

Trace elements in Dutch Paleogene clays



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Abstract: A disposal facility can be constructed in a stable geological formation to emplace packages containing radioactive waste. After closure of such a facility, the waste is isolated and the radionuclides are contained for the far future by a multibarrier system composed of engineered and natural barriers. Favourable Dutch geological formations may include Paleogene clays due to their presence in the subsurface. Radionuclides from the waste may enter the clay host rock if they have not decayed and are released from the engineered barriers. The low permeability physically retains them but there are also chemical retainment processes in the clay host rock that prevent radionuclides from entering the biosphere.

Non-radioactive counterparts of radionuclides in the waste and actinides are present in trace amounts in Paleogene clays. Their concentrations can be similar to those of long-lived radionuclides in the waste forms. Their variation in concentration in the sediments is statistically highly correlated with the variation in total clay content. Ion exchange has been hypothesized to be the main mechanism to chemically retain most of these trace concentrations for the following groups: alkali metals, rare-earth elements, some actinides, transition metals and perhaps even non-metals.

Supplementary material: Additional figures with coefficients of determination are available at <https://doi.org/10.6084/m9.figshare.c.8350450>

The Netherlands is currently at a conceptual stage of developing a geological disposal facility (GDF) for radioactive waste. Suitable disposal depths for high-level waste (HLW) are currently assumed to range from 200 to 1000 m. The minimum depth is determined by the isolation potential of the overburden on top of Paleogene clays, while an acceptable working temperature in the subsurface currently controls the maximum depth. During the Pleistocene, these Paleogene clays were only affected by glacial erosion in the northern part of the Netherlands. The polar ice cap did not advance into the southern part of the Netherlands during the Elsterian, Saalian and Weichselian glaciations (ten Veen 2015). The presence of Paleogene clays in the Netherlands in this range of depth covers almost the entire Dutch geographical area (Duin *et al.* 2006). Low level and short-lived intermediate-level waste (LLW and ILW) is disposed of at depths shallower than 100 m in Europe (Neeft *et al.* 2019) and this disposal depth is also considered to be an option for a

multilevel facility constructed in several Paleogene clays (Neeft *et al.* 2025).

The Paleogene clays were sedimented as marine deposits on the seafloor over the period from *c.* 23 to *c.* 66 Ma. The mineralogy of these Paleogene clays has changed little since their deposition. Some microbially mediated formation of pyrite, calcite and other calcareous minerals occurred during shallow burial of these sediments (De Craen *et al.* 1999). There is limited cementation caused by the formation of carbonates, which ensures that Paleogene clays can deform plastically (NIROND 2013). Illitization of smectite (e.g. Śródoń and Jewuła 2025) has not occurred or at least not fully. The content of smectite in these poorly indurated clays is greater than in indurated clays such as the Callovo-Oxfordian Clay and Opalinus Clay (Neeft *et al.* 2019). In the Netherlands, these clays are usually surrounded by sandy formations often containing saline porewater, more saline than brackish. This hydrogeological setting is favourable to

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minimize interactions with fresh groundwater activities. Paleogene clays are therefore preferred by COVRA (radioactive waste management organization) (Neeft *et al.* 2025).

Publications of conditional (i.e. not site-specific) safety cases for GDFs are aligned with the review of the National Programme (Verhoef *et al.* 2020). The backbone of a safety case is a safety assessment. This assessment quantifies the containment behaviour of multiple barriers and calculates the resulting radiation exposures from the disposed-of waste. In this multibarrier system, the radionuclides in the waste are contained by the waste form itself, other engineered barriers such as waste package and back-fill materials, and natural barriers (e.g. a clay formation and surrounding rock formations).

The clay formation is considered to be the primary barrier in the safety assessment (e.g. Verhoef *et al.* 2017). The low permeability of the clay minimizes access of water to the engineered barriers (Chapman *et al.* 1981), and also ensures that the clay porewater is stagnant, by which transport of dissolved radionuclides, if released from the engineered barriers, is dominated by diffusion. In this paper, we focus on chemical retainment processes of radionuclides in the Paleogene clays.

Many radionuclides are present in minor amounts in the waste but, frequently, the concentrations of their non-radioactive counterparts are greater, comparable with or lower than the concentrations in the clay host rock. Non-radioactive counterparts are stable isotopes of the same element of the radionuclide in waste. To illustrate this, Figure 1 provides examples of stable and radioactive isotopes and their concentrations in a Paleogene clay formation and radioactive isotopes in two engineered barriers: a waste form and concrete. The long-lived caesium isotope ^{135}Cs (half-life of 2.3 Ma), ^{94}Nb (half-life

of 20 300 years) and uranium (half-life at least 159 190 years) have been calculated to enter the biosphere in the post-closure safety assessment made in the third Dutch programme OPERA (Rosca-Bocancea *et al.* 2017). In a post-closure safety assessment, most radionuclides such as radioactive niobium, selenium, strontium and caesium are assumed to be absent in the clay host rock. Figure 1 shows that this assumption is not valid. The chemical gradient may go from the clay rock to the waste form instead of vice versa as assumed in post-closure safety assessments.

Even if the concentrations of radionuclides in the waste form are larger than in the clay host rock, the volumetric considerations become crucial. The volume of the waste form can be 10 000 times smaller than the volume of the clay host rock. Hence, the total inventory of these elements in the host rock will not be significantly affected if radionuclides are released from the engineered barriers. Consequently, the behaviour of natural radionuclides and chemical analogues in Paleogene clay formations can provide an indication of the fate of radionuclides if these radionuclides are released from the engineered barriers.

Geological surveys usually produce geochemical databases with measurements of trace elements in the geosphere. Interpreting these data for the purpose of geological disposal of waste can be useful to assess additional experimental research activities. Data concerning trace elements in the solid phases and dissolved in the aqueous phase are necessary to understand chemical retainment processes. Trace elements in the aqueous phase that can act as chemical analogues for radioactive counterparts in radioactive waste usually have a concentration that is too low to be measured with the equipment used (e.g. Breward 2007; Griffioen *et al.* 2016). In

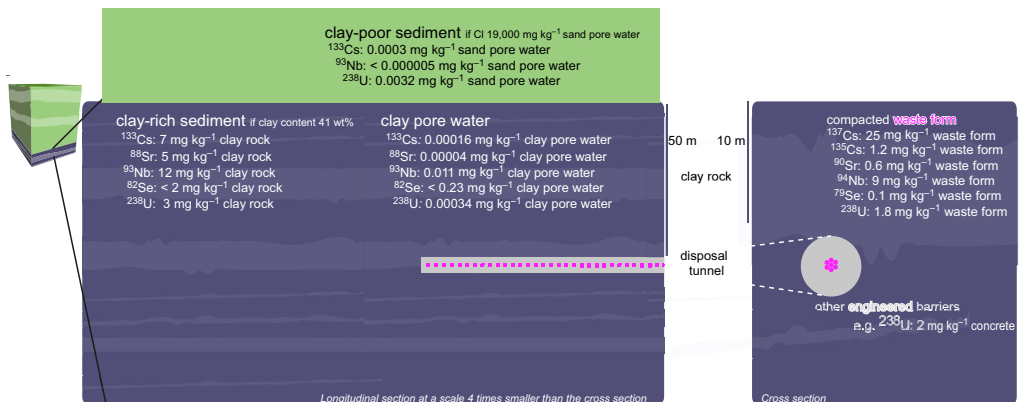


Fig. 1. Schematic depiction of a part of the clay host rock with the disposal tunnel and encapsulated compacted waste forms.

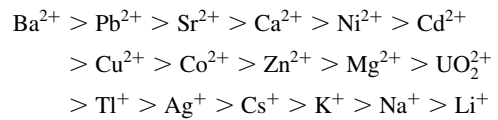
addition, the sampling regime may not have been appropriate for geological disposal of waste. [Breward \(2007\)](#) suggested new studies with specialized sampling systems to follow dispersion of (trace) elements for a well-defined host rock into soils, groundwater and surface drainage. The present study gives new measurements of trace elements in Dutch Paleogene clay formations in the bulk of the clay sediments, clay porewater and groundwater. Only trace elements that can act as chemical analogues for radionuclides in radioactive waste are presented in this paper.

The examples of concentrations in [Figure 1](#) are for clay rock with an average mineralogical content as shown in [Table 1](#) for Dutch Boom Clay porewater, which is Belgian clay porewater collected through piezometers present in the Connecting Gallery in the underground research laboratory (URL) in Mol – this URL in Belgium is also known as High Activity Disposal Experimental Site (HADES) – ([De Craen et al. 2023; Ma and Behrends 2026](#)) due to a lack of Dutch data. The composition of North Pacific seawater ([Nozaki 1997](#)) serves as an analogue for the marine depositional environment of the Paleogene clays as the chemical composition of depositional water can determine the exchangeable cations in clays for millions of years ([Jones and Capuano 2023](#)). Radionuclide concentrations in the waste form are based on the radionuclide inventory for compacted hulls and ends ([Verhoef et al. 2016](#)) divided by 850 kg (i.e. the weight of the waste). The uranium concentration in concrete has been determined from the activity concentration of ^{226}Ra in concrete ([Smeters and Bekhuis 2021](#)).

Two chemical retainment processes are considered in this study. The first is (co-)precipitation, which requires that water is saturated or supersaturated for a mineral. The radionuclide will be built in the crystal structure of the mineral. The second retainment process is ion exchange. Ions form complexes at the surface of minerals with a charged surface. These ions can be exchanged.

