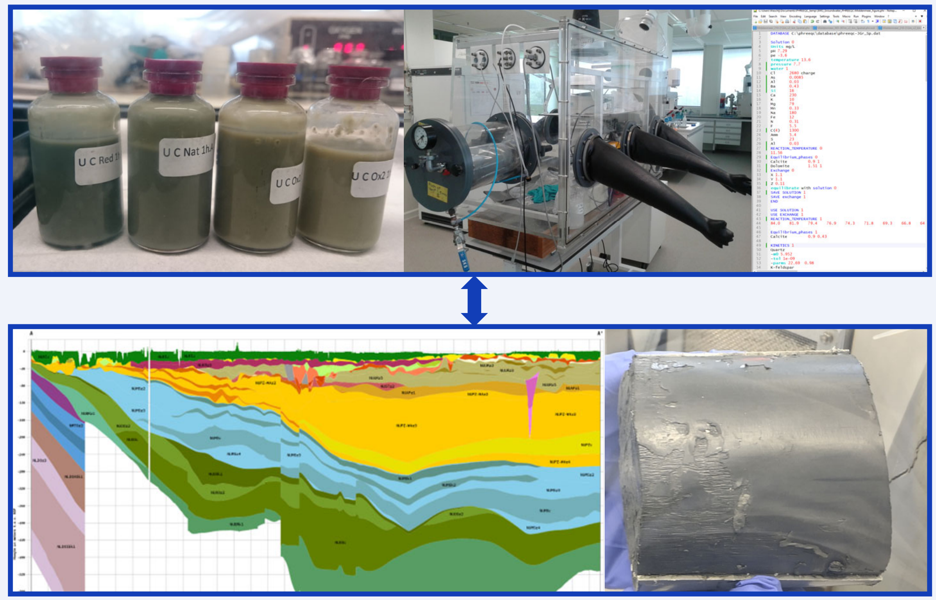
Se concentrations in Paleogene groundwater and sediments, the Netherlands

Natural radionuclides in host rock as analogue for radionuclides from waste

Behaviour of natural radionuclides and chemical analogues in Paleogene clay formations can provide an indication of the fate of radionuclides released from waste forms when entering these clay formations

This study:

- Characterize trace element content of Paleogene **sediments** of 2 different cores and identify minerals with which these trace elements are associated.
- Analyze trace element concentrations in **groundwater** of Paleogene aquifers in the region of one of these cores.



	Kd $_{\text{experimental/calculated}}$	Kd $_{\text{host rock}}$
Se	0 (Se^{VI})	
U	42	
Th	46	
Cs	1184	

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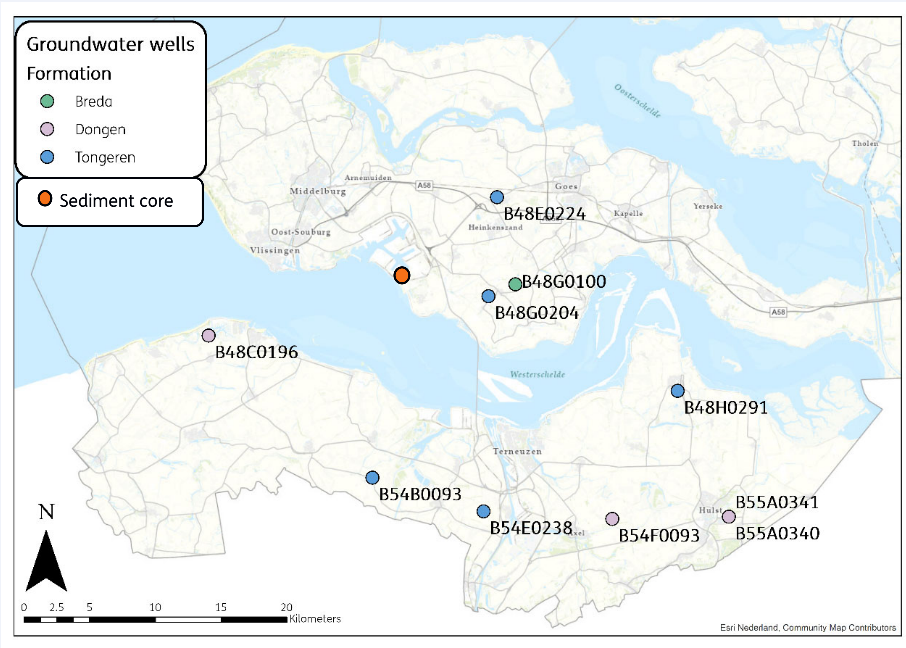
Groundwater sampling

- 10 sampled groundwater wells
- 8 wells with filters in Paleogene Tongeren/Dongen Formations
- 2 multi-level wells with filters in younger Formations
- 15 samples in total



