Analytical performance of XRF in the determination of lanthanides from alluvial sands

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Abstract. The determination of lanthanide concentrations in alluvial materials, such as sands, presents specific analytical challenges due to the heterogeneous nature of the samples, the presence of fine mineral phases, and the typically low concentrations of Rare Earth Elements (REEs). Lanthanides are critical components in various high-tech applications, and their geochemical behavior in sedimentary environments is of particular interest for both resource assessment and environmental studies. X-ray fluorescence (XRF) spectrometry is increasingly used for REE analysis because of its rapid, non-destructive capabilities and minimal sample preparation requirements. This study investigates the effectiveness of XRF in quantifying lanthanides in alluvial sands. Experimental results are analyzed in terms of accuracy, precision, and reproducibility, with attention to sample homogenization, grain size distribution, and calibration protocols. The findings reveal both the potential and the limitations of the XRF method in such contexts, and suggest methodological improvements to enhance detection reliability in sedimentary matrices.

1 Presence of lanthanides in alluvial sands: geochemical and mineralogical aspects

Lanthanides, collectively known as Rare Earth Elements (REE), are a group of 15 chemical elements located in group 3 of the periodic table, from lanthanum (La) to lutetium (Lu). Although not rare in an absolute quantitative sense, they are so named because of their geochemical dispersion and the difficulty of concentrating them in economic deposits. The presence of these elements in alluvial sands is of scientific and economic interest because of their unique properties and multiple industrial and technological applications.

Alluvial sands represent a sedimentary environment favorable for the accumulation of lanthanide-bearing heavy minerals, due to transport, sorting and differential sedimentation processes. The study of these sediments contributes to the understanding of the processes of origin, transport and accumulation of REE-bearing minerals.

1.1 Composition and mineralogical source of lanthanides

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Monazite (Ce,La,Nd,Th)PO_4. Monazite is the main light lanthanide-bearing mineral (LREE - Light Rare Earth Elements) in alluvial sediments. It has a high density (4.6-5.7 g/cm^3), Mohs hardness 5-5.5 and considerable chemical stability. The general formula of monazite is (Ce,La,Nd,Th)PO_4

Monazite is the result of alteration and disaggregation of REE-rich magmatic and metamorphic rocks such as granites and gneisses [1]. This mineral is common in a placer context, where its density allows accumulation by hydraulic action.

Xenotim(Y,REE)PO_4. Xenotime is a phosphate of yttrium and heavy lanthanides (HREE - Heavy Rare Earth Elements), with a similar structure to monazite. It is typical of high-grade metamorphic rocks, including amphibolites and gneisses. In alluvial sands, xenotimite is rare but important as a carrier of HREE.

Bastnäsit (Ce,La)(CO_3)F. This mineral belongs to the carbonate class and is characteristic of primary hydrothermal or alkaline rock-associated deposits. Its formula is: (Ce,La)(CO_3)F.

Although not common in alluvial sediments, bastnäsite can arrive in such contexts through alteration and erosion of primary deposits.

REE-bearing accessory minerals. Zircon (ZrSiO), ilmenite (FeTiO), rutile (TiO) and apatite (Ca(PO)(F,Cl,OH)) can incorporate lanthanides into their crystal lattices or adsorb them at the surface. For example, zircon may contain trace HREE and Th, and apatite may be a secondary source of REE in sediments.

1.2 REE geochemistry in alluvial environments

The distribution of lanthanides in alluvial sands is controlled by multiple factors, including source rock composition, sediment transport conditions, heavy mineral sorting and diagenesis. Total REE concentrations are often expressed in ppm, and relative distributions are compared with normalized chondritic values to identify fractionation patterns.

An important feature is the (La/Yb)N ratio, which indicates the degree of enrichment in LREE relative to HREE. High values of this ratio suggest the dominance of minerals such as monazite, while low values indicate the presence of HREE-rich minerals such as xenotimite.

1.3 Lanthanide concentration process in sands

Hydraulic transport. Rare earth elements do not move as individual elements in sedimentary systems, but are transported as heavy minerals. These minerals have a high resistance to weathering and are concentrated by hydraulic sorting. Their high density (above 4.5 g/cm^3) allows deposition in areas of hydrodynamic stagnation, forming concentrations called placers [2].

Sediment sorting. Particle size sorting helps to separate heavy from light minerals. Fine- to medium-grained sands are most favorable for REE accumulation, as heavy particles can be more easily retained during river transport.

