{O})_{1-2}$ and have validated this assumption with EXAFS.

In the carbonate free system, Schnurr *et al.* (2015) [44] also observe a further red shifted species with a central wavelength of ≈ 610 nm. Though this species only becomes dominant at elevated pH of ≈ 12 , its effect on the spectrum is already visible at pH 7.2, creating a similar shoulder as observed in this study (though not as far red shifted). After further investigation with added silicon to their solution, they concluded the possibility of a ternary surface complex of the form $>\text{SOCm}(\text{OH})_x(\text{SiO}_4)_y(\text{H}_2\text{O})_{4-x}$ (for $x, y = 1$ or 2). This complex may form due to trace amounts of mineral dissolution, causing an elevated silica content in solution. A similar structure is proposed for the sorption of curium onto kaolinite by Huittinen *et al.* (2012) for their observed emission peak at ≈ 610 nm with an elevated lifetime. Due to the lack single species spectra of ternary carbonate surface complexes of illite, deconvolution is performed using the single species spectrum of the ternary carbonate surface complex onto montmorillonite of Fernandes *et al.* (2016) [115] (not shown). Using this approach, a further species with an emission maximum at ≈ 608.5 nm remained with still a strong shoulder at 615 nm. This approach did not improve the data situation, since a peak maximum at 608.5 nm has not been observed in literature and still the shoulder at longer wavelengths remained. The ternary carbonate surface complex on illite likely shows a slightly further bathochromic shift in comparison to the complex on montmorillonite. A possible explanation on the shoulder may still be the similar formation of a ternary silica surface complex, but instead of simultaneous complexation with hydroxide on the surface, a carbonate molecule might be involved. The formed surface species might be in the form of $>\text{SOCm}(\text{CO}_3)(\text{SiO}_4)(\text{H}_2\text{O})_2$. The formation of a bidentate silicate surface complex is also briefly mentioned by Schnurr *et al.* (2015) [44], mentioning the further

water displacement on the surface to be a possibility. The observed speciation in this study is therefore likely a mixture of minor amounts of aquatic carbonate species and a majority of surface sorbed ternary carbonate complexes.

To validate the chosen approach, a synthetic clay is created from the single minerals in the same ratio as they are present in the sandy facies OPA sample. In the best-case scenario, this synthetic clay yields very similar results to the investigation of natural OPA. The obtained spectra hereof are shown in Figure 66.



Origin	Central λ / nm	Lifetime τ / μ s
This study 1 d	≈ 601.1	110 ± 30
This study 1 d	≈ 607.3	312 ± 7
This study 1 d	≈ 616	730 ± 7
This study 30 d	≈ 601.1	-
This study 30 d	≈ 607.8	341 ± 14
This study 30 d	≈ 616.4	1131 ± 59

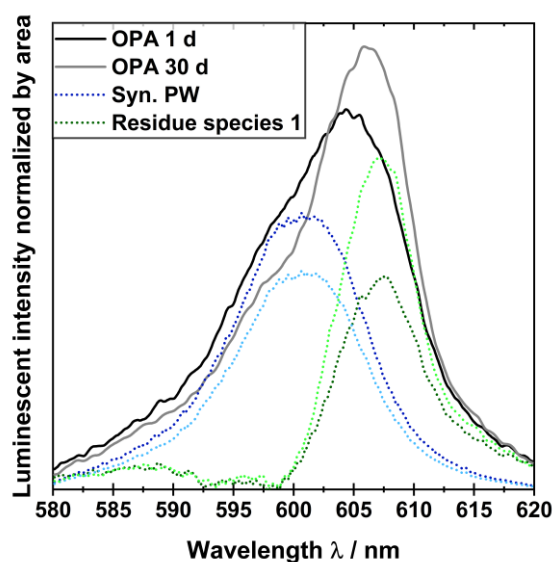
Figure 66: TRLFS spectra of Cm^{3+} in contact with “synthetic OPA” after 1 day (black) and 30 days (grey) of sorption time in the synthetic pore water. A peak deconvolution is shown in blue for the aquatic carbonate complexes and different shades of green for all further species. Dark colors indicate the deconvolution after 1 day and bright colors after 30 days of sorption time.

The spectrum after 1 day of sorption looks similar to the spectrum of illite, while the spectrum after 30 days of sorption looks more similar to the calcite spectrum after 30 days of sorption time. A peak deconvolution with the aquatic carbonate species reveals a broad residue after 1 day of sorption time, while a strong shoulder is visible after 30 days. Due to multiple species being present simultaneously, the lowest lifetime is only determinable with a comparatively high uncertainty. Still due to the positioning of the shoulder and the roughly matching lifetime, the presence of aquatic species is confirmed. The strong contribution to the overall spectrum can again be explained by the much higher FI factor of aquatic species. The residue shows a maximum around 607–608 nm, which is comparable to both the main peaks observed in the calcite and illite spectra. The observed lifetime is also comparable to both of these ternary carbonate surface complexes. Therefore, no precise distinction between the two possible surface species can be made for the spectrum after 1 day of sorption. From the general

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appearance of the spectrum, it looks more like the spectrum obtained for the sorption on illite, with similar shoulder to higher wavelengths. After very long delay times ($>500 \mu\text{s}$), a shoulder at $\approx 616 \text{ nm}$ can be adumbrated. This species is likely the cause of the third observed very long lifetime. From the water displacement and bathochromic shift, it is probably an incorporation species into calcite. After 30 days, a strong shoulder is visible after deconvolution. To this extent, this has only been observed in the calcite spectrum. The lifetime also matches a calcite incorporated species, which is also found after 1 day of sorption time. The synthetic OPA spectrum is therefore composed of a mixture of the previously examined minerals calcite and illite. No significant contribution of the other minerals is visible. Aquatic species are still visible, though the majority of the curium is adsorbed at mineral surfaces. From the bathochromic shifts and lifetimes, likely again ternary carbonate surface sorption species form.

To add onto this assumption of illite and calcite contributing to the adsorption, natural OPA is investigated. It has to be noted, that natural OPA contains much more iron, which is known to cause fluorescence quenching for Cm^{3+} as an ion in the aquatic phase and as a mineral constituent. The dissolution of iron from OPA has already been observed during the preliminary leaching experiment (see Table 21). This could lead to a significant reduction of the observed fluorescence lifetimes and quality of spectra concerning the signal-to-noise ratio. The results of the TRLFS investigation of the sandy facies OPA is shown in Figure 67.



Origin	Central λ / nm	Lifetime τ / μs
This study 1 d	≈ 601.1	95 ± 11
This study 1 d	≈ 607.4	263 ± 16
This study 1 d	≈ 616.8	-
This study 30 d	≈ 601.1	154 ± 17
This study 30 d	≈ 607.1	301 ± 14
This study 30 d	≈ 616.6	-

Figure 67: TRLFS spectra of Cm^{3+} in contact with sandy facies OPA after 1 day (black) and 30 days (grey) of sorption time in the synthetic pore water. A peak deconvolution is shown in blue for the aquatic carbonate complexes and different shades of green for all further species. Dark colors indicate the deconvolution after 1 day and bright colors after 30 days of sorption time.

The spectra of natural OPA has a slightly different appearance compared to the spectra of the synthetic OPA, but with similar characteristics. The effect of iron diminishing the quality of the spectrum is noticeable, with a reduced observed intensity and lower signal-to-noise ratio. The biggest difference to the synthetic OPA is the absence of a shoulder after 30 days of sorption time. The spectrum overall looks similar to the pure illite spectrum.

A peak deconvolution is again performed, subtracting an appropriate amount of the aquatic carbonate species. Compared to the illite and calcite spectra, more aquatic carbonates are visible. After 1 day of sorption time, the observed lifetime also matches the aquatic carbonate complexes. In contrast, during the batch sorption experiments with the same OPA, very strong sorption has been observed. Due to the differences in FI factors, they are still likely only present in minor amounts. The iron present in the mineral structure enhances the differences of the FI factors even further, causing more extinction of the adsorbed species. The deconvolution reveals the residue of a single species with a long shoulder, which indicates multiple species being present. The main maximum emission peak position again matches both illite and calcite surface sorbed ternary carbonate complexes. For the lifetime, it is comparatively shorter than the $\approx 300\text{--}400\text{ }\mu\text{s}$ observed for the ternary surface complexes so far. This might be caused by dynamic quenching of iron ions in solution. For the species causing the shoulder, the peak maximum may be at around $\approx 615\text{ nm}$. Due to the reduced intensity at increasing delay times, no lifetime could be assessed for this species and it is hardly visible at long delay times. This peak position is again similar to what has been observed in both the illite and calcite spectra. The suggested speciation here has been a ternary silica carbonate complex, though more investigation would be necessary for a definite statement.

In contrast to the 30 days sorption sample of synthetic OPA, no prevalent shoulder to higher wavelengths is observable. The missing calcite incorporation species indicates synthetic calcite being much more reactive in comparison to natural calcite. This is not surprising, since natural calcite has been in contact with pore water for millions of years and is therefore in equilibrium and unreactive [128]. Synthetic calcite, however, has not been equilibrated and a much faster recrystallization kinetic is expected, leading to more incorporation.

To summarize the findings of this chapter, most likely illite is the mineral dominating the adsorption of trivalent cations in natural clay rocks, but calcite may also play a minor role. The sorption on quartz, feldspars and muscovite seems negligible. There are hints on ternary sorption species with carbonate being present on these mineral surfaces. On kaolinite, a stronger sorption is observed with a more likely contribution of ternary carbonate surface sorption

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species. A curium species with more water molecules being displaced by silica on the surface is also hinted at, but no confirmation is possible. This possible species is also observed for illite, which would explain the broad peak and further red shift than a ternary carbonate surface complex. Synthetic calcite shows an even stronger adsorption of curium and the characteristic incorporation species. For synthetic OPA, the main sorbing minerals are either illite or calcite, while natural OPA shows sign of illite dominating the sorption process. The ternary carbonate surface complexes are also observed on natural OPA.

4.6 Rock Surface Sorption

From the previous investigations, illite has been identified as the dominant mineral regarding the sorption capacity in comparison to other mineral phases present in sandy facies OPA. For europium and cobalt, calcite may also play a subordinate role as a possible sorbent, based on the results from Chapter 4.4 and Chapter 4.5 [123, 218, 222]. In this chapter, the goal is the investigation of the sorption onto intact clay rock surface to visualize the effect the heterogeneity can have on the sorption process on a microscopic scale. The tool of choice for the detection of radiation after adsorption on a rock surface is autoradiography, yielding a spatially resolved activity map of the investigated surface. Prior to the rock surface sorption experiments, a mineral characterization of the intact surface is performed. The results are subsequently compared to the images of the autoradiography. The deployed characterization methods need to be spatially resolved, be able to process surfaces large enough to match the resolution of the autoradiography and be able to either identify mineral phases or elemental compositions. The two methods employed for this procedure are μ -XRF and SEM-EDX. Due to the size restrictions of the μ -XRF, a round sample is investigated to test the applicability of the detection method. The height of the sample is restricted to several cm, while the investigated surface may only be circular with a maximum diameter of one inch (≈ 2.5 cm). A high-resolution scan of the ≈ 5 cm² surface area is shown in Figure 68. This sample has been drilled from the preserved counterpart of the 7.00 m D2 disc and therefore contains a large amount of calcite with a high degree of heterogeneity. Various phases are visible, ranging from brown to fine black to diffuse dark grey brownish. Due to the visually high heterogeneity, a strong variation in the mineralogy and consequently sorption behavior is expected.

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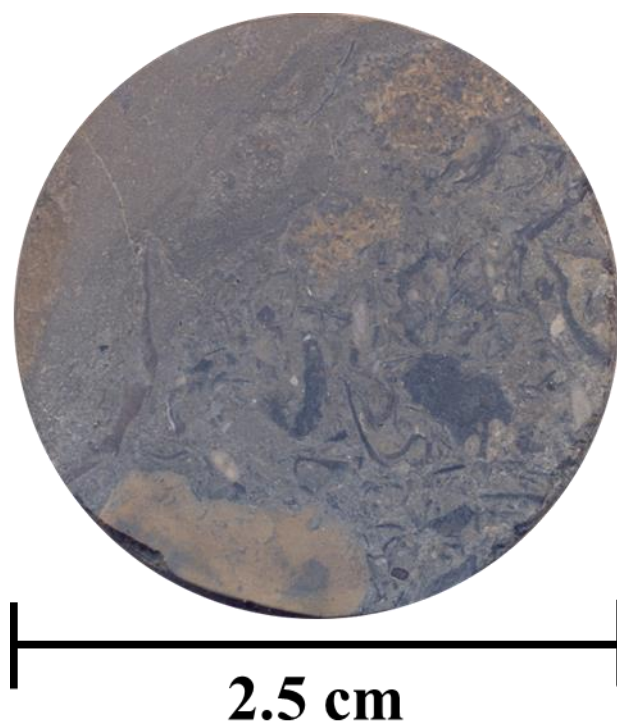


Figure 68: High-resolution scan of the sample surface for the cesium intact rock surface sorption experiment. $\approx 5 \text{ cm}^2$ of total investigated area.

Though the prepared sample fits the size restrictions of the μ -XRF, not the whole surface can be investigated at once. A region of interest has had to be chosen, indicated by the radiation damage on the surface caused by the μ -XRF in Figure 69 on the left. This radiation damage is abraded prior to further investigations. The obtained elemental distribution of the XRF is shown on the right.

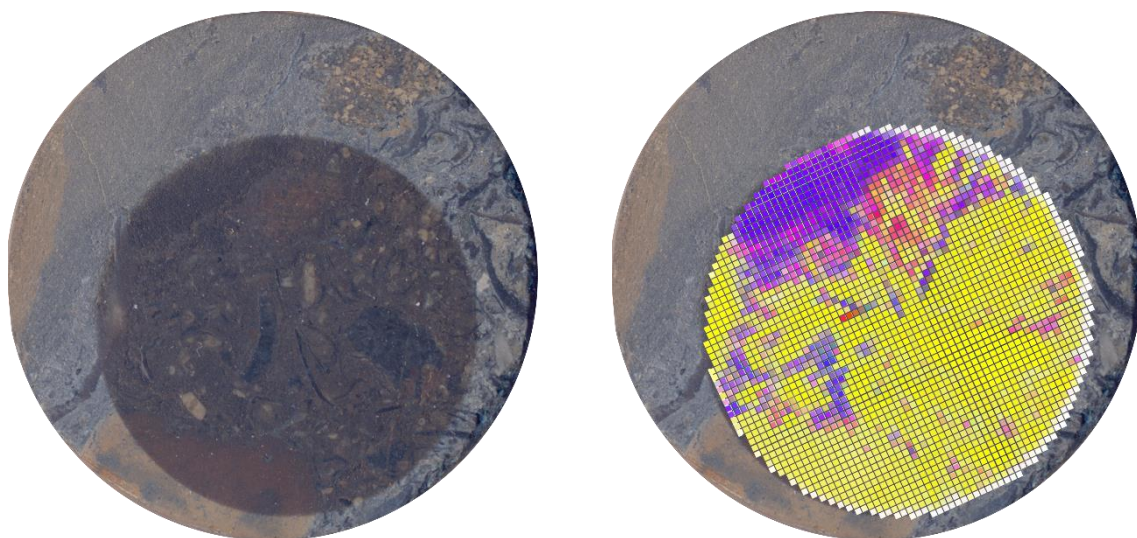


Figure 69: Radiation damaged surface of the cesium sorption sample on the left with the elemental mapping of the μ -XRF on the right. The area dominated by calcium is shown in yellow, silicon in red and mixed aluminum and silicon in purple.

Highlighted in yellow is the area covered mostly by calcium, consequently interpreted as being consisting largely of calcite. The areas marked in purple consist of a mixture of silicon and aluminum, and are interpreted as a mixture of clay minerals and feldspars. The sparse areas indicated in red mostly consist of silicon without the presence of aluminum and are therefore interpreted as quartz. Due to the sensitivity of the μ -XRF, only a superimposition of the most prominent elements could be done, rendering smaller phases invisible. The area at the bottom right with the thin black layers is dominated by calcite, while the top left brownish-grey mixture appears to be mostly consisting of clay minerals. No clear quartz agglomerates are visible, possibly due to the resolution of the μ -XRF. Trace elements have also been detected, but due to the lack of resolution could not be properly assigned to visible features. A rough mapping of a superimposition of these trace elements is shown in the Appendix E.

Due to the low resolution and the surface area restrictions of μ -XRF, SEM-EDX is also used to investigate the whole surface of the sample. SEM techniques are usually applied on a much smaller scale, visualizing even single minerals on the surface of the clay, so mapping such a large area proves to be rather challenging. The resulting image of the elemental mapping is shown in Figure 70.

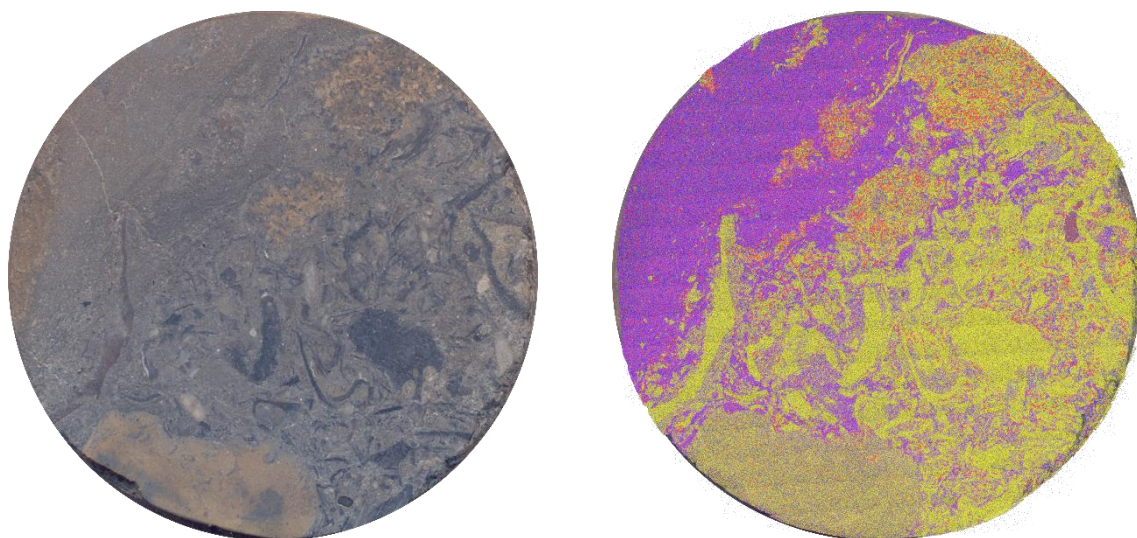


Figure 70: Surface mapping of the intact rock surface sample with the elemental distribution from the SEM-EDX of the main components shown on the right. In yellow calcium is shown, in purple aluminum and in red silicon.

The figure shows the elemental distribution of calcium in yellow, aluminum in purple and silicon without aluminum in red. The higher resolution of the SEM-EDX in comparison to the μ -XRF is striking, but a similar distribution is visible. The bottom right is dominated by calcium, while the top left mostly seems to consist of aluminum and silica. Pure silica phases are sparse and scattered. The dark areas of the surface almost exclusively consist of calcium

4. Results and Discussion

and are most likely calcite, while the brownish grey mixture in the top left seems to be clay minerals. The overall distribution of high calcite, medium clay minerals and low quartz is representative for the sample at this well-depth, where the XRD analysis of the powder has shown a similar distribution. The goal of obtaining a heterogeneously composed sample has therefore been achieved. From this elemental distribution map, a phase analysis is done to further identify present minerals. This mapping is shown in Figure 71.

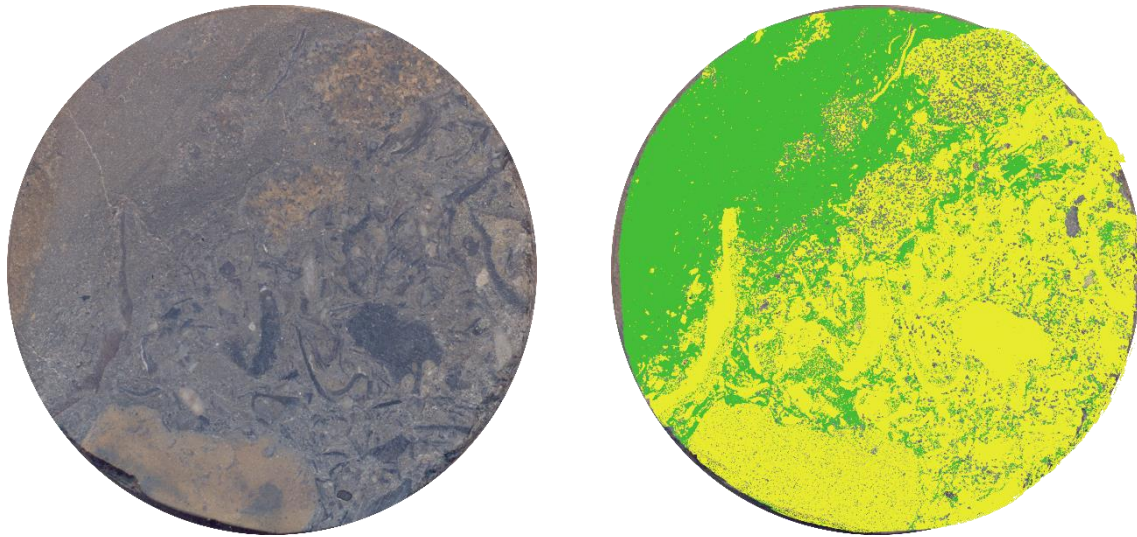


Figure 71: Surface mapping of the intact rock surface sample with the phase distribution from the SEM-EDX of the main components shown on the right. In yellow calcite is shown and in green a mixture of clay minerals, feldspars and quartz.

The figure shows the distribution of the two main phases, calcite and a mixed clay mineral phase. Due to the size of the investigated sample, the phase analysis needs to be adjusted. Instead of a single measurement, several areas have been measured separately and stitched together. From these spectra, the elemental composition is obtained and phases are derived. To find the same phases across the whole area, sufficient overlap of obtained spectra is necessary. Feldspars and quartz could therefore not be distinguished sufficiently from clay minerals; hence they are consequently interpreted as one single phase. Besides these main components, accessory minerals and a definite single quartz phase are also detected and shown in Figure 72.