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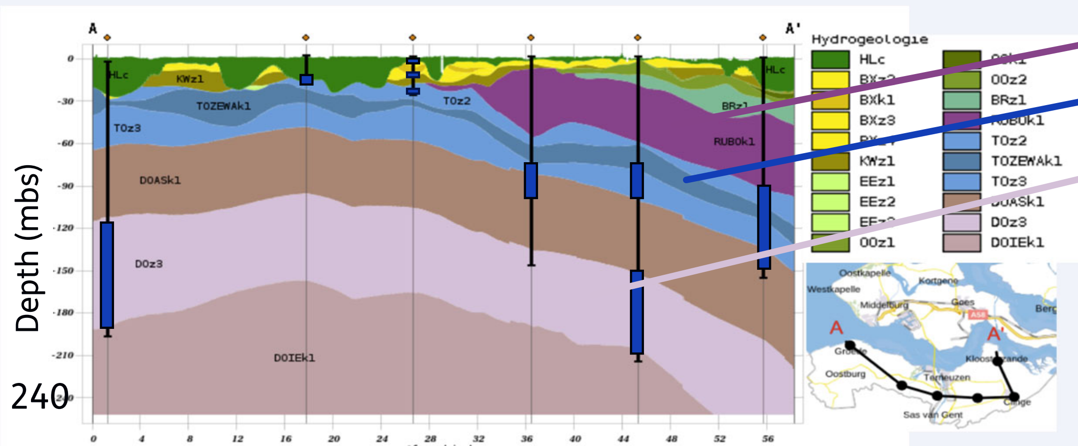
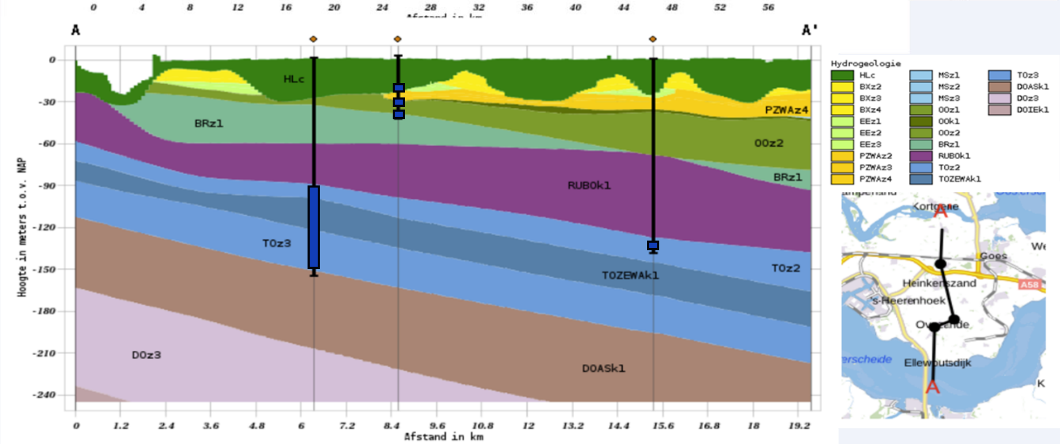
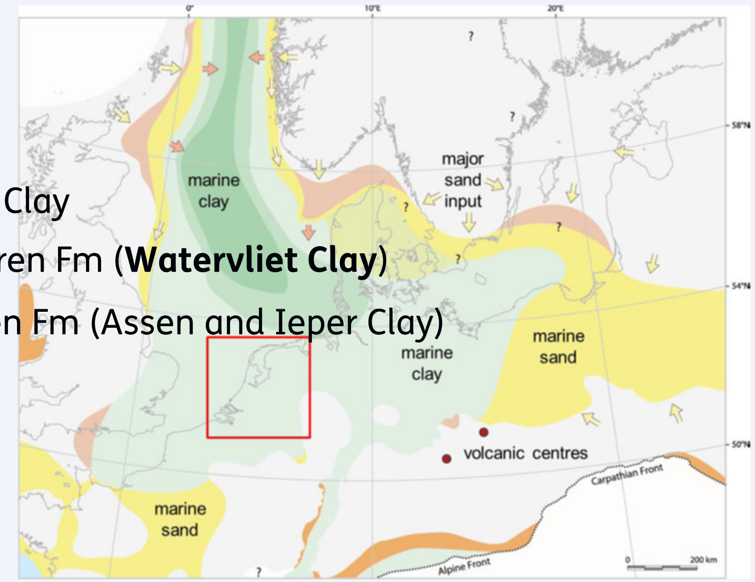
Cross sections