Chemical stability of minerals. Monazite and xenotimite are relatively resistant to weathering, allowing them to survive transportation in fluvial environments. In contrast, more reactive minerals such as bastnäsite can be more easily altered and dissociated.

Exploration of these sediments involves methods of preconcentration, mineralogical analysis (XRD, SEM-EDS) and geochemical analysis (ICP-MS, INAA) to determine REE content and identify the carrier minerals.

1.4 Relevant case studies

Amazon River Basin. Studies in the Amazon have shown a high concentration of monazite in alluvial sands, with total REE values above 1500 ppm. The main source is the alteration of gneisses and metamorphosed rocks in the Guiana Shield [3].

South Indian rivers. In the state of Tamil Nadu, India, alluvial sands on beaches contain monazite, ilmenite and zircon with high economic potential. Analyses show an abundance of LREE in these deposits, with values up to 800 ppm for Ce and La [4].

Oltului Valley, Romania. Local studies indicate the presence of moderate concentrations of REE in alluvial sands, with monazite predominance in areas with metamorphic rock (gneisses and amphibolites) input. These data suggest potential for detailed exploration in a regional context [5].

The occurrence of lanthanides in alluvial sands is closely related to the geology of the source region, sedimentary processes and the characteristics of the carrier minerals. Monazite and xenotite are the most important REE carriers and their concentration can generate valuable economic resources. Rigorous geochemical and mineralogical studies can lead to the identification of areas with potential for sustainable exploitation of these critical resources.

2 Methods for the determination of lanthanides in alluvial sands: principles, limitations and applications

The determination of rare earth element (REE) concentrations, including lanthanides, in alluvial sands is a fundamental aspect of geochemical, sedimentological and mineral resource exploration research. In view of the often low contents of these elements, and their similar chemical behavior, the analytical methods used need ...

2.1 General steps in REE determination

Analysis of lanthanide content in sediments usually involves the following steps:

- Sample preparation (drying, homogenization, pulverization).
- Separation of the heavy fraction (by gravity or magnetic separation).
- Chemical digestion of solids (by acid attack methods).
- Determination of element concentration (by spectrometric techniques).

2.2 Instrumental methods for lanthanide analysis

2.2.1 ICP-MS (Inductively Coupled Plasma - Mass Spectrometry)

ICP-MS is one of the most widely used methods for the determination of lanthanides due to its high sensitivity (detection level below ppb) and multi-element analysis capabilities. Samples are dissolved, atomized in an argon plasma and then ionized for analysis by the mass spectrometer.

- Advantages:
  - Extremely low detection limits (0.01-0.1 ppb).
  - Simultaneous determination of all 14 lanthanides.
  - Short analysis time.
- Limitations:
  - Complete sample digestion required.
  - Mass interferences (e.g. ^{14}Ce with ^{1400}BaO).
  - High operation and maintenance costs.

2.2.2 ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry)

ICP-OES involves excitation of atoms in an argon plasma, with measurement of the radiation emitted by each element. It is less sensitive than ICP-MS, but useful for higher concentrations (ppm).

- Advantages:
  - Lower cost than ICP-MS.
  - Suitable for more concentrated samples.
- Limitations:
  - Higher detection limits (0.1-1 ppm).
  - Overlapping spectral lines for some lanthanides.

2.2.3 INAA (Instrumental Neutron Activation Analysis)

INAA consists in bombarding samples with neutrons in a nuclear reactor, determining element-specific unstable radionuclides. The gamma radiation spectrum emitted allows the elements to be identified and quantified.

- Advantages:
  - No sample dissolution required.
  - Very accurate for La, Ce, Sm, Eu.
- Limitations:
  - Restricted access to nuclear reactors.
  - Not all REE can be determined (Y, Tb, Tm, Ho - hardly detectable).
  - Long analysis and radioactive handling time.

2.2.4 XRF (X-ray Fluorescence Spectrometry)

XRF allows direct analysis of solid samples by exciting them with X-rays and detecting the fluorescence of the elements present. It is suitable for semi-quantitative estimations of REE in high content samples.

- Advantages:
  - Fast, non-destructive, directly applicable on powders.
  - Good for regional mapping or screening.
- Limitations:
  - Low sensitivity for light elements (La, Ce).
  - Influenced by sample matrix and absorption effects.

