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**MINERALOGICAL AND CHEMICAL
CHARACTERIZATION OF BOTTOM ASHES
FROM WASTE INCINERATION**

Caratterizzazione Chimica e Mineralogica delle ceneri pesanti
provenienti dalla combustione dei rifiuti

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PREFACE

Waste generation is, today, a hot topic, strongly linked to environmental problems. Wastes have been produced since the dawn of civilization: the increasing world population and global development occur together with an increasing production of man-made objects, which at the end of their life become waste. Increasing industrial production in the last two centuries pose the problem of their disposal, and in more recent times of their management. Waste management is nowadays a global topic together with that of climatic changes and georesource shortage: it is foreseen to become more and more critical in response to the improvement in life standard in developing countries and in the increased consumption of raw materials.

Waste management is a complex issue, aiming to reduce the production and to recycle and reuse the waste, avoiding or minimising any dispersion in the environment. The goal in waste management can be summarised in the mantra “from waste to resource”.

Prominent among improvements and innovations concerning waste management are Waste-to-Energy (WtE) plants, systems that generate energy from the combustion of solid waste, mostly municipal. In WtE plants the solid waste is burned, with a positive energy balance, coming from the combustion of the wastes, which is used for the energy production. However, like any anthropogenic activity, this process generates wastes: Bottom Ashes and Fly Ashes. BA are the residual ashes in the bottom part of the combustion chamber, whereas FA are the residuals blowing out from the chamber. Also, BA from Municipal Solid Waste Incinerator (MSWI) can be recycled. Due to their physical and chemical-mineralogical characteristics, BA can be used as a secondary source of raw material or recycled into construction and cementitious materials. However, their recycling may be compromised due to the presence of Potential Toxic Elements (PTE), i.e. chromium, lead, and zinc, as their release may be harmful to the environment and human health.

The aim of this thesis is to provide a systematic and in-depth study on the BA, with special focus on the medium-fine fraction ($< 4\text{mm}$). This work has two goals, the mineralogical characterization of the BA and the assessment of their potential release. In both, special attention was paid to PTE. The goals are closely related, as the information on the mineralogical phases hosting the PTE is a key point for interpreting and assessing the potential release of the BA in the environment.

In this work BA from 5 WtE plants in Northern Italy were sampled and sorted by grain size. Each sampling was analysed by Thermo Gravimetric Analysis (TGA), X-Ray Powder Diffraction (XRPD), X-Ray Fluorescence (XRF), Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM - EDS) and X-ray Absorption. Synchrotron based Near Edge Spectroscopy (XANES) analyses were further conducted, to obtain a full chemical and mineralogical information.

The potential release of BA was investigated on particle sizes < 4mm by leaching test and sequential extraction procedure. From the results obtained, we found that several elements exceed the legal limits (chlorides, copper) already in the leaching test, where extraction is conducted only with ultrapure water at neutral pH.

The relation between grain size, composition, and leaching potential were assessed in the ashes to discuss the potential of grain size sorting in high value applications of them.

This thesis is organised as follows. In the **first chapter** the concept of waste is introduced, together with the figures on global and national waste production. The operational procedures and different types of waste-to-energy plants are described, and the characterization of BA is introduced. A literature review on the current state of the art on chemical, physical and mineralogical characteristics, together with the possible environmental problems and reuses of the BA is addressed.

In the **second chapter** the materials and methods used in this work are outlined, in what they are common to this investigation. Specific aspects are further discussed in the sub-chapters 3.1, 3.2, 3.3 and 3.4.

The **chapter 3** shows the results and discussion of the different topics addressed in this investigation. It is divided in four subchapters, each corresponding to a paper published, submitted, or in preparation. In the subchapter 3.1 the paper “*Particle size and Potential Toxic Element speciation in Municipal Solid Waste Incinerator (MSWI) Bottom Ash*”, published in 2021 in the journal Sustainability, is reported, giving a mineralogical characterization of the BA, with different grain size, from the Parma WtE plant. In the sub-chapter 3.2 the version submitted to the journal Frontiers of the paper “*Toward a deep characterization of bottom ashes from municipal solid waste incineration: new data from 5 plants of Northern Italy*” is reported. The BA from the WtE plants of Parma, Piacenza, Torino, Forlì-Cesena and Ferrara were examined. The mineralogy, geochemistry and leaching behaviour of the ashes were compared, and the trend outlined in the sub-chapter 3.1 were discussed in their generalization. In the sub-chapter 3.3 the version submitted to the journal Science of Total Environment of the paper “*Potential Toxic Elements speciation in Bottom Ashes from Municipal Solid Waste Incinerator: a combined SEM-EDS, XRF and XANES study*”, is reported. This investigation discusses the mineralogy of the PTE, combining a SEM-EDS information on the mineralogy of the host phases, with synchrotron based μ -XRF and XANES data, to outline the local distribution and mineralogy of the PTE at concentrations of the order of few ppm. In the sub-chapter 3.4 the results of a sequential extraction procedure on the BA from Parma and Piacenza are reported, and discussed together with a correlation between elements and grain size in the bulk material and in the leached products. A new protocol for the sequential extraction procedure in BA is proposed.

Finally, the *fourth chapter* reports the general conclusions from this work with a final focus on problems in the recycle of the BA.

1 INTRODUCTION

1.1 AGE OF HUMANS

Humanity is now a dominant geological actor, as human activities induce great, multiple and irreversible changes on Earth. The study of these human-associated changes led to the suggestion that we should not refer to the present time as pertaining to the Holocene epoch but to a new geological epoch called the “*Anthropocene*” (Crutzen, 2002; Steffen, 2021; Trischler, 2016; Zalasiewicz et al., 2011). In 2000, the first to propose the idea of the Anthropocene were the atmospheric chemist Paul Jozef Crutzen and the limnologist Eugene Filmore Stoermer; since then, the geological community has begun to take an increasing interest in this issue, analysing scientific evidence leading to a definition of the Anthropocene and establishing the “*Anthropocene Working Group*” (Trischler, 2016).

Other scientific branches (biology, ecology, ethology) also began to study the correlation between environmental changes and human activities and the idea of Anthropocene is now accepted and shared by most of the scientific community. However, the scientific debate is still open on establishing the “*starting point*” of this new epoch.

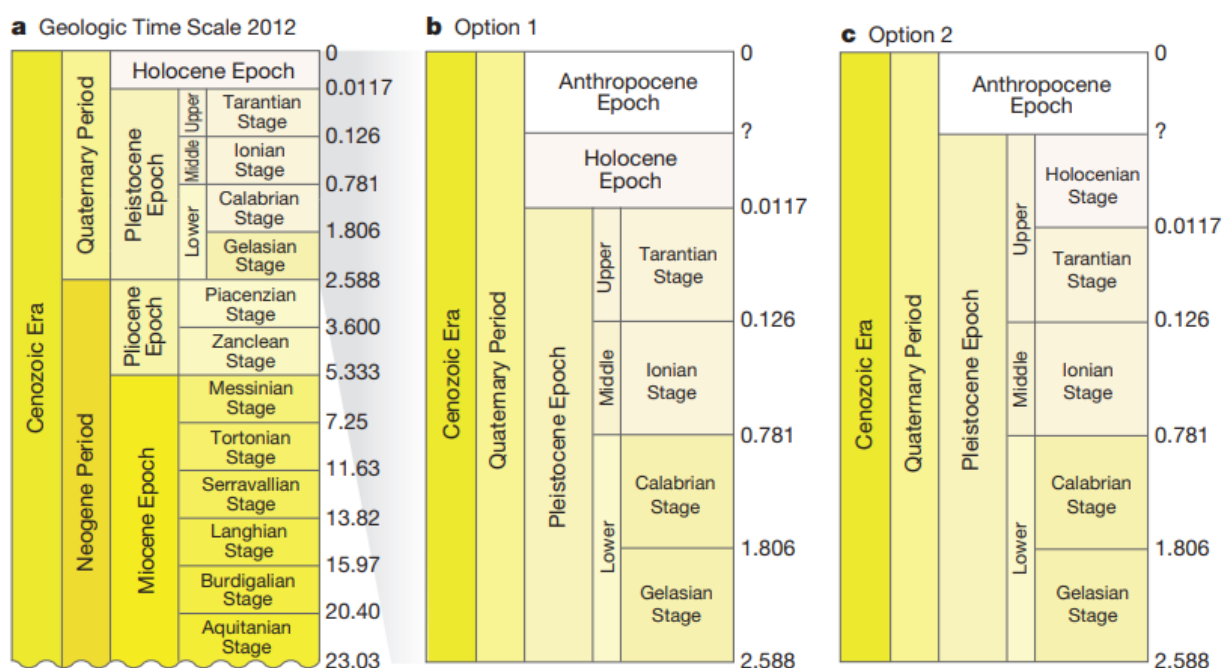


Figure 1.1.1 Comparison of the current Geologic Time Scale with two alternatives. (Lewis & Maslin, 2015)

For example, in **Figure 1.1.1** the current Geological Time Scale 2012 (a) is compared with two possible scenarios. In the first alternative (b) the Anthropocene Epoch directly follows the Holocene

Epoch, while in the second case the Holocene falls within the Pleistocene Epoch which is followed by the Anthropocene Epoch (Lewis S. L. & Maslin M. A., 2015).

To define where the “starting point” is, it is necessary to find the measurable signal of anthropic impact in the geological strata and how it is markedly different from the Holocene strata of the last 11.700 years.

Stratigraphic signatures were found in relation to:

- alterations in the processes of sediment creation, (i.e. due to eutrophication from fertilisers), use of dams sediment, erosion due to mining or deforestation;
- altered geochemical signals in sediments and ice caps, as the increase in polycyclic aromatic hydrocarbons, pesticide residues, nitrogen and phosphorus;
- presence in sediments and ice of radionuclides released by nuclear bomb testing;
- changes in the carbon cycle based on data from ice core samples;
- increase in global temperature and rising sea levels;
- alterations in biodiversity, for example homogenization due to agriculture and animal husbandry, and supplanting of established biota by invasive species introduced by humans
- new materials, such as elemental aluminium, concrete, plastic, slags, particulate matter and carbon particles (Trischler H., 2016).

The term “new materials” refers to a set of anthropogenic materials, which do not exist in nature, designed by man through the development of research and technology and born to satisfy the needs of our society. Among them, the BA of MSWI, which are the subject of this thesis.

1.2 GLOBAL WASTE PRODUCTION

An important input of anthropic material in environmental matrices is given by the production of waste. For the directive of the European Parliament and of the Council 2008/98/EC and for the Italian D. Lgs. 152/06 waste is *“any substance or object which the holder discards or has decided or is required to discard”*.

The production of waste occurred since the dawn of civilization, but now it increases due to the process of urbanisation, economic and demographic growth. World waste production in 2016 amounted to 2.01 billion tons. By 2050, waste generation across the world is expected to reach 3.40 billion tons (Kaza et al., 2018).

Wastes differ primarily by their composition. Waste composition is given by the material types making the waste. It is generally determined through a standard audit, in which samples of garbage are taken from generators or final disposal sites, sorted into predefined categories, and weighed (Kaza S. et al., 2018). The waste composition determines its final destination and method of disposal.

However, globally, almost 40% of waste is simply disposed of in landfills or open dumps (**Figure 1.2.1**). About 19% undergoes recovery through recycling and composting, and 11% is treated through modern incineration (Kaza S. et al., 2018).

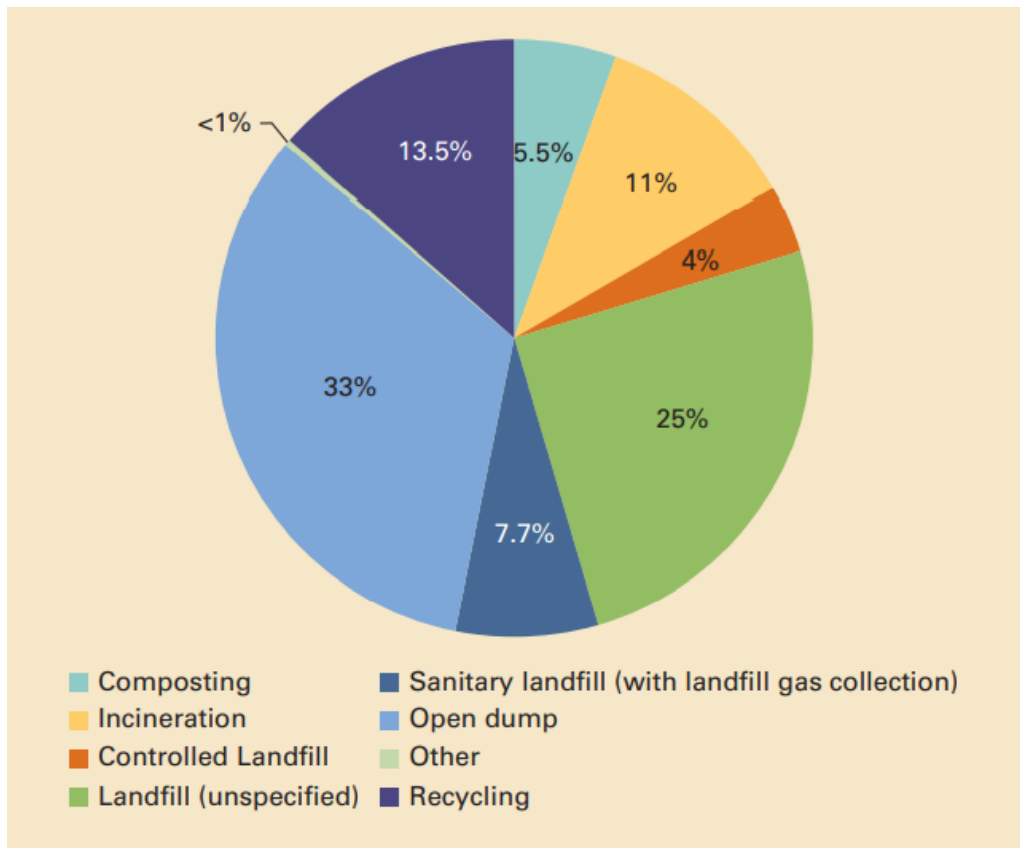


Figure 1.2.1 Global Waste Treatment and Disposal (Kaza S. et al., 2018)

The industrial plants that allow the incineration process can be divided in two categories:

- *incinerators*, older plants that simply reduce the mass and volume of incoming waste;
- *Waste-to-Energy (WtE) plants*, modern plants that reduce the mass and volume of waste obtaining energy as heat and electricity, from the combustion process.

1.3 EUROPEAN AND ITALIAN WASTE MANAGEMENT

In 2020, EU waste production amounted to 2.515 million tons. Most of the waste produced in Europe comes from construction and mining activities, with percentages equal to 37.1% and 23.4% respectively (**Figure 1.3.1**) (Eurostat, 2021).

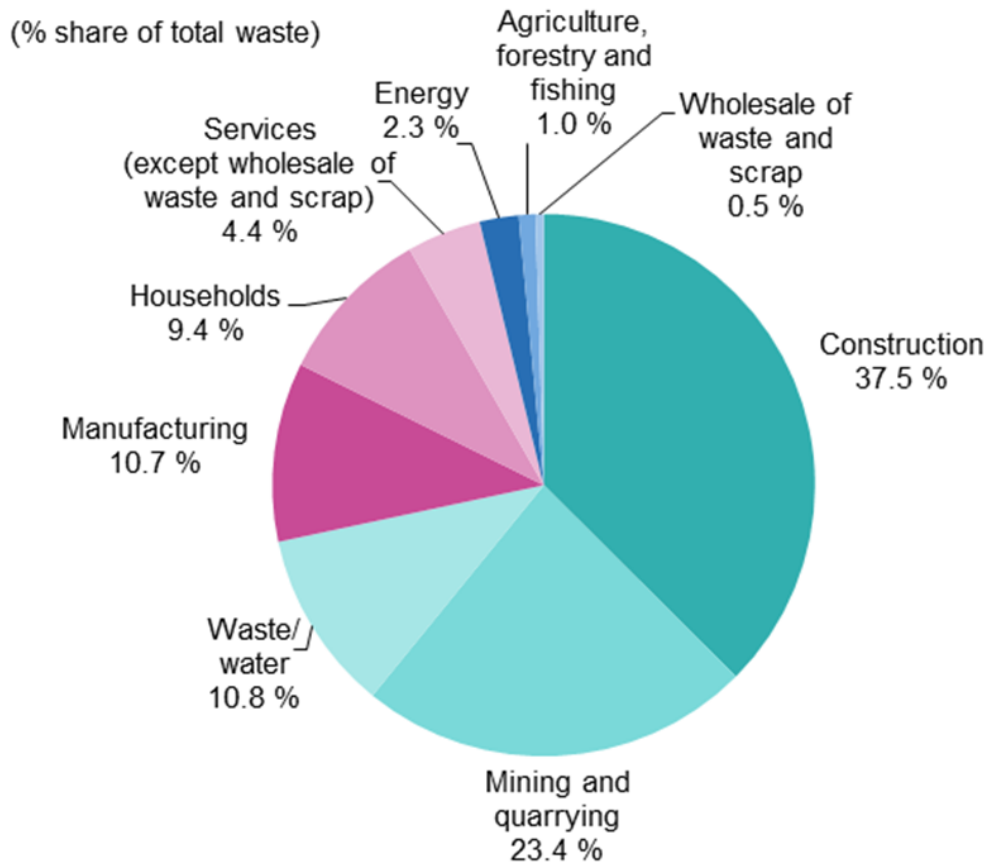


Figure 1.3.1 European waste generation by economic activities and household, 2020. (Eurostat, 2021)

The EU policy strategy for waste reduction and management is based on the following principles, in order of preference:

- *prevention*: measures taken to prevent the production of waste aimed at reducing the quantity and negative impacts on environmental matrices and on humans;
- *reuse*: operations (control, cleaning, disassembly, repair) through which an object, or components of an object, which would become waste is prepared for reuse without treatment;
- *recycling*: waste recovery operations aimed at obtaining products, materials and substances that can be used both for their original function and for other purposes;
- *recovery*: waste recovery operations other than recycling, such as energy recovery or solvent regeneration;
- *disposal*: where all the previous measures fail, the waste is disposed of in landfills. This is an actual failure in the waste management, and should be avoided as much as possible.

In 2020, 2.029 million tons of waste were treated in the EU. It should be noted that this value also includes waste imported from other nations and not produced in Europe; for these reasons it's difficult to create a direct link between waste production and treatment.

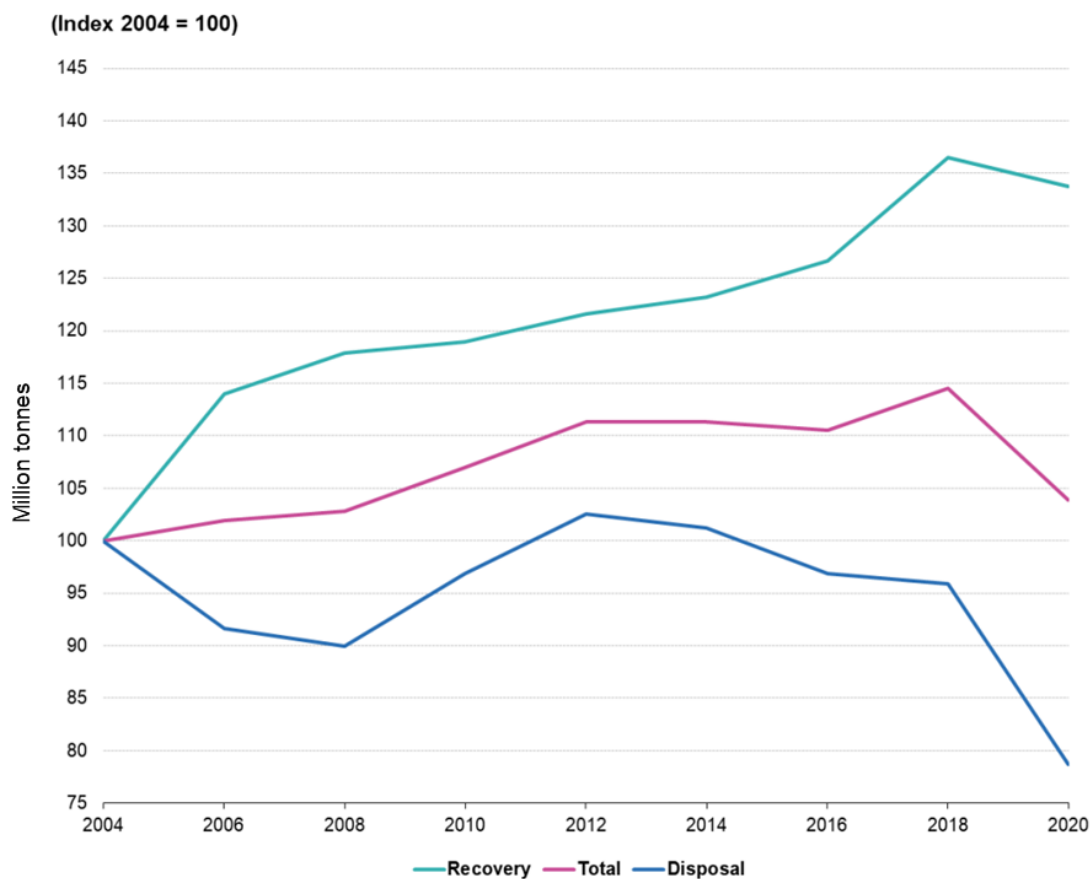
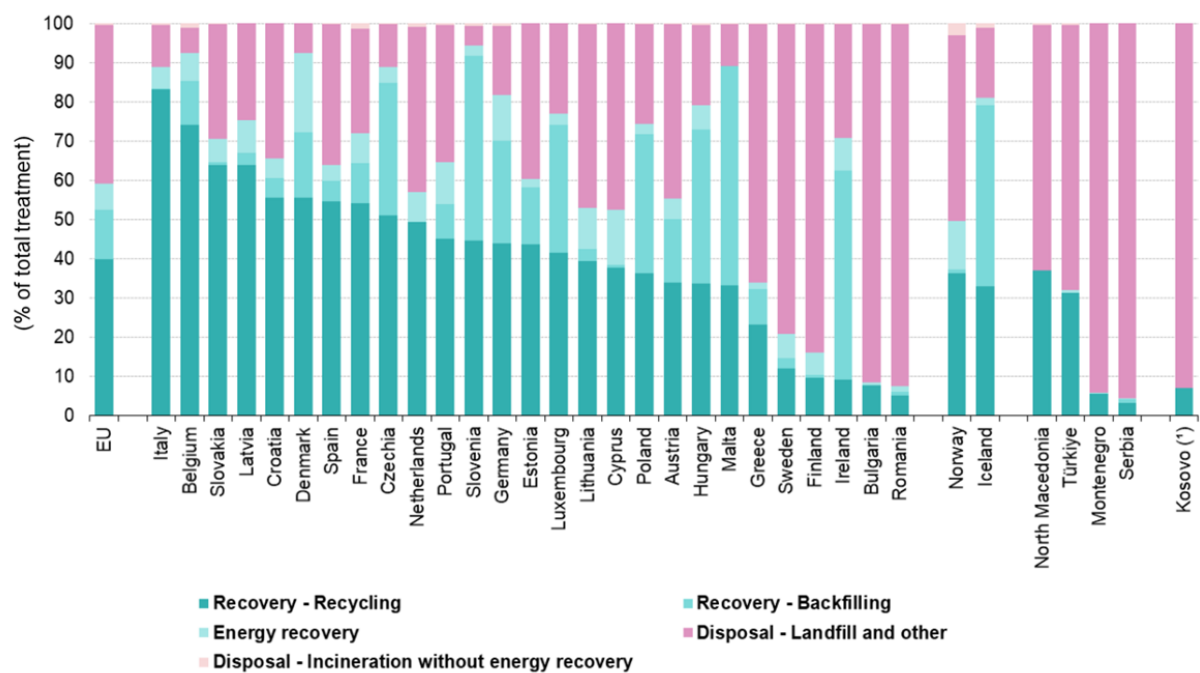


Figure 1.3.2 European waste treatment, 2004-2020. Relative percentage respect to the value in 2004 (Eurostat, 2021).



(*) This designation is without prejudice to positions on status, and is in line with UNSCR 1244/1999 and the ICJ Opinion on the Kosovo Declaration of Independence.

Figure 1.3.3 Waste treatment by type of recovery and disposal for each State of EU, 2020. (Eurostat, 2021)

The waste recovered (recycled, used to backfilling and recovered energy) grew by 40.3% from 870 million tons in 2004 to 1.221 million tons in 2020. In particular, 39.2% of the waste produced was sent for recycling, 14.6% was used for filling and 6.4% was used in energy recovery (**Figure 1.3.2**). Of the remainder, 39.8 was sent to landfill, 0.5% was incinerated without energy recovery and 8.1% was disposed in other ways (Eurostat, 2021).

As it can be seen in **Figure 1.3.3** the situation is heterogeneous among the different member states of the European Union.

In EU wastes are classified according to their:

- *origin*:

Urban waste: undifferentiated household waste (Municipal Solid Waste – MSW) and separate waste collection; waste from street sweeping and emptying waste bins; waste of any nature or origin, lying on roads and public areas, waste from the maintenance of public parks; waste from cemetery areas (D.Lgs 152/06);

Special waste: agricultural; waste from artisanal and industrial production; waste produced by commercial activities; waste produced by service companies; construction and demolition waste; waste produced by the disposal of waste itself; medical waste; sewage sludge (D.Lgs 152/06).

- *hazardousness*:

Hazardous: waste that contains a high percentage of pollutants. Oil waste, chemical industry waste, metallurgical industry waste, used oil, solvents, wastewater, sanitary waste, veterinary waste are classified as hazardous waste.

Non-hazardous: wastes that don't contain substances considered hazardous.

Each type of waste is marked with the “*European Waste Catalogue*” (EWC) code. EWC code provides a standardised description of the waste which is useful to decide the most appropriate type of treatment. Usually, the wastes that are sent to an energy recovery process are MSW and non-hazardous special waste.

In 2020, Italy produced 28.9 million tons of urban waste, recording a decrease of 3.6% compared to 2019 (ISPRA, 2021). In 2019, Italian special waste production was 164 million tons with an increase of 7.3% compared to previous years; in detail 154 million tons of non-hazardous special waste and 10 million tons of hazardous special waste was produced (ISPRA, 2021). Of the waste product, 6.25 million tons of urban waste and 2.04 million tons of special waste were incinerated with energy recovery (ISPRA, 2021).

1.4 WASTE TO ENERGY PLANTS

First generation incinerators were born to reduce waste mass and volume and the energy recovery wasn't a goal. Modern incinerators, called WtE plants, reduce mass and volume of input waste up to 25% and recover energy from waste in the form of heat and electricity (Brunner & Rechberger, 2015).

Figure 1.4.1 represents a schematic image of the WtE plant.

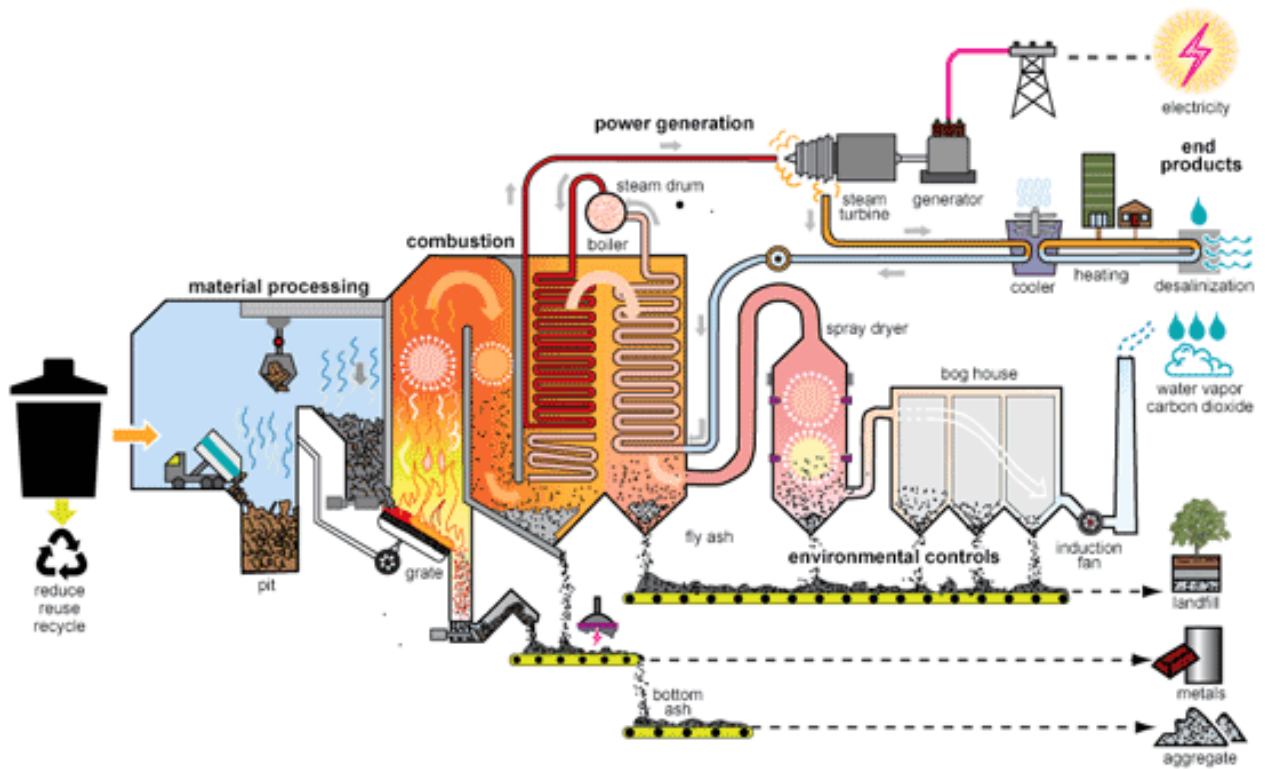


Figure 1.4.1 Waste to Energy plant. (Source: www.eia.gov)

A WtE plant is made by different sections involving:

- *control, accumulation and storage*: the waste is delivered to WtE plant and stored;
- *combustion*: the wastes are moved into the combustion chamber. The wastes remain in the combustion chamber for about 1h at a temperature between 850°C and 1200 °C
- *power generation*: the fumes originating from the combustion rise towards the boiler located above the combustion chamber and heat the water contained in it, generating water vapour; the pressure generated by the water vapour drives a turbine connected to a power supply and electricity is produced;
- *fumes treatment*: before being emitted into the atmosphere, the fumes are purified through several phases (removal of solid particles, acids, dioxins and heavy metals, sodium products and nitrogen oxides);

- *fumes expulsion*: the fumes are channelled into a chimney and expelled into the atmosphere at a temperature of about 120 °C;
- *ash collection*: the ashes obtained from the combustion of waste and the solid particles obtained from flue gas purification are collected in two separate lines, stored and sent to landfills or recycling companies.

The most variable part of waste-to-energy plants is the furnace. Three technologies are used (**Figure 1.4.2**):

- Grate furnace technology: this technique is most commonly used. The waste enters through the fuel chute and then it is pushed onto the grate by a feed mechanism. The fuel then moves along the (usually) sloping grate. The upper fuel surface-layer is exposed to radiation from the refractory structures of the furnace and the flames, formed by the volatile gases above the fuel layer, and heats up and dries. Subsequently, as the temperature of the fuel layer rises, the fuel devolatilises as it moves forwards on the grate. When the ignition temperature is reached, combustion starts, promoted by the primary air from the bottom sections: little air is supplied in the drying section, and the remaining primary air is adjusted in the various supply ducts beneath the grate according to the progress of combustion in the central section of the bed. The combustion front formed moves downwards into the bed against the air flow, while the bed moves forwards (Leckner, 2015). The combustion temperature is between 750 and 1000°C.
- Fluidised bed technology: in contrast to the fuel bed on the grate, the fuel is introduced to an inert fluidized bed, consisting of sand-like particles of about 0.5 mm in size, and mixes with this bed material and the remaining ashes from the waste. The advantage of the fluidized bed is the hot bed, which has a great thermal inertia for the fuel particles to burn in a controlled and thermally stable environment. This advantage is not entirely effective in waste combustion, though, because the volatile part of the fuels tends to burn in the freeboard above the bed in any case. The bed temperature is usually 850° C, but it could be higher as long as the bed does not sinter. The primary fluidization air is introduced through nozzles, traditionally covering the entire bottom of the furnace, the “distributor plate”. This leads to accumulation of larger and denser objects in the bottom region, originating from the waste, which eventually prevents proper air distribution, disturbs fluidization, and favours agglomeration. Therefore, fluidized bed combustion of waste has the reputation of requiring well sorted waste (Leckner B., 2015).
- Rotating furnace technology: the rotary furnace, or rotary kiln, is used for drying and other operations involving granular materials. In the field of waste treatment, it is most frequently

employed for combustion of hazardous waste. A rotary furnace consists of a cylindrical steel vessel, of 10 m in length and a few metres diameter, inclined by a few degrees from the horizontal plane. Inside, the vessel is protected by refractories. The cylindrical steel vessel rests upon rolls and is rotated at a speed between 0.05 and 2 revolutions per minute. The fuel is fed at one end and the ashes leave at the other end. Drying, devolatilization, and combustion take place, while the fuel is rotated and mixed, sometimes even enhanced by internals. The length and diameter of the cylinder, as well as its rotation speed, slope, and internals, all influence the residence time of the fuel particles. This ability to control the residence time even in wastes of different input is the main advantage of the device. However, the incineration often does not come to completion and usually an afterburner combustion chamber is needed (Leckner B., 2015).

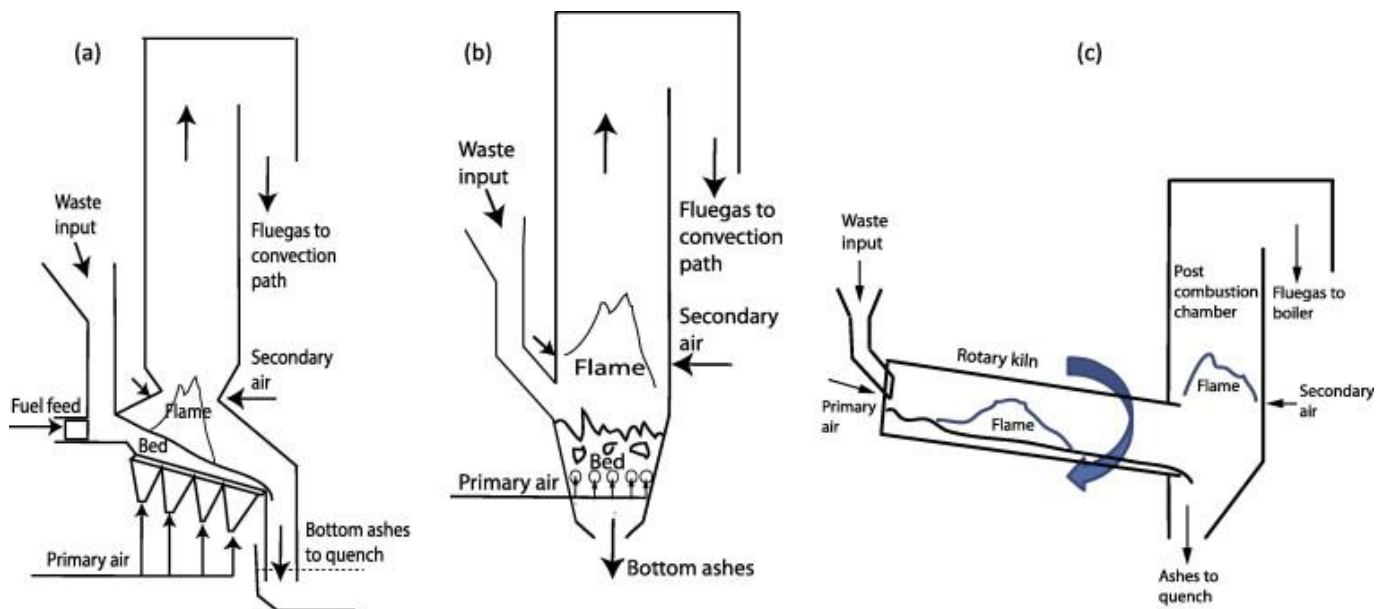


Figure 1.4.2 The most common conversion device for waste, here shown in the form of combustors: (a) grate furnace, (b) fluidized bed and (c) directly heated rotary furnace (Leckner B., 2015)

After an initial cooling phase, bottom ashes are screened manually or mechanically to remove oversized unburned residues. In addition, the ferrous metal fraction is removed with overhead magnetic separators and the non-ferrous metal fraction is removed by Eddy current. Subsequently, the material is stored on site awaiting aging.

As mentioned above, from the combustion of waste not only energy is obtained but also residual ashes. The ashes, which are also a waste, can be classified on the basis of its size and hazardousness:

- **Fly Ashes (FA):** their mass represents 2% -5% of the incinerated waste. The FA are the solid particles that are released with the combustion fumes and are removed after the purification process. Due to the high concentration of PTE, the FA are classified as hazardous waste (EWC

code 19.01.13 *: fly ash containing hazardous substances) and for this reason they cannot be recycled without pre-treatment and are usually collected and stored in specific landfills (Zhu J. et al., 2020; Qiu et al., 2017; D.Lgs 152/06).

- **Bottom Ashes (BA):** BA are one of the major by-products obtained during municipal solid waste incineration in waste-to-energy plants; their mass is 20% of the incinerated waste. Once the incineration process is complete, the BA are thrown into a tank full of water for rapid cooling. The BA are classified as non-hazardous waste (EWC code 19.01.12: bottom ash and slag other than those in 19.01.11 *).

1.5 BOTTOM ASHES: COMPOSITION AND PROBLEMS

The BA are made up of different fractions which, thanks to the non-hazardous nature of the unburned material, can be recycled becoming a resource. The fractions can be divided as:

- glass (soda-lime glass), coming from domestic items such as bottles and glasses. The amount of glass is highly dependent on the presence of a selective collection of urban waste.
- Synthetic ceramics, derived from clay-based materials (e.g. tiles and bricks), porcelain and concrete.
- Paramagnetic metals, which represent a 2-5 wt%; usually they originate from steel and iron pieces oxidised in the incineration furnace. Mineral phases such as magnetite (Fe_3O_4), hematite (Fe_2O_3) and wuestite (FeO) are characteristic of the BA fine fraction that is not removed by the magnetic separator.
- Minerals, such as feldspars calcite and quartz may have a natural origin (they are common in soil and rock), but they are also common components in ceramics or building materials as well as major weathering products in MSWI BA (calcite).
- Diamagnetic metals, which represent 10-12 wt% of the BA weight. They are mainly represented by aluminium and copper, and tend to be concentrated in the finest fraction (below 1 mm).
- Unburned organic matter which comes from the partial combustion of food residues, paper, fabric and bone fragments (Chimenos et al., 1999).

The composition of BA varies over time and from country to country, due to the differences in lifestyle and waste recycling processes of a country. To note, it is extremely heterogeneous and may change, also in the same plant, depending on the different mix of wastes burned each day; moreover, even within the same mix, there are seasonal differences (Dhir et al., 2017). This heterogeneity in the waste incoming material gives rise to a variation in compositions from grain to grain in the BA. Moreover, some inhomogeneity in the combustion temperature adds further heterogeneity in the

thermodynamic conditions of local equilibria. It must be emphasised that, despite this heterogeneity, some phases are commonly found (Chimenos et al., 1999; Forteza et al., 2004; Inkaew et al., 2016; Lynn et al., 2016; John Chandler et al., 1997c; Alam et al., 2019; Tyrer, 2013; Lam et al., 2010; Caviglia et al. 2019; Mantovani et al. 2021).

This complex chemical and mineralogical composition gives rise to numerous scientific questions regarding their reuse and non-hazardousness. Over the past 20 years, many research groups studied BA by implementing a multidisciplinary approach merging the contributions of environmental geology, geochemistry, and engineering.

The properties of the BA can be divided into chemical and physical properties. These properties are essential for a management of the waste: any proposed recycle must take into account the chemical and physical reactivity of the ashes, to optimise the industrial production, to assess and improve the performance of the recycled product, and to predict its long-term use in terms of pollution and durability.

1.5.1 Physical characterization

The mineral fraction of BA is typically light to dark grey and is a granular material (although it may also contain large fused lumps).

The physical characterization of the BA involves, preliminary to other investigations, an analysis of the grain size distribution. The grain size distribution is most important in the recycling in the construction industry, and, as discussed in the following, may be different in different incinerators. The particle size distribution is typical of well-graded materials and generally conforms with that of sandy gravel, with a content of 40mm oversize particles commonly below 5% by total mass as well as a low portion of fines (<63 micron) (Astrup et al 2016, Izquiero et al. 2011).

Broadly speaking we have that about 45 % of the mass of the BA is made by grains larger than 5 mm, whereas about 35 % of the mass falls in an intermediate grain size between 1 and 5 mm; fine-grained material between 0.1 and 1 mm make about 10 % in weight, whereas the remaining 10 % of the BA shows a grain size less than 0.1 mm (Dou X. et al., 2017; Šyc et al., 2018 Huber et al., 2020). Other physical properties that can describe BA are represented by the loss of ignition, usually 1-3% (Lynn et al., 2017) i.e. weight percentage lost when heated for 4 h at 500 °C, specific gravity, bulk density (t/m^3) that is typically 1.200-1.800 kg/m^3 , and water absorption (%).

1.5.2 Chemical and mineralogical characterization

The composition of the BA changes with the input material, the combustion technology, and the post combustion weathering. The input material depends on local lifestyle waste production, but also by

selective collection of household waste. Selective collection makes it possible to recover materials for which recycling options are available and economically viable. It was observed that, where separate collections were carried out, glass and paper/cardboard fraction sent to incineration fell by 10% and 8% respectively, while the proportion of other materials (e.g. textiles) increased by 30%. A lower silicon content in the of BA was found after the introduction of selective collection, which decreased the input in bottle glass to the incinerator (del Valle-Zermeno et al., 2017).

The composition of the ashes changes also as a function of the incineration technology: incineration is a complex technique to master because it involves several essential parameters as the storage and composition of incoming waste, the feeding to the furnace, the combustion temperature, the ignitability of the wastes, the oxygen supply and the process time in the furnace. These parameters have important effects in the mineralogical composition of the ashes and in the presence of organic matter. The same input material, burned with different furnace technologies, rotating, fluidized bed or grate, will produce a different mineralogical composition of the ashes. As mentioned before, the grate furnace is the most used in household waste incineration plants.

Also, the cooling after incineration affects the mineralogical composition of the ashes. The cooling can be with water or air. The water-cooling process is the most used and produces a rapid cooling together with chemical reactions between BA and water, loss of metals due to oxidation or adhesion of mineral matter to metals. Air cooling generates dust that requires special treatment but avoids the chemical interaction with water.

The maturation processes can reduce the environmental pollution potential of the material, as thermodynamically unstable compounds evolve into more stable secondary compounds in the presence of carbon dioxide, but also of oxygen or water. Usually BA are exposed to air for 1 to 12 months. Maturation changes the chemical and mineralogical composition, absorbing CO₂ to form carbonates, mostly calcite, and moisture vapour, to form cement minerals like ettringite.

For all these factors the ashes are very heterogeneous even from the same incineration plant. However, despite these variables, there are similarities among the different chemical compositions reported in the literature (**Table 1.5.2.1**).

Generally speaking, the major oxides in BA are CaO, SiO₂, Al₂O₃ and Fe₂O₃ that represent between 60 and 80 wt% of the chemical composition. The minor elements are Cu, Zn, Cr, Sb, Mo, Co and Ni, and make up about 1.5–2.0 wt% along with 1.5–5.0 wt% of chlorides and sulfates, the actual amount depending also on the size fraction of BA (Alam et al. 2020). For each element systematic differences are observed as a function of the grain size (Caviglia et al., 2019; del Valle-Zermeno et al., 2017; Loginova et al., 2019; Huber et al., 2019). Among the major elements, (Si, Ca, Al, and Fe) Si content

increases with grain size, while Ca follows an opposite trend. Al, Fe, Mg and K show definite trend as reported in (Caviglia et al., 2019; Funari et al., 2015; Loginova et al., 2019).

For minor and trace elements, on the other hand, greater variability has been reported but in the last literature data published the higher concentrations are found in the finer fraction (Caviglia et al., 2019; Funari et al., 2015; Loginova et al. 2019). The point will be discussed in the following in more detail. These elements combine together to form crystalline and amorphous silico-aluminates. In fact, BA are characterised by refractory (ceramic, metals unaffected by the combustion process) and melt (slag minerals formed during incineration) phases. Quenched BA are formed by agglomerated material, containing carbonates and hydrated phases (Inkaew et al., 2016). Usually, glass/amorphous phases form the particle core, while on the particle surface hydration products are found as calcium silicate hydrates (C-S-H), Friedel's salt/hydrocalumite, ettringite, gypsum and calcite. The cooling inside the tank can be a source of chlorides and sulphates due to the presence of Cl^- and SO_4^{2-} in the quenching water (Ito et al., 2008).

In general, glass and semi-fused metallic material is present in larger amounts in the coarser particle sizes, while slags are present in greater amounts in the finer grain size classes. The most common mineralogical phases are (i) silicates (quartz, melilites, feldspars), (ii) carbonates (calcite, vaterite), (iii) oxides (magnetite, hematite, corundum), and (iiii) hydrated phases typical of cementitious materials (hydrocalumite, portlandite, ettringite, stratlingite). For further details see **Table 1.5.2.2**, from Syc et al. (2020). In addition to these main phases, a high content of amorphous material is also present (Alam et al., 2019; Bertolini et al., 2004; Bayuseno & Schmahl, 2010; Caviglia et al., 2019; Yao et al., 2012). Mineralogical composition also varies as a function of grain size: for example, the amorphous content is higher in larger grains while carbonates are present in greater amounts in the finer grains.