- W-E and S-N Cross-sections with filter depth



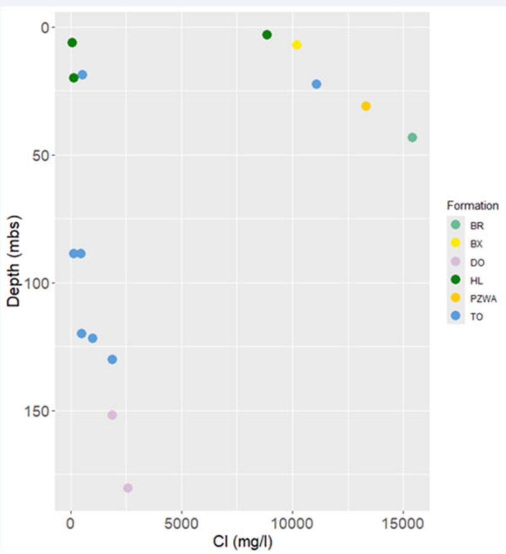


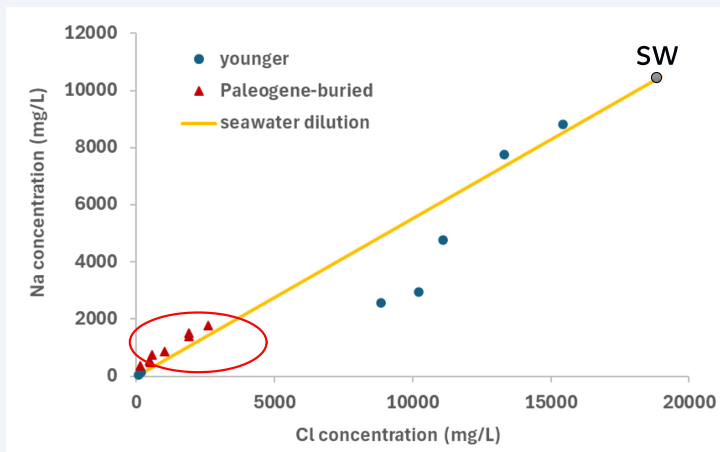


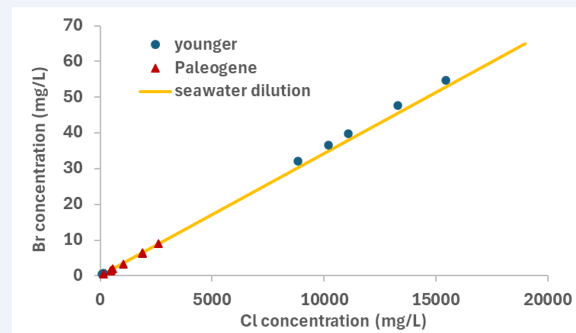
Chrono-stratigraphy (not on linear time scale)		Marine
Neogene	Pliocene	Oosterhout Formation - NUOO
	Miocene	Breda Formation - NUBR
23.03 Ma		Veldhoven Fm. - NMVE
Paleogene	Oligocene	Rupel Fm. - NMRU
		Tongeren Fm. - NMTO
	Eocene	Dongen Fm. - NLDO
66 Ma	Paleocene	Landen Fm. - NLLA

General groundwater composition

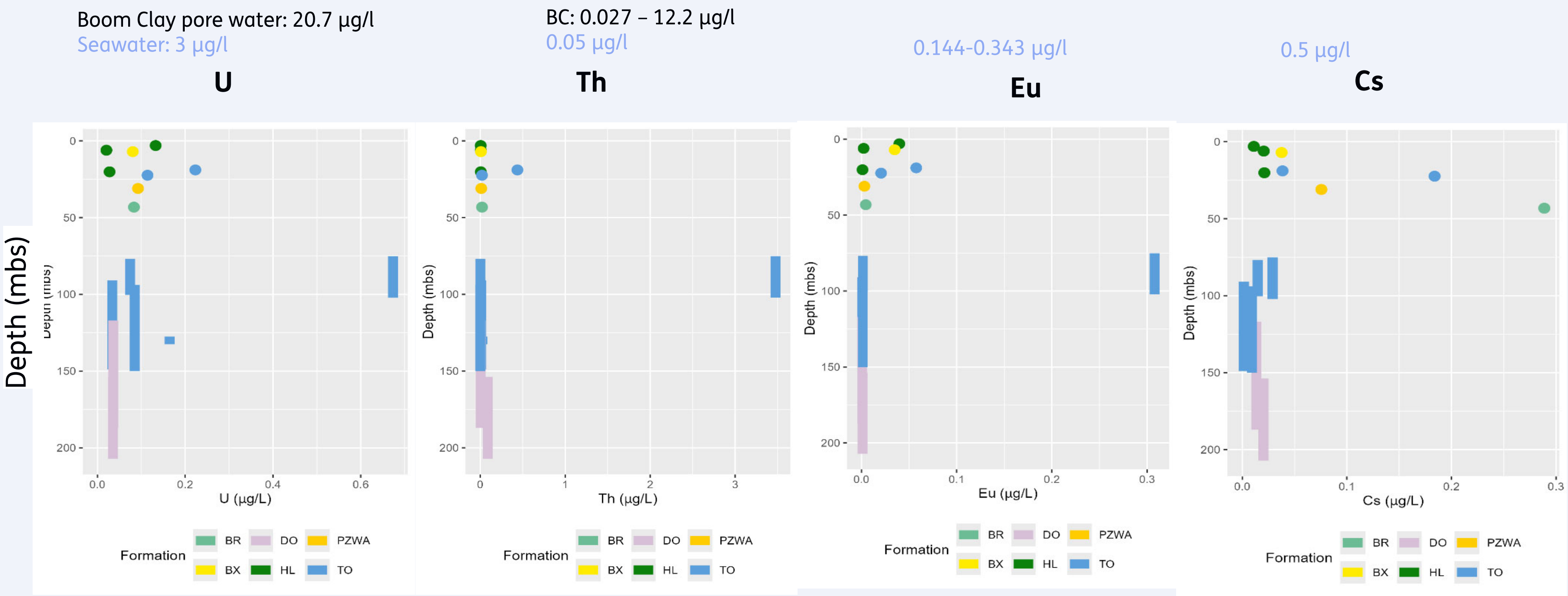
- Deeper samples (Tongeren & Dongen) are fresh to brackish-saline.
- Freshening occurred for the Paleogene samples (above mixing line Na/Cl).
- Based on C14 ages and $\delta^{18}O$ groundwater is from Holocene age.





