



# The fate of noble metals and rare earth elements during pelletized biomass combustion

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## ABSTRACT

The extraction of rare earth elements (REEs) and noble metals (NMs) from unconventional resources is playing a crucial role under the context of industrialization and reserve depletions. Plants used for phytoextraction are promising materials for the recovery of metals, but the biomass needs to be reduced to a manageable amount and volume prior to the extraction process. This paper investigates the combustion process of biomass focusing on NMs and REEs flow. The plants harvested from a brownfield land were pelletized and incinerated in a fixed-grate pilot-scale boiler, meanwhile, solid remains from various points in the combustion and flue gas system were captured and analyzed. The results show that levels of NMs in deposited ash and fly ash are greater than in bottom ash. Meanwhile, the higher REE concentration in bottom ash compared to that in other solid residuals demonstrates the less ability of these compounds to escape from the combustion chamber. Generally, the concentrations of REEs and NMs in the solid residues are significantly higher compared to biomass. SEM-EDS analyses of the contaminated solid remains indicate that gold forms individual particles with purity higher than 95 wt% in the bottom ashes, and this finding adds novel insights into gold phytomining.

## 1. Introduction

Noble metals (NMs) consist of Au (gold), Ag (silver), and six platinum group metals namely Ru (ruthenium), Rh (rhodium), Pt (platinum), Pd (palladium), Os (osmium), and Ir (iridium). In the economic aspect, noble metals are also called precious metals due to their high economic value. Rare earth elements (REEs) include 17 metallic elements that share similar chemical properties, encompassing Y (yttrium), Sc (scandium), and 15 lanthanide metals [1]. NMs and REEs generally refer to minerals that are rare, sparsely distributed, and arduous to extract from the natural surroundings [2]. These elements possess varieties of implementations in machinery, catalysts, metallurgy, and modern technology industries [3] due to their excellent physical and chemical properties [4]. Additionally, NMs and REEs are considered critical strategic resources [5,6] according to supply risk, economic importance, and cruciality to the progress of science and technology [7]. The demand for these elements has dramatically increased, while their natural ores are limited and unevenly distributed.

Phytomining has opened a new era in reclaiming valuable metals from brownfields where traditional mining techniques are not competitive [8]. The phytomining concept integrates three research areas: i) Accumulation of metals from brownfields to plants so called phytoextraction referred to as the first stage [8–10]; ii) Following that, enrichment process concentrates metals from biomass into solid residuals [11]; iii) Ultimately, extraction of high-value elements from the solid remains is the eventual step in the overall

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Fig. 1. Location for contaminated biomass sampling.

picture of phytomining [12–14]. As an example, the phytomining of nickel has been successfully demonstrated at different scales [15–19]. Meanwhile, the innovative phytomining approach is at a very early stage of development in terms of NMs and REEs, despite their potential for phytomining. The entire concept of NM and REE phytomining just has been disclosed recently [20,21].

The contaminated biomass derived from the phytoextraction is considered as the source of NMs and REEs. The valuable metals accumulated in the plants could be recovered through extraction techniques [22–24]. Nonetheless, prior to the extraction process, the amount and volume of the bulky polluted biomass must be significantly decreased, then concentrations of metals are enriched into solid remains as a result. The enrichment process lowers transportation costs and reduces the equipment sizes of subsequent processes. Enrichment methods such as composting, compaction, and thermal conversions (ashing, pyrolysis, gasification, combustion) have been mentioned previously [25]. Of these approaches, thermal conversions are feasible pathways to enhance metal concentrations from polluted plants. These enrichment techniques have been proven viable in the cases of heavy metals [26]. The behavior of these hazardous elements during the process of thermal conversion has been thoroughly investigated [27,28]. Several parameters have impacts on the fate of metals including reactors, elemental chemical speciation, material properties, operational conditions (resident times, heating rates, pressures, and temperatures), and so on [29,30]. The information on the enrichment of NMs and REEs from polluted biomass is limited, with only a few investigations conducted so far.

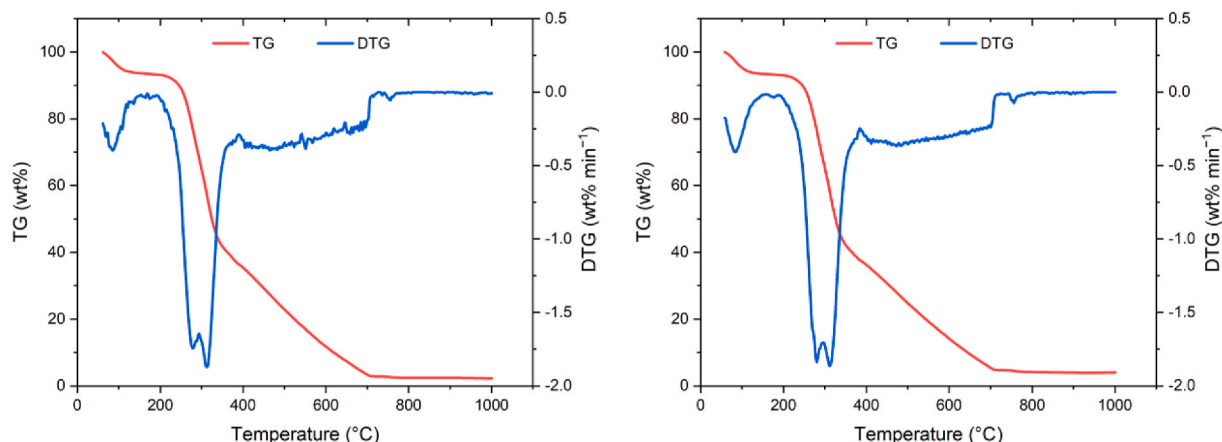
In one, harvested plants were incinerated at 550 °C aiming at eliminating organic substances [14]. After ashing at a temperature of around 300 °C, 100 kg tobacco used for Au phytomining was lessened to 5.54 kg ash, equating to 94.46 % mass reduction [13]. In another study regarding biomass combustion, 11.9 mg kg<sup>-1</sup> Ag and 3.06 mg kg<sup>-1</sup> Pt in gathered plants resulted in concentrations of 545 and 46.4 mg kg<sup>-1</sup>, respectively, in collected fly ashes [31]. It was observed that Au was not detectable in the biomass, but its concentration became high enough to be identified in the solid remain (4.10 mg kg<sup>-1</sup>) as a result of the enrichment process. The authors also investigated the impacts of flue gas temperatures on the metal flows. The concentration of Ag was substantially greater in the fly ash sample captured at the flue gas temperature of 150 °C versus the 250 °C case, demonstrating a significant temperature influence. Meanwhile, other precious metals were less dependent on the flue gas temperature. This was the first investigation regarding the effects of flue gas temperatures on the fate of metals including NMs during the incineration of polluted plants.

