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TRACE- AND RARE EARTH ELEMENT GEOCHEMISTRY OF PLIO - PLEISTOCENE FINE-GRAINED SEDIMENTS IN THE LOWER RHINE EMBAYMENT: DISCRIMINATION ACCORDING TO PROVENANCE

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Abstract

This case study demonstrates that trace element contents of fine-grained sediments can be used for the discrimination of provenance without regard to different lithological composition such as clay, silt or peat. Compared with heavy mineral analysis, this method allows more refined interpretations, e.g. in the case of mixed sediments with differing provenance. The study has been carried out on fine-grained sediments of Late Pliocene to Middle Pleistocene age from the tectonically subsiding area of the Lower Rhine Embayment. Sediments containing predominantly stable heavy minerals are characterised by high contents of TiO_2 and Zr. Deposits of the river Rhine containing predominantly unstable heavy minerals, show increased contents of Li, Sr, Rb and Cs.

Key words: Lower Rhine Embayment, Plio-Pleistocene, provenance, trace elements, Rare Earth Elements, ICP-MS, heavy minerals

Introduction

In the subsiding area of the Lower Rhine Embayment (e.g. Vinken, 1988, fig. 1), fluvial deposits of Late Tertiary and Quaternary age have been preserved at high

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thickness (e.g. Hager, 1981, Boenigk, 1978). These sequences are very well exposed in several open-cast browncoal pits. The drainage pattern of the region has been reconstructed mainly based on petrographic analysis of mostly coarse-grained sediments (e.g., Boenigk, 2002). Petrographic analysis also forms the base of lithostratigraphy and subsequent conclusions concerning chronostratigraphy (e.g., Kemna, 2005, 2008, Westerhoff et al., 2008).

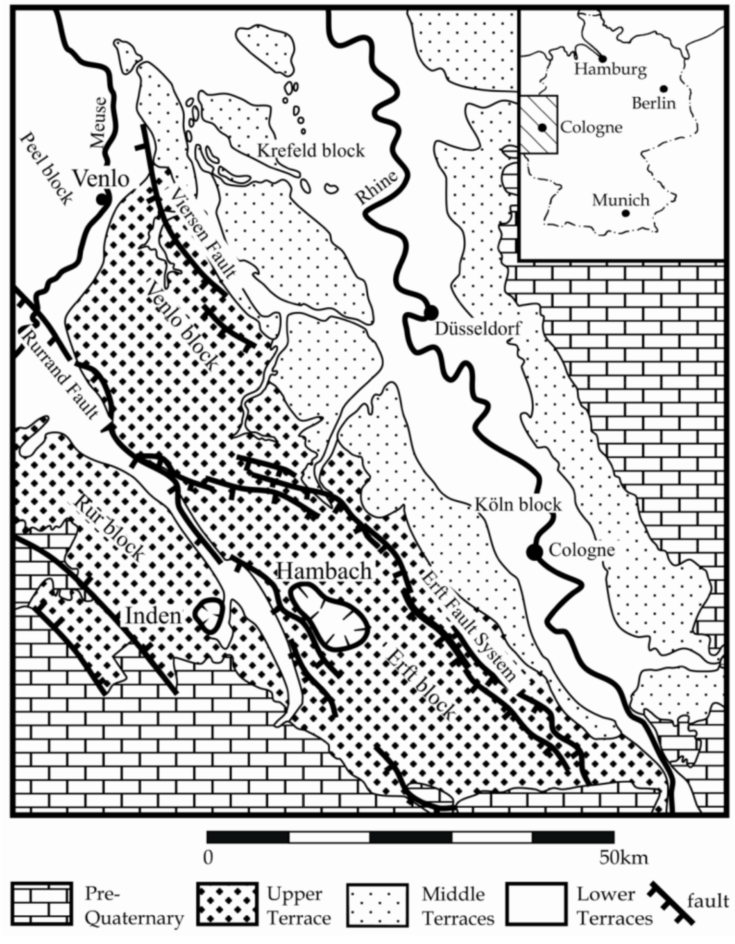

Fig. 1 The Lower Rhine Embayment with relevant rivers, cities, geomorphological features, tectonics and study areas, after Boenigk and Frechen (2006), modified

Petrographic characterisation of sediments can currently rely only on analysis of gravel content, heavy mineral analysis and clay mineralogy. While the latter method reveals mostly environmental or diagenetic aspects of deposits, the potential of the first two methods is restricted: in the case of gravel analysis to the occurrence of coarse-grained sediments and in the case of heavy mineral analysis to sandy material. The latter method has also been applied to fine-grained sediments (e.g. Boenigk, 1970). Still, it suffers from certain restrictions. Preparation as well as microscopic analysis demand increased effort and the results are distorted by grain size effects. Minor admixtures of material of different provenance usually cannot be detected, even in sandy deposits. In addition, heavy mineral analysis adresses opaque minerals only quantitatively in spite of their high potential for petrogenetic characterisation. However, fine-grained sediments, i.e. clays, silts and peats, represent the longest time involved in deposition and therefore have a high stratigraphic significance.

The bulk chemistry of Plio-Pleistocene clays in the Lower Rhine Embayment has been studied by (amongst others) Brinkmann (1976), Moura and Kroonenberg (1990), Hermanns (1992), Huisman (1998), Huisman and Kiden (1998), Huisman et al. (2000a, b), Tebbens et al. (2000). Some investigations have been dedicated to specific minerals (Tebbens et al., 1995). These studies often suffer from methodological limitations (e.g. due to the use of XRF) and are therefore mostly orientated towards the content of main elements such as Ca, Mg, Al, Na and K. Since most of these elements are mobile during weathering, research has been concentrated on environmental or diagenetic aspects.

In contrast to most of the main elements, several trace elements are immobile during and after deposition (e.g., Nesbitt et al., 1996). Moreover, the occurrence of several trace elements is connected to a few significant mineral phases which opens ways to distinguish sediments according to their mineralogic composition.

Petrogenetic characterisation of fine-grained sediments by means of ICP-MS offers a new opportunity to discriminate different provenance areas in detail. Aim of this study is the development of a tool to discriminate fine-grained sediments according to their provenance by means of geochemical analysis based on trace elements. The results should be applicable to clay, silt and peat equally and thus be independent of lithologic differences.

This study is based on a lithostratigraphic study of the Plio-Pleistocene of the Lower Rhine Embayment (LRE) (Kemna, 2005) which comprises detailed analysis of the successions at the open-cast pits of Inden (southwestern Lower Rhine Embayment) and Hambach (southern Lower Rhine Embayment) and in the type area of Plio-Pleistocene deposits at the Dutch-German border near Venlo (northern Lower Rhine Embayment).

Stratigraphy

For spatial reasons, the deposits of correlating provenance and age, i.e. the formations of the Pliocene and Lower Pleistocene in the LRE will be described only shortly in the following (fig. 2). For further information on the stratigraphy of this time-slice, the reader is referred to Boenigk and Frechen (2006) and Kemna (2005, 2008).

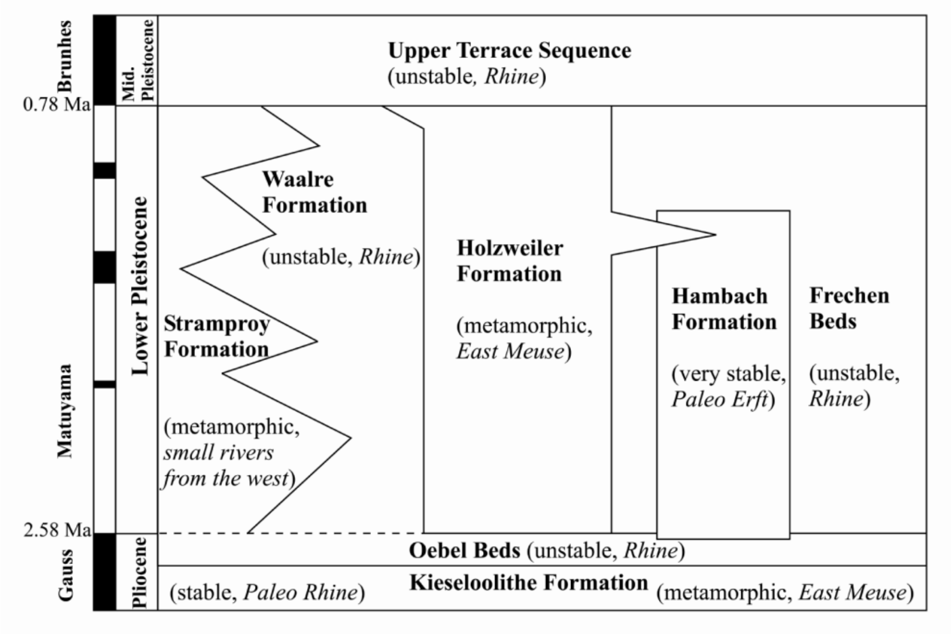

Fig. 2 Simplified stratigraphical scheme of the Plio-Pleistocene of the Lower Rhine Embayment including provenance and petrography of the units, after Kemna (2005), modified

1. Pliocene: “Kieseloolite Formation”: These whitish, quartz-rich, gravel-bearing sands with intercalated clays (e.g. “Reuver clay”) occur throughout the LRE. The sediments represent the pre-weathered detritus of the Rhenish massif and were mainly deposited by the “Palaeo Rhine river” (Boenigk, 2002) and in the southwestern LRE also by the Meuse river (Kemna, 2005, Westerhoff et al., 2008). Petrography: predominance of relatively stable heavy minerals (zircon, rutile, anatase, tourmaline and also the metamorphic mineral staurolithe). Meuse deposits also contain additional metamorphic minerals (disthene, andalusite, sillimanite), generally low overall content of heavy minerals, high percentage of opaque minerals of up to 50 % of all heavy mineral grains.