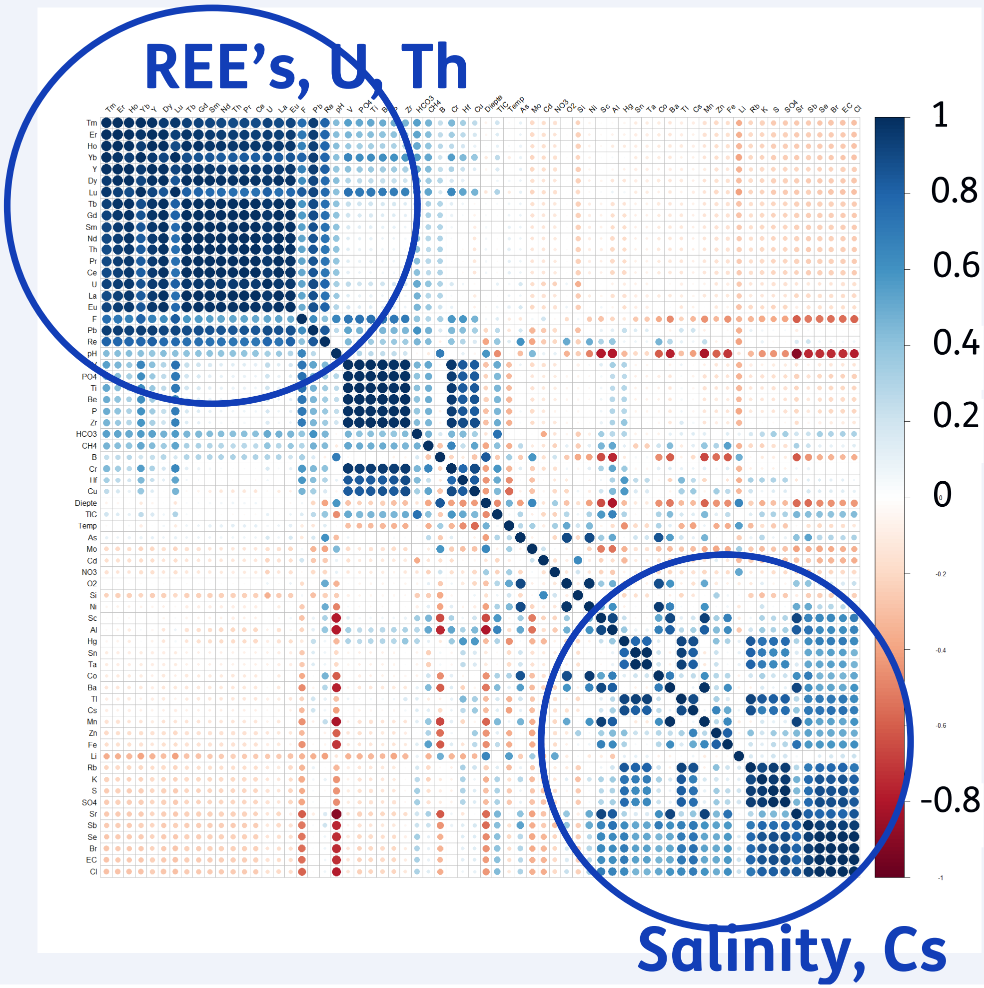


Trace elements in Paleogene groundwater



[82]Se: Analysis problematic due to high Br concentrations resulting in interference with HBr ion pair (M=82)

Correlations elements in groundwater



Correlation plot

- Two groups with high correlations:

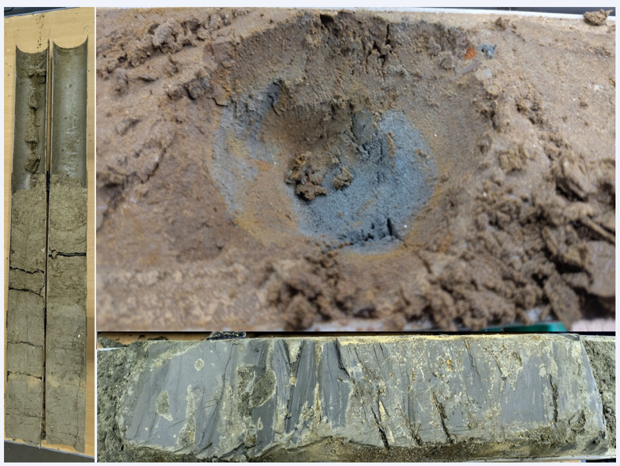
  1. Rare-earth elements (REE's) with U, Th, Re, Eu etc.

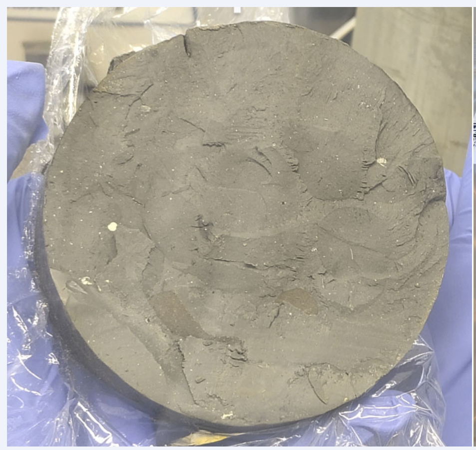
  2. Salinity-related elements: Cl, SO4, Cs

Summarizing results trace elements in Paleogene groundwater:
-Concentrations lower than respective seawater concentrations
-Immobilisation likely for U, Th, Re, Eu and Cs

Paleogene samples

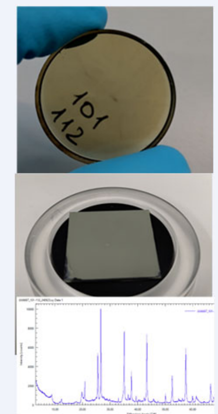
Location close to Groundwater wells: 24 samples of Watervliet clay’
DAPGEO borehole: 19 shoe samples, 3 fresh samples (porewater extraction, Utrecht University)

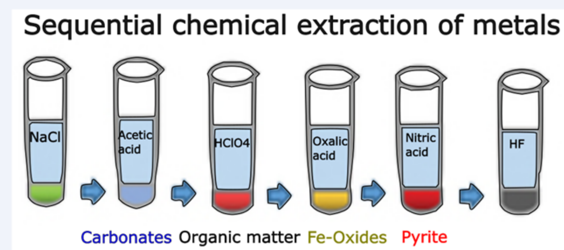


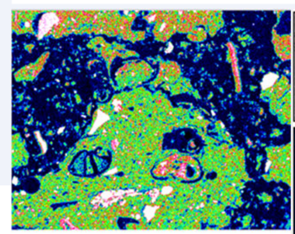


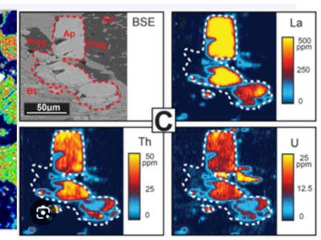
Analyses

- Elemental analysis by HF-digestion+ICP-MS, XRF and combustion (C, Corg and S)
- Mineralogical analysis by XRD (incl clay fraction)
- Trace elemental analysis by:
    - Sequential extraction + ICP-MS
    - SEM-EDX
    - Laser Ablation-ICP-MS









Minerals

The analyzed depth profiles are an alternation of clayey, silty and sandy layers. The sandy layers are glauconite rich.

