Introduction

The rare earth elements (REEs), the group of elements consisting of Y and the lanthanides, exhibit unique properties marking them as crucial for modern technologies [1, 2]. Nowadays, minerals containing REEs represent important strategic resources [3]. REEs are relatively abundant in the Earth’s crust [4, 5] but only very few minerals, assigned as primary sources (bastnaesite, monazite and rarely xenotime), exhibit minable concentrations [2].

At worldwide level, China is one of the most important REEs supplier [6, 7]. Most European countries have highly prevailing scarce primary sources [8, 9] and therefore are looking to identify alternatives to access REEs (e.g., e-waste recycling or using wastes from other mining activities). Although recycling is a suitable alternative source for REEs,
only about 1% of the REEs are recovered in this way due to production costs which are similar to those from primary sources [10]. However, in some of the most important mining areas (e.g., Mountain Pass—USA [11], Bayan Obo—China [12]) the sum of rare earths as oxides (REO) are not more than 5% [6]. This might indicate that even lower quality resources can become economically feasible in the near future due to increasing demand of REEs. Wastes from mining activities might be a suitable alternative for REEs extraction due to low ecological impact (REEs separation from tailings) and minimal sample preparation required (mechanical treatments already being applied in the original process). However, financial issues related to the implementation of a new REEs processing infrastructure or to the REEs prices variation are major drawbacks when the potential of this resource is considered [13, 14].

Nowadays, accurate quantitative analysis of REEs is usually performed by Neutron Activation Analysis (NAA) and on-line plasma ionization procedures. Inductively Coupled Plasma—Optical Emission Spectrometry (ICP–OES) and Inductively Coupled Plasma Mass Spectrometry (ICP–MS) are frequently used and the ICP–MS technique proved to be more sensitive and less susceptible for interferences [15, 16]. Although the ICP–MS technique allows time-efficient ultra-trace isotopic analysis [17, 18] its major limitation derives from the fact that only liquid samples (aqueous or organic solutions) can be investigated. Moreover, in ICP–MS analysis the total dissolved solids content (TDSC) must not exceed 1–2% [19, 20]. Even at this level the aerosols generated from the sample should be diluted with clean Argon prior entering the plasma to maintain optimal operating conditions.

For water, sediment, soil, mineral [21–26], and airborne particulate matter [27] samples, specific methods for REEs analysis by ICP–MS were developed over the years. Sample dissolution with *aqua regia* is a popular wet method but the procedure, depending on the matrix, may not lead to total dissolution of silicate-rich samples and can generate Cl-containing polyatomic interfering species [28, 29], especially noticeable in the case of low abundance analytes such as heavy REEs (HREEs: Y and elements from Gd to Lu). This may add to HREEs being negatively influenced by the interfering effect of light REEs (LREEs: elements from La to Eu) oxide species [30]. For geological samples, the wet digestion technique with HF or HF-containing mixtures of acids is one of the most suitable preparative method [31]. However, the technique has several drawbacks mainly associated with special ISO IEC operation procedures in the laboratory and high costs for specific instrument components. Moreover, the use of HF or HF-containing mixtures of acids does not guarantee total dissolution of granite and granodiorite as silicate-rich samples. [32, 33] For some matrices, the HF can be substituted with the less toxic NH₄F [34]. Slurry nebulization may also be used for the evaluation of REEs in geological samples [35] but the procedures are highly susceptible to be affected by increased contamination on the instrument, poor precision and accuracy variation driven by particle size.

The solid-state dissolution by fusion/sintering technique with alkali salts such as LiBO₂, Na₂CO₃, NaOH, Na₂O₂, is a feasible alternative to the wet digestion procedure. The technique was used for REEs digestion from several mineralogical samples [36–39]. Use of mixed oxidizing reagents may improve the dissolution efficiency for some matrices but may also increase the TDSC in the solution, a limiting factor for ICP–MS analysis. As most of the secondary sources for REEs contain some sort of silicates, the silicate content is one of the defining parameters controlling the dissolution efficiency of the preparatory procedure. For the silicate matrix, the dissolution efficiency is known to increase in the order: Na₂CO₃ < KOH < NaOH < Na₂O₂ [36, 38]. Sodium peroxide is the most efficient solid-state dissolution reagent for minerals [40]. Great emphasis must be given in selecting the appropriate processing temperature, as this may greatly influence the solubilization of the resulting products [41]. During the preparative steps, the use of platinum [40] or even zirconium vessels [42, 43] ensure minimal sample loss due to fusion. Longerich et al. were among the first claiming that combination of Na₂O₂ sintering and ICP–MS is an effective procedure for REE analysis in various samples. [33]