<i>Major Elements</i>	<i>Concentration range (min-max) in mg/kg</i>	<i>Potential toxic elements</i>	<i>Concentration range (min-max) in mg/kg</i>	<i>Rare earth elements</i>	<i>Concentration range (min-max) in mg/kg</i>	<i>Platinum metal group</i>	<i>Concentration range (min-max) in mg/kg</i>	<i>other precious and critical elements</i>	<i>Concentration range (min-max) in mg/kg</i>
Al	14000 – 79000	Ba	69 – 5700	Sc	1.3 – 22	Pt	0.074 – 0.53	Ag	0.2 – 36.9
Ca	8600 – 170000	Cd	0.3 – 70	La	2 – 30	Pd	0.03 – 1.8	Au	0.1 – 2.2
Fe	3100 – 150000	Cu	190 – 25000	Ce	11 – 51	Ir	0.0007 – 0.007	Sb	7.6 – 430
K	660 – 16000	Cr	20 – 3400	Pr	1.1 – 10	Rh	< 0.030	Be	1.2 – 6
Mg	240 – 26000	Mo	2.5 – 280	Nd	4 – 37	Ru	< 0.01	Co	6 – 350
Mn	77 – 3200	Ni	7.0 – 4300	Sm	0.93 – 5			Ga	7 – 24
Na	2200 – 42000	Pb	75 – 14000	Eu	0.25 – 2.6			Ge	0.78 – 2.7
P	440 – 10500	Se	0.05 – 10	Gd	0.88 – 5			In	< 1.7
Si	4300 – 308000	Sn	2 – 470	Tb	0.18 – 3			Nb	2 – 14
Ti	2783 – 7479*	Tl	0.0077 – 0.23	Gy	0.54 – 3			Ta	2.5 – 14
Cl	3644 – 37633	V	16 – 120	Ho	0.11 – 0.45			W	10 – 320
S	1310 – 16808	Zn	10 – 20000	Er	0.31 – 2			Li	2 – 29*
				Tm	0.01 – 0.18				
				Yb	0.31 – 5				
				Lu	0.02 – 0.23				

Table 1.5.2.1: some literature data on the chemical composition of BA (modified from Astrup et al. 2016 and Hjelmar et al. 2013)

<i>Mineral phase</i>	<i>Chemical formula</i>	<i>Unquenched BA</i>	<i>Quenched BA</i>	<i>Weatered BA</i>
quartz	SiO ₂	h, i	b, e, f, g, i	a, c, d, e, f
crystalbite	SiO ₂		g	a, g
gehlenite	Ca ₂ Al ₂ SiO ₇	h, i	b, e, f, g, i	a, e, f, g
akermanite	Ca ₂ MgSi ₂ O ₇		b, e	a, e
alkali feldspars	(K,Na)(Al,Si) ₃ O ₈		b, c (albite),g	g
plagioclase feldspars	NaAlSi ₃ O ₈ -CaAl ₂ Si ₂ O ₈	e, i	b, e, i	e
calcium pyroxene	Ca(Mg,Fe)Si ₂ O ₆		b, g	g
wollastonite	CaSiO ₃		b, f, g	f, g
lime	CaO	e, i	b	
portlandite	Ca(OH) ₂		c, g	
magnetite	Fe ₃ O ₄	e	e, f, g	a, e, f, g
hematite	Fe ₂ O ₃	h, i	i, f, g	d, f, g
wüstite	FeO		f, g	f, g
calcite	CaCO ₃	h, i	e, i, f, g	a, c, d, e, f, g
goethite	FeO(OH)			d
corundum	Al ₂ O ₃		e	e
gibbsite	Al(OH) ₃			d
anhydrite	CaSO ₄		c, e, g	d, g
gypsum	CaSO ₄ · 2H ₂ O			a, g
hydrocalumite	Ca ₂ Al(OH) ₆ Cl _{1-x} (OH) _x · 3H ₂ O		f, i	e
friedel's salt	Ca ₂ Al(OH) ₆ Cl · 2H ₂ O		i	
ettringite	Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ · 26H ₂ O			a, c, d, e

Table 1.5.2.2 most common mineralogical phases identified in BA. References: **a)** (Zevenbergen et al., 1998); **b)** (Eusden et al., 1999); **c)** (Chimenos et al., 2003); **d)** (Piantone et al., 2004); **e)** (Bayuseno and Schmahl, 2010); **f)** (Wei et al., 2011); **g)** (Santos et al., 2013); **h)** (Bourtsalas, 2015); **i)** (Inkaew et al., 2016).

The negative correlation that exists between grain size and carbonates, but also between grain size and hydrated phases, can be explained through a greater reactivity of the finer grains to the weathering process, as carbonates and hydrated phases are a product of hydration. We may compare the chemical composition of the average continental crust and that of bottom ashes from municipal solid waste incinerators (MSWI), much information on the human activity products can be obtained. **Figure 1.5.2.1(a)** represents the average composition of the oxides of common element (more an 1wt%) in MSWI BA (from Dijkstra et al. (2019), Hjelmar et al. 2013 and this work) vs the composition of the

average continental crust (from CRC Handbook 2016). In **Figure 1.5.2.1 (a)** is clearly visible that most abundant elements in BA (Al, Fe, Si, Ti, K and Na) are very close to that of the continental crust. Only two elements show strong enrichment in BA, Ca and P; also loss on ignition (LOI) content in BA is higher respect to the average crust. Despite the case of Ca and P, the average composition confirms that mineral wastes homogenise the products of industrial activity to obtain something close in composition to the natural continental crust.

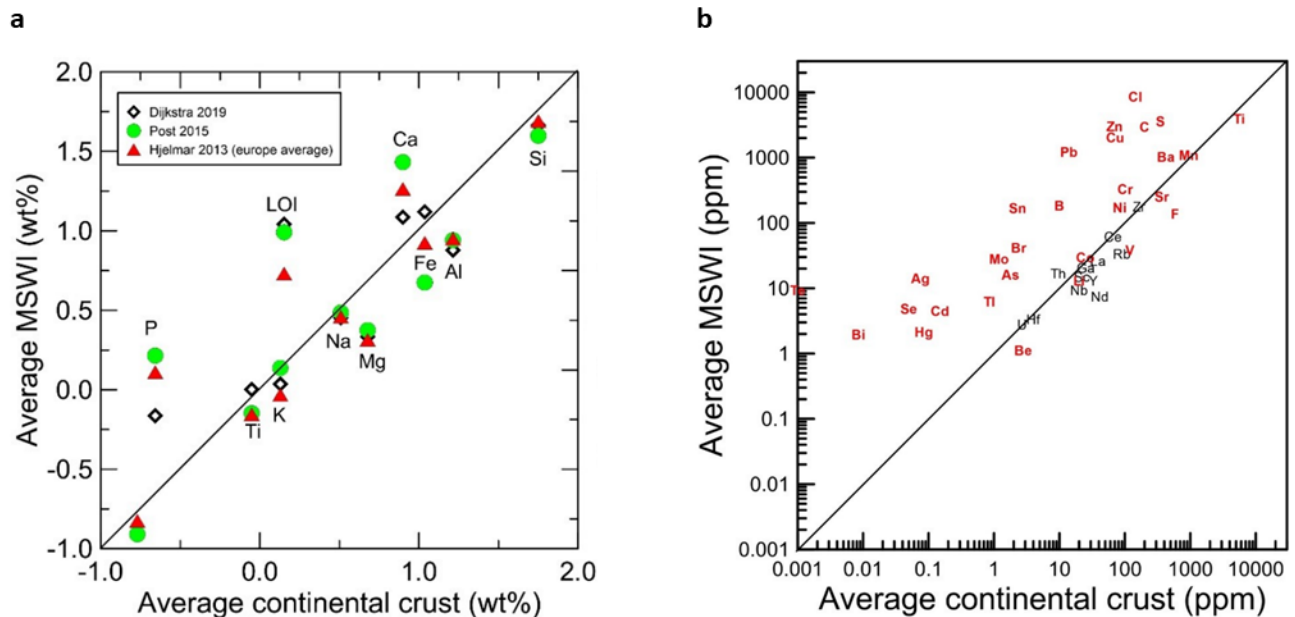


Figure 1.5.2.1 Average composition of major (a) and minor (b) elements in BA (from Dijkstra et al., (2019), Hjelmar et al. 2013 and this work) vs continental crust composition (from CRC Handbook 2016).

Figure 1.5.2.1(b) reports minor elements averaged in the MSWI BA respect to the continental crust. A first group of elements, among which Co, Zr, Li, Hf, Ti, Rb, F, V, Mn, Sr, Ga, U, Th shows an average composition in BA very close to the earth continental crust while a second group made by Cl, Zn, Cu, S, Pb, Br, Mo and Sn, show a significant enrichment in BA, between one and two orders of magnitude.

By some respect the chemical processes recorded BA could be similar to those in high temperature geochemistry. The overall composition is not far from that of the global earth, and the temperatures are in the range of the geological high temperature processes; a combustion chamber can be compared with natural high temperature systems. The difference lies in the extreme heterogeneity of the input material. During the incineration we observe in different grains multiple equilibria due to local compositional and temperature heterogeneities. At the local grain size scale the high temperature reactions can be interpreted as indicating the achievement or at least the progress to a thermodynamic

equilibrium, obeying to the Gibbs phase rule, whereas at the bulk scale this obviously does not occur. The multiphase, multiple equilibria lead to wealth of phases even in the grains where the high temperature glass and crystals are best preserved. Moreover, unreacted refractory material and low temperature weathering induce further mineralogical complexity.

1.5.3 Recovery and recycle of Bottom Ashes

In order to improve the properties of MSWI BA physically or chemically, to obtain a better material for application or to reduce the leaching concentration of contaminants from MSWI BA and lower its environmental risk potential, several treatments have been proposed. Today most plants are equipped with magnetic separators and non-ferrous separators for the recycling of pure metals such as iron or aluminium. From an economic point of view, the recycling of metals provides a financial benefit for the company in addition to obtaining a cleaner stony material. Some authors (Biganzoli & Grosso, 2013; Biganzoli et al., 2012) reported that the recovery level of metals is limited by their particle size. A focal point debated in the last years regards the extraction and immobilisation of contaminants as salts or heavy metals, and their extraction with water or chemical washing. However, it was not recommended to wash the MSWI BA due to the large amount of generated waste water or chemical reagents (Lin et al., 2011; Yang et al., 2012). Generally, the treatments on BA MSWI are matched with their applications, such as using bottom as in concrete and meanwhile, the binders in the concrete have an immobilisation effect on the heavy metals in the BA.

The polluting potential of BA is a key factor in deciding on its use as well as its storage in appropriate sites. Actually, each country has defined a regulatory and legislative framework on the management of BA with a view to identify recoverable and non-recoverable materials. The construction sector remains, for all European countries, the main re-use of BA, in order to limit the use of non-renewable natural resources. Unfortunately, the non-uniformity of Country standards act as an obstacle in the full valorisation of these materials. The EU legislation can be found in Directive 2010/75/EU on industrial emissions but each country has its national regulations implementation. Briefly, any waste incineration plant operated in a member state needs to adhere to the minimum requirements set out in the above mentioned directive in which the principal requires are to minimise the amount and potential hazard of combustion residues, and to have recycling strategies in place, after having assessed BA physical and chemical properties, as well as their polluting potential, including the determination of the total soluble fraction and soluble fraction of heavy metals.

The European Union requires Member States to carry out leaching tests according to the standards EN 12457/1 2002, EN 12457/2 2002, EN 12457/3 2002, and EN 12457/4 2002, with a liquid-to-solid (L/S) ratio ranging from 2 to 10 l/kg. If the BA respects these statements within the Community of

Member States in the European zone there is no legislation on the recycling of BA for the incineration of non-hazardous waste.

For these reasons, nowadays there are many attempts to reuse BA in various sectors. The principal recycling application regards road construction, pavement subbase layer or surfacing material in landfill as occurs in France, Germany, Italy, Portugal, Spain and UK. Other EU states like Austria and Sweden, don't recycle except as layering materials in landfills; in Denmark BA are re-use also in marine structures like dams and ports and in construction material for car parks.

The great possibility of reusing BA is, above all, given by the content of the main chemical elements and their similarity with other building materials, of natural and non-natural origin.

In the ternary diagram reported in **Figure 1.5.3.1** compositional data of BA from WtE plants in northern Italy (from this work) are plotted and compared with some compositions of igneous and sedimentary rocks, as well as Portland and alumina cements, glass and construction and demolition waste.

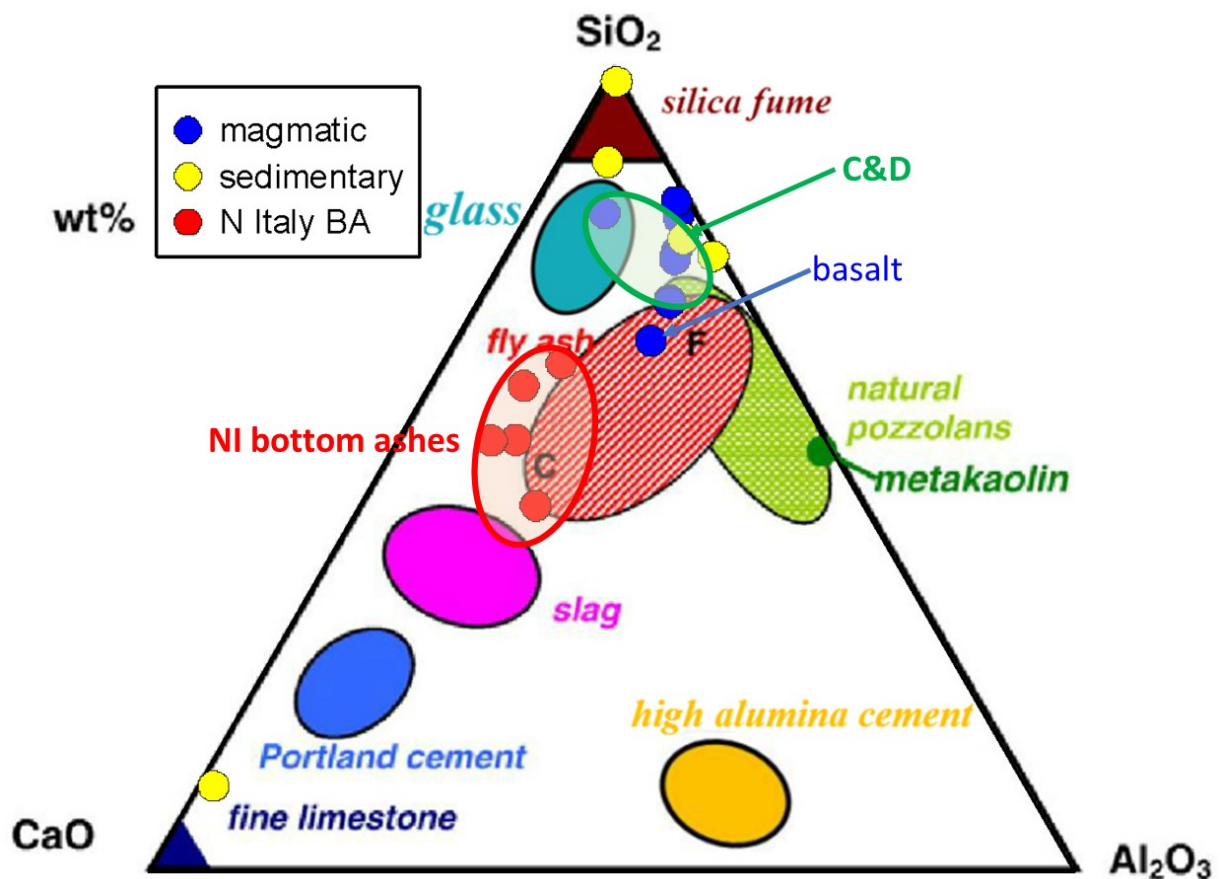


Figure 1.5.3.1 CAS (CaO–Al₂O₃–SiO₂) ternary diagram of cementitious materials modified from Lothenbach et al., (2011) and construction and demolition waste from Dijkstra et al. 2019. NI BA data are taken from this work.

The use as a road base is also due to its physical properties which are similar to normal aggregates, and its leaching behaviours could comply with the legislation established for road construction (Forteza et al., 2004). The use of MSWI BA in roads in some countries was successful and the leaching of metals during service life was reported to comply with standards (Dabo et al., 2009; Hjelmar et al., 2007; Izquierdo et al., 2008; Olsson et al., 2006). However, more application potentials for MSWI BA should be explored due to its increasing amount worldwide. Hence, the use of BA was introduced into building construction, such as being used as aggregates, binder alternatives, etc. Müller & Rübner (2006) used MSWI BA fractions (2-8, 2-32 mm) in concrete to replace natural aggregates.

Recently a hot topic in waste recycling research focused on recycling BA in ceramics. Thanks to the mineralogical composition of BA they could partially replace clay for the production of ceramics without preliminary processing. Senthamarai et al. (2005) shown the feasibility of recycling BA in the manufacture of ceramic tiles while Chen et al. (2021) suggested that the incorporation of up to 20% by weight of BA in ceramics does not substantially change the mineralogical and thermal properties of ceramic tiles. Conte et al. (2022) tests the use of BA in porcelain stoneware, exploring the technological properties, microstructure and phase evolution. An attempt to vitrified the MSWI BA at 1450 °C is reported by Ferraris et al. (2009) that obtained a dark brown glassy material that could be used as cement replacement for up to 20% wt. and as sand replacement in low strength mortar. Vitrification blocks heavy metals by including them in structures that are very strong to atmospheric agents attack but involves a considerable energy consumption (and therefore economic) that is not sustainable from an industrial point of view.

The employment of industrial wastes as raw materials in the production process of Alkali Activated Materials (AAMs) has been intensively promoted in recent years as low-carbon binder alternatives to Portland cements (PC) for building construction and cultural heritage conservation (Palomo et al., 2021; Barone et al., 2020). Many authors have investigated and exploited their strong ion exchange capacity for the stabilisation/solidification of toxic wastes containing appreciable amounts of heavy metals by their incorporation in a cementing material such as AAMs pastes (Palomo et al. 2021, Barone et al.2020). The mobility of the contaminant metals in waste decreases through mechanisms such as metal hydroxide precipitation, ion adsorption/substitution by hydration products and physical encapsulation (Tzanakos et al., 2014; Zhan et al., 2018; Luna Galiano et al., 2011) as demonstrated by leaching tests confirming the strong potentiality of AAM technology in the immobilisation of hazardous elements (El-eswed, 2020). On the other hand, other studies suggest that the immobilisation of highly soluble forms of heavy metal salts in geopolymers is less successful (El-eswed, 2017).

1.5.4 Mineralogy, PTE elements and environmental concern: aims of this thesis

As mentioned above, although classified as non-hazardous industrial waste (2008/98/EC). BA have a high concentration of PTE, most concentrated in the finest fraction. This poses an issue about the toxicity of the BA. The toxicity of an element depends on its oxidation state and/or its concentration in a given environment, which depends on its leachability. On its turn, the leachability of an element in environmental matrices depends on the mineralogical phase in which it is hosted. Investigating the chemical form of PTE and knowing the crystalline and amorphous phases that host them is a key point in assessing the actual toxicity of BA and to implement safer and viable material recycling strategies.

Among the most abundant contaminants, chlorides and sulphates are found, especially in the finer fraction. The chlorides content derived mainly from the incineration of plastic materials and food waste. They are found in mineralogical phases such as halite (NaCl) and sylvite (KCl) that are very soluble in water (Alam et al., 2019). The presence of chlorides represents an environmental issue as well as a limiting factor in the application of BA in steel reinforced concrete, due to the possible corrosion of steel bars (Chen and Chiou, 2007). Similar to chloride, sulphate content in BA are found on the particle surface of finer fraction. Usually, sulphates are associated with calcium, like in gypsum or as weathering products (e.g. ettringite) (Alam et al., 2019).

Among the PTE, the most commonly found are Cu, Mo, Cr, As and, Sb. Cu is related to the disposal of electronics devices, construction demolition wastes or kitchen utensils and (Chandler et al., 1997). Mo and Sb are used in special alloys, and some of their compounds are used in the pharmaceutical field, but little information is found about their behaviour during the incineration process (Chandler et al., 1997).

The presence of PTE poses several issues over the reuse of BA: (1) there are physical and environmental problems in using MSWI BA in construction without any pre-treatments - the heavy metals in BA which will leach out as the presence of water will pollute the groundwater and are harmful to human health; (2) the metal content in BA, especially metallic aluminium, will generate hydrogen with alkali content when used in concrete which contribute to the spalling and poor quality of concrete with BA; (3) treatments are needed to upgrade the quality of MSWI BA to meet the physical and environmental requirements on building materials; the economic factor of the treatments and the value of the treated BA for application are the main barrier in practice for BA application. Therefore, due to the fact that the MSWI BA contains heavy metals and has the potential to leach into the surrounding environment, the reuse of BA as secondary materials is limited.

In general, several points in the relations between the PTE and minerals are not clear:

1. the speciation of PTE. PTE become more or less hazardous depending on how they are bonded to the solid phases. The elements are leached when they are present in soluble phases, like sulphates or chlorides, and much less when they are encased in the structure of high temperature phases, like feldspar, melilite or a silicate glass. In spite of the number of previously published papers the data on the speciation of PTE are sparse, and seldom discuss the mineralogical speciation together with the effect on leaching;
2. What emerges from the latest published data is that in addition to a characterization of the BA from a chemical and mineralogical point of view, it is also necessary to have a detailed knowledge of the variation of the phases and compositions as a function of the grain size. Caviglia et al. 2019, Loginova et al., 2019 and Huber et al., 2020 demonstrate that the finest particles are richest not only enriched in Cl and S but also in PTE and that these elements are, more leachable from the smallest particles. Although it is clear that there are differences in the chemical composition with grain size of the elements, previous results are sparse, and no attempt to generalise the previous observations was done, i.e. to show consistent trends which relate the relations between geochemistry and grain size;
3. morphological aspects in crystals within grains were generally neglected, in spite of the different surface reactivity of the smaller and larger grains.

To address these points, we have investigated the chemical and mineralogical composition of the BA from five incinerators in northern Italy, and their leaching behaviour. In the following the description of the WtE plants where the ashes were obtained, the sampling and the analytical methods, and the results of the present investigations, are reported in the form of papers published, in publication or in preparation.

2. MATERIALS AND METHODS

In the following a general overview of the materials and methods used in this thesis is given. For the specific results and detailed description, the reader may go to the Results chapters.

2.1 DESCRIPTION OF THE WASTE-TO-ENERGY PLANT

The BA studied in this work were sampled from 5 WtE plants in northern Italy, one in Piedmont, and the other four in Emilia-Romagna, with different waste input, but with a large prevalence of MSW.

2.1.1 Parma WtE plant (Iren group)

The WtE plant of Parma, owned by the company Iren, is authorised to burn 195.000 t/y of waste. The wastes sent to the plant are MSW and non-hazardous special waste, such as sewage sludge, waste from recovery activities, non-hazardous special waste from non-recoverable production activities, and waste from handmade processing. The WtE plant consists of two combustion lines with grate steam generators for the production of superheated steam. In 2021, 163.701 t/y of waste was sent to combustion from which 33.353 t/y of BA originated (Dichiarazione Ambientale PAI, 2022).

1.6.2 Piacenza WtE plant (Iren group)

The Piacenza WtE plant is of the property of the Iren group, adopts grate furnace technology and has a waste disposal capacity of 120.000 t/y. The wastes that are sent to the plant are MSW and non-hazardous special wastes such as waste assimilable to municipal waste, sanitary waste and sewage sludge. In 2021, 107.692 tons of waste were processed from which 26,592 tons of total waste originated (BA and FA) (Dichiarazione Ambientale Termovalorizzatore di Piacenza, 2022).

1.6.3 Torino WtE plant (Iren group)

The Torino metropolitan city WtE plant (TRM) is licensed to treat MSW and non-hazardous special waste; it's equipped with three combustion lines using moving grate furnace technology. In 2021, 560.704 tons of waste were sent to the combustion process, from which 140.050 t of BA (Relazione Annuale TRM, 2022).

1.6.4 Ferrara WtE plant (Hera group)

The Ferrara WtE plant, owned by the company Hera, has a maximum authorised capacity of 142.000 t/y of MSW and special non-hazardous waste. The plant is equipped with two combustion lines with water-cooled grate furnaces. In 2021, 141.958 tons of waste were sent for combustion; specifically, 60.649 tons were special non-hazardous waste and the remaining were MSW. From the combustion process originated 29.491 tons of BA (Relazione annuale Termovalorizzatore di Ferrara, 2022).

1.6.5 Forlì-Cesena WtE plant (Hera group)

The Forlì WtE plant, owned by the Hera group, is authorized to treat 120.000 t/y. It's the only one of the five WtE plants that burns only MSW and has a single combustion line equipped with a grate furnace with water cooling. In 2021, 119.898 tons of waste were sent to Forlì-Cesena WtE plant. from the combustion of such waste originated 29.092 tons of BA (Relazione annuale Termovalorizzatore di Forlì-Cesena, 2022).

2.2 SAMPLING

The BA obtained from combustion are accumulated in areas dedicated to their storage to allow their maturation; after a few months they are disposed of in landfills or are taken by companies that recycle them into building materials. Our samplings of BA from the plants were done during process activity. The samples were taken randomly from a 2-3 m high stock, representative of more than one month of accumulation. The samples were taken in May 2019 at the WtE plants in Parma, Turin, and Piacenza, and in April 2020, during the pandemic freeze, in Ferrara and Forlì. Approximately 5 kg of BA samples were collected from each plant. Additional sampling (approximately 12 kg) was then conducted in June 2021 at the Parma plant.

2.3 SAMPLE PREPARATION

The BA sampled from the 5 waste-to-energy plants were first dried in an oven at 50°C for 24h (or until dried) and then sieved into ten grain size classes. The sequential sieving, to 16, 8, 4, 2, 1. 0.5, 0.3, 0.2 e 0.063mm, was performed according to the prescriptions of the European standards for aggregates EN 933-2 (Ente Nazionale Italiano di Unificazione, 2020).

2.4 GRAIN SIZE ANALYSIS

Each particle size class was weighed and, by calculating the percentage of material that passed through the sieves, cumulative particle size curves were made in order to evaluate their distribution and mechanical qualities. The obtained particle size curves were then compared with particle size curves from other works in the literature and with Fuller's curve, which represents the particle size distribution that an ideal concrete mix should have.

2.5 THERMO GRAVIMETRIC ANALYSIS (TGA)

Thermogravimetry is an analytical technique for evaluating the mass loss of a material with increasing temperature. Thermogravimetric analyses were conducted on samples taken from each particle size class. Each sample was ground with a mortar to obtain a fine and homogeneous powder (< 0.063mm);

a quantity of material equal to 3 -5mg was sufficient to perform the analysis. TGA were conducted by means of a Perkin Elmer 8000 instrument equipped with a Pt-crucible at a heating rate of 10 °C/min in the temperature range 35°C – 800 °C. All the measurements were run under a constant flux of dry air atmosphere (30 mL/min).

2.6 SEM-EDS OBSERVATIONS AND ANALYSIS

In a preliminary step, several BA granules chosen in the Parma WtE plant chosen in the grain size between 8 and 16 mm, to be investigated in the particle size characterization paper, and between 0.5 and 1 mm to be investigated for the paper focussed on XRF-XANES mineral characterization. The grains were embedded in epoxy resin stabs, cut longitudinally. After a preliminary optical observation, by a polarised stereomicroscope BX51, OLYMPUS, Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Spectroscopy (EDX) analysis was done.

Scanning Electron microscopy was used to determine the microscopic structure and composition of the phases which are present in the BA. The electron microscopy exploits the interactions that occur between an incident electron beam and the atoms in the sample by returning morphological and chemical information (**Figure 2.6.1**).

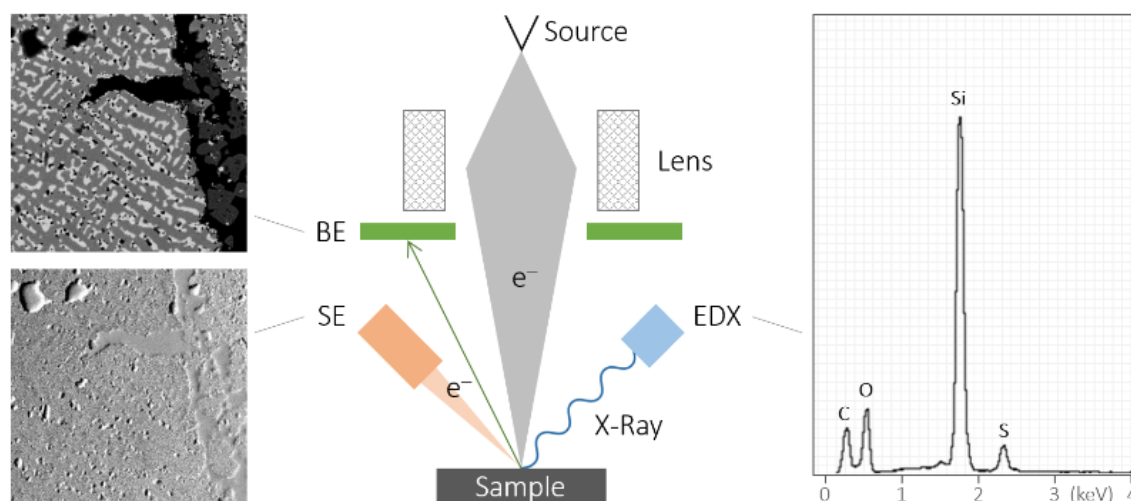


Figure 2.6.1 Scheme of electron-matter interactions arising from the impact of an electron beam onto a sample (www.rjl-microanalytic.de/en/)

The analyses were done using the SEM image obtained from backscattered electrons, together with EDS point or map analysis. A comparison with optic microscope images was done to highlight the correspondence between compositional and optical inhomogeneities, from the images obtained by backscattered electrons and SEM – EDS mapping.

The SEM – EDS analyses were performed at:

- Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale (Università di Parma) by a Scanning Electron Microscope coupled with Energy Dispersive System (SEM-EDS) JSM IT300LV Jeol 6400 equipped with an Oxford EDX microprobe. Microprobe analysis was performed with operating conditions 20 or 25 kV and 1.2 mA current, $\sim 1\mu\text{m}$ beam diameter and 75 s counting time;
- Dipartimento di Scienze della Terra (Università di Torino) by a JEOL JSM-IT 300LV Scanning Electron Microscope, equipped with Oxford INCA Energy 200 EDS SATW detector (WD 10, KV 15), at 15 kV, 1.2 mA current and $1\mu\text{m}$ beam diameter.

All data collected were processed using the AZTEC software (Oxford instruments, 2006)

2.7 X-RAY POWDER DIFFRACTION (XRPD) ANALYSIS

X – Ray Powder Diffraction was used for the identification and quantification of the phases in the samples. It was done on all grain sizes, before further analyses and treatments. The phase determination was done via powder diffraction, using the DIFFRAC.EVA software, whereas the quantitative assessment was done by Rietveld analysis of the diffraction patterns and the GSAS – II package. The samples were ground in an agate mortar in order to obtain a homogeneous powder ($< 0.063\text{mm}$). A 10% by weight standard (Al_2O_3 or Si) was also placed in each sample to perform quantitative analyses at a later time to assess the degree of crystallinity of the sample and the amount relative to each identified mineralogical phase.

The measurements were conducted at:

- Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale (Università di Parma) using a Bragg-Brentano Bruker 2D Phaser Diffractometer, with $\theta - \theta$ geometry, Cu $K\alpha$ radiation, 30 kV and 10mA and a solid-state detector;
- Dipartimento di Scienze della Terra (Università di Torino) using a Bragg-Brentano Rigaku Miniflex 600 Diffractometer, with $\theta - 2\theta$ geometry, Cu $K\alpha$ radiation, 40 kV - 15 mA, multistrip detector (128 strip) and $K\beta$ filter on incident beam;

The diffraction patterns collected were identified using the Bruker software DIFFRAC.EVA and the Crystallography Open (COD) and PDF-2005 databases. The identification was based on the fit with position and intensity of the main diffraction peaks. Problems in identification of phases with lower concentration came from the complexity of the diffraction patterns, due to the number of mineralogical phases in the BA, and the consequent peak overlapping. Moreover, the intensity of the diffraction pattern was greatly reduced by the presence of glass and amorphous unburned organics.

A further bias was that the position and intensity of the main diffraction peaks, in phases showing solid solutions like plagioclase and melilite, was shifted from those in the reference database.

By this respect, we can consider fully identified only phases with more than 1-2 wt% presence in the sample.

Quantitative analysis was done by means of the Rietveld method. The Rietveld refinement performs the analysis of the measured diffraction profile by modelling the crystal structure, unit cell and relative abundance of the crystalline phases identified in the diffraction pattern. The background, scale factor and sample related peak broadening are modelled as well, whereas instrumental parameters, like wavelength, zero position, and instrumental peak shape are defined by an instrumental file, but can also modelled if necessary (Rietveld, 1967 and 1969; Bish & Post, 1989). The quantitative analysis of the different crystalline phases present in a mixture is based on the principle that from the measured diffraction intensities the amount of the crystalline phases in the mixture can be modelled. In quantitative Rietveld analysis we assume that the pattern contains only crystalline phases, whose concentration is refined. Adding to the sample a known weight of a standard, the assumption is checked. In the case that the weight of the standard is higher than expected, the percentage of the crystalline phases is adjusted, with the addition of an amorphous phase. To note, the amorphous content is given by difference, and no further information on its homogeneity or nature is obtained.

2.8 X-RAY FLUORESCENCE (XRF) ANALYSIS

2.8.1 XRF spectroscopy: conventional source

X-ray fluorescence spectroscopy (XRF) is a quantitative analytical technique that is used to determine the elemental composition of a material. XRF is based on the property of atoms to emit X radiation characteristic of the element when they are excited by an X-ray beam. Fluorescence is induced by a beam of primary electromagnetic radiation with energy of the order of tens of keV. It is a multi-elemental experimental technique, that is, it allows the simultaneous detection of most of the elements present in the sample under investigation (major, minor and trace elements).

In this work, the elemental composition of all the grain sizes of the considered WtE plants was analysed by XRF. The BA were crushed and ground with an agate ball mill until a fine homogeneous powder with grain size < 0.063 mm was obtained. Tablets for conducting XRF analyses were prepared using 3 grams of BA ground with 7 grams of boric acid powder. The tablets were analysed at Dipartimento di Scienze Biologiche, Geologiche ed Ambientali (Università di Bologna) with a WDXRF Axios PanAlytical spectrometer, equipped with a Rh tube working at 4 kW. The analyses were performed on both major elements (expressed g/100g) and trace elements (expressed in g/Kg).

2.8.2 μ - XRF spectroscopy: synchrotron radiation

XRF done with conventional methods gives a bulk composition, average for the powdered tablet. The intensity and focussing which can be obtained from a conventional X-ray source are not sufficient to perform an analysis at the local scale. This can be overcome when synchrotron radiation is used.

Synchrotron radiation is an electromagnetic radiation produced when a charge particle of mass m (electron or positron) accelerated to relativistic velocity is being deflected in a magnetic field. When the speed of the charged particle increases to relativistic values ($v \approx c$) a radiation is generated with several specific characteristics: 1) it is strongly polarised; 2) it has a very low divergence; 3) it possesses a large and continuous range of energies (it's white), so scientists can pick whatever wavelength they need for their experiments, as infrared light, ultraviolet or X-rays (soft or hard); 4) it is very intense, several orders of magnitude greater than conventional X-ray tubes.

Using synchrotron radiation to excite the analysed area for fluorescence analysis we have a very intense and focussed beam, so that areas as small as $50 \times 50 \mu\text{m}^2$ can be analysed.

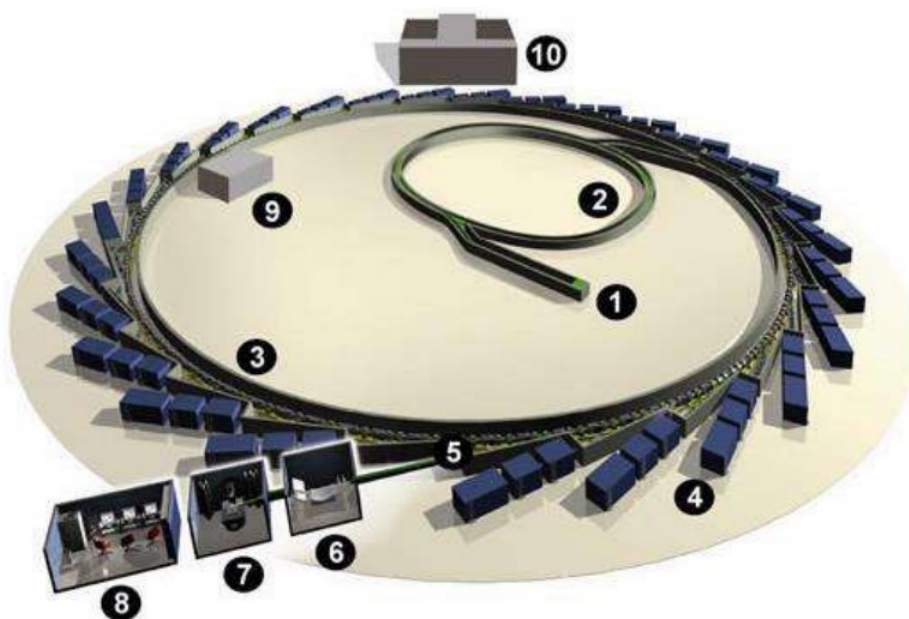


Figure 2.8.2.1 Scheme of a synchrotron. Legend: 1) Linac; 2) Booster; 3) Storage ring; 4) Beamline; 5) Front end; 6) Optics hutch; 7) Experimental hutch; 8) Control cabin; 9) RF cavities.

(www.diamond.ac.uk)

In this work synchrotron radiation was used to make μ - XRF maps and, as described in the following chapter, XANES analyses, at the XRF beamline at Elettra Sincrotrone Trieste (ETS) (**Figure 2.8.2.1**).

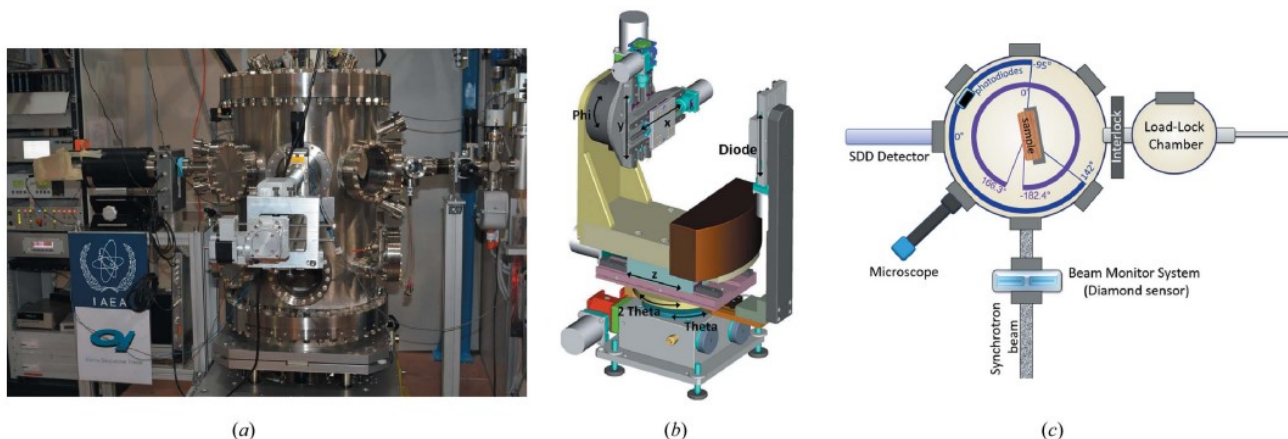


Figure 2.8.2.2 (a) Photograph of the IAEAXspe instrument installed at the XRF beamline of Elettra Sincrotrone Trieste (# Iain Darby/IAEA). **(b)** Seven-axis motorised manipulator. (Artwork courtesy of Huber Diffractionstechnik GmbH & Co. KG.) **(c)** Movement range of Theta/2Theta axes depicted in a horizontal cross-sectional view of the IAEA endstation (Karydas et al., 2018).

In this work, the experiment has been conducted using both HE multilayer for the collection of μ -XRF maps, with standard $45^\circ/45^\circ$ geometry for fluorescence mode measurements, using an XFlash 5030 SDD detector (Bruker, Berlin, Germany). The flat surface of the BA sample embed in epoxy resin has been mounted on a Teflon sample holder, with also reference metal foils mounted on the side (perpendicularly) for the energy calibration of the monochromator (in transmission mode, using an Hamamatsu Si-photodiode S3590-09, $10 \times 10 \text{ mm}^2$, $300 \mu\text{m}$ thickness). This setup was necessary to secure the sample and to have a system compatible with the working conditions of the Ultra High Vacuum Chamber (UHVC, 10^{-7} mbar) available at the XRF beamline. μ -XRF maps were collected with an incident beam energy of 14 keV and a beam size at the exit slits of $50 \times 50 \mu\text{m}^2$ (H*V). Higher order harmonics contaminations were suppressed by a pair of parallel plane mirrors intercepting the beam in grazing incidence (**Figure 2.8.2.2**).

2.9 X-RAY ABSORPTION SPECTROSCOPY (XAS)

Absorption spectroscopy refers to a number of experimental techniques used to acquire information on the electronic, structural and magnetic properties of the matter. They are based on the study of the variations of the linear absorption coefficient as a function of the energy of the incident photons. In the case in which X-ray are used as radiation we are talking about X-ray Absorption Spectroscopy (XAS). The linear attenuation coefficient depends both on the scattering phenomena (elastic or inelastic), and on the photoelectric absorption. In the range of energies used to perform XAS (1-40 KeV) the component due to the absorption clearly dominates that caused by diffusion; therefore, the

attenuation coefficient can be approximated as the coefficient of photoelectric absorption. On large energy ranges, absorption coefficient varies according to a law reported below:

$$\mu \approx \frac{dZ^4}{mE^3}$$

where Z is the atomic number of the target atom, m its mass, d the density of the sample and E the energy of the photon.

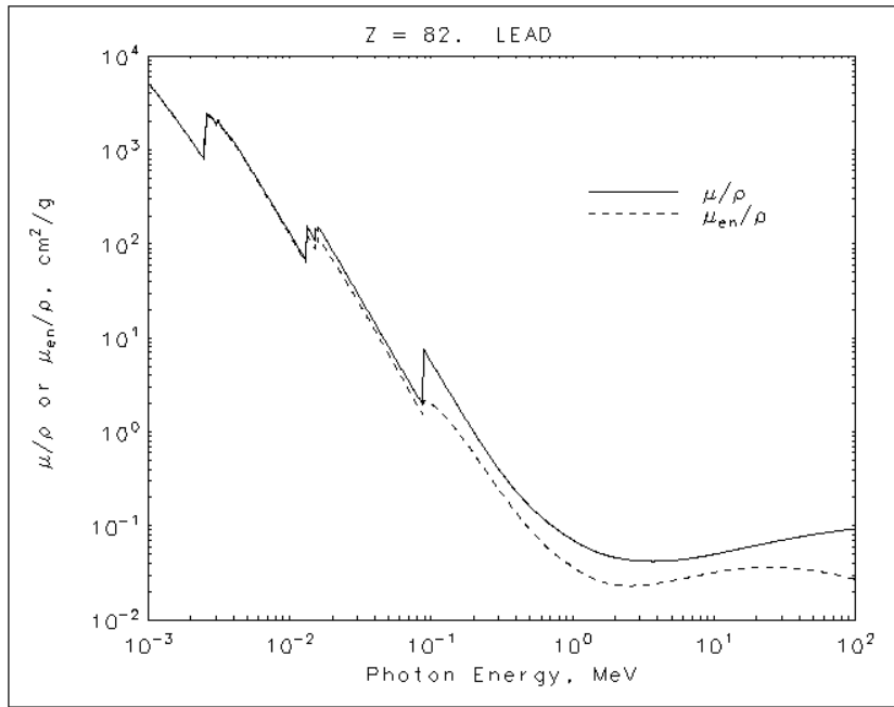


Figure 2.8.1 Graph of the absorption coefficient of Pb in function of the energy of the photons of the beam (www.physics.nist.gov)

In **Figure 2.8.1** it appears that absorbance shows some discontinuity in correspondence of particular energies. These are due to photoelectric absorption by quantized energy values. When the energy of the beam is sufficient to extract the electron in a given energy level a large number of photons is absorbed by the sample, dramatically decreasing the number of transmitted particles. This consequently causes the appearance, in the vicinity of that particular energy, of a discontinuity in the absorption spectrum. By studying these seemingly irregular structures and their energy distributions, it is possible to obtain that of the innermost electronic shells of the various chemical elements. Moreover, sinusoidal oscillations of the absorption coefficient occur around the value assumed in the peak, that is, of the presence of a fine structure.

When a XAS spectrum is analysed, is possible to obtain different information depending on the considered range of energy; for this reason, is convenient to divide the spectrum into three distinct regions:

- *Pre-edge region*: limited energy range to a few eV before the absorption edge. It's possible to detect the presence of weak discontinuities (pre-edge peaks) due to transition of core electrons to other bound states.
- *X-ray Absorption Near Edge Structure (XANES)*: it is the part of the spectrum which extends from 0 to 50 eV above the absorption edge; the combined study of XANES and pre-edge provides information on geometric and electronic local configuration. In other words it is particularly useful to obtain information on the state of chemical bond between different atoms of the sample and is strongly affected by the oxidation state of the absorber atom. This was the technique used in this work.
- *Extended X-ray Absorption Fine Structure (EXAFS)*: defines the region of the spectrum between 100 and 1000 eV beyond the absorption edge. From EXAFS analysis is possible to determine the geometric structure of the sample in the immediate vicinity of the absorber atom (up to 10 Å).