Clay minerals are the main cation exchangers in clayey sediments do their high surface area, negative charge and high content. Radionuclides dissolved as cations are exchanged by non-radioactive cations that are originally present on exchange sites on the clay minerals. Therefore, the amount of radionuclides that leaves the clay host rock is smaller than without this ion exchange process. Ion exchangers have a preference for cations with a higher valence, a smaller (solvated) equivalent volume, a greater polarizability, a stronger interaction with the fixed ionic group and for cations that participate least in complex formation. A fairly universal rule of thumb is that the cation that causes less swelling of the ion exchanger is preferentially retained. The affinity for ion exchange by cations decreases as

follows ([Helferich 1962; Stumm 1992; EPA 1999](#)):



However, this ranking should be applied cautiously as the formation of dissolved complexes with cations can alter the affinity for ion exchange. The total capacity of ion-exchanged cations in the clay rock is determined by the cation exchange capacity (CEC). For the average mineralogical composition of the Dutch Boom Clays with a total clay content of 41 wt%, the ‘theoretical’ CEC has been estimated to be 29.5 meq/100 g clay ([Griffioen et al. 2017](#)). Experimentally measured CEC values can vary significantly with the complex used. For a sample with a similar total clay content (45 wt%), the ‘measured’ CEC is 18.5 ± 4.5 meq/100 g clay using Cu(II)-triethylenetetramine complexes (Cu-trien) ([Behrends et al. 2015, 2016](#)). Higher experimentally measured CECs are obtained for Boom Clay using Ag-thiourea (30.0 ± 3.9 meq/100 g clay) and CsNO_3 (26.7 ± 2.5 meq/100 g clay) instead of Cu-trien ([Frederickx et al. 2018](#)). These higher measured CECs match better with the theoretical estimated CEC. Additional studies are needed to understand what causes these discrepancies (the presence of cations with a higher affinity than the complexes used to measure CEC or time for the complex to react with the clay sample, etc.).

Radionuclide retention in clay is commonly quantified in clayey sediments using distribution values, so-called K_d values. The concentration of a chemical element in the solid divided by the concentration of that element dissolved in water is the distribution value or the partition coefficient and is commonly used in safety assessments (e.g. [EPA 1999](#)). K_d values are usually obtained from batch experiments or modelling. A high K_d value corresponds to a large retention capacity for that chemical element by the clay host rock (i.e. a radioactive isotope with a high K_d value would barely leave the clay host rock). K_d values are typically determined from batch sorption experiments or geochemical modelling and serve as key input parameters for safety assessments. Experimental K_d determinations face several challenges. Theoretically, K_d values can only have positive values. However, negative K_d values are obtained experimentally. This erroneous experimental result is caused when the added concentration of the dissolved chemical element is lower than is naturally present in a sample of the clay host rock and becomes dissolved during the batch experiment (e.g. [Tournassat et al. 2007](#)). The added dissolved concentration has a huge impact on the

Table 1. Mineralogical content (wt%, mean $\pm$ SD) for the Dutch Boom Clay (Koenen and Griffioen 2014) and Watervliet Member (Hoving *et al.* 2024)

Group	Mineral	Boom Clay	Watervliet Member
Clay minerals	Kaolinite	41.0 $\pm$ 18.1	25.7 $\pm$ 6.9
	2:1 clay minerals	3.0 $\pm$ 4.0	6.2 $\pm$ 3.6
	KSS	35.9 $\pm$ 15.0	19.5 $\pm$ 4.0
	Chlorite	3.5 $\pm$ 2.9	n.m.
	Smectite	1.1 $\pm$ 1.0	b.l.
	ISS	16.2 $\pm$ 10.7	10.2 $\pm$ 2.5
	Illite	8.6 $\pm$ 5.1	7.7 $\pm$ 2.3
	Glauconite–smectite	5.3 $\pm$ 3.4	2.3 $\pm$ 0.7
Calcareous minerals		4.3 $\pm$ 5.9	n.m.
	Calcite	5.2 $\pm$ 1.6	5.6 $\pm$ 7.8
	Aragonite	5.6 $\pm$ 6.5	4.9 $\pm$ 7.8
	Ankerite/dolomite	1.9 $\pm$ 1.2	n.m.
	Siderite	0.7 $\pm$ 0.6	0.1 $\pm$ 0.4
Feldspars		1.0 $\pm$ 1.5	0.5 $\pm$ 0.2
	K-feldspar	9.0 $\pm$ 3.7	14.1 $\pm$ 2.7
	Microcline	6.6 $\pm$ 2.6	14.1 $\pm$ 2.7
	Orthoclase	n.m.	5.1 $\pm$ 1.0
	Albite	n.m.	4.1 $\pm$ 1.2
	Plagioclase	n.m.	4.9 $\pm$ 1.3
Quartz		2.5 $\pm$ 1.3	n.m.
Pyrite		41.5 $\pm$ 18.2	38.2 $\pm$ 11.9
Anatase/rutile		0.9 $\pm$ 1.4	0.6 $\pm$ 0.7
Ilmenite		0.5 $\pm$ 0.3	0.8 $\pm$ 0.2
Clinopyroxene		0.3 $\pm$ 0.1	n.m.
Hornblende		n.m.	0.8 $\pm$ 0.5
Clinoptinolite		n.m.	0.1 $\pm$ 0.1
Gypsum		2.1 $\pm$ 0.5	0.3 $\pm$ 0.1
Jarosite		1.2 $\pm$ 0.8	1.4 $\pm$ 0.7
Halite		2.0 $\pm$ 1.1	1.1 $\pm$ 1.1
Sylvite		0.7 $\pm$ 0.5	n.m.
		1.9 $\pm$ 0.3	n.m.

b.l., below detection limit of 0.5 wt%; ISS, illite stratified with smectite; KSS, kaolinite stratified with smectite; n.m., not measured.

measured K_d value, and the concentration should therefore be representative for disposal of radioactive waste. More fundamentally, the observed K_d value often logarithmically decreases with logarithmically increasing added concentration, with 10^{-5} M as a minimum concentration of dissolved chemical elements in the past for batch experiments (e.g. Baeyens *et al.* 1982; Hassan Loni *et al.* 2021). The detection limit of the available equipment may therefore control the experimentally determined K_d value. Innovative techniques have reduced this detection limit over the past decades and 10^{-5} M has recently been used as a maximum for the concentration of dissolved chemical elements (e.g. Montavon *et al.* 2022).

In previous studies, almost any chemical element that has a radioactive counterpart relevant for disposal of waste had a dissolved concentration in Boom Clay porewater that was below the detection limit (De Craen *et al.* 2004). Figure 1 shows some

preliminary results of Boom Clay porewater with lower detection limits (Ma and Behrends 2026).

The limitations of experimental K_d determination, including concentration artefacts, detection limit constraints and potential for erroneous results, motivated an alternative approach based on natural trace element distributions. Distribution values calculated from the *in situ* concentrations of non-radioactive elements and radioactive elements in Paleogene clays may provide more representative values for safety assessments than experimentally determined values, particularly those from earlier studies conducted at unrealistically high concentrations. This approach uses the fact that natural trace elements have undergone millions of years of equilibration under *in situ* geochemical conditions, providing a direct analogue for long-term radionuclide behaviour. The present study therefore aims to characterize trace element distributions in Dutch Paleogene clays and evaluate their utility for deriving

distribution values applicable to post-closure safety assessments.

in 2011 (PCR 2013) and in 2022 (Vardon *et al.* 2022; Munsterman 2023).

Sample materials

The best technique to obtain Dutch Paleogene (i.e. poorly indurated) clay samples is currently push-coring due to the absence of a URL in the Netherlands. Well-preserved or fresh Dutch Paleogene samples obtained by push-coring are scarce. Boom and Watervliet clay cores from the Oligocene, Asse and Ypresian clay cores from the Eocene, and Landen Clay cores from the Paleocene were obtained

Sediments

In OPERA – the third Dutch research programme into geological disposal of radioactive waste – Boom Clay samples were analysed. Figure 2 shows the locations at which these Paleogene clay samples were taken. Samples were taken at depths of 21–736 m. Most were from the core storage house of the Dutch Geological Survey in Zeist. This storage is at ambient conditions without any shielding from



Fig. 2. Boom Clay sample locations used in the third Dutch programme (Koenen and Griffioen 2014, 2016), the sampled water well nearest cored Watervliet Clay at location XVII (Hoving *et al.* 2024), and Ypresian and Landen clays samples at location XVIII (Vardon *et al.* 2022; Munsterman 2023).

the atmosphere. Oxygen and a limited amount of water vapour available in the air have caused oxidation of sulfide minerals and drying of the clay rock. Some cores also contained some fungi (Koenen and Griffioen 2014). An exception is Boom Clay obtained at location XVII in Figure 2 at a depth from 63 to 80 m. These samples were obtained with a push-coring technique in 2011. The clay core was pushed in a steel (Shelby) tube with a length of 55 cm. Melted micro-crystalline paraffin wax was poured into the top end of the tube and allowed to cool and harden in order to seal the sample and prevent moisture loss. Any void space in the top was then filled with clean sand and a flexible plastic cap was fitted onto the tube and wrapped with adhesive PVC tape. The bottom end of the sample was prepared in a similar fashion with wax, sand (if necessary) and a sealed end-cap (PCR 2013).

Watervliet is a geohydrological clay unit in the database of the national Regional Geohydrological Information System (REGIS) model. For clays, vertical permeabilities are available in REGIS. The lowest range in permeability is from 0 to $5 \times 10^{-5} \text{ m day}^{-1}$ in this hydrogeological model. This lowest range is for the Boom, Asse and Ypresian clays. The Watervliet Clay has a permeability in the range from 1×10^{-4} to $5 \times 10^{-4} \text{ m day}^{-1}$ in this model, but a lower permeability value of $2.3 \times 10^{-5} \text{ m day}^{-1}$ has been measured (PCR 2013). These samples are therefore named Watervliet Member cores in this study following the current stratigraphic nomenclature. These cores were also obtained with a push-coring technique in 2011 but the sampling device differed from that with which the Boom Clay cores were taken. The clay cores were directly pushed with a steel core shoe into a PVC sample tube with a length of 1 m. Directly after drilling, the PVC sample tubes were cut in half and the sediment was lithologically described. The two halves were put together with three wraps of PVC adhesive tape and placed inside storage tubes with sealed end-caps (PCR 2013). Despite these measures to shield the clay from air, cores had some areas that were oxidized after storage at ambient conditions after 13 years. From each core, the top 2 cm was stripped off to remove the material that was most oxidized. The middle of each core was sampled (Hoving *et al.* 2024).