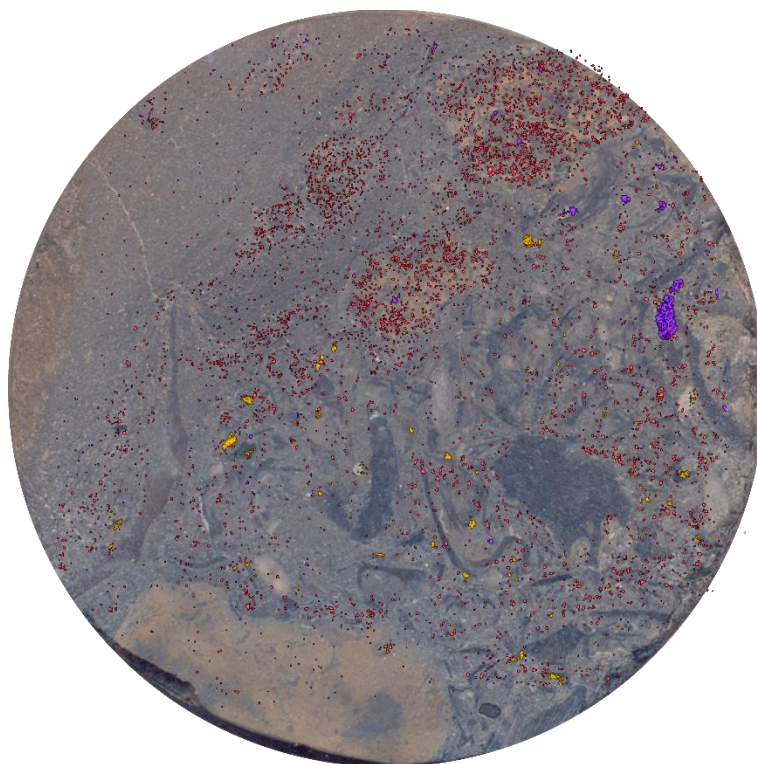


Figure 72: Surface mapping of the intact rock surface sample with the phase distribution from the SEM-EDX of the accessory components. In red quartz is shown, in purple pyrite and in orange apatite.

The pure quartz distribution is as scattered as assumed by the μ -XRF measurement and mostly found on visually brown diffuse areas. The low surface coverage of this phase suggests most quartz to be incorporated in the mixed clay mineral phase. Pyrite is present as rather big agglomerates in comparison to quartz. Apatite is also present in small agglomerates. The overall phase distribution is shown in Table 22 with a comparison to the average mineral distribution of the disc the sample originates from.

Table 22: Comparison of the surface analysis via SEM-EDX of the cesium sorption sample to the respective XRD results of the originating disc of core BDR-D2. Quartz content added to the clay minerals and feldspars to match the comparison.

Mineral phase	SEM-EDX / surf%	XRD / wt%
Calcite	59.2 ± 6.0	57.2 ± 6.6
Clay minerals, feldspars and quartz	40.5 ± 4.1	36.6 ± 6.3
Apatite	0.2 ± 0.1	0.7 ± 0.2
Pyrite	0.1 ± 0.1	0.3 ± 0.2

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The resulting surface composition reflects the average mineral powder composition of the disc nicely. Since the disc consistent not only of the fossil layer, differences would have been expected. With the surface mineralogy scrutinized, the sorption experiment with Cs-137 is performed. With an exposure time of two weeks, an acceptable autoradiographic image has been obtained and is shown in Figure 73 in comparison to the surface image.

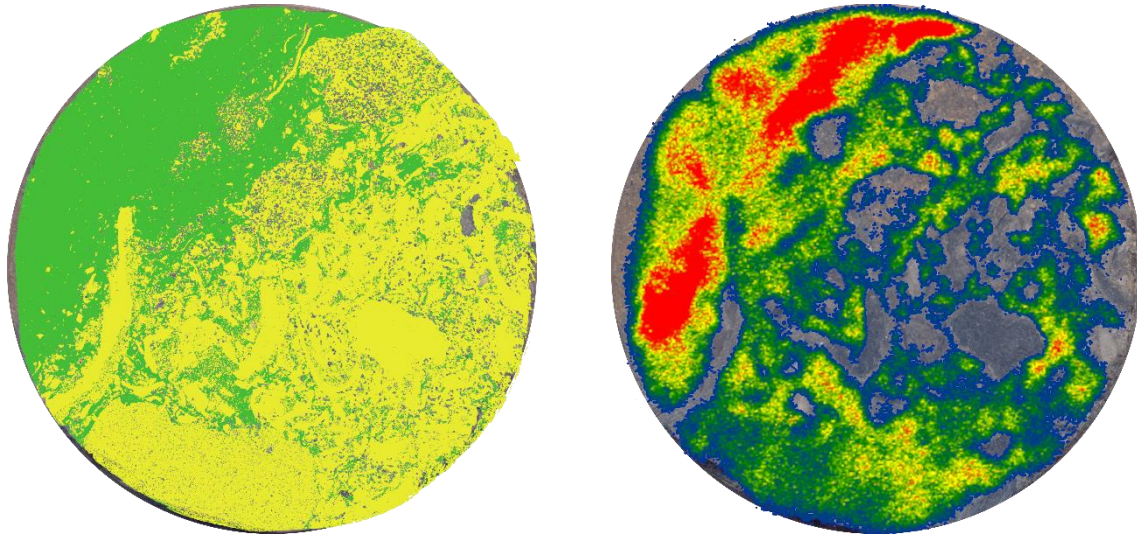


Figure 73: On the left the phase distribution from the SEM-EDX of the main components, in yellow calcite and in green a mixture of clay minerals, feldspars and quartz. On the right, an autoradiographic image showing the spatial distribution of the absorbed Cs-137. Low activity is displayed in blue to green, medium activity in yellow and high activity in red.

The figure shows from blue over yellow to red areas of low, medium and high activity. Since no calibration has been done, these areas cannot be assigned to specific activities. However, their intensity has been measured in so-called digital light units (DLUs), which can be compared to one another and are linearly correlated to the activity present. The background radiation of $\approx 130 \cdot 10^3$ DLU/mm² is subtracted from these units. The areas in without coloration have $\approx 260 \cdot 10^3$ DLU/mm², which is only double the background radiation. A color code for the other activities is shown in Table 23. It has to be noted, that this code is only valid for the cesium sorption and not the other investigated radionuclides, since these emit radiation of a different energy and subsequently may cause different illumination at similar activity.

Table 23: Color code for the interpretation of the autoradiographic images of the cesium sorption.

Coloration	Exemplary color	DLU/mm ²
Blue		$\approx 860 \cdot 10^3$
Green		$\approx 1.3 \cdot 10^6$
Green-Yellow		$\approx 1.6 \cdot 10^6$
Yellow-Red		$\approx 1.9 \cdot 10^6$
Red		$\approx 2.9 \cdot 10^6$

The assumption of the sorption being more oriented to the top left corner, where the clay minerals are present is correct. Moreover, the areas visually very dark and consisting of pure calcite show very low sorption. Slight sorption is observed on the mixed areas of the bottom and top right. Some high-activity-spots are also found in the bottom right, where clay minerals are present in the calcite dominant region. As the clay rock shows a strong tendency of swelling, the autoradiographs are of surprisingly high quality. They clearly demonstrate the cesium adsorption to be dominated by clay minerals, most likely illite, which is in agreement with literature data. The mineral dependent distribution of the sorption behavior is already visible after a very short contact time between rock surface and solution of 10 minutes, which is much shorter than the powder batch sorption experiments. Fortunately, the batch sorption experiments have already shown only a small deviation in adsorbed cesium with changes in sorption time (of course on a completely different scale).

For the cobalt rock surface sorption, μ -XRF has been discarded as an analytic technique, since it yields no additional information in comparison to SEM-EDX. This allows the investigation of rectangular surface samples, since SEM-EDX poses no restrictions on the samples' shapes. The sample used for the cobalt sorption is taken from the core BMB-A7. Figure 74 shows the high-resolution image of the surface of the sample used in the rock surface sorption experiment for cobalt on the left, together with the elemental mapping of SEM-EDX analysis on the right.

4. Results and Discussion

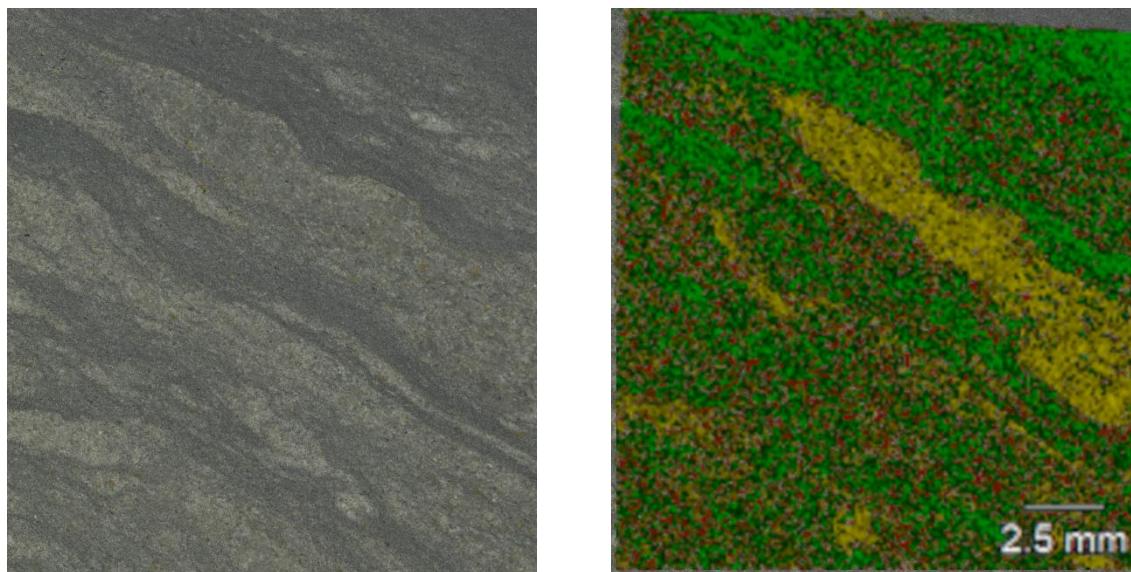


Figure 74: High-resolution scan of the sample surface for the cobalt intact rock surface sorption experiment on the left. Surface mapping of the intact rock surface sample for the cobalt sorption experiment, with the elemental distribution from the SEM-EDX of the main components shown on the right. In yellow calcium is shown, in green aluminum and in red silicon.

In the optical image of the surface, a clear layering structure and small lenses are visible. In the marbled structure, dark-grey and lighter tones alternate. None of the brownish phases visible in the cesium rock surface sorption sample are found, since this sample does not originate from a fossil-rich layer. On the right, a superimposed image of the elemental distribution gathered via SEM-EDX is shown, with calcium in yellow, aluminum in green and silicon in red. Unfortunately, the quality of the obtained image is reduced due to surface roughness, which prevents an adequate phase analysis. From the elemental distribution, it can be assumed that the areas indicated in yellow reflect calcite, while the areas in green are assigned to clay minerals and areas in red are either quartz or also clay minerals. Feldspars are again disregarded in these assignments, but can be present in both the green and the red phase. A comparison to the optical image indicates the bright areas to be calcite and in rare cases quartz, while the dark areas supposedly consist mostly of clay minerals. An autoradiography image of the adsorbed Co-60 in comparison to the EDX image is shown in Figure 75.

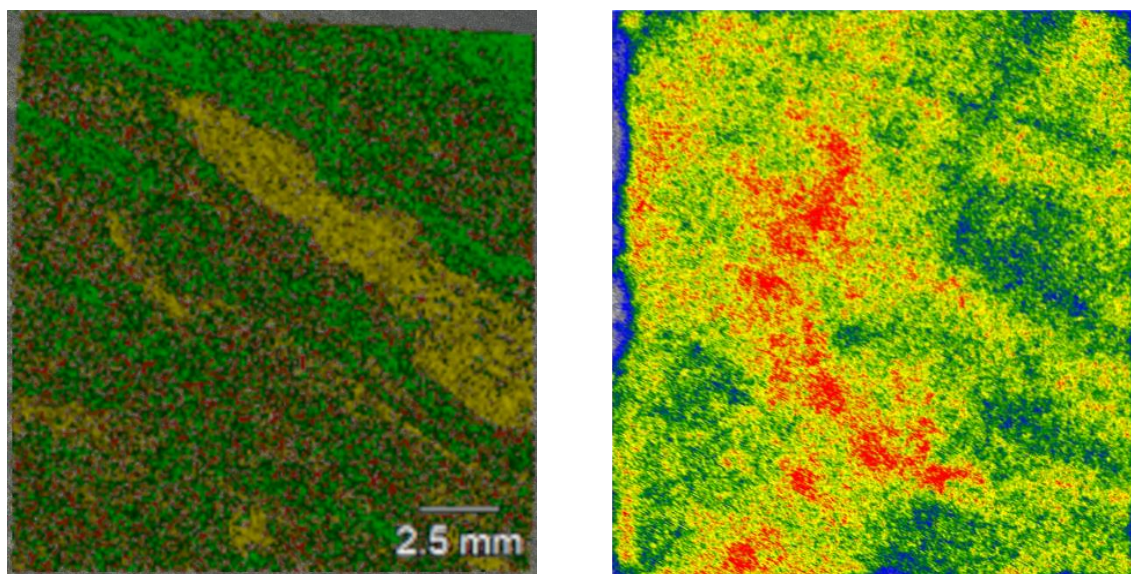


Figure 75: Autoradiographic picture showing the radioactive impulses received, mirroring the spatial distribution of the absorbed Co-60 on the right. Low activity is displayed in blue to green, medium activity in yellow and high activity in red.

The activity is again shown as a gradient from blue over yellow to red. The DLU array is much smaller compared to the cesium sorption, ranging only from $\approx 370 \cdot 10^3$ DLU/mm² for the blue area to $\approx 650 \cdot 10^3$ DLU/mm² for the areas in red. Since the relationship between DLU and activity is linear, the percentage differences also correlate. Therefore, the difference between blue and red areas is only 0.25 log units, which is lower than the uncertainty of general batch sorption experiments. The differences should therefore only be interpreted with some caution.

The layered structure appears only scattered and blurred in the autoradiography image. Only areas with the highest calcium content can be assumed to show a reduced sorption in comparison to the rest of the surface. The top right area, assumed to be quartz, also shows below average sorption behavior. A correct orientation of the autoradiographic image to the SEM-EDX image also proves to be more challenging due to the worse resolution. In general, the blurred look of the image is likely might be caused by the more diffuse sorption behavior of cobalt. The much more likely cause is the very low sorption time of only 10 minutes, which is not enough to reach equilibrium. Considering this limitation, one can nevertheless conclude cobalt sorption likely to predominantly take place on clay mineral rich regions.

Unfortunately, prior to the europium sorption, no surface characterization has been performed. A multitude of samples have been tested during the adjustment of the setup and only one Eu-152 containing sample remained intact, which has not been characterized before contact with tracer solution. Due to the contamination of the surface and the swelling of the clay, investigation via SEM-EDX after sorption is not feasible. Figure 76 shows an optical image of the sample on the left and the resulting autoradiography image on the right.

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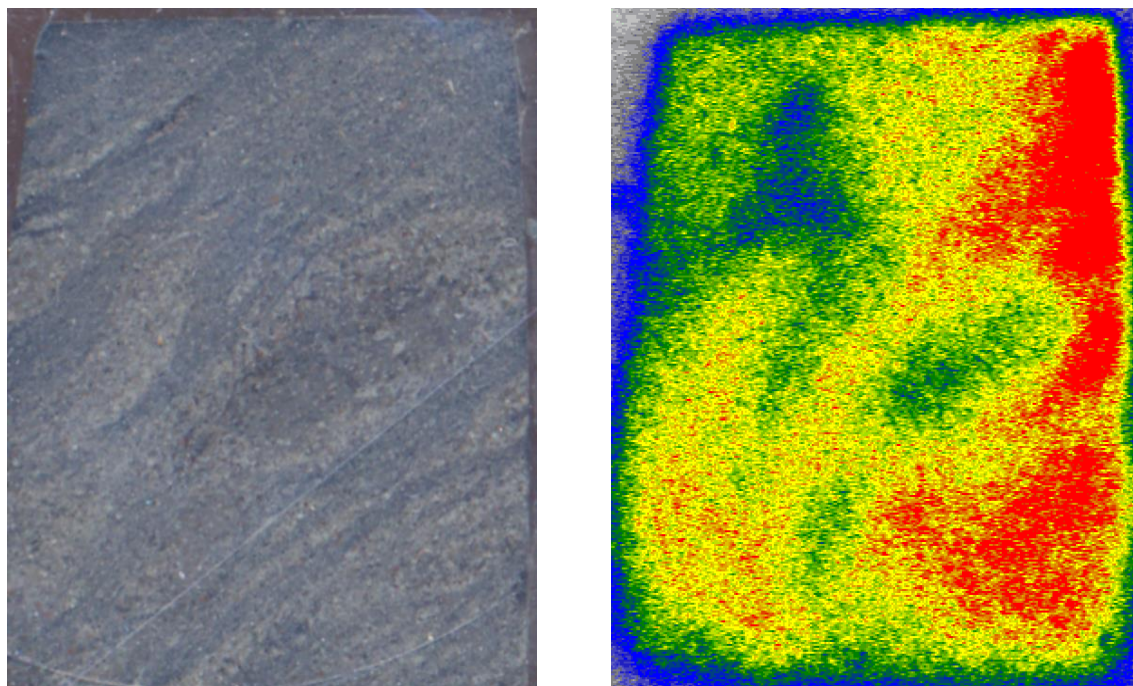


Figure 76: High-resolution scan of the sample surface for the europium intact rock surface sorption experiment on the left. Autoradiographic picture showing the radioactive impulses received, mirroring the spatial distribution of the absorbed Eu-152 on the right. Low activity is displayed in blue to green, medium activity in yellow and high activity in red.

The quality of the visual image is compromised as a result of its acquisition through a transparent foil, implemented to mitigate the risk of contamination. The image shows a thinly layered structure with alternating light-grey, presumably sand/carbonate layers, and dark-grey, presumably clay-rich areas. In the middle a concretion is visible as a big lens, exhibiting a shiny look not visible in the picture. This reflectiveness also carries on to the top left corner, hinting at a similar phase being present. The autoradiography image of the intact rock surface sorption of Eu-152 is shown on the right of Figure 76. The sorption is generally much stronger in comparison, with the blue areas already showing an activity of twelve times the background. On the linear color-scale, the red area exhibits $1.4 \cdot 10^6$ DLU/mm², which is only twice as much as the blue areas. This is again a difference of 0.3 log units, which is directly transferable to the surface activity. Interpretation of the differences in coloration should therefore not be overstated. The similarly shiny looking areas show a slightly decreased sorption capacity, whereas the right side of the sample shows stronger sorption. This is also the region dominated by the dark-grey areas. However, without analysis of the surface mineralogy, it is not possible to make a clear assignment to the mineral phases partaking in sorption.

Summarizing, it can be concluded that cesium sorption is dominated by the clay minerals and being completely absent in calcite phases shown in a spatially resolved autoradiographic image. The cobalt sorption on the intact rock surface shows a more diffuse image, still clay minerals are likely responsible for the sorption process. The europium sorption shows an even more diffuse image with visually multiple mineral phases likely taking part in the sorption process. Still, the image is not completely uniform and an impact of the heterogeneity is still visible. Taking the length of the equilibration time into account and the small differences in surface activity for cobalt and europium, these findings should not be overstated. Nevertheless, these are nice visualizations of the impact of the heterogeneity of sorption processes on the microscopic scale.

4.7 The Impact of the Heterogeneity

4.7.1 General Concept

As mentioned in Chapter 2, both a uniform description of homo- and heterogeneity and the general concept of representativeness are still under discussion. In this context often referred to, is the study of Bachmat and Bear (1987) [5], where a mathematical approach to the description representativeness for porosity is chosen. A more elaborate description on the continuum approach for modeling transport using a REV is published in the book by Bear (1988) [4]. In this present study, an adaptation of this concept of a REV is chosen in a more general approach, visualized in Figure 77.

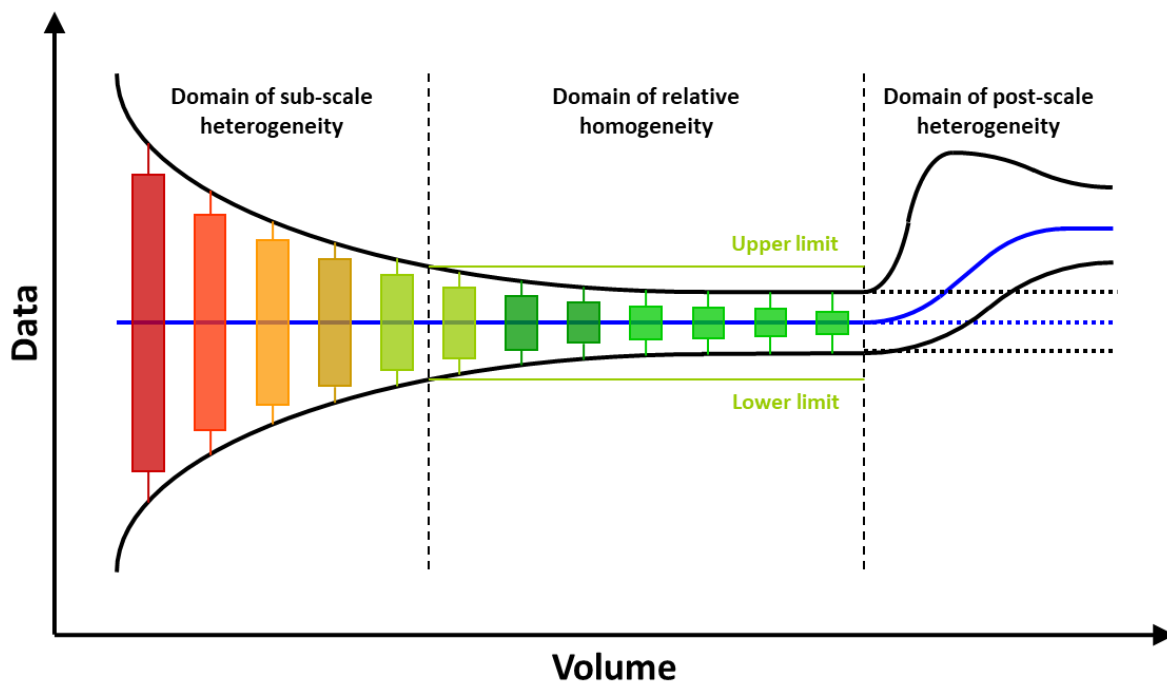


Figure 77: General approach for a conceptual definition of a REV chosen in this study. The bars indicate the data spread and the lines above and below the uncertainty of the measurement. In blue, the average of the investigated property is displayed. The dotted lines indicate the behavior of a theoretical infinite homogeneous medium. Concept adapted from Bachmat and Bear (1988) [5].

It has to be noted, that this concept always refers to a specific scale and parameter. If volumes on a different scale or different properties are investigated, the concept needs to be reevaluated. The colored bars indicate the observed data spread of a property or parameter, with the adjacent lines above and below showing the uncertainty in the determination. At small volumes, a large data spread is expected, as observed in Chapter 4.2 for the specific mineral contents. This area is termed the domain of sub-scale heterogeneity, encompassing the red to orange bars. Due to the large fluctuations in observable data, samples of this volume are deemed too small to be representative on the investigated scale.