DAPGEO

Mineral	MIN (wt%)	MAX (wt%)	AVERAGE (wt%)
Quartz	18	93	37
Clay minerals/ mica/ glauconite	4	66	48
Feldspars	1	12	7
Calcite	0	9	2
Ankerite	0	5	1
Pyrite	0	2	1
Anatase	0	2	1
Gypsum	0	5	2
Jarosite	0	3	1

Watervliet

Mineral	MIN (wt%)	MAX (wt%)
Quartz	13.5	60.5
clay minerals/ mica/ glauconite	13.9	41
Feldspars	**7.5**	**19**
Calcite	0.0	**29.1**
Ankerite	0.0	2.2
Pyrite	0.0	2.61
Anatase	0.8	1.6
Gypsum	0.1	2.2
Jarosite	0.0	4.8

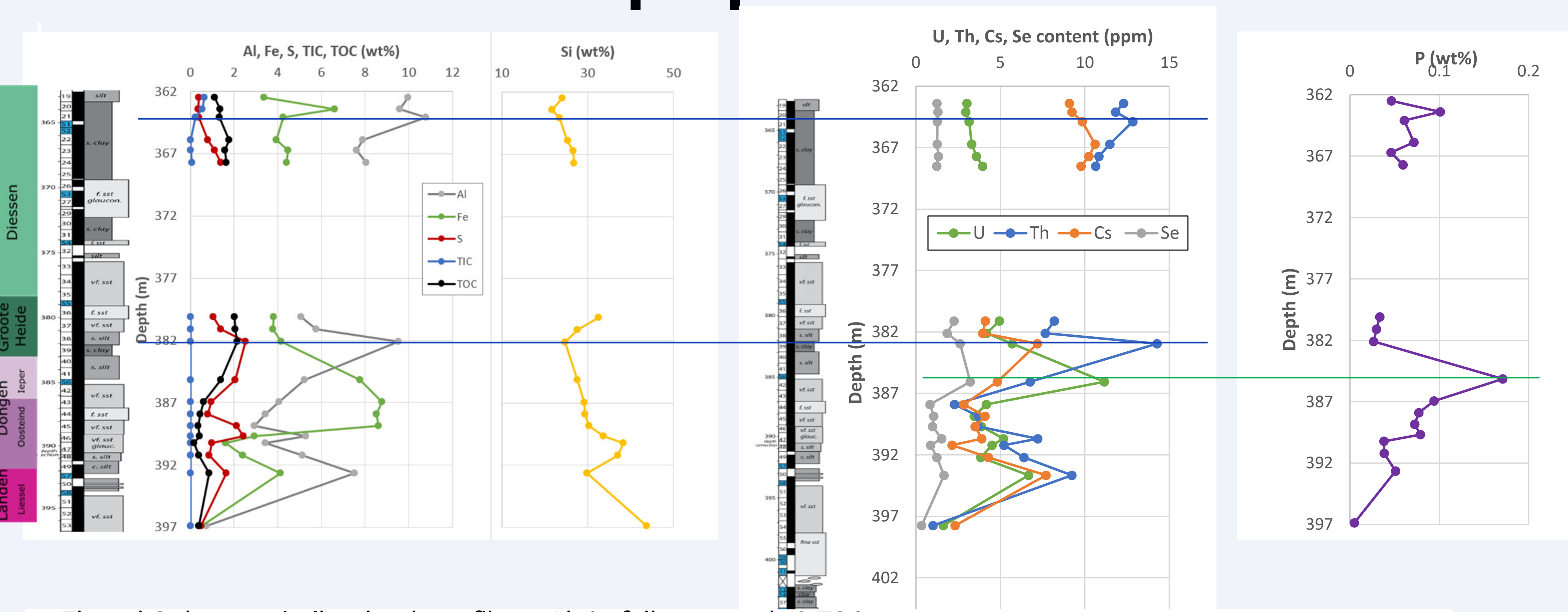
Secondary minerals → drying/oxidation

Trace elements

Comparison of average trace element content in Paleogene sediments of different Formations

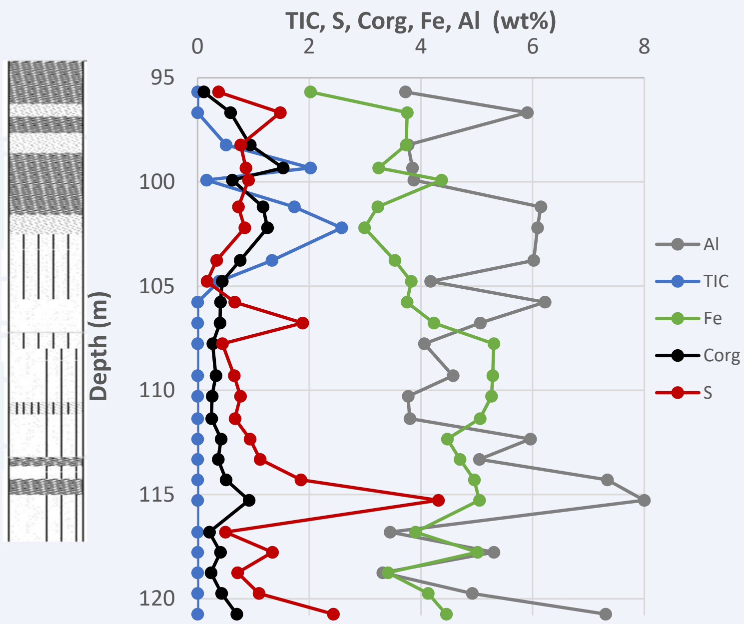
	DAP	Watervliet	Boom Clay	Callovo-Oxfordian
U	4 ± 2 ppm	2 ± 0.9 ppm	3.5 ± 2 ppm	0.5-4.4 ppm
Th	8 ± 4 ppm	7 ± 2 ppm	9 ± 3 ppm	
Cs	6 ± 3 ppm	5 ± 2 ppm	7 ± 3 ppm	
Se	1.5 ± 0.7 ppm	1 ± 0.3 ppm	1.2 ± 0.6 ppm	0.84 ppm