2. Upper Pliocene / Lower Pleistocene: “Öbel beds”, “Frechen beds”, “Waalre Formation”: These sands, gravels and clays were deposited by the Rhine from the Late Pliocene onward. The Rhine has been connected to the Alpine system since then (Boenigk, 2002, Boenigk and Frechen, 2006). High amounts of only slightly weathered

material from the Upper Rhine Graben led to a petrographic composition differing from that of the Kieseloolite Formation. Gravel is characterised by a lower percentage of quartz and higher amounts of rock fragments (e.g. lydite, silt- and sandstone, schist) in comparison to the Kieseloolite Formation. The heavy mineral assemblage is dominated by relatively unstable minerals (garnet, epidote, green hornblende and alterite). The overall content of heavy minerals is about ten times higher than in the deposits of the Kieseloolite Formation, whereas opaque minerals occur in rather low percentages of around 20 % of all heavy mineral grains. Light minerals other than quartz (feldspar, mica) are contained in higher quantity as well.

3. Upper Pliocene / Lower Pleistocene: “Hambach Formation”: These mainly fine-grained deposits (sandy silts, clays) occur in the open-cast pit Hambach (Kemna, 2005). They were deposited by a local river coming from the Eifel mountains in the south (“Palaeo Erft river”) and contain only stable heavy minerals (zircon, rutile, anatase, tourmaline) and large amounts of opaque minerals.

3. Lower Pleistocene: “Holzweiler Formation”: These sediments (sands, gravels, clay layers) were deposited in the middle of the LRE by the Meuse river (“East Meuse river”, Boenigk, 2002). Gravel content is predominantly composed of quartz, flintstones and locally with material from the Ardennes. The heavy mineral assemblages correlate with the Pliocene Meuse deposits with stable minerals (zircon, rutile, anatase, tourmaline) accompanied by several metamorphic minerals (staurolite, disthene, andalusite, sillimanite); low overall heavy mineral content, high percentage of opaque minerals.

4. Lower Pleistocene: “Stramproy Formation”: These sandy and clayey deposits occur deeply buried in the Rur block and at shallow depth in the type area near Venlo. They consist of Tertiary marine sediments which were reworked and deposited by small rivers coming from the west (Scheldt catchment area). The petrography resembles that of the Holzweiler Formation with stable and metamorphic heavy mineral assemblages. The two Formations can hardly be distinguished from each other by means of heavy mineral analysis.

5. Middle Pleistocene: “Upper Terrace Sequence”: These coarse-grained deposits of the Rhine (sands and gravels, few clay layers) overlay the Lower Pleistocene succession throughout the LRE. Their petrography resembles that of the Waalre Formation, e.g. with assemblages of predominantly unstable heavy minerals and high amounts of light minerals other than quartz e.g. such as feldspar and mica. Upper Terrace Sequence and Waalre Formation cannot be distinguished by heavy mineral analysis as well.

Based on this lithostratigraphy, four groups of sediments can be distinguished according to their petrographic characteristics or, respectively, provenance:

1. Predominance of stable heavy minerals with staurolite (“stable assemblage”): “Kieseloolite Formation” (Palaeo Rhine river),
2. Predominance of stable heavy minerals (“very stable assemblage”): “Hambach Formation” (Palaeo Erft river),

3. Predominance of unstable heavy minerals (“unstable assemblage”): “Öbel beds”, “Waalre Formation”, “Frechen beds” and “Upper Terrace Sequence” (Rhine river),
4. Predominance of stable heavy minerals accompanied by metamorphic heavy minerals (“metamorphic assemblage”): “Kieseloolite Formation” (East Meuse river, Pliocene), “Holzweiler Formation” (East Meuse river, Early Pleistocene) and “Stramproy Formation” (small rivers from the Scheldt catchment area).

Geochemical Behaviour of Analysed Trace Elements

Most concern has been given to the behaviour of trace elements during weathering in order to evaluate their significance concerning provenance. Information on this topic and on that of the following chapters was derived from (a.o.) Rösler and Lange (1976), Rösler (1991), Henderson (1984), Clark (1984), McLennan (1989), Hakstege et al. (1993), Cox et al. (1995), Nesbitt and Young (1996), and Morey and Setterholm (1997).

Ti: predominantly in (titano-)magnetite, ilmenite, rutile, titanite and anatase, the latter also being authigenous, similarly to Al immobile during weathering, then incorporated in clays, significance for highly weathered material and high clay content.

Li: mainly in muscovite and illite, also in amphiboles and tourmaline, adsorbed in clays.

Sc: in garnet, muscovite, tourmaline, pyroxenes and epidote, close resemblance to REE, also adsorbed in clays.

Mn, Co, Ni, Cu: very mobile during weathering.

Rb, Sr: mainly in white mica, illite and feldspar, also enriched in carbonate.

Y: in zircon and garnet, behaviour similar to Rare Earth Elements (REE).

Zr: only in zircon.

Nb: in rutile and anatase.

Cs: in mica, also adsorbed in clays.

Ba: in muscovite and feldspars, also enriched in carbonates.

REE: predominantly in zircon, monacite, titanite, also in garnet (heavy REE), immobile during weathering.

Pb: mobile during weathering, enriched in organic material.

Th: immobile during weathering, highly adsorbed on clays.

U: mobile during weathering, enriched in organic material.

Chemical Content of Important Minerals:

Important minerals and their typical contents of trace elements are listed below.

Zircon: $ZrSiO_4$, traces: Hf (up to 26 %), REE (up to 10 %), Y, U (both up to 4 %), Th (up to 2 %).

Tourmaline: $Na(Fe, Mg, Li, Al)_3Al_6[(OH)_{1+3}/(BO_3)_3/Si_6O_{13}]$, traces: Ti, Cr, Li, Be.

Rutile: TiO_2, traces: Ta, Nb, Zr, Cr.

Anatase: TiO_2, traces: Nb, Sn, Cr, Ta.

Garnets: (Mg, Fe^{2+}, Mn, $Ca)_3$(Al, Fe^{3+}, $Cr)_2(SiO_4)_3$, traces: Ti, Cr, Y, Zr, Sc, REE.

Epidote: $Ca_2(Fe,Al)Al_2(O/OH/SiO_4/Si_2O_7)$, traces: Ti, Ga, U.

Amphiboles: (Ca, Na, $K)_2$(Mg, Fe, Al, Mn, $Ti)_5$[(OH, F)/(Si, $Al)_4$ O_{11}], traces: Ti, Rb, Sr.

Apatite: Ca_5[F, Cl, OH/$(PO_4)_3$], traces: Ce, Sr, La, Y, Zr.

Muscovite: $KAl_2(OH, F)_2/AlSi_3O_{10})$, traces: Ba, Zn, Rb, Li.

Plagioclase: (Na, Ca)((Al, $Si)_4O_8$)vielleicht korrekt aber ungewöhnlich , traces: Ba, Rb, Sr.

Quartz: SiO_2, traces: Ti, U, Li.

Discriminative potential of trace elements

The relation between Zr/TiO_2 and Nb/Y as well as comparison of REE content have proved to be useful in order to characterise magmatic rocks petrographically (e.g. Rollinson, 1993). Since these elements are grossly immobile during weathering (e.g. Fleet, 1984), their analysis is expected to provide information concerning the petrography of soft sedimentary rocks as well. REE mostly occur in zircon and garnets.

Regarding the sedimentary record of the Lower Rhine Embayment, the content of zircon is decreasing simultaneously with increasing garnet content. Thus, total content of REE will probably not be a high-potential proxy for discrimination.

In the Lower Rhine Embayment, sediments containing predominantly stable heavy minerals are highly weathered in comparison to those containing assemblages of unstable minerals. This coincides with increased contents of mica, feldspars and carbonates and decreased content of zircon and opaque minerals. High concentration of Ti and Zr might therefore indicate a content of predominantly stable heavy minerals.

The high amount of opaque minerals should have an impact, too. Since Co, Ni, Cu, Pb, and U are mobile during weathering, the effect of high content of opaque minerals is not yet clear.

High contents of Li, Rb, Sr, Ba and also Sc might reflect high contents of mica, feldspars and carbonates in sediments displaying a predominance of unstable heavy minerals.