The European ENVIREE (Environmentally friendly and efficient methods for extraction of rare earth elements (REE) from secondary sources) project, under the ERA-MIN Program of the 7th Framework, was mainly aimed to demonstrate the economic viability of new methods for the production of rare earths from tailings to ensure a policy aimed to secure long-term access to non-energy raw materials at reasonable costs. The work at the “Alexandru Ioan Cuza” University of Iasi, one of the eleven partners from the eight countries involved in the consortium, was mainly devoted to the development of an effective and low-cost analysis method of REEs from various mining wastes selected be the Consortium. The quantification procedure presented in this study was developed around key parameters looking for (1) rapidity of analysis, with a main focus on optimizing the time-consuming preparatory step, (2) efficiency and robustness for silicate-rich matrix dissolution, (3) the use of relatively common reagents and materials and the ability to implement the procedure in regular laboratories; (4) low analysis costs, and (5) versatility regarding the matrix for which the procedure can be applied.

**Experimental**

**Reagents and materials**

Sodium peroxide, *puriss.*, p.a. ≥ 99% (Honeywell Fluka) was used as sintering reagent. Suprapur® nitric acid 65%...
(Merck) was used to obtain HNO₃ 3% for samples solubilization and dilution. Ultrapure water was obtained with an Advantage A10—Milli-Q water purification system. Tuning solution for ICP–MS, Agilent Technologies, containing 1 µg L⁻¹ Ce, Co, Li, Mg, Ti and Y was used for instrument tuning prior analysis. Rare earth elements mix for ICP–MS analysis, TraceCERT®, containing 50 µg L⁻¹ each: Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu (Sigma-Aldrich) was used to prepare the calibration standards. Indium ICP–MS standard solution, 1000 µg L⁻¹ (Merck), was used as internal standard. All chemicals were used without further purification.

**Investigated samples**

Seven certified reference materials (CRMs) were used for the development of an optimal analysis method applied for REEs measurement in nine mining wastes from Europe. CRMs from FLUXANA® GmbH & Co. KG have unique manufactures reference material number. Thus, for JA-1 (Andesite) is F0I007152; for JB-3 (Basalt) is FI000009; for JR-1 (Rhyolite) is FI000043, for JR-2 (Rhyolite) is FI000044, for JG-2 (Granite) is FI000037, for JG-3 (Granodiorite) is FI000038, and, lastly, for TILL-1 (Geochemical soil) is FI000154. These Igneous rock CRMs, excluding TILL-1, have been issued by The Geological Survey of Japan, from all over Japan, in 1982 (JA-1—Hakone Volcano, JR-1—Wada Toge obsidian), 1983 (JB-3—Fuji volcano, JR-2—Wada Toge obsidian), 1985 (JG-2—Naegi granite) and 1986 (JG-3—Mitoya granodiorite) [44]. The CRMs have certified values of concentration with associated uncertainties in µg g⁻¹, mg kg⁻¹ or any comparable SI units. The certified values of concentrations are compiled from 339 publications and 295 personal communications [45, 46] and for this reason great confidence is placed on the presented certified concentrations and associated uncertainties.

Table 1 presents details (sample code, location, short description) on the mining waste samples investigated in the present study. More information about the samples, the selection method, location, and sampling procedure are presented on the ENVIREE project site [47].

**Sample preparation by sintering method**

Weighed amounts of about 0.1 g from each investigated sample or CRM were subjected to thermal Na₂O₂ sintering process. The weighing was performed using a digital analytical balance (CPA26P-0CE—SARTORIUS) with a repeatability value of ± 0.004 mg. Prior weighing, both the investigated samples and CRMs were kept at 60 °C for at least 24 h to ensure slow removal of water and to have undertaken similar preparative conditions. After weighing, internal standard solution (50 µg of Indium 1000 µg L⁻¹) was added to each CRM and sample to be used for correcting the signal drift in the quantification step or for potential concentration underestimation due to sample loss during preparation.

The sintering step was performed in porcelain crucibles, in a closed Nabertherm P330 (Germany) electrothermal furnace. The porcelain crucibles were lined and covered with commercially available common aluminum sheets for the thermal processing. The efficiency of the sintering process was tested at several temperatures (350 °C, and from 400 to 480 °C with 20 °C increment step). A slow heating ramp of about 7.3 °C min⁻¹ was used to have a more accurate control of the sintering temperature and to reduce the impact of the induction effect. In this way the risk of reaching the melting point of Na₂O₂ (i.e., 480 °C) from the induction of the heating system, important especially for working temperatures close to this value, is significantly reduced or avoided.