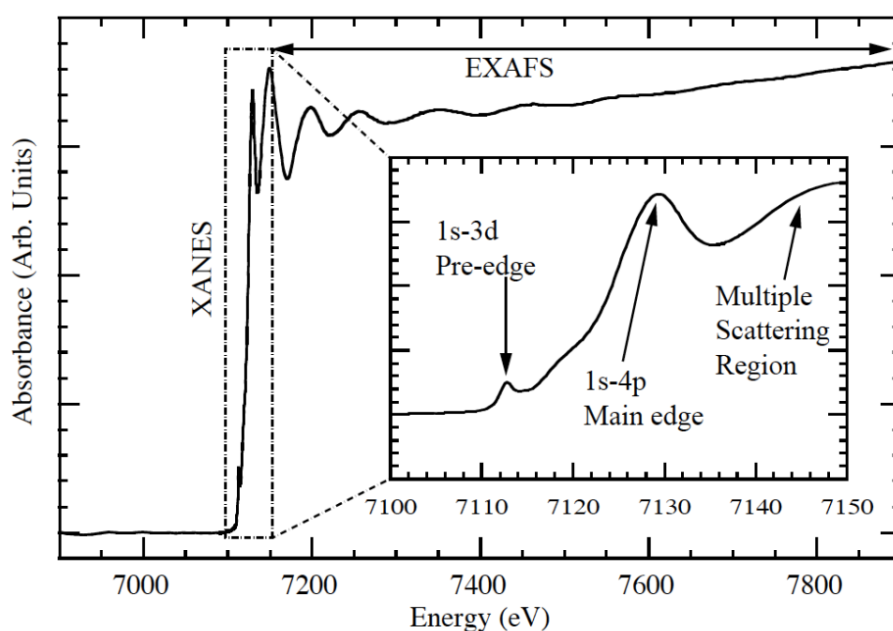


Figure 2.8.2 Example of an XAS spectrum of Fe and its components (www.commonswiki.org)

Since XANES is a much larger signal than EXAFS, XANES spectra can be collected even in sample containing lower concentrations of the target element. The interpretation of XANES spectra is complicated as there is not a simple analytic or physical description of XANES. However, the spectra can be interpreted by comparison with reference samples, and, as the edge position and shape is

sensitive to formal valence state, ligand type, and coordination environment, the XANES spectra can be used as a fingerprint to identify phases. An important and common application of XANES is to use the shift of the edge position to determine the valence state; the heights and positions of pre-edge peaks can also be reliably used to empirically determine oxidation states and coordination chemistry (**Figure 2.8.2**). A major advantage in XANES is to be element sensitive, and to detect an element even in ppm concentrations. Also, even when a given element under the beam is represented by more than one phase, a deconvolution can be done to assess the different contributions under the beam of the phases where the element is present.

In this work, some PTE (Cu, Cr, Zn, Pb, Ni, and Co) were analysed by XANES in order to investigate their oxidation state and the mineralogical environment in which they were hosted. XANES measurements were conducted at the Elettra XRF beamline. The experiment has been conducted using Si111 monochromators, with standard 45°/45° geometry for fluorescence mode measurements, using an X-Flash 5030 SDD detector (Bruker, Berlin, Germany). All spectra were collected using 5 seconds per step and a variable energy step as a function of the energy: Large step (5 eV) in the first 200 eV of the spectrum, smaller step (0.2 eV) in the near-edge region and a k-constant step of 0.05 Å⁻¹ further above the absorption edge. Multiple spectra have been collected and merged in order to increase the signal to noise ratio. The oxidation state will be determined using least-squares Linear Combination Fitting (LCF) based on reference spectra collected on compounds of known oxidation state. Background removal, normalisation of XANES spectra and LCF analyses will be performed using the Athena software package.

2.10 LEACHING TEST

The leaching test is a special type of chemical extraction. The material (soil, waste or sludge) undergoes a chemical attack with a reagent (liquid) in order to assess, through the analysis of the eluates, the elements released from the solid sample. The test makes it possible to estimate the potential long-term release of the compounds contained in soils or wastes, particularly those that could constitute potential pollution of the environmental matrices.

In this work, leaching tests and analysis of the leachates were performed following the **UNI EN 12457-2:2004 “Waste Characterization - Leaching - Compliance test for granular waste and sludge leaching - Part 2: Single-stage test with a liquid/solid ratio of 10 l/kg for materials with particle sizes less than 4 mm (with or without size reduction)”**, which in this case has been adapted for BA assessment. This is a single-stage test called “batch leaching method”, where a given volume of sample is placed in a volume of leachate solution for a given period of time. This method requires

some type of agitation to ensure constant contact between the sample and leachate. At the end of the leaching period, the liquid is removed and analysed.

Following guidelines which indicate a liquid to solid ratio of 10 to 1 (L/S = 10:1), the test was conducted in 50ml falcons into which 3g of BA and 30ml of ultrapure water (Milli-Q® 18.2 MΩ.cm at 25 °C and TOC < 5 ppb). The test was carried out on the particle size classes below 4mm from all the five WtE plants examined. Three replicates were prepared for each grain size class for greater accuracy of the data and a “blank” sample containing only 30ml of ultrapure water. The entire experimental procedure can be summarised as follows:

- the samples were placed in rotator shaker for 24h at 30 rpm;
- after 24h, each sample was centrifuged at 3600 rpm for 10 minutes in order to separate the eluate from the solid fraction;
- the samples were filtered and the eluates were collected; pH, temperature and electrical conductivity were noted;
- the samples were acidified with 3 drops of nitric acid

The leachates were diluted 1:2 and then 1:100 and were analysed by atomic absorption, ion chromatograph, and ICP-MS (analytical techniques that will be explained in detail later) in order to evaluate major elements, ions, and minor or trace elements.

2.11 SEQUENTIAL EXTRACTION PROCEDURE (SEP)

The SEP is a procedure where the sample undergoes a series of chemical etching to dissolve the solid phases, in response to their chemical behaviour. With this procedure, we may detect minor phases which from the X-ray diffraction of the original sample could be overlooked.

The Standards, Measurements and Testing (formerly BCR) program has proposed a three-step sequential extraction procedure for the analysis of sediment contaminants (Rauret et al., 1999). The procedure consists of three steps in which the sample to be analysed is attacked sequentially by different reagents and the eluates are analysed to assess which elements and in what amounts have passed into solution.

Several studies in the literature (Abramov et al., 2018; Alam et al., 2019; Haberl & Schuster, 2019; Pérez-Martínez et al., 2019; Tong et al., 2020; Akyniemi et al., 2020) apply and modify BCR 176 for the study of BA and FA. In this work, a sequential extraction procedure was developed based on the material's response to different chemical attacks which will be described below.

SEP was conducted on the Piacenza BA (sampled in 2019) and the Parma BA (sampled in June 2021). Specifically, for Piacenza material from 0.2 - 0.3mm grain size was analysed, while for Parma 2021 three particle size classes (0.063-0.2, 0.3 - 0.5, 2 - 4 mm) and a bulk made from the particle size

classes < 4mm were analysed. For each sample, 30g of material was taken and quartered to obtain samples of 1g each.

The final procedure consists of 5 steps described below, each of them promoting dissolution of a given portion of the material (**Figure 2.11.1**):

- STEP 1 (water-soluble fraction): the first step aimed to removing water-soluble phases, such as hydrated phases (ettringite). In centrifuge-tubes (50ml), 1g of BA and 40 ml of ultra-pure water were added. The samples were placed in an oscillating shaker at 30rpm for 16h (overnight) at room temperature. Then, the solid fraction was separated from the liquid fraction by centrifugation at 3000g for 20min (or until all suspended particles were precipitated). Through a filter apparatus with a vacuum pump, the eluate obtained was filtered, collected and stored with 3 drops of HNO₃ at a temperature of 4°C.
- STEP 2 (carbonate fraction): the second step is aimed to removing carbonate fraction, such as calcite and vaterite. In the centrifuge-tube (50ml), 40ml of 5mol/l acetic acid was added to each solid residue from the previous step. The samples were placed in an oscillating shaker at 30rpm for 16h (overnight) at room temperature. Then, the solid fraction was separated from the liquid fraction by centrifugation at 3000g for 20min (or until all suspended particles were precipitated). Through a filter apparatus with a vacuum pump, the eluate obtained was filtered, collected and stored at 4°C. Solid residues are washed with ultrapure water three times in a centrifuge and then proceed to the next step or are stored to conduct chemical-mineralogical analysis.
- STEP 3 (reducible fraction): the third step is aimed to removing reducible fractions, such as Fe – Mn oxyhydroxides. The residues from the previous extraction step are added to 40 ml of hydroxylammonium chloride 0.5mol/l. The samples are placed in an oscillating shaker at 30rpm for 16h (overnight) at room temperature. Then, the solid fraction is separated from the liquid fraction by centrifugation at 3000g for 20min (or until all suspended particles are precipitated). Through a filter apparatus with a vacuum pump, the eluate obtained is filtered, collected and stored at 4°C. The solid residues are washed with ultrapure water three times in a centrifuge and then proceed to the next step or are stored to conduct chemical-mineralogical analysis.
- STEP4 (oxidable fraction): this step is aimed to removing oxidable fraction, such as organic matter and sulphide. solid residues from the third step are transferred into glassy beakers with 10 ml of hydrogen peroxide. beakers are covered with a glass watch and digested at room temperature for 1h with occasional manual shaking. Digestion continues for 1h at 85°C in a thermostatic bath, then reduce the volume to less 3ml by further heating of the uncovered

beakers. After that, an aliquot of 10 ml of hydrogen peroxide is added, beakers are covered and the digestion continues at 85°C for another hour. The glass watches are removed and the volume of liquid part reduced to about 1 ml. The solid residues are transferred to a centrifuge tube and 50 ml of ammonium acetate 1.0mol/l are added the samples were placed in oscillating shaker at 30rpm for 16h (overnight) at room temperature. Then, the solid fraction was separated from the liquid fraction by centrifugation at 3000g for 20min (or until all suspended particles were precipitated). Through a filter apparatus with a vacuum pump, the eluate obtained was filtered, collected and stored at 4°C. Solid residues are washed with ultrapure water three times in a centrifuge and then proceed to the next step or are stored to conduct chemical-mineralogical analysis.

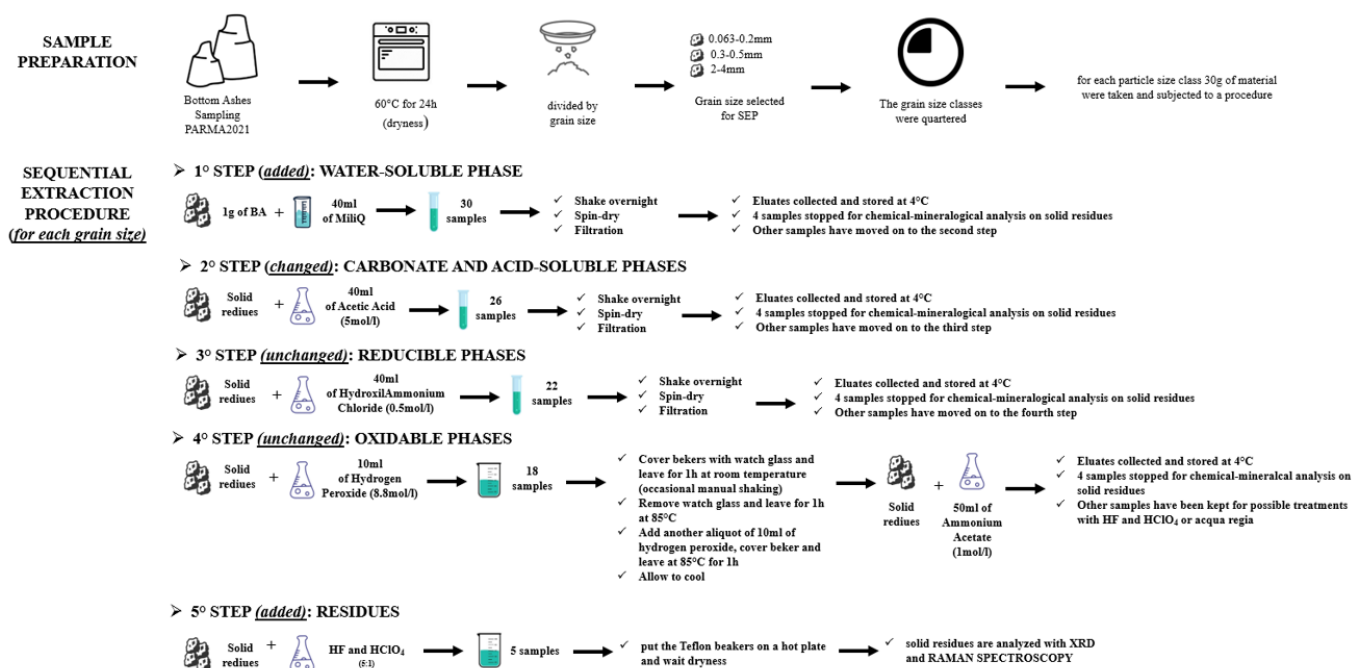


Figure 2.11.1 Sequential Extraction Procedure's scheme followed in this work.

- **STEP 5 (residues):** the last step is aimed to removed silicates and well-crystallized oxides. the solid residue from step 4 are transferred to Teflon beakers and digested with a 5:1 mixture of hydrofluoric and perchloric acids. First, a solution of concentrated HClO₄ (2 ml) and HF (10 ml) is added and wait for the almost dryness. Subsequently, another aliquot of HClO₄ (1 ml) and HF (10 ml) is add and wait for dryness. Finally, HClO₄ (1 ml) is added and wait the appearance of white fumes (Bruder - Hubscher et al., 2002). Any remaining solids are transferred in a centrifuge tube and washed three times with ultrapure water by centrifugation at 3000g for 20min.

Piacenza BA underwent all five extractions and the solid residues were analysed by diffraction. Parma BA sampled were processed to the fourth step and the solid residues were analysed by both fluorescence and diffraction. At the end of each step part of the solid residue is taken out, dried in an oven at 60°C and used to conduct XRPD and XRF analysis. Eluates are analysed by ICP-MS to evaluate the chemical elements passed into solution.

2.12 ATOMIC ABSORPTION SPECTROSCOPY (AAS) ANALYSIS

The Atomic Absorption Spectroscopy is a spectroscopic technique that uses the interaction between light and matter to quantitatively determine a metal in a solution.

In this work, the analysis of eluates from the leaching test conducted on the finest particle size classes of the 5 WtE plants were analysed at Dipartimento di Scienze Biologiche, Geologiche e Ambientali (Università di Bologna) using atomic absorption spectroscopy (Thermo S Series AA Spectrometer) for cations (Ca, Mg, Na, K).

2.13 IONIC CHROMATOGRAPH (IC) ANALYSIS

Ion chromatography (IC) allows the separation of components of a mixture provided they are in ionic form, such as cations or anions.

In this work, the analysis of eluates from the leaching test conducted on the finest particle size classes of the 5 WtE plants were analyzed at Dipartimento di Scienze Biologiche, Geologiche e Ambientali (Università di Bologna) using Ion chromatography (Metrohm Compact IC pro 881) for anions (Cl^- , SO_4^{2-} , F^- , Br^- , PO_4^{3-}), Atomic absorption spectroscopy (Thermo S Series AA Spectrometer) for cations (Ca, Mg, Na, K).

2.14 INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY (ICP-MS) ANALYSIS

The ICP-MS technique combines the use of an ultra-high temperature plasma and a mass spectrometer. Inside a quartz flashlight, housed in the instrument, Argon gas is heated through a mechanism that uses radio frequencies and magnetism, to temperatures in excess of 6000 °C. At these temperatures, which are found in nature on the surface of the sun or inside the Earth's core, a plasma is generated. Plasma is one of the four stages of matter and is composed of free electrons, positive ions and atoms or molecules with a neutral charge. In our case, only positively charged ions are selected to enter the mass spectrometer while neutral species, which have no electrical charge, are discarded by specific mechanisms. Inside the mass spectrometer, the ions enter a vacuum space in which they are subjected to a very refined electric field that manages to separate them with very high precision.

In this work, eluates from the leaching test conducted on the finest particle size classes of the 5 WtE plants were analyzed at Dipartimento di Scienze Biologiche, Geologiche e Ambientali (Università di Bologna) with an Inductively coupled plasma mass spectrometry (Perkin Elmer ICP-MS ELAN DRC-e) for the investigation of trace elements (Al, Ba, B, Cr, Co, Fe, Pb, Li, Mn, Mo, Ni, Se, Sr, Tl, Ti, V, Zn).

2.15 STATISTICAL ANALYSIS

The results obtained were investigated by statistical analysis to see if there were any correlations present between grain size and chemical composition. The indices that were used are:

- *Pearson's r index (r-index)*: which expresses whether there is a linear relationship between two parameters: it has a value between +1 and -1, where + 1 corresponds to a positive linear correlation, 0 corresponds to no correlation, and -1 corresponds to a negative linear correlation.
- *correlation index R (or p) by Spearman ranks*: which measures the degree of correlation between two variables. Spearman's coefficient does not measure a linear relationship even when intervallic measures are used. In fact, it allows us to determine how well a relationship between two variables can be described using a monotonic function. The relationship between two variables is significant when $p < 0.05$ and is highly significant when $p < 0.001$.

In addition, XRF and leaching test results are analysed by *Principal Component Analysis* (PCA).

3 RESULTS AND DISCUSSION

In the following the experimental results obtained in this investigation will be reported, as papers published, under revision or in preparation. Before each paper the summary of the main methods and results are reported.

3.1 MINERALOGICAL CHARACTERIZATION OF BOTTOM ASHES

In the first part of the work, the BA sampled from the Parma WtE plant in 2019 were characterized. After dividing the material into particle size classes and studying their trends, each of them was subjected to XRPD and XRF analysis on bulk samples in order to define the chemistry and mineralogy of the material. In addition, 11 large fragments were analysed by light microscopy and SEM – EDS, which showed great heterogeneity both structurally (crystalline phases, dendritic structures, bubbles, amorphous components) and chemically (different mineralogical phases and different chemical compositions of amorphous matrices). In this paper the main results are:

- 1) a relation between grain size and element composition is proposed, which will be verified on the 5 incinerators in the subsequent work, showing a trend by Ca, followed also by S and most chalcophile elements, and one by Si, followed by lithophiles;
- 2) the nature of BA, as a multiple phase and multiple equilibria material is outlined. It is shown that several amorphous phases are present, each with different composition, and in local equilibrium with different phases;
- 3) preliminary data, from SEM-EDS, on the speciation of PTE are given, showing a wealth of phases containing the elements. This will be further discussed in the paper where XRF-XANES results are reported.

The relevant publication is reported in section 3.1.1. *For simplicity, figures and tables have been re-numbered following the structure of this thesis.*

3.1.1 Particle size and Potential Toxic Elements speciation in Municipal Solid Waste Incineration (MSWI) Bottom Ash

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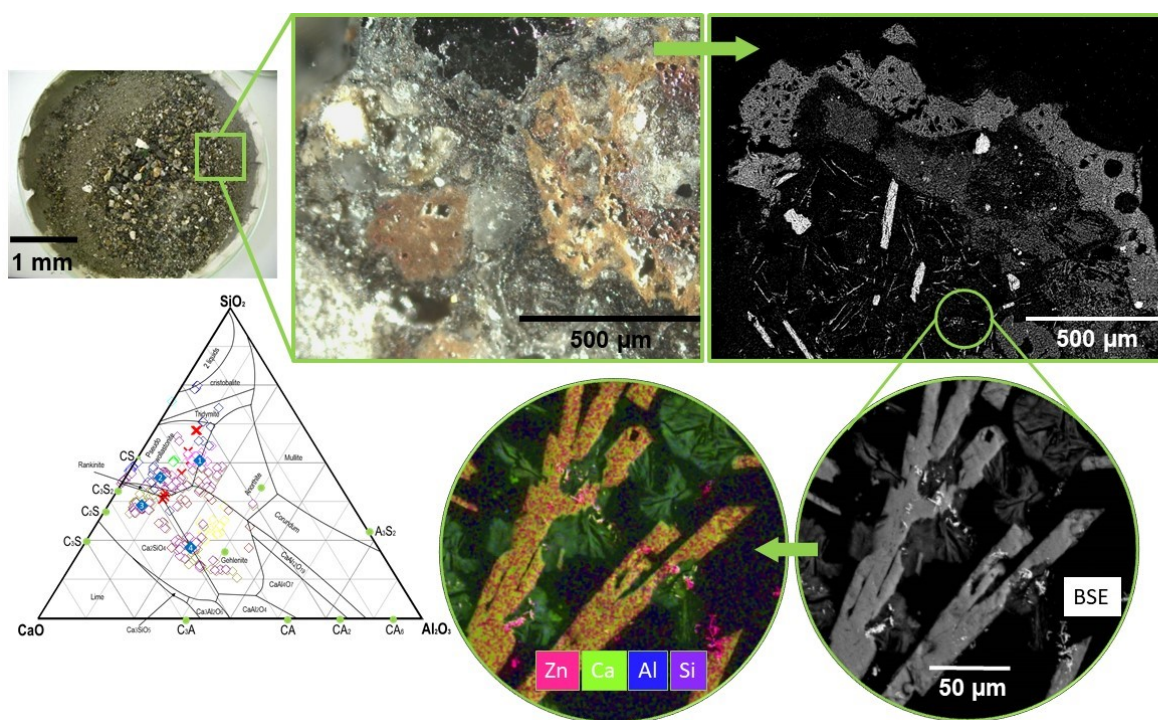
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Graphical Abstract



Abstract: The speciation of potentially toxic elements (PTE) in bottom ashes from municipal solid waste incineration (MSWI) and their relationship with grain size is investigated. The proposed enrichment of several potential toxic elements in lower sized grains is discussed, comparing the literature and new data on Parma's waste incinerator. Results from X-ray fluorescence spectrometry (XRF), SEM-EDS, and XRD analyses on different grain size show (1) a positive Si-trend, correlated with grain size and few lithophile elements, such as Zr and Rb. In Parma, Al, K, Mg, and Fe also correlate with Si for the portion below 2 mm; (2) a Ca-trend, with a strong negative correlation with Si and a positive correlation with loss on ignition (LOI), S, Cl, Ti, Zn, Pb, and Sn. Mineralogical composition shows a little change in grain size, as in previous investigations, but with substantial differences in amorphous content. SEM-EDS analysis shows that the amorphous portion is highly heterogeneous, with portions coming from melting during incineration, residual glass, and unburnt loss on ignition (LOI). The above results show that PTE elements are either present as metals (such as Cu and Ni, or Zn, Pb and Sn) in carbonate, sulfate, and amorphous residual LOI portions.

Keywords: Bottom ash; mineralogical characterization; potential toxic elements; grain size distribution; XRD, SEM-EDS, XRF

1. Introduction

The European Union has issued several directives on the management of waste that involve the prevention of waste formation, the reduction of the new dangerous material, the reuse and recycle

and, the use of waste to produce energy. These were implemented by the national laws, e.g., in Italy by the D.lgs. 152/2006.

The most recent communication from the European Commission is COM (2014)394 “Towards a circular economy: a zero-waste programme for Europe”. It proposes the recycling of 70% urban and 80% packaging wastes by 2030 and forbids landfill disposal of any recyclable waste from 2025 (COM 3998/2014). However, several waste categories cannot be recycled (i.e., hazardous waste with European Codes EWC signed with *). In order to recover some material and energy from the combustion process, waste-to-energy incineration plants are increasing in number. In the European Union, facilities burn over 131 kilos of waste per capita per year, but a very close fraction (117 kg per capita) ends in landfills (Eurostat, 2019). A major increase in waste burning is foreseen since, within a few years, all non-recycled waste must be reduced as much as possible to avoid landfilling. Incinerator plants produce combustion residues in the form of bottom ashes (BA), about 20% of the total waste mass, and in the form of fly ashes, about 4% (Izquierdo et al., 2002). In both cases, there is a growing need for the reuse of waste incinerator products. The current objective of reusing waste prompts the scientific community to analyze the chemical (composition, mineralogical phases, and heavy metal content) and physical (particle size distribution, bulk density, permeability, and porosity) properties of these ashes.

BA are very heterogeneous materials. They are composed of silicates, mainly in the form of amorphous glass; oxides; metallic part; and up to 5% unburned organics, but carbonates, sulphates, and chlorides are also present (Chimenos et al., 1999, 2003; Speiser et al., 2001; Šyc et al., 2018). The actual chemical and mineralogical composition of BA varies with respect to plant type, country, collection area and policy, season, etc.

A detailed analysis of the mineralogical composition has been conducted by different authors (Bayuseno & Schmahl, 2010; Chimenos et al., 1999; Wei et al., 2011a), but only in a few cases are the most recent plants referred to (Alam et al., 2019a; Caviglia et al., 2019; Inkaew et al., 2016). In fact, most investigations on BA focus on reuse and potential environmental hazards (Assi et al., 2020; Bertolini et al., 2004; Forteza et al., 2004; Hjelm et al., 2007).

Little or no consideration is generally paid to which phases host critical elements. Namely, it is not clear where metals and heavy metals in higher concentration, such as Cu, Zn, and Pb, are found, whether in a small reactive host, like a crystalline oxide, or in a more reactive one, such as glass or carbonate. This could become an important issue for reuse: BA are industrial non-hazardous waste (2008/98/CE), but in the presence of reactive mineral phases, with heavy metals embedded in their crystalline or amorphous structure, the ash would not be suitable for reuse. A focal point debated after

the European Council Regulation 2017/997 concerns the heavy metals glass and mineral-bearing phases, their identification and characterization, and their weathering behavior (EU 2017/997).

It is established that the smaller portion of the bottom ashes is the more polluted (Alam et al., 2020; Wiles, 1996). This was systematically verified in a recent investigation that sorted the BA in a range of different grain sizes. BA sorting produces new waste with the further disadvantage that smaller sized grains provide a larger reaction surface and, possibly, higher leaching of heavy metals already present at significant concentrations (Alam et al., 2020; Alam et al., 2019a; Caviglia et al., 2019; Loginova et al., 2019; Šyc et al., 2020). Recovery of the smaller fraction of the BA was proposed in regard to pyroxene glass ceramics by heating at a high temperature (Bourtsalas et al., 2014). However, characterization through different sizes of the BA is required to plan any process of recovery.

Previous investigations focused on the characterization of the mineral phases (Alam, et al., 2019a; Bayuseno & Schmahl, 2010) or the analysis of the portions sieved from bottom ashes (Caviglia et al., 2019; Šyc et al., 2020). A systematic investigation regarding mineralogy, composition, and grain size, to constrain the host for the potentially toxic elements (PTE) is still lacking. It is not clear whether the PTE are always concentrated in small grain sizes or whether their presence primarily depends on the waste input or the type of plant (Hyks & Astrup, 2009).

This study compares the average mineralogical and chemical composition for each fraction divided by grain size, using results from the literature and new data from the waste-to-energy plant (WtE) located in Parma. X-ray diffraction, chemical analysis of major and minor elements, and optical and electron microscopy, together with microprobe analysis observations, are used to clarify the trends followed by PTE in terms of grain size and BA mineralogy. The aim of this study is to determine how grain size affects the distribution of the different elements and any possible reuse and recycling implication

2. Materials and Methods

2.1 The Bottom ash sampling and sieving

Municipal solid waste incineration (MSWI) bottom ash was collected from the WtE plant of Parma (northern Italy), which is located in the first suburbs of the city in the PAIP (Polo Ambientale Integrato per la gestione dei rifiuti di Parma—Environmental Integrated Area for waste management). Designed and built by Iren Group, the plant has been operating since 2014, covering about 150.000 tons/year of material in 2019. The main feedstock waste includes a dry fraction selected from undifferentiated municipal solid wastes (70.000 t/year); special unrecycled wastes (18.000 t/year); discharges from waste recovery and disposal (15.300 t/year); sanitary wastes (3.500 t/year); cemetery wastes (200 t/year); industrial, handicraft, and commercial processes wastes (3.000 t/year); and dried

sewage sludge (20.000 t/year). The plant produces about 32.000 t/year of BA, as well as slag and fly ash (about 20% of the ashes).

Five samples, each weighing about 600 g, were taken, blending a larger amount of material from different points of the bottom ash pile located inside the plant on five different days (1–5 December 2018) to consider the variability of the material. The individual samples were mixed; the total sample of about 3 kg of fresh BA was dried in the oven at 50° C for 24 h and sieved in order to assess the grain size distribution. The openings standards used were chosen according to European standards for aggregate EN 933–2 (Ente Italiano di Unificazione, 2020), and the grain size used for further investigation was divided into nine classes (<0.063, 0.2, 0.3, 0.5, 1, 2, 4, 8, >16). The cumulative grain size distribution is shown in **Figure 3.1.1.1**.

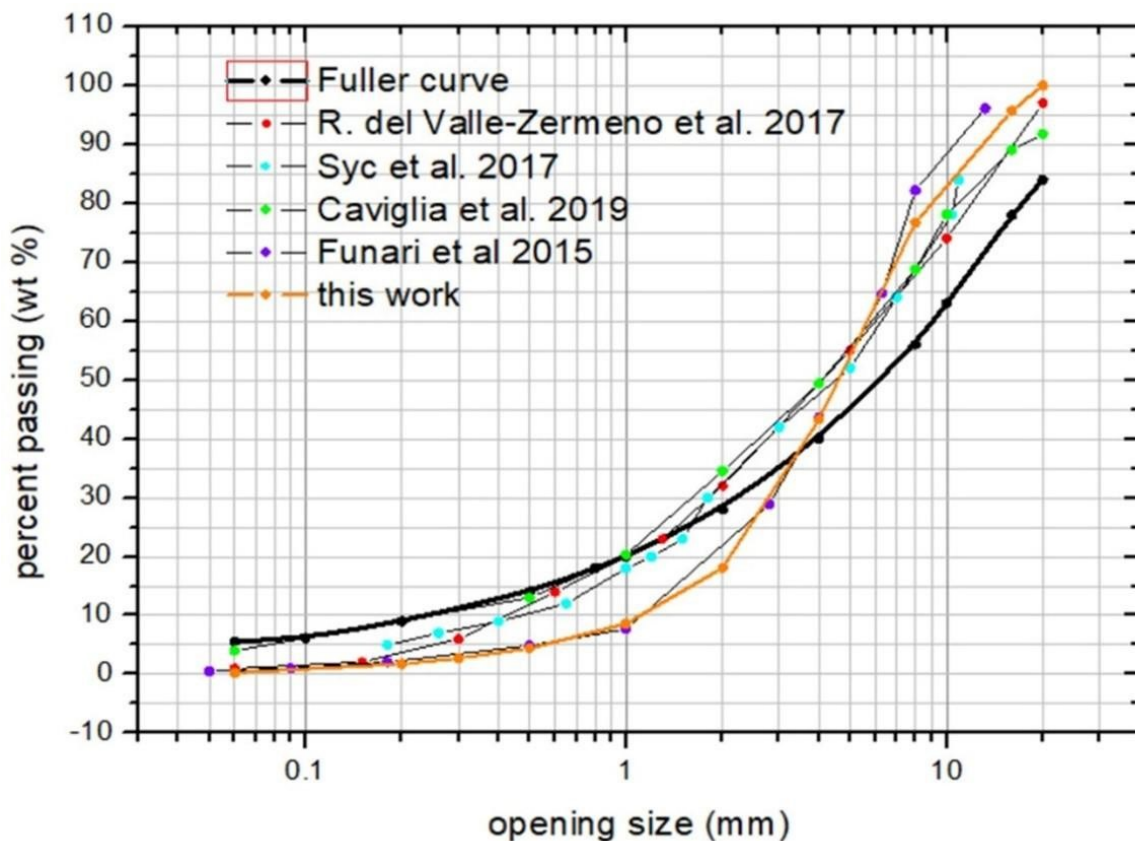


Figure 3.1.1.1 Cumulative particle size distribution and comparison with the Fuller curve and with literature data (Syc et al., 2018; Funari et al., 2015; Caviglia et al., 2019; del Valle-Zermeno et al, 2017; Fuller et al., 1907).

2.2 X-ray Fluorescence Spectrometry (XRF)

The bulk composition was measured for each granulometric class by means of X-ray fluorescence spectrometry (XRF). About three grams of the dried and milled material was used. Before analysis, each sample was first pressed in a boric acid binder to obtain a thin-layer pressed powder pellet (37

mm in diameter). A sequential wavelength dispersive X-ray fluorescence (XRF) spectrometer (Axios-Panalytical), equipped with a 4 kW Rh tube and SuperQ 3.0 software, was used. Total loss on ignition (LOI) was gravimetrically estimated after overnight heating at 950° C. The analytical results in **Table 3.1.1.1.** are provided with measured vs. certified values of the certified reference material (CRM) BCR-CRM176R. The estimated precision for elemental determinations is better than 5% for all elements, except those occurring at concentrations lower than 10 mg/kg, for which the precision is comparably worse (10–15%).

2.3 X-ray powder diffraction (XRPD) phase analysis

X-Ray Diffraction (XRD) was performed on each of the sieved portion, and on few mm-sized grains chosen in function of the optical appearance. A Bruker D2 Phaser powder diffractometer with Cu K α ($\lambda=1.54178$ Å) radiation, 30 kV and 10 mA, Ni filtered, 2θ between 5 and 70°, with steps of 0.02° and a sampling time of 1 s was used. The diffractometer acts with a θ - θ focalizing geometry and takes advantage of a solid-state detector. A sample rotation of 30 rpm was applied to minimize crystal preferential orientation effects. The diffraction patterns were identified using the Bruker software EVA and the Crystallography Open Database (COD). The complexity given by the number of mineralogical phases hindered a quantification through Rietveld refinement of all the phases present. The major crystalline phases, found in all samples, were quantified using the GSAS 2 software package (Toby & Von Dreele, 2013). The amorphous content was estimated by Rietveld analysis (Rietveld, 1993) using high purity Al₂O₃ corundum (10 wt %) as an internal standard. The refined phases and their abundance are listed in **Table 3.1.1.2.**

2.4 Optical and SEM-EDS microscopy

Twelve large fragments (>8 mm) were embedded in epoxy resin and cut longitudinally to obtain thin and polished sections for the analysis. The embedded grains were selected to avoid unburnt and refractory materials, which were instead part of the powder analyzed by XRD and XRF. The sections were first observed by a polarized stereomicroscope (BX51, OLYMPUS), and then with a Scanning Electron Microscope coupled with Energy Dispersive System (SEM-EDS) JSM IT300LV Jeol 6400 equipped with an Oxford EDS microprobe. Microprobe analysis was performed with operating conditions 20 or 25 kV and 1.2 mA current, ~1 μ m beam diameter and 75 s counting time. Analyses at 25 kV were performed in order to enhance the contribution of the higher energy peaks in metals and heavy metals.

2.5 Statistical analysis

A descriptive statistic is applied to selected chemical and mineralogical results based on grain size as a discriminant variable and used for comparative analysis with two suitable works recently carried out by Caviglia et al. (2019) and Loginova et al. (2019). The correlation was investigated by calculating the linear regression (r , Pearson) and Spearman's rank p order correlation coefficient. Statistical analysis of data distributions was performed using SPSS software (IBM corporation, 2017) and reported in **APPENDIX I**.

3. Results

3.1 Grain size distribution

In **Figure 3.1.1.1**, the granulometric curve of samples is shown and compared with that of other incinerators with similar technology and conditions as reported by Caviglia et al. (2019), Funari et al., (2015), Šyc et al., (2018) and del Valle-Zermeño et al. (2017). The Fuller curve, which represents the optimal aggregate distribution curve in terms of density and strength, is also plotted (Fuller & Thompson, 1907). Some of the difference may come from the sampling procedure: the curves vary in dependence on the portion of the ashes pile which is sampled, overestimating the larger size in the lower portion (A. F. Gualtieri, 2000), but for all the granulometric plots, the fraction lower than 4 mm accounts for about 55 wt%.

In particular, the cumulative particle size distribution of Parma shows that the most of BA (about 60%) lies in the range of 2-9 mm (range of coarse sand and gravel) while a 20% of the total weight has a grain size <2 mm and another 20% is the fraction >9 mm. A difference exists in the portion below 1 mm, which is just 6 wt% in Parma and Funari et al. 2015, whereas it is up to 20 wt% in others (Loginova et al. 2019). Comparing the shape of the Fuller curve to our samples, we have a lower percentage - about 5-10 wt% -of fine material (below the 3 mm).

3.2 Chemical analysis of MSWI bottom ash

The bulk chemical composition with grain size is reported in **Table 3.1.1.1**. Pearson's r -value and the Spearman rank p to test correlation between elements and with grain size is reported in **APPENDIX I**.

In the Parma bottom ashes, Si is enriched in the larger grains and Ca in the smaller ones. There are several elements that are positively correlated with Si or with Ca. The positive trend with Si is followed by Rb and Zr, and, among major elements, by Al, Fe, K, and Mg, when only the portions smaller than 2 mm are considered. In this case, the correlation is strong ($R^2 > 0.9$). Several other elements are positively correlated with Ca, and negatively with grain size: they are S, Cl, Zn, Cu, Ba, Pb, As, Sn, Ti, and Sr. Few elements, Cr, Ni, V, and Ce, do not seem to be related to Si or Ca.

major elements (g/100g)	grain size (mm)									
	>16	8-16	4-8	2-4	1-2	0.5-1	0.3-0.5	0.2-0.3	0.063-0.2	<0.063
SiO ₂	46.23	45.82	38.95	37.75	35.91	31.72	29.20	25.71	24.85	23.71
CaO	21.60	21.78	24.79	24.66	24.63	26.67	28.41	29.67	30.12	30.05
Al ₂ O ₃	8.59	8.26	8.92	10.39	10.05	9.63	8.96	8.27	8.46	8.27
MgO	3.71	3.95	3.64	4.33	4.42	3.91	3.59	3.26	3.15	3.23
Fe ₂ O ₃	3.04	3.01	3.60	3.63	4.05	3.74	3.48	2.64	2.49	2.21
Na ₂ O	3.92	3.69	2.78	2.49	2.36	2.20	2.18	2.14	2.26	2.20
P ₂ O ₅	1.52	1.30	1.59	2.22	2.11	2.10	2.19	2.00	1.91	1.82
K ₂ O	1.21	1.29	1.26	1.36	1.45	1.35	1.29	1.23	1.19	1.11
TiO ₂	0.69	0.64	0.78	0.86	0.90	0.97	0.92	0.90	0.90	0.90
MnO	0.09	0.08	0.11	0.09	0.10	0.10	0.10	0.09	0.09	0.10
LOI	9.40	10.19	13.60	12.22	14.02	17.62	19.69	24.08	24.58	26.40

Minor and trace elements (mg/Kg)										
S	8070	7780	9600	9500	10900	12840	14780	16910	17740	16420
Cl	5430	5430	7420	8050	8236	9780	10120	10530	10960	11600
Cu	1261	1413	1104	1669	1335	1640	1885	1664	1637	2041
Zn	1380	4400	1660	3630	3830	4270	5750	5940	6830	8740
Ba	955	907	1098	1684	1461	1681	1618	1631	1529	1879
Pb	1354	409	312	545	676	800	802	913	981	1172
Cr	880	629	573	434	651	644	697	592	621	627
Sr	429	378	436	681	499	485	517	571	568	572
Zr	256	212	186	207	196	173	169	155	156	143
Ni	119	183	140	135	174	144	179	132	134	160
Co	27	27	32	25	62	51	57	44	44	43
V	61	69	73	84	84	90	79	78	78	79
As	54	26	41	36	47	52	56	59	59	74
Ce	37	44	41	46	47	48	36	29	38	51
Sn	19	17	19	44	36	53	43	49	58	91
Rb	32	34	31	30	32	30	27	27	25	24
La	18	35	13	8	25	30	21	6	14	16
Y	14	16	16	17	19	15	14	12	12	11
Nd	18	19	10	10	22	18	20	2	19	5
Mo	15	10	15	11	17	14	13	15	14	14
Ga	14	13	12	13	13	13	14	14	13	14
Nb	11	10	11	12	12	11	10	10	11	10
Sc	<3	6	10	15	10	6	13	14	18	14
Th	13	7	6	5	7	7	7	8	9	9
Hf	<3	7	6	4	3	<3	<3	<3	<3	<3
U	<3	3	<3	<3	<3	<3	<3	<3	<3	<3

Table 3.1.1.1 X-ray fluorescence spectrometry (XRF) analysis of major, minor, and trace elements for the bottom ashes (BA) samples of Parma waste-to-energy (WtE) plant divided by grain size. Elements are in mg/kg, but major elements are expressed as g/100 g of their oxides and loss on ignition (LOI) values in %. The measured vs. certified concentrations of the certified reference material (CRM), BCR-CRM176R, is provided with the same unit of measure (n.a. is not available).

Thus, we find a Si-trend, which is followed by lithophile elements, i.e., those having an affinity for Si, incorporated in silicates, and a Ca-trend, for elements with an affinity for carbonates and sulfates (Ca, Ba, Zn, and Pb), sulfides (Sn and As), oxides (Ti), or possibly to the unburnt organics (LOI, Cl, and S).

Si-and Ca-trends are also present in other papers where the composition was determined with grain size. The differences with these observations are that Loginova et al. (2019) showed a strong correlation with Ca and S for Ni and Cr, and Caviglia et al. (2019) showed that Ni, but not Cu, follows the Ca-trend (Table S1). Moreover, the positive correlation with Si for Fe, Mg, K, and Al in the smaller grains is not confirmed; in Loginova et al. (2019), Fe has a negative correlation with Si. Within the above correlations, there is a strong difference in the actual compositional values (**Figure**

3.1.1.2). Si vs. Ca changed with a similar slope in this work and in that of Loginova et al. (2019), but shifted to lower Ca content in the work of Loginova et al. (2019); similar trends are found by Caviglia et al. (2019) but for the three finer grain sizes, which show higher Ca content than expected following the trend of Parma

(Figure 3.1.1.2 a). From the analyses of smaller grains, it appears that Ca from different plants changes similarly with S, with an apparent deviation from the main trend **(Figure 3.1.1.2 b)**. Pb and Zn follow a similar trend in the work of Loginova et al. (2019) and in this work, but they follow a different trend in the work of Caviglia et al. (2019) **(Figure 3.1.1.2 c)**. No correlation between S and Cr is found in any studies. It is likely that these differences in chemical composition may come from the waste input and different burning processes of the WtE plants, despite the fact that a correlation between final composition and waste input may be very difficult to predict with current knowledge.

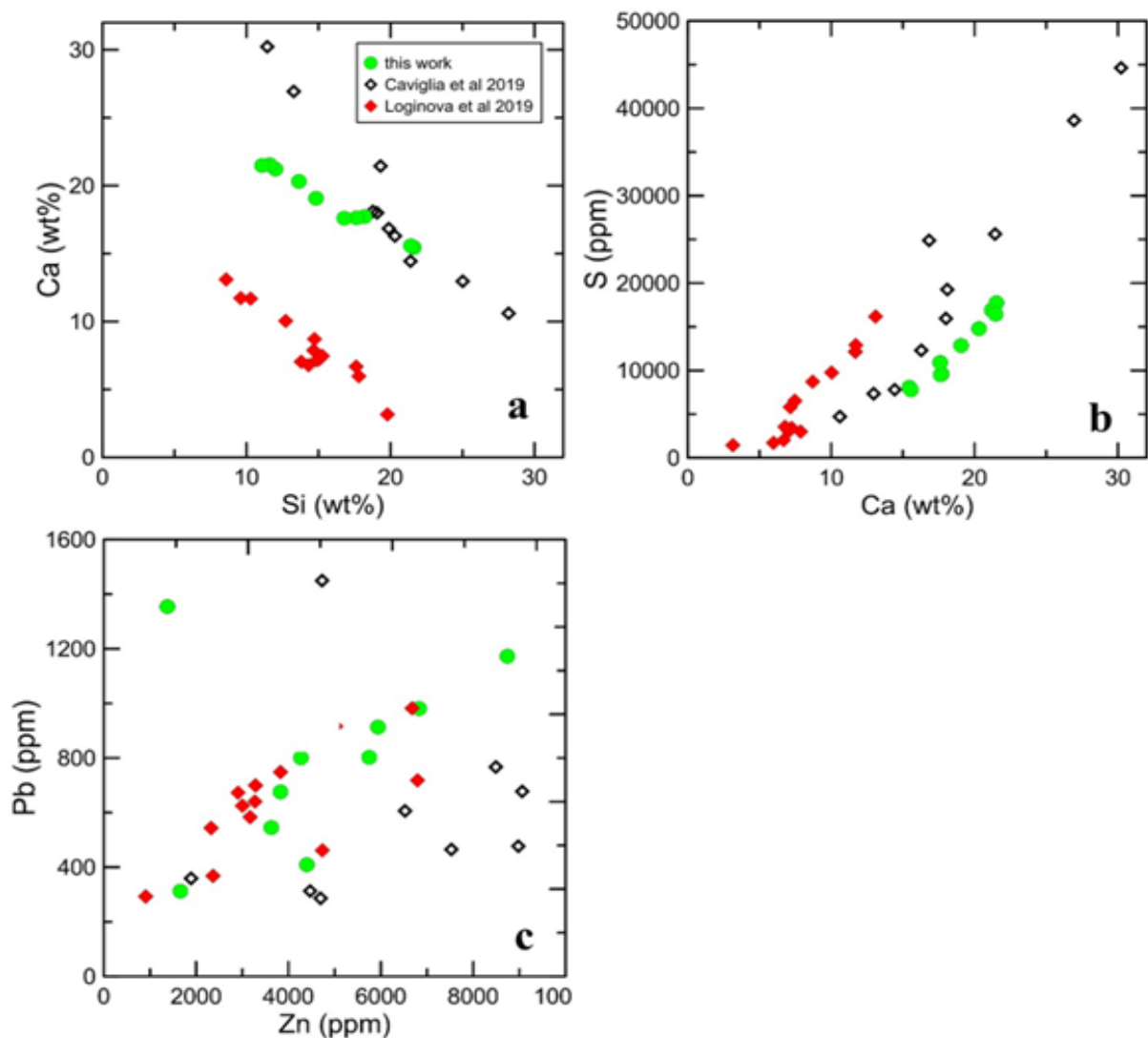


Figure 3.1.1.2 Comparison between a) Si vs Ca, b) S vs Ca, c) Pb vs Zn, values for this work (green bullet) data from Loginova et al. 2019 (red squares) and Caviglia et al. 2019 (dark squares).