In terms of REEs, by incinerating the harvested *Dicranopteris linearis* fern at 500 °C, 2032 mg kg<sup>-1</sup> of rare earth metals in plants was elevated to a concentration of 15956 mg kg<sup>-1</sup> in ashes; the solid remains accounted for the conversion of 93 % of the REE input from the plants [32]. Similarly, 92.3 wt% of fern species (*Dicranopteris linearis*) were lessened after ashing at a temperature of 550 °C [12]. Consequently, rare earth metals were concentrated in the solid residue consisting of 3000 mg kg<sup>-1</sup> REEs, which is over 11 times higher compared to biomass. In another research, pyrolysis was proposed to enrich REEs from contaminated biomass [33]. The solid residue obtained from pyrolysis of *Dicranopteris linearis* fern contained as high as 6160 mg kg<sup>-1</sup> REEs. In another study, hydroponically grown *Salix* (willow) containing 5678 mg kg<sup>-1</sup> of REEs was incinerated at 800 °C and 1000 °C [34]. The yields of ashes derived from biomass combustion at 800 °C and 1000 °C were 6.6 % and 6.3 %, respectively. The level of rare earth metals in the bottom ash formed at 1000 °C (8 %; equating to 80000 mg kg<sup>-1</sup>) was higher than at 800 °C (7 %; equating to 70000 mg kg<sup>-1</sup>). The retention rate for REEs in the solid remain at 1000 °C combustion temperature was also greater than at 800 °C. In both cases, the numbers of retention rates were greater than 80 %, that indicates the minor volatilizations of REEs during biomass incineration. This might be the first research regarding enrichment of REEs from *Salix* fern via combustion process as well as the influence of combustion temperature on the behavior of REEs.

**Table 1**  
Properties of pellet samples.

Sample	Element (wt%)					MC <sub>db</sub> wt%	AC <sub>db</sub> wt%	HHV <sub>db</sub> MJ kg <sup>-1</sup>	Density kg m <sup>-3</sup>
	N <sub>db</sub>	C <sub>db</sub>	H <sub>db</sub>	S <sub>db</sub>	O <sub>db</sub> <sup>a</sup>				
B1	0.40	46.75	6.05	0.01	33.43	11.07	2.30	18.16	422
B2	0.27	47.19	5.94	0.03	38.74	6.95	0.89	19.10	636

B1: biomass collected from a brownfield land, B2: biomass provided by a wood pellet manufacturer (MBH Zrt company), MC: moisture content; AC: ash content, HHV: higher heating value, db: dry basis, <sup>a</sup>: by difference.



**Fig. 2.** Thermogravimetric analysis of biomass samples.

The enrichment process is an essential step in the overall phytomining concept for the recovery of NMs and REEs, however, the available information about the method is sparse and scanty. This research investigates biomass combustion which contains REEs and NMs, and the influence of feedstocks and firing rates on the fate of these metals in the combustion and flue gas system. To the best of the author's knowledge, this is the first comprehensive study on the behavior of noble metals and rare earth elements in the burning system during biomass incineration. Additionally, the various ashes were analyzed with SEM-EDS which gives novel insights into phytomining, especially in the case of gold.

## 2. Materials and methods

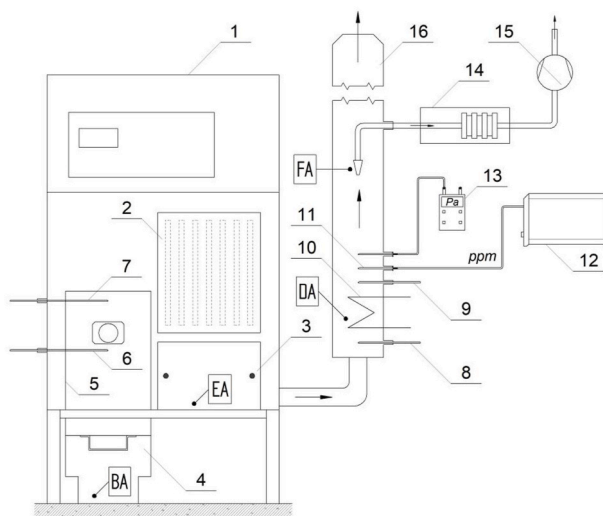
The source of contaminated plants primarily used in this study is a metal-polluted location situated in Gyöngyösoroszi, Hungary (Fig. 1). The brownfield used to be a mining region where zinc and lead were industrially produced until 1986.