The data spread narrows down when increasing the volume, entering the domain of relative homogeneity. This area is characterized by a much smaller data scattering, indicated by the green bars. These observable fluctuations are deemed sufficiently small to consider this domain homogeneous within a given range. This range is defined by setting up artificial upper and lower limits of parameter variation, shown as light-green lines in Figure 77. The smallest possible range is limited by the uncertainty of the determination method. In both of these domains, the average composition remains constant. A large enough number of measurements needs to be performed to observe this behavior experimentally, especially for low-volume samples where the randomly observed values scatter furthest. In a theoretical infinite, uniform system, the trend of lower data spread persists indefinitely (dotted lines in Figure 77). The deviation from the average is then only dependent on the uncertainty of the underlying measurement or the intrinsic heterogeneity of a given rock area. In reality, no domain extends infinitely and at elevated volumes a deviation from this trend needs to be expected. The beginning of this trend marks the start of the domain of post-scale heterogeneity, which is accompanied by a shift in the average composition, since an extending mixture of multiple systems is now observed. In the context of OPA, this could exemplarily be the extension of the investigated volume from one mineral grain into a homogenous mix of minerals, or the transition from a specific sedimentary layer, lamination or concretion into a mix of sedimentary layers, or the transition from one specific subfacies into another one. As mentioned above, on each of these scales a different REV could have to be defined. The transition beyond the homogeneous domain will in many cases be obvious, even visually in the example of the subfacies in OPA. In geological studies, REVs in the scale of multiple cubic meters are often proposed in structure studies [233-235]. These volumes are beyond the laboratory-scale of this study, so no specific upper boundary for a REV will be investigated.

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The borders for these three domains are indicated by the dashed lines in Figure 77, which mark the upper and lower limit of a REV. The upper limit for the REV defines the maximum volume a single sample may encompass while still only consisting of a uniform system and the lower limit offers the smallest volume which experimental samples need to cover to deliver representative data. Both volumes are important parameters. While the upper REV is defined by the system of interest, the lower REV can be varied. An acceptable data range for the lower REV should account for the uncertainty of the modeling procedure the data is collected for. The acceptable range can either be determined by the precision of the analytical method applied to characterize the sample or by the intrinsic heterogeneity of the system. Consequently, the definition of the acceptable data variation defines the range between the lower and the upper limit for the minimum REV.

4.7.2 Optical Heterogeneity

To obtain information on the impact of heterogeneity of the sandy facies OPA drill cores from the optical characterization, a similar procedure to Lauper et al. (2021) is chosen to assess representative elementary core lengths (RELs). This is a more or less one-dimensional analogue of the REA. In their study, they obtained RELs for each subfacies based on the “lenses to matrix” ratio derived from optical analysis and μ -CT scans. They increased the investigated drill core surface stepwise, until a significant flattening of the curve displaying the “lenses to matrix” ratio against the drill core depth is observed. The investigated drill core diameter has been 6.7 cm and the step size 0.5 cm. With this method, they obtained two RELs for each subfacies, based either on the surface composition (2D) and or on the three-dimensional CT scans, which only differ slightly.

In this study, the optical characterization has been performed in a similar way. Instead of a step size of 0.5 cm, the grids using for the characterization serve as the smallest step size. Thereby, a much larger total length can be investigated compared to the 5–7 cm maximum of Lauper et al. (2021) [6]. Also, in this first approach the three main components: Matrix, sand/carbonate concretions and sand/carbonate layers are taken into account. Note that the matrix is either the dark-grey clay matrix in case of the area identified as SF2 or the turbated light-grey matrix in case of SF3. In this process, areas which are optically significantly different from the average mixture of clay matrix, layers and concretions are disregarded. As the interpretation on the significant flattening of a curve may be somewhat subjective, as also mentioned by Lauper et al. (2021) [6] on their determination of a REL for SF4, a more distinct criterion for

representativeness is chosen. As limits, either the uncertainty of the determination method or an artificial boundary may be used. In the study of Yuan *et al.* (2022) [55] on the microstructure of digital OPA, the limit for representativeness is set at an allowed variation of 10 %. This is the same limit proposed by Houben *et al.* (2014) [56] in their optical analysis of the microscopic mineralogy. Coincidentally, this is also the uncertainty of the optical characterization method (see Chapter 3.6.2.1) in this study. Therefore, an acceptable deviation of $\pm 10\%$ when comparing the investigated surface composition to the next biggest area is chosen as the criterion for representativeness. It may be noted, that this method is very similar to the “box counting” method applied in microscopic studies for the determination of a REA [56, 236-238]. To differentiate this method with upcoming other methods for the determination of representative values, it will therefore be termed “optical box counting” method. The investigated areas are started from the lowest well-depth of each identified subfacies segment, until the desired deviation of less than 10 % is reached. Exemplarily, this procedure is shown for the beginning of the first segment (5.00–8.00 m well-depth) identified as SF2 of the drill cores BDR-D1 and -D2 on the bottom of Figure 78.

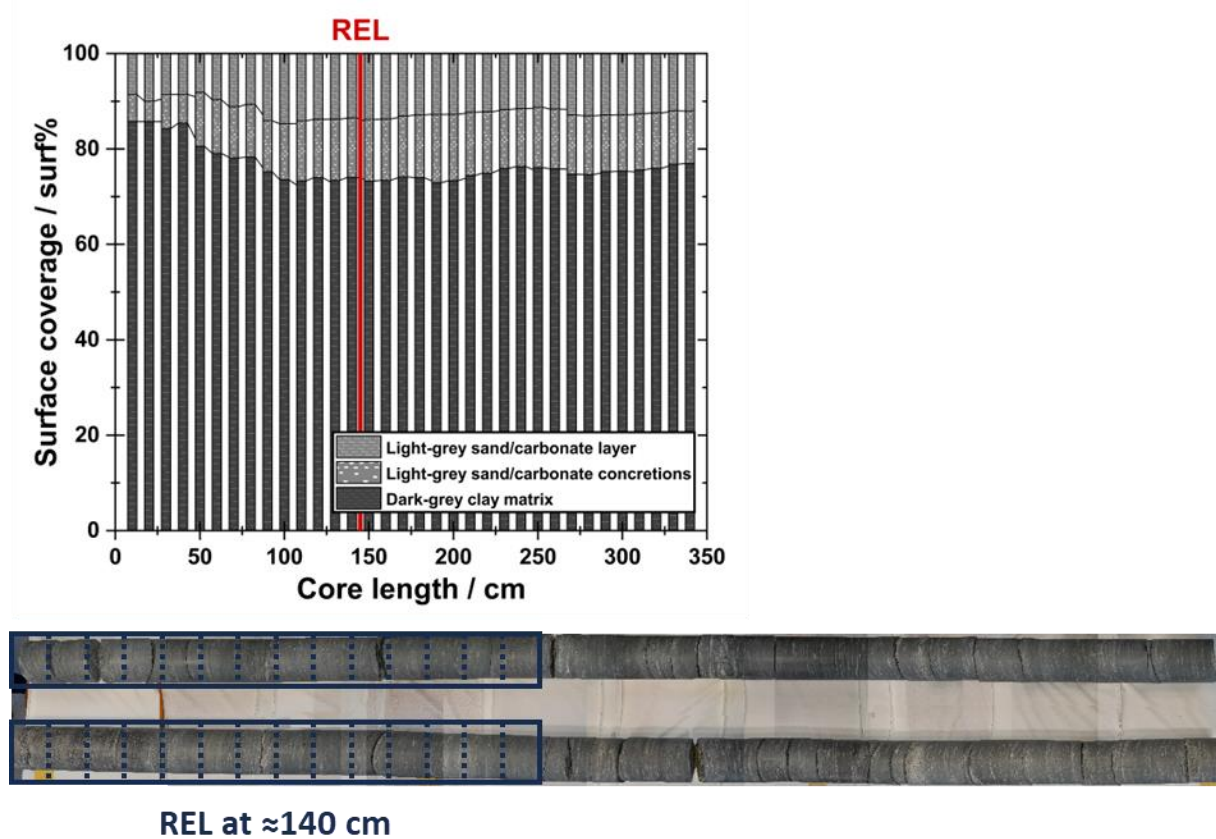


Figure 78: REL determination by the optical box counting method applied on the optical characterization of cores BDR-D1 and -D2. The image shows the cores at a well-depth from 5.00–8.00 m, classified as SF2. The postulated REL is indicated by a solid blue rectangle, with the individual summed segments highlighted by dashed lines.

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The resulting surface composition with increasing area is shown on top in Figure 78. A deviation in composition of less than 10 % for each of the three investigated components compared to the next biggest area is reached with a core length of ≈ 140 cm. The same REL is also determined for the second segment (11.00–15.50 m well-depth) identified as SF2. Though the optical composition of the area identified as SF3 looks comparatively homogeneous, the light-grey layers show a range in surface coverage between 2–11 surf%. One may estimate that the REL for SF3 lies in the same range as for SF2, but due to it only encompassing one meter in total, a REL determination for SF3 could not be done. The REL is subsequently validated by choosing different starting points for the areas, with a starting length of 140 cm. To confirm the REL, each of these areas must not deviate by more than 10 % in surface composition compared to an area with an increased side length to 150 cm. This procedure validates the first obtained REL of 140 ± 13 cm from this determination method.

All these determined RELs are longer when compared to the study of Lauper et al. (2021) [6], who have found the REL for SF2 and SF3 to be around 2.5 cm. However, they only differentiated between matrix and non-matrix, not subdividing between layers and concretions as it has been done in this study. Only considering two instead of three parameters consequently leads to smaller RELs. Furthermore, they investigated up to a length of 7 cm maximum, which is smaller than the size of some individual concretions found in this study. These differences may explain the larger obtained RELs in this study.

When varying the procedure to also only differentiating between matrix and non-matrix, a REL of ≈ 30 cm is obtained for SF2. This is significantly smaller in comparison to the first assessment. Also, with this approach a REL of ≈ 10 cm is obtained for SF3. Though still larger, these lengths are more comparable to the RELs found by Lauper et al. (2021) [6]. The finding of a larger REL for SF2 than for SF3 is surprising, since SF2 is ought to be comparatively more homogeneous [6]. Of the segments classified as SF2, on average ≈ 25 surf% is covered in non-matrix, while Lauper et al. (2021) [6] reported only ≈ 10 surf% (see Table 2). Judging from this higher non-matrix content, it is possible for the segments classified as SF2 to better be further subdivided into smaller fragments and assigned to separate distinct subfacies. Though this may likely lead to smaller RELs for the respective subfacies segments, the necessary resolution for this approach is not given with the grid size used in the optical characterization.

To compare this optical box counting method to other determination methods for representativeness, the deviation from the average composition with increasing core length is investigated. Due to the large variation in surface coverage of the smaller phases, only the main

matrix and non-matrix coverage is considered. As in the previous determination method, multiple consecutive grids are summed up to obtain an ever enlarging core length. However, these lengths are not compared to the next bigger area, but to the average surface matrix coverage of the respective subfacies segment. The length is increased until less than 10 % deviation from the average is observable. Figure 79 shows how the optical characterization is transformed into matrix and non-matrix for the respective subfacies, together with the average matrix surface coverage for each segment as a dotted line.

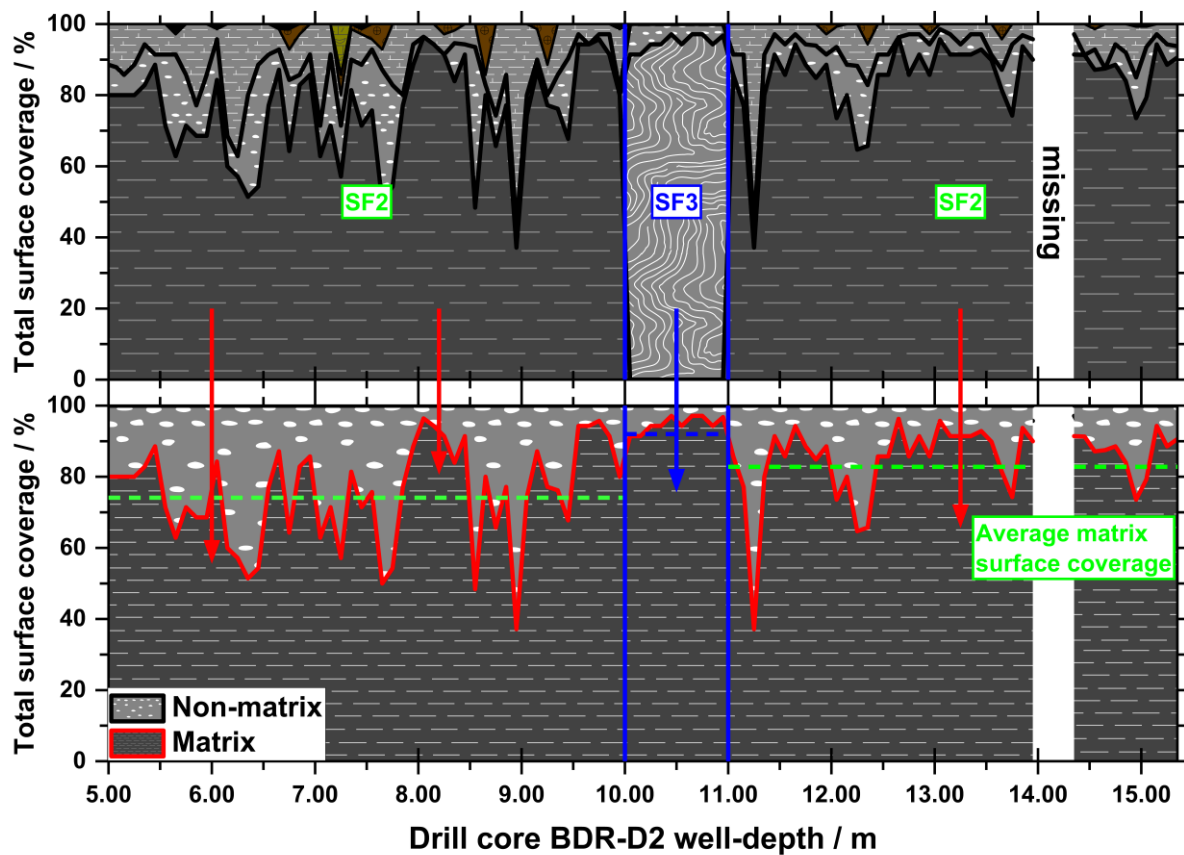


Figure 79: Transformation of the optical characterization to investigate the deviation from the average matrix surface coverage with increasing area on the example of drill core BDR-D2. Average coverage shown as a dotted green line for SF2 and as a dotted blue line for SF3.

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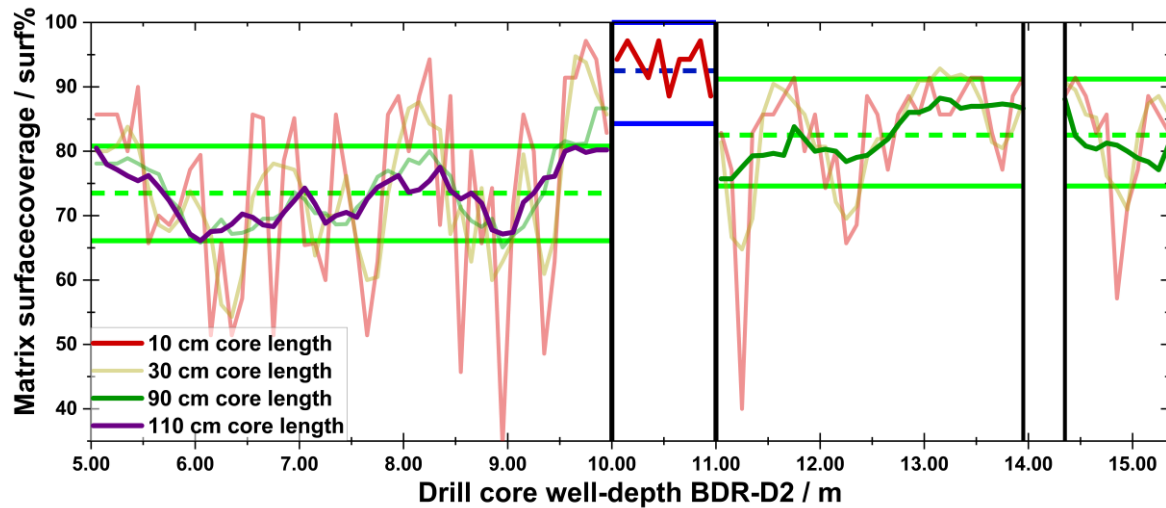


Figure 80: Main matrix surface coverage with increasing core length of drill core BDR-D2. The average composition is shown as a dashed line in green for SF2 and in blue for SF3, with the respective acceptable deviation of 10 % shown as a full line.

With increasing core length, a more average composition is observed. To reach the desired limit of less than 10 % deviation, a REL of 90–110 cm is necessary for the SF2 segments (purple and dark green data not going beyond the bright green line in Figure 80). In this approach, broad non-matrix layers and concretions do not cause as significant increases in the obtained RELs as in the optical box counting method. A REL of 10 cm is obtained for the region classified as SF3 (dark red data not going beyond the blue line in Figure 80). This is both comparable to the previously applied method.

The neglectable impact of significantly different non-matrix layers and concretions in this determination method for a REL highlights, how different methods can emphasize or conceal certain effects. Overall data trending in the optical composition is concealed with the optical box counting method, but taken into account when investigating the deviation from the average. Depending on the properties taken into account for the determination, a REL of 30–140 cm can be suggested for SF2. For SF3, it has to be noted that when taking all three main surface phases into account, the length of 100 cm has not been sufficient to identify a REL. Likely, it is in the same range or larger as for SF2, but more investigations would need to be carried out. Therefore, a REL of 10–100 cm can only be suggested. The obtained lengths may act as guidance for sampling, depending on the properties of interest. It has to be noted, that this visual assessment does not necessarily translate well into geochemical characteristics, as shown in Chapter 4.2. These RELs may be translated into REV_s of $\approx 2.6\text{--}12\text{ dm}^3$ for SF2 and $\approx 1\text{--}9\text{ dm}^3$ for SF3, taking the drill core diameter into account.

Since the drill cores BDR-D1 and -D2 have been drilled in from the same level (floor of the URL tunnel) in plane with a relative angle of 70° towards one another (see Figure 17), a correlation can be made to assess the heterogeneity parallel to the bedding. The resulting correlation graph is shown in Figure 81 together with a 90 % confidence interval, highlighting the area corresponding to less than 10 % deviation. A strong correlation between the two cores is observable, with a REL of ≈ 10 cm being enough to represent a layer across up to 20 m. Jaeggi *et al.* (2014) noted the correlation of intra-facies boundaries (later to be renamed to subfacies) over distances more than 10 m to be difficult in sandy facies OPA. However, larger alternations with a thickness of 10 cm and beyond are known to be traceable laterally at the scale of the whole URL Mont Terri [92, 201, 202] and even up to the Swiss northern basin [203]. Therefore, the scalability of the optical subfacies classification scheme for these distances is no surprise. Possibly, the REL parallel to the bedding might even be lower, but the minimum grid size investigated in this study limits the evaluation to 10 cm.

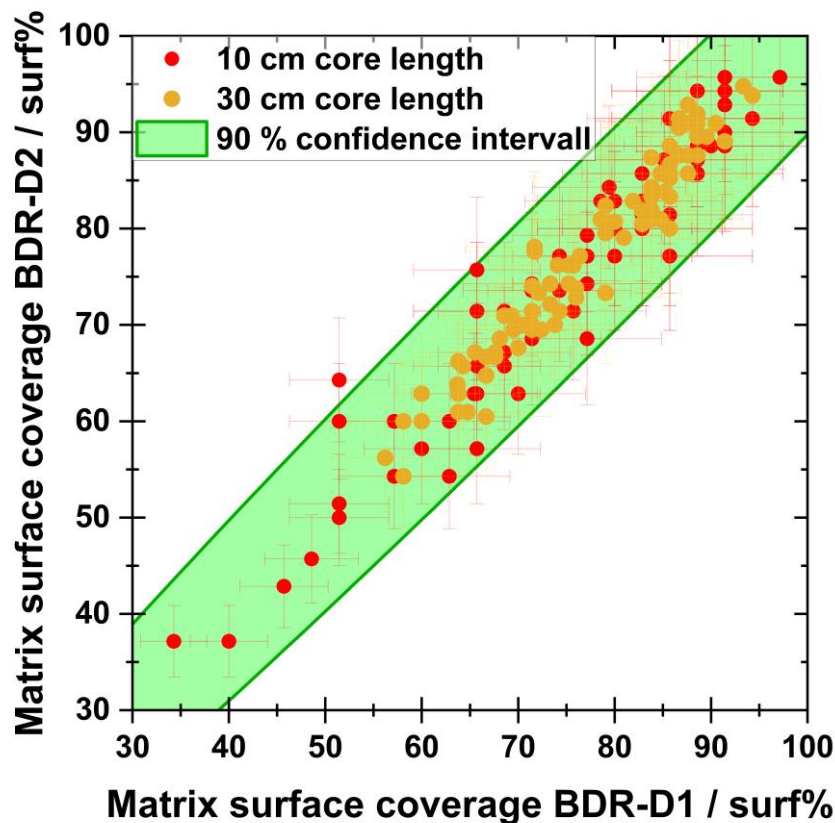


Figure 81: Correlation graph of the optical characterization with two different core lengths shown in red and orange. Only the matrix surface coverage is taken into account. Indicated as a green band is a 90 % confidence interval highlighting a maximum deviation of $\pm 10\%$.

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4.7.3 Mineralogical Heterogeneity

To investigate representative areas for the mineralogy of the sandy facies OPA on the microscopic scale, the box counting method is applied in its original form, as in Houben *et al.* (2014) [56]. The general method has already been used in previous studies [237, 238] and offers the determination of a REA on a two-dimensional sample. In the study of Houben *et al.* (2014) [56], the mineralogical composition is determined in a rectangular subregion, whose area is gradually increased. While in the studies of Klaver *et al.* (2012) [238] and Houben *et al.* (2013) [236] this process is continued until “no significant change” is observable, Houben *et al.* (2014) [56] stopped at a variation of less than 10 % in the mineralogy. This value for an acceptable deviation for representativeness is also used in this study. The SEM-EDX image already shown in Figure 37 is used to obtain a REA for the mineralogy. The starting points of the boxes are set on the corners of the SEM image and are gradually increased inwards (Figure 82, top left). This is different to the sampling method of Houben *et al.* (2014) [56], where the box is centered at a specific location and increased to all dimensions equally, causing the center to remain stationary. With the procedure in this study, a shift in the center of the ever larger box is caused, shown by the red arrows in Figure 83. Differences in these sampling methods are briefly addressed in the study of Huang *et al.* (2020) [239], though assuming a homogeneous distribution can be reached, both cases should yield comparable results. To compare the two approaches, three random locations on the SEM image are also chosen for another box counting method investigation.