High clay content is probably mirrored by high Ti, Cs and Th content. Organic-rich material is expected to contain high amounts of Pb and U.

Analytical Method

Acid Digestion: Acid digestion of samples by means of Microwave high-pT decomposition technique (260°C, max. 70 MPa; Paar PhysicaMultiwave Sample Preparation System) was carried out using in all stages Merck Suprapur® grade reagents (HF, $HClO_4$, HNO_3, and HCl).

100 mg of sample was weighed (Microbalance Sartorius MC21S) on weighing paper (Macherey-Nagel 226) and transferred carefully into the tightly closing TFM-vessels.

1. Step, Digestion (I): 2.5 ml HF, 2.5 ml $HClO_4$, 200°C, 40-45 Pa 10^5 (85 minutes)
2. Step, Digestion (II): 260°C, 50-55 Pa 10^5 (60 minutes)
3. Step, Evaporation (I): 180°C (40 minutes)
4. Step + 4 ml HCl, Evaporation (II): 160°C (40 minutes)
5. Step + 4 ml HCl, Evaporation (III): 160°C (35 minutes)
6. Step + 2 ml HCl, 5 ml H_2O, Reaction: 160°C (30 minutes)

After all evaporation steps, the residue should be nearly dry to avoid losses by sputtering of dry material. Finally the perfectly transparent solution was transferred with 2 % HNO_3 to PP bottles (50 ml).

ICP-MS Analysis: Geochemical analysis was performed with a Perkin Elmer/Sciex ELAN 6000 ICP-MS (inductively coupled plasma quadrupole mass spectrometer) following mainly the technique described by Dulski (2000).

The final digestion solution (50 ml) was diluted to up to 5000 (1 ml brought to 10 ml). Determinations of element concentrations were performed using as internal standards Ru-Re (each 10 $ng.ml^{-1}$) for drift corrections and a three-point external calibration (high purity grade chemical reagents; single and multi element solutions). Samples and procedure blanks were measured in batches of 5 and were bracketed by a calibration cycle. The precision of measurements following the described procedure is about +/- 5 %. The accuracy of all determinations was checked using reference materials in each batch. The RM (GSD 3, GSD 4, Govindaraju, 1994, and "Köln Loess", Potts et al., 2003) were treated the same way as samples. Analytical data for RM are listed in table 1.

Results

58 samples were measured for their content of Li, Mg, Al, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Cs, Ba, REE, Hf, Ta, Pb, Th and U.

Analysis was carried out on 14 samples from clay pit Hoher Stall in the Venlo area, 30 samples from open-cast pit Hambach and 14 samples from open-cast pit Inden. The results are presented in table 2.

Samples have been assigned to a defined provenance-related group of sediments (see above) based on their lithostratigraphic setting and heavy mineral analyses of genetically connected coarse-grained sediments. The local deposits at Hambach ("Hambach Formation") have been identified as consisting of a mixture of material with unstable (Rhine river) and very stable (Palaeo Erft river) heavy mineral content. Hence, transitions between the two groups of sediments (with predominantly unstable or stable heavy minerals) may occur.

The small amount of analysed samples may cause certain limitations of interpretation. This is especially the case with sediments from the Stramproy Formation and the Holzweiler Formation.

Selected Trace Elements: Average values have been obtained from quantitative analysis for each of the provenance-related groups and are presented in figure 3 normalised to AUC (Average Upper Crust, McLennan, 2001).

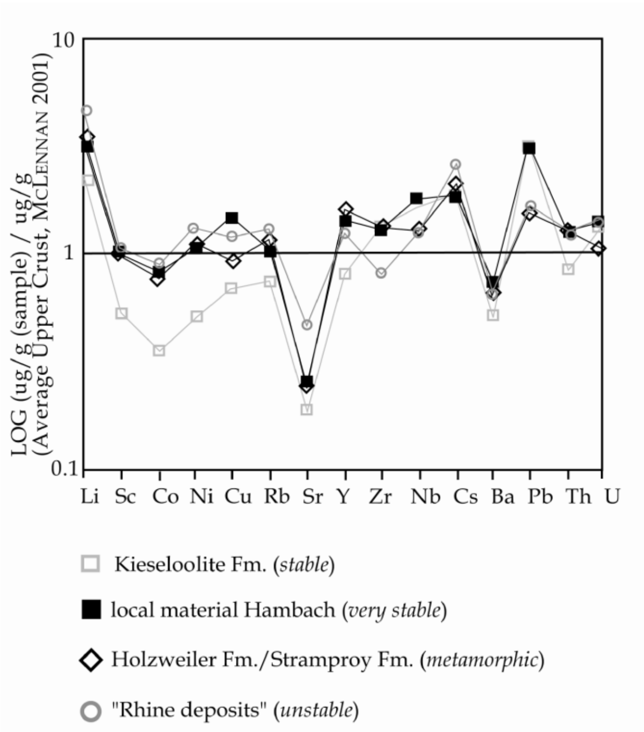

Fig. 3 Average content of selected trace elements of samples with a distinctive heavy mineral content, normalised to AUC (McLennan, 2001). Significant variations of the obtained values occur with, e.g., Li, Sr, Y, Zr, Cs and Pb

A positive deviation from the AUC values occurs regularly with the measured content of Li, Nb, Cs, Pb and U. With regard to Li and Cs, this can be explained by the high clay content of the samples which causes the deviation from AUC values. Values of Pb and U might be increased due to the presence of organic material or alternatively represent a provenance-related signal. High values of Nb are probably due to provenance as well. AUC values are derived from a large suite of rocks, most of which contain only small amounts of minerals with a significant Nb content (rutile, anatase). A regular negative deviation from the AUC values is noted for Sr and Ba. Sr values are probably decreased because the database for AUC values includes calcareous marine sediments containing more Sr than terrigenous fluvial deposits.

Significant variation of the obtained values occurs with elements such as Li, Sc, Cu, Rb, Sr, Zr and Pb.

Major and trace element concentration of samples from the Kieseloolite Formation are regularly the lowest ones, except for TiO_2, Zr, Nb and U. TiO_2 and Zr appear to be enriched by weathering, which causes depletion of most other elements. High values of Nb and U might be related to the specific provenance of the Kieseloolite Formation, i.e. the Rhenish Massif.

Pb is enriched in deposits belonging to the Kieseloolite Formation at Inden and in the local deposits occurring at Hambach. The latter deposits also contain high amounts of Cu and Nb.

Deposits of the Stramproy Formation can be characterised by high values of Zr and Y, especially.

Samples from the Holzweiler Formation contain smaller amounts of Y, but more Nb, compared to the Stramproy Formation.

In contrast, samples containing unstable heavy mineral assemblages are depleted from TiO_2, Zr, Nb and Pb and enriched in Li, Sc, Rb, Sr and Cs.

Rare Earth Elements: The content of Rare Earth Elements (REE) is shown as normalised to AUC (Taylor and McLennan, 1985, McLennan, 2001) in figure 4.

The diagram displays more or less even patterns for the set of average data. Variation of light and heavy REE is not significant. Hence, the distinction between light and heavy REE holds no potential for the discrimination of these sediments.

All average values are slightly increased in comparison to AUC, with the exception of samples of the Kieseloolite Formation. The enrichment is probably due to the siliciclastic, terrigenous character of the sediments, in correspondence to the high content of , e.g., Li and Cs.

Material containing heavy mineral assemblages with high amounts of metamorphic minerals (Holzweiler Formation, Stramproy Formation) and samples from the Hambach Formation (very stable assemblages) are characterised by a high content of REE when compared to sediments of a different provenance. Both groups have been generated from highly weathered material. This confirms the generally accepted interpretation that REE are immobile during weathering (e.g., Nesbitt et al., 1996).

The Eu/Sm ratio yielded another interesting result. Samples from the Venlo area regularly display values of around 0.15, whereas all other samples yield higher values (0.2-0.4) without regard to their stratigraphical setting and provenance. The reason for this phenomenon remains unclear.

Since there are little differences between the petrographic groups in the distribution patterns of REE, only the total REE contents will be considered further.