Bulk collection of biomass, along with the required sample preparation procedures, was conducted from the sampling point. *Populus tremula* a species of poplar native to the area was collected. The harvested plant parts including the trunk, branches, and leaf were left in a laboratory under natural conditions for a few weeks for air drying. The different parts of the biomass were individually shredded and then mixed in the proportion of 75 % trunk, 16 % branches, and 9 % leaf which corresponds to the weight distribution of a real tree. Afterward, the contaminated biomass mixture was pelletized to provide fuel for the operation of the boiler. In addition to contaminated biomass gathered from brownfield land (B1), the other biomass provided by MBH Zrt (Hungary) company (B2) was also utilized in this study for comparison purposes. Both of the pellets are 10–30 mm in length and 6 mm in diameter. The general properties of the two biomass samples are given in Table 1.

Their thermal analysis results are depicted in Fig. 2. The thermal measurement is conducted in a thermogravimetric analyzer branded MOM Derivatograph C/PC. The operating temperature is heated up to 1000 °C with a heating rate of 10 °C min<sup>-1</sup> under an air atmosphere.

To preliminarily investigate the fate of NMs and REEs during biomass combustion, three experiments employing biomass B1 were performed in a fix-grate pilot-scale boiler under similar operational circumstances to investigate the reproducibility of the combustion. The average values of the major parameters are firing rate:  $Q = 12.8$  kW, combustion temperature:  $T_c = 664$  °C, flue gas temperature:  $T_f = 118$  °C, fuel feeding rate:  $f = 4.9$  kg h<sup>-1</sup>, air flow rate:  $\dot{V}_{air} = 69$  m<sup>3</sup> h<sup>-1</sup>, and excess air ratio:  $\lambda = 3$ . During the incineration process, pellets are supplied automatically to the burner from an attached fuel tank by a screw conveyor. The combustion air is controlled by a variable frequency drive attached to the stack fan.

The influence of combustion parameters on the metal flows was also researched. Three incineration experiments utilizing biomass B1 were conducted under different firing rate levels of 10 kW ( $T_c = 693$  °C,  $T_f = 83$  °C,  $f = 4.6$  kg h<sup>-1</sup>,  $\dot{V}_{air} = 34$  m<sup>3</sup> h<sup>-1</sup>, and  $\lambda = 1.6$ ), 20 kW ( $T_c = 840$  °C,  $T_f = 106$  °C,  $f = 6.8$  kg h<sup>-1</sup>,  $\dot{V}_{air} = 47.4$  m<sup>3</sup> h<sup>-1</sup>, and  $\lambda = 1.5$ ), and 30 kW ( $T_c = 924$  °C,  $T_f = 149$  °C,  $f = 10$  kg h<sup>-1</sup>,  $\dot{V}_{air}$



**Fig. 3.** Schematic illustration of the measurement setup: (1) boiler body, (2) water heat exchanger, (3) chamber after the water heat exchanger, (4) ashtray, (5) combustion chamber door, (6, 7, 8, and 9) thermocouples, (10) air heat exchanger, (11) gas sampling probe, (12) portable flue gas analyzer, (13) manometer, (14) impactor, (15) pump, and (16) VFD controlled flue gas fan. Ash samples: BA – bottom ash, EA – after heat exchanger ash, DA – deposited ash, FA – fly ash.

$= 62.4 \text{ m}^3 \text{ h}^{-1}$ , and  $\lambda = 1.3$ ).

Additionally, an incineration experiment utilizing pellet B2 was implemented under the firing rate of 20 kW. The operational conditions were as follows:  $T_c = 895 \text{ }^\circ\text{C}$ ,  $T_f = 100 \text{ }^\circ\text{C}$ ,  $f = 6.3 \text{ kg h}^{-1}$ ,  $\dot{V}_{air} = 36.1 \text{ m}^3 \text{ h}^{-1}$ , and  $\lambda = 1.3$ . The combustion utilizing B2 pellet was conducted for the purpose of comparison with combustion employing biomass B1 aiming to study the effect of feedstocks on metal distributions in order to better understand the behavior of valuable metals during biomass incineration.

Combustion solid remains were collected from different positions in the burning system, illustrated in Fig. 3 along with the measurement setup. Bottom ash was taken from the ashtray of the combustion chamber, meanwhile, after heat exchanger ash was collected from the chamber after the water heat exchanger. The deposited ash was captured from the surface of the flue gas system. Fly ash was collected via an isokinetic sampling system employing a Dekati® PM10 three-stage cascading impactor. The collection of fly ash meets the ISO23210 standard, which was initiated after the stabilization of the boiler. The concentrations of fly ash in the flue gas were  $191 \text{ mg m}^{-3}$ ,  $383 \text{ mg m}^{-3}$ , and  $511 \text{ mg m}^{-3}$  for the combustion experiments of 10 kW, 20 kW, and 30 kW, respectively.

The woody biomass together with the combustion solid residuals were taken for elemental analysis. Woody biomass refers to pellet B1 gathered from a contaminated land and pellet B2 provided by a pellet manufacturer. The solid remains derived from biomass incinerations consist of FA (fly ash), DA (deposited ash), EA (after heat exchanger ash), and BA (bottom ash). An external Hungarian company conducted chemical analyses of the solid samples using inductively coupled plasma (ICP) spectrometry. ICP-MS (ICP mass spectrometry) and ICP-OES (ICP-optical emission spectrometer) PerkinElmer Avio 200 were utilized for the measurements. Sample preparation was carried out according to the MSZ EN 13346:2000 Hungarian standard. Concentrations of all NMs (Ru, Rh, Pt, Pd, Os, Ir, Au, and Ag) and most REEs (Yb, Y, Tm, Tb, Sm, Sc, Pr, Nd, La, Ho, Gd, Eu, Er, Dy, and Ce) were selected to be measured due to their importance and high economic value.