3.3 XRPD and Rietveld analysis

All of the X-ray powder diffractions show heterogeneous assembly of several crystalline phases, together with significant glass content (**Figure 3.1.1.3**). To identify the mineralogical phases, in addition to the standard X-ray diffraction pattern made on the different grain-sized portion, selected on the basis of their aesthetic appearance, they are taken from the total sample and discussed. The main goal of this procedure is the characterization of specific phases that are hardly recognizable due to their small quantities inside the sample. Microscopic images of the isolated clasts and their identification with XRD analysis are reported in **APPENDIX II**. Their composition is very heterogeneous and is represented by small pieces of green, brown, or transparent glass (point 3); white spongy granules of hydroxyapatite of bone residues (point 5); pieces of non-combusted piece of metal (point 4); and gray aggregates with red or dark areas, which are the typical product of the burning processes. The mineral phases found in these grey clast resemble those noted in the bulk sample and most of the portions after sieving.

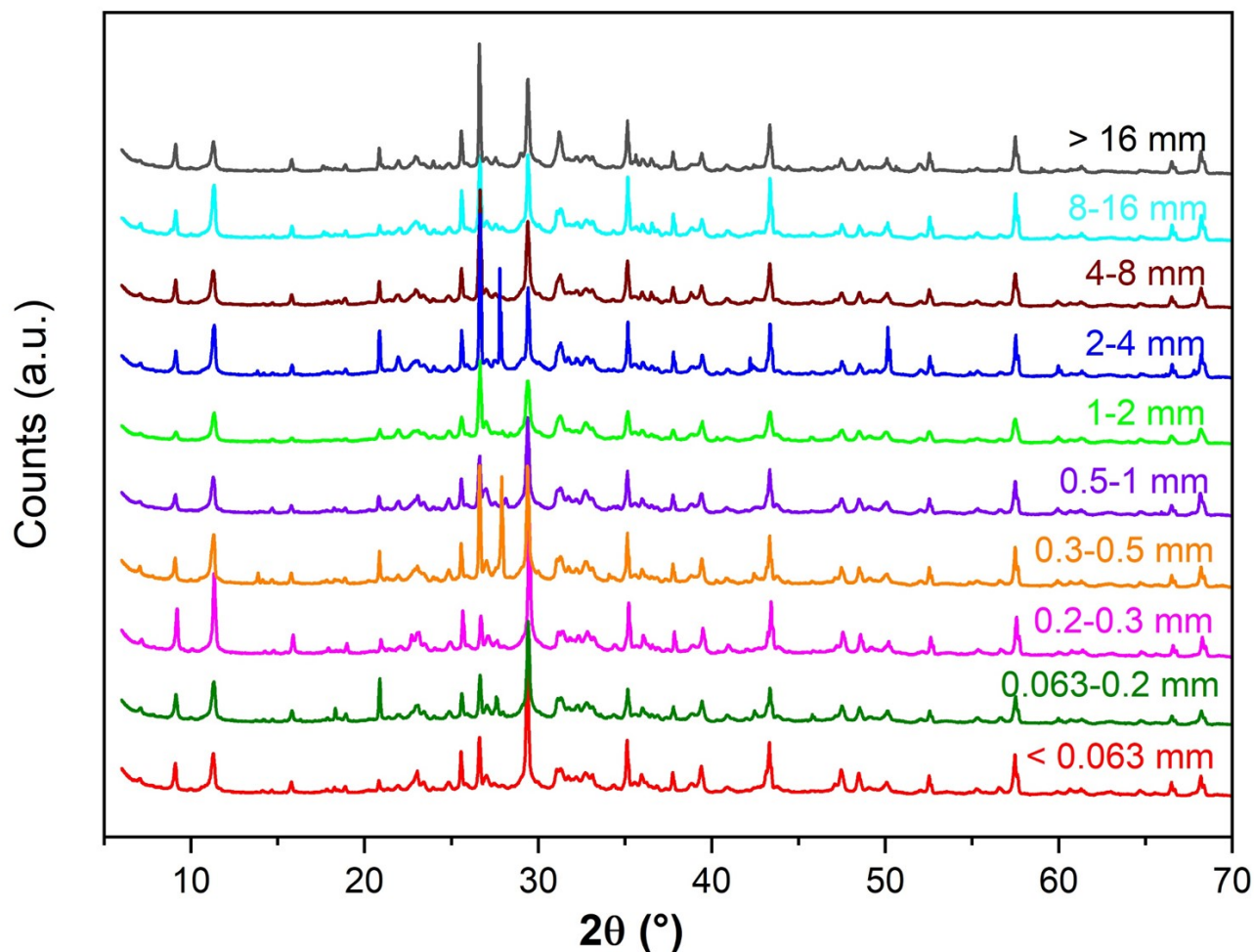


Figure 3.1.1.3. XRD patterns made on different grain sizes. Alumina (Al_2O_3) standard is used.

Phase identification was biased by the number of overlapping peaks, which concealed the peaks of the minor phases. Moreover, isomorphic substitutions in plagioclase, gehlenite, phosphates, and sulfates give rise to a shift in peak positions, again hindering correct identification. In **Table 3.1.1.2**, quantitative Rietveld analysis was conducted on the few phases that could be univocally identified. The results of the Rietveld refinement are given in weight percent normalized to 100%, including the amorphous fraction estimated with the aid of the corundum internal standard.

As shown in **Table 3.1.1.2**, the amorphous phases are the main constituents in BA. The amorphous phase is higher in the larger grain sized portions, between 75 and 70 wt%, and lower in the smaller ones, between 60 and 65%. The residual glass likely explains the higher amorphous phase content in the larger grains. Crystalline silicates (quartz and melilites) are present in higher percentage in larger grains, whereas carbonates, calcite, and vaterite occur more in smaller sized fractions. As expected, this agrees with the chemical analytical results, but as discussed below, most Ca and Si are present within the amorphous phases. Ettringite is concentrated more in the finer fractions, whereas less abundant hydrocalumite, strätlingite, and iron oxides appear to be unrelated to grain size. Calcite is the only crystalline phase present with a concentration higher than 10%. Its concentration in lower grain sized portion is likely related to the small size of crystals, which are formed during the carbonation process in air. Compared to other investigations, a difference in a minor content of feldspar is evident (Bayuseno & Schmahl, 2010; Loginova et al., 2019; Wei et al., 2011a), whose place is partially taken by Ca-Al-Si phases, such as ettringite, strätlingite, and hydrocalumite. Moreover, sylvite, another commonly found phase, is missing here. The amorphous phases here are more present than those in the works Bayuseno and Schmahl (2010) and Alam et al. (2019a), who found an amorphous of 33 and 36 wt%, respectively, but they are similar to those identified by Caviglia et al. (2019), i.e., about 70%. An intermediate value was found by Wei et al. (2011a) of about 50%.

Phases	Grain Size (mm)									
	< 0.063	0.063-0.2	0.2-0.3	0.3-0.5	0.5-1	1-2	2-4	4-8	8-16	>16
Calcite	10	11	10	9	8	8	5	7	5	7
Quartz	3	4	2	6	3	5	6	6	4	5
Stratlingite	2	2	2	2	2	1	1	1	1	1
Ettringite	4	6	5	3	3	2	1	1	3	3
Hydrocalumite	3	4	4	4	3	3	3	3	3	2
Anorthite	2	2	2	7	2	3	3	2	1	2
Vaterite	3	3	4	4	2	3	1	2	2	2
Gehlenite	2	3	3	2	2	2	2	2	2	2
Hematite	1	1	1	1	3	1	< 1	< 1	< 1	< 1
Magnetite	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Crystalline	30	36	33	36	28	27	23	24	20	25
Amorphous	70	64	67	64	72	73	77	76	80	75

Table 3.1.1.2 Rietveld refinement quantitative phase analysis (wt%) on different grain size. The estimated error is ± 1 .

3.4 Bottom ash morphology

3.4.1 Optical observation

Optical observation was done on few grains, chosen for different colour and lustre, from the portion larger than 4mm. Similar grains were also analysed by XRD (**APPENDIX II**). The grain colour varies with the crystalline and amorphous phase content, as revealed by XRD. The few whitish grains were made of hydroxyapatite, likely by the burning of cemetery residuals; green or colourless glass come from residual glass, which did not react during incineration. The rounded reddish-grey grains, which are most abundant here, in Chimenos et al., (1999,2003) and in Wei et al., (2011) are most made by a heterogeneous aggregation of residual refractory material and metals coexisting with crystals and amorphous (**Figure 3.1.1.4**). The amorphous acts as a matrix that binds the crystalline and metallic fractions of the original waste and the new-formed minerals. The original waste grains show rounded edges, indicating partial reabsorption (**Figure 3.1.1.4 a**), whereas new formed crystals are often present as sharp needles within the glass, like the wollastonite crystals in **Figure 3.1.1.4 b**. Vesicles and bubbles appear indicating that some degassing occurred (**Figure 3.1.1.4 c and 3.1.1.4 g**).

XRD and subsequent SEM-EDS analysis showed that the grey grains take their colour for the coexistence of gehlenite and wollastonite, mingled with metal, whereas the red portions take their colour from Fe oxides (**Table 3.1.1.2 and APPENDIX III**). Secondary carbonation is present as an external, fine grey cohesive material that coats the rounded clasts (**Figure 3.1.1.4 f**).

3.4.2 SEM-EDS investigation

SEM backscattered electron images show almost invariably crystals within an amorphous matrix. The prevailing amorphous was investigated in further detail. About 400 EDS point analyses were done on different amorphous areas, sampling five polished sections sized about 8-10 mm; in each five areas were examined, for a total of 20 areas. The point analyses on the amorphous are plotted in the ternary diagram $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ in **Figure 3.1.1.5**, together with the bulk XRF composition for the 9 granulometric classes (red crosses).

The amorphous material is made of an extreme heterogeneous composition, coexisting unmixed at the sub-millimetre scale even within the same grain. This kind of mingling, well known in igneous petrology is related to the crystal structure of silica-rich and silica-poor melts, here occurring at the microscale (Rankin, 1915). The composition of the amorphous within each volume is homogeneous (**Figure 3.1.1.4**).

Optically, this is apparent in the coexistence of reddish and whitish glasses. The chemical composition of the glassy materials is reported in the $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ ternary diagram. Most amorphous compositions fall near or above the cotectic lines, with a crowding on the ternary

minimum; this suggests that the amorphous glass forms from melt at eutectic conditions. About 80% of the analyses falls within the field with cornered by pseudowollastonite-gehlenite-larnite. As shown in **Figure 3.1.1.4** the average composition of the larger grains is Si-richer than almost all the analysed glasses.

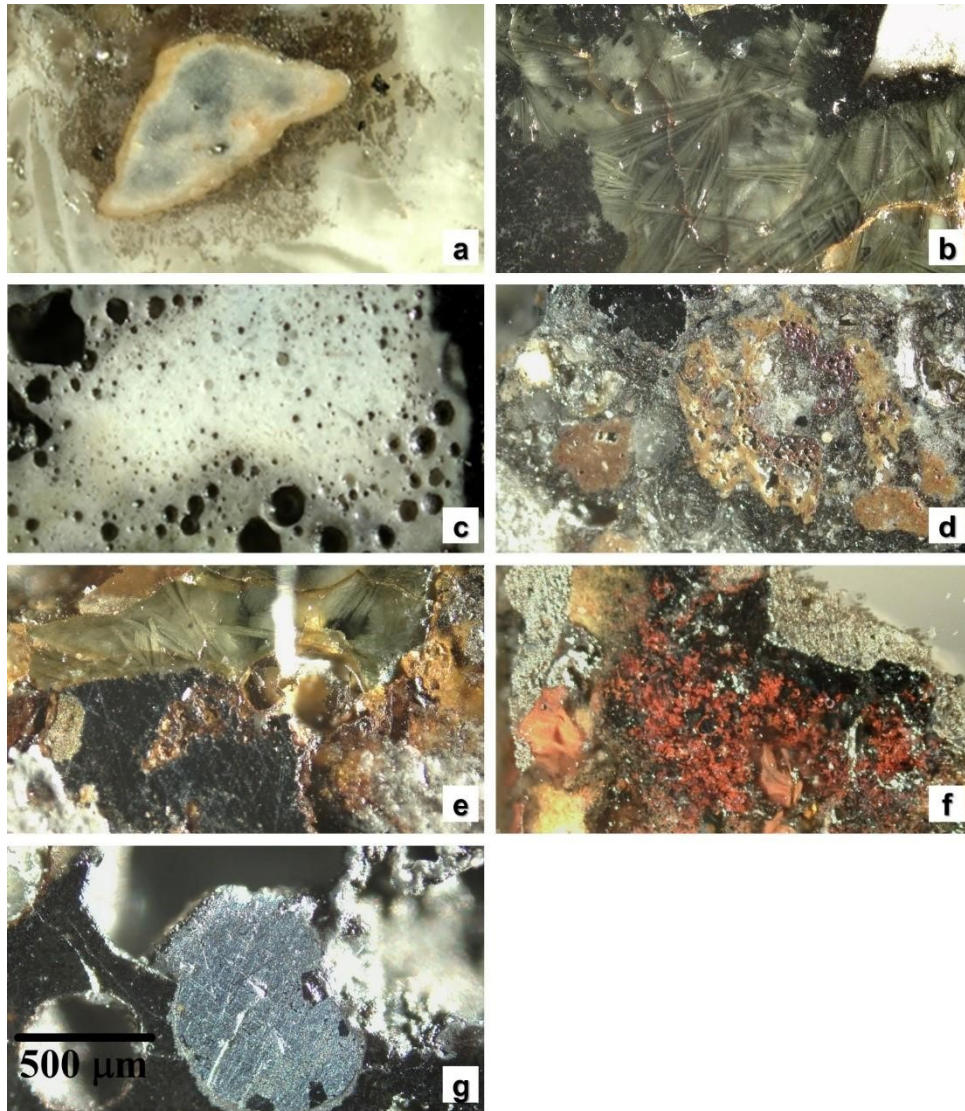


Figure 3.1.1.4 photomicrograph showing the inner part of the clasts cut longitudinally. Each of them appears different from the other in terms of morphology but we can observe frequently a part of a dark matrix (dm) **(b,e,f,g)** and within it areas of different color, sometimes white **(c)**, yellow/red **(e,f,d)** or transparent **(b,e)**. Many samples present little vesicles and bubble structures, indicating degassing processing **(c)**, metallic, alloy or refractory inclusions **(a,g)** sometime with reaction rims **(a)**. External grey crust surrounding related to carbonation is shown in figure **(d)**.

This likely occurs as XRF analyses consider also pure SiO₂ residual glass, which was discarded in the analysis of the grains. The glassy matrix is the host of Na, K, and Mg, elements which are not

found in crystalline phases reported by XRPD (**Table 3.1.1.2**), but are present in the XRF analyses between 1 to 5 wt% (in oxide).

Small crystals of silicate and oxides often with skeletal quenching structures are found, coexisting with the molten matrix. Most common are melilites, minerals that in nature crystallize at high temperature from alkaline rich magmas. Natural melilite is a solid solution between akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$), and gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$); here significant Fe is present so that the average formula is $\text{Ca}_2\text{FeAl}_{0.6}\text{Si}_{1.4}\text{O}_7$. Also, some Na and K exchange for Ca in melilites, like previously observed by Bayuseno et al. (2011) in soda-melilites. In this work no Cr, Ni, Cu, Zn was found in melilite, differently from Alam et al. (2019) (10-15% of the total content).

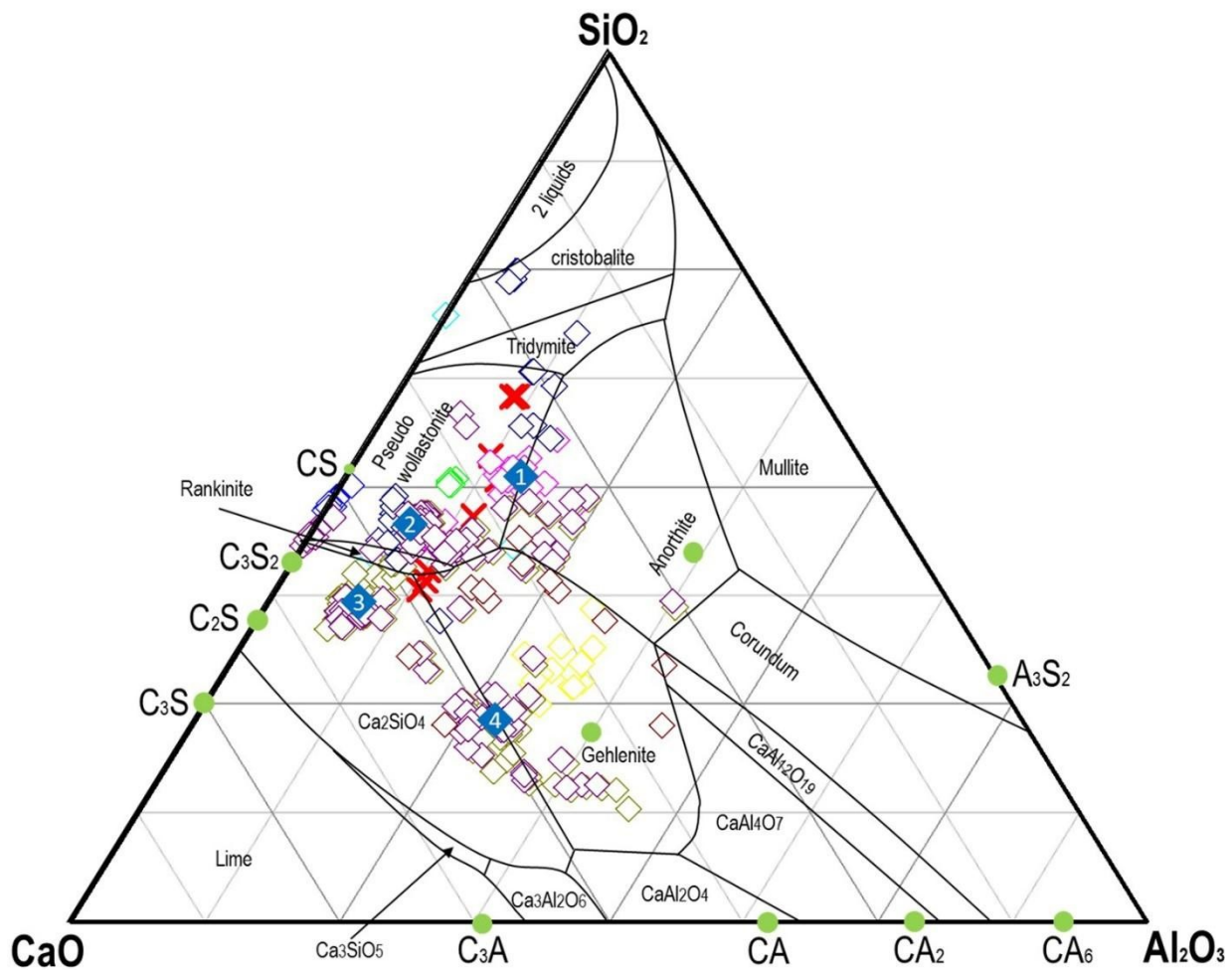


Figure 3.1.1.4 Phase diagram of the CaO - SiO_2 - Al_2O_3 system originally determined by Rankin and Wright (1915), representing the different regions where a given oxide component crystallizes from the corresponding melt. Specifically cement notation and stoichiometric formula of some compounds are given for the different phases that can be present in common cement clinkers and ceramics (green points). Red crosses represent the bulk XRF composition for the 9 grain size considered in this work.

Among other silicates, quartz, pyroxenes, pyroxenoid and plagioclase are found. Except quartz, they are hardly found in XRD pattern, as their major peaks are overlapped by more common phases. Plagioclase is bytownitic, with average chemical formula $\text{Na}_{0.2}\text{Ca}_{0.8}\text{Al}_{1.8}\text{Si}_{2.2}\text{O}_8$, while pyroxene is found with two different compositions, one hedenbergitic ($\text{CaFeSi}_2\text{O}_6$), and the other augitic $\text{Ca}_{0.9}\text{Na}_{0.1}(\text{Fe}_{0.3}\text{Al}_{0.7})\text{Si}_2\text{O}_6$. Skeletal wollastonite (CaSiO_3) and rankinite ($\text{Ca}_3\text{Si}_2\text{O}_7$) are also present (**APPENDIX III a, APPENDIX III b and APPENDIX III c**).

Among secondary minerals, most present are the carbonates, calcite and vaterite. They appear as incohesive and fine fragments around the clasts (**Figure 3.1.1.6 e**).

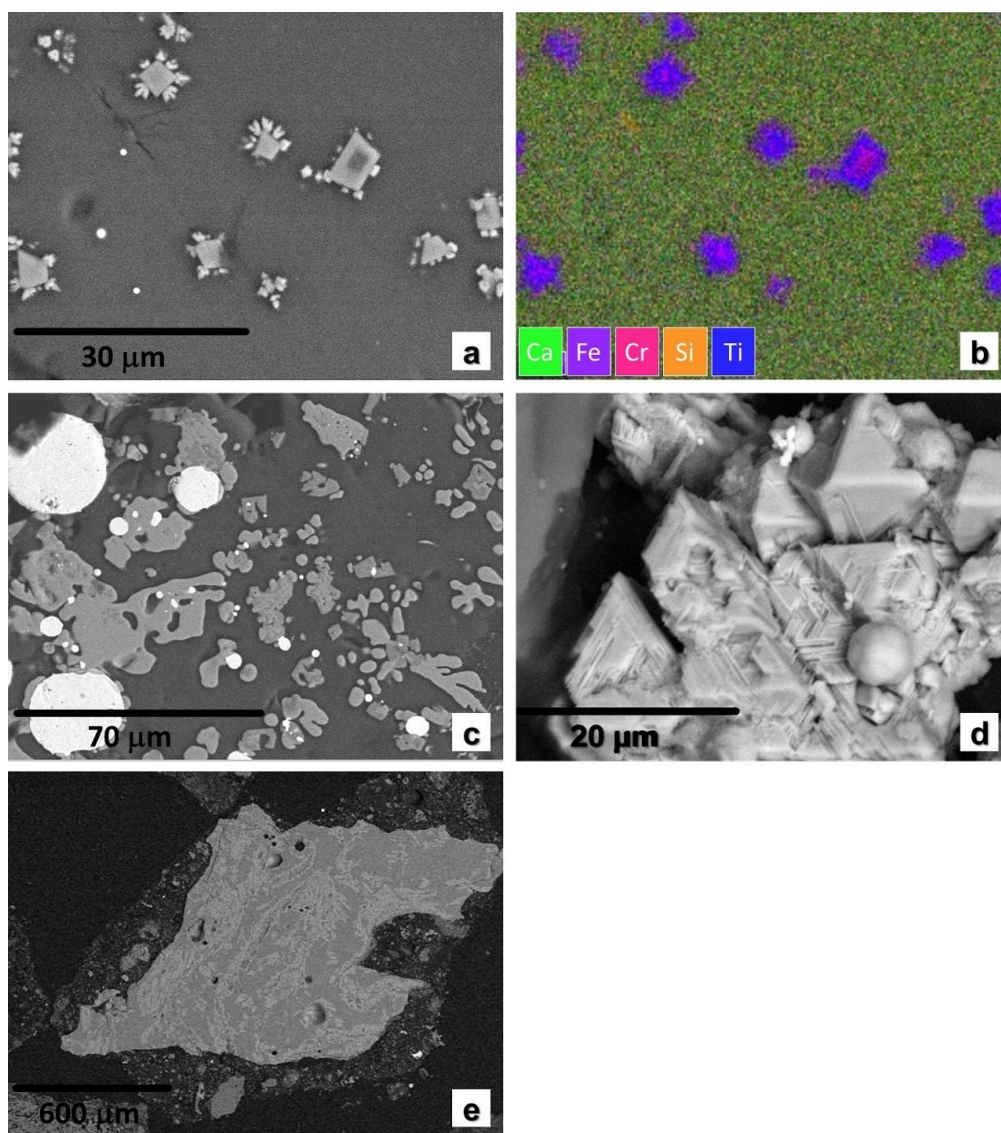


Figure 3.1.1.6 SEM images of metallic oxides found in bottom ash samples a) newly formed spinel crystals in glass matrix with their b) chemical maps. These crystals are Fe-Ti spinel with an inner core Cr rich; c) dendritic structure of iron oxides and few little square shapes of spinel. White and brightness (at BSE) drops are metallic Cu; d) regular octahedron of magnetite spinel in sample powder; e) large image of a clast: mingling of metallic phases and amorphous inner part surrounded by incohesive and fine fragments.

Other mineral phases ascribable to a secondary processes are hydrated silicates, aluminates and sulphates, like hydrocalumite $[\text{Ca}_8\text{Al}_4(\text{OH})_{24}(\text{CO}_3)\text{Cl}(\text{H}_2\text{O})_{9.6}]$ and ettringite $[\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}]$ as well as gypsum and anhydrite; they are reported by Meima et al. (2002) to form in a basic pH environment in air-dried material (pH 10–11). Simple (A_xO_y) and complex ($\text{A}^{2+}\text{B}_2^{3+}\text{O}_4$) metallic oxides are another important constituent. Most part of them are iron oxides, haematite (Fe_2O_3), and magnetite (Fe_3O_4). Magnetite, which belong to the spinel group of minerals is found both pure and with PTE and Ca exchanging for Fe. Spinel and simple oxides are found as residual resorbed or newly formed crystals in the glassy matrix (**Figure 3.1.1.6 a, 3.1.1.6 c, 3.1.1.6 d**). In the newly formed crystals Fe^{2+} is often partially replaced by Ca. The Ca-Fe substitution was found by Wei et al. (2011), who suggests a high-temperature crystal-melt exchange mechanism. Besides, exchange for Fe^{3+} and Ti^{3+} in the B site of the spinel-type minerals was observed, as well as the entrance of Cr and Zn (**Figure 3.1.1.6 a and 3.1.1.6 b**).

The secondary minerals are found mainly in the external part of the clast, covering the BA particles and weakly tied to them. These minerals are easily separated from larger grains during transport and sieving due to their breakable nature and low mechanical resistance and accumulate in the smaller fraction. Alteration phases are found despite our samples were sealed in a bottle just a few days after sampling and have not been air-aged like those of Alam et al. (2019) and Meima et al (2002), testifying early aging process as soon as the bottom ash are quenched in water after incineration.

4. Discussion

Combined chemical, SEM-EDS and XRD investigation with grain size allows to suggest the speciation of major and minor elements. Except Ca and Si, the major elements are poorly correlated with each other. They are present in silicates and non-silicates, although in Parma in the grain size below 2 mm Si is positively correlated with Mg, Fe, Al, Na, K, suggesting that they are present almost completely in silicate glass or crystals.

Fe was found to correlate with other metals, like Zn, Pb, Cr and Ni in Loginova et al. (2019). Such trend suggests that Fe is present as some metal or oxide, as the same elements are not correlated with Si. In Parma and Caviglia et al. (2019) a higher entrance of Fe in silicate glass is probably, as suggested by a Fe-Mg trend: Fe and Mg exchange in silicate and oxides, not in metals. We could expect that increasing Fe Mg increases if it is present in silicates or oxides. This is the case in this work and, albeit with poorer correlation, in Caviglia et al. (2019), but not in Loginova et al. (2019). Ti, commonly given as major element shows an opposite behavior to Si. In this work it is present in spinels and in metal alloys.

Although Ca is found in silicates, as in melilite, plagioclase, stratlingite, and wollastonite, Ca major concentration is in the smaller fraction and it is related to calcite-vaterite and ettringite, both Si free phases, or in spinel-like oxides.

About minor elements, the positive trend with Si and grain size for Zr and Rb indicates that they enter mostly as silicates. More elements are positively related with Ca: S, Cl, Ti, Sn, Zn, Pb, Sr, Ba, Mn, As, LOI and, in Loginova et al. (2019) and Caviglia et al. (2019), also Ni and Cu. The suggestion is that the positive correlation of Ca with so many elements comes from different sources of enrichment in lower sized grains. First, calcite-vaterite increase in the smaller grain size, such as elements hosted in the carbonate structure, like Ba, Zn, or Pb. The same elements exchange with Ca in sulphates like ettringite and gypsum, again seemingly more present in the smaller portion. Cl is likely present in the LOI: in silicates and glass, Cl is little present. We have found Ti, Mn, Ni with Fe and Ca in spinel oxides, but not in silicates. Cu is present as pure metal or in alloy with Fe. When present, Cu occurs at high concentrations according to EDS analysis (from 40 to 100 wt. %), with granules usually smaller than 10 μm . Correlation with Ca in Loginova et al. and Caviglia et al. suggests also that Cu may enter as a carbonate.

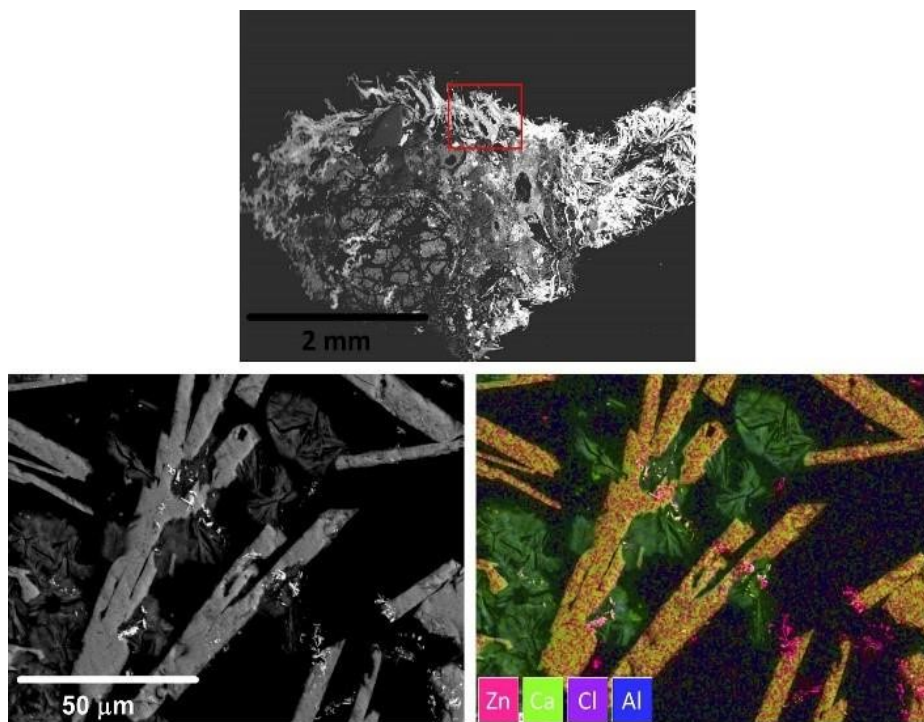


Figure 3.1.1.7 Optical and BSE images of a sample area with Zn compound. Chemical map is reported

However, to this general picture our ideas is that for a given element speciation may occur from different sources. An example is Zn, which was found throughout microprobe analysis in the following forms:

- 1) in solid solution in the spinel oxide with a remarkable heterogeneity between different granules. Zn exchanges with Fe^{2+} , between 2000 to 8000 ppm.
- 2) as a secondary constituent, in glasses of probable cement origin, with silicates or aluminates. There is substantial heterogeneity in the chemical composition of the glass, more or less rich in Al or Si, as well as Ca and Fe. The Zn is present in quantities at the limit of detection with punctual microprobe analyses, always less than 2000 ppm. Given the widespread presence of glass, it may account for a background value, always present of about 1000-2000 ppm. It may be the prevailing form in larger grains.
- 3) the presence of Zn in large amount was observed only in a single sample as hydroxides, pure or with Ca (up to 74 wt. % in pure hydroxide and 32 wt. % in that with Ca). Its presence as this mineralogical phase needs to be supported by other cases, not found here (**Figure 3.1.1.7**).

5. Conclusions

Bottom ash can be divided in different grain sizes. The size at about 4 mm divides approximately in two portions of similar weight. XRD showed that the amorphous phases are prevailing in any portion, more in the larger one. This is a general feature, even if the amount changes substantially in different incinerators. The mineralogical composition of the crystalline phases shows little difference between the grain size, with higher amounts of quartz in the coarser size and calcite in the finer one. The presence of ettringite and hydrocalumite suggest that an ageing process may take place in all samples, although they can be considered not exposed to weathering.

We found in minor elements two different trends: a Ca-trend, followed by LOI and a series of minor elements, and a Si trend, positively related with grain size and lithophile elements like Zr and Rb. This can be interpreted in terms of the abundance of crystalline minerals, and of the different amorphous phases present. Due to the prevalence and reactivity of the amorphous phases further investigation should discuss the different amorphous, their nature, if silicate or not, and their capability to incorporate transition elements.

Also, we have shown that bottom ash, despite the different waste composition, show similar enrichment in elements. The detailed trends, the value of the elements, especially the major ones, are an indication of waste composition, local use and separation, but also on how the incinerators work, and may suggest procedure to reduce environmental impact.

A few conclusions can then be drawn:

- a) in bottom ash the same crystal phases are observed at any grain size, albeit in different amount. However, at the electron microscope scale we observe a wealth of local situations, including residual

material made of silicate and metallic inclusions, silicate melts of different composition, droplets of metal phases, neo-formed minerals, with a variety of quenching structures.

b) The higher presence of amorphous phases at any grain size suggests that most of the observed compositional changes occur within the amorphous phases.

The presence of heavy metals in the finer fraction, suggested by numerous authors was here observed only for few elements. A separation process applied to the finer fractions to reduce the total heavy metal content would not reduce the overall presence significantly, being this fraction volumetrically almost negligible in terms of output flow, nor the enrichment is such to suggest as potential reuse as secondary raw material.

Author Contributions

Conceptualization, V.F.; Data curation, M.T. and **C.D.M.**; Investigation, L.M.; Methodology, **C.D.M.**; Supervision, M.T. and V.F.; Validation, L.M.; Writing–original draft, L.M.; Writing–review & editing, M.T. and V.F.. All authors have read and agreed to the published version of the manuscript

3.2 COMPARISON BETWEEN WtE PLANTS IN NORTHERN ITALY

In this second investigation the results on the first investigation on the Parma WtE plants are discussed with further data from 5 WtE plants from northern Italy. XRD, XRF and TGA analysis were conducted for each grain size; the XRF analysis showed higher concentrations of PTE in the finer grain size and for this reason the granulometric classes < 4mm were used for leaching test. The main results were:

- 1) a notable similarity in the major element composition, in spite of the different locations and input fluxes;
- 2) a strong difference in the content of the amorphous phase, between the Ferrara and Forlì-Cesena incinerators, respect to the others;
- 3) a partial confirm of the trend between grain size and composition found in the first paper, with elements like Al and Fe showing different composition and grain size relations in the 5 incinerators;
- 4) a varying leaching of the minor elements, among which PTE, with results following a trend and of the same order of magnitude in the samples from each incinerator;
- 5) a general trend where PTE are released more in the smaller grain size portion, often with values above regulatory limits.

The results obtained have been the subject of an article currently being submitted. The article is reported as paragraph 3.2.1. *For simplicity, figures and tables have been re-numbered following the structure of this thesis.*

3.2.1 Grain size and mineralogical constrains on leaching in the bottom ashes from municipal solid waste incineration: a comparison on 5 plants from Northern Italy

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Abstract

Introduction. Bottom ash (BA) from municipal solid waste incinerator (MSWI) are currently classified by the European Waste Catalogue as industrial non-hazardous waste. To promote their reuse, identification and characterization of the heavy metals bearing phases (both glass and minerals), as well as their weathering behavior must be addressed for what concern the chemical composition, mineralogical phases and in high concentrations and pollutants' mobility. An important point is whether the results from a given plant can be generalized.

Material and Methods. In this work BA from 5 northern Italy Waste to Energy (WtE) plants were sorted based on different grain sizes. The input waste of the plants is similar, coming from a culturally homogeneous area, and with similar collection management. For each grain size, a mineralogical, chemical and physical characterization has been done using of X-ray fluorescence (XRF), X-ray powder diffraction (XRD) and Rietveld refinement, Thermogravimetric analyses (TGA) and leaching test.

Results and Discussion. We found that for major elements the average chemical composition of the incinerators is similar, with some difference in minor elements. Ferrara (FE) and Forlì-Cesena (FC) BA show portlandite, higher ettringite and lower amorphous than the Torino (TO) Parma (PR) and Piacenza (PC) ones. This affects the pH and the release and toxicity of the leachates. In FE and FC ashes ettringite is not dissolved, and we have low sulphate, but also Ni and Ba beyond regulatory limits, suggesting that Ni and Ba are present as hydroxides with portlandite, which dissolves. In TO, PR and PC Cr and sulphates are beyond limits, suggesting that Cr comes from dissolution in ettringite. Cu and Cl are always beyond limits; the dissolution of chlorides accounts just for 30-35% of the global Cl leachate. We observe that in the assessment of potential toxicity of the ashes mineralogy has an effect higher than the bulk chemical composition.

Bulk and leachate composition show significant changes with grain size, but generally within an order of magnitude. Grain size sorting, although useful together with other techniques is not by itself able to comply with the PTE risk level.

1. Introduction

The world generates 2.01 billion tons of municipal solid waste (MSW) per year, where it has been estimated that at least 33% is not managed in an environmentally safe manner. On average, each individual generates 0.74 kg/day but with strong regional differences. The global waste production is expected to grow up to 3.40 billion tons by 2050 (Kaza et al., 2018).

Waste management in Italy is regulated by the legislative decree n°152/2006, which implements main European directives on waste. According to the decree n°152/2006 MSW incineration residues need to be treated before they are disposed of. Landfilling is the most common method used to manage MSW, but landfilling has also concerns about groundwater pollution and soil contamination. Among the different waste management options, waste incineration is most important and widespread: it reduces the volumes and weight of the waste, and in WtE plants it also provides a bonus for energy production (Bawab et al., 2021) .

Incineration produces two types of solid residues: bottom ashes (BA) and fly ashes (FA). The BA are the solid residues resulting from the combustion of household waste at the lower outlet of the furnace, after cooling in water tank, whereas the FA are the blown out fraction. In general, BA are about 20% of the total waste mass, and the FA, about 4% (Izquierdo et al., 2002). FA in Italy are usually excluded from recycling as they contain and release several hazardous elements (Setoodeh Jahromy et al., 2019).

The BA are composed by a mineral fraction (80–85%), ferrous metals (5–10%), non-ferrous metals (2–5%), and unburned organic matter (CEWEP, 2016). The chemical composition of the bottom ash depends on the MSW feed characteristics and on the combustion system; the content of major elements resembles on average the content of these elements in the soil and lithosphere. The content of minor and trace elements varies depending on the plant; for most elements it is depleted, and for some like Zn, Pb, Cl it is highly enriched with respect to the equivalent average concentrations found in the soil and lithosphere (Dijkstra et al., 2009). Compared with other combustion waste, BA is highly enriched in Cu, Mn, Zn, Pb, Cr, and Ni (Izquierdo et al., 2002). In a circular economy perspective, large quantities of BA can be considered as urban mines, from which it could be possible to extract and recycle materials and chemical elements. In this point of view, the chemical and mineralogical characterization of BA is of paramount importance.

In the last 20 years a number of studies investigated the technical and environmental properties, as well as recycling methods, leaching behavior, geochemical and petrological aspects of BA. All these literature data stressed the strong complexity of the BA due to an intrinsic heterogeneity of the material caused by a) selective collection of household waste, b) choice of incineration technology, c) furnace technology, d) cooling processes, e) maturation processes (among others: Zevenbergen et al., 1998; Eusden et al., 1999; Meima and Comans, 1999; Piantone et al., 2004; Ginés et al., 2009; del Valle-Zermeño et al., 2017; Dou et al., 2017; Alam et al., 2019).

An important point debated by other authors is the incomplete knowledge of the chemical, physical and mineralogical composition of the BA, thus making any approach to reuse very approximate (di Gianfilippo et al., 2018; Huber et al., 2020).

For example, the finer iron particles mingled within the mineral fraction can hardly be separated by magnets and form several compounds containing heavy metals, which can potentially be recycled (Wei et al., 2011b)

In recent years, much research has been conducted on the use of bottom ash as concrete in cements (Bawab et al., 2021; Kleib et al., 2021) in ceramic materials (Karamanov et al., 2021; Zanelli et al., 2021) and as fillers bituminous mixture (Suárez-Macías et al., 2021). It appears that any such application requires a focus on the chemical and physical features of the bottom ashes, giving attention to their strong heterogeneity, and to how their mineralogy affects the release of potentially toxic elements (PTE) in the environment.

The characterization of waste from incinerators in terms of chemical and mineralogical variation is preliminary to possible reuse paths. A critical parameter was found to be grain size. It was shown that chemical composition changes with grain size, and that several PTE are concentrated in the finer fractions (Chimenos et al., 1999; Wei et al., 2011a; del Valle-Zermeño et al., 2017; Šyc et al., 2018, 2020). More recent investigation, however, contend the above as a general rule, showing for a given element differences in grain size *vs* composition in different incinerators (Caviglia et al., 2019; Loginova et al., 2019; Huber et al., 2020; Mantovani et al., 2021). A limit in the above investigations is the lack of a quantitative mineralogical composition with grain size, together with leaching tests to determine the possible release of PTE.

In this work the chemical, physical and mineralogical analysis of BA from 5 plants located in Northern Italy has been done. The areas show similar MSW production, coming from a culturally homogeneous area, and with similar collection management. This will reduce the bias for possible differences in the input, which affect such comparison between incinerators. The samples were sorted according to the particle size and then analyzed to understand the variability coming from this parameter. XRD, XRF, TGA were performed on each portion, and followed by leaching tests. Grain size, elemental composition, and leachate products have been studied by PCA analysis.

The aims of this work are: a) to describe the mineralogical and chemical variability between the bottom ashes from different WtE facilities, arising from plant performance during incineration and weathering; b) to provide general relations between grain size and composition, and between the different elements, for bulk and leachates, in order to assess the potential of grain size sorting for a higher value use of the ashes; c) to provide new suggestions to foresee potential leaching from the mineralogical composition of the ashes.

2. Material and Methods

2.1 MSWI bottom ash sampling and sorting

The samples come from 5 WtE plants located in northern Italy, 3 of them owned by Iren Ambiente SpA (Parma, Torino and Piacenza, hereafter PR, TO and PC) and 2 by Herambiente Spa (Ferrara and Forlì Cesena, hereafter FE and FC) (**Figure 3.2.1.1**). **Table 3.2.1.1** summarizes for each plant the starting date of the activity, the type of waste input (tons/year) and the total weight of BA produced.

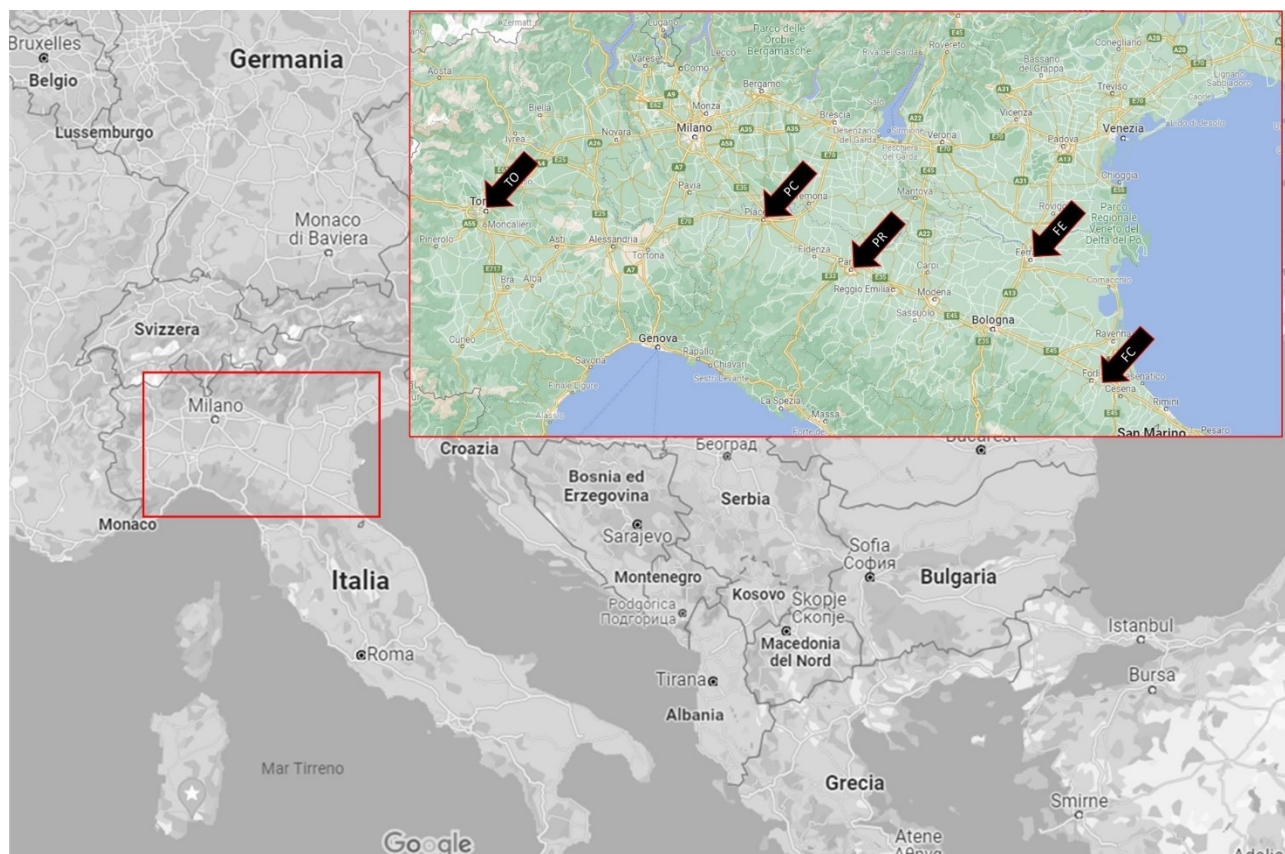


Figure 3.2.1.1: geographical distribution of WtE plants investigated in this work.

All the plants analyzed have a grate furnace technology that burns the waste for two to three hours at temperatures between 750 °C and 1000 °C. The input waste includes about 80% of undifferentiated fraction of separate collection (about 80%) and about 20% from special non-hazardous waste (industrial and household waste, sewage sludge, cemetery, biomedical waste, etc.). Only MSWI are burn in the Forlì plant (Iren Ambiente S.p.A., 2018; Hera Ambiente S.p.A., 2020).