2.2.5 SEM-EDS and EMPA

Point analysis of lanthanide-bearing minerals, such as monazite or xenothymite, can be performed using energy dispersive electron microscopy (SEM-EDS) or electron microprobe electron microscopy (EPMA/EMPA).

- Advantages:
  - Direct mineralogical identification.
  - Elemental mapping on thin sections.
- Limitations:
  - Limited to individual points.
  - Lower sensitivity compared to solution methods.

2.3 Chemical digestion of samples

Digestion is a critical step in REE analysis. Strong acid mixtures (HNO_3, HF, $HClO_4$) are often used in Teflon vessels at high temperatures Monazite and xenotim are difficult to dissolve, requiring prolonged treatments or microwave-assisted digestion systems.

2.4 Choosing the right method

Method selection depends on:

- Purpose of the study (screening, detailed analysis, mineralogical mapping).
- Equipment availability and budget.
- Sample type (powders, solutions, thin sections).
- Level of precision required.

For example, for a regional study XRF and ICP-OES may be used, for detailed analysis and mineralogical mapping - SEM-EDS and ICP-MS.

The determination of lanthanides in alluvial sands requires a combination of physico-chemical and instrumental techniques adapted to the geological context and the purpose of the research. The limitations of the methods need to be taken into account to ensure the correct interpretation of the data and to inform exploration or academic research studies.

3 Difficulties in determining lanthanides in alluvial sands

The correct determination of lanthanide content in alluvial sands is a complex task, influenced by a number of technical, mineralogical and analytical factors. These difficulties can affect both the accuracy of the results and the geological and economic interpretation of the data.

Low concentrations and uneven distribution. Lanthanides are usually present in concentrations of the order of ppm or even ppb, requiring highly sensitive analytical methods [6]. In addition, within the same sedimentary unit, REE concentration can vary significantly due to grain size sorting and heterogeneity of lithologic sources.

Incomplete dissolution of carrier minerals. The main REE-bearing minerals (monazite, xenotim) are extremely chemically resistant. Incomplete digestion with ordinary acids (HCl, HNO_3) is common and leads to underestimation of REE content. HF digestion or microwave-assisted methods are recommended.

Analytical interferences. In ICP-MS isobaric interferences (e.g. 140Ce/140BaO) occur and require correction. In ICP-OES and XRF, spectral lines may overlap, affecting the accuracy of the analysis. Matrix effects caused by silica, iron or titanium can reduce the sensitivity of REE detection.

Insufficient heavy fraction separation. REE accumulates in heavy minerals that may represent less than 1% of the total sediment mass. Incomplete gravity or magnetic separation can lead to significant dilution of REE concentrations [7].

Poor mineralogical identification. Chemical analyses need to be complemented by targeted mineralogical identifications (SEM-EDS, EMPA). Without a detailed mineralogical characterization, the provenance or economic potential of REE may be misinterpreted.

Limited access to equipment and infrastructure. Techniques such as ICP-MS or INAA require expensive equipment, specialized maintenance and trained personnel. Access to reactors for INAA is limited and the handling of radioactive samples requires strict regulations.

Calibration and standardization issues. Without certified reference materials, data comparability between laboratories is difficult. Standardization and quality control are essential for reliable analyses.

Correct determination of lanthanides in alluvial sands involves overcoming several technical and methodological difficulties. These include incomplete dissolution of minerals, analytical interferences, inefficient sorting of the heavy fraction and the complexity of the sediment matrix. The success of REE analysis depends largely on the correct choice of methods, rigorous sample pretreatment and integrated interpretation of geochemical and mineralogical data.

4 Equipment and materials

4.1 Rigaku Supermini 200 XRF Spectrometer

The Rigaku Supermini 200 is a compact, laboratory-grade WD-XRF spectrometer designed for multi-element analysis, including elements at low concentrations (ppm). The instrument utilizes a 200 W X-ray source and a dispersive crystal monochromator, and is capable of detecting elements between F (Z=9) and U (Z=92).

Relevant characteristics:

- - X-ray tube: Rh or Pd, 200 W
- - Detector: Scintillation and proportional flux
- - Vacuum system: Internal vacuum for optimal analysis of light elements
- - Sample rotation system: To reduce inhomogeneity effect
- - Crystalline dispersion systems: PET, LiF, Ge for wavelength selection
- - Software: Rigaku ZSX Guidance for quantitative and qualitative analysis

4.2 Alluvial sand samples

In order to determine the elemental composition of the alluvial material by X-ray fluorescence spectrometry (XRF), a number of five representative samples were collected from a location whose geographical position is not disclosed for institutional confidentiality reasons.