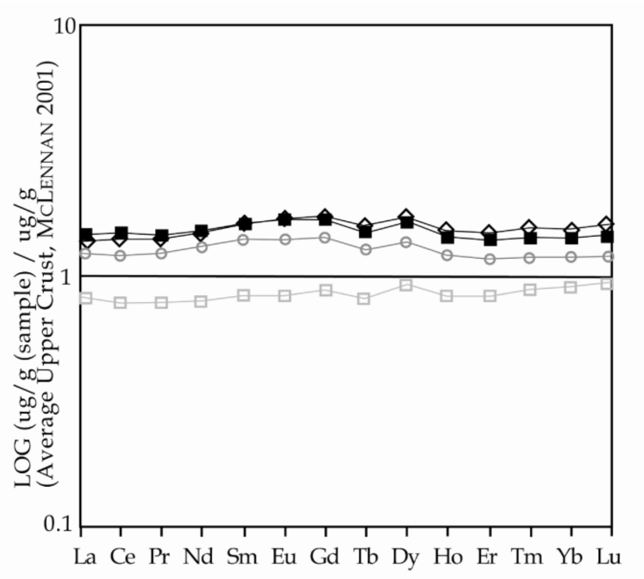

Fig. 4 Average content of Rare Earth Elements of samples with a distinctive heavy mineral content, normalised to AUC. No particular variation concerning light and heavy REE is noted. Deposits of the Kieseloolite Formation are slightly depleted in REE; signatures according to figure 3

Discrimination according to provenance

The diagram of Zr/TiO_2 versus Nb/Y (fig. 5) is of limited significance concerning the studied sediments. Values obtained for the two samples of the Stramproy Formation plot closely together. Other samples from the Lower Pleistocene succession at the Hoher Stall pit (Waalre Formation, predominance of unstable heavy minerals) plot in the same field. This might be interpreted as a sign of close resemblance of these deposits which regularly occur intercalated with each other.

Samples of the Kieseloolite Formation are widely scattered. Nevertheless with one exception they are distinctly differentiated from the field of samples containing unstable heavy mineral assemblages.

The sediments deposited mainly by the “Palaeo Erft river” at Hambach (Hambach Formation) indicate significant variation in the plot. Probably, this reflects the transitional character of the material between deposits with unstable and very stable heavy mineral assemblages. Samples of the Hambach Formation displaying unstable heavy mineral assemblages do not plot in the expected field. Hence, the strong impact of the unstable spectrum that often limits the resolution of heavy mineral analysis is not reflected by geochemistry.

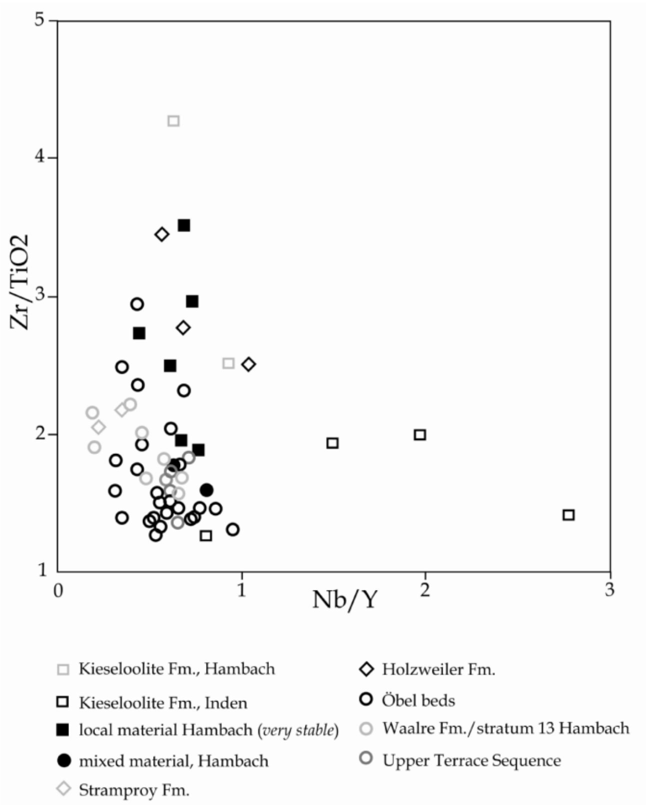

Fig. 5 Zr/TiO_2 versus Nb/Y. Significant variations occur with samples of the Kieseloolite Formation. Most of the samples containing unstable heavy mineral spectra plot closely together. Transitions occur within the local material from Hambach (Hambach Formation)

Samples with unstable heavy mineral assemblages may be more or less distinguished by means of a ternary diagram with Zr, Pb and Li+Rb as parameters (fig. 6a). The use of Li+Sr yields a similar result (fig. 6b). Sediments with metamorphic heavy mineral assemblages plot closely together in both diagrams. Similar results are obtained by TiO_2/Li/Sr (fig. 6c), or TiO_2/Σ REE content/Li+Rb diagrams (fig. 6d).

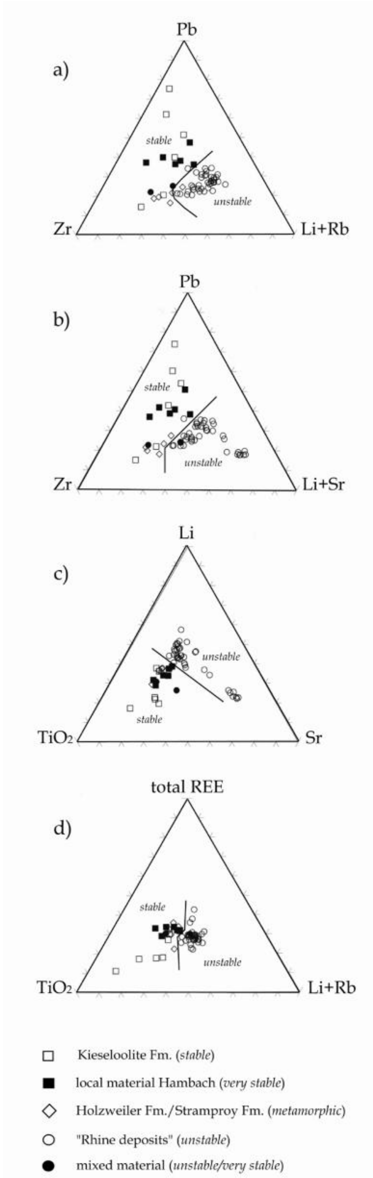

Fig. 6 Discrimination diagrams. Samples containing predominantly stable and unstable heavy minerals can be distinguished by their differing contents of TiO_2, Zr, Pb, Li, Sr, Rb and also REE

Considering the group of sediments containing predominantly stable heavy minerals, $Zr/Pb/TiO_2$ diagram (fig. 7a) shows that the deposits of the Kieseloolite Formation at Inden and the deposits of the Hambach Formation contain significantly more Pb than any other samples.

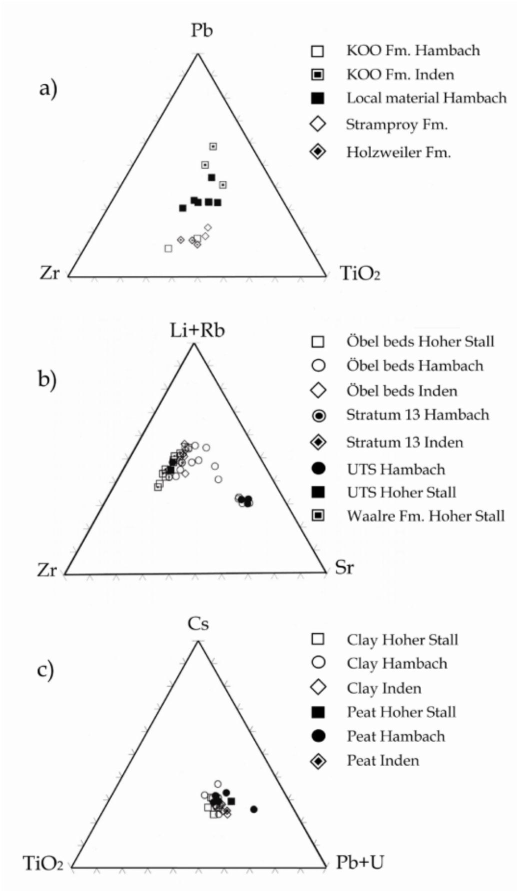

Fig. 7 Discrimination diagrams for deposits with (a) predominantly stable and metamorphic heavy mineral content and (b) predominantly unstable heavy mineral content. Diagram (c) shows that different lithologies within the Öbel beds are not reflected by trace element contents; KOO Fm.: Kieseloolite Formation; UTS: Upper Terrace Sequence

The group of sediments containing predominantly unstable heavy minerals has been examined in detail, e.g. with a diagram of Zr/Li+Rb/Sr (fig. 7b). Most samples plot close to each other, but several samples from the Öbel beds and from the Upper Terrace Sequence at Hambach show increased Sr content. This difference is probably related to higher amounts of feldspars in these samples.

The variation in samples from identical petrographic groups has been analysed in relation to lithology of the samples (e.g. clay/ silt or peat) but no dependency could be evidenced. A diagram with the lithologically significant parameters TiO_2 (clay content, weathering), Cs (clay content) and Pb+U (organic content) for samples of the Öbel beds (fig. 7c) did not show significant differences with regard to lithology or studied section.

Conclusions

This study is the first to test the potential of trace elements for provenance studies of fine-grained sediments in the LRE. Similar geochemical studies were focused on main elements or concentrated on coarse-grained deposits (e.g., Moura and Kroonenberg, 1990, Nesbitt and Young, 1996, Nesbitt et al., 1996, Huisman, 1998).

According to petrography, six groups of deposits from the Plio-Pleistocene succession of the LRE have been characterised due to their trace element geochemistry. This characterisation enables the discrimination between sediments predominantly containing unstable heavy minerals and sediments with a predominance of stable heavy minerals. Local and lithological effects are negligable. However, with regard to the small number of analysed samples, the interpretation of the results should be considered as preliminary.