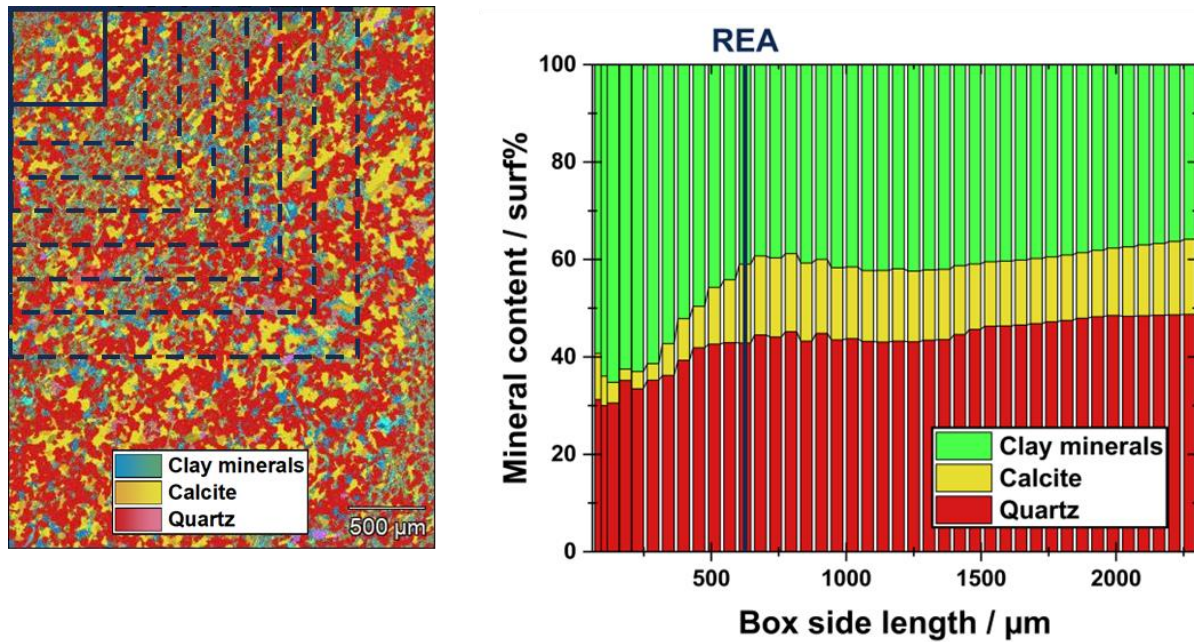


Figure 82: Left: Phases identified via SEM-EDX image mapping, with the obtained REA for the investigation starting at the top left corner highlighted by a dark blue square. The dashed squares indicate the stepwise increase up to the maximum investigated area. Right: The resulting mineral composition with increasing box side length from the investigation starting at the top left corner. Side length from which on less than 10 % deviation is observed, is indicated as the REA.

On the left of Figure 82, the SEM-EDX mapping is shown with the phases identified as quartz in shades of red, as calcite in yellow and the clay minerals in different shades of blue to green. Other mineral phases are disregarded due to their minor contribution to the overall mineralogy. Feldspars cannot be distinguished from clay minerals by SEM-EDX and, thus, no respective fractions can be quantified. Exemplarily, one of the areas deemed representative in all mineral contents is indicated by a dark blue square in the top left corner on the left of Figure 82. On the right, the resulting mineral composition is shown, indicating the obtained REA with a dark blue line.

The average REA from the seven investigations (four corners and three random spots) amounts to a square with an area of $0.34 \pm 0.17 \text{ mm}^2$. The highest REA of the seven investigations determined in this study is $0.55 \pm 0.1 \text{ mm}^2$ and the lowest is $0.16 \pm 0.03 \text{ mm}^2$. This is higher than what is reported by Houben et al. (2014) [56] for sandy facies OPA, who have identified an average REA of $0.04\text{--}0.06 \text{ mm}^2$ with the same 10 % deviation criterion. The different sampling method during the box counting method does not account for these differences, since the squares with a random center investigated in this study show similarly elevated REAs. Generally, in heterogenous material a certain variability for REA values is as well to be expected, when different samples are analyzed. Houben et al. (2014) [56] focused the imaging on specific sub-layers, like a specific clay layer within the sandy facies and stayed within this

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layer for the whole REA determination. In the present study, a much larger area is investigated and no specific focus is set. This may lead to the observed larger REAs. Also, the REA in this study is determined across multiple layers, which may be adumbrated in the top left corner of Figure 82 and are tried to be visualized in Figure 83, with the black lines delimiting areas of high and low clay mineral contents.

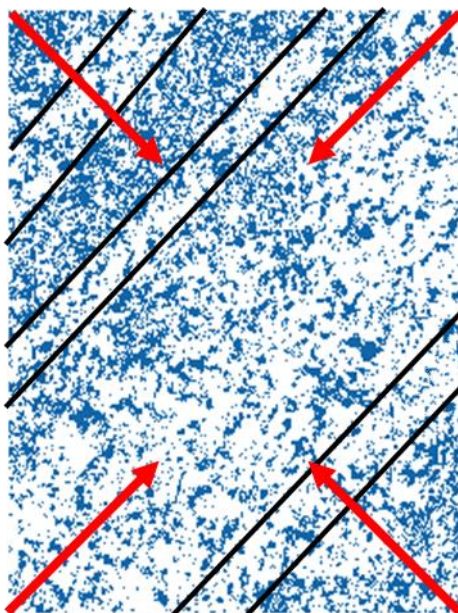


Figure 83: Illustration of the layered structure visible in the SEM-EDX image. The blue areas correspond to the clay mineral phase in Figure 82. The black lines highlight the layered structure which is prevalent in the top left corner of the image. The red arrows indicate the shift of the center in the REA determination starting in each of the four corners.

Even though this layered structure is hardly visible, it slightly impacts the obtained REAs in this study. The shift of the center is either perpendicular to the structure (starting top left or bottom right) or parallel (starting top right or bottom left), indicated by the red arrows in Figure 83. The corresponding REAs for the perpendicular shifted boxes are larger by a factor of 2–3, showing a small systematic difference when enlarging the boxes across the layered structure. The mineral composition with increasing box size starting in the four corners is shown in Figure 84, with the different REAs highlighted by a dark blue line. It has to be noted, that the differences in side lengths should nevertheless not be overstated in such a heterogeneously composed system, with the low amount of samples investigated.

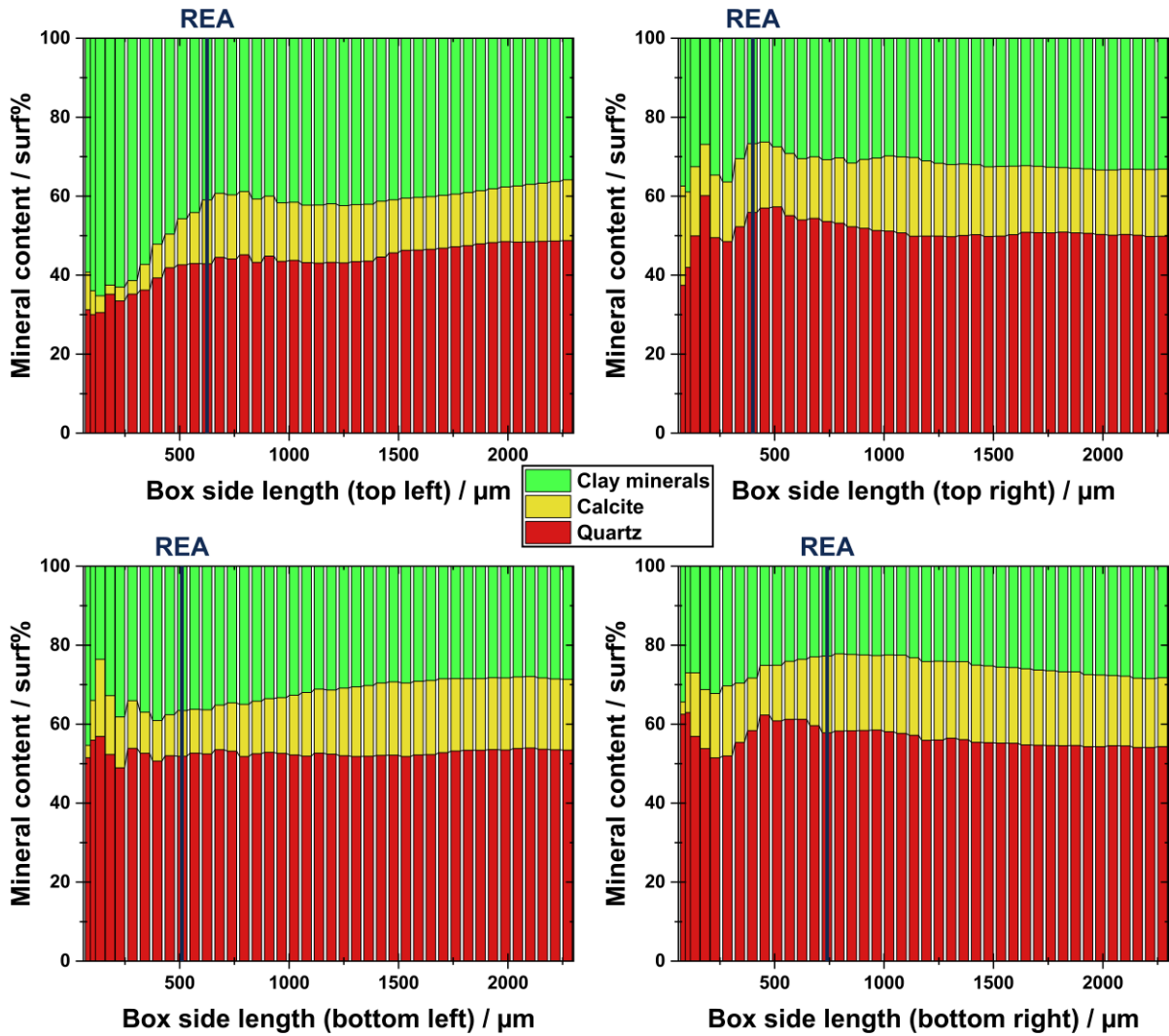


Figure 84: Mineral composition with increasing box length for starting at each of the four corners displayed in Figure 82 (left) with the resulting REA indicated by a dark blue line. When the center of the box shifts perpendicular to the bedding (top left and bottom right), a larger REA is concluded.

As already shown in Chapters 4.1 and 4.2, the optical characterization does not necessarily translate particularly well to the mineral composition. Where in the optical characterization, a comparatively high heterogeneity has been observed, the mineralogy remained more or less homogeneous, as shown in Figure 85. Therefore, a lower representative volume may be expected in comparison.

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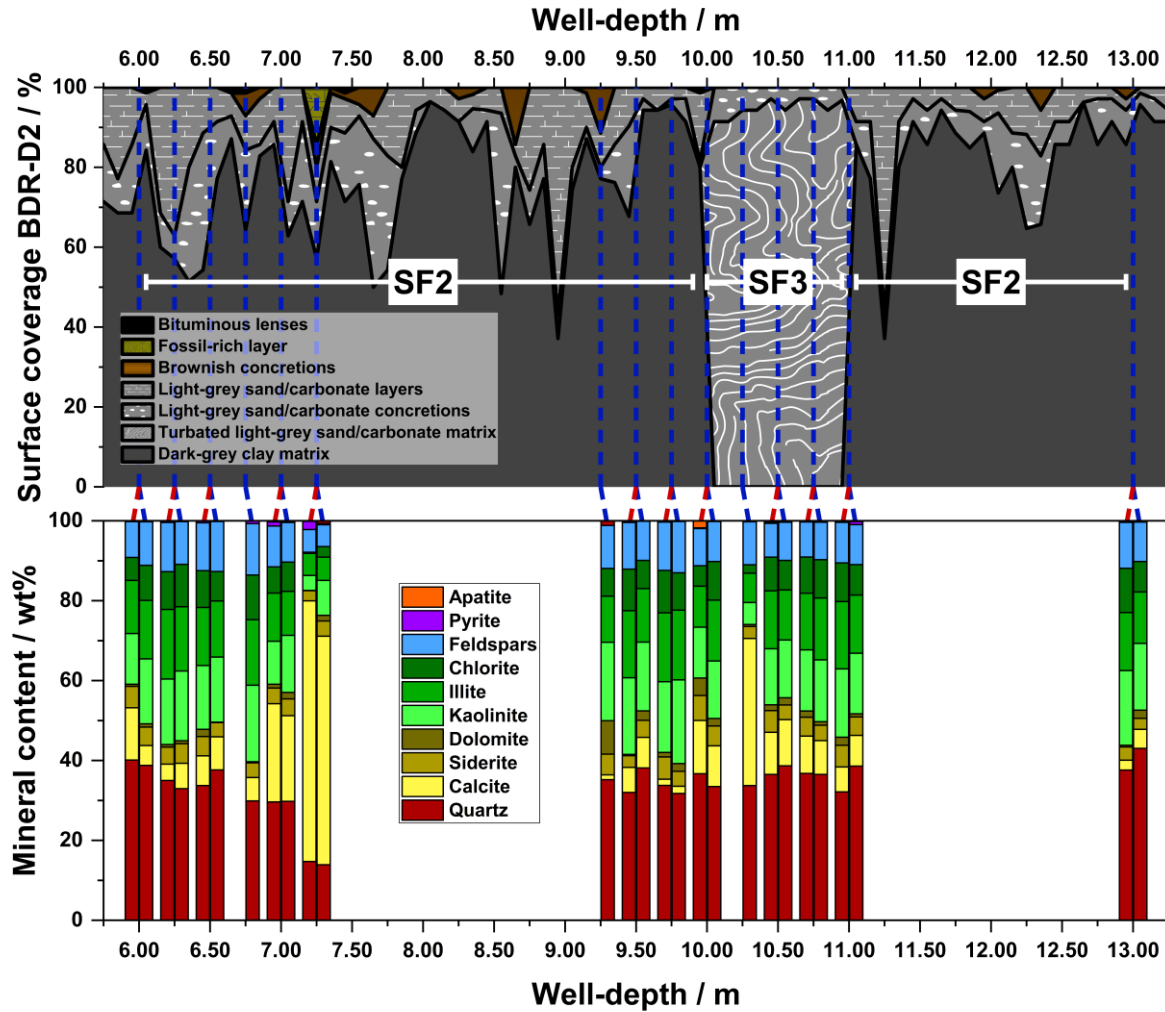


Figure 85: Comparison of the optical characterization of drill core BDR-D2 to the mineral composition of the two cores. For the mineral content, the left bar of the pairs (red dotted line) shows the mineralogy of drill core BDR-D1, while the right bar shows the mineralogy of drill core BDR-D2 (blue dotted line). The well-depth from which these samples have been obtained is in the middle of the mineral bar pairs.

While at a well-depth of 7.00 m and 7.25 m (position as the middle of the mineral composition bar pairs, see description of Figure 85), the calcite content dominates, the fossil layer identified via optical characterization only seems to occupy a marginal proportion of the surface. This effect is caused by the different resolution of the sampling methods. While in the optical characterization a grid with a length of 10 cm is used and merged into one data point, for the mineralogical characterization discs with a thickness of 2 cm are investigated. However, on the surface of the respective half discs, mostly the clay matrix is visible (see Figure 33), exhibiting a more or less uniform look. This may be caused by the fossil rich layer being overlayed by the clay matrix. A basic illustration of this possible occurrence is shown in Figure 86.

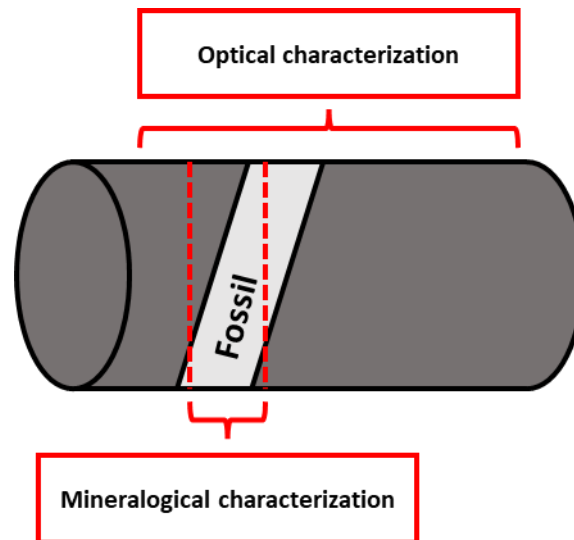


Figure 86: Illustration of the sampling through the fossil-rich layer, highlighting the different resolutions of the optical characterization and the sampling for the mineralogical characterization. The dotted lines indicate the resulting surface of the disc.

Besides this optically explainable strong deviation from the average mineral composition, only the sample at a well-depth of 10.25 m shows a strikingly high calcite content. A central point for the assessment of the samples so far has been the subfacies categorization of Lauper et al. (2021) [6]. In this classification, segments are assigned to specific subfacies based on their visual look. Of these segments, multiple samples have then been taken and the mineral composition analyzed. Thereby, ranges of the mineral composition have been derived, which may serve as limits for representativeness. Basically, if all samples of a certain volume have a mineral composition that is within the ranges observed by Lauper et al. (2021) [6], the volume can be considered representative for the subfacies. Then, the smallest volume of which all samples stay within the mineralogy of their assigned subfacies can be considered the minimum REV regarding this classification. To illustrate this approach, a somewhat modified version of the ternary diagram in Figure 45 is set up. In this process, only samples which can visually be assigned to a distinct subfacies are considered. Furthermore, the samples acquired for a specific mineralogy (SA, SH and the single-phase samples all of drill core BMB-A7) can also not be considered in an approach to identify a representative volume. The resulting diagram is shown in Figure 87.

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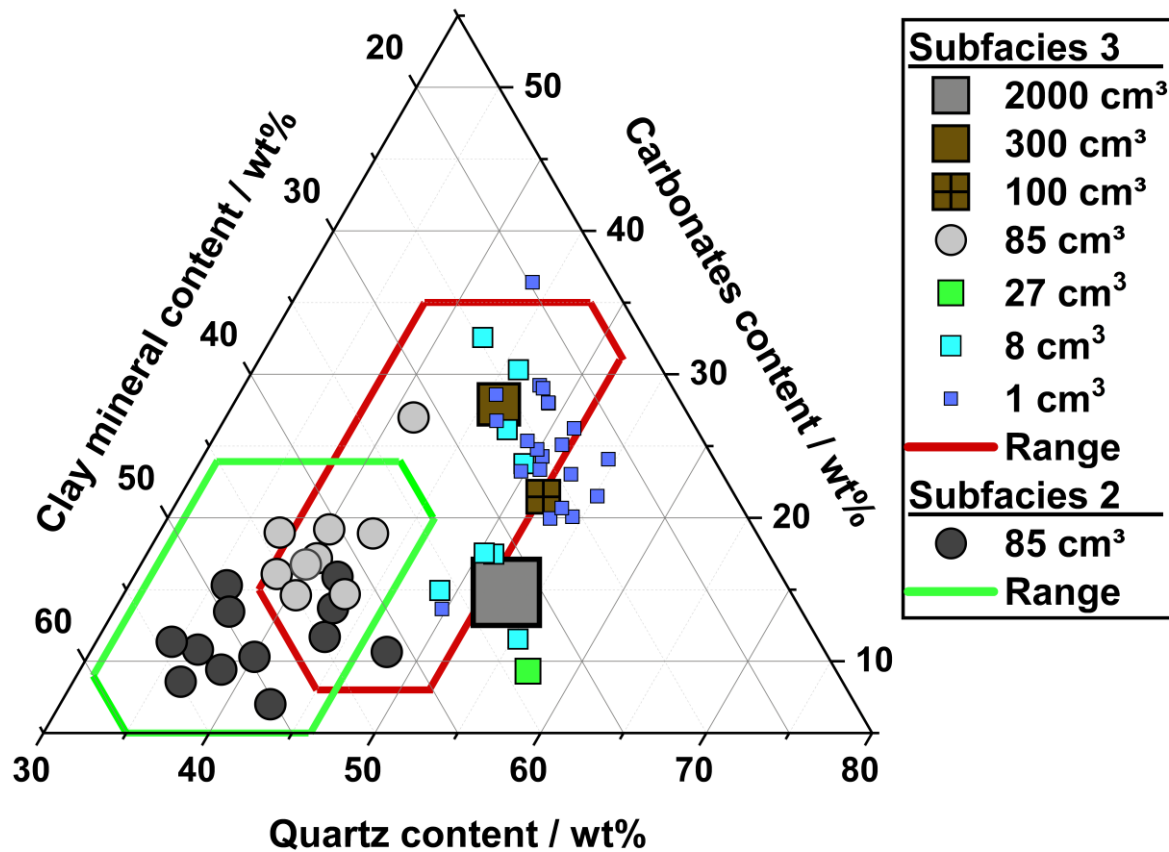


Figure 87: Ternary diagram of the samples included for the determination of a mineralogical REV. The mineral composition proposed for the subfacies classification by Lauper et al. (2021) [6] are shown in green for SF2 and in red for SF3.

The 1 cm³ samples are visually assigned to SF3, but the mineral composition of some of these samples deviates significantly from the ranges proposed by Lauper et al. (2021) [6]. Of the 8 cm³ samples only one is outside the proposed range, which may be classified as a single outlier. However, the 27 cm³ sample deviates even further, indicating that a representative volume for the subfacies classification is not yet reached. Starting with a volume of 85 cm³, the samples visually assigned to SF3 consist of the proposed mineral composition and stay within the red area highlighting the composition determined by Lauper et al. (2021) [6] for SF3. The investigated sample with a volume of 2000 cm³ (BU1) is on the edge of the assigned mineral range, but considering the uncertainties of the determination it may still be considered within the boundary. However, this might also be an indication for a volume of 2000 cm³ to be larger than the maximum REV for the mineralogy and this sample already encompassing multiple subfacies. This argument is opposed by no visual differences being observable between the drill core segment of the 2000 cm³ sample and the segment of the smaller samples. Furthermore, a look at the mineral ranges proposed for all subfacies reveals, that none would fit the mineral composition of this large sample. No mineral composition for a subfacies is reported with a

quartz content above 52 wt%. With a volume of 2000 cm³ it may be deducted, that the mineral composition is not a very specific outlier, which may be the case for very small samples. Therefore, arguments can be made to increase the range of the quartz content for SF3, which is the subfacies with the highest quartz content, up to 54 wt%. However, even with this enlarged quartz content range, the sample with a volume of 27 cm³ is still outside the proposed composition. The proposed minimum REV for the mineralogy regarding the subfacies classification for SF3 of 85 cm³ may therefore still apply.

For SF2 only one volume of samples (85 cm³) has been investigated, therefore the conclusions for a mineralogical REV for this subfacies are limited. Of these samples only one deviates from the assigned compositional range, shown as a green polygon in Figure 87. Taking into account the uncertainties in the determination, this sample may still be considered within the boundaries. Therefore, the REV for the mineral composition representing SF2 may be estimated to be similar to the REV proposed for SF3 at ≈ 85 cm³.