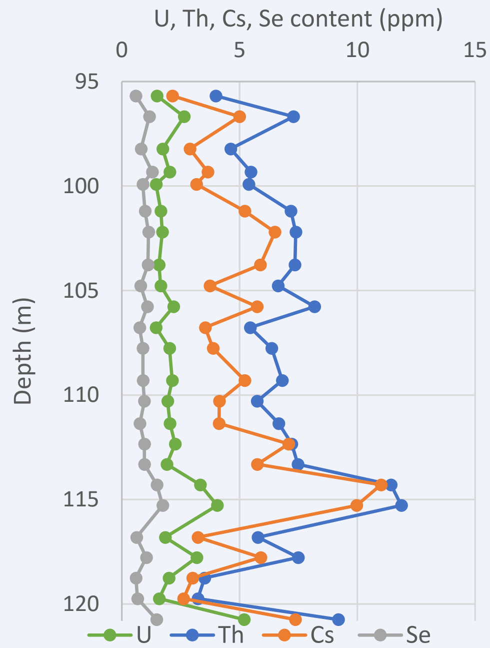
Trace elements – depth profile DAP core

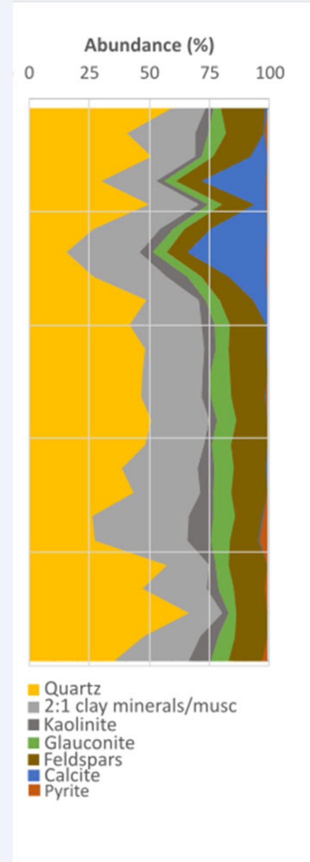


- Th and Cs have a similar depth profile as Al. Se follows trends S-TOC
- U peak at 385 m depth coincides with P peak. Groote Heide formation (former Breda Fm) known for phosphorites.