Nitric acid 3% was used for solubilization of the sintered mix, after slow cooling of the crucibles to room temperature. Lastly, sintered CRMs and samples were filtered on ashless filter paper Grade 41 (Whatman) and diluted to the final volume of 50 mL. Until analysis, the solutions were stored at ambient temperature in closed plastic containers.

| No. | Sample | Location | Short description |
|-----|--------|----------|-------------------|
| 1   | CZ-1   | Dolni Rozinka (Czech Republic) | Uranium deposit in metamorphic rocks |
| 2   | PL-1   | Zelazny Most (Poland) | Wastes from copper ore enrichment |
| 3   | PL-2   | Rudki (Poland) | Wastes from pyrite uranium mine tailings |
| 4   | PT-1   | Cumieira (Portugal) | Quartz veins and pegmatitic apophysis |
| 5   | PT-2   | Covas (Portugal) | Tungsten mineralization, sulfide and iron oxides |
| 6   | PT-3   | Elvideira (Portugal) | Quartz veins and altered granite |
| 7   | PT-4   | New Kankberg (Sweden) | Andalusite formation |
A flow sheet of the preparatory procedure is presented in Figure S.1 from the Supplementary Material (SM).

ICP–MS analysis

One of the key objectives of the experimental work was to contribute to the development of a direct ICP–MS analysis method of REEs in sintered and solubilized samples and CRMs, without any additional preparatory steps for matrix removal. The ICP–MS analysis was performed on the 7700×ICP–MS (Agilent Technologies) instrument using the “High Matrix Introduction Technology” (HMI) plasma conditions, implying the use of: (1) aerosol dilution with dry argon gas to reduce the aerosol load on the plasma, (2) short pre-defined cell stabilization time, and (3) relatively higher RF power and a lower carrier gas flow. Operation under these conditions enables analysis of samples with TDSC as high as 2%, together with the use of internal standard quantification procedure as mandatory. Relatively high contents of Na salts in final solutions are known to have negative effects on the signal stability [48, 49] but measurement strategies as those proposed in the present work were used also in other studies presenting ICP–MS analysis of geological samples solutions [20]. Although the dilution of sample aerosols might have a negative impact on instruments sensitivity, the quantification of REEs, even if present at lower concentrations than the average values observed in the upper continental crust, is possible (as later shown in “Method validation”).

Matrix removal or analytes separation from the matrix prior analysis require additional steps in the preparatory stage with uncertainty sources necessarily to be considered. However, they might lead to overall similar results for the expanded uncertainty of the measurements.

Instrument tuning conditions

Tuning of the ICP–MS was performed prior analysis to adjust to a minimum the instrument response to interfering species, especially those in the polyatomic form. From the elements in the tuning solution emphasize was given to Ce. Abundances for monitored masses, blanks and stability of the signal were identified to correspond to optimal analysis conditions. Stability of the signal was investigated in terms of RSD%. The 156/140 and 70/140 m/z ratios, corresponding to $^{140}\text{Ce}^{16}\text{O}^+/^{140}\text{Ce}^+$ and $^{140}\text{Ce}^{2+}/^{140}\text{Ce}^+$, were under scrutiny since these variables are good indicators for the occurrence probability of interfering oxides and doubly charged species formation potential. These parameters are especially important to be monitored since it is known that LREEs oxides might act as interfering species during HREEs analysis [28, 50] and the formation of doubly charged species reduces the sensitivity for some analytes.

| Instrument operating conditions of the 7700×ICP–MS (Agilent Technologies) instrument (a) and tuning conditions for representative low, medium, and high mass isotopes (b) |
|-----------------------------------------------|
| **Instrument** | **7700×ICP–MS (Agilent Technologies)** |
| Plasma mode | HMI |
| Aerosol dilution | Medium |
| Tune mode | No auxiliary gas |
| RF power (W) | 1600 |
| Plasma gas flow (L min$^{-1}$) | 15 |
| Carrier gas flow (L min$^{-1}$) | 0.37 |
| Dilution gas flow (L min$^{-1}$) | 0.9 |
| Nebulizer type | Concentric |
| Sample uptake rate (mL min$^{-1}$) | 0.4–1.2 |
| Mass analyzer | Quadrupole |
| Acquisition time (s) | 22.74 |
| Sampling period (s) | 0.311 |
| Integration time (s) | 0.100 |