Clay porewater

Extraction of clay porewater requires a piezometer (e.g. in a borehole in a URL or fresh or well-preserved cores that have been taken with a suitable drilling technique, for example the push-coring technique). Paleogene clay cores contained in steel and PVC tubes from locations XVII and XVIII in Figure 2 had been sampled just after drilling. In glove boxes to prevent oxidation of sulfide minerals,

samples of Boom Clay were taken from the steel tube (Behrends *et al.* 2015) and samples of Ypresian and Landen clays from PVC tubes (Fernández *et al.* 2025). The clay porewater obtained through mechanical squeezing as well as dilution experiments was found to be as saline as seawater based on the major chemical elemental composition (Behrends *et al.* 2016) or slightly more saline than seawater for clay porewater obtained through mechanical squeezing (Fernández *et al.* 2025). Dissolved chemical elements with a concentration $>0.010 \text{ mg l}^{-1}$ were measured for Boom Clay using inductively coupled plasma optical emission spectrometry (Behrends *et al.* 2015). These clay porewater studies focused on the major elements.

The clay cores contained in the PVC tubes from the drilling in 2011 (location XVII in Fig. 2) were thought to be too oxidized to obtain representative clay porewater after 13 years of storage but will be analysed here to confirm this hypothesis. Characterization of clay porewater from the most recently drilled cores (Vardon *et al.* 2022) and Boom Clay porewater from the URL in Mol with inductively coupled plasma mass spectrometry (ICP-MS) is executed (Ma and Behrends 2026).

Sand porewater

Sand porewater above and below a Paleogene clay may be an appropriate alternative where no clay porewater samples are available if the salinity above and below the clay layer is similar. We focus in this paper on the results obtained from well B48G0204 in which water is sampled at a depth from 91 to 149 m (i.e. a similar range in depth as the sampled Watervliet Member from 96 to 121 m) (see Fig. 2). Studies with chlorine isotopes show that the porewater is stagnant around the sampled Watervliet Member. More groundwater samples have been taken near the surface to a depth of 200 m using submersible pumps or peristaltic pumps, depending on the diameter of the wells (Hoving *et al.* 2024).

Characterization

Mineralogy

The main mineralogical reservoir for a trace element needs to be identified in order to substantiate whether its presence can give information on whether co-precipitation or ion exchange dominates the retention. The mineralogy of the Watervliet Member has been measured with X-ray diffraction (XRD) (Bruker D8 Advance with DAVINCI). For quantitative mineral analysis of the bulk samples, corundum was added as an internal standard (Hoving *et al.* 2024). The measurements for the Boom

Clay sample were performed with a Siemens D5000 XRD device in Bragg–Brentano configuration, equipped with a CuK_α X-ray source and a graphite monochromator (Koenen and Griffioen 2016). The mineralogical content was determined for Boom Clay samples at the locations with the following Roman numerals in Figure 2: III, IV, V, XI, XIII, XVI and XVII. Table 1 shows the mineralogy of both types of sediments. Clay minerals, feldspars, quartz and calcareous minerals are the main minerals. Minor amounts of gypsum, jarosite, halite and sylvite are formed by the ingress of oxygen and evaporation of porewater during storage of the samples.

The metal-oxide (SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , CaO , Na_2O , K_2O , TiO_2 , MnO , Cr_2O_3), phosphate, sulfur, and organic and inorganic carbon content were determined from all locations indicated in Figure 2 (Koenen and Griffioen 2014, 2016; Hoving *et al.* 2024; Hoving and Griffioen 2025).

Measurement of the concentrations of trace elements in the sample materials

Watervliet Member samples were freeze-dried. A subsample was ground in an agate mortar and dissolved in an $\text{HF-HNO}_3\text{-HClO}_4$ solution. The resulting solutions as well as the groundwater well samples were analysed by ICP-MS. In addition to acid digestion of the sediment samples, tablets were prepared to measure trace elements via X-ray fluorescence (XRF). Tablets were prepared from 10 g of ground sample mixed with 1.44 g wax and pressed (Herzog HP-PA) into a steal ring (Hoving *et al.* 2024).

Boom Clay samples were air dried ($<40^\circ\text{C}$) and pulverized to a 100 mesh (149 μm) in a mild-steel pulverizer, according to ASTM standard procedures. They were analysed for trace elements following digestion in aqua regia. The resulting solutions were analysed by ICP-MS (Koenen and Griffioen 2016).

Determination of the main reservoirs for each group of trace elements

Statistical analysis can help in the first identification of the main mineralogical reservoirs of the trace elements (e.g. Gaucher *et al.* 2004). Trace elements can have a detrital origin such as feldspars, quartz, anatase/rutile, calcite (fragments of shells) and organic matter, a depositional origin such as ion exchange with dissolved trace elements in seawater and clay minerals, can be microbially assimilated in minerals after deposition such as pyrite, calcite and other carbonates, and a diagenetic origin in which trace elements are incorporated during burial or uplift such

as pyrite and calcite (cementation). Linear relations between potential reservoirs and concentrations of trace elements in sediments are used in this study. The intercept with the trace element has been set equal to the concentration found in seawater (Nozaki 1997). If a single reservoir can be assigned to a trace element, these concentrations can be set to 0 since the concentration of dissolved trace elements in seawater is negligible compared to the range in concentration of the trace element in the sediments. Consequently, it is assumed that the concentration of the trace element would be 0 mg kg^{-1} sediment if the content of the identified reservoir was 0 wt%. This method is used for all minerals in order to statistically identify the main mineralogical reservoirs for the trace elements. The intercept cannot be 0 mg kg^{-1} sediment if a single reservoir cannot be assigned to a trace element. The best correlations are shown in the figures. The Supplementary material provides examples of discarded potential reservoirs due to their poor correlation with the considered trace elements. Interpretation of other experimental results can further substantiate whether the identified mineralogical phase can act as a trap for the trace elements. This substantiation is crucial for assessing whether ion exchange or co-precipitation is the main retention mechanism of a chemical element. In the case of ion exchange, the assumed concentrations in the solid and liquid phase need to be verified.

Alkali metals

The minerals with alkali metals in Table 1 are expected to be feldspars and clay minerals. Feldspars and clay minerals can theoretically have built-in caesium. The variation in caesium concentration in the sediments should be highly correlated with that specific feldspar or specific clay mineral if caesium was built-in. The variation in caesium concentration cannot be explained by the variation in feldspar content in the sediments; for example, for the Watervliet Member R^2 is -0.518 (see Supplementary material S1). Figure 3 shows that caesium is well correlated with the clay content in the Dutch Boom Clay samples as well as with the clay content in the Watervliet Member, despite the lower clay content for the Watervliet Member: 83% and 71% of the variation in the caesium concentration in the Boom Clay and Watervliet Member, respectively, can be explained by the variation in clay content. Clay minerals are therefore initially simplified to be the sole reservoir for caesium. Additional experimental results (e.g. laser ablation ICP-MS) interpreted with total mass balance with all minerals identified by XRD confirm this simplification (Hoving and Griffioen 2025).

Discrimination between the clay minerals kaolinite, kaolinite interstratified with smectite, chlorite,

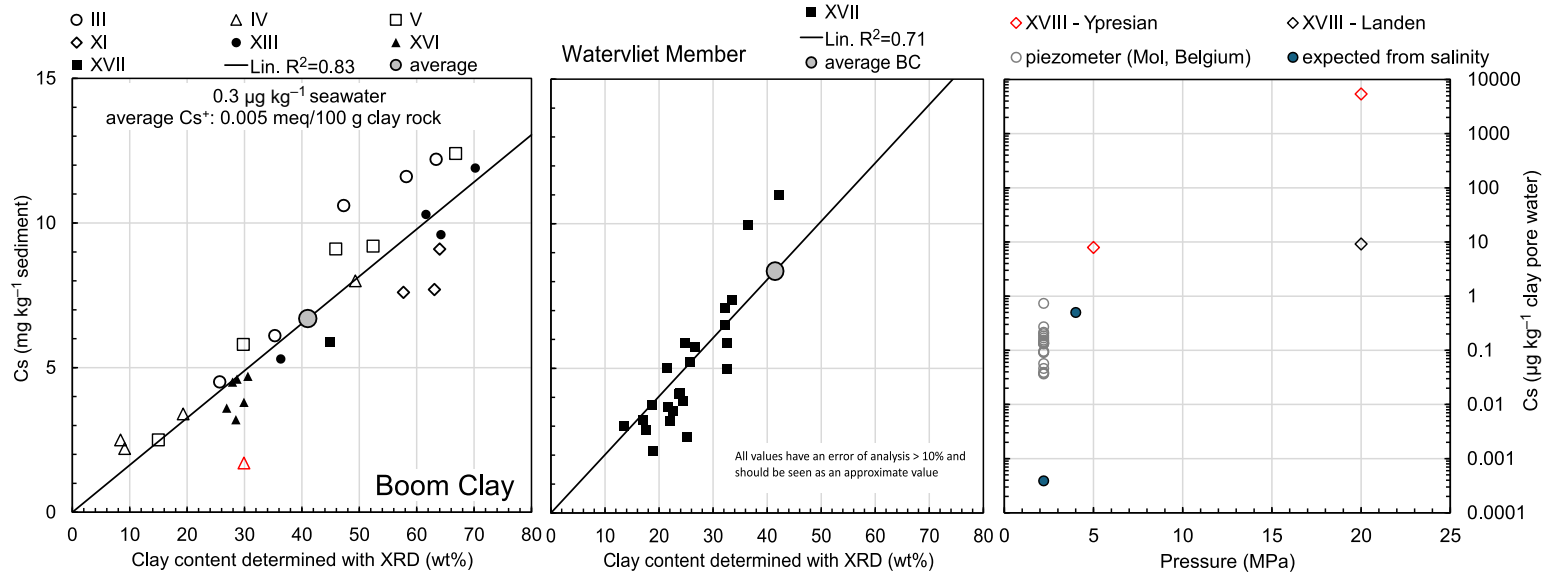


Fig. 3. Caesium concentration v. clay content in Boom Clay (BC) and in the Watervliet Member. Roman numerals are the locations shown in Figure 2. The red triangle has a high glauconite content. The indicated caesium concentration is representative for seawater (Nozaki 1997). All other data points come from the third Dutch programme (Koenen and Griffioen 2014) or are more recently obtained experimental results (Hoving *et al.* 2024; Ma and Behrends 2026). Clay porewater in circles as porewater pressure and in diamonds as mechanical squeezing pressure. XRD, X-ray diffraction.

smectite, illite interstratified with smectite, illite and glauconite–smectite for the Boom Clay samples (Koenen and Griffioen 2014) and kaolinite and 2:1 clay minerals/mica/glaconite for the Watervliet Member samples (Hoving *et al.* 2024) does not lead to an increase of the coefficient of determination (see Supplementary material S1). It is therefore hypothesized that the presence of caesium in the total clay content is caused by marine deposition in which clay minerals had been interacting with dissolved caesium in seawater.