Trace elements – depth profile Watervliet core

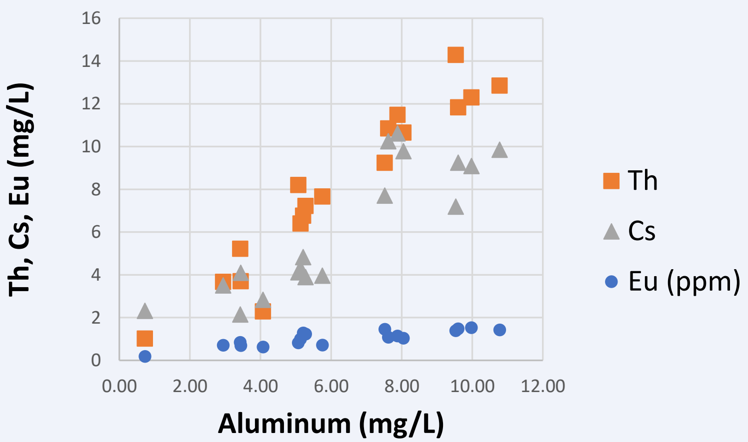


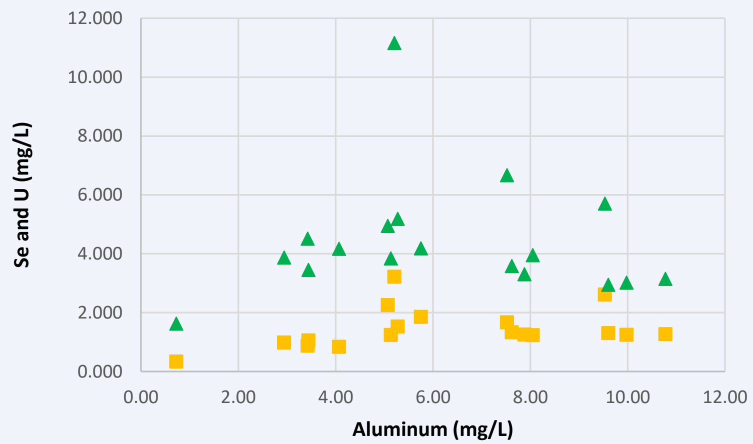




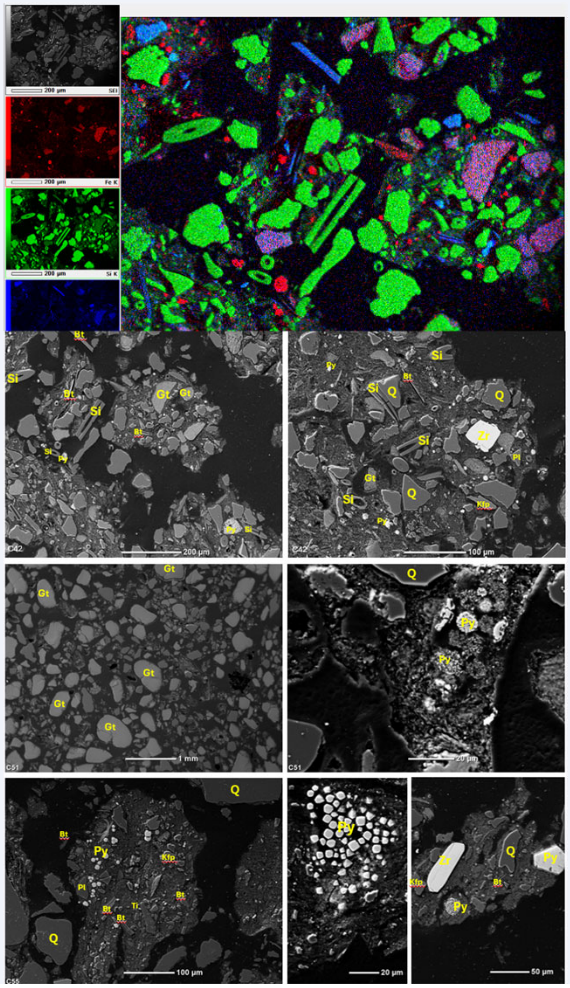
- Peaks of Al, S and TOC at same depths. Same holds for U, Th, Cs, Se
- Uranium does not seem correlated to calcite peaks

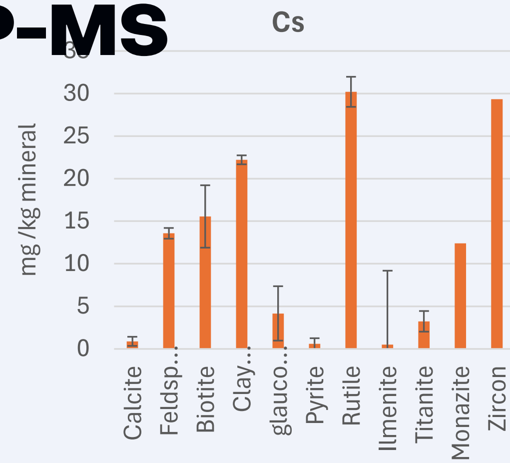
Correlations trace elements and clay (Al)