The BA sampling from the plants was carried out during a typical day of the process activity in different periods as reported in **Table 3.2.1.1**. Samples were randomly taken from a 2-3 m high stockpile which is representative of more than one month of accumulation. The homogeneity was checked by making X-ray diffractions on repeated days, without showing any significant difference. The samples were taken in May 2019 in PR, TO and PC WtE plants, and in April 2020, during the pandemic lockdown, in FE and FC. About 5 kg of BA samples were collected from each plant. Before

the analysis, the ashes were mixed, dried in an oven at 50°C for 24 h and sieved to different size classes. The sequential sieving (Φ : 16, 8, 4, 2, 1, 0.5, 0.3, 0.2 and 0.63 mm) was performed according to the European standards for aggregates EN 933–2(Ente Nazionale Italiano di Unificazione, 2020).

WtE plant	operating since (using this set up)	waste input (tons/y)	% of the waste type	total waste input	BA produced (tons/y)	data related to	sampling date for this work
PARMA	2014	undifferentiated municipal solid waste (MSW)	126 317	79	159 832	32 904	2019
		special wastes (SW)	33 515	21			
PIACENZA	2002	undifferentiated municipal solid waste (MSW)	110 041	96	114 231	21 135	2018
		special wastes (SW)	4 190	4			
TORINO	2014	undifferentiated municipal solid waste (MSW)	457 603	81	562 269	118 969	2019
		special wastes (SW)	104 666	19			
FERRARA	2008	undifferentiated municipal solid waste (MSW)	69 598	53	131 894	27 021	2020
		special wastes (SW)	62 296	47			
FORLI	2008	undifferentiated municipal solid waste (MSW)	119 215	100	119 215	53 308	2020

Table 3.2.1.1: waste input and output (only for BA) for each sampled WtE plant. Municipal Solid Waste: household and similar waste; Special Waste: waste from municipal sewage network and treatment, municipal construction and demolition waste, sanitary and cemetery wastes (Data from: Hera Ambiente S.p.A., 2020b, 2020a; Iren Ambiente S.p.A., 2018, 2020)

The cumulative grain size distribution curves are reported in **Figure 3.2.1.2**. Aggregates larger than 3 cm were removed to avoid loss of representativeness and distortion of the analytical results.

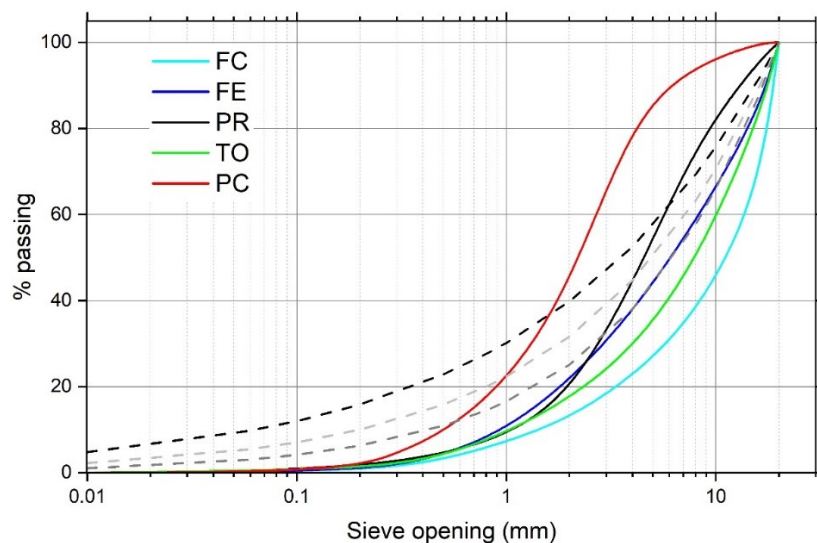


Figure 3.2.1.2: Cumulative particle size distribution of bottom ashes of the 5 plants analyzed. The dashed lines report the Fuller's curves with $n=0.4, 0.5$ and 0.6 ad $d_{max}=20$

2.2 XRD analysis

X-Ray powder Diffraction (XRD) was performed on each sieved fraction. A Bruker D2 Phaser powder diffractometer was used, operating at 30 kV and 10 mA with Cu K α ($\lambda = 1.54178 \text{ \AA}$) radiation. The collections were done at 2θ between 5 and 100° , steps of 0.02° , and 1sec/step sampling time. The diffractometer works with θ - θ focalizing geometry and takes advantage of a solid state detector. A 30 rpm sample rotation was applied to minimize crystal preferential orientation effects. The diffraction patterns were identified using the Bruker software EVA and the Crystallography Open Database (COD) (**Table 3.2.1.2**). GSAS 2 software package (Toby and von Dreele, 2013) was used to perform Rietveld analysis and quantify the major crystalline phases and the amorphous content. High purity Al₂O₃ corundum (10 wt%) was used as internal standard. **APPENDIX IV** reports the quantitative interpretation of XRD analysis with grain size for each WtE plant.

mineral phases		WtE plants				
Name	Formula	PR	PC	TO	FE	FC
Calcite	CaCO ₃	x	x	x	x	x
Vaterite	CaCO ₃	x	x	x	x	x
Quartz	SiO ₂	x	x	x	x	x
Cristobalite	SiO ₂	/	/	*	/	/
Anorthite	Ca(Al ₂ Si ₂ O ₈)	x	x	x	x	x
Bytownite	(Ca,Na)[Al(Al,Si)Si ₂ O ₈]	x	x	x	x	*
Albite	Na(AlSi ₃ O ₈)	*	*	*	/	/
Pyroxenes group	ABSi ₂ O ₆	/	/	x	/	/
Akermanite	Ca ₂ Mg(Si ₂ O ₇)	*	*	*	x	x
Gehlenite	Ca ₂ Al(AlSiO ₇)	x	x	x	*	*
Ettringite	Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ · 26H ₂ O	x	x	x	x	x
Hydrocalumite	Ca ₄ Al ₂ (OH) ₁₂ (Cl,CO ₃ ,OH) ₂ · 4H ₂ O	x	x	x	x	x
Portlandite	Ca(OH) ₂	x	x	x	x	x
Strätlingite	Ca ₂ Al ₂ SiO ₇ · 8H ₂ O	x	/	/	/	/
Apatite	Ca ₅ (PO ₄) ₃ (Cl/F/OH)	*	*	*	*	*
Larnite	Ca ₂ SiO ₄	*	*	*	x	x
Tobermorite	Ca ₄ Si ₆ O ₁₇ (H ₂ O) ₂ · (Ca · 3H ₂ O)	*	*	*	/	/
Sjogrenite	Mg ₆ Fe ₂ (OH) ₁₆ (CO ₃) · 4H ₂ O	/	/	/	*	*
Magnetite	FeFe ₂ O ₄	x	x	x	x	x
Ematite	Fe ₂ O ₃	x	x	x	x	x

Table 3.2.1.2: XRPD identification of bottom ash. The minerals are arranged in the following sequence: (x) major minerals (*) minor or trace minerals, (/) not found or very doubtful presence.

2.3 XRF analysis

The bulk composition of each grain size was measured using a wavelength dispersive X-ray fluorescence spectrometer (XRF), Panalytical Axios 4000, equipped with a Rh tube. About three grams of the representative samples were oven-dried at 50° C, homogenized and milled with an agate vibratory disk mill. Thin-layer pressed powder pellets for XRF analysis were prepared using a boric acid binder. The reproducibility, the general accuracy through calibration curve and corrections of the data are the same used in other works (Franzini et al., 1972; Toller et al., 2021). Major, minor and trace elements (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅, As, Ba, Br, Ce, Cl, Co, Cr, Cu, Ga, Hf, La, Mo, Nb, Ni, Pb, Rb, S, Sc, Sn, Sr, Th, U, V, W, Y, Zn, Zr) concentrations are calculated using a calibration curve built on a large number of certified reference materials and offline correction of Loss On Ignition (LOI) values. LOI, which is correlated with the influence of humidity, organic matter, and water, was gravimetrically estimated after overnight heating the samples at 950°C in a muffle furnace (Heiri et al., 2001)

2.4 Thermo Gravimetric Analysis

Thermal gravimetric analyses were conducted by means of a Perkin Elmer 8000 instrument equipped with a Pt-crucible (sample mass approximatively 3-5 mg) at a heating rate of 10 °C/min in the temperature range 35–800 °C. All the measurements were run under a constant flux of dry air atmosphere (30 mL/min).

2.5 Leaching tests and water elemental analysis

Standard leaching tests and analysis of the leachates were performed following the UNI EN 12457-2 (Ente Italiano di Normazione, 2004), a test of compliance for the leaching of granular waste and sludge, which in this case has been adapted for bottom ashes assessment. The test is based on a one stage batch at a defined liquid to solid ratio for materials with particle size below 4 mm. Samples have thus remained in ultrapure water (Milli-Q ® 18.2 MΩ.cm at 25 °C and TOC < 5 ppb) for 24 hours under mechanical oscillation in a controlled environment. The analysis of the leachate samples were conducted using Ion chromatography (Metrohm Compact IC pro 881) for anions (Cl⁻, SO₄²⁻, F⁻, Br⁻, PO₄³⁻), Atomic absorption spectroscopy (Thermo S Series AA Spectrometer) for cations (Ca, Mg, Na, K), and Inductively coupled plasma mass spectrometry (Perkin Elmer ICP-MS ELAN DRC-e) for trace elements (Al, Ba, B, Cr, Co, Fe, Pb, Li, Mn, Mo, Ni, Se, Sr, Tl, Ti, V, Zn). Finally, the metal extraction (from the solid to the leachate) was calculated as $X_{lea}/X_{bulk} * 100$ for each WtE plant in the grain size < 2 mm, where X_{lea} is the analytical determination of the a certain element on the leachate and X_{bulk} is the total concentration of the solid by XRF.

3. Results and discussion

3.1 Particle size distribution

Figure 3.2.1.2 shows the grain size curves of the samples. In all the BA samples the larger fraction prevails: below 1 mm the sieved portion represents between 5 and 8 wt.% of the total mass, and 50% of the mass does not pass the at 4 mm sieve. This was also found in previous investigations (del Valle-Zermeño et al., 2017; Šyc et al., 2018; Caviglia et al., 2019). An exception is the PC plant, where there is a higher percentage of fine and medium sized particles (the grains passage is almost 80% at 4 mm). It is not clear whether this is due to the sampling methodology or the intrinsic heterogeneity of MSWI residues. In order to test the recyclability of BA in cementitious formulations, we compared our results with the optimum size distribution for concrete according to the Fuller curve, which represents the optimal aggregate distribution curve in terms of density and strength (Fuller and Thompson, 1907). The Fuller curve calculates the optimum percentage of a given particle diameter d as: $P(d) = 100(d/d_{max})^n$. Three Fuller curves were calculated with an aggregate maximum value of $d_{max} = 20$ mm, i.e. the maximum opening sieves used here and n exponential factor $n = 0.4, 0.5$ and 0.6 . In no case the distribution falls completely within the curves, as the smaller dimensions are underrepresented in our sampling.

3.2 XRD

Tables 3.2.1.2 and **APPENDIX IV** show the mineralogical composition of the BA and their separated grain size classes. The bulk mineralogical composition of the ashes for each incinerator was obtained from that of each grain size and their proportion as:

$$C_{i,bulk} = C_{i,j} * w_j / w_{bulk}$$

where $C_{i,j}$ is the fraction of the mineral (i) in the sieved portion (j) (as reported in **APPENDIX IV**), w_j the weight of the sieved portion and w_{bulk} , the weight of the sum of the sieved portions.

The minerals reported in **APPENDIX IV** are those most present, whose abundance could be refined by Rietveld analysis. A number of minor phases is also present, which either showed very faint peaks in XRD or could be detected just from microprobe analysis (Bayuseno and Schmahl, 2010; Mantovani et al., 2021). During Rietveld analysis it was shown that the inclusion of a higher number of phases leads to refinement instability, so that a compromise was necessary between the number of phases to be included and the number that could be refined. In some cases, identification of mineral phases was doubtful due to the overlap of identificative reflections associated to certain peaks (**Table 3.2.1.2**). Most evident is the amorphous content, which is higher in the BA of the three plants (TO, PR, PC) so as that it overtakes the entire quantitative of crystalline component. In these plants, the amorphous is over 75% on average, and ranges in different grain size between 67 and 88 wt%. In the plants of

FE and FC, instead, bulk amorphous is, on average, less than 35% (depending on grain size between 7 and 55wt%). Furthermore, there is a slight inverse correlation between the logarithm of the grain size and the amorphous content, with $R^2 = 0.64, 0.53, 0.41$, for PR, PC, TO, respectively. For FE and FC the correlation is not significant ($p > 0.05$) (for statistical value see **APPENDIX VII**).

The large amount of amorphous is common in bottom ashes (among others Eusden et al., 1999; Bayuseno and Schmahl, 2010; Caviglia et al., 2019; Loginova et al., 2019; Šyc et al., 2020). More recently Mantovani et al. (2021) showed that several amorphous phases characterized by a different composition and formation, and likely micro-structure are present rather than a single homogeneous amorphous phase. Residual glasses coming from the input waste are most present in the larger grains, whereas in fine grain and in some areas of aggregates, partly melted glasses are also present. Microprobe analyses on these glasses portion showed that they are different in composition; in general, they coexist with crystals in eutectoid conditions, with the local composition depending on metal (transition, alkali and alkali earth) content.

The lower quantity of amorphous material in FE and FC occurs together with higher calcite, quartz and feldspar. Also ettringite content is higher in FE and FC than the other 3 plants sampled, indicating a probable greater reactivity of these ashes in the aging process. FE and FC showed the presence of larnite and portlandite, probably due to the high Ca content and ascribable to carbonation reaction and cementitious material in the input feed.

Among minerals, quartz, calcite, melilites, iron oxides and some alteration products such as sulphates, chlorides, and hydrated minerals are ubiquitous. An inverse relation with grain size is found in calcite, mainly in TO and PR incinerators ($R^2 = 0.95$ and 0.82 , respectively) and less in PC and FC (0.53 and 0.45). In FE bottom ashes, the relation is not significant, but the larger size shows a much lower calcite content than the finer portion. Calcite probably derives from secondary carbonation, during weathering in the temporary storage site, but we do not exclude that the higher calcite content in FE and FC may come from an unfinished decarbonation process during thermal decomposition. Portlandite, Ca(OH)_2 is found only in the BA ashes from FE and FC as a product of rehydration of CaO. The Ca-oxide forms at a temperature of approximately 700 °C at an initial atmospheric partial pressure (0.04 atm) and from the de-carbonation reaction (Criado et al., 2018):



In FC portlandite correlate with the amorphous content ($R^2 = 0.72$). Such positive correlation is also found, albeit with lower evidence also in with Ferrara ($R^2 = 0.34$).

Ettringite, hydrocalumite and strätlingite were formed during weathering. Ettringite and hydrocalumite are ubiquitous, whereas strätlingite is found only in the PR plant. Ettringite in TO is positively related to calcite and hydrocalumite ($R^2 = 0.82$ and 0.83 , respectively), and shows a

negative correlation with grain size ($R^2=0.78$). A milder correlation is found between ettringite and grain size also in PR and FE, whereas in FC no correlation is found. In PC ettringite shows an inverse correlation with calcite, and calcite a positive correlation with hydrocalumite.

Strätlingite is found only in the PR samples. This mineral is typical of cementitious materials and can be formed either from the degradation of gehlenite or from the reaction between calcium silicates (Ca_2SiO_4 - belite) with $\text{Al}(\text{OH})_3$ in hydration processes (Winnefeld and Lothenbach, 2010; Rungchet et al., 2017). In this case, the formation of strätlingite does not involve the degradation of gehlenite, as some evidence found in SEM analyses and reported in a previous work (Mantovani et al., 2021) showing that gehlenite has been formed in the combustion chamber (crystals with typical neoformation and rapid cooling shape).

Another cement related phase, larnite is present in significant amount in FE and FC. It is found in higher values in the smaller size fraction. Doubtful identification of tobermorite in PR, PC and TO would indicate that C-S-H formation is occurring.

Iron containing minerals as hematite and magnetite are revealed by X-ray diffraction, although likely other metal phases are present like Cu or Ni-Ti alloys, as found in Mantovani et al. (2021).

Last, a number of silicate phases, like pyroxene, gehlenite-akermanite, and anorthite, are found without significant difference with grain size, and are likely formed at high temperature in the combustion chamber.

3.3 XRF

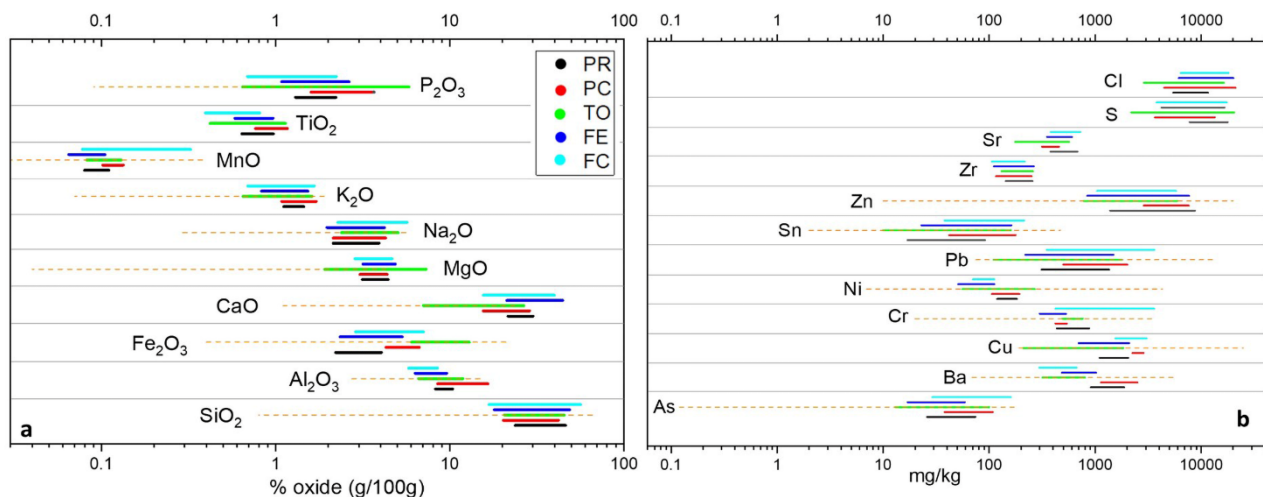


Figure 3.2.1.3: ranges observed for major (g/100g in oxides) and minor (mg/kg in elements) elements content of BA from the 5 WtE plants (different colour) examined. Orange dot lines represent the minimum to maximum range found in several literature source and reported by Asturp et al (2016).

As already observed by numerous authors, the bulk chemical composition of BA is represented by the major oxides of Si, Ca, Fe and Al (**APPENDIX V**) (among others Bayuseno and Schmahl, 2010; Funari et al., 2015; Caviglia et al., 2019). In fact, the sum of these elements (in oxides) represents from 60 to 77 g/100g. S and Cl are found in a range from 0.3 to 2 g/100g.

Among minor elements, Zn, Cu, Pb and Ba content is higher than 1000 mg/kg. **APPENDIX V** reports the content of major, minor and trace elements divided by grain size for all the investigated plants.

Figure 3.2.1.3 represents the value range (max and min) for each element and plant with a comparison to the range of the average composition of the incinerators value reported by Astrup et al. (2016). The compositional variability of the major elements shown by different grain size portions in the 5 incinerators is rather close, when compared to the variability reported by Astrup et al. (2016). The similarity between the bottom ashes from the plants investigated in this work is confirmed when we compare the weighted average composition. In **Figure 3.2.1.4 a**, the oxides show a rather similar pattern in the different plants, albeit with some slight difference: the BA from TO show higher Fe_2O_3 and lower CaO , and those from Piacenza shows lower SiO_2 and higher LOI than the others. Also for minor elements our data show that the compositional variability related to grain size is small compared with the variability shown by Astrup et al. (2016). However the difference in the average composition between the BA from different plants is more marked. In Piacenza higher value are found for Cl, and Cu, and overall, an higher compositional spread in S, Cl and Zn content (**Figure 3.2.1.4 b**). The analysis of the relation of composition, with grain size and between elements in the different grain size portions, was done by bivariate and PCA analysis (**APPENDIX VIII**).

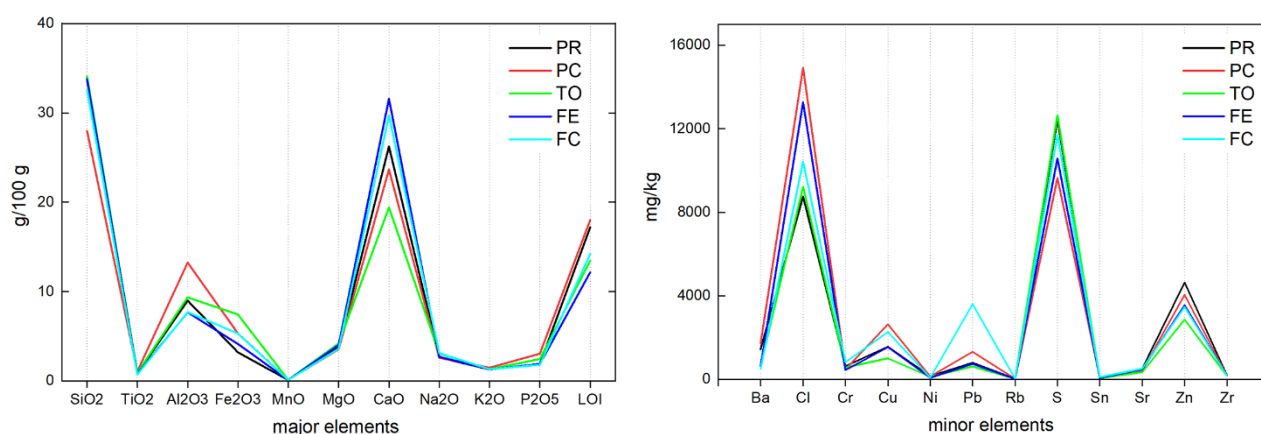


Figure 3.1.2.4: weighted average composition of the **a)** major (g/100g in oxides) and **b)** minor (mg/kg in elements) elements for each WtE plants analyzed.

Bivariate analysis (**APPENDIX VII**) shows that Si positively correlates with grain size ($p < 0.05$) probably due to the glass shards in larger grain size. Na as well correlates with Si, possibly for the addition of Na as a fining agent in glass production technology and for the presence of plagioclase solid solution. Ca, Ti, S, loss on ignition, LOI (in all the plants) and Cl (in PR, PC, FE) correlate negatively with grain size. The smaller fraction is richer in Ca due to the faster carbonation occurring in smaller particles with larger surface area. The higher Ca in smaller particles goes together with the higher Ca-carbonate content. Higher decarbonation means also higher weight loss in LOI, which is greater in smaller particle sizes having higher active surfaces. We suppose that S follows the same trend due to the sulfation process and the formation of the ettringite phase, which, as shown in XRD analysis, is more present in finer sized grains. Most of the PTE like Cu, Pb and Cr are negatively related with grain size. To note, the differences in the minor elements concentration between plants are within an order of magnitude, and could be related to the different waste input. Other elements, like Al, Fe, Mg, P and Cr show little change between samples of different grain size. An exception is in Torino MgO and Al₂O₃, which show a significant increase in the smaller sized grains.

S and Cl (**Figure 3.2.1.5**) are contained in the BA in considerable quantities, causing metal erosion if they are used as supplementary cementitious material in reinforced concrete (Ito et al., 2006). In BA examined in this work, S and Cl range between 2000 to 21000 mg/kg. These two elements are positive correlated in all incinerators and show an inverse correlation with the grain size, as already pointed out by Alam et al. (2020) suggesting that they are mostly present as weathering of the products.

Principal component analysis (**APPENDIX VIII**), was done on the element composition and grain size, for the BA from each incinerator, to seek the variability and trends for each element.

In the analysis of previous data on Parma WtE plant Mantovani et al. (2021) found a relation between CaO, LOI, S and Cl which have an opposite variation with SiO₂, grain size and lithophile elements like Zr and Rb. This is confirmed also in the analysis of the PCA of other incinerators, with Zn and Sn that, with the exception of Piacenza, follow the LOI and S. Ni, Cr and Pb do not follow one of the two trends, and do not show a definite grouping with other PTE. In Piacenza and Ferrara Ni and Cr are opposite related by the second component; Pb also is unrelated with the above elements, with the exception of Ferrara where it goes with S, and a possible grouping with As. More complex, non-linear relations, are also observed.

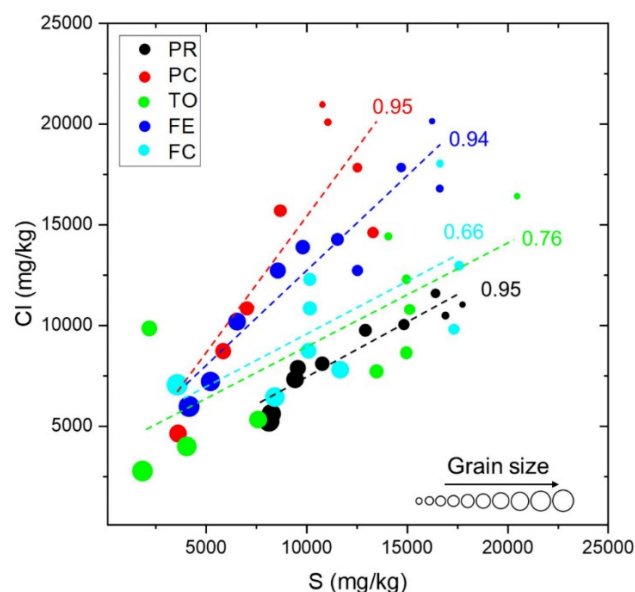


Figure 3.2.1.5: correlation between S, Cl and grain size for the 5 WtE plants examined. The number reported is the Pearson correlation coefficient while the diameter of the dot represents the grain size dimension (not to scale).

For instance, the Na_2O oxide in the larger grains, is negatively related with Cl, whereas as soon as Cl exceeds 5000 mg/kg, the Na_2O does not change while Cl increases. Higher Na content is locked in the glass and high temperature minerals in the larger grains, whereas in smaller ones the Na becomes more linked to Cl in chlorides, probably due to decomposition of the glasses by weathering (**Figure 3.2.1.6**). This will be confirmed by further analysis of the leachates.

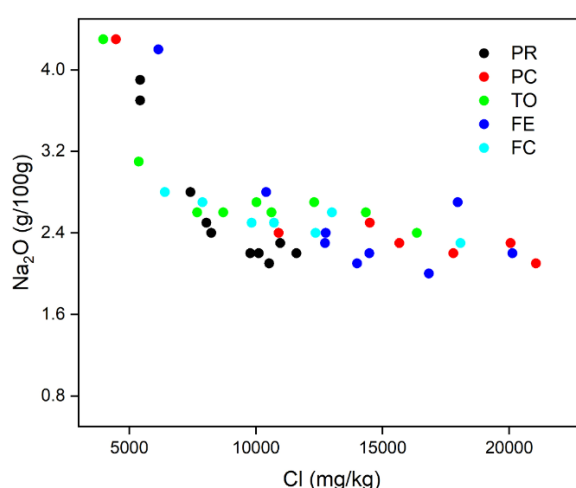


Figure 3.2.1.6: Correlation between Na_2O (g/100g) and Cl (mg/kg) content for each plants and in different grain size analyzed.

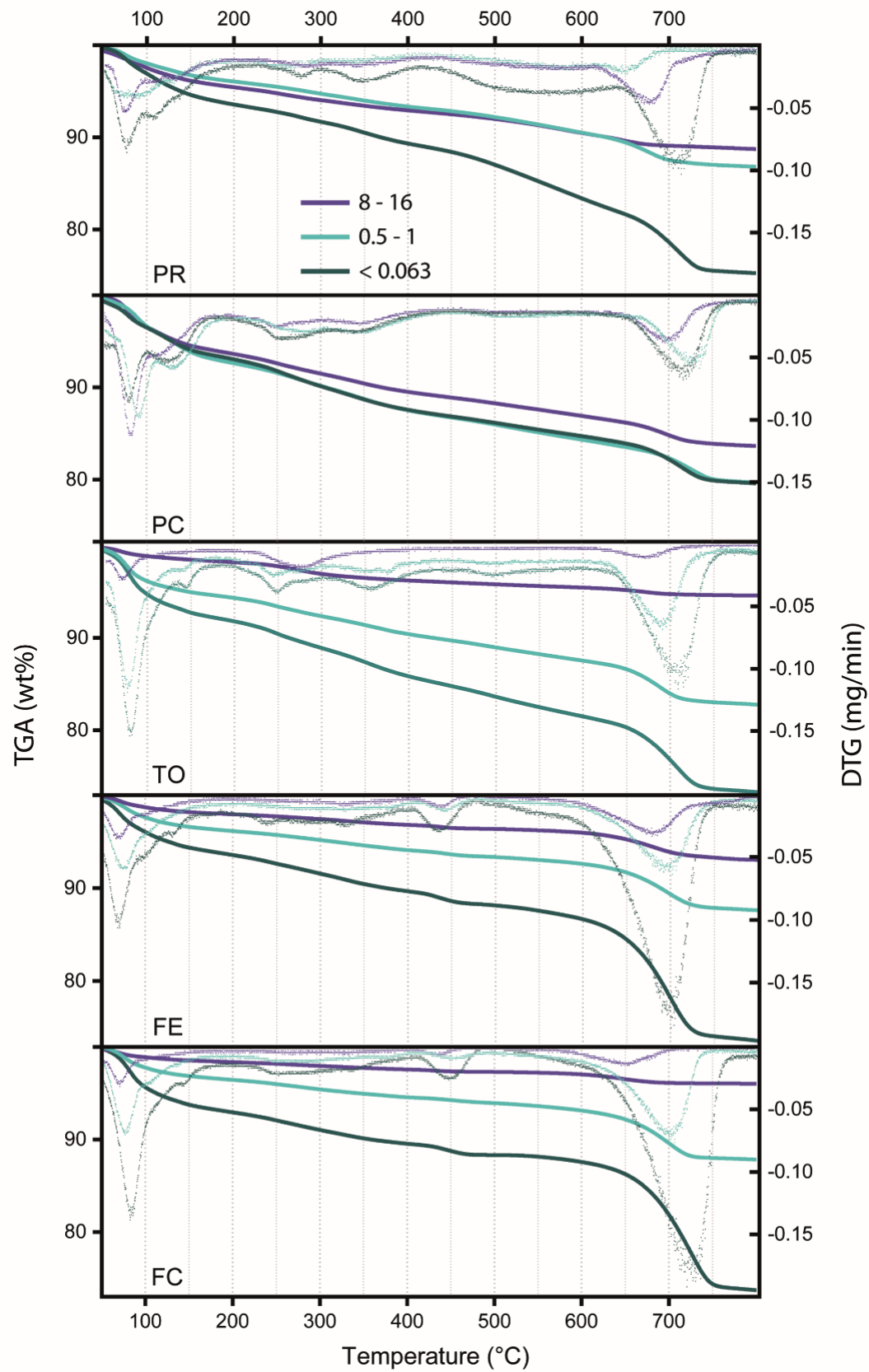


Figure 3.2.1.7: TGA (line) and DTG (dots) of 3 selected grain size (<0.063, 0.5-1 and 8-16 mm) of the 5 WtE plants.

Thermo Gravimetric Analysis shows a continuously weight decreases with temperature for any grain size. The weight loss is higher in the smaller grain size, where the mass loss at 800°C is about 25%. For the larger grain size, the loss is about 5-10% and for intermediate ones about 15%. An exception is PC, where the weight loss is similar for every grain size (**Figure 3.2.1.7**).

The analysis of the first derivative shows few temperature ranges where higher weight loss is present. A moderate (3-4%) weight loss occurs in the interval 50-100 °C, likely ascribable to two reactions: one at 50-60°, likely due to surface water, and another just above 100°C, related to the first dehydration of ettringite with further dehydration possibly revealed by the faint peaks at 250 and 350°C (Fridrichová et al., 2016).

The second loss is 1-2 wt% and appeared over the range 250-450°C and a 4-7 wt% in the interval 620-760°C. The 250-450°C reaction is likely due to plastic combustion residue (molecular decomposition), as suggested by Trifunovic et al. (2010) while the 620-760°C loss is ascribable to the transformations involving carbonate (decarbonation) phases. The first mass loss around 100°C can be related with

In FE and FC the de-carbonation loss is greater than in the other plants, accordingly with XRD and XRF data that show a higher carbonate content.

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In FE and FC the de-carbonation loss is greater than in the other plants, accordingly with XRD and XRF data that show a higher carbonate content.

Despite the general shape of the TGA curves appear similar, some difference with particle size dimension and between plants is found. A peak at 450°C has been found only in FE and FC BA. The peak is more apparent in the finer portion, and it is likely due to the de-hydration of portlandite (Menéndez et al., 2012) which occurs between 450 and 500°C. Portlandite is present only in the two incinerators of FE and FC, between 5-10 wt% in the finer portion, and between 1 and 2% in the larger grains.

3.5 Leaching Tests

Leaching tests were done on particle sizes below 2 mm, as XRF analyses showed that they are richer in PTE. The leaching was done on particles of different size, and their variability was analyzed by PCA. The results are reported in **APPENDIX VI** and **APPENDIX IX**.

PCA analysis shows that the two major components describe more than 80% of the variability in all WtE. A number of ions, among which Cl, K, Li, Na and Cu show an opposite trend respect to grain size, i.e. show higher leaching in smaller grain sized samples. SO_4^{2-} follows Cl in TO, PR, PC and FC. In FE and FC the sulphates leached are one order of magnitude less than in other incinerators. Ni and Cr follow Cl and sulphates in TO, PR and PC, but not in FE and FC. Pb does not follow a definite trend, with little change with grain size. Al is leached in significant amount only in TO, PR and PC, but not in FE and FC.

Marked differences in leaching behavior have been found between the two different owner corporation that is IREN for PR, PC and TO and HERA for FE and FC.

Although generally the leaching is higher in smaller grain size portion, great difference, within one order of magnitude, is found. Higher differences are observed between WtE plants.

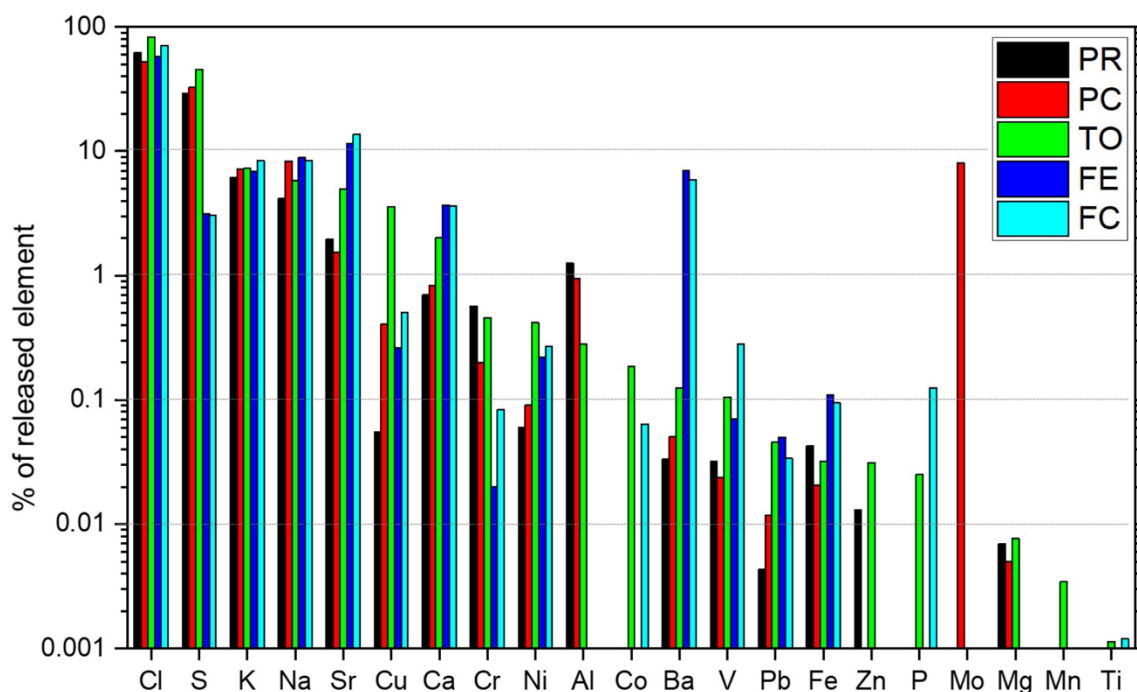


Figure 3.2.1.8: percentage of released elements calculate as $(X_{\text{bulk}}/X_{\text{lea}})*100$ for each WtE plant in the grain size < 2 mm

With respect to a given particle size, the leaching of an element has been compared to the total content in the bulk sample (from XRF analysis) and calculated in percentage (all referred to mg/kg of material). The most released element is Cl with a release percentage of about 70/90%, higher in the finer fraction (**Figure 3.2.1.8 and 3.2.1.9, APPENDIX VI**).

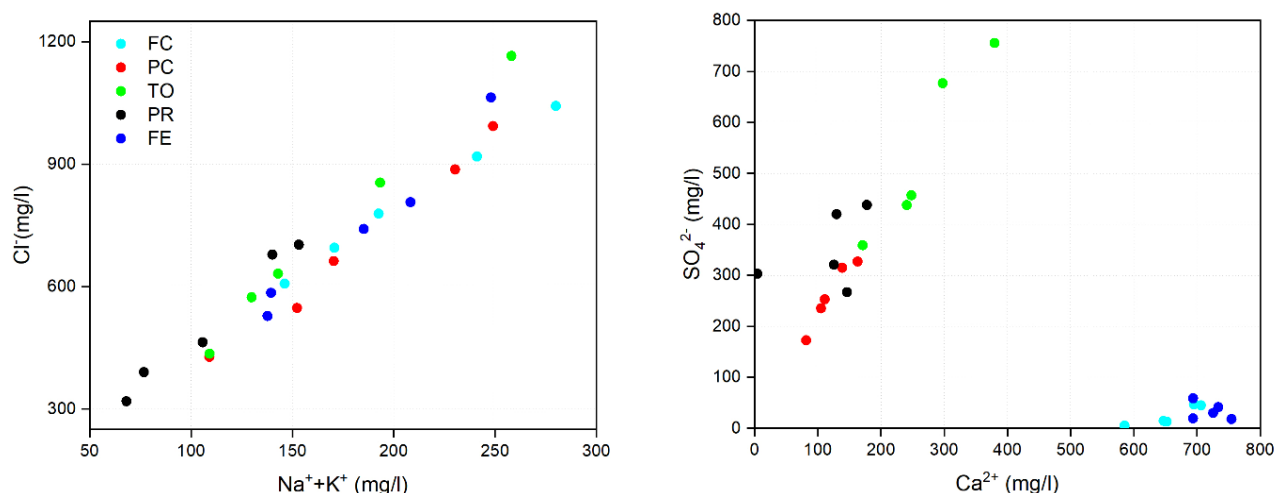


Figure 3.2.1.9: a) correlation between the leached $\text{Na}^+ + \text{K}^+$ vs Cl^- and b) SO_4^{2-} vs Ca^{2+} (mg/l).

The extraction efficiency in the smaller portion is almost twice that in the larger one. In agreement with Alam et al. (2020) we suggest that Cl is present in very soluble salts, like NaCl and KCl, dispersed on the surface of the grains. This suggestion is confirmed by the linear relation found in leached Na+K with Cl (**Figure 3.2.1.9 a**), whereas such relation does not exist in the sample composition determined by XRF as most Na and K are likely caged within the amorphous and silicates structures. However, the amount of chlorides in leachate are considerably greater than the Na+K value (and not in a 1:1 ratio), suggesting that the release of Cl is not only attributable to the dissolution of the Na/K salts. Therefore, no diffraction peaks attributable to Na,KCl are found in XRD analysis, suggesting that not all the Cl is bound to Na and K in salts, and that a significant release of Cl may be originate by the dissolution of ettringite.

Therefore, probably the contribution of ettringite dissolution is minor, due to the very similar ratio in Na+K/Cl in the 5 plants, in spite of the different amount and solubilization of ettringite (**Figure 3.2.1.10**).

EDS analyses of the ashes from PR, (Mantovani et al., 2021) showed that Cl is often associated with silicate glassy phases. We suggest therefore that chloride is most released by dissolution of weakly bonded Cl at the surface of the amorphous phases. This would explain the higher leaching in smaller grains, with higher surface.

All tests exceeded the legal limits for Cl (Legislative Decree 152/06) suggesting that washing and selection of larger grains may be combined technique to reduce Cl for a correct reuse.

S shows a release, about 30% for PR, PC and TO and 3% for FE and FC, with no dependence on the particle size. S is present in the ettringite structure which is observed in XRD in all the plants, especially in FE and FC. However the release in SO_4^{2-} is lower in the two HERA WtE plants, whereas the Ca is higher (**Figure 3.2.1.9 b**). Moreover, Al is released by at least two order of magnitude less in HERA than in IREN plants. Another relevant difference is that the measured pH in the leached IREN plants is between 10 and 11, whereas in the HERA plants it varies between 12 and 12.5. We suggest that in the HERA plants, the dissolution of portlandite, which is absent in the IREN plants, gives rise to a basic environment, where ettringite is less prone to dissolution. In the IREN plants, ettringite dissolves, with sulphate and Al hydroxide solubilization.

Other elements like Mg and Fe do not show a significant leaching, indicating that they are bonded in non-soluble oxide or silicate structures.

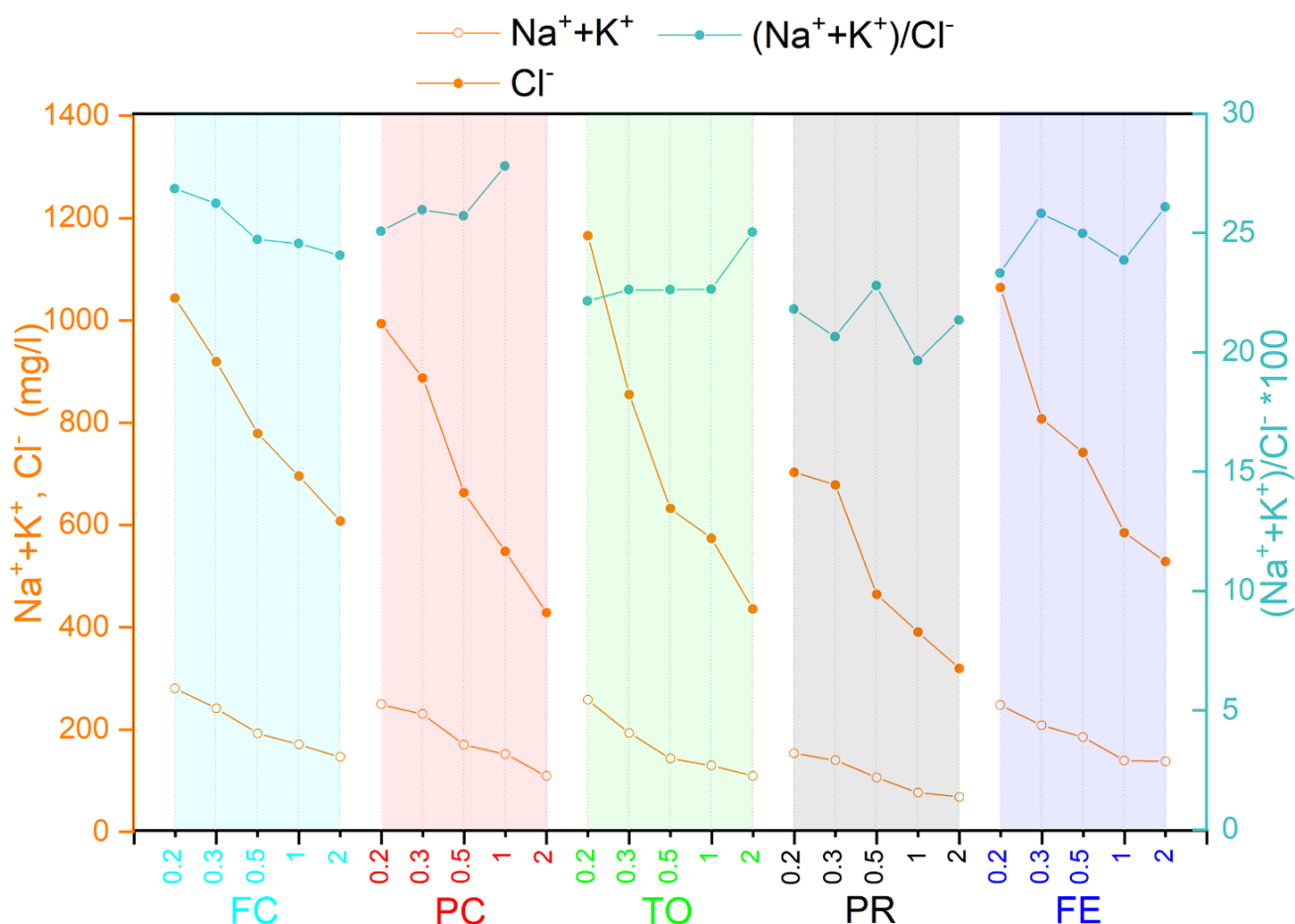


Figure 3.2.1.10: trend of the $\text{Na}^+ + \text{K}^+$, Cl^- and $\text{Na} + \text{K} / \text{Cl}$ in the leachate in function of the grain size (<2mm) for the 5 WtE plants.

The different mineralogy in IREN and HERA plants, and the consequent different leaching in major elements has an effect also on minor elements. Minor elements are often present in solid solution within phases more or less prone to dissolution at different pH, and the dissolution of the host phases releases also the exsolved element. Therefore the release in minor elements is different in the different WtE plants, often by two order of magnitude. In a plant the leaching could be above legal limits, whereas in others it could be not (**Table 3.2.1.3**).