Studies of exchangeable cations in clay formations are typically focused on calcium, magnesium, sodium and potassium for Belgian Boom Clay (Frederickx *et al.* 2018), Callovo-Oxfordian Clay (Gaucher *et al.* 2004) and Opalinus Clay (Marques Fernandes *et al.* 2024). Caesium is also an alkali metal and therefore is expected to be present as an exchangeable cation in clay in particular because it has a higher affinity than sodium. Another line of reasoning is that the caesium could only be measured from Boom Clay porewater obtained through mechanical squeezing while the caesium concentration in porewater collected through piezometers was below the detection limit of $0.5 \mu\text{g l}^{-1}$ at that time (De Craen *et al.* 2004). Recent preliminary results confirm that the caesium concentration is below the detection limit of $0.5 \mu\text{g l}^{-1}$, except for one measurement taken from a silt-rich clay layer (Ma and Behrends 2026). Assuming the dissolved caesium concentration follows the salinity (Nozaki 1997), a concentration of chloride of 24.8 mg l^{-1} (De Craen *et al.* 2004) would give a caesium concentration in clay porewater of $0.0004 \mu\text{g kg}^{-1}$. Figure 3 shows higher measured caesium concentrations in Boom Clay porewater. The elevated caesium concentration in this clay porewater is therefore tentatively attributed to marine deposition (i.e. from >23 Ma), with ongoing release of caesium due to the high retention capacity of the clay minerals for caesium in the Boom Clay.

A caesium concentration of 0.0038 mg l^{-1} was measured in clay porewater obtained by mechanical squeezing of Boom Clay samples with a pressure of six times the formation pressure (De Craen *et al.* 2004). Recently, a mechanical squeezing pressure of 7.5 MPa (i.e. less than two times the formation pressure) was used (De Craen *et al.* 2023). The hypothesis is that surface-sorbed water, or water that is part of the diffuse layer surrounding the clay mineral surfaces, may be expelled during squeezing by the collapse of the pore space so that more soluble caesium could be extracted from the squeezed sample than porewater collected from piezometers representing the caesium concentration at the formation pressure at the URL. The measured caesium concentration obtained from mechanical squeezing is also greater than would be expected from the chloride

concentration (see Fig. 3). Collection of clay porewater by other techniques and lower mechanical squeezing pressures is in progress (Ma and Behrends 2026).

The mean value for caesium in mudstone is 5 mg kg^{-1} (Breward 2007). A Cs concentration of $7 \pm 3 \text{ mg kg}^{-1}$ Boom Clay rock would be the result with an average of $41 \pm 18 \text{ wt\%}$ clay content in Boom Clay (see Fig. 3). A Cs concentration of 7 mg kg^{-1} can be transferred into the ion-exchanged amount by the molar mass and the charge of a dissolved cation, leading to 0.005 meq/100 g clay rock. This ion-exchanged amount is insignificant with the measured CEC of $18.5 \pm 4.5 \text{ meq/100 g}$ clay (Behrends *et al.* 2016) and not considered if only the major ion-exchanged cations are investigated (e.g. Gaucher *et al.* 2004; Wersin *et al.* 2020; Marques Fernandes *et al.* 2024; Frederickx *et al.* 2018). The exchangeable sodium and potassium content can be c. 8 and 3 meq/100 g for Belgian Boom Clay (Frederickx *et al.* 2018), c. 3 and 1 meq/100 g for Callovo-Oxfordian Clay (Gaucher *et al.* 2004), and 5 and 1 meq/100 g for Opalinus Clay (Marques Fernandes *et al.* 2024). The measured exchangeable sodium and potassium in these studies support the interpretation that trace amounts of caesium can also be ion-exchanged from the marine depositional environment. Determining a rough approximation of the *in situ* K_d value by the average caesium concentration in the sediments divided by the caesium concentration in seawater gives a value of $21\,000 \text{ l kg}^{-1}$.

The Watervliet Member has a lower clay content, but a Cs content of 8 mg kg^{-1} sediment would be the result using also 41 wt% clay mineralogical content and the linear relation as found for the Watervliet Member and presented in Figure 3. This Cs difference of 1 mg kg^{-1} between the Boom Clay and the Watervliet Member is considered insignificant compared to the variation in the clay content as indicated in Table 1.

The presence of caesium in the Watervliet Member given in Figure 3 is also attributed to the high retention capacity of the clay minerals and marine deposition more than 34 Ma. Groundwater has been sampled from wells near location XVII in Figure 2. The sand porewater is less saline (i.e. brackish) at the deeper Watervliet Member from 96 to 121 m than the Boom Clay located nearer the surface at a depth from 63 to 80 m (PCR 2013). Boom Clay porewater is almost as saline as seawater (Behrends *et al.* 2016). The chloride concentration at the depth of the Watervliet Member is 496 mg l^{-1} while $19\,000 \text{ mg l}^{-1}$ is a common value for seawater. However, the dissolved caesium concentration was below the detection limit of $0.003 \mu\text{g l}^{-1}$ at the depth of the Watervliet Member (Hoving *et al.* 2024) while a concentration of $0.008 \mu\text{g l}^{-1}$ was expected with a chloride concentration of 496 mg l^{-1} .

Alkaline-earth metals

The radioactive isotope ^{90}Sr is frequently present in waste (e.g. Verhoef *et al.* 2016) but has a relatively short half-life of 29 years, like the short-lived ^{137}Cs with a half-life of 30 years (Figure 1). A Paleogene clay formation does not need to be at a minimum depth of 200 m for disposal of short-lived waste. The minerals with alkaline earth metals in Table 1 are expected to be carbonate and clay minerals. Carbonate as well as clay minerals can theoretically have built-in strontium, but the sand porewater at the depth of the Watervliet Member is supersaturated with respect to calcite and dolomite (Hoving *et al.* 2024). Alkaline-earth metallic trace elements are therefore first assumed to be correlated with carbonate minerals (i.e. a built-in trace element). Figure 4 shows that the strontium concentration in the sediment is indeed well correlated with the content of carbonate minerals for the Watervliet Member (calcite, ankerite/dolomite and siderite from Hoving *et al.* 2024) but not as well correlated for the Boom Clay samples (calcite, aragonite, ankerite/dolomite and siderite from Koenen and Griffioen 2014) perhaps due to the lower carbonate mineral content in these Boom Clay samples. The carbonate mineral content is, however, about five to eight times lower than the clay content (see Table 1). With a carbonate mineral content of c. 5 wt%, the strontium concentration in carbonate minerals should be about 20 times larger than the bulk of the sample in order to be the main reservoir in the clay host rock. Laser ablation and sequential extraction experiments would provide further evidence. The mean value for strontium in mudstone is 400 mg kg^{-1} (Breward 2007).

Assuming another reservoir (i.e. intercept is not 0 mg kg^{-1}) increases the correlation coefficient (see Fig. 2). Strontium has been measured to be ion-exchanged with clay minerals in indurated clay (e.g. Gaucher *et al.* 2004; Marques Fernandes *et al.* 2024). However, the variation in strontium concentration cannot be explained by the variation in clay content. The coefficient of determination (R^2) for the strontium concentration v. the clay content is -0.064 for the Watervliet Member and -0.066 for the Boom Clay samples (see Supplementary material S2). Discrimination between clay minerals does not lead to an increase in the coefficient of determination.

The dissolved strontium concentration almost follows the salinity of seawater (Nozaki 1997). The measured strontium concentration near location XVII in Figure 2 at the depth of the Watervliet Member is $233 \mu\text{g l}^{-1}$ for porewater with a chlorine concentration of 496 mg l^{-1} (Hoving *et al.* 2024), i.e. similar to the expected Sr concentration of $200 \mu\text{g l}^{-1}$ with this salinity. Figure 2 shows that all strontium concentrations in Boom, Ypresian

and Landen clay porewater are higher than expected from the salinity. Strontium has been measured in the Paleogene Clay porewater obtained by mechanical squeezing in samples at location XVII at 30 MPa and location XVII in Figure 2 (Behrends *et al.* 2015; Ma and Behrends 2026). The solubility of carbonate minerals can be enhanced at high pressure during collection of porewater through mechanical squeezing (Mazurek *et al.* 2023). Ion exchangers can also enhance the dissolution of solids (Helfferich 1962). The measured exchangeable strontium and calcium in Opalinus Clay (Marques Fernandes *et al.* 2024) and in the Ypresian and Landen clays (Fernández *et al.* 2025) may be caused by the dissolution of strontium and calcium carbonate. A comparison should be made between the exchangeable strontium concentration in the clay rock and the strontium concentration as measured in the bulk of the sample as performed in this paper in order to provide further evidence of whether co-precipitation or ion exchange dominates the chemical retainment process for strontium in the clay host rock.