Ash samples derived from combustion experiments utilizing biomass B1 were examined by scanning electron microscopy (SEM). The imaging information and elemental composition of ash samples are provided via the SEM examination. The analysis was conducted by using a scanning electron microscope of ZEISS EVO MA10 which is outfitted with secondary and backscattered electron detectors along with energy dispersive spectroscopy (EDS). This scanning electron microscope employs high-energy electron beams scanning on a sample surface area of  $3 \text{ }\mu\text{m}$ , going below  $1 \text{ }\mu\text{m}$  depth of the surface. To prepare for SEM-EDS analysis, representative portions of the solid residues were either sprinkled onto double-sided carbon tapes or suspended onto aluminum plates or glass plates. Noble metals and rare earth elements are major interests of the scanning.

### 3. Results and discussion

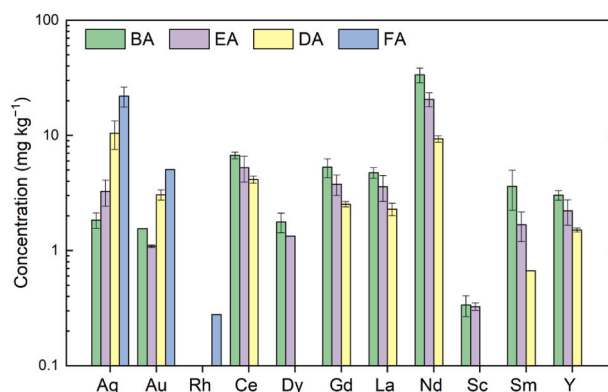
The chemical results are generally separated into 2 elemental categories. The elements which are not detectable (under detection limits) in all the samples are classified into the first metal division. This classification consists of some NMs (Ir, Os, Pd, Pt, and Ru) and REEs (Er, Eu, Ho, Pr, Tb, Tm, and Yb). No further investigation nor discussion was made for this metal group. The second chemical categorization comprises a couple of noble metals (Ag, Au, and Rh) and several rare earth metals (Y, Sm, Sc, Nd, La, Gd, Dy, and Ce) which are detectable in at least one sample. The second metal group was used for further investigations and calculations.

**Table 2**

The average metal concentration and its standard deviation of the solid remains (FA-fly ash, DA-deposited ash, EA-after heat exchanger ash, and BA-bottom ash) obtained from the three similar combustion experiments utilizing B1 sample (average values of combustion parameters: firing rate  $Q = 12.8$  kW, combustion temperature  $T_c = 664$  °C, flue gas temperature  $T_f = 118$  °C).

Element		Mean $\pm$ SD (mg kg <sup>-1</sup> )			
Symbol	Name	BA	EA	DA	FA
<b>Noble metals</b>					
Ag	Silver	1.84 $\pm$ 0.28	3.26 $\pm$ 0.83	10.45 $\pm$ 2.89	21.93 $\pm$ 4.29
Au	Gold	1.55	1.09 $\pm$ 0.03	3.05 $\pm$ 0.31	5.05
Rh	Rhodium	<0.01*	<0.01*	<0.01*	0.28
<b>Rare earth elements</b>					
Ce	Cerium	6.72 $\pm$ 0.45	5.26 $\pm$ 1.32	4.13 $\pm$ 0.29	–
Dy	Dysprosium	1.77 $\pm$ 0.34	1.34	<2*	<7.5*
Gd	Gadolinium	5.29 $\pm$ 0.98	3.76 $\pm$ 0.76	2.53 $\pm$ 0.13	<0.2*
La	Lanthanum	4.74 $\pm$ 0.5	3.58 $\pm$ 0.91	2.29 $\pm$ 0.29	–
Nd	Neodymium	33.57 $\pm$ 4.94	20.57 $\pm$ 2.89	9.32 $\pm$ 0.61	–
Sc	Scandium	0.34 $\pm$ 0.07	0.33 $\pm$ 0.02	<0.01*	–
Sm	Samarium	3.61 $\pm$ 1.37	1.68 $\pm$ 0.48	0.67	<0.2*
Y	Yttrium	3.02 $\pm$ 0.29	2.21 $\pm$ 0.54	1.51 $\pm$ 0.06	–

<\*: below detection limit; "–" not available; Mean: the average value; SD: standard deviation.



**Fig. 4.** The average metal concentration of the solid remains obtained from the three similar combustion experiments utilizing pellet B1.

### 3.1. The fate of NMs and REEs during combustion utilizing contaminated biomass

The metal concentrations of solid remains obtained from the three combustion experiments utilizing pellet B1 are given in Table 2 and Fig. 4. Several NMs such as Ag, Au, and Rh were identified in the ash samples. Rhodium was solely detectable in FA with a level of 0.28 mg kg<sup>-1</sup>. This is a valuable finding from the scientific point of view since this element was rarely reported before. Other noble metals, including Ag and Au, were found in each ash sample. The highest concentrations of Ag (21.93 mg kg<sup>-1</sup>) and Au (5.05 mg kg<sup>-1</sup>) were observed in FA. These numbers are 12 and 3 times greater than the metal grades in bottom ash for Ag and Au, respectively. In general, the higher concentration of the detectable NMs in FA, DA, and EA compared to that in BA indicates these metals can leave the combustion chamber.