Deposits of the river Rhine containing unstable heavy mineral assemblages can be characterised by a high content of Li, Cs, Sr and Rb. This is due to a high content of carbonates, feldspars and also mica, in comparison to the other provenance-related groups of sediments.

A differing clay mineralogic content may also be relevant, especially concerning the high content of Li and Cs. The Öbel beds have been studied by Hermanns (1992) at Hambach. Huisman (1998) analysed the sediments of the Reuver clay *s.s.* and the Öbel beds in the Venlo area. Both found a shift in clay mineralogy that coincides with the shift in heavy minerals. The Öbel beds contain smectite accompanied by caolinite and illite, whereas the underlying sediments of the Kieseloolite Formation contain only caolinite and illite. This is not only due to a higher degree of in-situ weathering having altered the underlying material but also to a different provenance. Deposition of comparatively “fresh” material provided by the Alpine Rhine caused the occurrence of unstable heavy minerals and also of unstable clay minerals such as smectite.

Data from the Öbel beds show a highly homogenous pattern without regard to the geographical setting or the vertical location of samples in the profiles. The results are also independent of changes in lithology. In accordance to the results of a rockmagnetic study (Kemna, 2005), this is interpreted to indicate comparatively high sedimentation rates during deposition of the Öbel beds.

The highly weathered deposits of the Kieseloolite Formation contain increased amounts of TiO_2 and Zr, whereas most other elements are depleted.

Deposits of the Kieseloolite Formation from Inden and local deposits from Hambach (Hambach Formation) contain high amounts of Pb. This cannot be explained by increased abundance of humic material, since this would also occur within the humic sediments of the Öbel beds. Moreover, non-humic material of the local deposits shows the same anomaly.

The local material has been derived from the Eifel mountains in the south, most probably from the major Pb deposits near Mechernich (Schalich et al., 1986). Detrital material (e.g. opaque heavy minerals) from this deposit most probably caused the high Pb content of the material at Hambach. The same appears to hold true for the deposits of the Kieseloolite Formation at the open-cast pit Inden. This provenance is additionally evidenced by increased values of other metals such as Cu that occur within the local deposits at Hambach. This signature is missing in the weathered material of the Kieseloolite Formation at Inden due to the mobility of Cu during weathering.

Hence, a local provenance-related geochemical signature occurs in the southwestern LRE during the time of the Kieseloolite Formation. Later during the Late Pliocene, the same signal is observed about 30 km further to the east. This is interpreted as a tectonically induced shift of the local river ("Palaeo Erft river") due to tilting of the tectonic unit (Erft block).

Several samples from the Hambach Formation yielded unstable heavy mineral spectra. The geochemical analysis has shown that these deposits still show a local influx. Hence, a complex pattern of mixed deposits of the Rhine and of the local river could be evidenced. This was not recognised by means of heavy mineral analysis.

Deposits with "metamorphic" heavy mineral assemblages (Stramproy Formation, Holzweiler Formation) are characterised by a high content of Zr and TiO_2 in that resembling the Kieseloolite Formation. Their discrimination is possible based on the higher amounts of REE and differing Nb/Y and Zr/TiO_2 ratios. With regard to the small number of analysed samples (5 samples), additional data are in need to confirm the results.

This study demonstrates that the provenance-related petrography of deposits is reflected in their trace element pattern. Trace element studies can contribute valuable results concerning lithostratigraphical and paleogeographical problems.

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Tab. 1 Analytical data for Certified Reference Material (CRM). Official reference data are listed in grey rows. Note that analysed values for Zr exceed the given data for GSD4

	601N GSD3	624N GSD3	639N GSD3	647 GSD3	CRM GSD3	568 GSD4	609 GSD4
Al_2O_3 (wt.%)	9.56	10.30	11.06	9.83	12.04	12.85	12.85
TiO_2 (wt.%)	1.12	1.12	1.14	1.13	1.06	0.97	0.97
MnO (wt.%)	0.05	0.05	0.05	0.05	0.05	0.10	0.09
Li	33	33	34	34	33	61	57
Sc	12	13	12	11	14	15	14
V	181	214	137	123	120	192	173
Cr	62	65	62	93	87	63	61
Co	11	11	11	11	12	19	18
Ni	26	26	27	26	26	43	41
Cu	180	182	189	183	177	41	40
Zn	101	104	111	122	52	149	172
As	39	48	21	19	18	56	55
Rb	79	79	83	77	79	132	132
Sr	90	91	96	92	90	143	146
Y	20	20	21	20	22	25	25
Zr	184	174	180	169	220	161	167
Nb	14	15	15	15	16	16	17
Cs	7	7	7	7	8	9	9
Ba	554	567	581	573	615	410	416
La	32.8	33.7	34.7	34.1	39	34.0	34.3
Ce	62.3	64.4	66.6	65.2	64	76.1	76.4
Pr	6.8	7.0	7.2	7.2	8	7.7	7.7
Nd	25.8	26.5	27.6	26.9	30	29.3	29.4
Sm	4.7	4.8	4.9	4.9	5	5.4	5.4
Eu	1.04	1.06	1.09	1.1	1	1.06	1.05
Gd	3.9	3.9	4.1	4.05	5	4.6	4.8
Tb	0.6	0.6	0.6	0.6	1	0.7	0.7
Dy	3.7	3.7	3.8	3.8	4	4.4	4.5
Ho	0.8	0.8	0.8	0.8	1	0.9	0.9
Er	2.2	2.3	2.3	2.3	2	2.5	2.6
Tm	0.3	0.3	0.3	0.3	0	0.4	0.4
Yb	2.2	2.2	2.3	2.3	3	2.6	2.8

Lu	0.3	0.3	0.3	0.4	0	0.4	0.4
Hf	5	5	5	5		4	5
Ta	1	1	1	1	1	1	1
Pb	42	41	42	42	40	30	31
Th	10	9	9	9	9	15	15
U	2	2	2	2	2	3	3
(mg/kg)							
Zr/Hf (36-37)	35	38	38	32		38	37
Nb/Ta (17-18)	11	15	14	12	16	17	13
Y/Ho (28)	26	26	27	25	22	29	27

Tab. 1 (continued)

	621 GSD4	659 GSD4	CRM GSD4	585 "Köln Loess"	586 "Köln Loess"	CRM "Köln Loess" (prelim. results)
Al_2O_3 (wt.%)	13.68	13.13	15.67	5.27	5.10	6.20
TiO_2 (wt.%)	0.94	0.92	0.89	0.45	0.44	0.42
MnO (wt.%)	0.10	0.09	0.11	0.06	0.06	0.06
Li	55	53	51	24	24	22
Sc	15	12	15	5	5	6
V	189	113	118	96	80	38
Cr	54	78	81	63	63	106
Co	18	18	18	6	5	6
Ni	42	41	40	44	43	43
Cu	41	40	37	11	11	11
Zn	148	168	101	71	62	34
As	52	20	20	38	33	7
Rb	133	127	130	51	50	51
Sr	146	140	142	282	280	279
Y	26	23	26	20	20	23
Zr	174	147	118	148	150	
Nb	18	17	18	7	7	9
Cs	9	9	10	3	2	3
Ba	418	429	470	186	186	201
La	34.8	34.6	40	25.3	25.1	26
Ce	77.5	76.9	78	52.9	52.5	53
Pr	7.9	7.8	9	6.3	6.2	6
Nd	30.5	28.8	32	24.3	24.6	24

Sm	5.6	5.1	6	4.9	4.8	5
Eu	1.06	1.03	1	0.8	0.8	1
Gd	4.8	4.8	5	4.2	4.1	4
Tb	0.8	0.7	1	0.6	0.6	1
Dy	4.5	4.4	5	3.6	3.5	4
Ho	0.9	0.9	1	0.7	0.7	1
Er	2.7	2.5	2	2.0	1.9	2
Tm	0.4	0.4	0	0.3	0.3	0
Yb	2.6	2.6	3	2.0	1.9	2
Lu	0.4	0.4	0	0.3	0.3	0
Hf	5	4.5		4	4	9
Ta	1	2	1	1	0	1
Pb	31	30	30	11	11	11
Th	15	15	15	9	9	8
U	3	3	3	3	3	3
(mg/kg)						
Zr/Hf (36-37)	37	32		35	36	
Nb/Ta (17-18)	13	10	18	13	14	9
Y/Ho (28)	28	26	26	29	29	23

Tab. 2 Analytical data for sample material including stratigraphical assigning and lithology