This mineralogical REV is much larger than what may be expected from the SEM imaging and clearly shows the inability of upscaling beyond the mm-scale of this SEM-EDX based data, as projected by Houben *et al.* (2014) [56]. A comparison to the REV of other mineralogical characteristics like the porosity [56, 59] ($\approx 10^{-3}$ mm³) also shows these results to be on a completely different order of magnitude. Fernandes *et al.* (2012) [240] investigated the porosity of sandstones with a much larger pore size and even in those rock systems, a REV of ≈ 2.7 mm³ for the porosity is observed. This shows the strong fluctuations a REV can have, depending on the investigated material and on the investigated property. The experimentally determined REV for diffusivity by Yuan *et al.* (2022) [55] is ≈ 7 cm³, when allowing a deviation of 23 % and is estimated to around 100 cm³ when considering a deviation by 10 %, like it has been done so far in this study. This is therefore a parameter showing a REV on the same scale as the mineralogy determined in this study, with which it is strongly related [80].

Another approach to determine a REV for the mineral composition is to investigate the maximum deviation from the average composition. Due to the large percentage variation of the minerals only contained in low amounts and the general importance of the clay mineral content for the sorption, only the total clay mineral content is taken into account for this investigation. Each sample will be compared to the average of the respective investigated drill core segment and subfacies. For the optical characterization, a deviation of 10 % from the average composition has been deemed an acceptable limit to determine representativeness. This is also in the same range as the uncertainty of the determination method used, with multiple optical

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characterizations of the same segment yielding the same composition with $\pm 10\%$ accuracy (see Chapter 3.6.2.1). Therefore, an appropriate limit for the determination of representativeness for the mineralogy may be the uncertainty in the determination of the clay mineral content through the XRD measurement and subsequent Rietveld refinement. This would amount to an acceptable deviation of $\pm 20\%$. Similarly to the approach to determine the mineralogical REV in regards to the subfacies classification, the samples with an obvious strong deviation from the average composition (e.g. fossil-rich layer) are disregarded. The maximum deviations from the average composition of each volume are summarized in Table 24.

Table 24: Maximum deviation from the average mineralogy of each sample volume. The proposed limit for representativeness is $\pm 20\%$.

Sample volume	Percentage deviation range from the average clay mineral content	
	SF3	SF2
2000 cm³ (BU1)	-3.0	-
300 cm³ (BU2)	15.1	-
100 cm³ (EV)	12.9	-
85 cm³ (BDR)	-15.3–20.0	-16.8–19.8
27 cm³	-27	-
8 cm³	-17.0–21.1	-
1 cm³	-22.1–35.0	-

Below a volume of 85 cm³, the maximum deviations still exceed the proposed limit of $\pm 20\%$, indicated by the bold line in the table. Therefore, a REV of at least 85 cm³ is proposed regarding the mineral composition. With the data obtained in this study, a mineralogical REV of 85 cm³ is suggested, since it also fits the approach of the subfacies classification as the criterion for representativeness.

For the mineralogy, also a correlation between the two in-plane drilled cores BDR-D1 and -D2 can be drawn. A correlation plot of the main mineral constituents of the respective discs is shown in Figure 88. To obtain a sense of representativeness for the mineral contents of these samples, deviation ellipses are added. These show a deviation by the uncertainty of the XRD measurement and Rietveld refinement, as proposed for the criterion of representativeness for the previous investigation. Since each mineral content is determined with a different uncertainty, this amounts to an allowed deviation of 7 % for the quartz content (red), 14 % for the carbonates content (yellow) and 20 % for the clay mineral content (green).

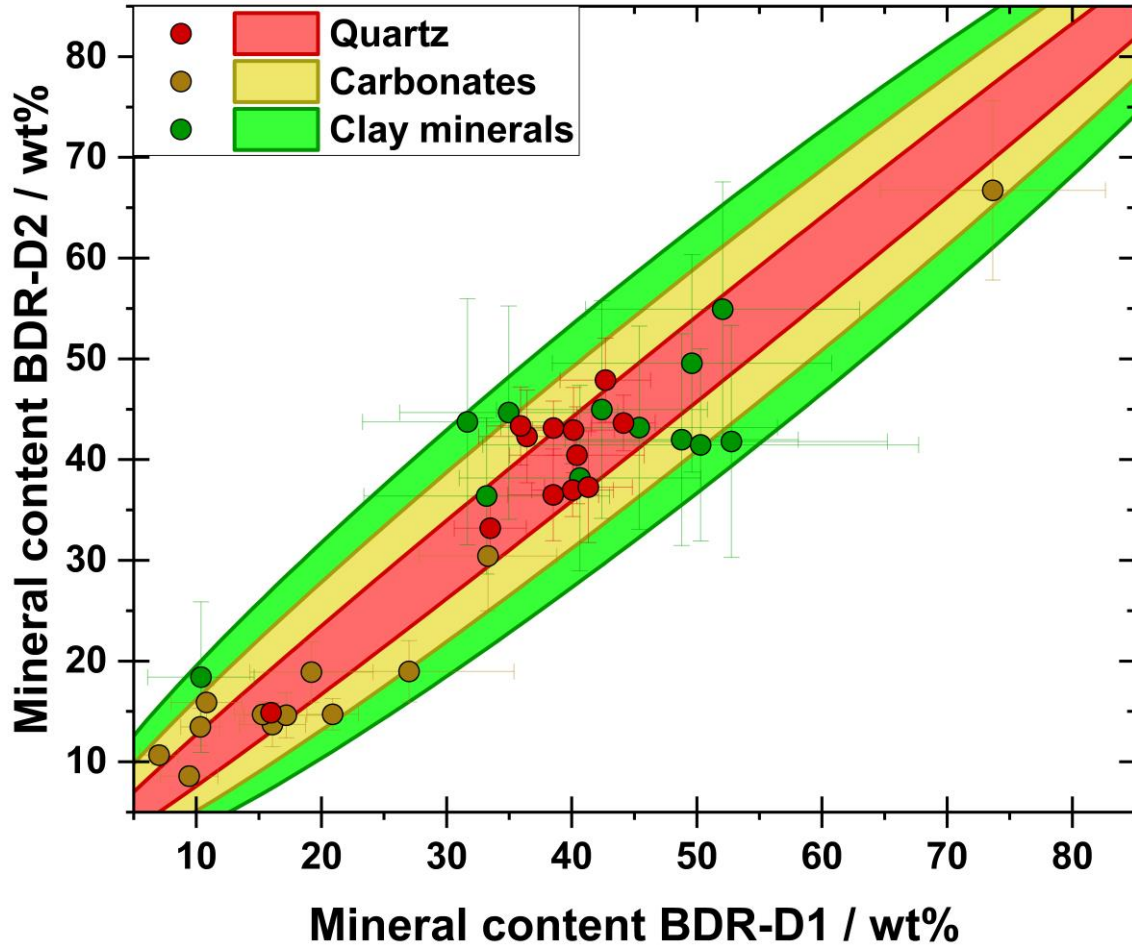


Figure 88: Correlation of the mineral composition of the cores BDR-D1 and -D2. The deviation ellipses show the average uncertainty of the measurement of the respective mineral group.

All samples fall within the respective deviation band and can therefore be considered representative for one another, for ranges up to 20 m apart. The same volume deemed representative in regards of the subfacies classification can definitely be considered representative for its 2 cm thick layer for a range of at least 20 m. This also leads to the conclusion, that the REL parallel to the bedding for the mineralogy might be as small as 2 cm. This is even smaller than the 10 cm estimated from the optical analysis and more in line with what Lauper et al. (2021) [6] report. A single drill core could be used to sufficiently describe the mineralogy of a big voxel of several meters in length parallel to the bedding, excluding external perturbation effects.

The CEC is strongly related to the mineral composition, especially the clay mineral content. In the study of Kneuker et al. (2023) [93], specific CEC ranges are attributed to each OPA subfacies. However, estimating a REV for the CEC determination based on the data scattering of the 20 g ($\approx 8 \text{ cm}^3$) samples from Kneuker et al. (2023) [93] may not be feasible. Likely, this

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would lead to samples from this study with a volume of 8 cm³ to show similar scattering, which would lead to them being considered representative. Furthermore, the detection method is afflicted with a comparatively large uncertainty, as seen for the determination of the CEC for the 27 cm³ samples of 3.5 ± 1.1 cmol_c(+)/kg. Dohrmann et al. (2012) [241] determined an uncertainty of 0.7–2.1 cmol_c(+)/kg, when repeatedly measuring bentonite samples with a CEC of 11–87 cmol_c(+)/kg. A very rough estimate for a REV regarding the CEC may therefore be in the same range as for the mineral composition at ≈ 85 cm³.

However, a correlation between the two in-plane drill cores BDR-D1 and -D2 may again be drawn. This correlation is shown in Figure 89 for the CEC at the same well-depth. Since the CEC is highly dependent on the clay mineral content, a similar allowed deviation of 20 % (yellow area) as for correlation of the clay mineral content in Figure 88 is proposed. Taking this into account, only one sample pair deviates slightly from the proposed range. Considering the uncertainty in the determination, the samples may be considered to be representative to one another for ranges up to 20 m apart parallel to the bedding in regards of the CEC. Therefore, again a REV of 85 cm³ in parallel to the bedding may be concluded.

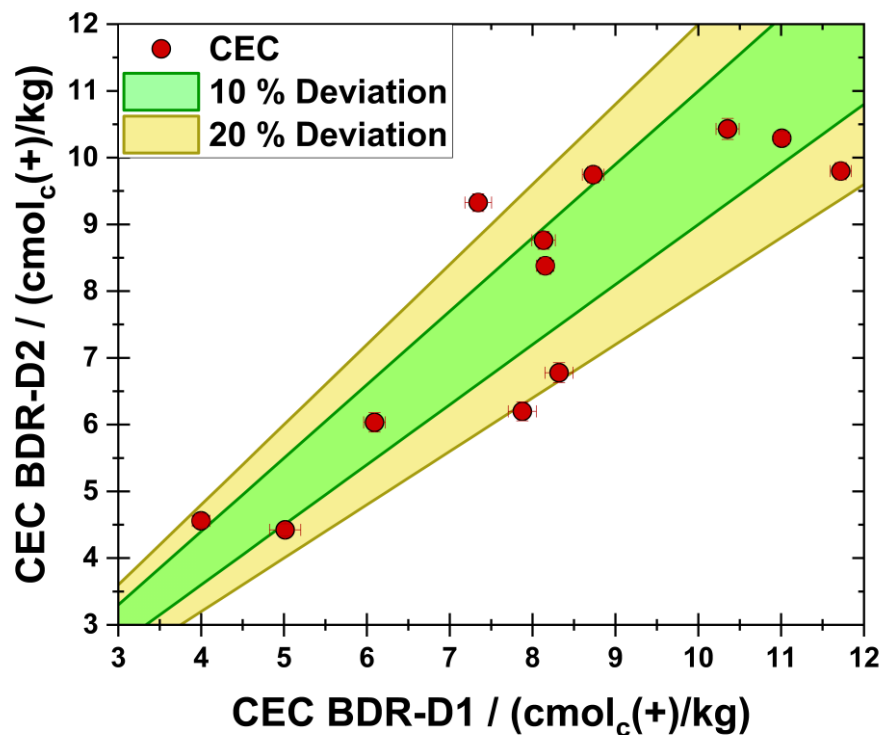


Figure 89: Correlation of the CEC of drill cores BDR-D1 and -D2 at the same well-depth. Bands indicate the deviation, with the yellow area highlighting the proposed allowed deviation of 20 %, as for the clay mineral content, which is considered the criterion for representativeness.

4.7.4 Heterogeneity of the Sorption of Cesium, Cobalt and Europium

To define representativeness for the batch sorption data, again limits need to be set to define the domain of relative homogeneity. The beforementioned, well-established estimate for the uncertainty of $\log(R_d)$ -values of strongly adsorbing cations is used: ± 0.3 log units ($\log(\text{L/kg})$) [38, 199]. This uncertainty is often used to account for experimentally observed deviations in repeated experiments with the same material under the same conditions. Though analytical precision is often much higher than this uncertainty, the variation in natural material often causes these fluctuations.

With this limit established, the maximum positive and negative deviation for each sample volume from the overall average $\log(R_d)$ -value are shown in Table 25. The smallest volume of which all samples deviate less than ± 0.3 log units ($\log(\text{L/kg})$) can be deemed the REV for the specific cation. This volume is highlighted by being separated with a bold black line.

Table 25: Deviation ranges from the average sorption coefficient of the batch sorption experiments at each distinct sample volume. *For europium, these values need to be considered with care, due to the vicinity of the obtained data to the detection limit.

Sample volume	Deviation range from the average sorption coefficient		
	Cesium / $\log(\text{L/kg})$	Cobalt / $\log(\text{L/kg})$	Europium* / $\log(\text{L/kg})$
2000 cm ³ (BU1)	-0.05	0.27	-0.23
300 cm ³ (BU2)	-0.1	0.23	-0.22
100 cm ³ (EV)	-0.1	0.21	-0.21
85 cm ³ (BDR)	-0.26–0.14	-0.28–0.24	-0.3–0.25
27 cm ³	-0.14	-0.18	-0.24
8 cm ³	-0.09–0.14	-0.16–0.18	-0.07–0.56
1 cm ³	-0.24–0.41	-0.46–0.11	-0.54–0.78

It has to be noted, for the europium samples the obtained $\log(R_d)$ -values have been obtained close to the detection limit for the samples of drill core BMB-A7 and partly even above it for the samples of the BDR drill cores. These deviations and conclusions should therefore be considered with care.

For the cesium and cobalt batch sorption experiments, all samples with a volume of 1 cm³ still deviate by more than 0.3 log units. Starting at a volume of 8 cm³, the fluctuations narrow down and relative homogeneity is obtained considering the allowed deviation. This is smaller by a factor of 10 compared to the REV of the mineralogy and even more so compared to the optical characterization. The impact of the heterogeneity seems to diminish greatly when looking at

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sorption data. Notably, since all volumes fall into the representative criterion, a single measurement of a block as small as 8 cm³ is sufficient to describe the retention capability of a whole sandy facies segment (either upper or lower). This is even true across multiple subfacies categories, since both the samples classified as SF3 and SF2 show no larger deviation from the average.

For europium, strictly obeying the limits chosen for representativeness leads to a REV of 27 cm³ being suggested. The smaller samples show a much stronger scattering and fluctuation from the average compared to the other two investigated cations. However, the sorption of europium is generally significantly stronger than what is observed for cesium and cobalt. Comparatively strong variations in the observed $\log(R_d)$ -values do not correspond to significant changes in the percentage of adsorbed europium. The difference from the average percentage of adsorbed europium of the samples of drill core BMB-A7 to the lowest observed adsorption on a single sample is only 0.2 %, changing from 99.8 % to 99.6 % adsorption. Thus, the uncertainty with respect to $\log(R_d)$ -values may even be larger than ± 0.3 log units in case of europium. Europium adsorption is not significantly correlated with the mineralogy, especially the illite content. This has been shown by experimental data and geochemical modeling. Even small clay contents ensure almost quantitative adsorption.

In Figure 90 the lateral correlation of the obtained batch sorption data is shown, comparing the $\log(R_d)$ -values of cores BDR-D1 and -D2 at similar well-depths. This is done to assess, if the chosen REV's for the sorption are also valid for the comparison parallel to the bedding, or if a larger REV needs to be proposed. To visualize the criteria for representativeness, deviation bands ranging from ± 0.1 – 0.3 log units ($\log(L/kg)$) are added in yellow to green, to indicate significant deviations in the correlation.

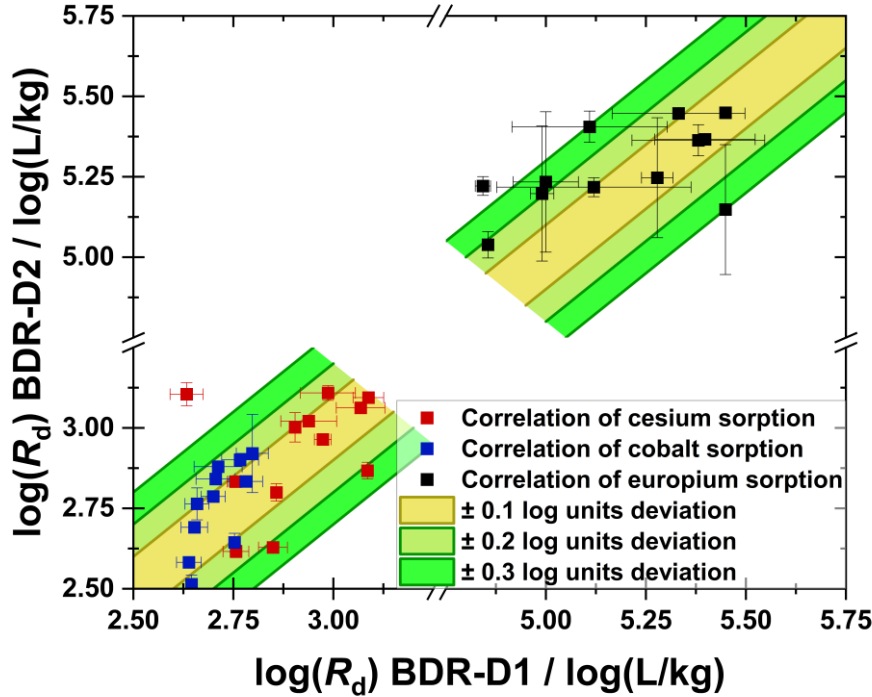


Figure 90: Correlation graph of the batch sorption experimental data, showing the obtained $\log(R_d)$ -values for cesium in red, for cobalt in blue and for europium in black. Deviation bands of ± 0.1 – 0.3 log units are added for comparison as the criterion for representativeness.

For a better visualization, a break was added on both axes to enable presentation of the europium sorption data in the same diagram. Besides two outliers, all samples fall into the green ± 0.3 log unit band. For the cesium and cobalt sorption experiment, excluding the one outlier, all values even fall into the light green ± 0.2 log unit deviation band. The samples with a thickness of 2 cm can therefore be considered representative for their layer not only mineralogically but also with respect to their sorption behavior for all three investigated cations. The proposed REV_s of 8 cm³ and 27 cm³ therefore may still apply.

Another approach to determine representativeness for an investigated parameter is to base it on the precision it needs to have for its interpretation. In the case of this study, the mineral composition has been correlated with the sorption of cations. Like taken for the criterion for representativeness, the sorption of strongly sorbing cations like Cs⁺, Co²⁺ and Eu³⁺ is commonly regarded to be accompanied with an uncertainty of ± 0.3 log units [38, 199]. The experimentally determined sorption coefficients have been modeled in Chapter 4.4, taking into account these ± 0.3 log units for the $\log(R_d)$ -values. From these modeling approaches, ranges can be determined for the precision of the illite content necessary for the analysis of homogeneity. This general approach is visualized in Figure 91 at the example of cesium in the BMB-A7 system.

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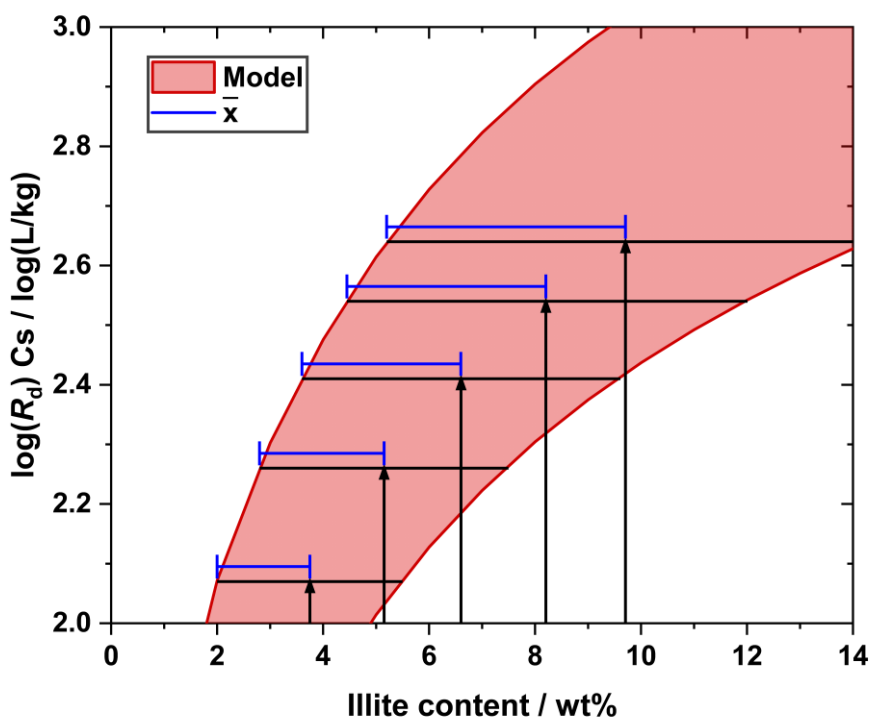


Figure 91: Geochemical model for the cesium sorption under the conditions present in the batch sorption experiment with the samples of drill core BMB-A7. The procedure for the determination of the allowed deviation $\bar{x}$ in blue is shown by the black arrows and lines.

While the geochemical model has been set up to determine sorption coefficients based on the illite content, it can be used in reverse. For each $\log(R_d)$ -value, the model determines a range of possible illite contents which can lead to this sorption coefficient. This is indicated by the horizontal black lines. From the center of these ranges, a deviation of $\pm \bar{x}$ (in blue) would be allowed to stay within the modeled sorption curve.

In a single system, the minimum allowed deviation could be determined by the lowest observed sorption coefficient in the batch sorption experiments. For the cesium sorption on the BMB-A7 samples, this would consider the deviation at the $\log(R_d)$ of 2.2 $\log(\text{L/kg})$. The same can be done for the maximum and average deviation. Since the model for europium has shown significant deviation from the experimentally determined sorption data, it is not considered here. For the cesium and cobalt systems, the values are shown in Table 26.

Table 26: Deviations in the illite content to stay within the modeling range for the sorption coefficients.

Drill core	Sorbing Cation	$\bar{x}_{min} / \text{wt\%}$	$\bar{x}_{average} / \text{wt\%}$	$\bar{x}_{max} / \text{wt\%}$
BMB-A7	Cesium	2.2	3.5	5.2
BDR	Cesium	2.2	3.5	5.3
BMB-A7	Cobalt	3.7	8.0	13.5
BDR	Cobalt	3.3	6.1	9.7

Apparently, a wide range of illite contents in a rock sample lead to a certain log R_d -value within a range of ± 0.3 log units. As the average illite content in all collected samples varies only between 6 to 11 wt%, it is clear that sorption data mostly fall into this range. Moreover, these results show, that even a low clay mineral content is sufficient to result in a comparable and strong sorption for the investigated cations. Judging from the observable illite ranges of drill core BMB-A7 shown in Figure 42, a REV of 8 cm³ may be proposed for the representativeness of the illite mineral content in regards to the sorption of cesium and cobalt. This is in line with what has been concluded on the REV for the sorption of these cations, where 8 cm³ have also been deemed the REV.

4.7.5 Synopsis on the Impact of the Heterogeneity

To summarize, the definition of homogenous domains and what may be regarded as representative samples is highly dependent on the chosen boundary conditions, often the variability considered acceptable and the scale investigated, as well as the parameter of interest. The suggested representative values are summarized in Table 27.