Some rare earth metals were observed in the derived residues. The highest concentrations were found for neodymium, with 9.32 mg kg<sup>-1</sup> in DA, 20.57 mg kg<sup>-1</sup> in EA, and 33.57 mg kg<sup>-1</sup> in BA. Conversely, scandium was observed in trace grades in the combustion ashes. The concentrations of rare earth minerals in FA are either unavailable or fall under detection limits. The behavior of these elements in the system shows a consistent trend, their concentrations follow the decreasing orders of BA > EA > DA (Fig. 4). The greater metal concentrations in BA versus other solid remains indicates the minor volatility of REE compounds during biomass combustion.

The identified elemental concentrations in EA, DA, and FA also indicate that a noticeable amount of valuable metals might leave the combustion chamber, which later ends up at other positions of the burning system and emits into the environment in large part. Basically, throughout the combustion process, a portion of the metals input in biomass stays in the chamber of combustion and can be captured with BA. The other part goes through the water heat exchanger and is partially found in the ash collected after the water heat exchanger. The fly ash captured from flue gas contains a certain metal content. Another quantity of metals is detected in deposited ash, which is taken from the surfaces of the flue gas system. Eventually, the remaining metal proportion in both solid and volatile forms along with flue gas leaves the burning system.



**Table 3**  
Metal concentrations of solid samples collected from biomass combustion experiments.

Sample		Concentration (mg kg <sup>-1</sup> )									
		Ag	Au	Ce	Dy	Gd	La	Nd	Sc	Sm	Y
WB	B1	<0.5*	<0.05*	0.526	<1*	0.026	<0.25*	<0.5*	<0.01*	0.026	<0.25*
	B2	<0.5*	<1*	<0.5	<1*	<0.5*	<0.25*	<1*	<0.25*	<0.5*	<0.25*
BA	10-kW	3.87	<1*	4.72	2.08	6.06	3.96	26.5	0.271	2.59	2.37
	20-kW	2.94	<1*	6.4	2.22	7.49	5.23	30.7	0.372	3.12	3.13
	30-kW	2.01	1.52	6.42	2.5	7.5	5.08	39.1	0.404	5.79	3.11
	20-kW*	1.32	<1*	16.1	<1*	7.64	8.53	6.57	2.04	1.55	5.83
EA	10-kW	5.13	2.64	1.69	<1*	2	1.29	9.39	<0.25*	<0.5*	0.961
	20-kW	8.44	<1*	5.58	1.4	5.3	3.84	18.4	0.38	1.64	2.51
	30-kW	11.4	1.34	4.98	1.82	5.6	3.85	30.5	0.384	2.68	2.39
	20-kW*	1.78	<1*	10	<1*	5.03	5.08	4.24	1.26	0.905	3.52
DA	10-kW	12.4	1.9	2.17	<1*	2.5	1.54	7.51	<0.25*	<0.5*	1.08
	20-kW	15.4	3.04	1.61	<1*	1.56	1.07	4.02	<0.25*	<0.5*	0.809
	30-kW	23.6	2.98	3.42	<1*	3.42	2.45	12.5	<0.25*	0.787	1.49
	20-kW*	3.46	<1*	4.18	<1*	2.34	2.22	1.61	0.508	<0.5*	1.46
FA	10-kW	24.3	<9*	<4.5*	<9*	<4.5*	<3*	<9*	<3*	<4.5*	<3*
	20-kW	19.2	3.52	<1.5*	<3*	<1.5*	<1*	<3*	<1*	<1.5*	<1*
	30-kW	13.1	<9*	<4.5*	<9*	<4.5*	<3*	<9*	<3*	<4.5*	<3*
	20-kW*	2.94	<9*	<4.5*	<9*	<4.5*	<3*	<9*	<3*	<4.5*	<3*

< \*: Below detection limit; WB: woody biomass, B1: biomass collected from a brownfield land, B2: biomass provided by a wood pellet manufacturer (MBH Zrt company); FA, DA, EA, and BA: fly ash, deposited ash, after exchanger ash, and bottom ash, respectively; 10-kW, 20-kW, 30-kW: combustion experiments of 10 kW, 20 kW, and 30 kW utilizing pellet B1; 20-kW\*: combustion experiment of 20 kW utilizing pellet B2.

### 3.2. Influence of combustion parameters and feedstocks on the behavior of NM and REEs during biomass combustion

Basically, three combustion experiments utilizing biomass B1 were conducted with three boiler performance levels of 10 kW, 20 kW, and 30 kW to study the effect of combustion variables, specifically the firing rate on the metal flows. The influence of feedstocks was investigated by comparing the results of the two experiments carried out under the same 20 kW firing rate but using different feedstocks of pellet B1 and pellet B2. The levels of NMs and REEs in the collected solid samples are given in Table 3.

#### 3.2.1. Influence of combustion parameters

The concentration of individual metals in the solid remains captured from the three different combustion experiments utilizing pellet B1 conducted with the firing rate of 10 kW, 20 kW, and 30 kW is visualized in Fig. 5. On the basis of the figure, the concentration of Ag in BA and FA collected from the 10-kW experiment is significantly greater compared to the higher performance levels. The opposite trend was observed in the case of EA and DA indicating a strong combustion parameter dependence. That could be explained by that Ag rather escapes the firing chamber, thus the higher firing rate or combustor temperature results in less Ag concentration in BA. On the other hand, low flue gas temperature (<100 °C) in the low-performance case enhances metal condensation leading to higher Ag concentrations in FA. In the case of Au, the dependence is minor and uncertain, further experimental and theoretical examinations are required for a better understanding of the behavior of this element.