Optimized instrument operating conditions are presented in Table 2. Additional information about the tuning conditions and results of the tuning procedure are presented in Table S.1 from the SM. Since the background signal is almost zero its contribution can be neglected. For all monitored masses the signal RSD was below 5% indicating suitable signal stability. For high mass isotopes, $^{140}\text{Ce}^{16}\text{O}^+/^{140}\text{Ce}^+$ (m/z 156/140 ratio) ratio of 1.1% was obtained indicating limited formation of oxides as polyatomic interfering species. The experimental

| Table 2 | Calibration curves ranges, detection, and quantification limits with $^{115}\text{In}$ at 1000 µg L$^{-1}$ as internal standard |
|-----------------------------------------------|
| **Isotope** | **Calibration curve range (µg L$^{-1}$)** | **LOD (µg L$^{-1}$)** | **LOQ (µg L$^{-1}$)** |
| $^{89}\text{Y}$ | 5–100 | 0.27 | 0.92 |
| $^{139}\text{La}$ | 2.5–50 | 0.15 | 0.51 |
| $^{140}\text{Ce}$ | 5–100 | 0.23 | 0.75 |
| $^{141}\text{Pr}$ | 0.5–10 | 0.07 | 0.22 |
| $^{146}\text{Nd}$ | 2.5–50 | 0.33 | 1.08 |
| $^{147}\text{Sm}$ | 1–25 | 0.31 | 1.02 |
| $^{153}\text{Eu}$ | 0.5–10 | 0.05 | 0.16 |
| $^{157}\text{Gd}$ | 2.5–50 | 0.16 | 0.53 |
| $^{159}\text{Tb}$ | 0.25–5 | 0.03 | 0.09 |
| $^{161}\text{Dy}$ | 1–25 | 0.21 | 0.69 |
| $^{163}\text{Ho}$ | 0.25–5 | 0.01 | 0.03 |
| $^{166}\text{Er}$ | 1–25 | 0.13 | 0.43 |
| $^{169}\text{Tm}$ | 0.25–5 | 0.02 | 0.08 |
| $^{172}\text{Yb}$ | 0.5–10 | 0.15 | 0.48 |
| $^{175}\text{Lu}$ | 0.25–5 | 0.04 | 0.12 |
140Ce^{2+}/140Ce^{+} (m/z ratio of 70/140) ratio (3.01%) is higher than the set value of 2%, which might suggest occurrence of doubly charged species during analysis. Considering that there are no other elements that at half of their mass can generate interfering species for the REEs analysis, this parameter is rather an indicator of the probability that REEs themselves may undertake this process. Under these circumstances signal loss and sensitivity loss might occur in the quantification of REEs. However, the obtained value of 3.01% does not significantly influence the analysis.

Instrumental performances: calibration and sensitivity characterization

Analysis range, detection, and quantification limits with $^{115}$In at 1000 µg L$^{-1}$ as internal standard are presented in Table 3.

The expanded uncertainties of the measurements were estimated using the formula:

$$\text{LoD} = \frac{3 \times \text{SD}_{\text{CPS (1st standard)}}}{\text{CPS}_{\text{IS}} \times \text{slope}},$$  \hspace{1cm} (F.1)

with assignments of the contributors presented in Table 4. The evaluation of the expanded uncertainty is exclusively based on type A uncertainties since these can be accurately calculated from direct observations [52]. Similar formulas for the estimation of the expanded uncertainty are reported in the literature [53]. In Eq. (1) the first five contributors belong to sample preparation steps (including contributions from stock standard solutions) and the last three are associated with the ICP–MS measurements.

### Table 4 Description of factors used for the overall uncertainty estimation

| Factor | Term | Description |
|--------|------|-------------|
| 1      | $u_{(W_{sp})}$ | Uncertainty of sample weight (g) |
| 2      | $u_{C_{IS}}$ | Uncertainty of concentration of the internal standard stock solution (mg L$^{-1}$) |
| 3      | $u_{V_{IS}}$ | Internal standard stock solution concentration (mg L$^{-1}$) |
| 4      | $u_{c_{St}}$ | Uncertainty of the internal standard pipetting—expressed as the precision resulting from weighing of ten consecutive pipetting of the same volume of internal standard added to both samples and CRMs (µL) |
| 5      | $u_{V_{St}}$ | Internal standard volume (µL) |
| 6      | $\text{SD}_{\text{CPS}_{St}}$ | Standard deviation of the signal (3 replicates) for the internal standard (CPS) |
| 7      | $\text{SD}_{\text{CPS}_{St}}$ | Internal standard average signal (CPS) |
| 8      | $u_{CC}$ | Uncertainty related to the calibration (residual CPS_{analyte}/CPS_{IS})—for each analyte individually |
| 9      | $R_{A/IS}$ | Analyte to internal standard signal ratio (CPS_{analyte}/CPS_{IS})—for each analyte individually in each investigated CRM |
Results and discussions