Stratigraphy	Sample No.	Lithology	Al_2O_3 (wt.%)	TiO_2 (wt.%)	MnO (wt.%)	Li (mg/kg)	Sc	Co	Ni
HOHER STALL:									
Oebel beds	25513	clay, siderite	10.01	0.67	0.04	66	9	13	55
Oebel beds	25516	clay, siderite	11.23	0.83	0.07	80	13	15	59
Oebel beds	25517	clay, siderite	13.32	0.85	0.02	95	15	12	61
Oebel beds	25518	peat	13.74	0.87	0.01	152	14	16	79
Oebel beds	25519	clay, siderite	15.25	0.92	0.01	112	13	13	48
Stramproy Fm.	25531	clay, humic	14.47	1.18	0.01	78	16	12	58
Stramproy Fm.	25533	clay	12.69	1.36	0.01	83	15	10	52
Upper clays, HS 2	25562	clay/silt	14.22	0.98	0.02	105	15	9	45
Upper clays, HS 2	25567	clay/silt	15.58	0.95	0.02	121	16	11	56
Upper clays, HS 2	25572	clay	13.24	0.88	0.19	106	14	22	56
Upper clays, HS 2	25573	clay	11.96	1.03	0.05	93	13	20	51
Upper clays, HS 2	25574	clay	12.68	0.97	0.02	106	14	30	72
Upper clays, HS 2	25585	clay/silt	7.99	0.80	0.04	68	7	16	45
UTS	25606	silt	13.51	0.91	0.02	89	14	22	76

HAMBACH:									
UTS	25833	clay	16.83	1.05	0.02	103	15	16	59
UTS	25839	clay/silt	10.46	0.57	0.11	61	9	14	49
UTS	25841	clay/silt	11.47	0.60	0.15	62	10	14	48
UTS	25815	clay	10.38	0.57	0.10	66	10	12	45
KOO Fm.	25756	clay/silt, humic	8.01	0.95	0.03	57	9	11	23
KOO Fm.	25768	silt, sandy	9.26	0.95	0.02	59	8	5	20
Oebel beds	25771	clay, molluscs	12.95	0.75	0.12	83	13	14	56
Oebel beds	25774	peat	15.77	0.90	0.02	109	16	15	72
Oebel beds	25776	peat	12.05	0.53	0.02	80	16	19	94
Oebel beds	25777	clay	17.68	0.76	0.04	110	18	17	75
Oebel beds	25778	clay	14.78	0.74	0.07	85	15	19	78
Oebel beds	25779	peat	18.36	0.79	0.05	121	16	18	78
Oebel beds	25780	clay	10.23	0.59	0.09	57	10	12	47
Oebel beds	25781	clay	9.97	0.56	0.14	56	10	12	47
Oebel beds	25782	clay, molluscs	10.95	0.59	0.08	60	10	12	45
Oebel beds	25785	clay/silt, sandy	10.90	0.65	0.02	58	10	12	46
Oebel beds	25789	peat	16.51	0.89	0.02	95	17	15	58
Oebel beds	25861	clay/silt	11.23	0.62	0.08	67	12	12	51
Oebel beds	25865	clay	13.96	0,72	0,02	77	12	19	70
Oebel beds	25866	peat	11.11	0.64	0.01	59	9	9	36
stratum 13, Rhine	25792	clay/silt, humic	19.83	1.12	0.02	109	18	30	81
stratum 13, Rhine	25794	clay/silt	21.72	1.35	0.01	97	19	7	43
stratum 13, local	25797	clay, humic	9.62	0.93	0.01	44	8	9	27
stratum 13, local	25799	clay	15.98	1.24	0.01	72	16	19	48
stratum 13, local	25801	clay/silt, sandy, humic	11.88	1.05	0.03	64	13	11	45
stratum 13, local	25802	clay/silt, sandy, oölites	8.10	0.76	0.15	33	11	11	23
stratum 13, Meuse?	25808	clay	18.62	1.15	0.01	80	17	36	81
stratum 13, local	25869	clay/silt	22.80	1.35	0.02	103	19	10	50
stratum 13, mixed	25822	clay/silt	10.93	1.09	0.28	51	12	37	58
stratum 13, mixed	25825	clay/silt	12.20	1.07	0.16	50	12	9	31
INDEN:									
Oebel beds	25636	clay	15.10	0.94	0.02	129	13	10	44
Oebel beds	25637	clay	14.62	0.88	0.02	84	12	6	26
Oebel beds	25638	clay	14.41	0.82	0.06	87	15	14	63
Oebel beds	25639	clay, oxidized	14.54	0.85	0.02	85	15	24	93
Oebel beds	25640	clay, humic	17.96	0.91	0.09	116	15	17	44
Oebel beds	25641	Torf, Top	16.45	0.87	0.02	103	14	16	49
KOO Fm.	25649	clay, peaty	4.80	1.14	0.01	35	5	2	16
KOO Fm.	25650	clay	7.58	1.29	0.00	24	4	3	17
KOO Fm.	25652	clay/silt	10.36	1.54	0.01	49	9	6	30
KOO Fm.	25659	peat	4.24	0.93	0.01	25	4	6	26
Rhine deposits	25673	clay	14.43	1.00	0.06	111	13	16	64

Meuse deposits	25677	clay/silt	10.34	0.95	0.01	62	11	8	21
Meuse deposits	25679	clay/silt	7.78	0.80	0.03	48	8	24	28
Meuse deposits	25681	silt	11.31	1.06	0.05	45	11	18	46

Tab. 2 (continued)

Stratigraphy	Sample No.	Lithology	Cu	Rb	Sr	Y	Zr	Nb	Cs
HOHER STALL:									
Oebel beds	25513	clay, siderite	21	111	78	27	198	11	8
Oebel beds	25516	clay, siderite	26	126	88	30	196	13	10
Oebel beds	25517	clay, siderite	27	148	86	23	163	10	14
Oebel beds	25518	peat	51	107	97	31	119	15	17
Oebel beds	25519	clay, siderite	39	144	89	16	121	15	15
Stramproy Fm.	25531	clay, humic	24	149	82	48	241	11	11
Stramproy Fm.	25533	clay	26	135	84	48	294	17	9
Upper clays, HS 2	25562	clay/silt	27	148	94	30	178	18	11
Upper clays, HS 2	25567	clay/silt	29	164	95	38	180	7	13
Upper clays, HS 2	25572	clay	27	153	92	28	146	13	13
Upper clays, HS 2	25573	clay	19	129	83	29	207	13	11
Upper clays, HS 2	25574	clay	25	145	90	39	213	15	10
Upper clays, HS 2	25585	clay/silt	22	102	78	18	204	13	9
UTS	25606	silt	27	151	99	54	195	10	12
HAMBACH:									
UTS	25833	clay	29	166	98	28	191	20	12
UTS	25839	clay/silt	26	121	332	20	90	12	9
UTS	25841	clay/silt	30	132	328	20	82	13	10
UTS	25815	clay	25	119	301	21	95	12	9
KOO Fm.	25756	clay/silt, humic	11	89	60	30	404	19	7
KOO Fm.	25768	silt, sandy	13	85	53	19	239	18	7
Oebel beds	25771	clay, molluscs	23	136	208	23	111	15	12
Oebel beds	25774	peat	37	159	103	25	125	18	16
Oebel beds	25776	peat	48	111	105	28	93	12	14
Oebel beds	25777	clay	30	179	145	29	97	15	18
Oebel beds	25778	clay	33	156	179	26	99	15	13
Oebel beds	25779	peat	60	158	114	22	111	16	18
Oebel beds	25780	clay	23	108	289	22	92	12	8
Oebel beds	25781	clay	24	112	307	22	77	11	8
Oebel beds	25782	clay, molluscs	24	114	273	21	94	7	9
Oebel beds	25785	clay/silt, sandy	20	118	91	19	150	13	8
Oebel beds	25789	peat	64	130	117	29	127	17	15
Oebel beds	25861	clay/silt	30	116	279	22	93	12	11
Oebel beds	25865	clay	26	141	87	41	179	15	11
Oebel beds	25866	peat	22	120	88	21	131	13	10

stratum 13, Rhine	25792	clay/silt, humic	36	173	125	26	180	21	15
stratum 13, Rhine	25794	clay/silt	34	160	120	37	239	23	11
stratum 13, local	25797	clay, humic	37	47	52	26	326	18	4
stratum 13, local	25799	clay	36	138	92	34	241	23	9
stratum 13, local	25801	clay/silt, sandy, humic	45	134	91	31	261	19	9
stratum 13, local	25802	clay/silt, sandy, oölites	39	71	48	30	208	14	4
stratum 13, Meuse?	25808	clay	28	152	98	33	195	22	14
stratum 13, local	25869	clay/silt	37	169	126	36	211	24	12
stratum 13, mixed	25822	clay/silt	19	85	68	29	320	21	7
stratum 13, mixed	25825	clay/silt	23	99	122	28	201	21	9
INDEN:									
Oebel beds	25636	clay	27	122	103	18	142	11	13
Oebel beds	25637	clay	19	125	119	21	153	13	14
Oebel beds	25638	clay	34	141	97	28	148	9	11
Oebel beds	25639	clay, oxidized	41	156	89	45	119	16	12
Oebel beds	25640	clay, humic	22	177	95	23	134	18	15
Oebel beds	25641	Torf, Top	33	159	96	26	153	17	13
KOO Fm.	25649	clay, peaty	25	52	77	9	227	18	9
KOO Fm.	25650	clay	24	27	44	8	182	21	8
KOO Fm.	25652	clay/silt	21	137	102	16	195	13	13
KOO Fm.	25659	peat	17	106	71	11	180	16	10
Rhine deposits	25673	clay	39	153	102	21	146	18	15
Meuse deposits	25677	clay/silt	11	110	64	16	239	17	8
Meuse deposits	25679	clay/silt	13	84	55	24	274	13	7
Meuse deposits	25681	silt	23	114	59	28	295	20	7