Rare earth elements

Lanthanides are part of the rare earth elements (REEs). REEs are dissolved as carbonated species in the ocean (Schijf and Byrne 2021). REEs such as europium have been measured to exchange with calcium for the clay minerals present in Boom Clay (Baeyens *et al.* 1982). Europium is an analogue for the following trivalent actinides: americium, curium and plutonium (Hassan Loni *et al.* 2021). The europium concentration in Dutch Boom Clay as well as the Watervliet Member is below 2 mg kg^{-1} (Koenen and Griffioen 2014; Hoving *et al.* 2024). Figure 5 shows the europium concentration as measured by ICP-MS; Eu shows interference with XRF and was therefore not measured by XRF. The average concentration of 1 mg kg^{-1} for a Boom Clay with a clay content of 41 wt% ($1 \mu\text{g g}^{-1}$) is similar to the measured europium concentration of $0.9 \mu\text{g g}^{-1}$ in Callovo-Oxfordian Clay (Hassan Loni *et al.* 2021). The REEs with the highest concentrations in these clays are lanthanum and cerium. The best correlated mineralogical reservoir has been identified to be clay minerals. However, the variation in lanthanum cannot solely be attributed to the variation in the clay content (see Fig. 5). The second best correlated mineralogical reservoir appeared to be rutile (see Supplementary material S3).

Cerium, samarium, europium and ytterbium can be present in different oxidation states (i.e. these elements are redox sensitive). Figure 5 shows that no significant difference can be deduced between lanthanum and europium despite the much lower europium compared to lanthanum concentration.

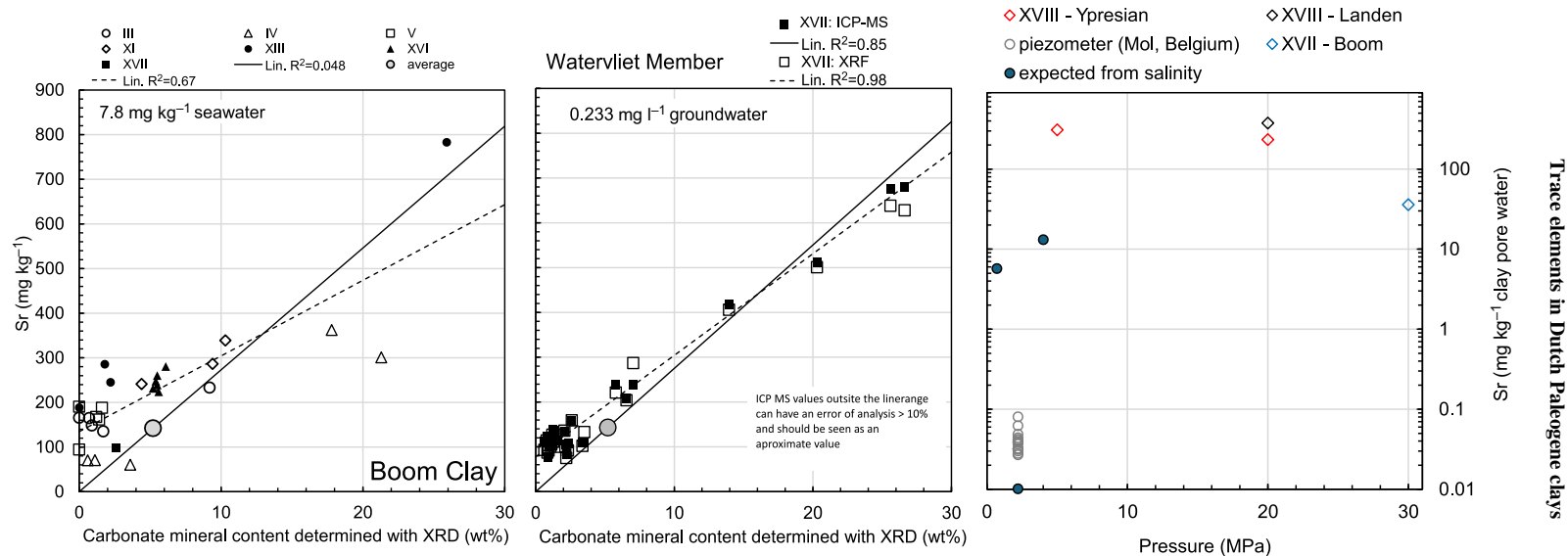


Fig. 4. Strontium concentration v. the content of carbonate minerals in Boom Clay (BC) and in the Watervliet Member. Roman numerals are the locations shown in Figure 2. The indicated strontium content is representative for seawater (Nozaki 1997). All other data points come from the third Dutch programme (Koenen and Griffioen 2014) or are more recently obtained experimental results (Hoving *et al.* 2024; Ma and Behrends 2026). Clay porewater in circles as porewater pressure and in diamonds as mechanical squeezing pressure. ICP-MS, inductively coupled plasma mass spectrometry; XRD, X-ray diffraction; XRF, X-ray fluorescence.

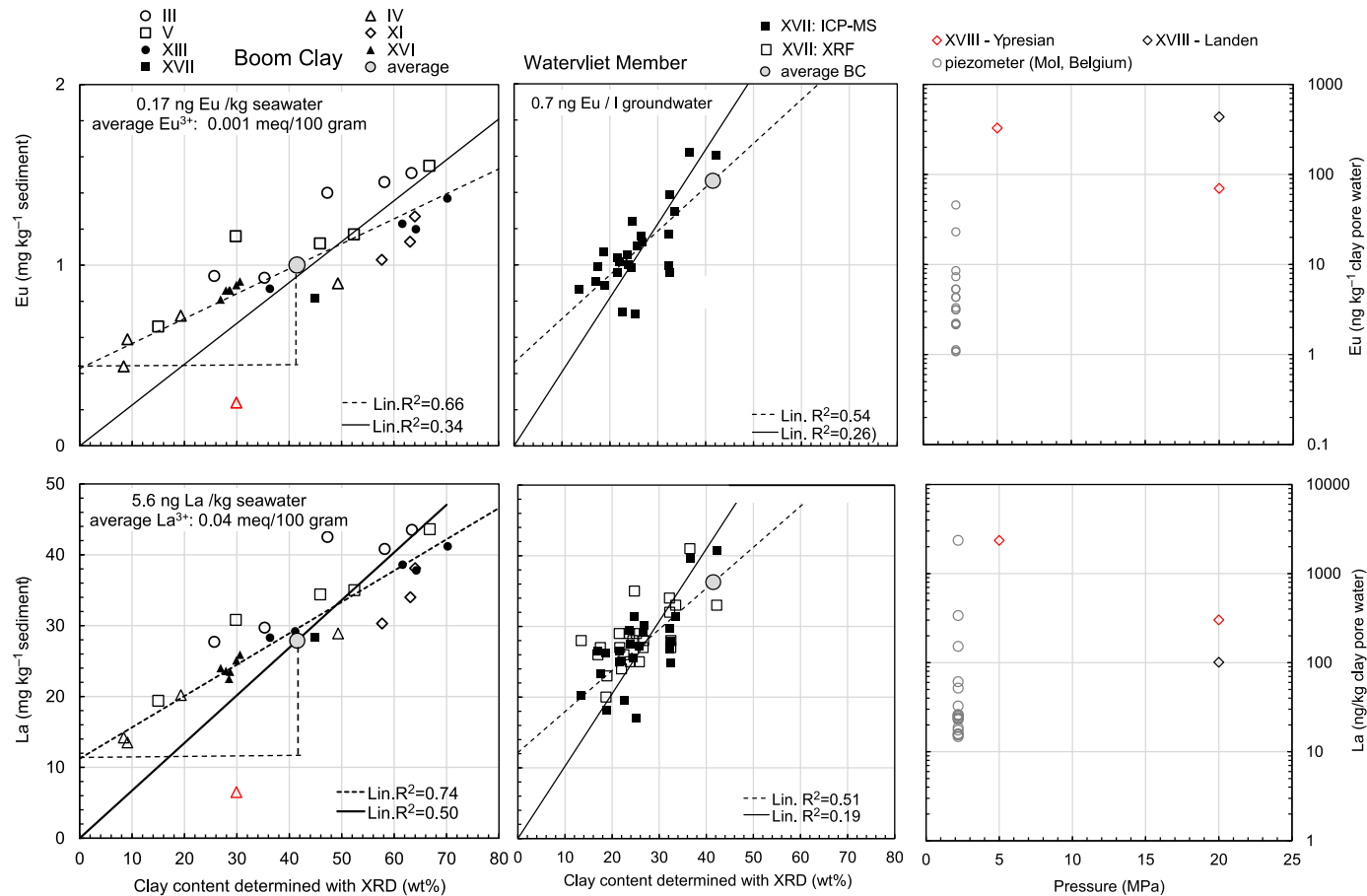


Fig. 5. Europium and lanthanum concentration v. clay content in Boom Clay (BC) and in the Watervliet Member. Roman numerals are the locations shown in Figure 2. The red triangle has a high glauconite content. The indicated europium and lanthanum concentration is representative for seawater (Nozaki 1997). All other data points come from the third Dutch programme (Koenen and Griffioen 2014) or have been obtained recently (Hoving *et al.* 2024). Clay porewater in circles as porewater pressure and in diamonds as mechanical squeezing pressure. ICP-MS, inductively coupled plasma mass spectrometry; XRF, X-ray fluorescence; XRD, X-ray diffraction.

The mean value for lanthanum in mudstone is 40 mg kg^{-1} (Breward 2007).

Clay minerals have also been identified to be the main reservoir for europium in Callovo-Oxfordian Clay with laser ablation ICP-MS measurements (Hassan Loni *et al.* 2021). The statistical correlations of europium in Figure 5 support that europium is mainly contained by clay minerals in Paleogene clays, but we cannot exclude other reservoirs due to the poor correlation with an intercept of 0 mg kg^{-1} . The second best correlation is with rutile/anatase (see Supplementary material S3) but the mineral contents are less than 1 wt% (see Table 1). The europium concentration in rutile/anatase should be at least 100 times larger than the value in the bulk of the samples in order to be the main reservoir in the clay host rock. Laser ablation experiments have been performed to provide further evidence (Hoving and Griffioen 2025).