Table 27: Summary of the representative values obtained in this study. Averages are written in italic. *value limited by the resolution of the method applied.

Characterization	Applied method	Limit for representativeness	REL REA REV	
			Perpendicular	Parallel
Optical	Box counting	$\pm 10\%$ to next area	10–140 cm*	10 cm*
Optical	Deviation from average	$\pm 10\%$ to average	10–110 cm*	
Mineralogical (μm -scale)	Box counting	$\pm 10\%$ to next box	0.16–0.55 mm ² <i>0.34 $\pm$ 0.04 mm²</i>	
Mineralogical	Subfacies Range	Within range	85 cm ³	2 cm 85 cm ³
Mineralogical	Deviation from average	$\pm 20\%$ to average clay content	85–100 cm ³	
Sorption (cesium)	Deviation from average	± 0.3 log units	8 cm ³	2 cm 85 cm ³
Sorption (cobalt)	Deviation from average	± 0.3 log units	8 cm ³	2 cm 85 cm ³
Sorption (europium)	Deviation from average	± 0.3 log units	27 cm ³	2 cm 85 cm ³

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From the optical characterization, a REL of ≈ 140 cm is determined when taking the three main surface components into account. When only considering the matrix and non-matrix surface coverage, this decreases to ≈ 30 cm for SF2 and to ≈ 10 cm for SF3 with an allowed deviation of 10 %, which is comparable to literature data. When instead comparing the surface coverage to the average and allowing the same deviation, the REL marginally shifts to ≈ 90 – 110 cm for SF2, while it remains at ≈ 10 cm for SF3. Parallel to the bedding, a high degree of homogeneity is observable with a suggested REL of ≈ 10 cm, possibly even lower.

For the microscopic analysis of the mineralogy, an average REA of 0.34 ± 0.17 mm² is determined via the box counting method, allowing a deviation of 10 % to the next box. Taking the total investigated area into account, this is comparable to literature data. When comparing the REAs perpendicular to parallel to the layered structure, a difference by a factor of 2–3 is observable, already showing a strong impact of the sedimentary heterogeneity on the microscopic scale.

For the mineralogical composition on the cm-scale, samples with a volume of 85 cm³ can be considered representative for their respective visually assigned subfacies. This is significantly smaller than what is observed by the optical characterization. Comparing the clay mineral content of the samples to the average of the respective segment and subfacies yields a similar REV of 85–100 cm³ for the mineralogy. Again, a high degree of homogeneity is visible parallel to the bedding, showing discs with a thickness of 2 cm (85 cm³) to be representative for their respective layer up to 20 m. This indicates the REL for the mineralogy to be as small as 2 cm and further suggests the assumption of the parallel REL determined from the optical characterization to be smaller than 10 cm.

Regarding the representativeness for the batch sorption, the REV shrinks significantly. Samples with a volume as low as 8 cm³ can be considered representative for the sorption capability towards both cesium and cobalt, which shows a very low impact of the optical and mineralogical heterogeneity on this property. For the europium adsorption, an REV of 27 cm³ is suggested. In this case, very small amounts of clay minerals being present are sufficient for an almost quantitative retention. Again, parallel to the bedding a homogeneous behavior is observed with the discs with a width of 2 cm being representative for up to 20 m. For the sorption, the REL of 2 cm therefore also applies.

Thus, this work demonstrates that, while the heterogeneity is very prominent in optical assessments, its effect already diminishes significantly when investigating the mineral composition, and is almost negligible when quantifying the sorption behavior.

5. Conclusions

In the present Ph.D. study, a thorough optical and mineralogical analysis of the sandy facies OPA has been performed. Three drill cores have been investigated to gather information on this less studied facies and to extend the array of methods used for the characterization. The mineralogical composition has been determined and validated with various analytical techniques, leading to the drill cores being assigned to the respective subfacies. These results have been compared to similar investigations on the sandy and shaly facies and agree well. Volume dependent and well-depth dependent mineralogical analysis have been performed to gather insight into the impact of the heterogeneity on the mineralogical composition. These have revealed the sedimentary heterogeneity to be much more impactful perpendicular than parallel to the bedding. From the optical characterization, a REL of around 10–140 cm is proposed, depending on the matrix and surface phases considered. This is equivalent to a REV of 1–12 dm³. Parallel to the bedding, a high degree of homogeneity is observed and a REL of 10 cm is proposed. For the mineral composition, in contrast a volume of 85 cm³ has been sufficient to represent a subfacies and also respective sedimentary layers on length-scales of up to 20 m.

Batch sorption experiments have been performed with the radiotracers Cs-137, Co-60 and Eu-152 to estimate the impact of the heterogeneity on radionuclide retention. Measured sorption coefficients ($\log(R_d)$ -values) are within the range of established literature of the shaly facies. They add to the literature reports, with comparatively high pH and high carbonate content in the synthetic pore water. The impact of the heterogeneity on these sorption parameters is low, finding a REV for the sorption of cesium and cobalt of only 8 cm³ and for europium at 27 cm³. In total, very minor variation in sorption behavior is found on the total of the investigated scale, both perpendicular and parallel to the bedding. Again, a high order of similarity has been found parallel to the bedding, shown by highly correlated results between the BDR-D1 and -D2 drill cores in up to 20 m distance from each other.

Due to the before mentioned lack of literature data on the sorption on the sandy facies and to better interpret the obtained results, geochemical modeling has been performed. Simulations applying a simplified bottom-up approach considering exclusively sorption on illite validate the sorption data of cesium and with minor deviations also those of cobalt. For the europium sorption, the model underestimates the observed sorption coefficients. However, though the sorption is very strong and $\log(R_d)$ -values close to- or at the detection limit are observed, both model and data agree on adsorption of more than 99.5 %.

To validate the assumptions made for the geochemical modeling and gather information on the sorption behavior of the trivalent Eu^{3+} , TRLFS investigations of the chemical equivalent Cm^{3+} have been carried out in the carbonate containing synthetic pore water. The sorption species on multiple minerals contained in OPA have been investigated via luminescence spectroscopy, applying peak deconvolutions and luminescence lifetime investigations. Indications for ternary carbonate surface adsorbed species have been found for all investigated minerals, though much more pronounced on kaolinite, calcite and illite. This shows the potential impact of the carbonate in a synthetic pore water with respect to the sorption behavior. The hypothesis of illite being the most relevant mineral phase for the sorption of trivalent cations could be confirmed, but contributions of calcite are also likely.

As an integral approach towards investigating sorption heterogeneity on the μm – cm -scale, intact clay rock surface characterization and sorption experiments have been performed. Via SEM-EDX imaging, a REA of $0.34 \pm 0.17 \text{ mm}^2$ is determined for the mineralogy of the rock surface on the microscopic scale via the box counting method. The affinity for the cesium towards clay mineral surfaces has been confirmed via autoradiography. The intact clay rock surface sorption procedure shows a clear impact of the heterogeneity on the mm -scale, being responsible for the distinct sorption pattern measurable via autoradiography.

The obtained results provide a significant contribution to understanding the sorption behavior of mono-, di- and trivalent cations on OPA. They demonstrate that, while heterogeneity may be prominent in optical assessments, its effect diminishes significantly when investigating the mineral composition, and is almost negligible when quantifying the sorption behavior. These findings may guide upscaling approaches for the assessment of the long-term safety of nuclear waste repositories constructed in clay rock.

Further investigations could span a more in-depth study on the lateral homogeneity of sedimentary layers, possibly allowing to estimate the mineralogy and sorption behavior across a whole sedimentary basin based on only few drillings. Furthermore, the volume dependent sampling procedure could be significantly improved by introducing many more samples, prepared from randomly chosen core segments into the analysis. A larger total volume should be investigated to compensate for the cm -scale heterogeneities and prevent single layers to dominate the mineralogy of the experiment. A bigger spread in investigated volumes might help narrow down representative elementary volumes on this macro-scale.

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Appendix

Appendix A

Cs Sorption

TITLE Cs sorption calculation

```

PHASES                                #pH control
Fix_pH
H+ = H+
log_k 0.0

EXCHANGE_MASTER_SPECIES               #definition of additional present species
Xa  -                                #strong sites
Xb  -                                #weak sites
Xc  -                                #planar sites

EXCHANGE_SPECIES                       #equilibrium constants of the exchange sites
Xa- = Xa-                             #equilibrium constants of the strong sites
log_k = 0.0
Xa- + Na+ = NaXa
log_k      0.0
NaXa + K+ = KXa + Na+
log_k      2.4
NaXa + Cs+ = CsXa + Na+
log_k      7.0
NaXa + Rb+ = RbXa + Na+
log_k      4.6

Xb- = Xb-                             #equilibrium constants of the weak sites
log_k = 0.0
Xb- + Na+ = NaXb
log_k      0.0
NaXb + K+ = KXb + Na+
log_k      2.1
NaXb + Cs+ = CsXb + Na+
log_k      3.6
NaXb + Rb+ = RbXb + Na+
log_k      2.6

Xc- = Xc-                             #equilibrium constants of the planar sites
log_k = 0.0
Xc- + Na+ = NaXc
log_k      0.0
NaXc + K+ = KXc + Na+
log_k      1.1
NaXc + Cs+ = CsXc + Na+
log_k      1.6
NaXc + Rb+ = RbXc + Na+
log_k      1.6

2NaXc + Mg+2 = MgXc2 + 2Na+
log_k      1.04
2NaXc + Ca+2 = CaXc2 + 2Na+
log_k      1.04
END

SOLUTION 1                             #composition of background solution
units mol/kgw
pH      7.24
Na      0.14959

```

Appendix

```

K          0.00211
Mg         0.01184
Ca         0.00897
Sr         0.0004817
Cl         0.16524 charge
S(6)      0.0095
C          0.00292
Co         3.7E-7
Eu         5.0E-10
Ni         5.5E-7
Zn         1.0E-6
Rb         4.65E-7
Ba         5.1E-7
Cs         2.05E-7
SAVE SOLUTION 1
END

```

```

EXCHANGE 1
Xa 5E-8;      Xb 4E-6;      Xc 1.6E-5;      END;  #1% Illite
EXCHANGE 2
Xa 1E-7;      Xb 8E-6;      Xc 3.2E-5;      END;  #2% Illite
EXCHANGE 3
Xa 1.5E-7;    Xb 1.2E-5;    Xc 4.8E-5;      END;  #3% Illite
EXCHANGE 4
Xa 2E-7;      Xb 1.6E-5;    Xc 6.4E-5;      END;  #4% Illite
EXCHANGE 5
Xa 2.5E-7;    Xb 2E-5;      Xc 8E-5;        END;  #5% Illite
EXCHANGE 6
Xa 3E-7;      Xb 2.4E-5;    Xc 9.6E-5;      END;  #6% Illite
EXCHANGE 7
Xa 3.5E-7;    Xb 2.8E-5;    Xc 1.12E-4;     END;  #7% Illite
EXCHANGE 8
Xa 4E-7;      Xb 3.2E-5;    Xc 1.28E-4;     END;  #8% Illite
EXCHANGE 9
Xa 4.5E-7;    Xb 3.6E-5;    Xc 1.44E-4;     END;  #9% Illite
EXCHANGE 10
Xa 5E-7;      Xb 4E-5;      Xc 1.6E-4;      END;  #10% Illite
EXCHANGE 11
Xa 5.5E-7;    Xb 4.4E-5;    Xc 1.76E-4;     END;  #11% Illite
EXCHANGE 12
Xa 6E-7;      Xb 4.8E-5;    Xc 1.92E-4;     END;  #12% Illite
EXCHANGE 13
Xa 6.5E-7;    Xb 5.2E-5;    Xc 2.08E-4;     END;  #13% Illite
EXCHANGE 14
Xa 7E-7;      Xb 5.6E-5;    Xc 2.24E-4;     END;  #14% Illite
EXCHANGE 15
Xa 7.5E-7;    Xb 6E-5;      Xc 2.4E-4;      END;  #15% Illite
EXCHANGE 16
Xa 8E-7;      Xb 6.4E-5;    Xc 2.56E-4;     END;  #16% Illite
EXCHANGE 17
Xa 8.5E-7;    Xb 6.8E-5;    Xc 2.72E-4;     END;  #17% Illite
EXCHANGE 18
Xa 9E-7;      Xb 7.2E-5;    Xc 2.88E-4;     END;  #18% Illite
EXCHANGE 19
Xa 9.5E-7;    Xb 7.6E-5;    Xc 3.04E-4;     END;  #19% Illite
EXCHANGE 20
Xa 1E-6;      Xb 8E-5;      Xc 3.2E-4;      END;  #20% Illite
EXCHANGE 21
Xa 1.05E-6;   Xb 8.4E-5;    Xc 3.36E-4;     END;  #21% Illite
EXCHANGE 22
Xa 1.1E-6;    Xb 8.8E-5;    Xc 3.52E-4;     END;  #22% Illite
EXCHANGE 23

```

```

Xa 1.15E-6;      Xb 9.2E-5;      Xc 3.68E-4;      END;  #23% Illite
EXCHANGE 24
Xa 1.2E-6;      Xb 9.6E-5;      Xc 3.84E-4;      END;  #24% Illite
EXCHANGE 25
Xa 1.25E-6;      Xb 1E-4;      Xc 4E-4;      END;  #25% Illite
EXCHANGE 26
Xa 1.3E-6;      Xb 1.04E-4;      Xc 4.16E-4;      END;  #26% Illite
EXCHANGE 27
Xa 1.35E-6;      Xb 1.08E-4;      Xc 4.32E-4;      END;  #27% Illite
EXCHANGE 28
Xa 1.4E-6;      Xb 1.12E-4;      Xc 4.48E-4;      END;  #28% Illite
EXCHANGE 29
Xa 1.45E-6;      Xb 1.16E-4;      Xc 4.64E-4;      END;  #29% Illite
EXCHANGE 30
Xa 1.5E-6;      Xb 1.2E-4;      Xc 4.8E-4;      END;  #30% Illite

USER_punch                                     #data output
-headings amount_illite log_Rd total_Cs
-start
10 punch      ((tot("Xb"))/4.0E-6)              #Illite calc
20 punch      log10((sys("Cs")-tot("Cs"))/(tot("Cs"))*100)  #log Rd calc
30 punch      sys("Cs")                          #Cs control calc
-end
SELECTED_OUTPUT
-file Cs sorption model.dat
-reset false
-molalities CsXa CsXb CsXc
-totals Cs
END

#Calculation
use SOLUTION 1; use EXCHANGE 1; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0; -f; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 2; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 3; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 4; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 5; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 6; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 7; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 8; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 9; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 10; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 11; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 12; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 13; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 14; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 15; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 16; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;

```

Appendix

```
use SOLUTION 1; use EXCHANGE 17; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 18; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 19; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 20; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 21; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 22; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 23; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 24; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 25; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 26; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 27; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 28; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 29; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use EXCHANGE 30; EQUILIBRIUM_PHASES 1; Fix_pH -7.24 NaOH 1;
CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
```

Co and Eu Sorption

TITLE Co and Eu sorption

```

PHASES                                     #pH control
Fix_pH
H+ = H+
log_k 0.0

SURFACE_MASTER_SPECIES                   #definition of additional phases
Clay_s  Clay_sOH                         #strong sorption sites

SURFACE_SPECIES                           #equilibrium constants
Clay_sOH = Clay_sOH
log_k 0.0
Clay_sOH + H+ = Clay_sOH2+
log_k 4.0
Clay_sOH = Clay_sO- + H+
log_k -6.2

Clay_sOH + Ni+2 = Clay_sONi+ + H+
log_k 0.7
Clay_sOH + Ni+2 + H2O = Clay_sONiOH + 2H+
log_k -8.2
Clay_sOH + Ni+2 + 2H2O = Clay_sONi(OH)2- + 3H+
log_k -17.3

Clay_sOH + Co+2 = Clay_sOCo+ + H+
log_k 0.0
Clay_sOH + Co+2 + H2O = Clay_sOCoOH + 2H+
log_k -7.0
Clay_sOH + Co+2 + 2H2O = Clay_sOCo(OH)2- + 3H+
log_k -16.5

Clay_sOH + Eu+3 = Clay_sOEu2+ + H+
log_k 1.9
Clay_sOH + Eu+3 + H2O = Clay_sOEuOH+ + 2H+
log_k -4.6
Clay_sOH + Eu+3 + 2H2O = Clay_sOEu(OH)2 + 3H+
log_k -12.8
Clay_sOH + Eu+3 + 3H2O = Clay_sOEu(OH)3- + 4H+
log_k -24.0

Clay_sOH + Eu+3 + CO3-2 = Clay_sOEuCO3 + H+
log_k 9.8
Clay_sOH + Eu+3 + CO3-2 + H2O = Clay_sOEuOHCO3- + 2H+
log_k 1.4

EXCHANGE_MASTER_SPECIES                 #definition of exchange sites
X  X-
EXCHANGE_SPECIES                         #equilibrium constants
X- = X-
log_k 0.0
Na+ + X- = NaX
log_k 0.0
Ni+2 + 2X- = NiX2
log_k 1.1
Co+2 + 2X- = CoX2
log_k 1.3
Eu+3 + 3X- = EuX3

```

Appendix

```
log_k 1.9
NaX + H+ = HX + Na+
log_k 1.0
NaX + K+ = KX + Na+
log_k 12.9
2NaX + Mg+2 = MgX2 + 2Na+
log_k 11.0
2NaX + Ca+2 = CaX2 + 2Na+
log_k 11.0
END
```

```
SOLUTION 1
units mol/kgw
pH 7.24
Na 0.14959
K 0.00211
Mg 0.01184
Ca 0.00897
Sr 0.0004817
Cl 0.16524 charge
S(6) 0.0095
C 0.00292
Eu 2.005E-7
Co 1.7E-7
Ni 5.5E-7
Zn 1.0E-6
Ba 5.1E-7
Cs 5.0E-9
Rb 4.6E-7
SAVE SOLUTION 1
END
```

#definition of background electrolyte

```
EXCHANGE 1 #exchange sites of 1% illite
X 2E-5; END;
EXCHANGE 2 #exchange sites of 2% illite
X 4E-5; END;
EXCHANGE 3 #exchange sites of 3% illite
X 6E-5; END;
EXCHANGE 4 #exchange sites of 4% illite
X 8E-5; END;
EXCHANGE 5 #exchange sites of 5% illite
X 1E-4; END;
EXCHANGE 6 #exchange sites of 6% illite
X 1.2E-4; END;
EXCHANGE 7 #exchange sites of 7% illite
X 1.4E-4; END;
EXCHANGE 8 #exchange sites of 8% illite
X 1.6E-4; END;
EXCHANGE 9 #exchange sites of 9% illite
X 1.8E-4; END;
EXCHANGE 10 #exchange sites of 10% illite
X 2E-4; END;
EXCHANGE 11 #exchange sites of 11% illite
X 2.2E-4; END;
EXCHANGE 12 #exchange sites of 12% illite
X 2.4E-4; END;
EXCHANGE 13 #exchange sites of 13% illite
X 2.6E-4; END;
EXCHANGE 14 #exchange sites of 14% illite
X 2.8E-4; END;
EXCHANGE 15 #exchange sites of 15% illite
X 3E-4; END;
```

EXCHANGE 16	#exchange sites of 16% illite
X 3.2E-4; END;	
EXCHANGE 17	#exchange sites of 17% illite
X 3.4E-4; END;	
EXCHANGE 18	#exchange sites of 18% illite
X 3.6E-4; END;	
EXCHANGE 19	#exchange sites of 19% illite
X 3.8E-4; END;	
EXCHANGE 20	#exchange sites of 20% illite
X 4E-4; END;	
EXCHANGE 21	#exchange sites of 21% illite
X 4.2E-4; END;	
EXCHANGE 22	#exchange sites of 22% illite
X 4.4E-4; END;	
EXCHANGE 23	#exchange sites of 23% illite
X 4.6E-4; END;	
EXCHANGE 24	#exchange sites of 24% illite
X 4.8E-4; END;	
EXCHANGE 25	#exchange sites of 25% illite
X 5E-4; END;	
EXCHANGE 26	#exchange sites of 26% illite
X 5.2E-4; END;	
EXCHANGE 27	#exchange sites of 27% illite
X 5.4E-4; END;	
EXCHANGE 28	#exchange sites of 28% illite
X 5.6E-4; END;	
EXCHANGE 29	#exchange sites of 29% illite
X 5.8E-4; END;	
EXCHANGE 30	#exchange sites of 30% illite
X 6E-4; END;	
Surface 1	#sorption sites of 1% illite
-no_edl	
Clay_sOH 2.0e-7;END	
Surface 2	#sorption sites of 2% illite
-no_edl	
Clay_sOH 4.0e-7;END	
Surface 3	#sorption sites of 3% illite
-no_edl	
Clay_sOH 6.0e-7;END	
Surface 4	#sorption sites of 4% illite
-no_edl	
Clay_sOH 8.0e-7;END	
Surface 5	#sorption sites of 5% illite
-no_edl	
Clay_sOH 1.0e-6;END	
Surface 6	#sorption sites of 6% illite
-no_edl	
Clay_sOH 1.2e-6;END	
Surface 7	#sorption sites of 7% illite
-no_edl	
Clay_sOH 1.4e-6;END	
Surface 8	#sorption sites of 8% illite
-no_edl	
Clay_sOH 1.6e-6;END	
Surface 9	#sorption sites of 9% illite
-no_edl	
Clay_sOH 1.8e-6;END	
Surface 10	#sorption sites of 10% illite
-no_edl	
Clay_sOH 2.0e-6;END	
Surface 11	#sorption sites of 11% illite