Tab. 2 (continued)

Stratigraphy	Sample No.	Lithology	Ba	La	Ce	Pr	Nd	Sm	Eu
HOHER STALL:									
Oebel beds	25513	clay, siderite	293	29.4	61.5	7.07	27.5	5.2	1.0
Oebel beds	25516	clay, siderite	290	33.5	71.7	8.4	32.8	6.3	1.2
Oebel beds	25517	clay, siderite	328	36.05	71.2	7.9	29.8	5.2	1.0
Oebel beds	25518	peat	278	36.5	76.7	8.9	34.8	6.9	1.5
Oebel beds	25519	clay, siderite	332	30.9	61.07	6.6	24.2	3.9	0.7
Stramproy Fm.	25531	clay, humic	377	52.02	109.4	12.8	50.4	9.6	2.04
Stramproy Fm.	25533	clay	360	46.3	96.8	11.2	44.0	8.4	1.7
Upper clays, HS 2	25562	clay/silt	309	38.7	75.02	9.2	35.5	6.6	1.3
Upper clays, HS 2	25567	clay/silt	323	44.2	87.5	10.8	43.6	8.2	1.7
Upper clays, HS 2	25572	clay	330	33.6	74.4	8.7	34.4	6.5	1.3
Upper clays, HS 2	25573	clay	318	38.02	80.6	9.3	35.7	6.7	1.3
Upper clays, HS 2	25574	clay	319	43.5	83.9	9.8	38.3	7.1	1.4
Upper clays, HS 2	25585	clay/silt	294	23.9	58.07	5.8	22.2	4.03	0.8

UTS	25606	silt	398	50.3	101.6	12.6	51.2	10.1	2.1
HAMBACH:									
UTS	25833	clay	386	44.8	94.2	10.6	40.7	7.5	1.5
UTS	25839	clay/silt	314	25.1	51.8	5.9	22.8	4.4	0.8
UTS	25841	clay/silt	349	26.4	54.0	6.1	23.8	4.5	0.8
UTS	25815	clay	296	24.6	50.5	5.8	22.6	4.3	0.8
KOO Fm.	25756	clay/silt, humic	280	31.2	69.4	7.7	30.3	5.8	1.2
KOO Fm.	25768	silt, sandy	234	29.5	60.4	6.8	26.03	4.6	0.9
Oebel beds	25771	clay, molluscs	304	31.3	64.4	7.4	28.8	5.2	1.04
Oebel beds	25774	peat	341	39.2	82.9	9.4	36.3	6.7	1.3
Oebel beds	25776	peat	263	25.7	52.8	6.4	26.3	5.9	1.3
Oebel beds	25777	clay	344	43.03	92.3	10.6	41.3	7.9	1.6
Oebel beds	25778	clay	319	35.5	72.0	8.3	32.4	6.09	1.2
Oebel beds	25779	peat	359	34.6	68.6	7.7	29.02	5.2	1.03
Oebel beds	25780	clay	257	26.3	53.8	6.2	24.2	4.7	0.9
Oebel beds	25781	clay	259	25.7	51.9	6.03	23.6	4.6	0.9
Oebel beds	25782	clay, molluscs	270	26.3	54.7	6.3	24.02	4.6	0.9
Oebel beds	25785	clay/silt, sandy	312	28.0	58.01	6.6	25.05	4.68	0.8
Oebel beds	25789	peat	408	37.2	77.02	9.00	35.6	6.9	1.4
Oebel beds	25861	clay/silt	269	28.3	57.9	6.8	26.5	5.1	1.06
Oebel beds	25865	clay	300	56.4	122.5	14.3	58.3	11.7	2.3
Oebel beds	25866	peat	243	27.2	55.4	6.1	23.3	4.2	0.7
stratum 13, Rhine	25792	clay/silt, humic	464	47.1	99.0	10.8	40.5	7.3	1.4
stratum 13, Rhine	25794	clay/silt	489	56.5	120.7	13.08	49.8	8.9	1.8
stratum 13, local	25797	clay, humic	289	31.0	68.4	7.4	28.7	5.3	1.06
stratum 13, local	25799	clay	436	52.01	117.2	12.6	48.07	8.5	1.7
stratum 13, local	25801	clay/silt, sandy, humic	438	43.3	92.3	10.3	39.8	7.5	1.5
stratum 13, local	25802	clay/silt, sandy, oölites	269	27.9	61.8	6.9	27.2	5.4	1.1
stratum 13, Meuse?	25808	clay	428	49.7	103.01	11.3	42.7	7.6	1.6
stratum 13, local	25869	clay/silt	499	59.06	125.8	13.6	51.5	9.1	1.8
stratum 13, mixed	25822	clay/silt	278	33.5	69.2	7.8	30.2	5.7	1.2
stratum 13, mixed	25825	clay/silt	315	36.4	77.9	8.6	33.03	6.09	1.2
INDEN:									
Oebel beds	25636	clay	326	30.8	62.03	6.9	25.7	4.5	0.8
Oebel beds	25637	clay	356	34.4	67.5	7.5	27.6	4.8	0.9
Oebel beds	25638	clay	336	37.0	80.3	9.4	37.0	7.4	1.4
Oebel beds	25639	clay, oxidized	327	51.4	112.4	13.4	53.3	10.9	2.3
Oebel beds	25640	clay, humic	320	38.1	80.00	8.5	32.00	5.6	1.07
Oebel beds	25641	Torf, Top	321	39.09	79.6	8.7	33.3	5.9	1.2
KOO Fm.	25649	clay, peaty	241	17.8	33.5	3.6	13.0	2.2	0.5
KOO Fm.	25650	clay	183	10.3	21.2	1.9	6.6	1.2	0.3

KOO Fm.	25652	clay/silt	489	27.6	54.02	5.7	20.6	3.4	0.7
KOO Fm.	25659	peat	276	17.5	34.5	3.7	13.9	2.4	0.5
Rhine deposits	25673	clay	403	34.6	71.5	8.02	30.2	5.4	1.08
Meuse deposits	25677	clay/silt	294	26.2	49.6	5.7	21.0	3.6	0.6
Meuse deposits	25679	clay/silt	258	33.7	85.1	8.6	33.7	6.3	1.2
Meuse deposits	25681	silt	350	39.7	92.2	9.6	36.8	6.8	1.3

Tab. 2 (continued)

Stratigraphy	Sample No.	Lithology	Gd	Tb	Dy	Ho	Er	Tm	Yb
HOHER STALL:									
Oebel beds	25513	clay, siderite	4.8	0.7	4.4	0.9	2.6	0.4	2.6
Oebel beds	25516	clay, siderite	5.6	0.9	5.3	1.06	3.02	0.4	3.0
Oebel beds	25517	clay, siderite	4.3	0.7	3.9	0.8	2.3	0.4	2.4
Oebel beds	25518	peat	6.4	1.0	5.8	1.1	3.1	0.5	3.00
Oebel beds	25519	clay, siderite	2.8	0.4	2.7	0.6	1.6	0.3	1.7
Stramproy Fm.	25531	clay, humic	9.2	1.4	8.3	1.7	4.7	0.7	4.4
Stramproy Fm.	25533	clay	7.8	1.2	7.3	1.5	4.3	0.6	4.1
Upper clays, HS 2	25562	clay/silt	5.9	0.8	4.9	1.6	2.8	0.4	2.8
Upper clays, HS 2	25567	clay/silt	7.9	1.08	6.5	1.3	3.5	0.5	3.4
Upper clays, HS 2	25572	clay	5.7	0.8	4.9	1.00	2.7	0.4	2.7
Upper clays, HS 2	25573	clay	6.0	0.9	5.3	1.06	2.9	0.4	2.9
Upper clays, HS 2	25574	clay	6.2	1.0	5.6	1.1	3.2	0.5	3.1
Upper clays, HS 2	25585	clay/silt	3.5	0.6	3.2	0.7	1.9	0.3	2.0
UTS	25606	silt	10.3	1.5	8.7	1.8	4.8	0.7	4.3
HAMBACH:									
UTS	25833	clay	6.1	0.9	5.3	1.05	3.0	0.4	2.9
UTS	25839	clay/silt	3.8	0.6	3.5	0.7	2.0	0.3	2.0
UTS	25841	clay/silt	3.8	0.6	3.5	0.7	2.0	0.3	1.9
UTS	25815	clay	3.9	0.6	3.7	0.7	2.07	0.3	2.03
KOO Fm.	25756	clay/silt, humic	5.6	0.8	5.3	1.1	3.2	0.5	3.3
KOO Fm.	25768	silt, sandy	3.9	0.6	3.5	0.7	2.02	0.3	2.07
Oebel beds	25771	clay, molluscs	4.5	0.7	4.03	0.8	2.3	0.3	2.2
Oebel beds	25774	peat	5.4	0.8	4.5	0.9	2.4	0.4	2.4
Oebel beds	25776	peat	5.4	0.9	5.2	1.07	3.0	0.4	2.8
Oebel beds	25777	clay	6.4	1.0	5.4	1.05	2.9	0.4	2.6
Oebel beds	25778	clay	5.00	0.8	4.6	0.9	2.6	0.4	2.4
Oebel beds	25779	peat	4.5	0.7	4.09	0.8	2.4	0.4	2.3
Oebel beds	25780	clay	4.1	0.6	3.7	0.7	2.1	0.3	2.06
Oebel beds	25781	clay	4.04	0.6	3.7	0.7	2.08	0.3	2.0
Oebel beds	25782	clay, molluscs	4.1	0.6	3.9	0.8	2.1	0.3	2.06
Oebel beds	25785	clay/silt, sandy	3.9	0.6	3.5	0.7	2.03	0.3	2.08
Oebel beds	25789	peat	6.00	0.9	5.4	1.08	3.07	0.4	2.9