Lanthanides such as europium have, however, been assumed to be trapped by immobile dissolved organic matter as input for the post-closure safety assessment in the third Dutch programme (Meeussen *et al.* 2017). The coefficient of determination (R^2) for the lanthanum concentration v. organic carbon content is negative: -6.268 for the Watervliet Member and -2.101 for the Boom Clay samples (see Supplementary material S4); that is, the variation in the lanthanum concentration cannot be explained by the variation in the organic carbon content in the clay rock. The europium and lanthanum concentrations in organic carbon would need to be at least an order of magnitude larger than measured in the clay rock due to their low contents, with a maximum of 2.5 wt%, if their presence is mainly attributed to interaction with organic matter. We therefore believe that clay minerals can be more representative traps for lanthanum than organic carbon.

Another line of reasoning is that lanthanum could be measured from Boom Clay porewater but only for porewater obtained with mechanical squeezing with a pressure six times the formation pressure. A maximum lanthanum concentration of $63\,000 \text{ ng l}^{-1}$ was measured in Boom Clay porewater collected at 30 MPa (De Craen *et al.* 2004). A recent study (Ma and Behrends 2026) confirms that all lanthanum concentrations are below 500 ng l^{-1} except for one measurement taken from a silt-rich clay layer. Unlike caesium and strontium, the measured lanthanum concentration in Ypresian and Landen clays porewater obtained from squeezing is not always higher than collected from the URL in Belgium. Collection of clay porewater by other techniques and other mechanical squeezing pressures is in progress (Ma and Behrends 2026).

The measured europium concentration was $0.0007 \text{ } \mu\text{g l}^{-1}$ and the lanthanum concentration was below the detection limit of $0.004 \text{ } \mu\text{g l}^{-1}$ (Hoving

et al. 2024). Lanthanum and europium are so-called nutrient-type elements in seawater (i.e. elements that are depleted in surface water due to biological uptake and are enriched in deep water by regeneration from particulate matter). The concentrations of nutrient-type elements therefore increase with increasing depth in the ocean. This increase in concentration from the surface of the ocean to 4–5 km depth is less than ten times the surface concentration (Nozaki 1997). We have not indicated values that can be expected from salinity in Figure 5 since their behaviour does not follow the salinity as strontium and caesium.

Actinides

Only two actinides are naturally present in Paleogene clays: thorium and uranium. Although the uranium concentration in the clay rock can be lower than the uranium concentration in waste (see Fig. 1), the volume of the waste form is 10 000 times smaller than the volume of the clay host rock. Understanding how these natural radionuclides behave in Paleogene clay formations is therefore valuable for predicting what controls the naturally present soluble amount of uranium in the clay host rock.

Thorium in seawater is dissolved as a hydroxide and uranium as a uranyl-carbonate (Murray 1992). Figure 6 shows that the majority (69 and 67%) of the variation in the thorium concentration can be explained by the variation in clay content. This is not the case for the uranium concentration, but the variation in clay content does have the highest correlation with the variation in uranium concentration, the second best correlation was found with rutile/anatase (see Supplementary material S5) but the uranium and thorium concentration in these Ti oxides should be very high due to their low content of less than 1 wt % as explained for REEs. No statistically significant correlations have been found for uranium with the carbonate mineral content, content in pyrite, inorganic carbon, organic carbon or phosphorus. Organic carbon (see Supplementary material S6) shows that the uranium concentration does not increase with increasing organic carbon content (i.e. similarly as measured by Montavon *et al.* (2022), who also measured a uranium concentration in organic matter of 0.069 mg kg^{-1}).

The mean value for uranium in mudstone is 3.5 mg kg^{-1} (Breward 2007). Analysis of individual mineral phases in Callovo-Oxfordian Clay identified the clay minerals as the main mineralogical reservoir but also revealed that phosphate minerals can contain on average a ten times higher concentration of uranium than clay minerals (i.e. 2.5 mg kg^{-1} in clay minerals and 32 mg kg^{-1} in phosphate nodules) (Montavon *et al.* 2022). Such high uranium spikes may hamper statistical analysis. Apatite is a

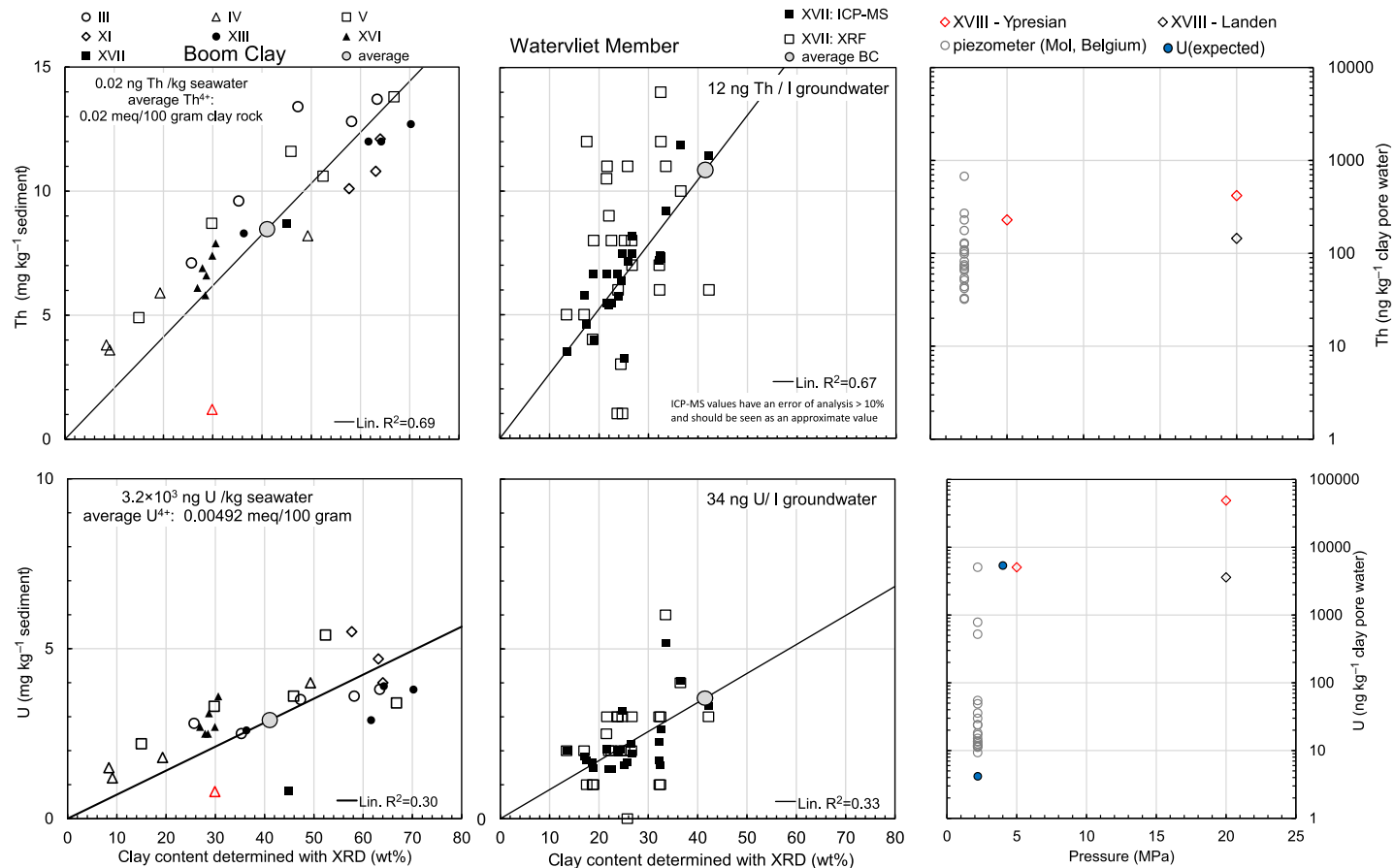


Fig. 6. Thorium and uranium concentration v. clay content in Boom Clay (BC) and in the Watervliet Member. Roman numerals are the locations shown in Figure 2. The red triangle has a high glauconite content. Thorium and uranium concentrations in seawater from Nozaki (1997). All other data points come from the third Dutch programme (Koenen and Griffioen 2014) or are more recently obtained experimental results (Hoving *et al.* 2024). Clay porewater in circles as porewater pressure and in diamonds as mechanical squeezing pressure. ICP-MS, inductively coupled plasma mass spectrometry; XRF, X-ray fluorescence; XRD, X-ray diffraction.

phosphorus mineral that has been measured to be present in trace amounts in Belgian Boom Clay (Honty and De Craen 2012). A detailed study on phosphorus minerals in Dutch Paleogene clay may elucidate the major mineralogical trap for uranium. Nevertheless, higher uranium and thorium concentrations were measured in porewater extracted from the squeezed sample than porewater collected from piezometers (De Craen *et al.* 2004) (i.e. the same behaviour as already described for alkali metals (caesium) and REEs). The more recent data in Figure 6 confirm the large variation in uranium concentration in clay porewater in the Belgian URL (De Craen *et al.* 2004).

Thorium is a so-called scavenged type of element in seawater (i.e. the thorium concentration in seawater is very low due to scavenging by particulate matter). Like REEs, the thorium concentration increases with increasing depth of the ocean but not by an order of magnitude (Nozaki 1997). We have therefore not indicated a value that can be expected from salinity for thorium in Figure 6. The concentration measured in groundwater in the Watervliet Member is higher than in seawater but the Th of 12 ng l^{-1} is still very small compared to the 9 mg kg^{-1} in Boom Clay rock (i.e. orders in magnitude smaller than measured in the sediment). The K_d value would be greater than 10^5 l kg^{-1} if the presence of thorium in clay minerals in Paleogene clays can entirely be attributed to ion-exchange. The mean value for thorium in mudstone is 12 mg kg^{-1} (Breward 2007).