Appendix

```
-no_edl
Clay_sOH  2.2e-6;END
Surface 12                                #sorption sites of 12% illite
-no_edl
Clay_sOH  2.4e-6;END
Surface 13                                #sorption sites of 13% illite
-no_edl
Clay_sOH  2.6e-6;END
Surface 14                                #sorption sites of 14% illite
-no_edl
Clay_sOH  2.8e-6;END
Surface 15                                #sorption sites of 15% illite
-no_edl
Clay_sOH  3.0e-6;END
Surface 16                                #sorption sites of 16% illite
-no_edl
Clay_sOH  3.2e-6;END
Surface 17                                #sorption sites of 17% illite
-no_edl
Clay_sOH  3.4e-6;END
Surface 18                                #sorption sites of 18% illite
-no_edl
Clay_sOH  3.6e-6;END
Surface 19                                #sorption sites of 19% illite
-no_edl
Clay_sOH  3.8e-6;END
Surface 20                                #sorption sites of 20% illite
-no_edl
Clay_sOH  4.0e-6;END
Surface 21                                #sorption sites of 21% illite
-no_edl
Clay_sOH  4.2e-6;END
Surface 22                                #sorption sites of 22% illite
-no_edl
Clay_sOH  4.4e-6;END
Surface 23                                #sorption sites of 23% illite
-no_edl
Clay_sOH  4.6e-6;END
Surface 24                                #sorption sites of 24% illite
-no_edl
Clay_sOH  4.8e-6;END
Surface 25                                #sorption sites of 25% illite
-no_edl
Clay_sOH  5.0e-6;END
Surface 26                                #sorption sites of 26% illite
-no_edl
Clay_sOH  5.2e-6;END
Surface 27                                #sorption sites of 27% illite
-no_edl
Clay_sOH  5.4e-6;END
Surface 28                                #sorption sites of 28% illite
-no_edl
Clay_sOH  5.6e-6;END
Surface 29                                #sorption sites of 29% illite
-no_edl
Clay_sOH  5.8e-6;END
Surface 30                                #sorption sites of 30% illite
-no_edl
Clay_sOH  6.0e-6;END

USER_PUNCH                                #data output
-headings amount_Illite log_Rd total_Eu
```

```

-start
10 punch      tot("X")/2E-5
20 punch      log10((sys("Eu")-tot("Eu"))/(tot("Eu"))*100)
30 punch      sys("Eu")
-end
SELECTED_OUTPUT
-file Eu_sorption model.dat
-reset false
-molalities  EuX3   Clay_sOEu+2   Clay_sOEuOH+   Clay_sOEu(OH)2
-totals Eu
END

                                #Calculation
use SOLUTION 1; use SURFACE 1; use EXCHANGE 1; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 2; use EXCHANGE 2; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 3; use EXCHANGE 3; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 4; use EXCHANGE 4; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 5; use EXCHANGE 5; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 6; use EXCHANGE 6; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 7; use EXCHANGE 7; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 8; use EXCHANGE 8; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 9; use EXCHANGE 9; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 10; use EXCHANGE 10; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 11; use EXCHANGE 11; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 12; use EXCHANGE 12; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 13; use EXCHANGE 13; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 14; use EXCHANGE 14; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 15; use EXCHANGE 15; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 16; use EXCHANGE 16; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 17; use EXCHANGE 17; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 18; use EXCHANGE 18; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 19; use EXCHANGE 19; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 20; use EXCHANGE 20; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 21; use EXCHANGE 21; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 22; use EXCHANGE 22; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 23; use EXCHANGE 23; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 24; use EXCHANGE 24; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 25; use EXCHANGE 25; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;

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Appendix

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use SOLUTION 1; use SURFACE 26; use EXCHANGE 26; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 27; use EXCHANGE 27; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 28; use EXCHANGE 28; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 29; use EXCHANGE 29; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
use SOLUTION 1; use SURFACE 30; use EXCHANGE 30; EQUILIBRIUM_PHASES 1;
Fix_pH -7.24 NaOH 1; CO2(g) -2.0 1.0 ; -f ; Calcite 1.0 0.03; END;
```

Appendix B

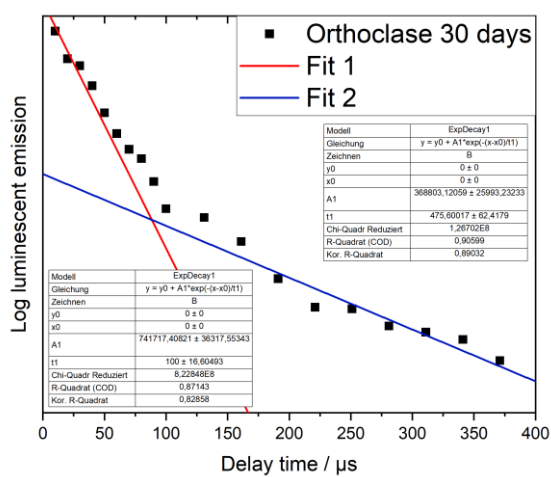
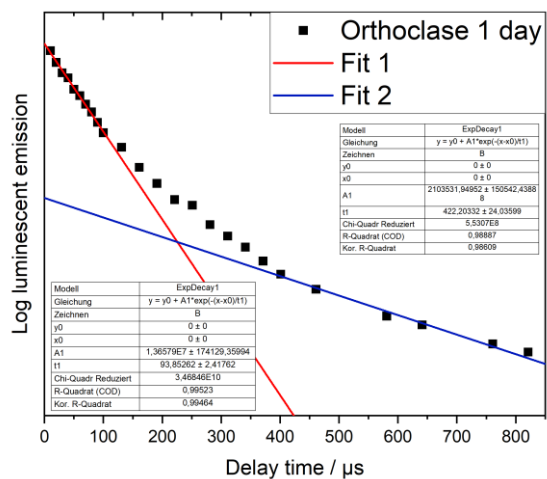
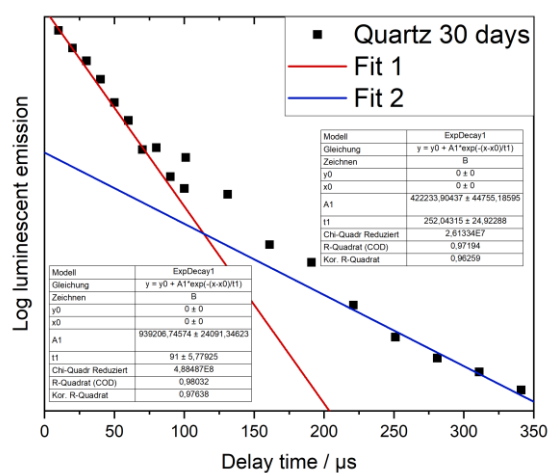
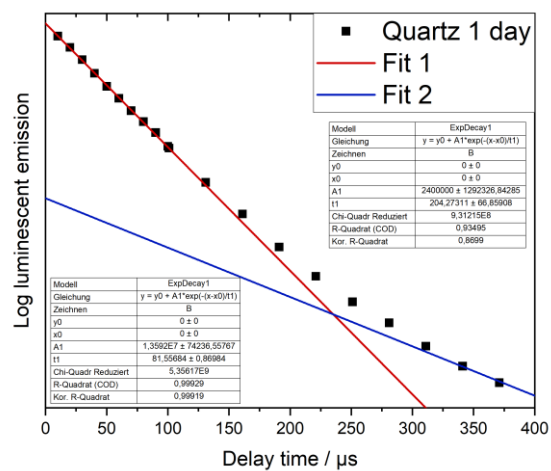
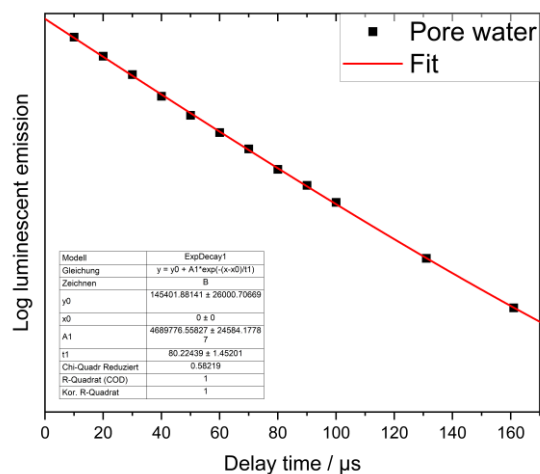
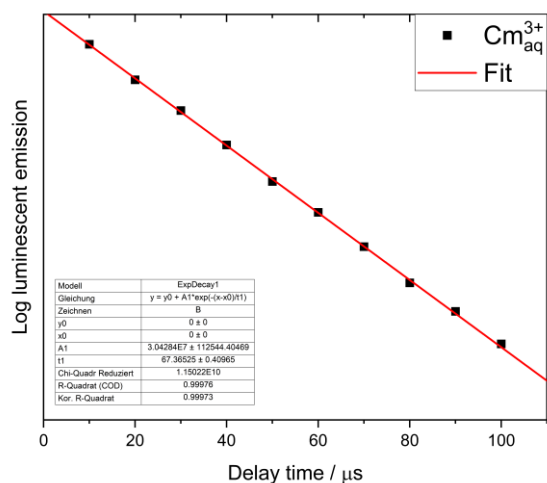


Appendix C

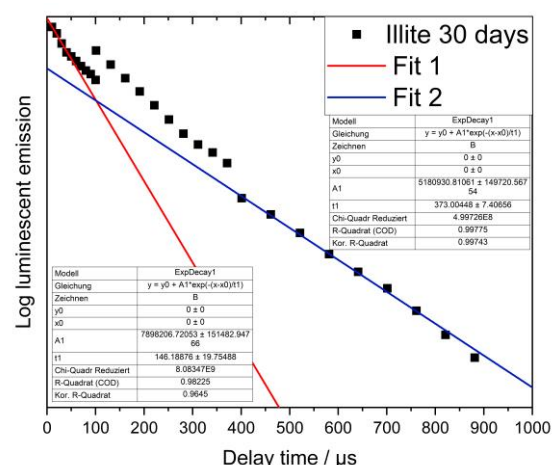
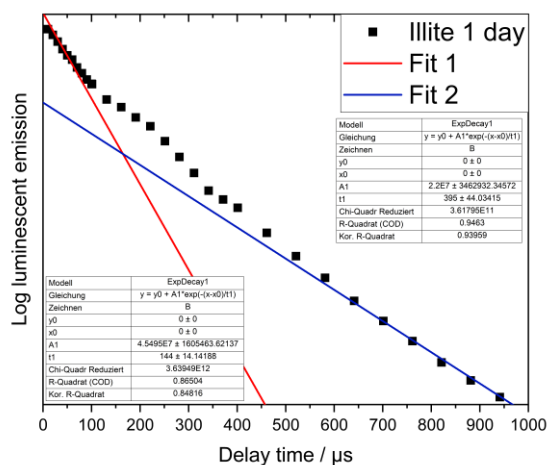
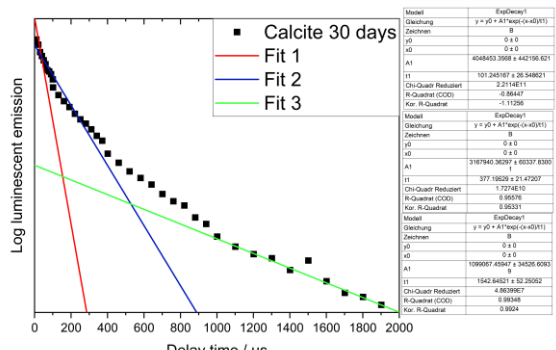
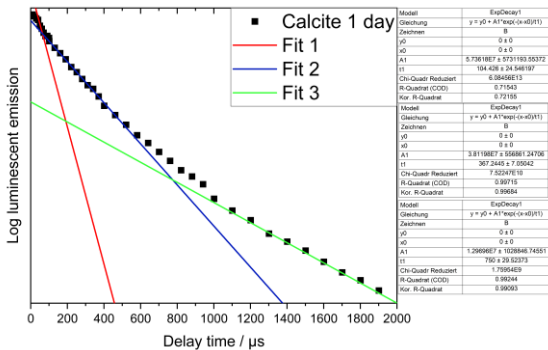
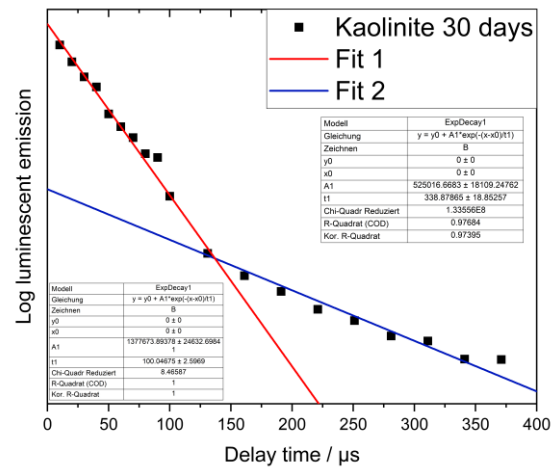
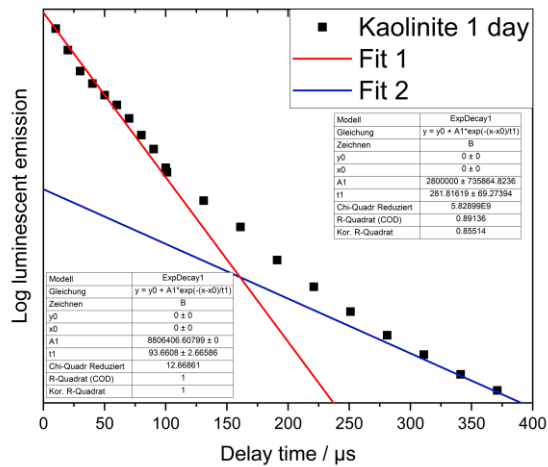
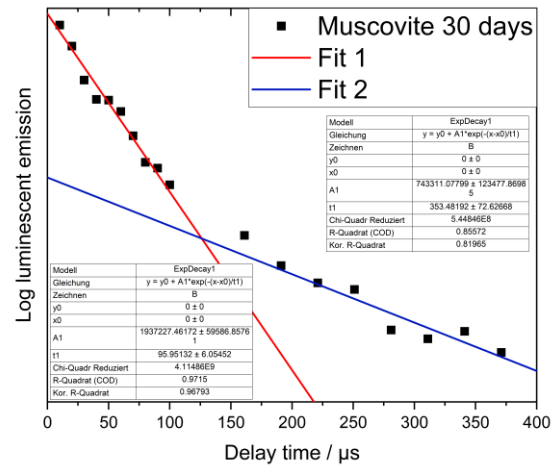
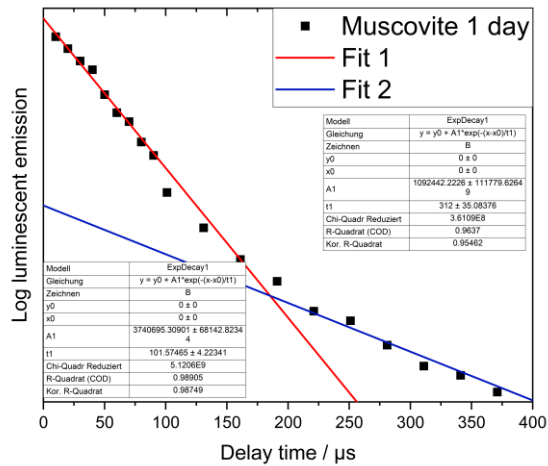
Elements / at.%	Quartz (SiO ₂)	Calcite (CaCO ₃)	Muscovite	Clay minerals and feldspars
O	53.61 ± 1.19	61.09 ± 1.21	54.44 ± 1.08	53.68 ± 1.19
Si	18.71 ± 0.26	4.11 ± 0.07	18.51 ± 0.22	14.33 ± 0.23
C	12.58 ± 0.95	12.34 ± 0.34	12.05 ± 0.64	12.74 ± 0.87
Al	6.31 ± 0.17	1.44 ± 0.06	7.00 ± 0.13	6.44 ± 0.19
Na	5.67 ± 0.2	<1	<1	<1
Ca	1.11 ± 0.06	18.86 ± 0.21	<1	<1
Fe	<1	<1	1.01 ± 0.05	6.88 ± 0.14
Ca	<1	<1	<1	1.91 ± 0.08
Mg	<1	<1	<1	2.11 ± 0.15
K	<1	<1	4.78 ± 0.04	<1

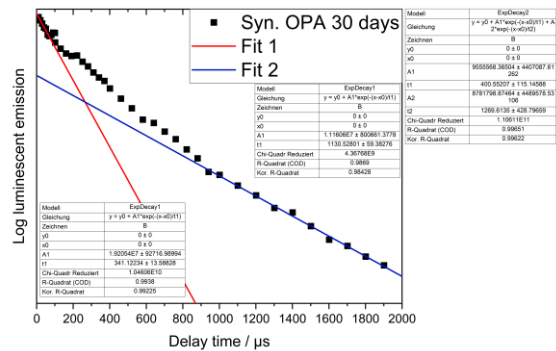
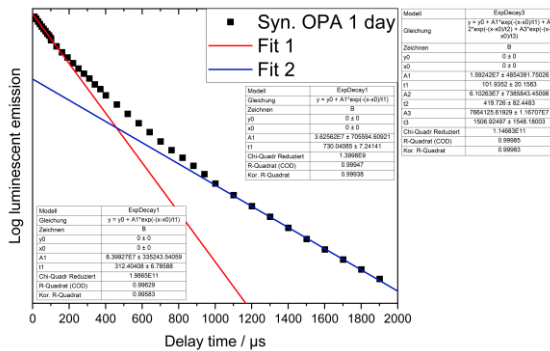
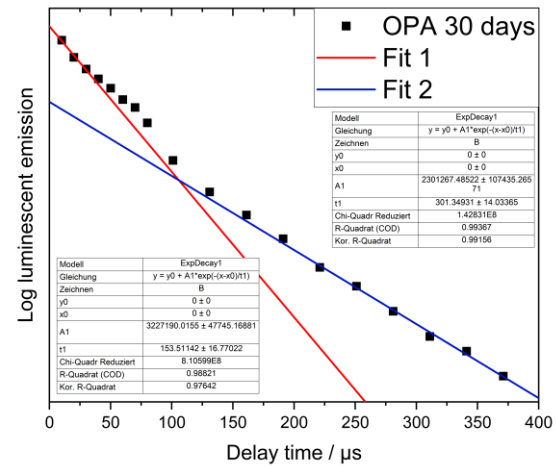
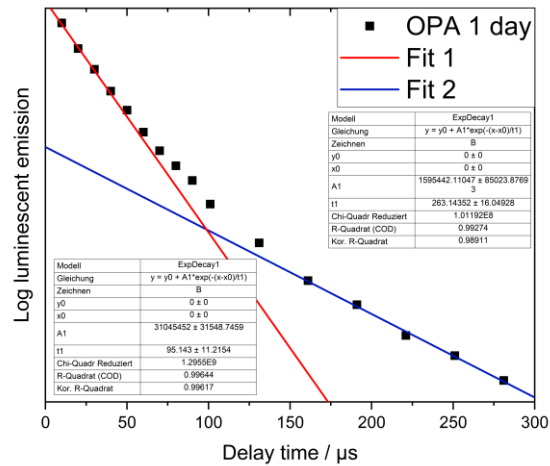
Elements / at.%	Rutile (TiO ₂)	Apatite (Ca ₅ [F](PO ₄) ₃)	Celestine (SrSO ₄)	Pyrite (FeS ₂)
O	60.68 ± 5.07	54.74 ± 3.98	57.91 ± 2.98	47.65 ± 3.24
Si	9.95 ± 0.53	3.85 ± 0.36	<1	8.99 ± 0.42
C	6.72 ± 2.03	11.25 ± 1.90	18.96 ± 2.61	16.30 ± 2.65
Al	3.51 ± 0.46	1.55 ± 0.27	1.10 ± 0.32	3.64 ± 0.37
Fe	1.21 ± 0.19	1.03 ± 0.14	<1	7.15 ± 0.39
Ca	<1	15.02 ± 0.41	<1	4.09 ± 0.26
Ti	15.78 ± 0.50	<1	<1	<1
P	<1	8.45 ± 0.42	<1	<1
S	<1	<1	11.07 ± 0.41	10.67 ± 0.38
F	<1	2.11 ± 0.52	<1	<1
Sr	<1	<1	7.34 ± 0.93	<1
Ba	<1	<1	2.21 ± 0.11	<1

Appendix D



Appendix





Appendix E

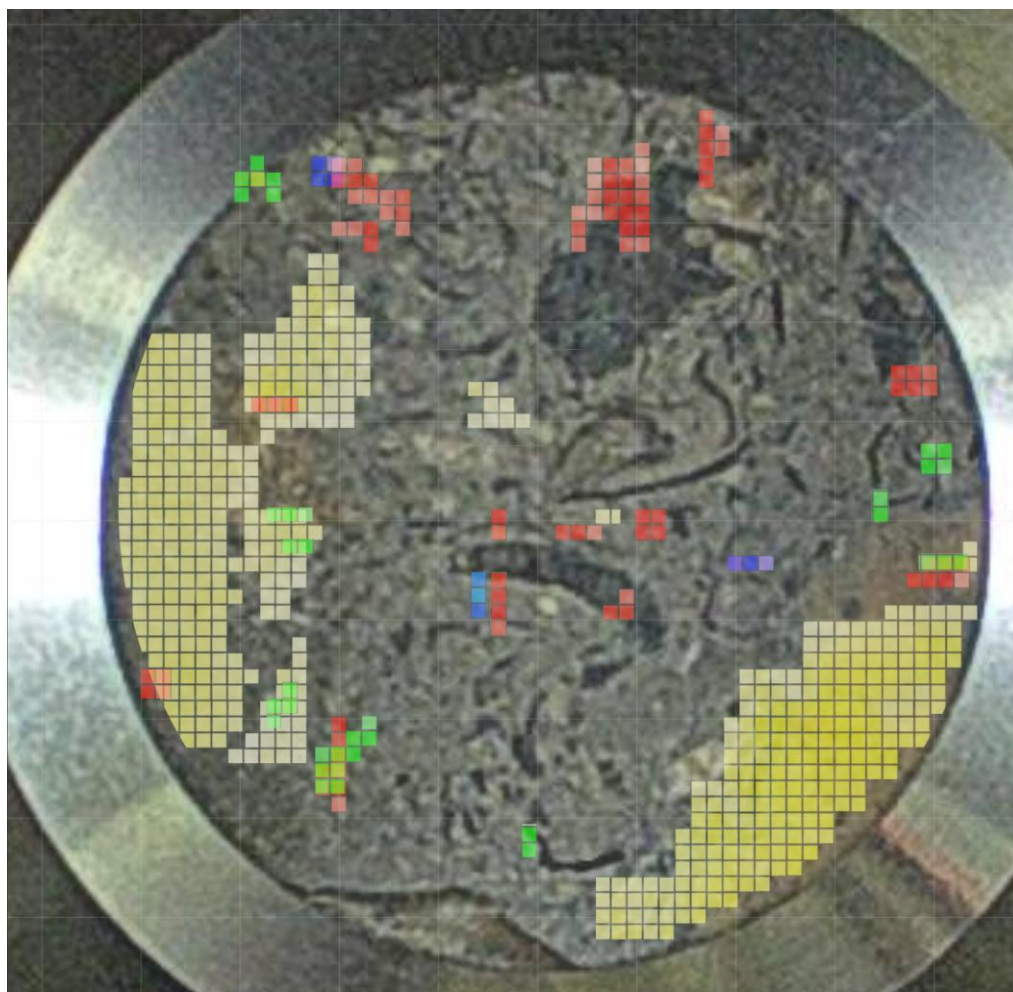


Figure 92: μ -XRF data of the minor elemental contents, titanium in blue, iron in yellow, sulfur in red and phosphorus in green.

Appendix F

In this appendix, the optimization procedure of the whole rock surface sorption sample preparation is described. For the first sample preparation, cubic cutouts of OPA are embedded into epoxy resin and their face is carefully abraded to obtain a smooth and flat surface without intrusions. For contamination protection and ease of use, a long screw is drilled into the backside of these samples. The cap of a 50 mL vial (Sarstedt, PP) is perforated and a nut is attached, to easily slide the mounted sample up and down via rotation of the screw, while the vial remains closed. The resulting setup is shown in Figure 93. With this design, the first experiments with europium as a tracer have been conducted with a sorption time of one day.