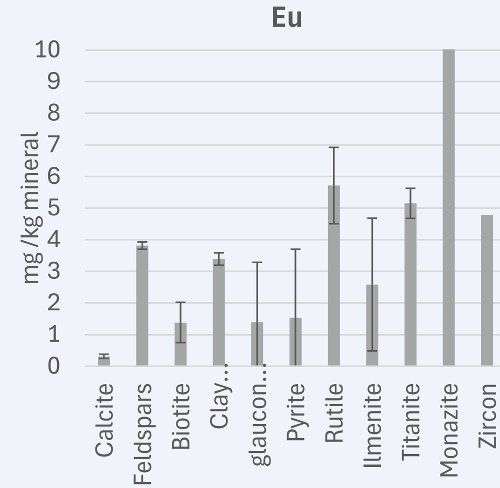


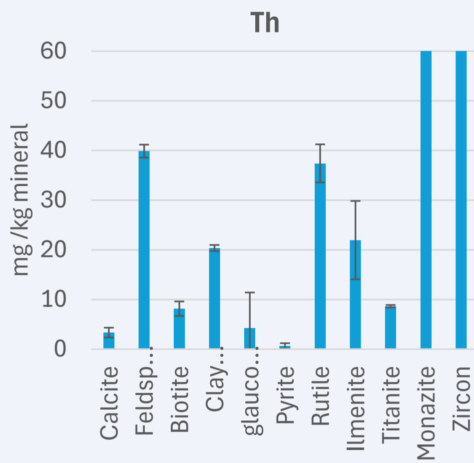


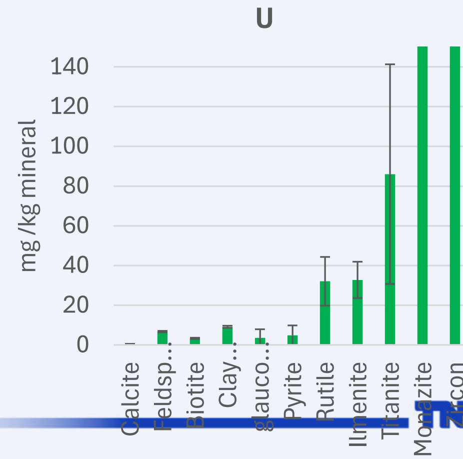
Laser ablation ICP-MS











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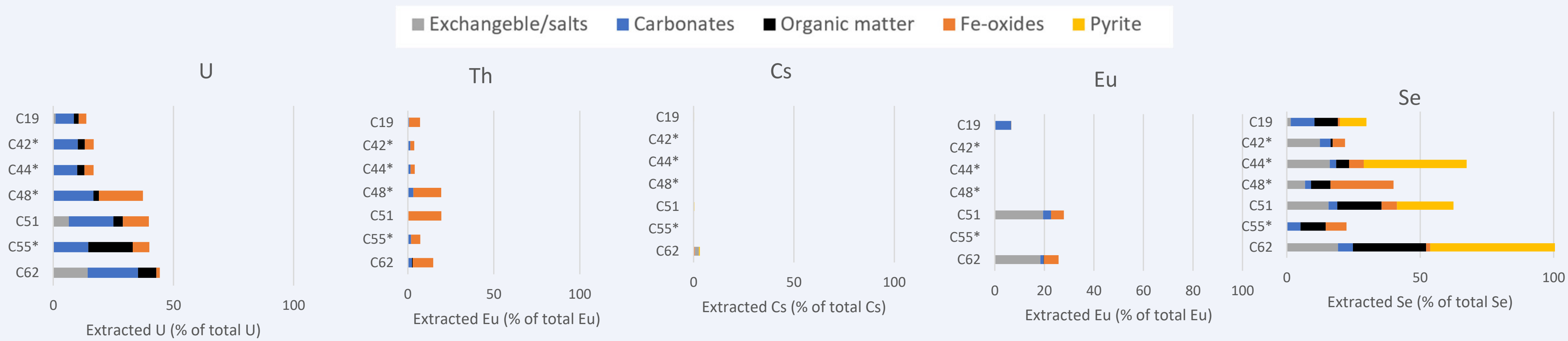
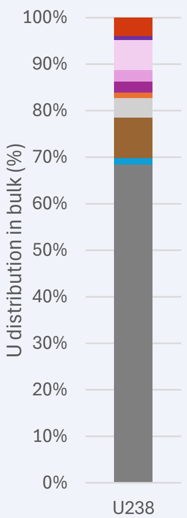
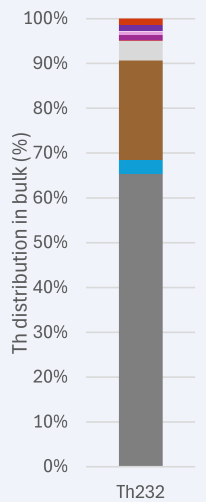
Trace elements - extractions and LA-ICP-SMS

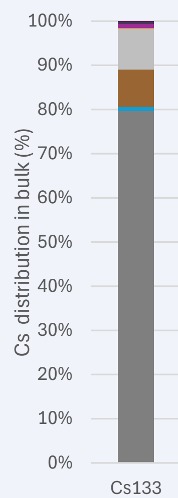


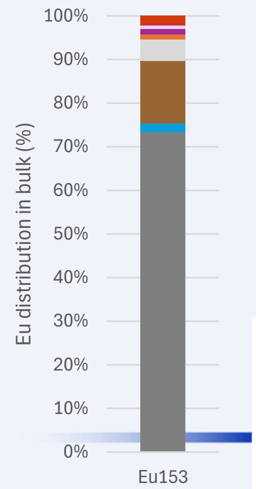


COx
U: 65 % in clay

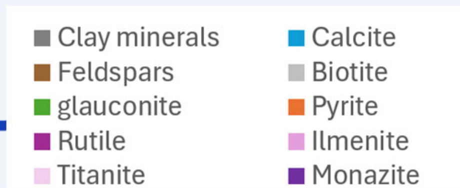
Phosphates also important.
Organic matter and calcite had low content







COx
Se:
77 % in NOM
2% exchange sites
13% pyrite+residual



Conclusions sediment

- The analyzed depth interval of the two boreholes consisted of an alternation of more **clayey** and **sandy** layers. The top contained higher carbonate content
- The average content of natural analogues, **U, Th, Cs, Se** and rare earth elements (REE) is very similar to other clay formations (e.g. Boom Clay), only U appears to be slightly enriched.
- The natural analogues Th and Cs and Eu were predominantly associated with **aluminosilicates.** Se was present in exchangeable fraction, organic matter and pyrite. U was associated with aluminosilicates but also in accessory heavy minerals

	Kd safety case	Kd experimental	Kd watervliet (ml/g)	Kd DAP (ml/g)
Se	0 (Se^{VI})	-	1100	-
U	42	3200-32000	55000	4400
Th	46	3200-32000	670000	8082
Cs	1184	600-18600	500000	60800

Thank you!

- 1. Exchangeable ions (1 M $MgCl_2$ solution, 1h),
  2. Carbonates and carbonate-bound ions (1 M Na-acetate/acetic acid pH 4.5, 24h),
  3. Organic matter (0.7M Na-hypochlorite, 85°C, 3 x 15 min),
  4. Fe/Mn-oxides (0.2M oxalate/oxalic acid, 97°C, 30 min)
- 5.Pyrite (concentrated HNO3)
- Pyrite and residual fraction were analyzed by LA-ICP-MS. However total counts for Se were too low..

They identified the clay minerals to be main mineralogical reservoir for U. Phosphate minerals in their samples contained on average ten times more uranium than clay minerals i.e. 2.5 mg kg^{-1} in clay minerals and 32 mg kg^{-1} in phosphate nodules. Our samples had on average a higher U content in clay minerals of 9 mg/kg clay mineral. The U content in carbonates in our samples (0.6 mg/kg carbonate) was similar to that in COx Clay (0.4-1 mg/kg calcite). The uranium content in organic matter was 0.07 mg/kg in COx while in this study there was a high variation from 0.06 to 1 mg/kg. The U content in pyrite (0.013 ± 0.004 mg kg^{-1}) was very low in COx, while it was higher in our samples, although highly variable (4.9 ± 5 mg/kg).

Europium in COx clay was mainly present in the clay fraction (1.2 ± 0.5 mg/kg of clay fraction) but was also present in the less abundant calcite (0.33 ± 0.15 mg/kg of calcite). Our samples had a slightly higher Eu content in clay minerals (3.4 ± 0.2 mg/kg of clay fraction) and very similar Eu content in calcite (0.3 ± 0.07 mg/kg of calcite).