The concentration of dissolved uranium follows salinity as with caesium (Nozaki 1997). A U concentration of 81 ng l^{-1} would be expected at a Cl salinity of 496 mg l^{-1} . This calculated concentration is larger than the measured U concentration of 34 ng l^{-1} . For caesium, the measured concentration as measured in the groundwater well (Hoving *et al.* 2024) was also lower than expected based on salinity. The uranium concentration in porewater collected through mechanical squeezing from samples of the Ypresian and Landen clays (Ma and Behrends 2026) is of similar order of magnitude as expected from the salinity (see Fig. 6).

Uranyl-carbonate complexes are proposed to be ion-exchanged with clay minerals (Montavon *et al.* 2022). Such complexes therefore not only retain uranium in the waste but also radionuclides such as ^{14}C . This feature (i.e. retention of non-metals by clay minerals) is further explored for selenium in the 'Other non-metals' section.

Transition metals

Radioactive niobium had also been calculated to enter the environment in the post-closure safety assessment made in the third Dutch programme (Rosca-Bocancea *et al.* 2017). Most transition metals

were assumed to be trapped by immobile dissolved organic matter in that assessment, except for niobium and molybdenum. These two transition metals were assumed to be dissolved as anionic dissolved complexes that were not chemically retained by a solid or immobile phase (Meeussen *et al.* 2017). Figure 7 contradicts this assumption, showing that the majority (57 and 74%) of the variation in the niobium concentration can be explained with the variation in the clay content. The mean value for niobium in mudstone is 20 mg kg^{-1} (Breward 2007) and Figure 7 clearly shows that results obtained with ICP-MS lead to a higher measured concentration than with XRF.

Naturally present niobium in water is extremely low and therefore difficult to quantify. The niobium concentration in groundwater was below the detection limit of $0.2 \mu\text{g l}^{-1}$ (Hoving *et al.* 2024) and below the detection limit in seawater of 5 ng kg^{-1} (Nozaki 1997). Our equipment could handle lower concentrations by which even the lowest Nb concentrations in the Belgian URL could be measured. The porewater collected through mechanical squeezing from samples of the Ypresian and Landen clays will be extended with more mechanical squeezing pressures and other methods to collect porewater (Ma and Behrends 2026). For now, there is sufficient evidence that niobium is chemically retained, and radioactive niobium is not expected to enter the biosphere if released from the waste form (Neeft *et al.* 2025).

Other non-metals

The four groups of elements that have not yet been treated in this paper are other metals, metalloids, halogens, noble gases and other non-metals. The radioactive counterparts of other metals and metalloids are very rarely present in radioactive waste; halogens have not been measured in the sediments and a chemical retention process with noble gases is not expected. Selenium belongs to the group of other non-metals. Like niobium, selenium has been assumed not to be chemically retained by a solid or immobile phase (Meeussen *et al.* 2017) and radioactive selenium has also been calculated to enter the biosphere in the post-closure safety assessment made in the third Dutch programme (Rosca-Bocancea *et al.* 2017). Figure 8 shows, however, that most (64%) of the variation in the concentration of selenium can be explained by the variation in clay content for the Watervliet Member. The detection limit for selenium (0.5 mg kg^{-1} sediment) was too high to measure selenium accurately enough at the time that the Boom Clay samples were measured, and the mean value for selenium in mudstone of 0.6 mg kg^{-1} (Breward 2007) is close to this detection limit. Figure 8 also shows that chemical concentration in this sediment is almost three

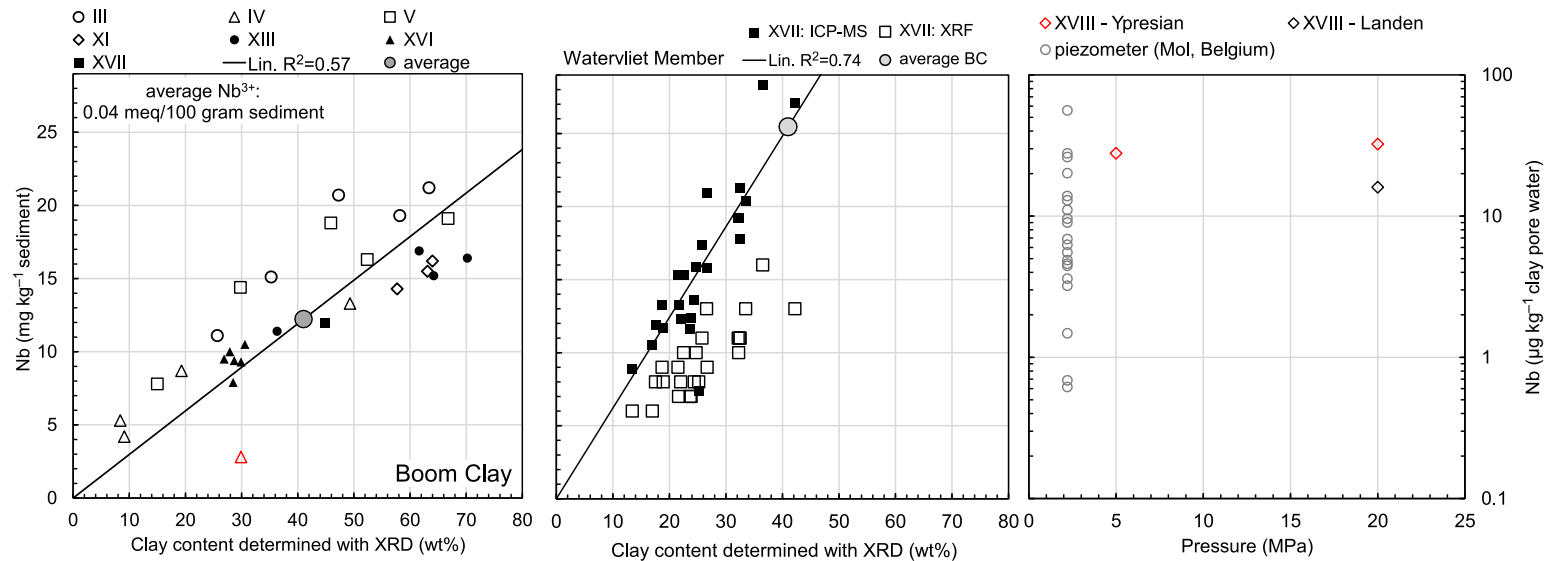


Fig. 7. Niobium v. clay concentration in Boom Clay (BC) and in the Watervliet Member. Roman numerals are the locations shown in Figure 2. The red triangle has a high glauconite content. All data points come from the third Dutch programme (Koenen and Griffioen 2014) or are more recently obtained experimental results (Hoving *et al.* 2024; Ma and Behrends 2026). Clay porewater in circles as porewater pressure and in diamonds as mechanical squeezing pressure. ICP-MS, inductively coupled plasma mass spectrometry; XRF, X-ray fluorescence; XRD, X-ray diffraction.

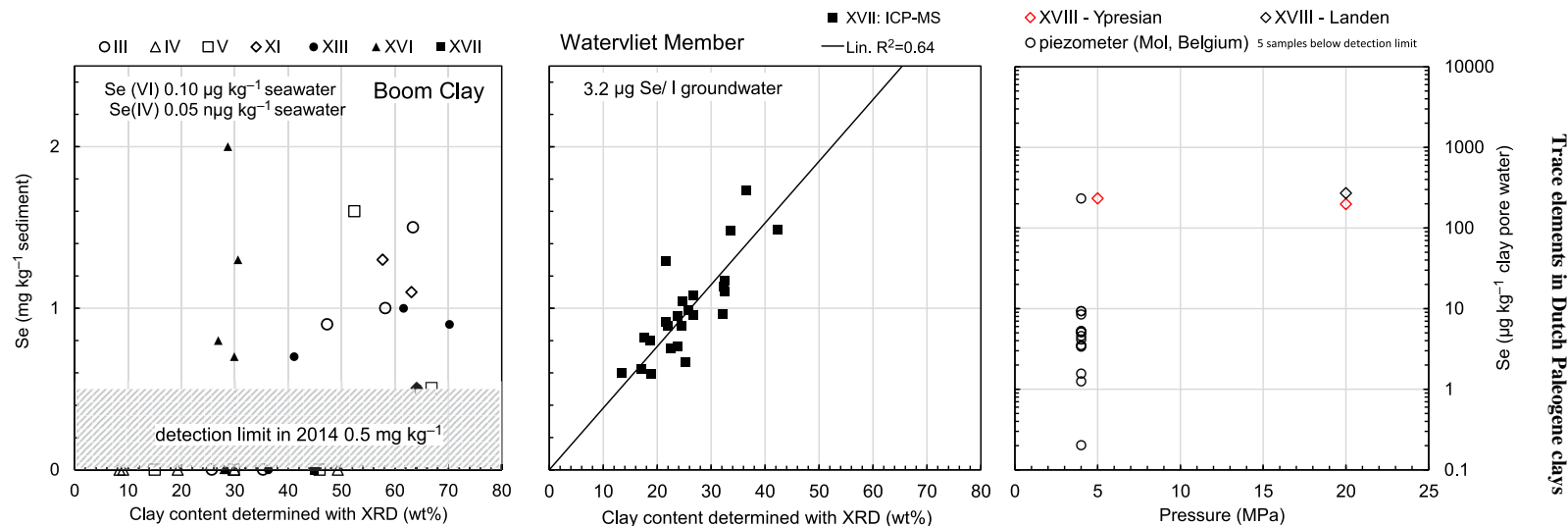


Fig. 8. Selenium concentration v. clay content in Boom Clay (BC) and in the Watervliet Member. Roman numerals are the locations shown in Figure 2. Selenium concentration in seawater from Nozaki (1997). All other data points come from the third Dutch programme (Koenen and Griffioen 2014) or are more recently obtained experimental results (Hoving *et al.* 2024). ICP-MS, inductively coupled plasma mass spectrometry; XRD, X-ray diffraction; XRF, X-ray fluorescence.

orders of magnitude larger than the dissolved concentration in groundwater (i.e. the sediment is chemically enriched with selenium in the solid phase). Figure 8 shows that the concentrations measured in groundwater (Hoving *et al.* 2024) are higher than measured in seawater (Nozaki 1997). This has also been observed for europium (see Fig. 5) and thorium (see Fig. 6). Frequently, the selenium concentration in Belgian Boom Clay porewater was too low to be measured. The selenium concentrations in porewater samples that could be measured are below $10 \mu\text{g kg}^{-1}$ except for one measurement taken from a silt-rich clay layer. Measuring collected porewater with more mechanical pressures and other methods is in progress (Ma and Behrends 2026)

The study by Montavon *et al.* (2022) shows that uranyl-carbonate complexes ion-exchange with clay minerals by which not only would uranium be chemically retained but also radioactive ^{14}C . A similar feature is also expected for selenium, by which selenium would also be chemically retained by the clay minerals in the clay host rock. More detailed studies specific to selenium are needed to confirm this hypothesis.