REEs show a consistent trend during biomass incineration utilizing pellet B1 as seen in Fig. 5. REEs are low volatile metals, their concentrations in BA, EA, and DA tend to increase with the performance of the boiler. Rare earth elements are below detection limits in all fly ash samples. High-performance levels or combustor temperatures have an advantage for the enrichment of REEs from biomass into solid residuals.

#### 3.2.2. Influence of feedstocks

The chemical analysis results of the solid samples obtained from the two same firing rate experiments utilizing different materials of pellet B1 collected from a contaminated land and pellet B2 provided by a manufacturer are compared. The comparison aims to investigate the effect of feedstocks on the distribution of valuable metals during biomass incineration. Based on Table 3, concentrations of NMs in solid samples of the biomass combustion using pellet B1 are substantially greater compared to that of the combustion utilizing pellet B2. Silver levels fold approximately 2, 5, 4, and 7 times in BA, EA, DA, and FA, respectively. Gold is undetectable in samples of the experiment employing B2 biomass, but this element is found in the ashes of combustion utilizing B1 biomass. The superior concentrations of NMs in contaminated solid samples indicate that the harvested contaminated biomass is favorable for the investigation of precious metals. Developing NM hyperaccumulators is also necessary to increase the concentrations of NMs in biomass ashes.

The behavior of NMs and REEs during incineration using pellet B1 and pellet B2 performs the similarity as seen in Table 3. The concentrations of NMs in FA and DA are greater versus in EA and BA. On the contrary, the concentration of rare earth metals consistently follows the descending orders of BA > EA > DA > WB. The findings completely align with the previous outcomes described in section 3.1.

Enrichment factor (EF) is the ratio of the metal concentration in the ash to that in biomass as seen in the equation below. This metric is utilized to characterize the effectiveness of the enrichment process in enhancing concentrations of metals.

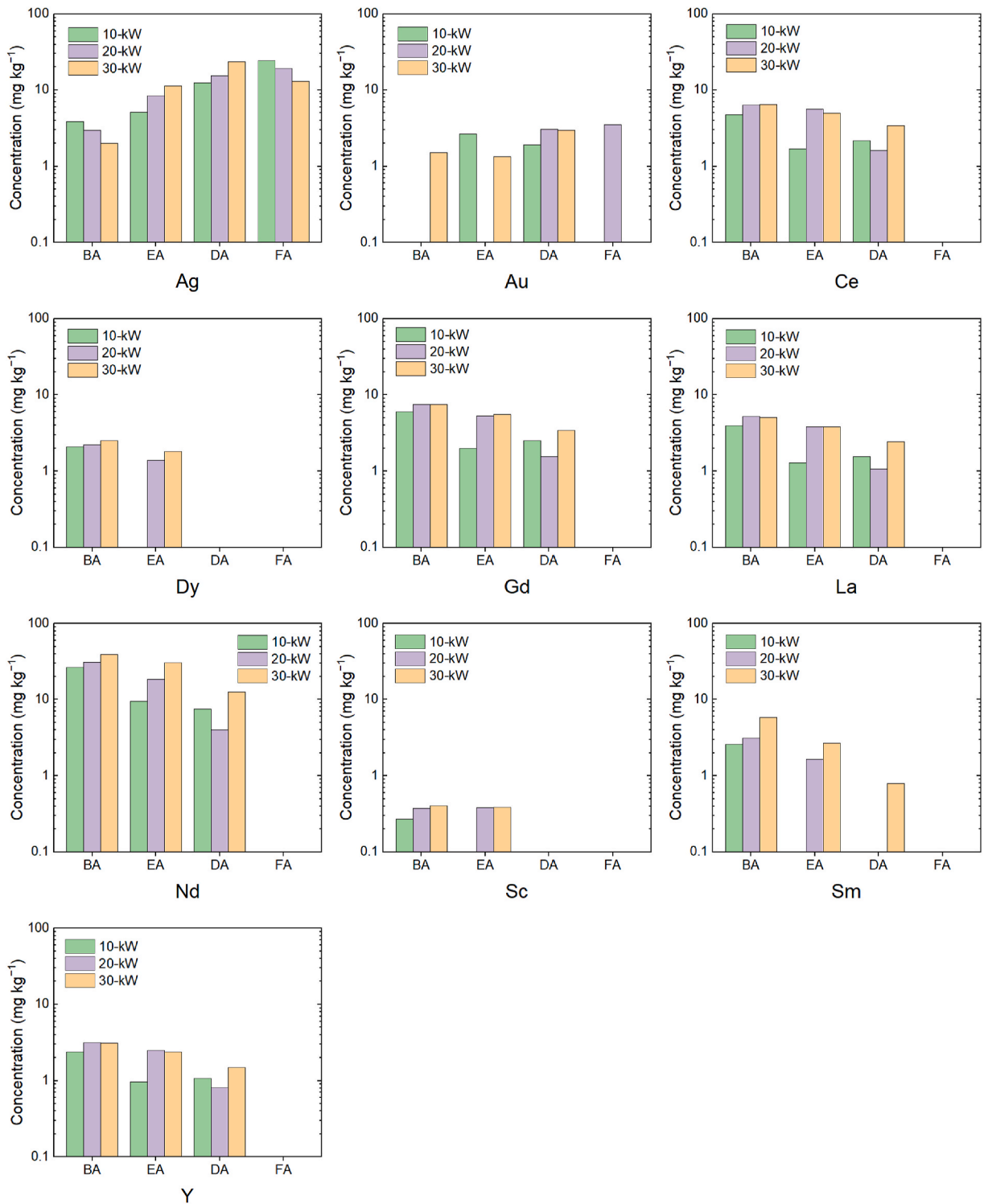


Fig. 5. The concentration of NMs and REEs in the solid remains under different conditions of combustion utilizing pellet B1.