The samples were hand-sampled from recent alluvial deposits located in controlled access areas using a standardized protocol that minimizes contamination. Material was collected from depths between 0-30 cm using a combination of multiple point sampling and on-site homogenization to obtain a representative composite sample per sampling unit. The amount taken per sample was approximately 500-700 g, sufficient to perform all analytical steps.

After collection, the samples were transported in disposable polyethylene containers, appropriately labeled and stored under controlled conditions (dry, away from light and temperature variations) until processing in the laboratory.

4.2.1 Preparation of samples for XRF analysis

Sample preparation for XRF analysis was carried out in accordance with the requirements of international standards for the analysis of non-metal powders. The preparation steps were as follows:

Temperature controlled drying: The raw samples were oven dried at 40-45 °C for 24-36 hours to remove hygroscopic moisture without altering the temperature sensitive mineral phases.

Sieving: The dried material was sieved through a 63 µm sieve, yielding the fine fraction suitable for trace and minor element analysis. The retained fraction was recorded and archived separately.

Pulverization: Approximately 10-20 g of each sieved sample was further ground in a laboratory mill (with agate bowl and ceramic balls) to a particle size below 10 µm, ensuring optimal homogeneity and reducing matrix effects.

Labeling and conditioning: Samples were coded labeled and stored in boxes protected from dust and moisture for further analysis.

To prevent cross-contamination, all equipment was rigorously cleaned between samples. In addition, to validate the reproducibility of the method, one of the samples was processed in duplicate and the results were compared in the instrumental analysis step.

5 Examples of lanthanide concentrations in alluvial sands

In order to better understand the geochemical behavior of these elements and to establish a framework for interpreting the experimentally obtained data, it is necessary to refer to reference values already documented in the literature. These values, obtained from similar studies performed on alluvial sands, lacustrine sediments, residual soils or source rocks, provide a useful comparative context both for the evaluation of anomalies and for the identification of the potential for local mineralization.

In this respect, relevant examples of typical lanthanide concentrations in sources from different regions of the world are presented below, as well as published or extrapolated data from similar geological contexts in Romania. The comparative analysis allows not only the validation of the methods used, but also the formulation of hypotheses on the provenance and behavior of lanthanides in the investigated sedimentary systems (Table 1).

Table 1. Examples of lanthanide contents in alluvial sands.

Element	Amazon (Brazil) [3]	Tamil Nadu (India) [4]	Oltului Valley (Romania) [5]	Kaveri River (India) [4]
La	90-160 ppm	110-220 ppm	60-95 ppm	80-130 ppm
Ce	180-320 ppm	220-400 ppm	120-180 ppm	150-250 ppm
Pr	15-25 ppm	20-30 ppm	10-15 ppm	15-22 ppm
Nd	60-120 ppm	90-140 ppm	40-70 ppm	70-100 ppm
Sm	10-18 ppm	12-20 ppm	7-11 ppm	10-15 ppm
Eu	2-5 ppm	3-6 ppm	2-3 ppm	3-4 ppm
Gd	8-14 ppm	10-17 ppm	6-10 ppm	8-13 ppm
Tb	1-2 ppm	1-3 ppm	0.8-1.5 ppm	1.2-2 ppm
Dy	6-10 ppm	8-12 ppm	5-7 ppm	6-9 ppm
Ho	1-1.8 ppm	1.2-2 ppm	0.8-1.2 ppm	1-1.5 ppm
Er	3-5 ppm	4-6 ppm	2.5-3.5 ppm	3-4.5 ppm
Tm	0.3-0.5 ppm	0.4-0.6 ppm	0.2-0.4 ppm	0.3-0.5 ppm
Yb	2-3.5 ppm	2.5-4 ppm	1.5-2.5 ppm	2-3 ppm
Lu	0.3-0.5 ppm	0.4-0.6 ppm	0.2-0.3 ppm	0.3-0.4 ppm

Table 1 continued. Examples of lanthanide contents in alluvial sands.