Approach for validation of the parameters in a post-closure safety assessment

Figure 9 shows the total clay content and the concentration of caesium, niobium and uranium in the sediments with depth for the Watervliet Member. These elements show the same pattern in their distribution with depth.

Representative parameters for the post-closure safety assessment can be derived by obtaining a good fit between the mechanistically modelled profile and the measured concentration in multiple clay samples from a single location (e.g. Mazurek *et al.* 2009). A similar approach is proposed for chemical elements that are chemically retained in clay rocks.

A start to bound the K_d and diffusion values to be used in the post-closure safety assessment has been made in COPERA, a Dutch acronym for COVRA's programme for research into geological disposal of waste. A period of 10 Ma was used for modelling the caesium profiles with a range in K_d values and transport parameters and the same geometry and boundary conditions as used in the post-closure safety assessment (see Fig. 10).

For caesium, the dissolved caesium concentration in seawater of $0.003 \mu\text{g l}^{-1}$ and 7 mg kg^{-1} in the sediment are used in the determination of the K_d value. The K_d value for Boom Clay with a clay content of 41 wt% becomes $21\,000 \text{ l kg}^{-1}$. This value is slightly larger than the maximum of $18\,600 \text{ l kg}^{-1}$ as used in the Belgian programme (Bruggeman and Maes 2017) but more than an order of magnitude larger than the maximum of 1038 l kg^{-1} used in OPERA and orders of magnitude larger than the minimum of 183 l kg^{-1} used in OPERA (Schröder *et al.* 2017).

The caesium profile calculated with a K_d value of $21\,000 \text{ l kg}^{-1}$ would hardly show any migration of caesium in the clay rock (i.e. a concentration profile controlled by diffusion and retention; so-called retarded diffusion). Calculation with the low K_d value of 183 l kg^{-1} would lead to disappearance of caesium. However, we can measure caesium in

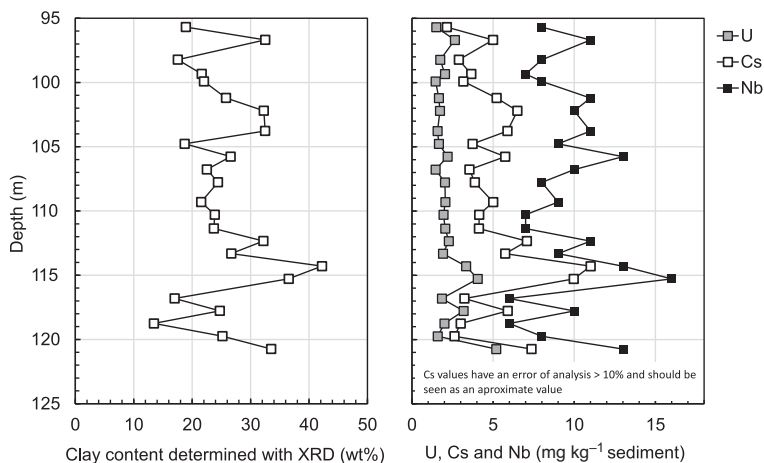


Fig. 9. Clay (left) and caesium, niobium and uranium (right) concentration measured with inductively coupled plasma mass spectrometry v. depth for the Watervliet Member. XRD, X-ray diffraction.

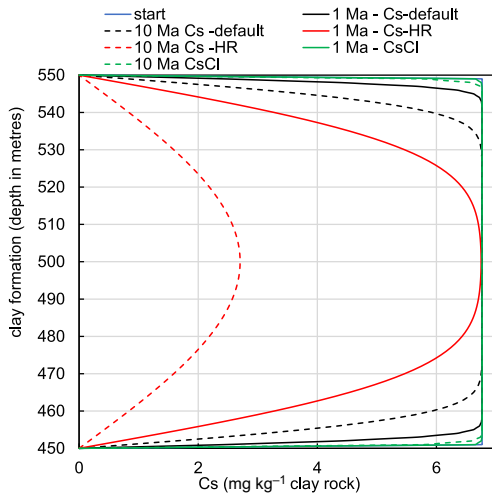


Fig. 10. Modelled caesium concentration for a hypothetical clay formation with a thickness of 100 m and an initial average concentration of 7 mg Cs per kg sediment. Red (high release (HR): K_d 183 l kg⁻¹, diffusion value (D) 34×10^{-10} m² s⁻¹) and blue (default: K_d 605 l kg⁻¹, D 3×10^{-10} m² s⁻¹) curves with OPERA parameters; green curves (K_d 21 000 l kg⁻¹, D 0.8×10^{-10} m² s⁻¹) with retention as assumed with experimental data with trace elements; D for CsCl is a calculated fraction of the diffusion value for water in clay (Neeft *et al.* 2025).

Paleogene clays even at lower mineralogical clay contents. The experimentally obtained high K_d value is therefore expected to be more representative for a post-closure safety assessment than the calculation performed with a K_d value of 183 l kg⁻¹ since Figure 9 also shows a lack of caesium migration. The dissolved caesium concentration in the clay porewater as well as the amount of naturally exchanged caesium are needed to confirm this expectation. If confirmed, the Dutch programme would be more in line with programmes from other countries such as the Swiss programme in which radioactive caesium would not leave clay host rock in the post-closure safety assessment (NAGRA 2002).

In the future, location-specific experimental studies for the presence of chemical elements in the sediment and clay porewater should be done to validate the parameters used in the post-closure safety assessment.

Further work

In this study, a simple model is used in which a trace element is linearly related to carbonate or clay minerals. For the trace elements examined, we hypothesized that their distribution reflects the original

depositional environment and subsequent ion exchange with clay minerals, analogous to the behaviour of major elements (Jones and Capuano 2023). However, additional evidence is needed to confirm this interpretation and refine the derived distribution values.

Laser ablation ICP-MS measurements were performed to determine the concentration of trace elements in specific minerals and interpreted based on total mass balance with all minerals identified by XRD. In addition, sequential extractions have been made, but the removal of trace elements of clay sediments appears to be difficult (Hoving and Griffioen 2025). The time evolution of solutions was previously investigated in the third Dutch programme (Behrends *et al.* 2016) and may need to be further explored to obtain appropriate results with sequential extractions. The porewater from the clay cores extracted in 2022 in Delft (Vardon *et al.* 2022) is being analysed (Ma and Behrends 2026). Measurement of the CEC with complexes (e.g. Cu-erien and Ag-thiourea) needs to be followed up with the measurement of the chemical composition of the resulting solutions. The concentrations of exchanged cations (and anions to deduce complexes with cations) in these solutions will reveal whether the clay minerals are the main reservoir for the trace elements.

Conclusion

The concentrations of trace elements in clay host rock are usually higher than those of most of their radioactive counterparts in the solid waste form. The total inventory of these elements in the natural system far surpasses that in the waste form considering the larger volume of the clay host rock. Exceptions are some actinides such as plutonium. The natural presence of lanthanides has been used as chemical analogues for these actinides. The main mineralogical reservoir of trace elements in Paleogene sediments has been identified, with the best correlations between the variation in concentration of chemical elements and the variation in content of groups of minerals. Importantly, the same correlations were observed for the Boom Clay and Water-vliet Member samples despite their differences in clay content, suggesting that the fundamental controls on trace element distribution are consistent across these Paleogene formations. The main mineralogical reservoir for trace amounts of alkali metals, REEs, actinides, transition metals and non-metals has been identified to be clay minerals. These trace elements are hypothesized to be exchangeable cations or cationic complexes with this identification and interpretation from the supporting literature. The naturally ion-exchanged amount of these trace elements is negligible compared to the major

components sodium, potassium, magnesium and calcium, and therefore is easily overlooked.

Trace amounts of alkaline-earth metals may not correlated with the clay content. The groundwater in the sand formations surrounding the clayey sediments was saturated with carbonates. Strontium was well correlated with the calcareous mineralogical content. The radioactive part of that alkaline-earth metal would therefore barely enter the clay host rock if that radionuclide is released from the engineered barrier system but co-precipitate as a carbonate.

Most radionuclides in radioactive waste will meet their non-radioactive counterparts in the clay host rock if radionuclides are released from the engineered barrier system. The behaviours of the non-radioactive counterparts of radionuclides in the clay host rock, equilibrated over millions of years under *in situ* conditions, are expected to be representative for a post-closure safety assessment. Studying the natural distribution of trace elements in Paleogene clays provides a robust framework for deriving representative parameter values for post-closure safety assessments. This natural analogue approach complements experimental studies and offers distribution values that reflect long-term geochemical equilibrium relevant to the million-year timescales of containment of radionuclides.

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Data availability All data generated or analysed during this study are included in this published article and, if present, its supplementary information files.

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