Elements		Cl ⁻	SO ₄ ²⁻	F ⁻	PO ₄ ³⁻	Ba	Cu	Zn	As	Be	Co	Ni	V	Cd	Cr	Pb	Se
Legal Limits		100 mg/l	250 mg/l	1.5 mg/l	2 mg/l	1mg/l	0.05 mg/l	3 mg/l	50 ug/l	10 ug/l	250 ug/l	10 ug/l	250 ug/l	5 ug/l	50 ug/l	50 ug/l	10 ug/l
WtE plants	grain size (mm)	mg/l					ug/l										
PR	0.063 - 0.2	703	438	0	0	0.04	0.12	0.06	0	0	0	8	2	0	458	6	17
PR	0.2 - 0.3	678	420	0	0	0.04	0.09	0.06	0	0	0	8	2	0	354	0	17
PR	0.3 - 0.5	463	321	0	0	0.04	0.07	0.06	0	0	0	7	2	0	248	2	13
PR	0.5 - 1	391	267	0	0	0.05	0.05	0.04	0	0	0	8	2	0	212	4	19
PR	1 - 2	319	303	1.0	0	0.04	0.04	0.05	0	0	0	4	2	0	198	2	8
PC	0.063 - 0.2	993	327	4.5	0	0.08	1.15	0	0	0	0	4	2	0	119	4	62
PC	0.2 - 0.3	887	315	0	0	0.06	1.17	0	0	0	0	2	2	0	105	2	56
PC	0.3 - 0.5	662	253	11.4	0	0.06	0.88	0	0	0	0	2	2	0	74	2	46
PC	0.5 - 1	547	236	3.0	8	0.08	0.95	0	0	0	0	38	2	0	75	59	32
PC	1 - 2	428	173	3.9	0	0.04	0.36	0	0	0	0	0	0	0	31	0	34
TO	0.063 - 0.2	1170	756	0	0	0.09	5.31	0.11	0	0	11	57	4	0	306	19	15
TO	0.2 - 0.3	855	677	0	0	0.08	4.08	0.06	0	0	6	44	6	0	229	17	11
TO	0.3 - 0.5	632	457	0	0	0.07	3.36	0	0	0	6	42	6	0	219	33	13
TO	0.5 - 1	574	438	4.6	0	0.07	3.39	0.07	0	0	4	40	8	0	171	15	13
TO	1 - 2	436	359	4.3	1	0.06	3.43	0.12	0	0	4	23	13	0	147	25	11
FE	0.063 - 0.2	1064	59	1.8	0	5.53	0.53	0	0	0	0	15	6	0	6	44	21
FE	0.2 - 0.3	807	30	3.4	0	4.52	0.39	0	0	0	0	15	4	0	4	33	19
FE	0.3 - 0.5	741	42	7.7	0	2.95	0.36	0	0	0	0	16	2	0	6	33	14
FE	0.5 - 1	584	20	3.4	0	1.80	0.30	0	0	0	0	17	2	0	4	36	15
FE	1 - 2	528	18	6.4	0	1.45	0.32	0	0	0	0	15	2	0	11	29	13
FC	0.063 - 0.2	1043	5	0	0	38.53	1.05	0	4	0	2	19	27	0	31	13	31
FC	0.2 - 0.3	919	15	4.6	0	37.32	0.89	0	2	0	2	17	15	0	27	13	20
FC	0.3 - 0.5	779	13	15.5	1	25.20	0.93	0	0	0	2	19	10	0	23	16	10
FC	0.5 - 1	695	45	5.1	4	12.50	0.88	0	0	0	2	21	8	0	37	55	14
FC	1 - 2	608	47	5.1	0	0.80	0.74	0	0	0	2	21	6	0	41	10	14

Table 3.2.1.3: leaching test results for elements subject to regulation for plants (d.lgs 156/2006). In red, concentrations exceeding legal limits.

For instance, sulphate and Cr are above regulatory limits only in IREN BA, but Ba and Ni (with the exception of TO) only in the HERA plants. Sr leaching is observed in high percentages in FE and FC (10-15% of the bulk), and less in the IREN plants (4-6% in TO and 1-2% in PR and PC). A likely interpretation is that Cr could have a significant concentration in ettringite, which is dissolved in

IREN plants, whereas Ba, Ni and Sr could exchange with Ca in significant amount in portlandite, which is dissolver in HERA plants.

Zn and Mg are released only in the TO and PR plants, possibly in relation with ettringite dissolution. In TO the leaching of SO₄, Co, Cu, Mg and Zn is higher than in other plants, and in PC B and Mo show higher leaching. These differences, which are more than one order of magnitude look specific of an WtE, or at least of the analyzed sampling from that plant.

Cu, Cr and Ni are, among the PTE, the most released in all plants with values below 0.5%, except for TO where the Cu stands at 3%. On the other hand, the release of Ti, Pb and Zn is relatively low (<0.01%), never exceeds law limits (Legislative Decree 152/06) suggesting their presence in a non-soluble structure, like glass or silicate minerals.

4. Conclusions

The bottom ashes from the WtE plants show an average composition remarkably similar in major elements, just with higher iron in TO, and lower Si/higher LOI in PC. The chemical composition of major and minor elements changes with grain size, but within an order of magnitude and similarly in the different plants. The similar BA composition could be related to a similar waste management approach in the area.

The mineralogy is different between HERA (FE and FC) and IREN (TO, PR and PC) BA. In the former we have lower amorphous and higher portlandite and ettringite, in the latter we do not have portlandite and the amorphous phases are between 60 and 90%. This affects leaching, which occurs in different basic environment: the leachates show higher sulphate and Al in IREN plants, and lower sulphate-higher Ca in HERA plants. Leaching up to two orders of magnitude lower in Ba and Sr, and higher in Cr occurs in IREN. The balance of Cl leaching shows that alkaline chlorides account just for about 30-35% of the global Cl, a fraction which does not show significant changes with grain size and between WtE, and that is similar to the findings of Alam et al. (2020).

Composition and leaching is for most elements size dependent, but almost invariably within an order of magnitude. Some elements like Cl, Zn, S, and the LOI decrease with grain size, but for other PTE like Ni, Cr, Co and Pb this is not a rule. Leaching increases in smaller grains for almost any element, but again within an order of magnitude, whereas between WtE plants we find higher variability in leaching efficiency. From a circular economy perspective, reuse of BA as a supplementary material in concrete is possible: the presence of cement related minerals such as portlandite in FE and FC supports reuse in the concrete, facilitating the setting and hardening reactions. However, significant concentrations of Cl and S, especially in the finer grain size, could be disadvantageous for cement application and a pre-treatment before application as cement bind could be envisaged. Grain sorting

could be useful in cases where leaching of the larger grain size falls below the legislative limits for a given element, while the smaller grains do not, like Cr in PC and Cu in PR. It could be more profitable to gain acquaintance with the mineralogical and chemical dissolution behavior of the BA from a given plant being the differences in the leaching of minor elements look more dependent to the mineralogy than to grain size.

Author contributions

LM, MT: conceptualization, methodology, data collection, data calculation, writing—original draft, and writing—review and editing. **CDM**, PP, ED, ST, VF, TB: methodology, data collection, data curation, editing. LM, MT, **CDM**, PP, ED, ST, VF, TB have read and agreed to the published version of the manuscript

3.3 PTE SPECIATION: COMBINED SEM-EDS ANALYSIS, XRF AND XANES BY SYNCHROTRON RADION STUDY

The focus of this third work was PTE (Pb, Cu, Zn, Ni, Co and Cr). For this reason, BA sampled from the Parma waste-to-energy plant (0.5 - 1mm grain size class), was studied through a multi-technical approach. Previously, as shown in the first two papers, this particle size class was analysed by diffraction and fluorescence techniques to gain an overview of the chemistry and mineralogy of the material. Subsequently, some BA grains were analysed by SEM - EDS and XRF mapping and XANES analysis conducted by synchrotron facility. In this way, information was obtained regarding not only the mineralogical environment in which the PTE are housed but also their oxidation state, information of crucial importance in assessing the potential toxicity of the material under study. From the results obtained, it can be seen that the chemical elements analysed are present in different chemical forms, especially zinc, which turns out to be the element found in a greater variety of mineralogical phases but not in metallic form. Chromium has never been found in +VI oxidation state, its most toxic form. In general, PTE has been found in the form of metal (sheet or alloy), oxide (or hydroxides), carbonates, sulphates, silicates, or as substituted in other crystal structures or amorphous matrices.

The results obtained are coming from an article that is in the process of being submitted. The article is reported as paragraph 3.3.1. *For simplicity, figures and tables have been re-numbered following the structure of this thesis.*

3.3.1 PTE speciation in Bottom Ashes from Municipal Solid Waste Incinerator: a combined SEM-EDS, XRF and XANES by synchrotron radiation study

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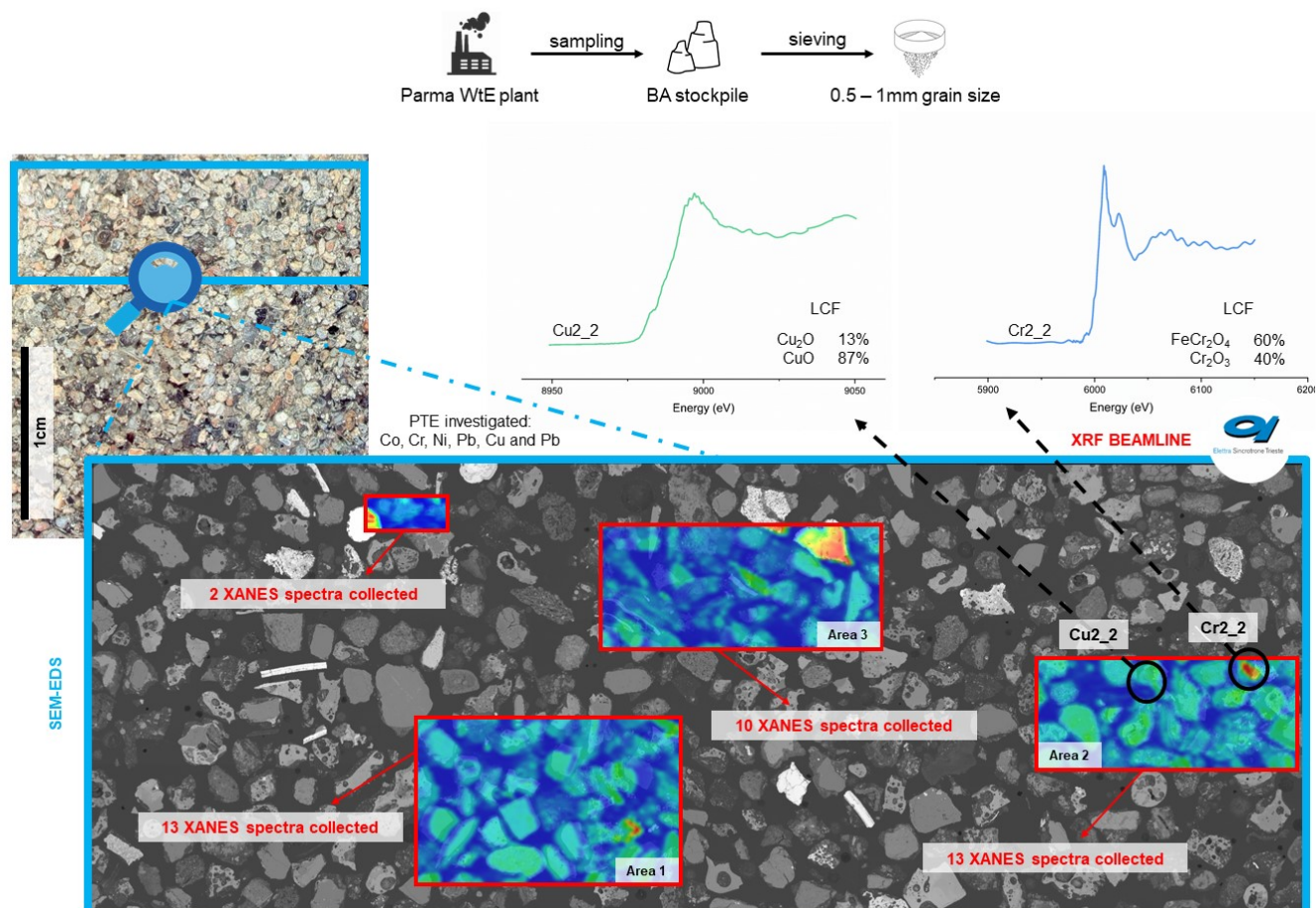
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Abstract

Potential Toxic Elements (PTE) in Municipal Solid Waste Incinerator Bottom Ash (MSWI-BA) may be toxic depending of their oxidation state and mineralogical environment. In this work, Cr, Ni, Pb, Co, Zn and Cu chemical speciation are investigated on BA from Parma Waste to Energy (WtE) plant by means of SEM-EDS, μ -XRF and XANES measurements by synchrotron radiation. This multi-technique approach allowed to examine PTE providing a general picture of mineralogical and chemical properties such as the oxidation state. SEM-EDS analyses show the presence of Zn and Pb in minerals and in glass matrix. Cr oxide and chromite has found whereas Cu and Co are present as metal inclusions or alloy. μ -XRF mapping reveals that Cu, Ni and Cr are generally together with Na, K and Si suggesting their presence in glass matrix. XANES spectra show that Cu has a variable oxidation state suggesting its presence as oxide, hydroxide, acetate and metal form. Zn is mainly in the +II oxidation state confirming the SEM-EDS data. Cr has been found always as +III, whereas the +VI oxidation state was never identified. Pb spectra have a good match with oxides. Ni and Co were found either as oxides and in metal form.

Graphical abstract



Keywords

BA-MSWI, PTE, Chemical-mineralogical characterization, XANES, speciation, leaching

1. Introduction

A considerable input of anthropogenic material in the environment is given by waste. In 2016, world waste production was equal to 2.01 billion tons and due to economic and demographic growth will reach the 3.40 billion tons in 2050 (Kaza et al., 2018).

The waste can be sent to recycling, composting, incineration processes or deposited in landfills. A considerable amount of waste, as much as 11% of the global production, is incinerated (Kaza et al., 2018). In industrialized countries, the incineration is entrusted to WtE plants, which recover energy as heat and/or electricity through controlled combustion of MSW.

FA and BA are the main outputs of WtE processes. FA are classified as hazardous waste and constitute 4% of MSW mass, while BA are non-hazardous waste and represent 20% of MSW mass (Bertolini et al., 2004; Izquierdo et al., 2001; Nazionale, 2002).

BA are formed by an extremely complex and heterogeneous mineral fraction. In recent years several studies aimed to characterize BA from a chemical, geochemical, mineralogical and physical point of view (Alam, Schollbach, van Hoek, et al., 2019; Assi et al., 2020; Bayuseno & Schmahl, 2010; Caviglia et al., 2019; Huber et al., 2020; Loginova et al., 2019; Mantovani et al., 2021).

BA are made of silicates, carbonates, hydrated minerals, sulphates, phosphates, oxides and an amorphous component that in the larger particle size classes can be up to 80% - 90% of the global content (Alam, Schollbach, van Hoek, et al., 2019; Assi et al., 2020; Bayuseno & Schmahl, 2010; Caviglia et al., 2019; Inkaew et al., 2016). The major elements are Si, Ca, Al, Mg, Fe, K, S, P and Na whereas among the minor few potentially toxic elements (PTE) such as Pb, Cu, Cr, Zn and Ni are found (Alam, Schollbach, van Hoek, et al., 2019; Caviglia et al., 2019; Funari et al., 2015; Mantovani et al., 2021).

With respect to the global Earth Crust composition, Dijkstra et al. (Dijkstra et al., 2019) showed an enrichment in Ca, S and P, and slightly less in Si. To note, PTE are strongly enriched respect to the Earth Crust. This poses a bias in re-using BA due to the possible release of PTE in environment.

Several investigations on the leaching behaviour of BA were done, demonstrating that PTE release is major in finer grain size because of both the particle dimension and the great presence of water-soluble mineralogical phases such as ettringite and hydrocalumite (Alam, Schollbach, van Hoek, et al., 2019; Caviglia et al., 2019; Feng et al., 2007; Huber et al., 2020; Loginova et al., 2019; Mantovani et al., 2021; Šyc et al., 2020; Wei et al., 2017; Yao et al., 2012).

The mobility of an element towards an environmental matrix is strictly connected to chemical and mineralogical characteristics: PTE in silicates or glasses are released only after a strong acid attack, whereas PTE in soluble phases may be easily released in the environment. Therefore, several authors carried out sequential extractions to investigate the association between elements, crystalline or amorphous phases and their leaching behaviour (Abramov et al., 2018; Alam, Schollbach, van Hoek, et al., 2019; Goodarzi & Huggins, 2001; Haberl & Schuster, 2019; Zhu et al., 2018).

However, due to the complexity of the material and the low concentration of PTE it is difficult not only to obtain an unambiguous correspondence between mineralogical and chemical information but also to analyse the PTE at a detailed scale, determining its concentration and oxidation state in the different phases. This information is crucial to predict and assess the potential release and toxicity, but also for a valuable reuse of BA (Rissler et al., 2020).

Synchrotron-based XAS is one of the techniques that can be used to investigate the chemical speciation of elements. The main advantage of XAS is to determine the local atomic environment and oxidation state of a given element. It is a very sensitive method, able to investigate elements also in low concentration.

In literature, there are few studies in the use of synchrotron-based XAS for MSWI investigation. In details, the most part of the data focused on Cu and Zn speciation in FA (Hsiao et al., 2001, 2002, 2006), less on BA (Lassesson & Steenari, 2013; Rissler et al., 2020; Steenari & Norén, 2008; Tiberg et al., 2021) and no data are found on others critical elements like Pb, Cr and Ni.

A limit in XAS methods regards the lack of analytical data on the other elements present in the same point. Therefore, the textural information, like crystal size, clustering, shape and/or inclusions of other phases in the areas of analysis is lost. This affects the reliability of the XAS analyses in showing the distribution of the different phases in the sample. Synchrotron radiation-based micro-XANES together with micro-XRF provides a powerful alternative. With a narrowly focused beam, sized as little as $50\mu\text{m}^2$, micro-XRF analysis shows the local composition, with a sensitivity down to the ppm for the minor elements. The distribution of the PTE can be revealed, and in chosen points the XANES analysis can be done, showing the local environment for specific elements.

Micro-XRF and XANES were combined in environmental and cultural heritage studies, where an heterogeneous matrix is present (Kostomitsopoulou Marketou et al., 2021; Liu et al., 2020), but not in BA from incinerator yet.

The novelty of the present study is to present for the first time the combined micro-XRF and XANES data on BA, with the aim to determine not only the chemical form and speciation of PTE, but also their textural distribution and association with other elements. SEM-EDS analyses have been performed on the same studied sample, as well. In respect with micro-XRF, the analytical resolution

of SEM-EDS analysis is lower, being possible to reveal elements at least 0.1 wt%, but with a spatial resolution of 1 μm^2 in analysis or less in imaging.

In this work, sample of BA from Parma WtE plant with particle size 0.5 - 1mm were investigated throughout a multi-technique approaches with SEM-EDS, micro-XRF and micro-XANES. A preliminary mineralogical and chemical characterization of the bulk material (XRD and XRF) were carried out on the same grain size and are reported.

2. Materials and methods

2.1 Sample Description

The BA samples come from Parma WtE plant (northern Italy), property of Iren Ambiente S.p.A. The plant operating since 2014 and has an authorized disposal capacity of 160.000 t/y of waste. The materials treated are MSW and non-hazardous special waste (Iren Ambiente, 2022). WtE plant has a grate furnace technology and burn at about 1000°C. BA were taken from 2-3m high stockpile in May 2019.

BA were mixed, dried in an oven at 60°C for 24 h and sieved. The 0.5-1mm grain size was selected to conduct this study and then, to have more representative samples, it was quartered. The bulk composition of this grain size was measured by XRF (Mantovani et al., 2021). The results are shown in **Table 3.3.1.1**.

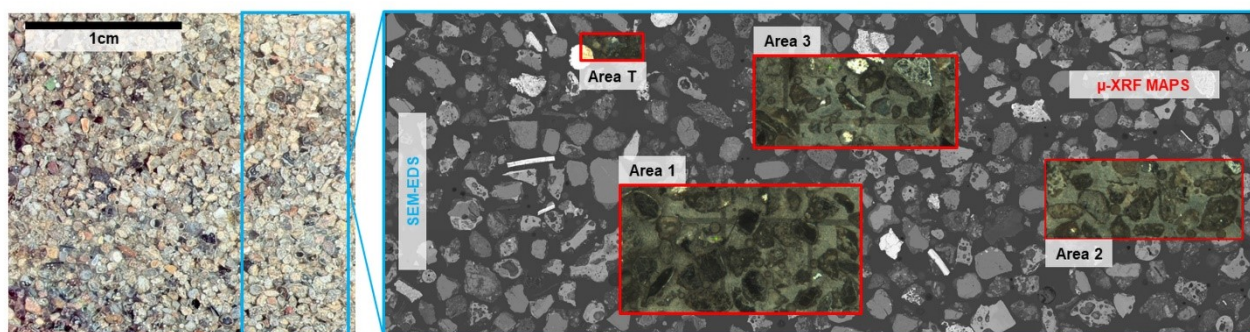


Figure 3.3.1.1 Left: stab containing the polished grains of the BA, with the area where SEM-EDS analyses were performed; right: SEM backscattered electrons image of the same area, with frames indicating the areas of XRF and XANES analyses.

About 1 g of the sample was used for XRD powder analyses, while another part of sample was embedded in epoxy resin and cut longitudinally to obtain a polished section for SEM-EDS, synchrotron XRF and XANES analyses. The stab was 2x2cm². A selected area of the stab was

chosen and a chemical map with SEM-EDS was acquired (**Figure 3.3.1.1**); within this selected area, 4 smaller areas were selected for XRF mapping and XANES analyses.

Major Elements (g/100g)	
SiO ₂	29.20
TiO ₂	0.92
Al ₂ O ₃	8.96
Fe ₂ O ₃	3.48
MnO	0.10
MgO	3.59
CaO	28.41
Na ₂ O	2.18
K ₂ O	1.29
P ₂ O ₅	2.19
LOI	19.69
Minor Elements (mg/kg)	
As	56
Ba	1618
Ce	36
Cl	10120
Co	57
Cr	697
Cu	1885
Ga	14
Hf	< 3
La	21
Mo	13
Nb	10
Nd	20
Ni	179
Pb	802
Rb	27
S	14780
Sc	13
Sn	43
Sr	517
Th	7
U	< 3
V	79
Y	14
Zn	5750
Zr	169

Table 3.3.1.1 X-Ray Fluorescence (XRF) analysis of major, minor and trace elements for the BA of 0.5-1mm grain size from WtE of Parma. Minor and trace elements are in mg/kg while major elements are expressed as g/100g of their oxides and loss of ignition (LOI) values %.

2.2 X-Ray Powder Diffraction Analyses

XRPD was performed with a Bruker D2 Phaser powder diffractometer, operating at 30 kV and 10 mA with Cu K α ($\lambda = 1.54178 \text{ \AA}$) radiation. The collections were done in the 2θ range 5-100°, with a

step of 0.02°/sec. The diffractometer works with θ - θ focalizing geometry and takes advantage of a solid state detector. A 30 rpm sample rotation was applied to minimize crystal preferential orientation effects. The diffraction patterns were identified using DIFFRAC.EVA software (Bruker, Germany). The Crystallography Open Database (COD) and the ICDD PDF-2 database were used for phase identification.

GSAS 2 software package (Toby & Von Dreele, 2013) was used for Rietveld analysis (Gualtieri, 2000; Pagani et al., 2010) and to quantify the major crystalline phases and the amorphous material; a 10% Al₂O₃ corundum was used as standard. XRD results are reported in **Table 3.3.1.2**.

2.2 SEM-EDS

The SEM-EDS analyses were performed on a 2.0 x 0.8 cm² slice, using a JEOL JSM-IT 300LV Scanning Electron Microscope, equipped with Oxford INCA Energy 200 EDS SATW detector (WD 10, KV 15), at 15kV, 1.2mA current and 1 μ m beam diameter. The data were collected and processed using the AZTEC software (Oxford Instrument). The mapping was done on 33 frames, which were subsequently merged, each with a 1024 x 768 pixel resolution, under a 50 times magnification, dwell time 1500 μ sec. The whole collection lasted about 14 hours. Each analytical point sized 2.5 μ m².

2.3 Synchrotron radiation

μ -XRF mapping and XANES measurements were conducted at Elettra synchrotron radiation source, at the 10.1L XRF beamline (Jark et al., 2014; Karydas et al., 2018; Wrobel et al., 2016). The experiment was performed using both HE multilayer (for the collection of XRF maps) and Si111 (for the collection of XANES spectra) monochromators, with standard 45°/45° geometry for fluorescence mode measurements, and an XFlash 5030 SDD detector (Bruker, Berlin, Germany). A pair of parallel plane mirrors intercepting the beam in grazing incidence suppressed higher order harmonics contaminations.

The flat surface of the BA sample embedded in epoxy resin has been mounted on a Teflon sample holder, with also reference metal foils mounted on the side (perpendicularly) for energy calibration of the monochromator (in transmission mode, using a Hamamatsu Si-photodiode S3590-09, 10x10 mm², 300 μ m thickness) prior to XANES measurements.

XRF maps were collected with an incident beam energy of 14 keV and a beam size at the exit slits of 50x50 μ m² (H x V).

XANES measurements were performed on 37 points, which were chosen based on the higher content in PTE (Co, Cr, Ni, Cu, Zn and Pb) from μ -XRF maps. The spectra collected on the point positions are reported in supplementary.

All spectra were collected using 5 seconds per step and a variable energy step as a function of the energy: large step (5 eV) in the first 200 eV of the spectrum, smaller step (0.2 eV) in the near-edge region and a k-constant step of 0.05 Å⁻¹ further above the absorption edge.

When necessary, multiple spectra were collected and merged in order to increase the signal to noise ratio. The oxidation state was determined using least-squares Linear Combination Fitting (LCF) based on reference spectra collected on compounds of known oxidation state. Background removal, normalization of XANES spectra and LCF analyses were performed using the Athena software package (Ravel & Newville, 2005).

3 Results

3.1 X-Ray Powder diffraction

Mineral Phase	Formula	Wt%
<i>calcite</i>	CaCO ₃	8 (1)
<i>vaterite</i>	CaCO ₃	2 (1)
<i>quartz</i>	SiO ₂	3 (1)
<i>melilite</i>	(Ca, Na) ₂ (Mg, Fe, Al, Si) ₃ O ₇	2 (1)
<i>plagioclase</i>	(Ca,Na)[Al(Al,Si)Si ₂ O ₈]	2 (1)
<i>strätlingite</i>	Ca ₂ Al ₂ SiO ₇ ·8H ₂ O	2 (1)
<i>ettringite</i>	Ca ₆ Al ₂ (SO ₄) ₃ (OH)12*26H ₂ O	3 (1)
<i>hydrocalumite</i>	Ca ₄ Al ₂ (OH) ₁₂ (Cl,CO ₃ ,OH) ₂ ·4H ₂ O	3 (1)
<i>hematite</i>	Fe ₂ O ₃	3 (1)
<i>magnetite</i>	Fe ²⁺ Fe ³⁺ ₂ O ₄	< 3 (1)
<i>amorphous</i>		72 (6)
<i>larnite</i>	Ca ₂ SiO ₄	x
<i>portlandite</i>	Ca(OH) ₂	x
<i>tobermorite</i>	Ca ₄ Si ₆ O ₁₇ (H ₂ O) ₂ ·(Ca·3H ₂ O)	*
<i>apatite</i>	Ca ₅ (PO ₄) ₃ (Cl/F/OH)	*

Table 3.3.1.2 Quantitative mineralogical composition of the major phases in the examined grains; X: present, but not refined, * dubious.

XRPD results (**Table 3.3.1.2**) shows that amorphous material is the main component. As reported in Mantovani et al. (Mantovani et al., 2021), in the analysis of BA from the same plant, the amorphous portion is on itself heterogeneous, showing areas more or less Fe and Ca rich. The amorphous fraction is made in part by residual glass, already in amorphous state before incineration (i.e. bottle glass),

and in part by the melt during incineration. In the latter case it was found in local equilibrium with different crystalline phases.

Crystalline phases identified by XRD can be divided into three groups: a) phases, like quartz, apatite and refractory materials which were present before combustion, b) phases like melilite, anorthite, magnetite, and hematite which are formed during combustion, or c) phases formed during the quenching and the subsequent aging of the ashes, as carbonates (calcite and vaterite), and a number of typical cementitious materials phases. This is in agreement with what is reported in the literature (Bayuseno & Schmahl, 2010; Caviglia et al., 2019; Mantovani et al., 2021). To note, the phases in which PTE are present as a main component, observed by XANES and SEM-EDS, were not revealed by XRD.

3.2 SEM-EDS

SEM-EDS mapping was done to show where the critical elements (Zn, Cr, Ni, Pb, Cu, Co) are most concentrated, and where they form phases as major components, like zincates, plumbates or Cu alloy. Quantitative analyses were done on point and/or area of grains with higher concentration of PTE to determine the stoichiometric compositions. Due to the overlap of the strong L_{α} line of Zn with the K_{α} of Na, and of the M_{α} line of Pb with the K_{α} of S, K_{α} and L_{α} of Zn and Pb respectively were used to chart the presence of these elements.

Spatial resolution was another issue: in several cases the PTE bearing phase could not be analysed due to the size of the crystals, below the spatial resolution of the SEM-EDS analysis. In few larger sized grains, it was possible to retrieve the composition without overlap of the neighbouring phases and to identify phases by stoichiometry. In **Figure 3.3.2.2** the images of a few grains including phases with PTE as major components are shown.

As a rule, PTE are found in solid solution with more common elements, so that the stoichiometric mineral formula deviates from that of the pure mineral phase, as following.

Zn was found in a single grain as Mg-rich willemite. Willemite is a Zn orthosilicate, with stoichiometric formula Zn_2SiO_4 , here with significant Mg content exchanging for Zn in solid solution. The Mg-willemite composition is $Zn_{1.74}Mg_{0.23}SiO_4$. It coexists with a Na-rich hardystonite $[(Ca_{1.7}Na_{0.3})(Mg_{0.1}Zn_{0.8}Al_{0.1})(Si_{1.9}Al_{0.1})O_7]$. (**Figure 3.3.1.2 a**). Hardystonite is a Zn-bearing melilite, with nominal composition $Ca_2ZnSi_2O_7$; in our sample there is a strong deviation from nominal composition, due to an exchange of Na for Ca, Mg and Al for Zn, and Al for Si. The willemite-hardystonite assemblage in the ZnO - CaO - SiO_2 system is stable below $1301^{\circ}C$, at which temperature it melts incongruently to zincite (ZnO) and melt (Shevchenko & Jak, 2019). In another grain, zincite (ZnO) was found seemingly coexisting with a $Zn_4Al_2O_7$ phase, in a silica free environment. The

$\text{Zn}_4\text{Al}_2\text{O}_7$ phase is reported after decarbonation of Zn,Al-carbonate (Pshinko et al., 2013); it is not expected to form starting from oxides, as in the Al_2O_3 -ZnO phase diagram the intermediate phase between oxides is the gahnite spinel (ZnAl_2O_4) (Sharma & Yoo, 2018). Gahnite spinel is present in the same grain, but not mingled with ZnO. Zincite is also found in grains without coexisting phases, with stoichiometric composition, or in solid solution with Mn ($\text{Zn}_{0.43}\text{Mn}_{0.57}\text{O}$), in this case coexisting with glass and Ca-carbonate. Moreover, in one grain zincite crystals are found crowning non stoichiometric gehlenite, with composition $(\text{Ca}_{1.8}\text{Mn}_{0.2})(\text{Zn}_{0.3}\text{Al}_{0.7})(\text{Si}_{1.9}\text{Al}_{0.1})\text{O}_7$ (**Figure 3.3.1.2 b**). SEM-EDS analysis revealed also several grains with Zn content up to 2 wt%, dissolved in Na- and Mg-rich silicate glass.

Cr is found in several grains as a background peak with concentration below 1 wt%. As a major constituent, Cr was observed in three grains: in one grain as stoichiometric FeCrO_3 oxide and in two others as chromite spinel (FeCr_2O_4), coexisting with glass. Both indicate the association with Fe, and the speciation in oxides (**Figures 3.3.1.2 e and 3.3.1.2 h**).

Cu was found in one metal grain in alloy with Sn, without coexisting phases (**Figures 3.3.1.2 c**). Partial oxidation is revealed by the presence of a small O peak. The measured stoichiometry, with O measured as a separate element, i.e not constrained by cation stoichiometry, is $\text{Cu}_{0.73}\text{Sn}_{0.07}\text{O}_{0.20}$. In the same sample two small EDS peaks of $\text{Cl}(\text{K}_\alpha)$ and $\text{S}(\text{K}_\alpha)$ may indicate alteration to sulphate and chloride of the metals. Cu was also found in small sized metal drops throughout the sample.

Co was found in one metal grain, in alloy with Mo and in an alumina matrix. No grains containing Ni in a major amount were found.

Pb was generally too low to be revealed as major phase. In one grain it was found a Pb bearing phase, Ca-plumbate (Ca_2PbO_4), together with lime (CaO) and glass (**Figure 3.3.1.2 f**). The Ca_2PbO_4 phase was found in oxidizing conditions by Suzuki et al. (Suzuki et al., 1998), and can be obtained by reaction of a Pb-bearing compound with lime. It is a phase soluble in hot water and decomposes in weakly acid environment, which might be a source of potential leaching (JERNEJCIC J et al., 1969). On the other hand Wang et al. (Wang et al., 2016) report that the Ca-plumbate phase controls Pb volatilization during incineration.

3.3 Synchrotron-based μ -XRF

μ -XRF elemental maps (**APPENDIX X**) show the distribution and relative quantities of the different elements (major and minor), together with the BSE and optical images of the investigated areas. μ -XRF results are here discussed together with morphological information from SEM-EDS.

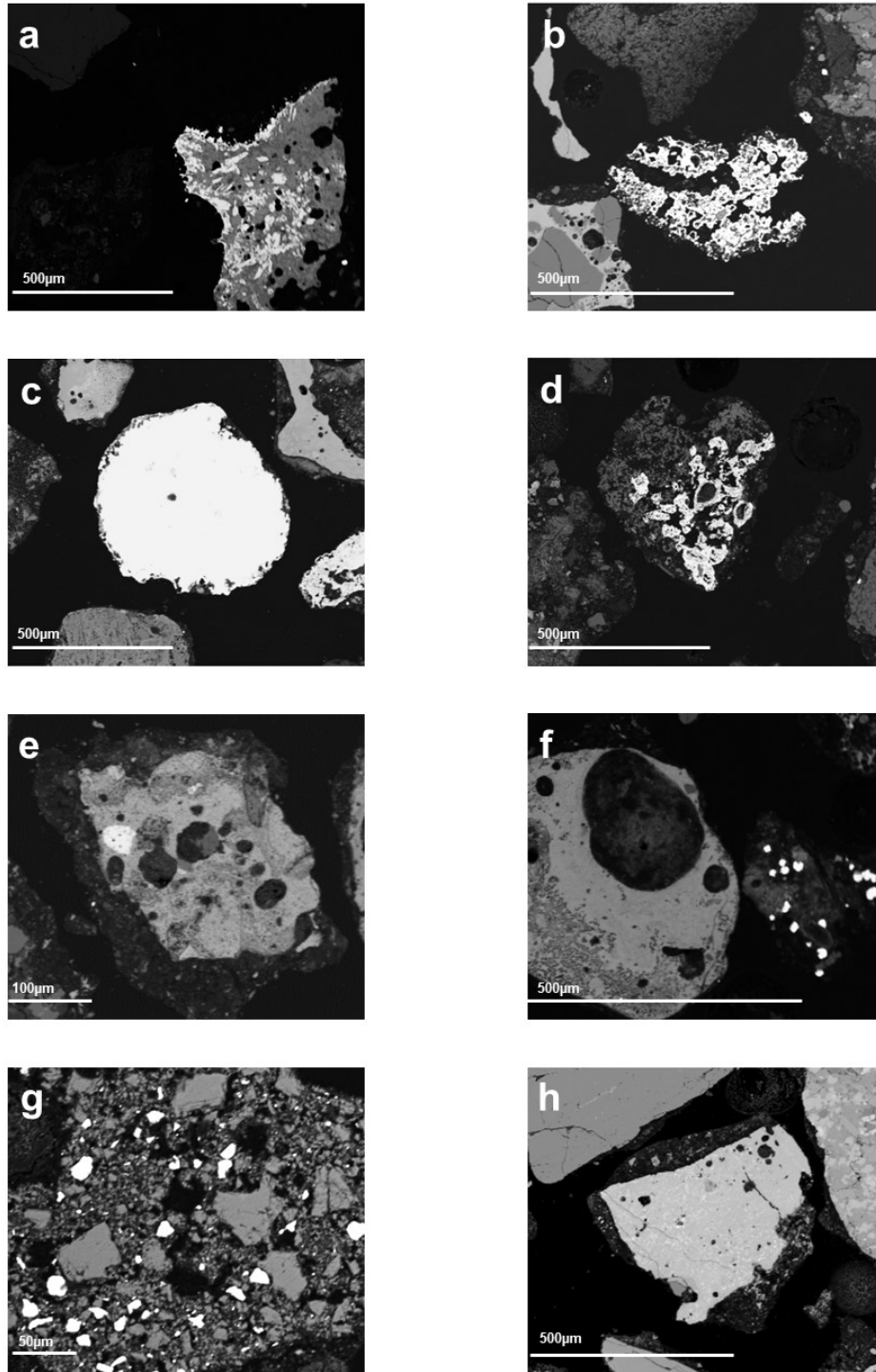


Figure 3.3.1.2 SEM-BSE image of grains with PTE: **a)** Willemite-hardystonite assemblage (willemite white, hardystonite gray); **b)** ZnO (white), overgrowing non stoichiometric Zn bearing gehlenite (gray); **c)** Cu-Sn oxidized alloy (white); **d)** Zn-Mn oxide (white); on the left of the image we find Ca-carbonate, gray, and glass, dark gray; **e)** FeCrO₃, white, coexisting in a composite grain with Ca-rich glass (light grey) and alumina (dark gray round phases); **f)** Ca-plumbate (Ca₂PbO₄), shown by white squared grains, together with lime (light gray), and silicate glass; **g)** Pb with TiO₂ oxide (white rounded grains) ; **h)** glass matrix with Cr-oxide inclusions (white points).

The embedded grains are generally made by a core, with the shape neatly appearing from the epoxide in BSE images. A rim usually borders the core, with smaller crystals embedded in a darker matrix. SEM-EDS analysis on the rims could be done just in few larger crystals, finding that they have a different composition from the core, i.e., among others, Ca-carbonate, phosphates, residual plagioclase, sulphates and chlorides.

μ -XRF maps show that some elements, namely Ca and Si, but also Mg, Al, Fe, P, Cr, Ti, Co, and Pb are generally present within the core of the grains. Zn and Cu are found both in the rims and in the core, whereas others, like S and Cl and, to a lesser extent, Na and K, mostly at the rims. The different mineralogical composition between rim and the core grains suggests a formation of very small crystals of chloride and sulphate during weathering.

Leaching tests on the same sample showed that Cl and S are the most leachable, supporting the hypothesis of their presence at the rim of the grains, and not within silicate glasses.

Also, the core of the grains is heterogeneous: SEM-EDS observations at higher resolution indicate the coexistence of several crystals as silicates, oxides, carbonates, metals inclusions and glass (**Figure 3.3.1.2**). μ -XRF data show a more detailed distribution of the PTE than SEM-EDS results: this is expected, as PTE are generally below SEM-EDS analytical resolution. However, in few cases when the μ -XRF indicates a higher concentration of a given element, it is not possible to find a counterpart in the SEM-EDS maps. Although the two methods analyse the same areas, the detected volume is different: in μ -XRF the beam probes a depth of few tens of microns, whereas the SEM-EDS probes 1-2 μ m maximum. The PTE rich phase may not be present at the surface of the grain, so to be revealed by SEM-EDS, but just few microns below, and detected instead by μ -XRF.

Due to the spatial resolution of acquired μ -XRF maps, lower than that of SEM-EDS, and the heterogeneous nature of BA, a given μ -XRF analytical pixel may sample a number of different phases.

Throughout the overlaps of single elements μ -XRF maps, the distribution of PTE was analysed and associated to major elements (Si, Ca, Mg, Na, etc) obtaining the mineralogical environment in which PTE are incorporated. Among the PTE, Cu is present generally together with Na, K and Si, in glass morphologies observed with SEM-EDS. To note, in the same areas EDS analysis do not revealed the presence of Cu-bearing phases, indicating that Cu is below the instrumental resolution or in tiny grains under the surface. Cu was found in one grain as a Cu-Sn alloy also with Ni; Cu was also found as alloy/metal inclusions and droplets dispersed within the glass as observed by Mantovani et al. (Mantovani et al., 2021).

In a grain, Ni occurs in alloys with Co and Mn, and with Co and Cr. Generally, however, Ni appears together with Fe and Cr, in a phase that was confirmed as chromite by XANES analysis, and, most

frequently, together with Na, K, Si and Al in an assemblage likely a glass. To note, Ni was not found together with S and Cl.

Co was found together with Ni, likely in alloy; overlap with O indicates some degree of oxidation. In the same grain, an overlap of Co and Cl might indicate formation of chlorides.

Cr is generally associated with Fe, but also with Si, Ca, Fe, Na and K. The suggestion is that it is dissolved in a glass, or in tiny chromite crystals. Cr was not present together with S and Cl.

Pb is found most in larger grains, in the core and in the rims of the grains. It is associated with Ca and Zn, but not with Si. This could suggest a carbonate phase. Pb occurs with S in few grains, where S is present within the core. This is not unlikely, in view of the strong affinity of Pb for sulphides. Pb is also found with Si, Na, K and Mg in Pb-rich glass.

Zn is found in core as trace in amorphous material and in rims, together with S and Cl suggesting their presence in sulphates and chlorides and together with Ti, in spinel-like structure.

3.4 XANES

A major advantage of XAS is to be element specific, modelling the X-ray Absorption Edge of a given electron transition for a given atomic species. It provides information on the local environment and oxidation state of the considered element, but it does not provide a chemical information of the specific phase where the element is present. As the element may be in different oxidation states and different phases within the area sampled by the beam, a deconvolution of the different contributions is often necessary. Comparing XANES results with those from SEM-EDS and μ -XRF analysis, the disadvantage of not having the composition of the emitting phase, is compensated by the sensitivity of the XANES emission, able to probe an element at few ppm concentrations and within submicrometric phases. Oxidation state and possible host phases for each of the PTE are here reported.

Cobalt

XANES spectra were recorded at the Co K-edge in one clast, on which higher resolution SEM-EDS analysis showed that the grain is made by a partially oxidized Co-Mn alloy, mingled with Al_2O_3 and a Ca-silicate phase (**Figure 3.3.1.3**).

XANES results confirm that Co is present in a partially oxidized alloy: LCF analysis indicates that Co is present at 68(7)% in the form of metal Co and at 32(4)% as Co-oxide. In the same grain, a single XRF spectrum extracted from the map highlight the presence of also Ni, present below the analytical resolution of SEM-EDS. A XANES spectrum collected at the Ni K-edge (labelled as Ni3_1). indicates that also Ni is present as a partially oxidized alloy: LCF results shows indeed that

metal Ni [84(5)%] coexists with divalent Ni-oxide [16(20)%]. Hereafter, the label of the spectra will be reported as Xa_b where X is the element, a is the area and b the point analysed. (APPENDIX XVI).

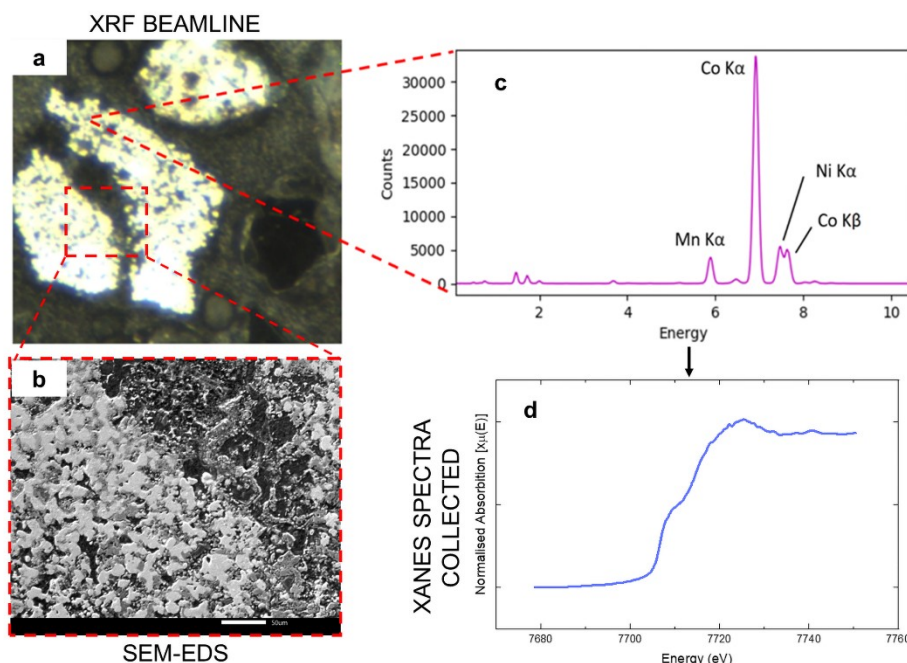


Figure 3.3.1.3 Co-bearing grain. a) Image of the grain taken with the microcamera available at the XRF beamline; b) SEM-BSE image on the same area with a three phases assemblage: metal cobalt (white), oxidized area with Co/Mn ratio 2/1 (gray) and mixture of alumina and Ca-Al silicate (black); c) XRF spectrum representative of the clast, with label of the main fluorescence lines; d) Normalized XANES spectrum collected on the same grain at the Co K-edge.

Copper

XANES spectra collected at the Cu K-edge in different clasts are reported in **Figure 3.3.1.4**. LCF analysis (**Table 3.3.1.3**) suggests that Cu chemical environment and oxidation state are heterogeneous even in the same area, ranging from metallic to Cu +II.