Optimization of the sintering temperature

For selected samples the results obtained during the experiments performed to establish the optimal sintering temperature are presented in detail in Table S.2 from the SM. Data in Table S.2 give information on the JR-1 (rhyolite), JG-2 (granite) CRMs and on the Covas (Portugal) real sample. The JR-1 (rhyolite) CRM is a slightly simple matrix which can be used to evaluate the optimal processing temperature in terms of energy consumption, JG-2 is a complex and difficult matrix while the Covas real sample was selected due to its “sand-like” aspect. For the interest CRMs the dissolution efficiency investigated from 400 to 480 °C showed not significant changes from one temperature to another, with recoveries of investigated REEs close to 1 even at 350 °C. For the real sample the recoveries slightly increased with increasing the temperature, except for 480 °C. This may be related to sample loss due to fusion with the crucible, as 480 °C is the melting point of Na₂O₂, and thus the melt formation is favored in this case. Here we should stress that use of the internal standard may correct the signal variation due to sample loss if this occurs. According to data in Table S.2 and if considering that the recoveries of the interest REEs from the investigated CRMs is high enough at 460 °C, use of temperatures higher than this value is not justified. This observation allows selecting 460 °C as optimal operation temperature for the interest silicate-rich CRMs in the present study.

When processing temperatures below the melting point of Na₂O₂ are used, there is a risk that part of the sample will remain undisolved if the sample and the oxidizing reagent particles mixture is not appropriately homogenized. Experiments performed in the present work showed that the oxidizing reagent particle size might have great influence on the sample dissolution efficiency. Optimal results were obtained when the oxidizing reagent particles were intimately mixed with the sample particles prior thermal processing. It is worthy to mention that Na₂O₂ is usually supplied as pellets and not as fine powder, such to increase its shelf time especially due to the fact that Na₂O₂ retains water [54, 55] and carbon dioxide [56]. Although both NaOH and Na₂CO₃ possess oxidizing properties, their dissolution efficiency on silicate-rich samples is much weaker than that of Na₂O₂. To develop an experimental working strategy suitable to overcome some of these difficulties, in the present work appropriately stored and handled Na₂O₂ was finely grinded before its use to have the oxidizing effect at optimum. Coarse particles sodium peroxide can also be used but with increased sample to Na₂O₂ ratio which might be disadvantageous for the ICP-MS quantification since it will increase the TDSC.

Influence of the mixing approach on the sintering efficiency

Several mixing strategies were tested in the present work to maximize the effect of the oxidizing agent on the sample and to minimize the unwanted fusion of the mix with the support. When the sample and the finely grinded Na₂O₂ were plainly but thoroughly mixed, optimal results were generated in terms of both dissolution efficiency but also the TDSC in the final solution. This is important due to the fact that the sintering temperature does not allow melt formation and, thus, if the Na₂O₂ is not in direct contact with the sample the maximum oxidizing effect is not reached. Moreover, tests performed in the present work led to the conclusion that lining porcelain crucible with aluminum foil removes the risk of sample loss, expected due to the fact that the oxidizing agent can lead to fusion and even attack of the crucible [42]. This is an accessible, cheap alternative to the crucibles presented in the literature for similar tasks, like iron [42], nickel [33], corundum [38], and even more expensive platinum [39, 40]. In this case the porcelain crucible is acting only as a support, with the reaction between sample and the oxidizing reagent taking place on the aluminum foil. Although in few cases fusion of the mix with the aluminum foil was observed, this aspect was not considered as a critical factor for the REEs quantification. As shown in Figure S.2 from the SM, analysis of several analytical blanks (concentrated and diluted HNO₃, original and neutralized Na₂O₂, similarly processed as the samples in the aluminum foil) revealed that Al, Mg, Mn, Fe, Ga, and Pb were the most significant contaminants from the aluminum foil. However, none of these elements act or form polyatomic species that could interfere during the REEs analysis. Moreover, for the present study, the initial sample mass, the corresponding oxidizing reagent mass, and the final volume for sample dilution were selected such as to maintain the TDSC below 2%.

For the present study, a sample to Na₂O₂ ratio of 1:6.5 proved to be optimal for total dissolution of the interest samples with a dissolved solid content in the final solutions kept at minimum. On the base of the experimental observation from the present work the established operating conditions are consistent with other studies in the literature reporting sample to Na₂O₂ ratios varying from 1:3 [40], 1:4 [33, 57], 1:6 [58], 1:8 [42], and as high as 1:12 [59] depending on the sample matrix. The optimized procedure was also applied for the analysis of samples regarded as potential secondary sources for REEs.