**Table 4**  
The enrichment factor of 20 kW experiments utilizing B1 pellet and B2 pellet.

Metal	BA		EA		DA		FA	
	B1	B2	B1	B2	B1	B2	B1	B2
Ag	5.9*	2.6*	16.9*	3.6*	30.8*	6.9*	38.4*	5.9*
Au	-	-	-	-	60.8*	-	70.4*	-
Ce	12.2	32.2*	10.6	20.0*	3.1	8.4*	-	-
Dy	2.2*	-	1.4*	-	-	-	-	-
Gd	288.1	15.3*	203.8	10.1*	60.0	4.7*	-	-
La	20.9*	34.1*	15.4*	20.3*	4.3*	8.9*	-	-
Nd	61.4*	6.6*	36.8*	4.2*	8.0*	1.6*	-	-
Sc	37.2*	8.2*	38.0*	5.0*	-	2.0*	-	-
Sm	120.0	3.1*	63.1	1.8*	-	-	-	-
Y	12.5*	23.3*	10.0*	14.1*	3.2*	5.8*	-	-

\* Minimum enrichment factor; Colouring rule: red > yellow > green; BA, EA, DA, and FA: bottom ash, after exchanger ash, deposited ash, and fly ash, respectively; B1: biomass collected from a brownfield land, B2: biomass provided by a wood pellet manufacturer (MBH Zrt company).

$$EF = \frac{MA}{MB} \quad (1)$$

where:

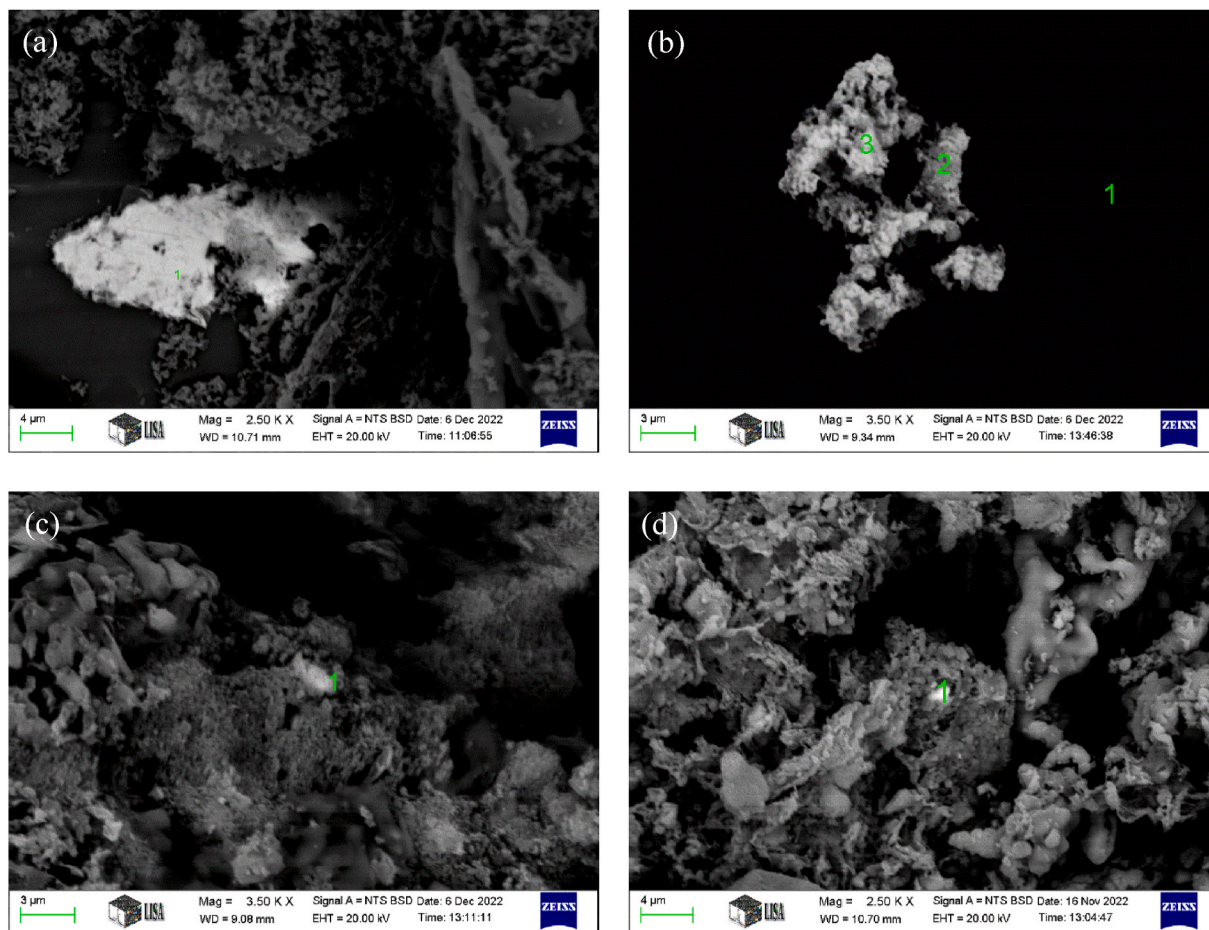
- EF: Enrichment factor
- MA: Metal concentration in ash ( $\text{mg kg}^{-1}$ )
- MB: Metal concentration in biomass ( $\text{mg kg}^{-1}$ )