Three spectra (Cu1_1, Cu2_1 and Cu2_2) have a broad white line peak at about 8997 eV, together with a minor pre-edge peaks at about 8981 and 8985 eV, respectively. They fit with divalent Cu-oxide, but the contribution of monovalent Cu-oxide, and, in one spectrum, of residual metal, are necessary to obtain the best fit. In another grain (Cu3_1) we find a doublet at 8994 and 8998 eV, possibly indicating the presence of cupric acetate.

SEM-EDS analysis on the same areas did not show phases with sufficient enrichment in Cu to show significant emission in Cu-Kα peaks. It is possible that Cu in the areas is below the analytical

resolution of SEM-EDS, i.e. few thousands of ppm, but it could be also an effect of the different sampling size of SEM-EDS and XANES analyses. Only in one case Cu was found by SEM-EDS analysis as well, in a Cu-Ni-Sn alloy (**Figure 3.3.1.2 c**).

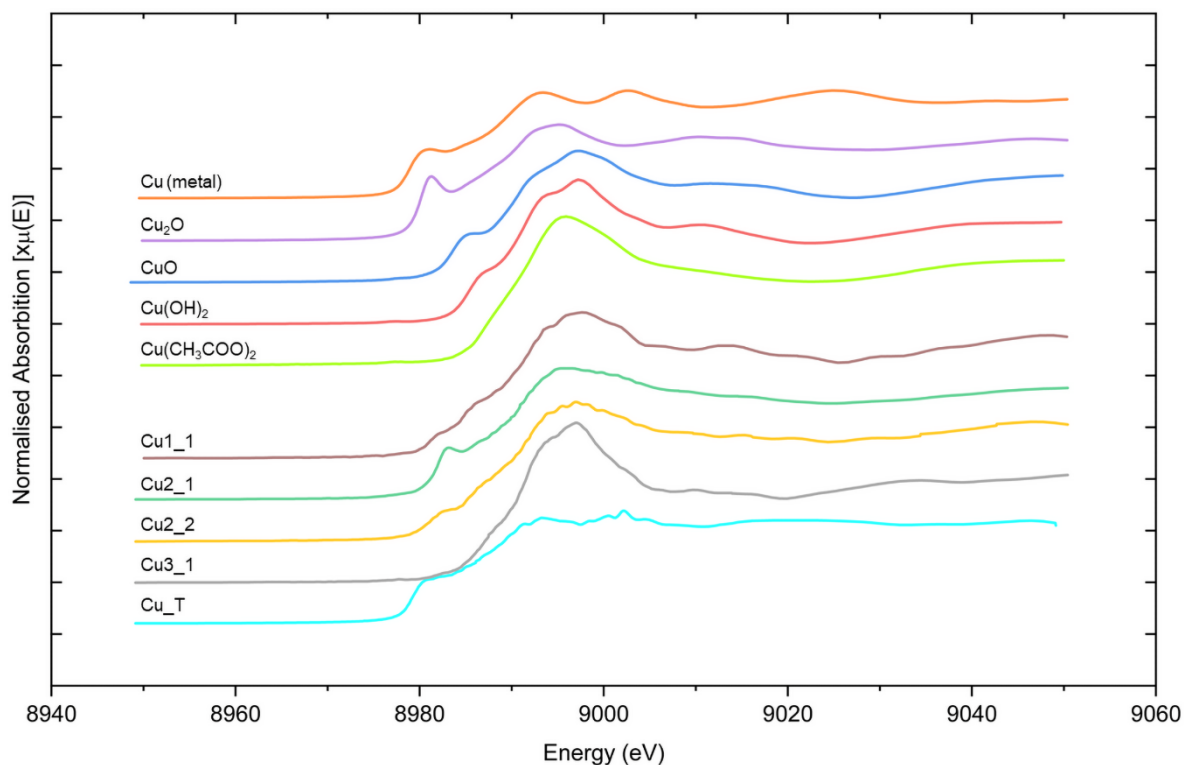


Figure 3.3.1.4 Normalized Cu XANES spectra of reference materials (top) and collected on various clasts of the BA samples (bottom).

Compounds	<i>Cu1_1</i>	<i>Cu2_1</i>	<i>Cu2_2</i>	<i>Cu3_1</i>	<i>Cu_T</i>
<i>Metal Cu</i>		10 (4)			80 (3)
<i>Cu₂O</i>	6 (4)	24 (5)	13 (4)		16 (4)
<i>CuO</i>	94 (2)	66 (3)	87 (3)		4 (2)
<i>Cu(OH)₂</i>				11 (6)	
<i>Cu(CH₃COO)₂</i>				89 (6)	

Table 3.3.1.3 Results of the LCF analysis performed on the spectra collected at the Cu K-edge on BA clasts (reported quantities are %; sigmas in brackets).

In this grain, XANES spectrum fits with metal Cu (Cu_T in **Figure 3.3.1.4**), showing the typical triplet at 8981, 8994 and 9004 eV, and indeed confirmed by LCF results. The Cu speciation in BA showed that Cu is present in different oxidation states (0, +I and +II); this was also observed by Rissler et al. (Rissler et al., 2020), and interpreted as an effect of zones in the fuel bed with different access to the oxygen. Here, however, we observe coexistence of different oxidation states within the same grain.

Zinc

Zn was found in BA in a number of different phases, some of them well visible also in SEM-EDS. Various XANES spectra (12 in total) at the Zn K-edge were collected on different clasts; a selection of the most representative ones is reported in **APPENDIX XI** where is visible that the edge position of all the spectra is similar and shifted with respect to reference Zn foil, indicating that Zn is not present as a metal but mainly occurred in oxidation state +II (**Table 3.3.1.4**).

Clast Zn2_3 is the only one to have a weak pre-edge, whereas two peaks at about 9665.3 and 9667.9 eV are clearly distinguishable in all the spectra except that of clast Zn1_2, which has only one peak at about 9666.5 eV. The LCF proved difficult because of the heterogeneity of the collected spectra. In all the spectra, a great fit is obtained with Zn-carbonate, in the form of smithsonite (ZnCO_3) or hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$). Smithsonite is here first observed, but Zn in solid solution within carbonate was reported by Piantone et al. (Piantone et al., 2004b) in an investigation on weathering phases. Hydrozincite was found by Rissler et al. (Rissler et al., 2020) and dubiously by EXAFS analysis by Tiberg et al. (Tiberg et al., 2021). Zincite (ZnO) was found in few grains, confirming SEM-EDS results and previous XAS data by Rissler et al. (Rissler et al., 2020) and Tiberg et al. (Tiberg et al., 2021).

Compounds	Zn1_1	Zn1_2	Zn1_3	Zn2_1	Zn2_2	Zn2_3	Zn3_1	Zn3_3	Zn3_4	Zn3_5	Zn3_6	ZnT
ZnO				29 (6)			32 (5)	36 (6)				28 (6)
ZnS	27 (3)	51 (3)	33 (3)						54 (2)	62 (2)	51 (2)	
ZnCO ₃		15 (2)		45 (7)	39 (4)	44 (3)	28 (4)	21 (5)				64 (6)
ZnAl ₂ O ₄						34 (3)						
Zn ₅ Si ₂ O ₇ (OH) ₂ ·(H ₂ O)							41 (6)		17 (3)	9 (3)	24 (5)	
Zn ₃ (PO ₄) ₂	42 (4)		41 (5)		27 (10)							
ZnFe ₂ O ₄					34 (7)			43 (4)				
Zn ₅ (CO ₃) ₂ (OH) ₆	31 (5)	34 (0.9)	26 (1)			22 (4)			29 (4)	29 (4)	26 (2)	
ZnCl ₂				26 (10)								8 (2)

Table 3.3.1.4 Results of the LCF analysis performed on the spectra collected at the Zn K-edge on BA clasts (reported quantities are %; sigmas in brackets).

Due to the similarity of the XANES spectra of zincite and Zn-hydroxide, $\text{Zn}(\text{OH})_2$ could be also present. In five of the examined spectra the fit required the ZnS phase in substantial amount. The phase is here first observed, and could be present by reduction of sulphates during weathering. The presence of Zn-phosphate is not surprising, as several Zn phosphate phases were found by (Piantone et al., 2004b). However, Zn-phosphate was not found by Rissler et al. (Rissler et al., 2020). Also, spinel phases like gahnite and Zn-ferrite (ZnFe_2O_4) are present, as well as the silicate hemimorphite [$\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$]. Both are common findings in Rissler et al. (Rissler et al., 2020), and Tiberg et al. (Tiberg et al., 2021). However, a possible misinterpretation can be done due to the absence of a standard for Zn in silicate glass, where it was found here and in Mantovani et al. (Mantovani et al., 2021) (**Table 3.3.1.5 2**). Last, the ZnCl_2 was found only in one spectrum (Zn2_1); this compound was found mainly in FA (Cai et al., 2015; Kitamura et al., 2020) but also in BA where its presence can be explained by the encapsulation of chloride within sintered BA particles (Rissler et al., 2020). It is possible that Zn is dispersed in small quantities, but being a highly soluble salt, its presence poses environmental concern.

Chromium

The LCF analysis results showed that three of the four collected spectra (Cr1_1, Cr2_1, Cr2_2) fit mainly with FeCr_2O_4 , with a percentage ranging from 60-77% (**APPENDIX XIV and Figure 3.3.1.5**). In the spectra Cr1_1 and Cr2_1 was also found metal Cr (23% and 27%, respectively) and 40% of Cr_2O_3 in Cr2_2. In one spectrum (Cr3_1) metal Cr (24%) and Cr_2O_3 (76%) were found, in agreement with SEM-EDS analytical results of chromium-aluminium oxide ($\text{Cr}_{1.81}\text{Al}_{0.19}\text{O}_3$). In all XANES spectra Cr was present in the Cr 0 and Cr III+ oxidation state. No evidence of Cr VI+, which would show the typical high intensity pre-edge peak at about 5993 eV, was found.

Lead

Several XANES spectra at the Pb L_3 -edge were collected, which show the same features and are almost identical: a very broad white line peak at 13052 eV is invariably present (**APPENDIX XII**). From the comparison of the edge position with respect to Pb metal foil and Pb oxide standard compound spectra, Pb is expected to be oxidized in all the clasts. The LCF analysis results showed fits with PbCO_3 (29-43%) and Pb_3O_4 (57-71%) (**APPENDIX XV**). In these compounds, Pb is present in +II and +III chemical forms. Other reference compounds, like PbO, PbO_2 , and PbCl_2 were tested, but none gave a satisfactory fitting. Also, in the same areas, S fluorescence lines were not detected, which discarded PbS and PbSO_4 as possible candidates. As for Zn, we did not try to fit Pb in a glassy environment, so we cannot rule out the presence of Pb in an alkali rich silicate glass, which could be

compatible with the chemical composition of some of the investigated clasts (from XRF data). XANES spectra of Pb in PbO-Ga₂O₃ glasses show, similarly to our sample, a single broad white line peak, which is also similar to the XANES spectrum of Pb in a silicate structure (Choi et al., 1999; Dubraille et al., 2009).

Nickel

Like Cu, Ni is found in SEM-EDS only in the above described grain together with Co, and is revealed just by XRF. The XANES spectra at the Ni K-edge (**APPENDIX XIII**) were compared with Ni metal foil, NiO and Ni(OH)₂.

LCF analysis shows that Ni, like Cu and Co, is present in metal and oxidized form, but hydration is also possible. The results of LCF analysis (**APPENDIX XVI**) indicate that the metal is always partially oxidized and hydrated.

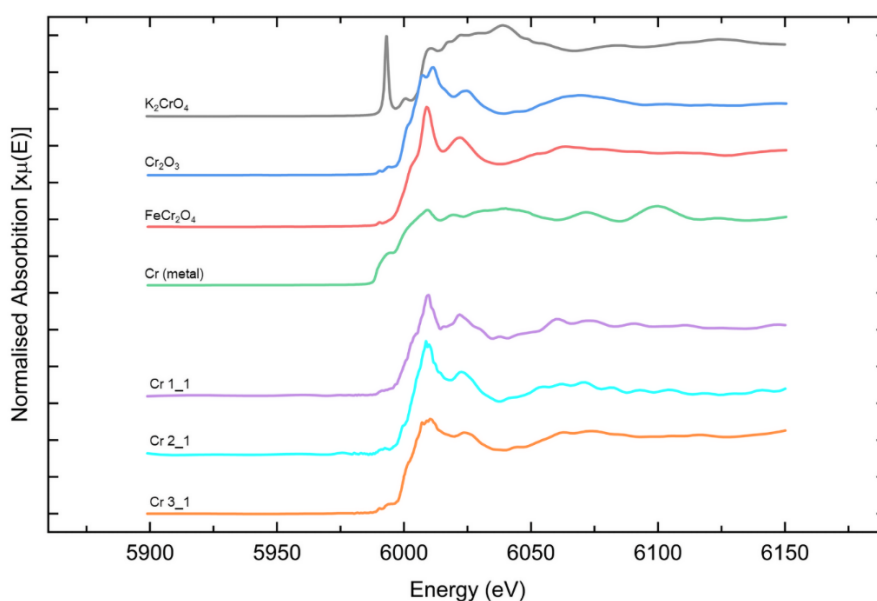


Figure 3.3.1.5 Normalized Cr XANES spectra of reference materials (top) and collected on various clasts of the BA samples (bottom).

4. DISCUSSION

The fate of PTE

In previous investigations on the speciation of PTE, several potential host minerals were suggested [11, 23, 56, 27, 29, 50–55]. This investigation confirmed the previous results, and possibly widened somehow the list (**Table 3.3.1.5.1, 3.3.1.5.2, 3.3.1.5.3**). However, being silicate glasses the major

phases of BA, a significant speciation in the glassy phases can be expected. In BA, where local equilibria are a rule, we may find glasses with different composition, although generally enriched in alkalis (Mantovani et al., 2021), able to host the different atomic species in their structure. The glass formed by the high temperature of the combustion chamber is easily detected in BSE images: it is present in the core of the grains, it embeds the crystals, and shows a composition of a Ca-Al silicate enriched in alkalis. The same compositional pattern was shown by XRF, in areas where SEM-BSE images showed a glass. SEM-EDS analyses on the glass in the core found in few grains Zn, Cr or Pb just above detection limits, although evidence of PTE in silicate glasses was not confirmed by XANES. In BA several glassy phases coexist with different composition likely hosting PTE. Because of the lack of reference standards for glass, XANES spectra might miss the contribution of PTE present in glasses.

Mingling with crystalline phases, and with a non-definite chemical composition, the characterization of this heterogeneous matrix is rather complex task. Even combining μ -XRF and SEM-EDS analysis, only in few grains distinct phases hosting the investigated PTE can be detected. In previous investigations [23, 29], without the use of μ -XRF, the XAS spectra were always interpreted with crystalline phases standards, overlooking possible contribution of the glass. Bearing this in mind we may suggest a possible speciation for each of the PTE.

Cu is found in different oxidation states. It was mainly found in metal forms, pure or as an alloy, which is partially oxidized as Cu I⁺ and Cu II⁺. It was observed as tiny droplets in the silicate glasses. This work and Rissler et al. (Rissler et al., 2020) suggest that it may also undergo weathering as a hydroxide or a chloride. Co is mostly present as an alloy, where found, with Mn, Ni or Fe, and only partially oxidized to Co II⁺. XRF shows that Pb, differently from Cu, is distributed mainly in larger grains, both in the core and in the rim, host in glasses and carbonate minerals in agreement with the XANES results. Besides, in SEM investigation, Pb was also found as a Ca-plumbate phase possibly formed by Pb-rich glass and lime. In a previous studies on the speciation of Pb in FA, it was found as metal Pb, PbCl₂, PbO and PbCO₃ (Zhu et al., 2018). Cr in higher concentration is generally found as an oxide, like spinel chromite or an Al-Fe-Cr oxide. In lower concentration, Cr occurs in glasses. No evidence of Cr VI⁺ or correlation with sulphate was detected. Ni is present as a metal or in spinel solid solution together with Cr and Fe. However, it looks more prone to alteration than Cr, forming Ni-bearing oxides and hydroxides.

Last, Zn is present in a number of phases, some of them probed by SEM-EDS, others mingled within a single 50x50 μ m² area, identified by XANES spectral deconvolution. Zn is observed in silicates like willemite, hardystonite or hemimorphite, in oxides and hydroxides, like gahnite spinel and zincite, in ZnS, in the very soluble form of ZnCl₂ and in carbonates like smithsonite or hydrozincite that can be

an alteration product of hemimorphite. Moreover, the presence of Zn in a silicate glass is suggested by a locally enrichment revealed by SEM-EDS. It was not found in sulphates or as a metal.

In **Tables 5.1, 5.2, 5.3** a list of the minerals containing the investigated PTE in BA in this work and previous investigations is reported. PTE were found in two mineralogical occurrences, like it was here observed: as minor components in silicates, metals, oxides and hydroxides, including glassy phases, or as phases in their own, as an effect of their local concentration. A further difference is in phases present as tiny inclusions, well below 1 μm , which could be revealed just by XAS or TEM, or, when in significant amount, by XRD. An example is the Cu oxides inclusions, i.e. tenorite and cuprite, which are likely present for oxidation of metal Cu, or that of ZnCl_2 and hemimorphite, observed only by XANES in this work and in Rissler et al. (Rissler et al., 2020). The nanoscopic minerals show higher surface and different size-related properties which should be taken care in any geochemical modelling (Hochella et al., 2019). The presence of PTE in submicrometric crystals or glasses was revealed by the XRF mapping, showing significant concentration of them, in areas where they were not found within single phases by SEM.

Moreover, in the enclosed list, several minerals appear just in one single paper, like $\text{Zn}_2\text{P}_2\text{O}_7$, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ or $\text{Zn}_2\text{PO}_4(\text{OH})$. These phases were identified by XRD, assumingly in significant amount, but they didn't find by other authors. In Meima and Comans (Meima & Comans, 1999) as much as 26% of the examined particles were containing Zn in metal form, while here in none of the investigated samples it was found. Likewise, it was observed for Pb. This indicates that each WtE plant has its own mineralogy, and that for any use of the BA, a specific investigation should be done. However, from the list it appears that comparing with different WtE plants, we can see that PTE are found in some common mineralogic phases.

For Cu the commonly observed is in metal Cu, which is more or less altered as Cu I+ or Cu II+ oxides or $\text{Cu}(\text{OH})_2$. The carbonate form, commonly observed in alteration of mining deposits, is less reported. In few cases it may enter in the complex spinel oxide structure. Cu associated in silicates did not find in this work, but this was reported by Rissler et al. (Rissler et al., 2020) and Meima and Comans (Meima & Comans, 1999). If present, Cu-silicates together with metal Cu are probably combustion products, while the others are related to subsequent weathering.

Zn is found in a wealth of different phases. As a high temperature Zn dominant phase, zincite is the main mineral, but also silicate willemite and the spinels franklinite and gahnite are commonly found. Zn-phosphates and metal Zn are also found, but not in this investigation. Zn is also present as an impurity in other oxides, in silicate glasses, in feldspars and pyroxenes. The alteration products are silicate hydrated, hydroxides, carbonates and chlorides. All of them have been observed by XAS, indicating their presence as nanosized grains. Such rather complex mineralogy of Zn produces an

equally complex leaching behaviour depending of: a) degree of weathering and consequently ratio between high temperature and alteration phases; b) grain size, which may affect the solubility; c) mineralogical species of the weathering phases, which are specific of each WtE plants.

Cr in a stable glass or oxide is a common finding. Cr weathering phases were not found, apart from a possible entrance in the ettringite structure, as yet demonstrated only by Piantone et al. (Piantone et al., 2004a).

Pb was found as a major component in oxides, or as an impurity in silicate glass. Weathering phases, where Pb may enter as an impurity were observed in carbonates and ettringite. Last, we did not find in previous literature indications about the speciation of Ni and Co.

Speciation and leaching

Prediction of leaching behaviour in a complex system like BA involves the phases within the ashes, their proportion, and their thermodynamic properties in multiple equilibria. A problem in this approach is that it assumes equilibrium, which is not present globally, but might be achieved only at a local microscale; moreover, the thermodynamic properties of several constituents, either in terms of modelling solid solution in the host minerals, or for the properties of the glass lack. In previous investigation it was shown that the glass, which is the main constituent of the ashes, is not a unique phase with its own thermodynamic properties, but that there are several glasses, with different composition and assumingly different thermodynamic properties. The different glasses have compositions loosely falling within the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ field, but they may differ by K and Na content, by Fe and possibly organic dispersed matter, and last, by the content in minor metal elements. A major problem observed is the coexistence of a heterogeneous material in which connection between the different grains is not granted; moreover weathering, which occurs at the rim of the grains promotes further local complexity. This may lead to significant differences between each WtE plants. For example, from chemical data not yet published (XRF) on BA sampled from Parma and others WtE plants in Northern Italy, appear that major and minor elements content is similar within the same order of magnitude. However, the elements leaching using the same procedure (UNI EN-12457-2, at pH 7) are much different. Between WtE plants the leached fraction diverges by one order of magnitude for Cr, Ni, Pb and Zn, and by two orders of magnitude for Cu. The PTE leached from the 0.5-1 mm grain size of the Parma WtE plant (the same taking into account in this work) are compared with the bulk mineralogical composition. Due the pH utilized; the released fraction would involve only very soluble phases. The results varied from 0.7% to 0.002% for Cr and Pb, respectively, and 0.07 and 0.08% for Cu and Ni. In Alam et al. (Alam, Schollbach, van Hoek, et al., 2019) a sequential extraction procedure (SEP) showed that Zn is among PTE the most leachable, a result which was

confirmed by preliminary SEP data on Parma BA. Leaching promotes an almost complete solubilisation of Cl, which is released by 70%. We may assume that only minor content of Cl is locked within a glass or some stable crystal forms, and that it is present as well as highly soluble chlorides. Highly soluble Cu-chlorides may therefore account for the leached Cu. In the case of Ni, no evidence of Ni chlorides was found, but a wider transformation in hydroxide could account for the leached Ni. Pb was found in insoluble oxides and carbonates. The higher concentration of Cr in leachate is puzzling: Cr was invariably found in phases highly stable, like in chromite, or in metals. A possible suggestion, although with no evidence in the investigation, may come from dissolution of Cr in ettringite as CrO_4^{2-} replacing SO_4^{2-} (Song et al., 2019).

5. CONCLUSIONS

The distribution and speciation of PTE like Pb, Cu, Zn, Co, Cr and Ni has been determined. The main results are:

- 1) core and rim structures were generally found for each grain. The core consists of high temperature phases, mingled with glass of different composition, in local equilibrium, whereas the rim is made by fine grained carbonates, sulphates, oxides, hydroxides, chlorides and organic residual matters, likely coming from weathering;
- 2) among PTE, Zn and Cu are present at the grain rims, whereas the others are generally found in the core;
- 3) the speciation of Cu and Ni involves the transformation from metal to oxide and hydroxide. Cu shows also the coexistence of Cu I+ intermediate oxidation state;
- 4) Pb is generally found in carbonates or in oxides; Zn has a wide mineralogical speciation, in carbonates, oxides and silicates;
- 5) Cr is found in insoluble oxides, and never in Cr VI+ oxidation state. The results from leaching experiments however suggest that wider solubility might be achieved by some neglected contribution of Cr III+ exchanging with Al or of Cr VI+ exchanging with S in SO_4^{2-} in the highly soluble ettringite;
- 6) the speciation of PTE occurs in a wide range of minerals, due to different waste input, combustion temperature, local equilibria, grain size and ageing; these variables affect the elements leaching, and the predictions of the potential leaching results obtained in one WtE plant should be extended to others with extreme care.

Element	Suggested form/Mineral	Tecnicue	References
Copper	<i>CuO (tenorite)</i>	TEM, SEM-EDS + XRD	(Meima & Comans, 1999)
		XRD, EPMA	(Bayuseno, 2011)
		SEM-EDS	(Wei et al., 2011)
		XANES + EXAFS	(Lassesson and Steenari, 2013)
		XANES + EXAFS	(Olsson et al., 2009)
		XANES	(Rissler et al., 2020)
		EXAFS	(Tiberg et al., 2021)
		XANES	this work
	<i>Cu₂O (cuprite)</i>	XRD	(Meima and Comans, 1999)
		XANES + EXAFS	(Lassesson and Steenari, 2013)
		XANES	(Rissler et al., 2020)
		XANES	this work
	<i>Cu₂(OH)₃Cl (atacamite/paratacamite)</i>	XRD	(Piantone et al., 2004)
	<i>Cu(OH)₂</i>	XANES	(Rissler et al., 2020)
	<i>CuSiO₃ · H₂O</i>	XANES	(Rissler et al., 2020)
	<i>Cu₁₉Cl₄SO₄(OH)₃₂ · 3H₂O (connellite)</i>	XRD	(Piantone et al., 2004)
	<i>Cu₂Zn₄Al₂(OH)₁₆CO₃ · 4H₂O</i>	XRD	(Piantone et al., 2004)
	<i>Cu₂S</i>	XRD	(Bayuseno, 2011)
	<i>CuS</i>	XRD	(Bayuseno, 2011)
	<i>Cu₁₁(OH)₁₄(CrO₄)₄</i>	XRD	(Piantone et al., 2004)
	<i>CuCr₂O₄</i>	XANES + EXAFS	(Lassesson and Steenari, 2013)
		XANES	(Rissler et al., 2020)
	<i>CuFe₂O₄</i>	XANES	(Rissler et al., 2020)
	<i>Cu metal (or alloy)</i>	SEM-EDS	(Meima and Comans, 1999)
		XANES + EXAFS	(Lassesson and Steenari, 2013)
		SEM-EDS	(Wei et al., 2011)
		XANES	(Rissler et al., 2020)
		SEM-EDS	(Mantovani et al., 2021)
		EXAFS	(Tiberg et al., 2021)
		SEM EDS + XANES	this work
	<i>Cu₂(OH)₂CO₃ (malachite)</i>	Geochemical model	(Dijkstra et al., 2006)
		XANES	(Rissler et al., 2020)
	<i>Cu adsorption to Fe/Al-hydroxides</i>	Geochemical model	(Meima and Comans, 1999)
		Geochemical model	(Dijkstra et al., 2006)
	<i>Cu substitution in different minerals</i>	SEM-EDS + XRD	(Meima and Comans, 1999)

Table 3.3.1.5.1 Cu species found in literature data (ref, in brackets) and implemented with data of this work.

Element	Suggested form/Mineral	Technique	References
Zinc	<i>ZnO</i> (zincite)	Crystal-chemical data and XRD	(Piantone et al., 2004)
		XRD + SEM-EDS	(Piantone et al., 2004)
		XANES + EXAFS	(Steenari and Norén, 2008)
		XANES	(Rissler et al., 2020)
		EXAFS	(Tiberg et al., 2021)
		SEM-EDS + XANES	this work
	<i>ZnS</i>	XANES	this work
	<i>ZnCl₂</i>	XANES	(Rissler et al., 2020)
		XANES	this work
	<i>ZnCO₃</i> (smithsonite)	XANES	(Rissler et al., 2020)
		XANES	this work
	<i>Zn₂P₂O₇</i>	XRD	(Tang et al., 2015)
	<i>Zn₂(PO₄)(OH)</i> (descloizite)	XRD	(Piantone et al., 2004)
	<i>Mn₂Zn(PO₄)₂</i>	XRPD	(Crannell et al., 2000)
	<i>Zn₃(PO₄)₂</i>	XRPD	(Crannell et al., 2000)
		XANES	(Rissler et al., 2020)
		XANES	this work
	<i>Zn₃(PO₄)₂ · 4H₂O</i>	XRPD	(Crannell et al., 2000)
	<i>ZnFe₂O₄</i> (franklinite)	XANES	(Rissler et al., 2020)
		EXAFS	(Tiberg et al., 2021)
		XANES	this work
	<i>ZnFe₂(SO₄)₄</i> (lishizhenite)	XRD	(Piantone et al., 2004)
	<i>ZnAl₂O₄</i> (gahnite)	XANES	(Rissler et al., 2020)
		EXAFS	(Tiberg et al., 2021)
		SEM - EDS + XANES	this work
	<i>Zn₂AlO₇</i>	SEM-EDS	this work
	<i>Ca₂ZnSiO₇</i> (hardystonite)	SEM-EDS	this work
	<i>Zn₂SiO₄</i> (willemite)	Geochemical model	(Dijkstra et al., 2006)
		XANES + EXAFS	(Steenari and Norén, 2008)
		XANES	(Rissler et al., 2020)
		EXAFS	(Tiberg et al., 2004)
		SEM-EDS	this work
	<i>Zn₄Si₂O₇(OH)₂ · (H₂O)</i> (hemimorfite)	XANES	(Rissler et al., 2020)
		EXAFS	(Tiberg et al., 2021)
		XANES	this work
	<i>Zn(OH)₂</i>	XANES + EXAFS	(Steenari and Norén, 2008)
		EXAFS	(Tiberg et al., 2021)
	<i>Zn₅(CO₃)₂(OH)₆</i> (hydrozincite)	XANES	(Rissler et al., 2020)
		SEM-EDS	(Meima and Comans, 1999)
	<i>Zn metal (or alloy)</i>	SEM-EDS	(Meima and Comans, 1999)
		SEM - EDS	(Wei et al., 2011)
		XANES	(Rissler et al., 2020)
	<i>Zn adsorption to or surface precipitates on Fe/Al-hydroxides</i>	Geochemical model	(Meima and Comans, 1999)
		Geochemical model	(Dijkstra et al., 2006)
	<i>Zn substitution in spinel crystals</i>	SEM - EDS	(Wei et al., 2011)
		SEM-EDS	(Mantovani et al., 2021)
	<i>Zn substitution in calcite</i>	Mapping by microprobe	(Piantone et al., 2004)
	<i>Zn substitution in Fe oxides/oxyhydroxides</i>	Mapping by microprobe	(Piantone et al., 2004)
	<i>Zn substitution in ettringite</i>	Mapping by microprobe	(Piantone et al., 2004)
	<i>Zn in solid solution with carbonates</i>	Mapping by microprobe	(Piantone et al., 2004)

Table 3.3.1.5.2 Zn species found in literature data (ref, in brackets) and implemented with data of this work.

Element	Suggested form/Mineral	Technique	References
Chromium	$FeCrO_3$	SEM-EDS	this work
	$FeCr_2O_4$	SEM-EDS	this work
	$Ca_6Cr_2(SO_4)_3(OH)_{12} \cdot H_2O$ (bentorite)	XRD	(Piantone et al., 2004)
	<i>Cr substitution in spinel crystal</i>	SEM - EDS	(Wei et al., 2011)
		SEM - EDS	(Mantovani et al., 2021)
	<i>Cr in glass matrix</i>	SEM - EDS	this work
Lead	Ca_2PbO_4	SEM-EDS	this work
	$PbCO_3$	Geochemical model	(Meima and Comans, 1999)
		XANES	this work
	Pb_3O_4	SEM-EDS	this work
	$PbCrO_4$ (crocoïte)	XRD	(Piantone et al., 2004)
	$Pb_4Cu_4O_4Cl_8 \cdot 5H_2O$ (cumingite)	XRD	(Piantone et al., 2004)
	<i>Pb substitution in calcite</i>	Mapping by microprobe	(Piantone et al., 2004)
	<i>Pb substitution in Fe oxides/oxyhydroxides</i>	Mapping by microprobe	(Piantone et al., 2004)
	<i>Pb substitution in ettringite</i>	Mapping by microprobe	(Piantone et al., 2004)
	<i>Pb substitution in spinel crystal</i>	SEM - EDS	(Wei et al., 2011)
	<i>Pb substitution in TiO_2</i>	SEM - EDS	this work
	<i>Pb metal (or alloy)</i>	SEM - EDS	(Meima and Comans, 1999)
Nickel	NiO	XANES	this work
	$Ni(OH)_2$	XANES	this work
	<i>Ni (metal or alloy)</i>	XANES	this work
Cobalt	CoO	XANES + SEM - EDS	this work
	<i>Cu (metal or alloy)</i>	XANES + SEM - EDS	this work

Table 3.3.1.5.3 Cr, Pb, Ni and Co species found in literature data (ref, in brackets) and implemented with data of this work.

Credit authorship contribution statement

Chiara De Matteis: methodology, data curation, investigation, writing – original draft, writing – review & editing, validation. **Simone Pollastri:** methodology, investigation, data curation. **Luciana Mantovani:** data curation, writing – review & editing, funding acquisition, supervision. **Mario Tribaudino:** conceptualization, data curation, writing – original draft, validation, funding acquisition, supervision. All authors have read and agreed to the published version of the manuscript.

3.4 SEQUENTIAL EXTRACTION PROCEDURE AND ENVIRONMENTAL CONCERN

In this section the results, yet to be published, on Sequential Extraction Procedure (SEP), are reported. SEP was performed on Piacenza (0.2 – 0.3mm) and Parma (<0.063 – 0.2mm, 0.3 – 0.5, 2 – 4mm, bulk < 4mm) samples. The solid residues collected during procedures are analysed by XRD and XRF. Results from extractions give further information on the speciation of PTE, which can be interpreted with respect to the results in the mineralogy of the BA.

The BA sampled from the Piacenza and Parma WtE plants were processed using a SEP described in detail in Section 2.8.2.1. In **Table 3.4.1** are reported XRD results for each step of procedure for Parma and Piacenza samples (this work) and Alam et al., (2019). Steps 0 (S0) represent the mineralogical composition of BA not yet subjected to any treatment, highlighting mineralogical differences between Parma and Piacenza WtE plants. Specifically, ettringite isn't present in the Parma BA, and hydrocalumite is present in a smaller amount, as can be seen from the peak intensity (**Figure 3.4.1**). These differences are due to the ageing of the material, as the Piacenza BA were sampled in 2019 while the Parma BA were sampled in June 2021, just a couple of weeks before the beginning of the SEP.

Summarizing what was said in section 2.8.2.1:

STEP 1 aims to remove water-soluble phases,

STEP 2 aims to remove carbonate phases,

STEP 3 aims to remove reducible phases,

STEP 4 aims to remove oxidizable phases.

In **Figure 3.4.2** the mass loss after each step is outlined. After the first step there is a mild, but significant mass loss for each size portion, higher in the smaller sized portion, up to 8% in the 0.063-0.2 fraction. A more considerable loss occurs after the second step of decomposition of carbonates and sulphates. This reduces the mass by 65% of the original value in the smaller fraction. In Alam et al. 2019 the acid reaction reduced the smaller fraction (≤ 0.125 mm) and the larger one (0.125 – 1 mm) by 35 and 20% of the original value, respectively. The higher dissolution in the second step could be an effect of the higher concentration of the acetic acid used in this work. The third step takes just to minor mass reduction, whereas in the fourth step there is a higher mass decrease.

With the third and fourth step the difference between grain size is hardly noticeable, like it was found in Alam et al. 2019. In this the Piacenza WtE plant differs, showing inverse relation, with higher loss of reducible phases, and less for oxidable ones. However globally the mass loss is not much different for similar grain size, respect to Parma.

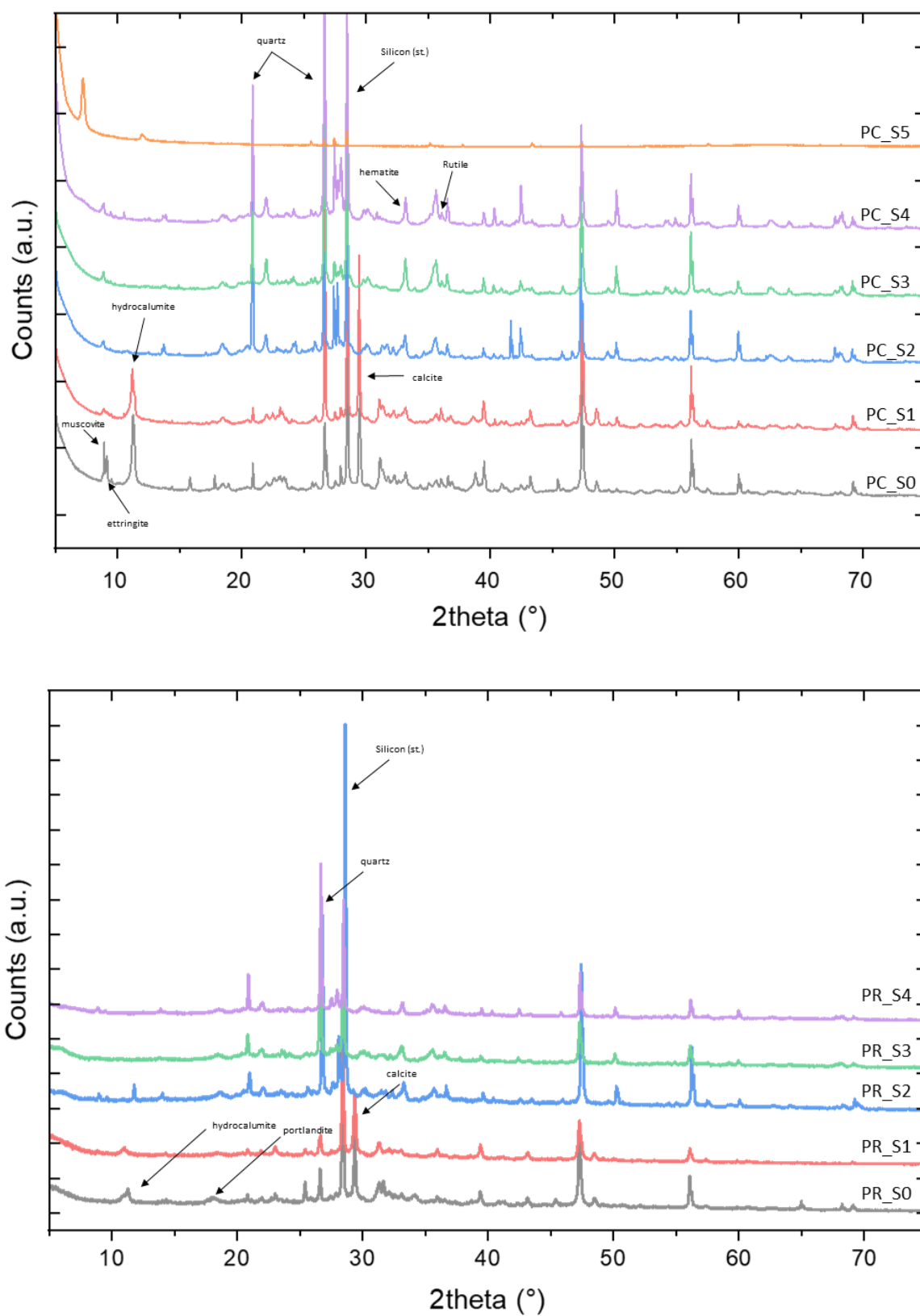


Figure 3.4.1: XRD pattern collected for Piacenza samples (PC) and 0.063 – 0.2 samples Parma (PR) for each extraction.

		Alam et al., 2021 ≤ 0.125mm					Alam et al., 2021 0.125 - 1 mm					PC 0.2-0.3 mm					PR 0.063 - 0.2 mm					PR 0.3-0.5 mm					PR 2 - 4 mm					PR < 4 mm					
Mineral	Chemical formula	S0	S1	S2	S3	S4	S0	S1	S2	S3	S4	S0	S1	S2	S3	S4	S5	S0	S1	S2	S3	S4	S0	S1	S2	S3	S4	S0	S1	S2	S3	S4	S0	S1	S2	S3	S4
halite	NaCl	x					x					x						x					x					x								x	
gypsum	CaSO ₄ · 2H ₂ O	x	x																																		
ettringite	Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ · 26H ₂ O	x										x																									
hydrocalumite	Ca ₄ Al ₂ (OH) ₁₂ (Cl,CO ₃ ,OH) ₂ · 4H ₂ O											x	x					x	x				x	x			x	x				x	x				
portlandite	Ca(OH) ₂																	x	x				x														
zeolite	X(AlO ₂)n(SiO ₂)1-n · mH ₂ O	x	x																																		
calcite	CaCO ₃	x	x				x					x	x					x	x				x	x			x	x				x	x				
apatite	Ca ₅ (PO ₄) ₃ (Cl/F/OH)	x	x	x	x		x	x	x	x	x	x	x	x				x	x	x						x	x				x	x					
anhydrite	CaSO ₄																	x	x	x	x		x														
larnite	Ca ₂ SiO ₄																	x	x				x	x													
spinel	XY ₂ O ₄	x	x	x	x		x	x	x	x	x																										
magnetite	Fe ²⁺ Fe ³⁺ ₂ O ₄													x	x					x	x	x			x	x	x			x	x			x	x		
hematite	Fe ₂ O ₃	x	x	x	x	x	x	x	x	x	x			x	x	x				x	x	x			x	x	x			x	x			x	x		
rutile	TiO ₂	x	x	x	x	x	x	x	x	x	x			x	x	x	x				x	x	x			x	x			x	x	x	x				
corundum	Al ₂ O ₃															x	x	x									x	x	x								
Cu-Ti oxide														x																							
Pb-Fe oxide														x																							
wustite	FeO						x	x	x	x	x																										
muscovite	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂											x	x	x	x	x																					
melilite	(Ca, Na) ₂ (Mg, Fe, Al, Si) ₃ O ₇	x	x	x			x	x	x	x	x	x	x	x				x	x				x	x			x	x	x	x		x	x	x	x		
plagioclase	(Ca,Na)[Al(Al,Si)Si ₂ O ₈]	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		
pyroxene	ABSi ₂ O ₆	x	x	x	x	x	x	x	x	x	x																x	x	x	x	x		x	x	x		
quartz	SiO ₂	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		

Table 3.4.1: mineralogical phases found (x) after each extraction in Alam et al. (2019), Piacenza BA and Parma BA

XRD analyses were performed at the end of each step, and the results obtained were compared with those reported by Alam et al., 2019. X-ray diffraction (**Table 3.4.1**) showed that after the first step halite is removed in all samples; ettringite, present in Piacenza and found by Alam et al. (2019), and portlandite, present only in Parma samples, are removed after treatment with ultrapure water. After the second step calcite and hydrocalumite are no more present in all samples. Melilite is partially removed in Alam et al., 2019, in this work Piacenza sample and in the 2 - 4 mm and bulk ≤ 4 mm Parma samples. The dissolution of melilite is complete in 0.063 - 0.2mm and 0.3 - 0.5mm Parma grain size melilite. After the acid attack, new mineralogical phases are identified, no more overlapped by the removed phases. In the Piacenza sample and in Parma smaller grain size (0.063-0.2mm and 0.3-0.5) hematite, magnetite and rutile are identified. In the Piacenza sample Cu-Ti and Pb-Fe oxides were also identified, but were not found after the extraction occurred in the third step. After the third step melilite residual is totally removed and in Piacenza sample appears corundum. In the fourth step plagioclase intensity decreases, indicating the onset of a dissolution, and there are no significant changes from the previous residue. Only the Piacenza samples were undergoing to the fifth step and, after attack with HF and HClO₄, only quartz, rutile and corundum are present.

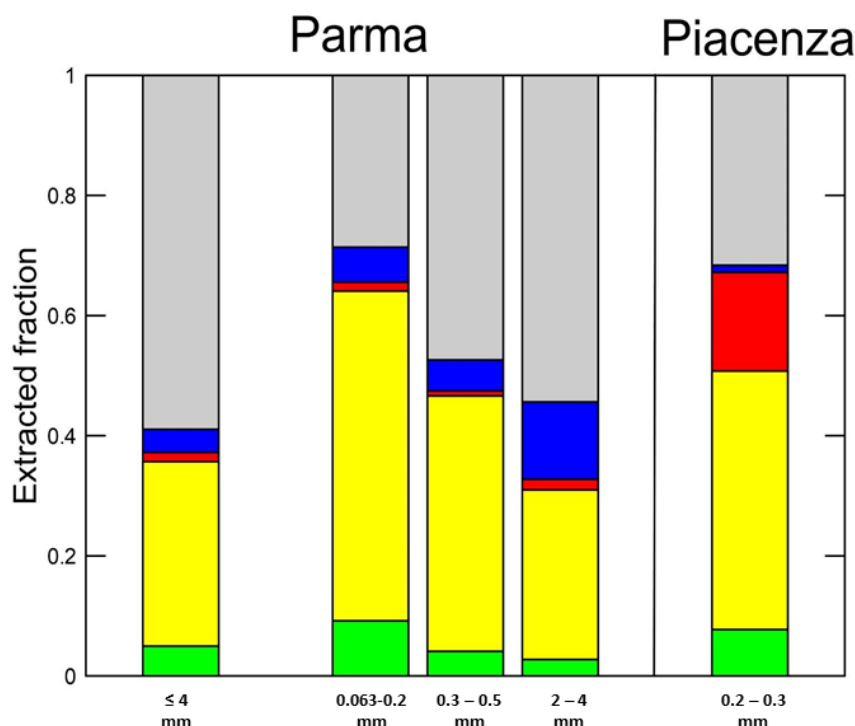


Figure 3.4.2 Weight loss in progressive extracted fraction. Green areas corresponding at first step (S1); yellow areas corresponding at second step (S2); red areas corresponding at third step (S3); blue areas corresponding at fourth step (S4); grey areas corresponding at residues

In **APPENDIX XVII** the results of the XRF analyses of the bulk samples at the different steps are reported. These results are averaged to 100% of the residue; to obtain the residual amount of each oxide (for major elements), and atomic concentration (for minor elements), the analytical value was recalculated by multiplying the analytical value with the ratio between the residual value and the one before the SEP. Moreover, the concentrations obtained from the four grain size in the SEP from Parma WtE were averaged. As shown in figure 3.4.2.3 we have for some elements like Cr and Fe, and, to a minor amount Ni, that the corrected value does not show a decreasing value, i.e, the element stays in the residual portion, at least within the experimental uncertainty. Other elements, like S and Zn do show a strong dissolution during the steps.