Method validation

Concentration values (in mg kg⁻¹ units) for rare earth elements (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm,
Yb, and Lu) quantified from seven representative silicate-rich geological CRMs are presented in Table 5. The correlation ($y = 1.076x$ and Pearson coefficient, $R$, of 0.998 at $p < 0.01$) between measured REEs quantified concentrations versus their certified concentrations are presented in Fig. 1. The individual values for each CRM are presented in Table S.3 from the SM. Figure 1 was generated using Origin PRO

| Table 5 | Quantified concentrations accompanied by the estimated expanded uncertainty (±) (line indicated by 1) and certified concentrations (line indicated by 2) for REEs in the investigated CRMs, in mg kg$^{-1}$ units (certified values for JA-1 (andesite), JB-3 (basalt), JG-2 (granite), JG-3 (granodiorite), JR-1 and JR-2 (rhyolite) in [45, 46] and for TILL-1 (geochemical soil) in [60]) |
|---------|---------|---------|---------|---------|---------|---------|
|         | Y       | La      | Ce      | Pr      | Nd      | Sm      |
| JA-1    |         |         |         |         |         |         |
| 1       | 31.3 ± 3.5 | 569 ± 0.73 | 14.5 ± 1.5 | 2.22 ± 0.28 | 11.9 ± 1.3 | 3.62 ± 0.39 |
| 2       | 30.6 ± 3.0 | 524 ± 0.86 | 13.3 ± 1.3 | 1.71 ± 0.64 | 10.9 ± 1.3 | 3.52 ± 0.32 |
| JB-3    | 29.0 ± 2.0 | 959 ± 0.81 | 23.5 ± 1.6 | 3.37 ± 0.30 | 17.2 ± 1.0 | 4.71 ± 0.39 |
| 2       | 26.9 ± 3.0 | 881 ± 0.77 | 21.5 ± 1.7 | 3.26 ± 0.42 | 15.6 ± 2.1 | 4.27 ± 0.24 |
| JG-2    | 98.3 ± 14.0 | 20.7 ± 2.5 | 47.7 ± 5.3 | 5.9 ± 0.69 | 25.5 ± 2.8 | 8.09 ± 0.88 |
| 2       | 86.5 ± 8.0 | 21.8 ± 3.8 | 46.3 ± 7.3 | 4.73 ± 0.55 | 17.2 ± 2.5 | 3.19 ± 0.55 |
| JG-3    | 17.7 ± 2.5 | 21.9 ± 3.97 | 50.3 ± 9.8 | 5.78 ± 1.24 | 25.0 ± 4.7 | 6.02 ± 1.06 |
| 2       | 17.3 ± 1.5 | 19.7 ± 1.77 | 39.9 ± 5.7 | 4.79 ± 0.54 | 20.1 ± 2.8 | 5.44 ± 0.92 |
| JR-1    | 47.2 ± 8.4 | 47.2 ± 4.3 | 38.8 ± 5.1 | 4.75 ± 0.76 |
| JR-2    | 52.9 ± 7.6 | 47.2 ± 4.3 | 38.8 ± 5.1 |
| TILL-1  | 40.8 ± 5.8 | 47.2 ± 4.3 | 38.8 ± 5.1 |

|         | Eu      | Gd      | Tb      | Dy      | Ho      | Er      |
|---------|---------|---------|---------|---------|---------|---------|
| JA-1    |         |         |         |         |         |         |
| 1       | 1.82 ± 0.20 | 5.65 ± 0.70 | 0.84 ± 0.10 | 5.57 ± 0.59 | 1.16 ± 0.13 | 3.45 ± 0.34 |
| 2       | 1.20 ± 0.13 | 4.36 ± 0.37 | 0.75 ± 0.14 | 4.55 ± 0.64 | 0.95 ± 0.10 | 2.04 ± 0.32 |
| JB-3    | 1.88 ± 0.15 | 6.67 ± 0.50 | 0.89 ± 0.063 | 5.27 ± 0.38 | 1.04 ± 0.08 | 3.08 ± 0.40 |
| 2       | 1.32 ± 0.12 | 8.01 ± 2.13 | 1.96 ± 0.23 | 13.4 ± 1.35 | 1.67 ± 0.15 | 1.67 ± 0.15 |
| JG-2    | 0.23 ± 0.067 | 3.30 ± 1.31 | 0.40 ± 0.20 | 2.64 ± 1.44 | 0.54 ± 0.22 | 1.34 ± 0.14 |
| 2       | 0.10 ± 0.044 | 2.92 ± 0.28 | 0.46 ± 0.05 | 6.37 ± 1.25 | 0.54 ± 0.22 | 1.30 ± 0.24 |
| JG-3    | 0.85 ± 0.206 | 8.52 ± 1.54 | 1.09 ± 0.18 | 6.63 ± 1.11 | 1.30 ± 0.24 | 1.39 ± 0.16 |
| 2       | 0.36 ± 0.074 | 7.74 ± 1.12 | 1.08 ± 0.13 | 6.29 ± 0.67 | 1.25 ± 0.18 |
| JR-1    | 0.15 ± 0.077 | 5.83 ± 0.95 | 1.08 ± 0.17 | 6.65 ± 1.05 | 1.39 ± 0.32 | 1.25 ± 0.18 |
| JR-2    | 2.46 ± 0.28 | n.a     | 1.1   | 6.65 ± 1.05 | n.a     | 1.25 ± 0.18 |
| TILL-1  | 1.3       | 6.65 ± 1.05 | 1.1   | 6.65 ± 1.05 | n.a     | 1.25 ± 0.18 |