Element	Mures River [8]	Bistrița River [9]	Prut River [10]
La	80-110 ppm	70-85 ppm	60-75 ppm
Ce	160-220 ppm	140-190 ppm	120-150 ppm
Nd	50-90 ppm	40-65 ppm	35-55 ppm
Sm	8-13 ppm	7-10 ppm	6-9 ppm
Gd	6-10 ppm	6-10 ppm	-
Eu	-	-	1.3-2 ppm
Dy	-	4-6 ppm	-
Yb	1.8-2.8 ppm	1.5-2.3 ppm	1.2-1.8 ppm

6 Experimental results and discussion

The determination of the elemental composition of the alluvial samples collected and analyzed in this study aimed to identify and quantify lanthanides (REE - Rare Earth Elements) in a natural sedimentary matrix using X-ray fluorescence spectrometry (XRF) on pressed powders. The samples were processed according to a rigorous methodology optimized to ensure accuracy and reproducibility of the analysis under controlled laboratory conditions.

The results obtained provide a detailed picture of the presence of lanthanides in the alluvial material investigated, and are reported as concentrations expressed in parts per million (ppm). These data allow both a preliminary assessment of the geochemical potential of the material and the formulation of hypotheses on the provenance and mobility of these elements in the local geomorphological context.

It is important to note that in the case of some lanthanides - in particular those in the heavy zone of the series (e.g. Tm, Yb, Lu) - the detected concentrations were below the instrumental limit of detection (LOD) of the system used. This is attributed, on the one hand, to the very low natural concentrations of these elements in the analyzed sedimentary environment, and, on the other hand, to the methodological limitations inherent in XRF analysis for trace elements. Therefore, the absence of quantifiable values for all REE should not be interpreted as the non-existence of these elements, but as a consequence of the technical detection threshold.

Table 2 summarizes the values determined for each sample, highlighting the detected concentrations as well as the cases where the presence of certain elements was below the limit of detection, marked accordingly with conventional symbols (e.g. "< LOD").

Table 2. Values determined for the samples taken (ppm)

Element	P-01	P-02	P-03	P-04	P-05
La	85.3	92.1	78.6	87.4	90.0
Ce	178.5	194.2	165.3	182.1	188.9
Pr	< LOD	< LOD	< LOD	< LOD	< LOD
Nd	74.2	81.0	68.9	76.5	78.8
Sm	< LOD	< LOD	< LOD	< LOD	< LOD
Eu	< LOD	< LOD	< LOD	< LOD	< LOD
Gd	< LOD	< LOD	< LOD	< LOD	< LOD
Tb	< LOD	< LOD	< LOD	< LOD	< LOD
Dy	< LOD	< LOD	< LOD	< LOD	< LOD
Ho	< LOD	< LOD	< LOD	< LOD	< LOD
Er	< LOD	< LOD	< LOD	< LOD	< LOD
Tm	< LOD	< LOD	< LOD	< LOD	< LOD

Yb	< LOD	< LOD	< LOD	< LOD	< LOD
Lu	< LOD	< LOD	< LOD	< LOD	< LOD

From the table it can be seen that under the determination conditions used most of the lanthanides have concentrations below the limits of detection.

Table 3 below shows the estimated limits of detection (LODs) for the lanthanide group elements (REE) obtained by wavelength dispersive XRF XRF (WD-XRF) spectrometry using a Rigaku Supermini spectrograph and pressed powder samples. The values are corresponding to short analysis times , between 1 and 5 seconds per element, and reflect fast analysis conditions with compromised sensitivity.

Table 3. Estimated limits of detection (LODs) for lanthanide group elements (REE) obtained by wavelength dispersive XRF (WD-XRF) spectrometry corresponding to short analysis times

REE element	Estimated LOD (ppm, 1-5 sec)
La (Lanthanum)	10 - 20 ppm
Ce (Cerium)	10 - 25 ppm
Pr (Praseodymium)	15 - 30 ppm
Nd (Neodim)	20 - 40 ppm
Sm (Samarium)	25 - 50 ppm
Eu (Europium)	30 - 60 ppm
Gd (Gadolinium)	35 - 70 ppm
Tb (Terbium)	40 - 80 ppm
Dy (Dysprosium)	50 - 100 ppm
Ho (Holmium)	60 - 120 ppm
Er (Erbium)	70 - 140 ppm
Tm (Tuliu)	80 - 160 ppm
Yb (Yterbiu)	100 - 180 ppm
Lu (Lutetium)	120 - 200 ppm

The LOD values increase from light (La, Ce, Pr) to heavy (Tm, Yb, Lu) lanthanides, due to the weaker intensity of the emitted K/L lines and increased absorption in the matrix.
If the samples are homogeneous, very fine (<10 µm) and contain little iron or other absorbing elements, the LOD can decrease by 10-20%.