All NMs and most REEs were not detectable in biomass materials. However, due to the incineration process, their levels increased sufficiently to be identifiable in one sample of the resulting ash at least. Their EFs in this case are computed using the detection limits, which represent the worst-case scenarios or the lowest possible values. The EFs of 20 kW combustion experiments utilizing pellet B1 and pellet B2 are shown in Table 4, the magnitudes are color-coded in ascending order, ranging from green to yellow and red. The EFs exhibit a broad range of variation, spanning from roughly one to nearly 300. The exceptional outcomes were obtained for Gd (EF-DA = 60, EF-EA = 203.8, and EF-BA = 288.1) and Sm (EF-EA = 63.1 and EF-BA = 120) for combustion utilizing pellet B1. Additionally, the minimum enrichment factors of NMs are relatively high in terms of DA and FA obtained from the combustion using B1 biomass (Ag: EF-DA = 30.8, EF-FA = 38.4; Au: EF-DA = 60.8, EF-FA = 70.4). Conclusively, the significant EFs demonstrate the efficacy of the combustion process in concentrating valuable metals from biomass into solid residues, which is favorable for subsequent stages of extracting and reclaiming high-value metals from biomass combustion ashes.

### 3.3. SEM-EDS analysis of contaminated combustion ash samples

SEM-EDS examination aims to investigate forms of valuable metals in the ashes derived from the combustion utilizing pellet B1 (contaminated ashes) as well as to find evidence for the ICP measurement outcomes. Gold was found in all the contaminated bottom ashes even in the samples where Au was below the detection limit. Fig. 6a is an imaging example of gold in bottom ash obtained from combustion experiments utilizing pellet B1. Gold was observed in the bottom ash in pure particle form having minor elemental contaminations. The depicted particle contains >95 % of Au. Other similar particles were detected in BA samples indicating that gold





**Fig. 6.** SEM imaging examples of (a) Au in BA; (b) Au in FA; (c) Ag in FA; (d) Ce in BA.

clearly forms neat particles in the bottom ash. This finding also means that the extraction of gold from bottom ashes as a subsequent processing step might be significantly easier and might open novel pathways in gold phytomining.

Gold was also observed in the contaminated fly ash sample as seen in Fig. 6b, where number 1 in the figure represents the surrounding vicinity containing mainly carbon. Meanwhile, the highlighted numbers 2 and 3 denote the presence of gold in the fly ash particle. Unlike in bottom ash, the formation of gold in fly ash behaves differently. This precious metal was primarily found as a thin coating on potassium sulphate. The association of gold and potassium sulphate might stem from their almost identical melting point (1064 °C for Au and 1069 °C for  $K_2SO_4$ ).

Silver was detected only in the contaminated fly ash sample via SEM-EDS analysis (Fig. 6c). This element is typically associated with potassium sulphate as well in a form of a coating on the surface of the particle. Its behavior is similar to the formation of gold in fly ash.

In addition to NMs, SEM-EDS examination showed REEs in the contaminated residues, an example can be seen in Fig. 6d, where cerium can be seen as a coating on a particle surface primarily associated with calcium, oxygen, and potassium. The presence of REEs in contaminated biomass ashes is difficult to observe. That might arise from these elements are associated or intermixed with other substances becoming an integral part of solid particles or a surface phenomenon. The question about the occurrence of REEs is in limbo, which requires further theoretical and experimental studies.

#### 4. Conclusion

Biomass harvested from a brownfield land and biomass provided by a wood pellet manufacturer were incinerated in a pilot-scale boiler to investigate the fate of NMs and REEs. Woody biomass and solid remains from various points of the combustion and flue gas system were captured and analyzed. The analytical results show that the concentrations of NMs in FA, DA, and EA are higher than in BA. Meanwhile, the higher levels in BA compared to other solid remains indicates the minor volatility of REE compounds during the combustion of biomass.

The significant EFs demonstrate the efficiency of the process of combustion in concentrating NMs and REEs from biomass into solid

residuals. The highest numbers were found for Gd (EF-DA = 60, EF-EA = 203.8, and EF-BA = 288.1). NMs such as Ag and Au also had relatively high enrichment factors (Ag: EF-DA = 30.8, EF-FA = 38.4; Au: EF-DA = 60.8, EF-FA = 70.4). Elevated levels of NMs and REEs in biomass-derived ashes are advantageous for subsequent stages of extracting and reclaiming these valuable metals from unconventional resources. Combustion parameters and feedstocks have substantial effects on the distribution of NMs and REEs during the incineration of biomass. For Ag, the greater firing rate results in less concentration in BA and FA, but higher levels in EA and DA. Meanwhile, the levels of rare earth metals in biomass-derived ashes tend to increase with boiler performance. Under the same firing rate condition, the concentrations of NMs in the ashes captured from the combustion utilizing pellet B1 collected from a contaminated land are remarkably greater than that of the one using pellet B2 provided by a manufacturer. It indicates the cruciality of the harvested contaminated biomass for phytomining.

SEM-EDS examination demonstrates that gold forms individual particles in the bottom ashes with at least 95 % purity. Noble metals comprising Ag and Au are observed as a coating on particle surfaces of FA. The SEM-EDS outcomes are vital to comprehending the formation of valuable metals during contaminated biomass incineration.

In the following stage, biomass-derived ashes will be subsequently subjected to the extraction process to recover high-value metals. It will be the last brick to complete the entire phytomining pathway for reclaiming NMs and REEs from secondary minerals.

### Additional information

No additional information is available for this paper.

### CRedit authorship contribution statement

**Truong Dinh:** Data curation, Formal analysis, Investigation, Writing - original draft, Visualization, Writing - review & editing. **Helga Kovacs:** Conceptualization, Methodology, Resources, Writing - review & editing, Project administration. **Zsolt Dobo:** Conceptualization, Investigation, Methodology, Writing - review & editing, Supervision.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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