|         | Tm      | Yb      | Lu      |
|---------|---------|---------|---------|
| JA-1    |         |         |         |
| 1       | 0.53 ± 0.069 | 3.23 ± 0.37 | 0.51 ± 0.050 |
| 2       | 0.47 ± 0.071 | 3.03 ± 0.72 | 0.47 ± 0.065 |
| JB-3    | 0.43 ± 0.073 | 2.66 ± 0.24 | 0.42 ± 0.027 |
| 2       | 0.42 ± 0.051 | 8.70 ± 1.04 | 0.39 ± 0.059 |
| JG-2    | 1.34 ± 0.14 | 1.61 ± 0.32 | 1.22 ± 0.14 |
| 2       | 1.16 ± 0.74 | 4.44 ± 0.78 | 0.26 ± 0.049 |
| JG-3    | 0.24 ± 0.140 | 3.44 ± 0.78 | 0.71 ± 0.08 |
| 2       | 0.24 ± 0.048 | 5.15 ± 0.67 | 0.88 ± 0.093 |
| JR-1    | 0.63 ± 0.102 | 5.15 ± 0.67 | 0.88 ± 0.093 |
| JR-2    | 0.75 ± 0.08  | 5.15 ± 0.67 | 0.88 ± 0.093 |
| TILL-1  | 0.55 ± 0.1   | 5.15 ± 0.67 | 0.88 ± 0.093 | 0.6
v2022 software, as all subsequent figures presented in the manuscript and the SM.

The concentration values measured in the present work are compared with certified data for igneous rocks, in the form of Andesite (JA-1), Basalt (JB-3), Rhyolite (JR-1, JR-2), JG-2 (Granite), JG-3 (Granodiorite) and data in Fig. 1 show the excellent correlation between the two variables. For the TILL-1 reference material certified values of concentration are not available for Pr, Gd, Dy, Ho and Tm elements. However, in the present study these elements were quantified. The highly significant correlation between the quantified and certified concentrations (p value < 0.001) for the rest of the REEs allows suggesting that, for the Till-1 CRM, the concentrations quantified in the present work can be used either to confirm the provisional values reported in the literature or as reference for further studies involving REEs for which provisional concentration are not provided. In Table 5 presented data are accompanied also by the expanded uncertainty of the measurements which seems to be within the limits of the uncertainties presented in the literature [45, 46]. On average (considering all analytes in all the investigated CRMs), the contribution of the expanded uncertainty of the measurements relative to the estimated concentration values is of about 16%. The percentage contribution of each identified uncertainty source is presented in Tables S.4.1 to S.4.7 from the SM while Fig. 2 presents the variation of the relative contribution for each contributor to uncertainties accounting to the quantified value.

Method uncertainty assessment

Sample preparation and elements measurements analysis steps are the major classes of contributors to the expanded uncertainty. The average contribution of the sample preparation step can go as high as 32% of the expanded uncertainty, with the contributing sources varying in the order: sample weighing > analytes stock solution pipetting > internal standard concentration in stock solutions > analytes concentration in standard solution > internal standard pipetting. Moreover, as shown in Fig. 2 and Tables S.3.1 to S.3.7 from the SM, both internal standard and the analyte signal variations bring the highest contribution to the expanded uncertainty of the ICP–MS measurements (described by factors 6 and 7 respectively from Eq. (1) and Table 4). The uncertainty associated with the calibration step is also important, especially for the analytes for which the calibration was performed on a relatively lower range of concentrations. This observation is
consistent with similar literature reports [61]. The uncertainty associated with the calibration step is also important, especially for the analytes for which the calibration was performed on relatively lower range of concentrations. Taking the advantage of the high dynamic range operational for the Agilent 7700 Series ICP–MS instrument used in the present work, relatively high concentration of the internal standard was used to diminish the contribution of the internal standard signal variation. Under these circumstances, measurement’s precision, regarded as relative standard deviation (RSD, %) of 3 replicates measurements, improves with about 6% for most elements measured in all investigated CRMs. For the REEs with a relatively lower abundance in some CRMs, and especially for HREEs, improvements in signal stability could go as high as 40%. The observations from the present study indicate that the addition of the internal standard immediately after weighing of the sample/CRM will bring all the advantages of this quantification process.