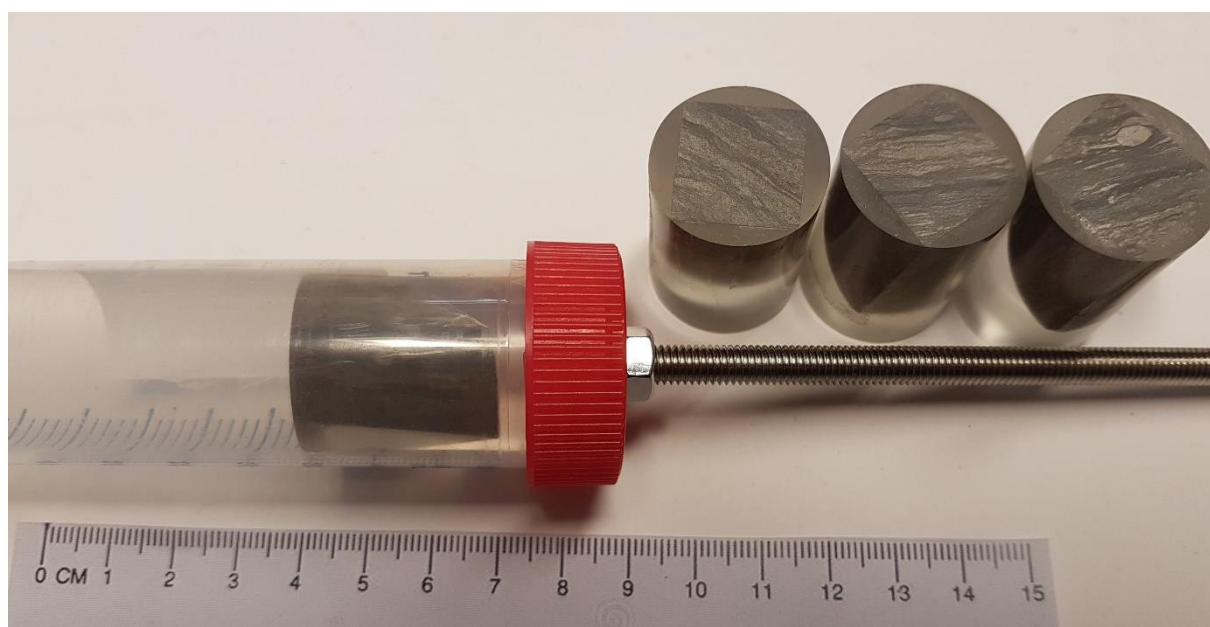


Figure 93: First samples for the rock surface sorption experiments. Sandy facies OPA cutouts embedded into epoxy resin with a screw mounted to a vial for easier handling of sample position.

The small diameter difference of the sample and the vial causes an air bubble to form on the surface, when lowering the sample into the spiked solution, due to surface tension. Though shaking removes some of this air, a full immersion of the sample cannot be ensured. To address this problem, the setup is changed to a bigger vessel, which solved this problem. The sample stayed intact despite possible dissolution or swelling. After drying, the first autoradiography imaging has been done. The exposure time has been chosen to be one day only, due to concerns about overexposure of the film. The resulting image is shown in Figure 94, only presenting a diffuse adsorption, in contrast to the optical image clearly showing heterogeneities and

Appendix

sedimentary lenses and layers. This first led to the assumption of the autoradiography not having sufficient spatial resolution.

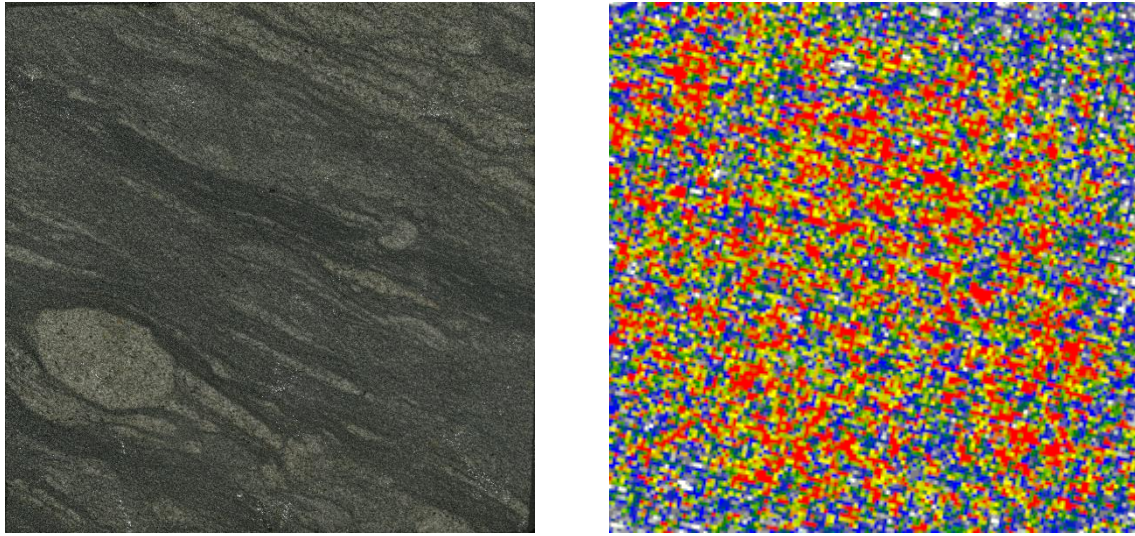


Figure 94: High-resolution optical image of the intact rock surface sorption sample prior to contacting with Eu-152 and the resulting autoradiographic image obtained during the testing of the setup.

Consequently, another setup is developed for samples of a much bigger size, to contact a whole disc of one of the cores BDR-D1 or -D2 with a spiked pore water solution. For embedding the samples into epoxy resin, a new Teflon casting mold is prepared. This casting construction features three layers of Teflon, screwed together with a multitude of screws to lessen the tension on the soft material. The mold is prepared as a cuboid with a cut edge to obtain an orientation in the autoradiography image.

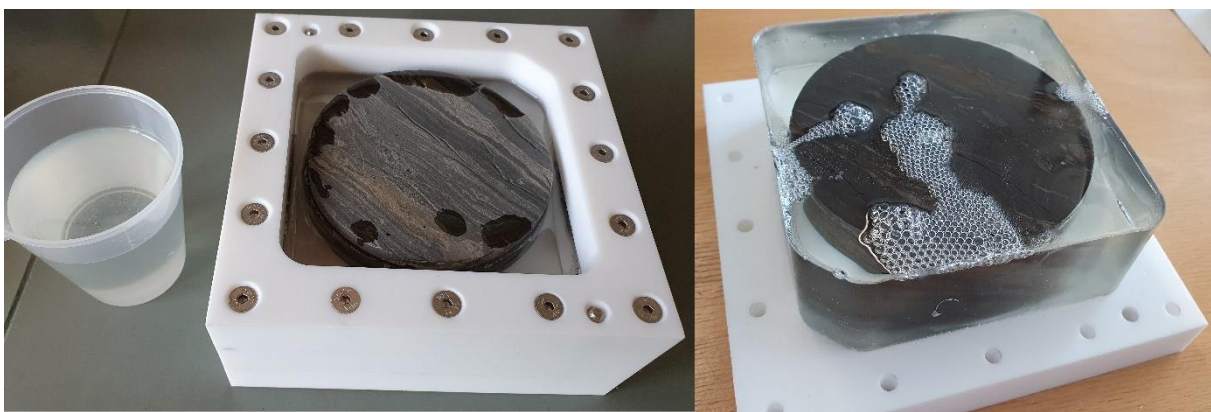


Figure 95: Casting form for the big autoradiography samples during the casing of the sample (left) and the resulting embedded disc (right).

Figure 95 shows the casting of a sample on the left and one of the resulting samples on the right. Prior to the embedding, the surface has been sealed using superglue to prevent any intrusions

of the epoxy resin. Due to the size of the sample, two days of hardening time have been necessary. During the embedding, air bubbles form and rise to the surface, displacing air from the inside of the sample. These bubbles also harden, together with the rest of the epoxy resin. The removal of the sample from the mold has proven to be more difficult than first envisioned. Despite the soft material chosen for the casting mold, a rather strong force (a hammer) is needed to retrieve the sample. The sealed surface is polished similarly to the previous samples and an image of one of these samples before and after the polishing is shown in Figure 96.



Figure 96: Intact clay rock samples before (left) and after (right) the abrasion of the protruding residue on the surface.

A tub has been built with four stands docking on the edges of the samples, preventing any movement during the sorption process and not blocking any of its surface. This tub is shown in Figure 97. Equipped with these new samples and a new setup, the next rock surface sorption experiments are conducted. One of the most prominent features of clay, making it a suitable host rock in the first place, causes severe problems in this setup. The swelling capability of the clay in contact with water completely destroys the sample. Though embedding has been done to have a confining pressure towards five of the six swelling directions of the cube, the open surface expands to a high degree. More than one centimeter of overhang is caused after two hours of sorption time and most of the surface is even breaking off. The results of some of these attempts are shown in Figure 97, clearly depicting these samples not being fit for any further investigation. The sorption time is stepwise reduced down to 10 minutes without any improvement, destroying a multitude of samples in the process.



Figure 97: Results of contacting the big rock surface sorption samples with synthetic pore water.

Being set back to the drawing board, some further testing has revealed the low resolution asserted prior not be caused by the autoradiography in general but by the exposure time. It turns out that after one day of exposure, not even one percent of the maximum illumination is reached. Therefore, new small samples are prepared and the experimental setup is adjusted to is the final design, described in Chapter 3.6.5. The testing also revealed a significant difference in swelling capabilities of the core BMB-A7 and the cores BDR-D1 and -D2. Samples of the cores BDR-D1 and -D2 are so swellable, that almost all samples show big cracks or are destroyed even after a contact time of one minute with synthetic pore water, while some samples of core BMB-A7 could be submerged for more than an hour without a significant impact on the stability of the surface.

Appendix G

In this appendix, further analyses of the sample BU1 are shown, which were not deemed relevant for the present study.

Mössbauer spectroscopy

Mössbauer spectroscopy is a nuclear spectroscopic technique, offering insights into the electronic and magnetic properties of materials. This method takes advantage of the recoilless emission and absorption of gamma-ray photons by nuclei in a solid, yielding precise information about local environments and electronic states. This technique provides details on hyperfine interactions, isomer shifts, and magnetic interactions, enabling the identification of oxidation states, coordination environments, and crystalline structures. Often, as in this study, this analytical tool is used to differentiate the oxidation state and coordination of iron. The sample BU1 is analyzed using a Mössbauer spectrometer from *WissEl* with a Rh/Co source. The procedure has been performed at the TU Dresden by S. A. Bräuninger. This task has been commissioned by M. Vogt, prior to the start of this study.

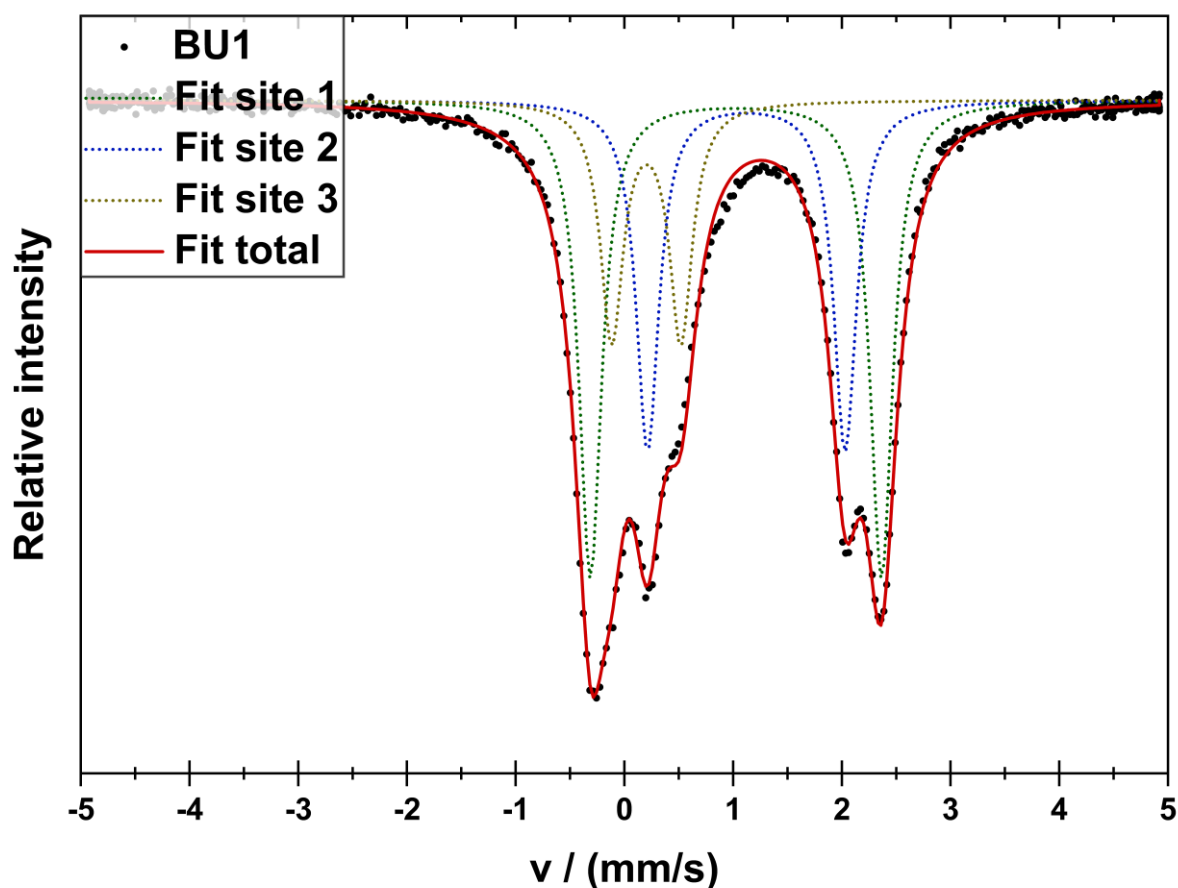


Figure 98: Mössbauer spectrum of BU1 with the proposed total fit (sum) in red and the three adjusted Fe-sites in dotted lines in green, blue and yellow. The isomeric shifts are stated relative to α -Fe.

The observed isomeric shifts of site 1 and 2 are consistent with Fe^{2+} ions in a high spin ($S = 2$) configuration, with values of 1.14 mm/s and 1.23 mm/s, respectively. Additionally, site 1 shows a quadrupole splitting of 2.67 mm/s, consistent with iron-substituted phyllosilicates. The mineral that most closely matches these features is chlorite, with an isomeric shift of 1.13 mm/s and a quadrupole splitting of 2.68 mm/s [242]. However, it is worth noting that other minerals, such as biotite, also exhibit similar Mössbauer behavior with isomeric shifts ranging from 1.12–1.14 mm/s and quadrupole splittings ranging from 2.57–2.63 mm/s [243]. Therefore, site 1 may not be unambiguously assigned to a single species but could be a combination of phases.

In contrast, site 2 clearly indicates being siderite. The isomeric shift of 1.23 mm/s, as well as the quadrupole splitting of 1.81 mm/s, align with descriptions of Vandenberghe *et al.* (2013) [243]. The relatively weak ligand CO_3^{2-} would lead to a small ligand field splitting, resulting in the observed high spin state of $S = 2$. An additional marker suggesting siderite as the source of site 2 is the subtle asymmetry of the spectral lines. In pure siderite spectra, one line is usually

notably deeper than the other, although their widths are the same [244], a phenomenon firstly explained as the Goldanskii-Karayagin effect [245].

Regarding site 3, the isomeric shift of 0.31 mm/s can be described by Fe^{3+} ions in either a low spin ($S = 1/2$) or a high spin ($S = 5/2$) state or alternatively, by Fe^{2+} ions in a low spin ($S = 0$) state. The hyperfine parameters, encompassing the isomeric shift and the quadrupole splitting of 0.63 mm/s are in good agreement with published Mössbauer spectra of pyrite [243], whose presence in BU1 is already proven by other characterization methods. On the other hand, Fe^{3+} ions in phyllosilicates like the before mentioned chlorite or biotite exhibit analogous patterns with $\delta\text{Fe} = 0.35$ mm/s and $\Delta Q\text{Fe} = 0.67$ mm/s [243]. Therefore, site 3 likely results from a mixture of different phases. In summary, the sites 1–3 cover 44.5 %, 33.2 % and 22.3 % of the total spectrum area, respectively. This indicates a distribution of >77.7 at% Fe^{2+} and <22.3 at% Fe^{3+} . Likely 33.2 % of the present iron is present in the form of siderite and at most 22.3 % as pyrite.

MIP

Mercury intrusion porosimetry is a versatile technique, pivotal in characterizing the pore structure of materials. By subjecting a sample to stepwise increasing pressure of liquid mercury, MIP measures the intrusion of mercury into pores, enabling the determination of pore size distribution and total pore volume. In this study, an AutoPore IV 9520 porosimeter from *micrometrics* is used to identify the pore size distribution of three OPA samples. These samples are fragments of BU1 before the grinding. They have been chosen to represent firstly, a clay mineral rich sample, visually consisting of a lot of darkish areas, secondly a fragment containing a lot of quartz and carbonates, visually consisting of a lot of sand lenses and lastly, an evenly-mixed fragment. These fragments are displayed in Figure 99. The procedure has been performed at the KIT-AGW by H. Steger. This task has been commissioned by M. Vogt, prior to the start of this study.

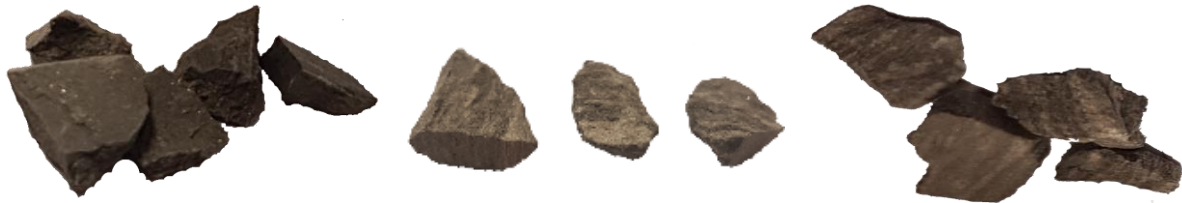


Figure 99: Investigated MIP samples of BU1 with the clay-rich sample on the left, sand-rich sample in the middle and evenly-mixed sample on the right.

The results of this procedure are shown in Figure 100, with the sand-rich sample in brown, the clay-rich sample in green and the evenly-mixed sample in blue. The main pore diameters of the sample mostly consisting of sand lenses is ≈ 180 nm, the average pore size of the clay fraction is much smaller with a main pore diameter ≈ 15 nm. The pore size distribution of the composite sample is a combination of the beforementioned constituents, with a broad distribution including two shallow maxima at ≈ 50 nm and ≈ 140 nm. Presumably, due to the bigger pore sizes, reactive transport in a heterogeneous environment would take place faster in the sand lenses rich fraction of the OPA. The ascertained pore size data bears close resemblance to the data obtained by Houben et al. (2014) [56], who have found maxima at around ≈ 20 nm for the clay fraction of sandy OPA, ≈ 80 nm for the carbonate-rich fraction and ≈ 110 nm for the sand fraction in a similar experiment.

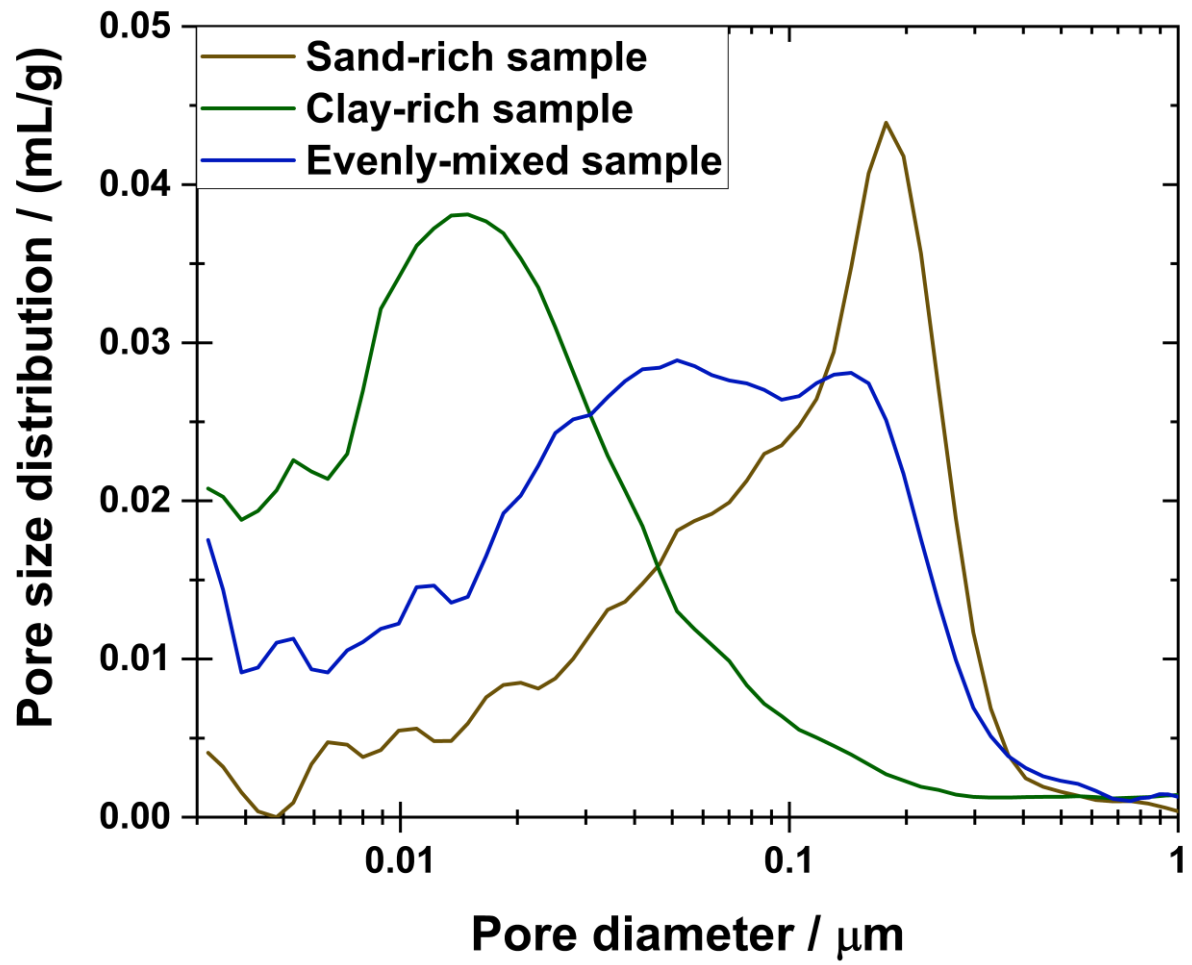


Figure 100: Distribution of the pore sizes of the three investigated samples from the BU1.