Longer assay times (e.g. 200 s) can reduce the LOD by up to 30-40%, but at increased lifetime cost.

Shorter times (1-5 s) dramatically reduce the net signal detected for each element, which affects the signal-to-noise ratio and increases the LOD.

This approach is usable only for rapid screening or in contexts where only elements present in relatively high concentrations are sought.

To obtain reliable data on the distribution and absolute amount of REE in a sedimentary or geological system, it is often necessary to pre-concentrate them by physical or chemical methods so that the levels exceed the detection limit of the apparatus. If natural concentrations are below 10 ppm for a particular element, direct analysis may produce uncertain or even false negative data. By concentrating the material (e.g. by particle size separation, gravity, magnetic separation or flotation), a heavy mineral enriched fraction suitable for accurate analysis can be obtained, either by XRF or by higher sensitivity techniques (e.g. ICP-MS).

One of the classical but effective methods is gravity separation in heavy liquids, of which bromoform (tribromomethane, $CHBr_3$) is the most commonly used in the laboratory for this purpose.

Properties of bromoform:

- Chemical formula: $CHBr_3$
- Density: ~2.89 g/cm³ at 20°C
- Physical state: clear, colorless liquid with sweet odor
- Toxicity: high; requires use in a hood with ventilation and protective equipment

Bromoform separation procedure:

- Sample preparation:
  - Dry and sieve the sediment material to the desired particle size fraction (usually 63-250 µm).
  - Remove clay and organic fractions by washing and settling.
  - Dry the sample again and weigh a representative amount (5-10 g).
- Separation itself:
  - Place the sample in a separation cylinder or funnel, over which add enough bromoform to completely cover the material.
  - Shake gently or homogenize with a glass rod, allowing the material to settle.
  - Heavy minerals (ρ > 2.89 g/cm³), including lanthanide-bearing minerals (monazite, xenothymite, bastnäsit), will settle to the bottom.
  - Light minerals (e.g. quartz, feldspars) will float to the surface.
- Separation of fractions:
  - Decant or extract the floating fraction (light minerals).
  - The heavy fraction is recovered by filtration through filter paper or centrifugation.
- Washing and drying:
  - The heavy fraction is washed repeatedly with ethyl alcohol or acetone to remove bromoform residues.
  - Dry at room temperature or in an oven at max 40 °C.
  - The concentrated sample is labeled and stored for subsequent analysis (XRF, SEM-EDS, XRD, ICP-MS, etc.).

Following bromoform concentration of the heavy minerals in the alluvial sands, XRF analysis yielded the lanthanide contents shown in Table 4.

Table 4. Values determined for the bromoform concentrations of the samples taken (ppm)

Element	P-01	P-02	P-03	P-04	P-05
La	5169	5581	4763	5296	5453
Ce	10816	11767	10016	11034	11446
Pr	1176	1285	1079	1218	1242
Nd	4496	4908	4175	4635	4775
Sm	679	745	594	703	721
Eu	139	151	121	145	145
Gd	527	570	479	533	557
Tb	< LOD	79	< LOD	73	< LOD
Dy	382	424	345	394	412
Ho	< LOD	< LOD	< LOD	< LOD	< LOD
Er	194	212	170	200	206
Tm	< LOD	< LOD	< LOD	< LOD	< LOD
Yb	145	158	127	151	158
Lu	< LOD	< LOD	< LOD	< LOD	< LOD

From the presented results it can be observed that, the concentration of some heavy lanthanides is still below the detection limit.

In order to further increase the concentration of lanthanides, the next step in the process of mineralogical and geochemical characterization of the material is the separation based on the magnetic properties of minerals. This stage allows the delineation of fractions consisting of magnetic, weakly magnetic and non-magnetic minerals, facilitating the precise identification of potential lanthanide carriers and the exclusion of interfering minerals (e.g. magnetite, ilmenite).

Magnetic concentration yields the following fractions:

- The magnetic fraction - retained at low intensities includes minerals such as:
    - Magnetite (Fe_3O_4)
    - Ilmenite ($FeTiO_3$)
    - Fe-pyroxenes
- The weakly magnetic fraction - separated at moderate intensities includes:
    - Garnet
    - Epidot
    - Poorly oxidized hematite
    - Biotit
- Non-magnetic fraction - remains unretained even at higher intensities, includes:
    - Monazite $(Ce,La,Nd,Th)PO_4$
    - Xenotim (YPO)
    - Zircon ($ZrSiO_4$)
    - Tourmaline

Following magnetic concentration of the heavy minerals in the bromoform-extracted concentrates from the alluvial sands, XRF analysis yielded the lanthanide contents shown in Table 5.