The distribution presented in Fig. 2 allow us to infer that with the exception of JG-3 CRM all other silicate-rich CRMs present similar percentage contributions to the expanded uncertainty from each factor. The similarity might come from the fact that andesite is found in associations with basalt and/or rhyolite rocks [62]. When considering all analytes in the investigated samples the lowest expanded uncertainty of about 8.5% was found for the JB-3 CRM and the highest value of about 32% was found for the JG-3 CRM. The larger contribution for the JG-3 CRM is associated with higher uncertainty due to measurements related sources. For this CRM, an analysis of the uncertainty’s contributions for measurements of heavy versus light REEs is presented in Fig. 3. In the granodiorite sample, the contributions from the analytes and internal standard measurements uncertainties for HREEs seem to change by a factor of two in comparison with those specific for LREEs. The effect can be attributed to the relatively lower abundances of HREEs, influencing the precision for these analytes. Nevertheless, the granodiorite is known as complex and difficult matrix. Literature data reports about incomplete digestion of this matrix when using microwaves and mixtures of strong acids (e.g., HF, HNO$_3$, HCl and H$_3$BO$_3$) [32] and for this reason the higher expanded uncertainty obtained also in our case for the measurements of HREEs might be seen as acceptable.

Besides the ability of total dissolution of granite and granodiorite matrices, the Na$_2$O$_2$ sintering method has also some other advantages over the wet digestion with HF-containing mixes of acids which requires special laboratory conditions and strict safety measures. Moreover, if the HF-containing mix of acids used for digestion includes also HCl, the probability of polyatomic interfering species in the form of MCl$^+$ occurrence at $m/z$ +35 and $m/z$ +37 is significantly increasing. When HCl is used there is always a great risk that Ba and light REEs can lead to interfering species during heavy REEs analysis [17, 28, 50]. Nevertheless, since for the HF method the aerosols dilution procedure is not mandatory, the sensitivity of the quantification method in this case might be improved. However, for the HF method an additional step must be considered, involving removal of HF excess prior analysis, that will contribute to the overall uncertainty associated with the preparatory step. Although the discussion is mainly focused on the granodiorite matrix data from the present study clearly shows the suitability of the Na$_2$O$_2$ sintering method also for basalt and andesite type rocks samples.

**REEs concentrations in secondary sources of potential economic interest**

For the samples selected within the ENVIREE project to check for their potential to be used as secondary sources for REEs, the concentrations of the interest elements were measured accordingly with the method developed in the present study. Measured concentrations together with uncertainty values representing two times standard deviation for three replicates measurement (with both in mg kg$^{-1}$ units) are presented in Table 6. The distribution of the Upper Continental Crust (UCC)-normalized concentrations of all measured REEs in the investigated potential secondary sources samples is presented in Fig. 4. The UCC-normalization [63] was applied to the data-set for a better comparison between the samples and also with the average values in the continental crust. Data presented in Fig. 4 clearly show that samples from Sweden (SW-1) and Czech Republic (CZ-1) are
the only one standing out with normalized concentrations higher than 1. In the SW-1 sample, measured concentrations of LREEs have values even 3 times higher than the UCC, but the HREEs are close to the UCC values. Among HREEs only Tb, Dy, Tm, Yb and Lu are presenting values higher than 1. Opposite behavior is observed for the CZ-1 sample with significant enrichment for HREEs and some LREEs in the form of Sm, Eu and Gd. Moreover, the $\Sigma_{\text{REEs}}$ for SW-1 is 375 ± 7 mg kg$^{-1}$ and for the CZ-1 sample is 188 ± 3 mg kg$^{-1}$. Although significantly higher than the UCC, the values do not really recommend the samples as potential secondary sources for the REEs especially due to the fact that the concentrations equivalent in REO is around 0.09% in SW-1 sample and slightly below 0.05% for CZ-1 sample. The estimated $\Sigma_{\text{REOs}}$ (%) is of about 50–100 times lower for SW-1 and CZ-1 samples in comparison with some primary important deposits for the REEs at the Mountain Pass and Bayan Obo [11, 12]. Although the results reported in the present work represent only a small contribution to the ENVIREE project main aim, the developed analysis method proved to be suitable for the investigation of REEs in various complex samples of less economical value with REEs concentrations below the UCC values. However, in the future such samples might become some of the most valuable REEs resources.

Conclusions

The analytical performance of Na$_2$O$_2$ sintering as a suitable preparatory procedure prior the quantification of REEs by ICP–MS was investigated in the present work using seven silicate-rich geochemical CRMs. The excellent correlation observed between the quantified and certified REEs concentrations ($p$ value < 0.001) proves that the analysis method leads to accurate data. For Till-1, the obtained results can be used either to confirm the provisional values reported in the literature or as reference for further studies involving REEs for which provisional concentration are not provided.

The results obtained in the present work indicate that the procedure is an accessible alternative to the HF wet
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