Oebel beds	25861	clay/silt	4.4	0.7	4.07	0.9	2.3	0.4	2.2
Oebel beds	25865	clay	10.4	1.5	8.04	1.5	3.7	0.5	3.3
Oebel beds	25866	peat	3.4	0.5	3.2	0.7	2.0	0.3	1.9
stratum 13, Rhine	25792	clay/silt, humic	5.7	0.9	4.9	1.0	2.7	0.4	2.7
stratum 13, Rhine	25794	clay/silt	7.1	1.1	6.8	1.3	3.8	0.5	3.6
stratum 13, local	25797	clay, humic	4.9	0.8	4.5	0.9	2.6	0.4	2.6
stratum 13, local	25799	clay	7.1	1.05	6.3	1.2	3.4	0.5	3.3
stratum 13, local	25801	clay/silt, sandy, humic	6.4	1.00	5.8	1.1	3.2	0.5	3.2
stratum 13, local	25802	clay/silt, sandy, oölites	5.5	0.8	5.2	1.05	3.0	0.4	2.9
stratum 13, Meuse?	25808	clay	6.8	1.0	6.1	1.2	3.4	0.5	3.4
stratum 13, local	25869	clay/silt	7.4	1.1	6.6	1.3	3.6	0.5	3.6
stratum 13, mixed	25822	clay/silt	5.2	0.9	5.1	1.07	3.06	0.5	3.06
stratum 13, mixed	25825	clay/silt	5.3	0.8	4.9	1.0	2.7	0.4	2.7
INDEN:									
Oebel beds	25636	clay	3.5	0.5	3.1	0.6	1.9	0.3	2.0
Oebel beds	25637	clay	3.8	0.6	3.6	0.7	2.09	0.3	2.1
Oebel beds	25638	clay	6.4	0.9	5.4	1.04	2.9	0.4	2.8
Oebel beds	25639	clay, oxidized	10.3	1.6	8.9	1.7	4.6	0.6	3.9
Oebel beds	25640	clay, humic	4.4	0.7	4.07	0.8	2.3	0.3	2.3
Oebel beds	25641	Torf, Top	4.8	0.8	4.4	0.9	2.7	0.4	2.6
KOO Fm.	25649	clay, peaty	1.9	0.3	1.9	0.4	1.05	0.2	1.1
KOO Fm.	25650	clay	1.1	0.2	1.4	0.3	0.9	0.1	1.02
KOO Fm.	25652	clay/silt	2.9	0.5	2.9	0.6	1.8	0.3	1.7
KOO Fm.	25659	peat	2.09	0.3	2.01	0.4	1.2	0.2	1.2
Rhine deposits	25673	clay	4.6	0.7	4.09	0.8	2.3	0.3	2.3
Meuse deposits	25677	clay/silt	2.9	0.4	2.8	0.6	1.8	0.3	2.0
Meuse deposits	25679	clay/silt	5.2	0.8	4.4	0.9	2.4	0.4	2.4
Meuse deposits	25681	silt	5.8	0.9	5.2	1.03	3.0	0.4	3.03

Tab. 2 (continued)

Stratigraphy	Sample No.	Lithology	Lu	Hf	Ta	Pb	Th	U
HOHER STALL:								
Oebel beds	25513	clay, siderite	0.4	5	1	20	12	3
Oebel beds	25516	clay, siderite	0.4	5	1	21	13	4
Oebel beds	25517	clay, siderite	0.4	5	1	25	15	3
Oebel beds	25518	peat	0.4	3	1	39	13	7
Oebel beds	25519	clay, siderite	0.3	3	1	28	13	4
Stramproy Fm.	25531	clay, humic	0.7	7	1	30	16	4
Stramproy Fm.	25533	clay	0.6	8	1	28	15	3
Upper clays, HS 2	25562	clay/silt	0.4	5	1	24	15	3

Upper clays, HS 2	25567	clay/silt	0.5	5	1	26	15	3
Upper clays, HS 2	25572	clay	0.4	4	1	26	12	3
Upper clays, HS 2	25573	clay	0.4	6	1	24	13	3
Upper clays, HS 2	25574	clay	0.5	5	1	24	13	6
Upper clays, HS 2	25585	clay/silt	0.3	6	1	20	10	2
UTS	25606	silt	0.7	5	1	26	15	3
HAMBACH:								
UTS	25833	clay	0.4	5	2	31	15	7
UTS	25839	clay/silt	0.3	2	1	21	10	3
UTS	25841	clay/silt	0.3	2	1	23	11	3
UTS	25815	clay	0.3	3	1	20	11	3
KOO Fm.	25756	clay/silt, humic	0.5	11	1	18	12	3
KOO Fm.	25768	silt, sandy	0.3	6	1	20	10	3
Oebel beds	25771	clay, molluscs	0.3	3	1	19	11	3
Oebel beds	25774	peat	0.4	3	1	29	14	4
Oebel beds	25776	peat	0.4	3	1	24	12	27
Oebel beds	25777	clay	0.4	3	1	27	14	4
Oebel beds	25778	clay	0.3	3	1	25	13	4
Oebel beds	25779	peat	0.4	3	1	35	15	4
Oebel beds	25780	clay	0.3	3	1	19	10	3
Oebel beds	25781	clay	0.3	2	0	19	10	3
Oebel beds	25782	clay, molluscs	0.3	3	0	19	10	3
Oebel beds	25785	clay/silt, sandy	0.3	4	1	22	12	3
Oebel beds	25789	peat	0.4	4	1	31	14	4
Oebel beds	25861	clay/silt	0.3	3	1	21	10	3
Oebel beds	25865	clay	0.5	5	1	26	15	3
Oebel beds	25866	peat	0.3	4	1	19	10	3
stratum 13, Rhine	25792	clay/silt, humic	0.4	5	2	41	18	4
stratum 13, Rhine	25794	clay/silt	0.5	6	2	51	17	4
stratum 13, local	25797	clay, humic	0.4	8	1	49	10	4
stratum 13, local	25799	clay	0.5	7	2	55	14	3
stratum 13, local	25801	clay/silt, sandy, humic	0.5	7	1	52	14	3
stratum 13, local	25802	clay/silt, sandy, oölites	0.4	6	1	41	9	3
stratum 13, Meuse?	25808	clay	0.5	6	2	77	15	4
stratum 13, local	25869	clay/silt	0.5	6	2	54	18	5
stratum 13, mixed	25822	clay/silt	0.5	8	2	26	12	3
stratum 13, mixed	25825	clay/silt	0.4	5	2	23	12	3
INDEN:								
Oebel beds	25636	clay	0.3	4	1	40	13	3
Oebel beds	25637	clay	0.3	4	1	34	12	3
Oebel beds	25638	clay	0.4	4	1	31	15	3
Oebel beds	25639	clay, oxidized	0.6	3	1	28	14	3
Oebel beds	25640	clay, humic	0.3	4	1	35	13	3

Oebel beds	25641	Torf, Top	0.4	4	2	36	14	4
KOO Fm.	25649	clay, peaty	0.2	6	1	102	7	4
KOO Fm.	25650	clay	0.1	5	1	141	6	5
KOO Fm.	25652	clay/silt	0.3	6	1	81	9	4
KOO Fm.	25659	peat	0.2	5	0	41	5	5
Rhine deposits	25673	clay	0.3	4	1	40	13	4
Meuse deposits	25677	clay/silt	0.3	6	1	16	11	2
Meuse deposits	25679	clay/silt	0.4	7	1	19	10	2
Meuse deposits	25681	silt	0.5	8	1	22	14	3

Note: Editorial Board will apologize for any discomfort caused by the presentation of tables 1 and 2 in this form, for editorial reasons.