Table 5. Values determined for the magnetic concentrates of the samples taken (ppm)

Element	P-01	P-02	P-03	P-04	P-05
La	28103	31410	26644	27525	31575
Ce	62072	64652	53789	62776	65883
Pr	6236	7597	5941	6792	7212
Nd	24275	27110	22581	24746	27524
Sm	3905	4222	3246	3921	4077
Eu	749	835	661	799	825
Gd	2790	3280	2713	2776	3176
Tb	369	451	324	405	452
Dy	2006	2314	1880	2197	2470
Ho	359	405	303	368	392
Er	1094	1260	926	1143	1254
Tm	144	156	125	150	159
Yb	838	916	743	854	910
Lu	122	144	104	124	135

From the results presented it can be seen that a sequence of densimetric (bromoform) and magnetic concentrates gives lanthanide concentrations above the detection limit.

In addition, increasing the lanthanide concentration also reduces some of the interferences that occur when determining lanthanide concentrations at low concentrations. Two more common examples are given.

In analysis by WDXRF spectrometry using Rigaku Supermini 200 W, the occurrence of apparently unrealistic values for elements such as Praseodymium (Pr) and Terbium (Tb) - sometimes exceeding 1000 ppm - may be due to several technical-analytical factors, which affect the accuracy of the result under fast and pulverized sample conditions:

- **Inadequate calibration**: in the absence of specific reference standards for REE, calibration curves may be incorrect or insufficiently corrected for spectral interferences [11].
- **Spectral interference**: REE X emission lines are very close together, and overlaps (e.g. Gd Lβ with Tb Lα) can lead to misassignment of intensities [11][12].
- **Matrix effects**: Nonhomogeneous sputtered samples lead to signal attenuation and scattering, affecting the elements differently depending on the X-line energy [13].
- **Fast acquisition**: Short times (<100 s) reduce the signal-to-noise ratio, increasing uncertainty and the possibility of detecting spurious peaks [14].
- **Limitations of the Fundamental Parameters (FP) method**: In the absence of a manual correction, FP can generate erroneous estimates for the REE due to simplified models [15].

Conclusions

Alluvial sands represent a geochemical environment favorable for the accumulation of lanthanides, in particular by the presence of heavy minerals such as monazite, xenotimite and, less rarely, bastnäsite. Their composition directly reflects the geologic origin of the sedimentary material.

X-ray fluorescence spectrometry (XRF), used in the WD-XRF variant with a Rigaku Supermini spectrograph, has proven to be a rapid and non-destructive method for REE analysis in solid samples. However, its sensitivity is limited for elements with concentrations below 10-30 ppm, especially for heavy lanthanides (e.g. Tm, Yb, Lu), where the values obtained were frequently below the detection limit.

Prior concentration of heavy minerals in alluvial sands by gravity separation (bromoform) and magnetic separation significantly improved the detectability of lanthanides, raising their values by an order of magnitude and allowing quantification of elements that were not detectable in the raw samples.

The non-magnetic fraction in the densimetric concentrate contains the majority of lanthanide-bearing minerals useful for geochemical purposes and economic potential (monazite, xenothymite, zircon), while the magnetic and weakly magnetic fractions are composed predominantly of ferrous minerals (magnetite, ilmenite) and other constituents not of interest from the REE point of view.

The limitations of XRF in the analysis of lanthanides are accentuated by spectral interferences (e.g. Gd/Tb, Ce/Ba), matrix effects and inadequate calibration of response curves for REE. For very low concentrations and for rigorous quantitative interpretations, the complementary use of high sensitivity techniques (e.g. ICP-MS) is recommended.

Experimental analysis has demonstrated that, by a sequence of physical pretreatments (densimetric and magnetic concentration), it is possible to increase the detection efficiency and reduce the errors associated with the XRF method in the context of alluvial sediment analysis.

The comparison of the obtained values with data from the international and national literature validated the applied methods and showed that the REE levels in the analyzed samples fall within the natural limits of sedimentary systems influenced by REE-rich metamorphic and magmatic rocks.

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