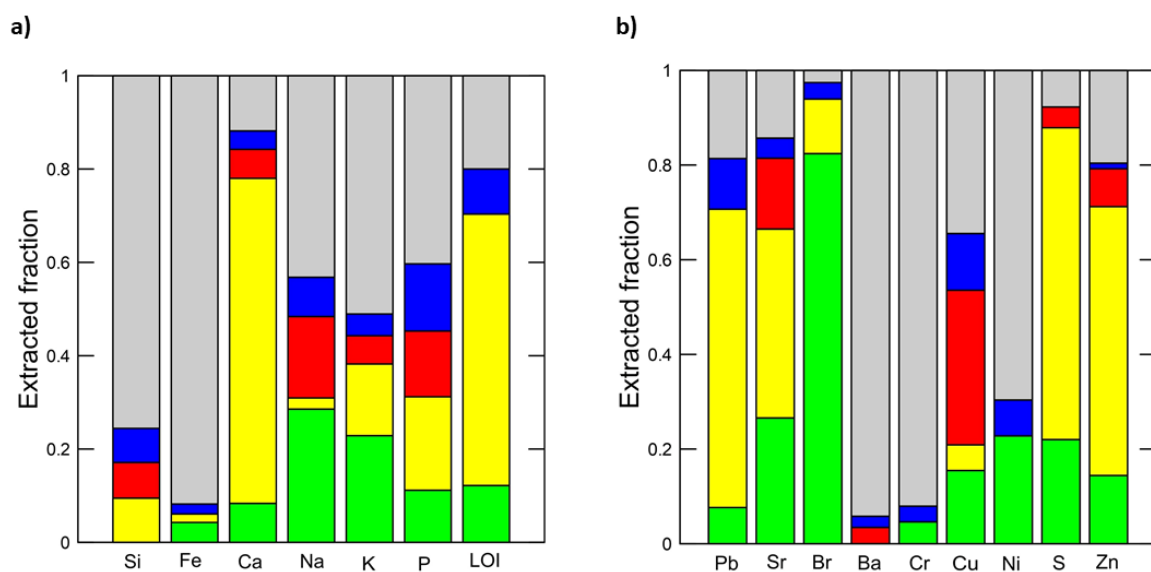


Figure 3.4.3 Sequential extraction of major (a) and minor (b) elements. Green areas corresponding at first step (S1); yellow areas corresponding at second step (S2); red areas corresponding at third step (S3); blue areas corresponding at fourth step (S4); grey areas corresponding at residues

The average of each element residual after the different steps from the four fractions was used to obtain **Figure 3.4.3**. The fraction extracted after each step is outlined for the major and minor elements. Although with the uncertainties related to possible sample in homogeneities, we find that Ba, Cr and Fe are almost completely in the residuals, whereas Pb, Zn, LOI, S, Ca and Sr do show a strong decrease after the acid etching. In the first step Br is almost completely extracted, and Na and K show a significant decrease, suggesting that they are present in a highly soluble phase, like chlorides. This is observed for any grain size, whereas Zn and S (**Figure 3.4.4**) content decrease in the first step only in the smaller grain size, and for Pb the decrease is just observed in one grain size. A strong decrease of the residual in the reducing stage is observed mainly for Cu, indicating possible reduction of hydroxides and oxides to metal.

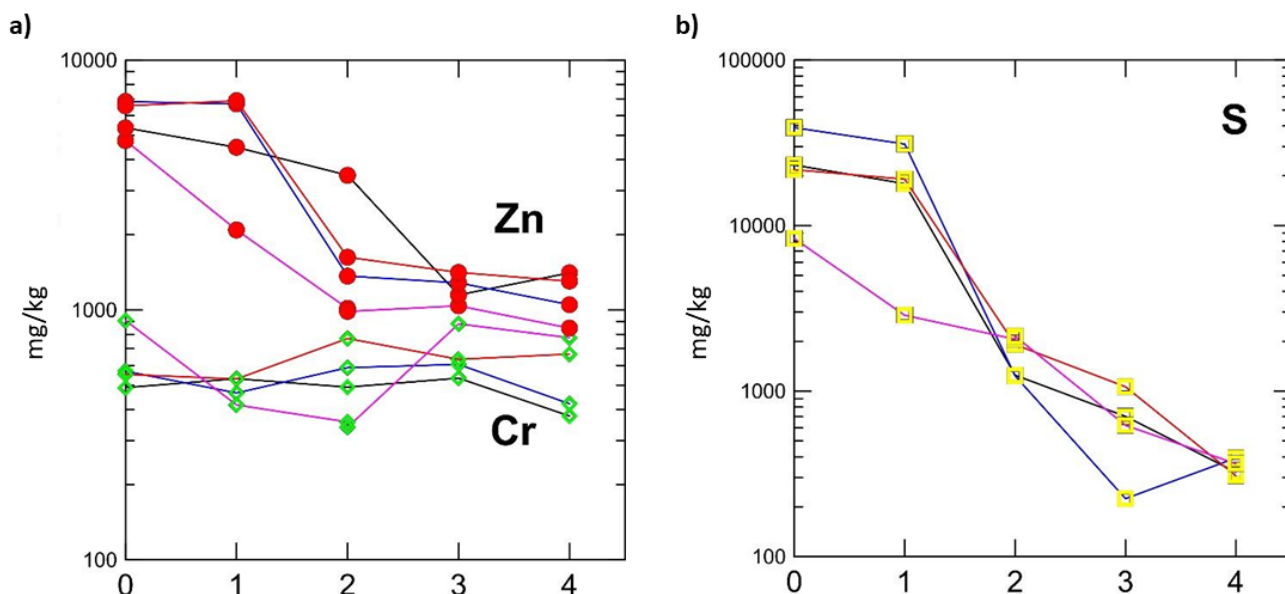


Figure 3.4.4: Elements (mg/kg) in solid residues from XRF data

At the end of step 4, some elements are almost completely leached, like S, Zn, Sr, Pb and Ca, indicating that they are not concentrated in resistant oxides, like spinels or in silicate crystals or glass. Still, for these elements a significant concentration of the element is present in the residual, likely indicating their presence in a silicate phase, as willemite or Zn-rich glass, for Zn, or in solution in feldspars for Sr (Tribaudino et al., 2005). Other elements like Cr and Ba are concentrated in the residual. For Cr this confirms its concentration in non-soluble oxides, whereas for Ba the suggestion is that the element is present in silicates, possibly in feldspars. It is not clear whether Ni has some significant leaching.

4 CONCLUSIONS

The mineralogy, chemical composition and properties of the BA in five incinerators in Northern Italy were examined. The average composition, and the changes of the composition with grain size follow quite similar trends in all the incinerators. As shown in **Figure 3.2.1.3** of chapter 3.2 the major and minor elements compositions are very close, and are well grouped in the compositional variation of the incinerators worldwide. This may indicate that, in spite of the different numbers of waste input between municipal and special waste, the input is comparable, at least in the unburned fraction. On the other side, as shown in **Figure 3.2.1.6** in chapter 3.2 there are orders of magnitude in the leached fraction between the different incinerators, with higher differences between the incinerators of Ferrara and Forli-Cesena, and the others. The difference is related to the mineralogical composition, and to where a given element occurs in a more soluble phase, and affects also whether the ashes are beyond legislation limits, as shown in chapter 3.4. The presence of portlandite in Ferrara and Forli-Cesena buffers the pH to higher values, to stabilise ettringite, which does not dissolve with sulphates. The quantitative mineralogical differences (amorphous, carbonates) found between the WtE plants of IREN and HERA groups could be related to different burning temperatures, operating procedures or weathering conditions, and make an example on how the mineralogy may affect the properties of the ashes.

The combined SEM-EDS, XRF-XANES, XRD analyses on different grain size and different grains enabled to find a number of new mineral hosts of the PTE (Co, Zn, Ni, Cu, Pb, Cr), found in metallic inclusions, oxides, carbonates, and amorphous matrices. As such combined investigation was not previously done, we may assume that the mineralogical variety which has since now been determined in BA, already represented by a considerable number of phases, is just a fraction of the actual one. As long as SEM-EDS is used on single grains, we observe that each grain shows chemically different bulk composition, and mineralogical assemblages. Just for an example Zn was found in BA in 27 mineral phases, of which 15 were confirmed or discovered in this work. Also, what is generally and simply described as an amorphous or glassy phase, is in fact a number of different phases, each of them in local equilibrium with the embedded crystals. This makes the prediction of the leaching behaviour of the ashes a risky task: the leached fraction for PTE is just a very small fraction, between 10^{-3} and 10^{-6} of the global content of the element, and a slight change in mineralogy, hardly or not detectable by XRD, may have a profound effect on the leaching of the samples. The precipitation of a small amount of a highly soluble phase containing PTE may increase dramatically the leached fraction.

We observed that the mineral fraction of BA is extremely heterogeneous, being made by slags, glass, metallic components, each of them chemically and mineralogically heterogeneous; chemical and mineralogical compositional differences were observed as a function of grain size, among different slags and within a single grain. This comes from a combined effect of the heterogeneous input, but also of the temperature gradients in the combustion chamber, promoting different equilibria at the different temperatures, and, last but not least, by the different weathering conditions, like position in the pile, moisture, different exposure time.

There are however some regular features in the compositional relations between the elements, which could be outlined by the analysis of different portions of the same sample, sorted by grain size. Two opposite trends are observed: one shown by Si and grain size, the other, opposite correlated to the first, is shown by Ca, Cl, S and the residual loss on ignition. The first trend is followed also by some more lithophile elements, like Zr and Rb, the latter likely present in feldspar or silicate glass. The second trend is followed by PTE elements like Cu and Zn, but with some exceptions: in the WtE from Piacenza Zn does not follow a specific trend, and in the Forlì-Cesena plant, Cu follows the Si trend. Pb, Ni and Cr do not follow neither trend, with the exception of the Ferrara WtE, where Pb goes with S. It appears that Cu and Zn are hosted in carbonate, sulphate or chlorides in the different grain size, whereas Pb, Ni, Co and Cr may have different host minerals in the different compositions. As for the leaching behaviour it is generally observed that leaching increases as the grain size decreases, for Cl, Na (and K) and Cu, but other elements, like Cr and Ni follow a different trend in the WtE plants of Torino, Piacenza and Parma, where they follow the trend of Cl and Na, respect to Ferrara and Forlì-Cesena, where they seem unrelated to the grain size. This again, highlights the difference between the different plants.

For a possible recycle of the BA, the results in leaching tests indicate that all the grain size below 2 mm, from any incinerator are beyond legal limits for some element. Chlorine and Cu are always beyond legal limits, and again we find a difference between incinerators: Ba, Ni, F are above limits in the Ferrara and Forlì-Cesena plants, SO_4^{2-} and Cr for the other incinerators. Ni and Other elements, like Pb and Zn were always leached below limits, although in Ferrara the Pb leaching is close to the critical value.

Therefore, to make any use other than as insulator fillers, some kind of treatment is needed. The observation that PTE decrease with increasing grain size, is not always correct, and for Cu and Cl, in the examined grain size the leaching is so high that it is not expectable that simply sieving the larger portion will solve the issue. However, the larger grain size could be easier to wash, and the reactivity in the grains could be slower: our SEP showed that the leached fraction, no matter its toxicity, is higher in finer grains. The highly reactive nature of the ashes can be used as an aggregate in cement,

most for highly matured material where cement minerals are present. Concrete obtained using BA as aggregate could fix the PTE in a structure where leaching occurs less. By this respect an investigation on the performance and on the leaching of concrete, obtained using ashes of different grain size as aggregates in concrete, before and after washing could be promising. Also, in light of the observed differences in the mineralogy of the different incinerators, we may expect different performances in concrete using ashes from different plants. Preliminary washing at some pH value should be useful, as our observation showed that most of the coarser grains do show a rim, made by smaller grains, and likely the more reactive part. The washing should be made as to disaggregate the rim portion, whose sewage could be subject of further recovery of metals.

Finally, a note on the analysis of the ashes, considering as a geological material: generally speaking, BA are on average a material which can be chemically described within the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system, not far from the composition of basaltic rocks. The main difference is that the average composition comes from an average of micro or submicrometric equilibria, occurring within each grain. Equilibrium is not always achieved, and weathering plays a major role. To predict the thermodynamic behaviour would require preliminary homogenization, which is not economically feasible, and therefore the predictions on the fate of the incinerated material are a risky task. However a wealth of information is retained in the grains size reactions, which involve the temperature and thermodynamic conditions of the reactions in the incinerator, whose knowledge could allow to better constrain the operating conditions, to minimise the particle leaching and obtain a more suitable material for higher value uses.

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APPENDIX I

Linear Pearson's r (lower triangle) and Spearman's ρ rank correlation (upper triangle) for evaluating correlation grade between elements and the grain size ($\log_{10}$) for **a)** this work and for those of **b)** Caviglia et al. (2019) and **c)** Loginova et al. (2019). Correlation table for $< 2\text{mm}$ grain size with major elements are also reported **(d)**. Pearson's r represents the linear correlation. $r = 0$ no correlation. $r = 1$ completely correlated. while Spearman's rank is significant (correlated) if $p < 0.05$.

a) Data from this work

	Log(10) size	Si	Ca	Fe	Al	Na	Mg	Ti	K	P	Mn	LOI	S	Cr	Cu	Ni	Zn	Pb	Sr	Cl	Ba	Zr	Rb
Log(10) size		0.000	0.000	0.107	0.518	0.007	0.072	0.017	0.189	0.185	0.627	0.000	0.000	0.535	0.005	0.786	0.000	0.277	0.094	0.000	0.003	0.000	0.000
Si	0.954	-	0.000	0.207	0.628	0.001	0.063	0.003	0.306	0.077	0.582	0.000	0.000	0.470	0.014	0.976	0.003	0.362	0.067	0.000	0.002	0.000	0.000
Ca	-0.936	-0.992	-	0.152	0.484	0.002	0.030	0.008	0.214	0.117	0.639	0.000	0.000	0.479	0.016	0.902	0.004	0.378	0.079	0.000	0.006	0.682	0.072
Fe	0.541	0.437	-0.489	-	0.003	0.974	0.003	0.781	0.000	0.345	0.372	0.058	0.096	0.745	0.190	0.580	0.042	0.100	0.670	0.281	0.702	0.079	0.063
Al	0.233	0.175	-0.251	0.822	-	0.470	0.004	0.299	0.003	0.050	0.447	0.267	0.337	0.264	0.738	0.966	0.292	0.308	0.299	0.785	0.463	0.890	0.030
Na	0.786	0.881	-0.846	-0.012	-0.259	-	0.553	0.000	0.831	0.004	0.281	0.011	0.009	0.148	0.062	0.819	0.062	0.984	0.036	0.000	0.000	0.720	0.654
Mg	0.591	0.606	-0.680	0.831	0.821	0.214	-	0.714	0.001	0.603	0.996	0.013	0.019	0.603	0.278	0.448	0.094	0.157	0.855	0.098	0.604	0.250	0.894
Ti	-0.729	-0.828	0.777	0.101	0.365	-0.958	-0.133	-	0.701	0.001	0.270	0.029	0.018	0.351	0.071	0.967	0.126	0.682	0.043	0.001	0.000	0.228	0.005
K	0.452	0.360	-0.431	0.914	0.826	-0.078	0.891	0.139	-	0.243	0.838	0.107	0.176	0.473	0.330	0.378	0.172	0.079	0.921	0.370	0.889	0.051	0.042
P	-0.456	-0.583	0.528	0.335	0.631	-0.819	0.188	0.888	0.407	-	0.655	0.267	0.170	0.283	0.131	0.985	0.402	0.890	0.013	0.051	0.004	0.505	0.052
Mn	-0.176	-0.199	0.170	0.317	0.272	-0.378	0.002	0.386	0.075	0.162	-	0.713	0.866	0.743	0.568	0.685	0.651	0.720	0.986	0.505	0.564	0.000	0.434
LOI	-0.957	-0.973	0.979	-0.616	-0.389	-0.757	-0.748	0.685	-0.540	0.389	0.134	-	0.000	0.654	0.017	0.938	0.001	0.250	0.151	0.000	0.014	0.000	0.009
S	-0.918	-0.973	0.980	-0.554	-0.339	-0.772	-0.721	0.723	-0.465	0.470	0.061	0.981	-	0.744	0.023	0.878	0.003	0.228	0.136	0.000	0.016	0.434	0.997
Cr	0.223	0.259	-0.254	-0.118	-0.391	0.493	-0.188	-0.331	-0.257	-0.377	-0.119	-0.162	-0.119	-	0.574	0.891	0.558	0.048	0.068	0.434	0.221	0.009	0.745
Cu	-0.805	-0.744	0.730	-0.451	-0.121	-0.609	-0.381	0.592	-0.344	0.511	-0.206	0.728	0.704	-0.203	-	0.545	0.001	0.280	0.061	0.009	0.004	0.009	0.264
Ni	-0.099	0.011	-0.045	0.200	0.015	-0.083	0.272	-0.015	0.313	-0.007	-0.147	-0.028	-0.056	-0.050	0.218	-	0.403	0.269	0.433	0.997	0.969	0.019	0.148
Zn	-0.922	-0.833	0.822	-0.650	-0.370	-0.608	-0.558	0.517	-0.468	0.299	-0.164	0.874	0.833	-0.211	0.865	0.298	-	0.357	0.179	0.004	0.023	0.018	0.603
Pb	-0.381	-0.323	0.313	-0.550	-0.359	0.007	-0.483	0.149	-0.580	0.050	-0.130	0.402	0.419	0.636	0.379	-0.387	0.327	-	0.662	0.382	0.495	0.176	0.017
Sr	-0.557	-0.599	0.579	-0.155	0.366	-0.664	-0.066	0.646	-0.036	0.745	-0.007	0.490	0.506	-0.598	0.610	-0.280	0.462	0.158	-	0.055	0.005	0.170	0.003
Cl	-0.954	-0.994	0.979	-0.378	-0.099	-0.905	-0.552	0.868	-0.318	0.630	0.239	0.951	0.947	-0.280	0.770	-0.001	0.819	0.311	0.621	-	0.001	0.866	0.008
Ba	-0.829	-0.847	0.799	-0.139	0.263	-0.897	-0.187	0.907	-0.051	0.819	0.208	0.740	0.731	-0.425	0.822	0.014	0.703	0.245	0.804	0.888	-	0.001	0.781
Zr	0.945	0.950	0.284	0.651	0.493	0.842	-0.436	0.396	-0.718	-0.325	-0.967	-0.919	-0.924	-0.661	-0.805	-0.744	-0.201	0.257	-0.488	0.627	0.067	-	0.069
Rb	0.939	0.927	0.350	0.777	0.684	0.704	-0.439	0.645	-0.636	-0.207	-0.920	-0.911	-0.873	-0.754	-0.714	-0.732	-0.541	0.099	-0.647	0.848	0.098	-0.411	-0.319

b) Caviglia et al., 2019

	Log (10) size	Si	Ca	Fe	Al	Na	Mg	Ti	K	P	Mn	S	Cr	Cu	Ni	Zn	Pb	Sr	Cl
Log(10) size		0.00	0.00	0.94	0.89	0.09	0.64	0.00	0.16	0.00	0.03	0.00	0.40	0.50	0.00	0.00	0.00	0.05	0.00
Si	0.91	-	0.00	0.76	0.38	0.28	0.40	0.00	0.57	0.00	0.02	0.00	0.35	0.69	0.00	0.00	0.00	0.04	0.00
Ca	-0.91	-0.96	-	0.66	0.44	0.39	0.75	0.00	0.52	0.00	0.05	0.00	0.44	0.39	0.00	0.02	0.00	0.06	0.00
Fe	0.03	-0.11	-0.16	-	0.84	0.23	0.02	0.95	0.78	0.62	0.21	0.75	0.52	0.43	0.59	0.35	0.89	0.99	0.94
Al	-0.05	0.31	-0.28	-0.07	-	0.11	0.87	0.85	0.14	0.96	0.90	0.37	0.61	0.77	0.52	0.89	0.88	0.65	0.54
Na	0.57	0.38	-0.30	-0.42	-0.54	-	0.10	0.03	0.04	0.06	0.02	0.40	0.29	0.37	0.45	0.04	0.08	0.54	0.21
Mg	-0.17	-0.30	0.12	0.72	-0.06	-0.54	-	0.41	0.96	0.42	0.04	0.76	0.39	0.64	0.86	0.05	0.65	0.24	0.64
Ti	-0.90	-0.83	0.84	-0.02	0.07	-0.69	0.29	-	0.04	0.00	0.01	0.01	0.18	0.26	0.01	0.00	0.00	0.10	0.00
K	-0.48	-0.21	0.23	-0.10	0.51	-0.65	0.02	0.65	-	0.15	0.30	0.78	0.28	0.50	0.72	0.18	0.15	0.55	0.42
P	-0.91	-0.88	0.82	0.18	-0.02	-0.62	0.29	0.87	0.49	-	0.05	0.01	0.59	0.77	0.02	0.00	0.00	0.07	0.00
Mn	-0.67	-0.72	0.62	0.44	-0.05	-0.72	0.66	0.78	0.37	0.63	-	0.05	0.03	0.32	0.07	0.01	0.08	0.26	0.02
S	-0.85	-0.92	0.97	-0.11	-0.32	-0.30	0.11	0.79	0.10	0.75	0.64	-	0.38	0.22	0.00	0.05	0.00	0.17	0.00
Cr	0.30	0.33	-0.27	-0.23	0.18	0.37	-0.30	-0.46	-0.38	-0.19	-0.68	-0.31	-	0.41	0.45	0.22	0.63	0.55	0.29
Cu	0.24	0.14	-0.31	0.28	-0.10	0.32	0.17	-0.40	-0.24	-0.11	-0.35	-0.43	0.29	-	0.29	0.85	0.44	0.23	0.28
Ni	-0.89	-0.90	0.97	-0.20	-0.23	-0.27	0.06	0.76	0.13	0.72	0.60	0.97	-0.27	-0.37	-	0.06	0.00	0.11	0.00
Zn	-0.81	-0.83	0.72	0.33	-0.05	-0.66	0.63	0.85	0.46	0.86	0.80	0.63	-0.42	0.07	0.62	-	0.01	0.01	0.01
Pb	-0.96	-0.85	0.88	-0.05	0.05	-0.58	0.17	0.88	0.49	0.93	0.58	0.81	-0.17	-0.28	0.84	0.77	-	0.07	0.00
Sr	-0.63	-0.66	0.61	0.00	-0.16	-0.22	0.41	0.55	0.22	0.60	0.39	0.47	-0.22	0.42	0.53	0.80	0.59	-	0.14
Cl	-0.89	-0.94	0.95	-0.03	-0.22	-0.43	0.17	0.89	0.29	0.85	0.72	0.96	-0.37	-0.38	0.90	0.75	0.83	0.50	-

c) Loginova et al., 2019

a)	Log (10) size	Si	Ca	Fe	Al	Na	Mg	Ti	Mn	S	Cr	Cu	Ni	Zn	Pb	Ba	Sb
Log (10) size		0.000	0.000	0.001	0.025	0.663	0.778	0.001	0.035	0.000	0.000	0.000	0.000	0.017	0.000	0.074	0.000
Si	0.914	-	0.000	0.000	0.017	0.580	0.214	0.000	0.009	0.000	0.003	0.000	0.000	0.001	0.000	0.008	0.000
Ca	-0.919	-0.954	-	0.004	0.113	0.627	0.356	0.000	0.001	0.000	0.001	0.000	0.000	0.002	0.000	0.018	0.000
Fe	-0.797	-0.817	0.719	-	0.005	0.674	0.385	0.047	0.159	0.010	0.001	0.004	0.000	0.024	0.001	0.179	0.001
Al	-0.595	-0.624	0.442	0.706	-	0.404	0.667	0.164	0.896	0.056	0.058	0.023	0.021	0.080	0.037	0.042	0.032
Na	0.128	-0.162	0.142	0.124	-0.242	-	0.000	0.976	0.255	0.518	0.614	0.733	0.515	0.138	0.722	0.296	0.976
Mg	-0.083	-0.354	0.267	0.252	0.126	0.855	-	0.636	0.294	0.977	0.864	0.228	0.961	0.022	0.262	0.014	0.623
Ti	-0.769	-0.847	0.865	0.539	0.394	0.009	0.139	-	0.005	0.000	0.012	0.002	0.005	0.073	0.003	0.015	0.000
Mn	-0.564	-0.671	0.781	0.398	0.038	0.326	0.302	0.706	-	0.010	0.013	0.010	0.058	0.015	0.004	0.075	0.019
S	-0.956	-0.894	0.935	0.663	0.521	-0.189	-0.008	0.876	0.661	-	0.001	0.000	0.000	0.027	0.000	0.052	0.000
Cr	-0.823	-0.737	0.803	0.770	0.518	-0.148	-0.050	0.648	0.643	0.805	-	0.001	0.000	0.053	0.000	0.161	0.000
Cu	-0.915	-0.936	0.943	0.711	0.601	0.100	0.344	0.754	0.664	0.891	0.767	-	0.000	0.001	0.000	0.004	0.000
Ni	-0.928	-0.810	0.839	0.810	0.608	-0.190	-0.014	0.706	0.517	0.883	0.916	0.839	-	0.098	0.000	0.121	0.000
Zn	-0.625	-0.788	0.753	0.597	0.484	0.417	0.604	0.493	0.636	0.587	0.527	0.806	0.460	-	0.002	0.003	0.027
Pb	-0.921	-0.919	0.930	0.775	0.560	0.104	0.322	0.726	0.715	0.872	0.827	0.963	0.881	0.743	-	0.021	0.000
Ba	-0.491	-0.672	0.622	0.381	0.549	0.301	0.638	0.633	0.490	0.528	0.396	0.720	0.434	0.723	0.609	-	0.019
Sb	-0.917	-0.924	0.932	0.779	0.573	-0.009	0.144	0.910	0.618	0.934	0.821	0.869	0.897	0.589	0.846	0.618	-

d) this work: data from < 2mm grain size

	Log (10) size	Si	Ca	Fe	Al	Na	Mg	Ti	K	P	Mn	LOI
Log (10) size		0.00	0.01	0.01	0.01	0.16	0.02	0.91	0.00	0.00	0.73	0.00
Si	0.91	-	0.00	0.01	0.00	0.04	0.00	0.75	0.00	0.02	0.82	0.00
Ca	-0.86	-0.99	-	0.01	0.00	0.05	0.00	0.84	0.00	0.04	0.60	0.00
Fe	0.89	0.90	-0.90	-	0.01	0.28	0.00	0.65	0.00	0.01	0.66	0.00
Al	0.86	0.99	-0.98	0.89	-	0.03	0.00	0.87	0.01	0.03	0.70	0.00
Na	0.60	0.79	-0.76	0.48	0.79	-	0.06	0.16	0.21	0.26	0.85	0.05
Mg	0.85	0.98	-1.00	0.91	0.97	0.74	-	0.85	0.00	0.05	0.55	0.00
Ti	-0.05	-0.15	0.09	0.21	-0.08	-0.60	-0.09	-	0.84	0.98	0.29	0.82
K	0.93	0.92	-0.92	0.97	0.89	0.54	0.93	0.10	-	0.02	0.72	0.00
P	0.93	0.84	-0.77	0.87	0.80	0.50	0.76	0.01	0.84	-	0.58	0.01
Mn	-0.16	0.10	-0.24	0.21	0.18	-0.09	0.27	0.47	0.17	-0.26	-	0.87
LOI	-0.92	-1.00	0.98	-0.92	-0.98	-0.76	-0.97	0.11	-0.93	-0.87	-0.08	-

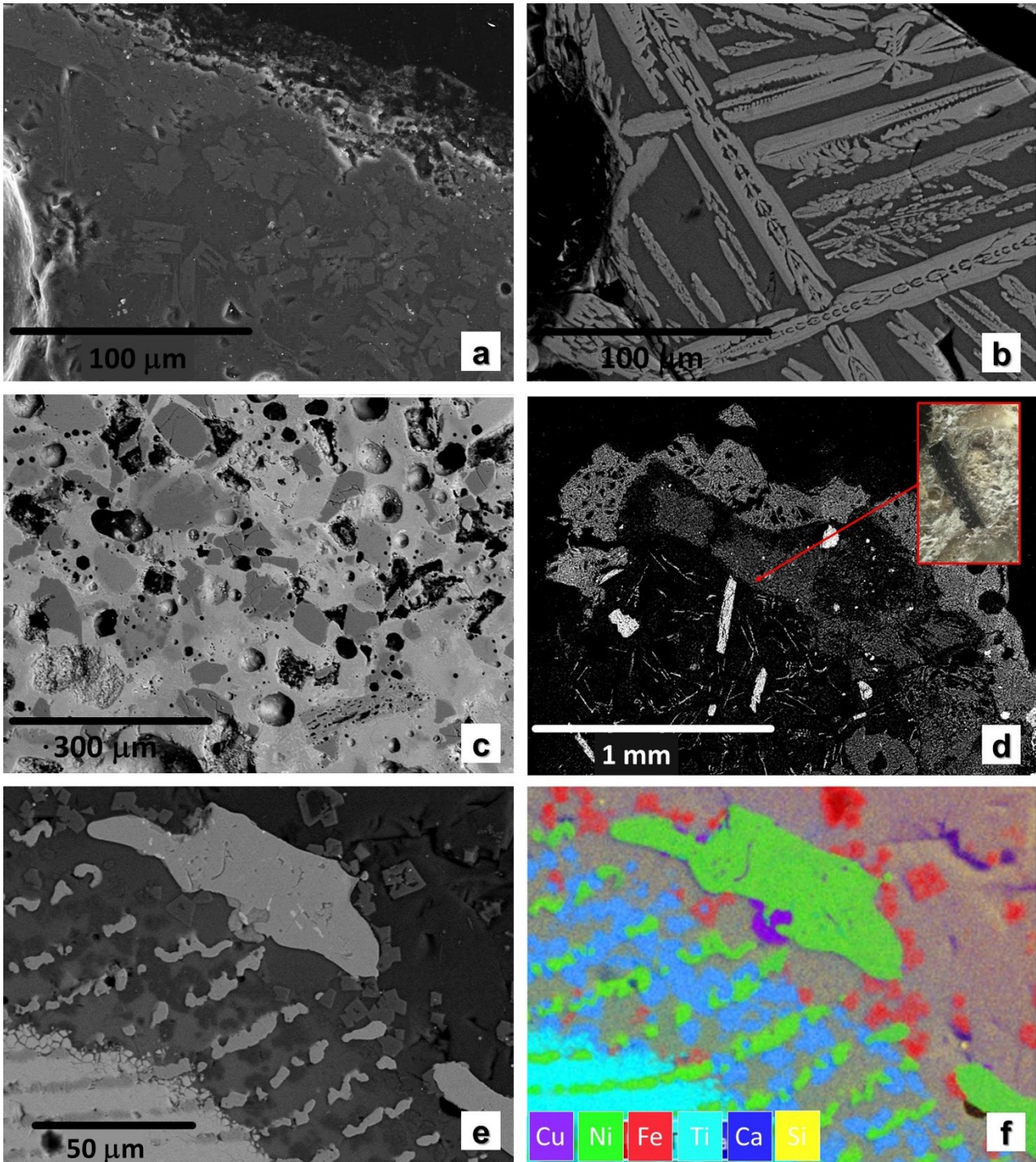
APPENDIX II

XRD analysis: phase identification and semi-quantitative estimation in XRD pattern of bulk sample (1) and colour-based selected clast: (2) gray. (3) green/transparent. (4) metallic part. (5) white. and (6) red/dark. The semi-quantitative content are represented as: xxxx= 70-100 wt%. xxx = 40-70 wt%. xx=10-40wt%. x=<10 wt%. *=uncertainty presence. Estimated error ± 10 .

						
Phase identification	Xrd bulk (1)	Gray clast (2)	Green/transparent clast (3)	Metallic part (4)	White clast (5)	Red/dark clast (6)
quartz	xx	x	*			x
calcite	xxx	x			x	xx
gehlenite	xx	x				x
hydroxylapatite					xxx	
stratlingite	x	x				x
ettringite	x	x				x
idrocalumite	x	x				x
vaterite	x	x				x
hematite	*	*		xxx		x
magnetite	*	*		*		*
amorphous	xxx	xxx	xxx			xx

APPENDIX III

SEM images of particles catted longitudinally: **a)** melilites, **b)** pseudowollastonite and **c)** quartz crystals inside an amorphous matrix; **d)** fine and heterogeneous materials that cover the BA particles core and a metallic part inside a clast with their original shape; **e)** BSE image of a metallic inclusion and their chemical maps **f)**. To note the inclusion is made of strip structure of Ni and Ti which react partially with the amorphous matrix.



APPENDIX IV

Quantitative analysis made by Rietveld refinement (wt%) for crystalline and amorphous phases:

a) from < 0.063mm grain size to 0.5 – 1mm grain size

Mineral name	Chemical formula	PR	PC	TO	FE	FC	PR	PC	TO	FE	FC	PR	PC	TO	FE	FC	PR	PC	TO	FE	FC	PR	PC	TO	FE	FC
		< 0.063					0.063-0.2					0.2-0.3					0.3-0.5					0.5-1				
Calcite	CaCO ₃	10.5	7.2	9	32.4	29.6	11.4	6.8	6.2	15.5	20.6	10.4	7.8	5.3	13.1	14.6	9.1	5.6	5.3	17.2	17.9	8	5.1	2.8	18.7	17
Quartz	SiO ₂	3	4.2	4	5.6	2.8	4	3.7	6.7	19.3	7.3	2.1	6.2	5.8	17.6	8.7	5.5	8.7	10.6	21.4	19.4	3.5	4.3	17	10.7	10.4
Plagioclase	(Na,Ca)(Si,Al) ₄ O ₈	2.4	4	1.3	4.9	6.1	2.4	3.4	3.7	7.3	7.3	2.6	2.3	6.6	10.3	11	6.7	1.9	8.8	15	3	2.1	2.8	8.2	7.8	6.9
Ettringite	Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ · 26H ₂ O	3.8	3.5	7.5	10.2	6.8	5.8	5	4.8	11.3	15.1	5.2	5.4	4	5.4	13.7	2.9	4.7	5	9.8	9.8	3	6.3	5.1	8.2	16.9
Hydrocalumite	Ca ₄ Al ₂ (OH) ₁₂ (Cl,CO ₃ ,OH) ₂ · 4H ₂ O	3.5	6.3	1.5	6.4	8.7	3.9	6.7	1.3	4.7	5.2	4	6.5	1	2.3	3.7	3.9	6.4	0.9	4.7	1.2	3.2	6.6	1.4	6.1	3.4
Strätlingite	Ca ₂ Al ₂ SiO ₇ · 8H ₂ O	1.6					1.6					1.5					1.8					1.7				
Pyroxenes	ABSi ₂ O ₆			6					2.2					1										0.8		
Vaterite	CaCO ₃	2.7	0.5		0.9	1.2	3.3	0.3		0.7	1.8	3.6	0.3		0.4	1.6	3.9	2.2		0.8		1.7	0.4		0.7	0.3
Gehlenite	Ca ₂ Al(AlSiO ₇)	1.8	1.1	1.8			2.7	2.2	1.7			2.8	1.8	1.5			1.5	2.5	2.3			1.9	2.5	1.8		
Akermanite	Ca ₂ Mg(Si ₂ O ₇)				3.9	10.5				3	4.2				3.3	4.5				3.6	3				3.8	4.4
Cristobalite	SiO ₂			0.4					0.2					0.4										0.2		
Larnite	Ca ₂ SiO ₄				7	16.3				5.9	8.5				5.9	7.8				6	5.2				5.4	6.9
Portlandite	Ca(OH) ₂				10.1	8.6				5.7	6				2.2	5.7				6.1	4.3				7	6.1
Hematite	Fe ₂ O ₃	0.7	0.7	0.5	1.1	1.7	0.7	0.8	0.4	0.5	1.4	0.8	0.8	0.4	1.1	1.3	0.6	1	0.1	1.1	0.9	2.8	1.1	0.5	1.1	1.3
Magnetite	Fe ²⁺ Fe ³⁺ ₂ O ₄	0.1	1.4	0.3	0.5	0.4	0.1	0.1	0	0.9	0.5	0.2	0.2	0.1	0.4	0.4	0.4	0	1.5	0.4	0.5	0.2	0.1	0.1	0.4	0.5
crystalline		30	28.8	32.3	83	92.6	36	29	27.3	74.8	78	33.1	31.3	26.2	62.1	73	36.3	33	34.5	86	65.3	28	29.2	38	69.8	74.1
amorphous		70	71.2	67.7	17	7.4	64	71	72.7	25.2	22	66.9	68.7	73.8	37.9	27	63.7	67	65.5	14	34.7	72	70.8	62	30.2	25.9

b) from < 0.063mm grain size to 0.5 – 1mm grain size

		PR	PC	TO	FE	FC	PR	PC	TO	FE	FC	PR	PC	TO	FE	FC	PR	PC	TO	FE	FC	PR	PC	TO	FE	FC
Mineral name	Chemical formula	1_2					2_4					4_8					8_16					> 16				
Calcite	CaCO ₃	7.5	3.4	3.4	12.7	17.3	5.3	5.7	1	19	12.6	6.6	4.4	0.5	14.8	14.9	5.2	2.8	0.1	20.3	6.1	6.6		0.2	6	19.7
Quartz	SiO ₂	5.4	4.4	9.4	10.8	5.9	6.5	5.7	8.2	11	6.9	5.8	0.9	1.7	9.4	4.9	3.8	3.4	11	8.9	3.1	5.2		3.2	9.7	7.7
Plagioclase	(Na,Ca)(Si,Al) ₄ O ₈	2.8	2.2	8.8	1.9	8	3.4	2.2	5.7	8.2	9.2	2.1	2.5	4.3	6.9	7.1	1	1.4	8.1	12.8	8.8	1.9		3.2	11.6	7.2
Ettringite	Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ · 26H ₂ O	1.6	6	5.2	3.7	19.7	1.2	6	1.9	6.7	19.8	0.6	7.6	1.4	6.2	14.1	3.1	6.6	1.7	6.9	5.6	3.4		1.6	3.1	16.8
Hydrocalumite	Ca ₄ Al ₂ (OH) ₁₂ (Cl,CO ₃ ,OH) ₂ · 4H ₂ O	2.5	5.9	1.4	3.6	4.4	2.6	4.4	0.2	5.8	11.8	3.2	5	0.3	5	4.5	2.6	3.3		5.3	3.6	2.2		0.4	2.3	6
Strätlingite	Ca ₂ Al ₂ SiO ₇ · 8H ₂ O	1.2					0.6					1.3					0.5					1.2				
Pyroxenes	ABSi ₂ O ₆			0.6					0					0.5										-		
Vaterite	CaCO ₃	2.9	1.1		0	0.8	1.5	1.1		1.3		2	1.1		1.6	1.7	1.7	0.5		6.4	2.7	1.8		1.7	3.5	
Gehlenite	Ca ₂ Al(AlSiO ₇)	2.1	1.8	1.6			1.6	2.8	1.8			2	1.5	1			1.6	1.2	3.1			2.2		2.1		
Akermanite	Ca ₂ Mg(Si ₂ O ₇)				2.2	4				3.6	5.8				4.4	4				6.6	8.4			4.6	4	
Cristobalite	SiO ₂			1					0.7										1.1					0.1		
Larnite	Ca ₂ SiO ₄				2.3	7.9				5.9	9.2				5.5	7.5				8.4	6			2.9	7.8	
Portlandite	Ca(OH) ₂				3.6	7.2				4.2	6.1				3.2	5.5				1.3	0.3			0.6	3.5	
Hematite	Fe ₂ O ₃	0.6	1.3	0.4	0.6	1.3	0.4	1	0.4	1.7	0.2	0.5	0.5	0.2	1.3	1.2	0.4	0.7	0.6	1.6	1.9	0.6		0.6	0.8	1.3
Magnetite	Fe ²⁺ Fe ³⁺ ₂ O ₄	0.1	0.1	0.2	0.6	0.5	0	0.2	0.2	0.7	1.6	0.1	0.1	0.2	0.8	0.5	0	0.3	0.3	0.7	1.4	0.1		0.2	0.7	0.4
crystalline		26.6	26.1	31.9	42	77.1	23.2	29.1	20.2	68	83.2	24.2	23.7	10.1	58.9	66	20	20.2	26	79.2	47.9	25.1		11.4	44.1	78
amorphous		73.4	73.9	68.1	58	22.9	76.8	70.9	79.8	32	16.8	75.8	76.3	89.9	41.1	34	80	79.8	74	20.8	52.1	74.9		88.6	55.9	22

APPENDIX V

Major (a) and minor (b) elements divided by grain size for all the investigated plants

a)		MAJOR ELEMENTS (g/100g)										
WtE	grain size	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI
PR	20	46.2	0.7	8.6	3.0	0.1	3.7	21.6	3.9	1.2	1.5	9.4
PR	16	45.8	0.6	8.3	3.0	0.1	3.9	21.8	3.7	1.3	1.3	10.2
PR	8	38.9	0.8	8.9	3.6	0.1	3.6	24.8	2.8	1.3	1.6	13.6
PR	4	37.7	0.9	10.4	3.6	0.1	4.3	24.7	2.5	1.4	2.2	12.2
PR	2	35.9	0.9	10.1	4.0	0.1	4.4	24.6	2.4	1.4	2.1	14.0
PR	1	31.7	1.0	9.6	3.7	0.1	3.9	26.7	2.2	1.3	2.1	17.6
PR	0.5	29.2	0.9	9.0	3.5	0.1	3.6	28.4	2.2	1.3	2.2	19.7
PR	0.3	25.7	0.9	8.3	2.6	0.1	3.3	29.7	2.1	1.2	2.0	24.1
PR	0.2	24.9	0.9	8.5	2.5	0.1	3.1	30.1	2.3	1.2	1.9	24.6
PR	0.063	23.7	0.9	8.3	2.2	0.1	3.2	30.0	2.2	1.1	1.8	26.4
PC	20											
PC	16	42.1	0.8	8.5	6.7	0.1	3.0	15.6	4.3	1.1	1.6	16.3
PC	8											
PC	4	29.2	1.1	12.4	4.7	0.1	3.9	24.3	2.5	1.7	3.5	16.7
PC	2	33.2	1.1	10.8	6.3	0.1	4.4	19.1	2.4	1.7	2.9	17.9
PC	1	22.9	1.1	13.9	4.9	0.1	3.5	26.1	2.2	1.5	3.7	20.2
PC	0.5	26.5	1.1	14.3	5.6	0.1	3.6	23.7	2.3	1.6	3.6	17.6
PC	0.3	21.7	1.2	16.6	4.6	0.1	3.3	28.7	2.3	1.4	3.1	17.0
PC	0.2	20.3	1.1	16.2	4.3	0.1	3.2	28.2	2.1	1.3	3.0	20.3
TO	20	27.4	0.4	6.6	4.7	0.1	1.9	7.1	2.7	0.6	0.6	5.0
TO	16	44.4	0.6	7.9	13.0	0.1	2.9	14.4	4.3	1.3	5.8	5.3
TO	8	45.3	0.9	8.5	11.2	0.1	3.6	15.3	5.0	0.8	1.4	7.8
TO	4	43.2	0.8	7.9	6.7	0.1	7.3	17.4	3.1	1.5	2.6	9.5
TO	2	37.3	1.0	8.9	6.5	0.1	5.5	21.5	2.6	1.5	2.3	12.9
TO	1	35.9	1.1	9.8	6.1	0.1	4.9	22.6	2.6	1.6	2.2	13.2
TO	0.5	31.6	1.1	10.5	6.0	0.1	4.2	22.8	2.6	1.5	2.4	17.1
TO	0.3	29.6	1.1	11.7	6.8	0.1	4.1	23.5	2.7	1.5	2.6	16.3
TO	0.2	25.8	1.1	11.9	7.1	0.1	3.7	23.1	2.6	1.4	2.5	20.8
TO	0.063	20.6	1.0	9.8	6.1	0.1	3.6	26.6	2.4	1.2	2.0	26.6
FE	20	44.8	0.6	6.9	2.3	0.1	3.2	26.6	4.2	1.5	1.9	8.0
FE	16	48.7	0.6	7.3	5.0	0.1	3.8	21.3	4.1	1.1	1.1	6.9
FE	8	37.4	0.7	7.9	5.3	0.1	3.6	27.5	2.8	1.2	1.6	11.8
FE	4	35.4	0.8	8.1	4.8	0.1	4.7	30.3	2.4	1.5	1.9	10.0
FE	2	34.3	0.9	8.0	4.7	0.1	4.9	30.9	2.3	1.5	2.0	10.5
FE	1	33.7	0.9	7.4	4.8	0.1	4.7	30.4	2.2	1.5	2.1	12.3
FE	0.5	20.8	0.8	7.9	3.2	0.1	3.4	36.8	2.2	1.0	1.9	21.9
FE	0.3	34.8	0.8	7.5	4.2	0.1	4.1	29.6	2.1	1.3	2.0	13.7
FE	0.2	29.4	1.0	9.6	4.1	0.1	4.6	44.5	2.7	1.4	2.6	0.0
FE	0.063	18.0	0.7	6.3	2.8	0.1	3.2	37.9	2.0	0.8	1.7	26.4
FC	20											
FC	16	56.4	0.4	7.8	4.5	0.3	3.2	15.6	5.7	1.7	0.7	3.9
FC	8	42.6	0.8	7.5	6.8	0.1	3.3	26.7	4.0	1.2	2.2	4.8
FC	4	34.9	0.7	7.9	7.1	0.1	4.2	26.9	2.5	1.3	1.9	12.4
FC	2	35.9	0.8	8.0	6.8	0.1	4.7	26.7	2.4	1.6	1.9	11.2
FC	1	33.2	0.8	8.5	6.7	0.1	4.2	28.1	2.8	1.6	2.0	12.2
FC	0.5	29.4	0.7	7.9	5.0	0.1	3.7	31.8	2.7	1.4	2.2	14.9
FC	0.3	24.7	0.7	7.8	4.5	0.1	3.3	35.1	2.3	1.3	2.2	18.1
FC	0.2	19.2	0.6	8.0	3.5	0.1	3.0	36.3	2.6	1.1	1.9	23.6
FC	0.063	16.8	0.6	5.8	2.9	0.1	2.9	39.9	2.5	0.7	1.7	26.3

b)		MINOR ELEMENTS (mg/kg)																										
WtE	Grain size (mm)	As	Ba	Ce	Cl	Co	Cr	Cu	Ga	Hf	La	Mo	Nb	Nd	Ni	Pb	Rb	S	Sc	Sn	Sr	Th	U	V	W	Y	Zn	Zr
PR	20	53.5	955.2	36.9	5430.0	27.1	879.7	1260.8	13.5	<3	17.5	14.8	11.4	17.9	118.8	1353.9	31.7	8070.0	<3	18.9	429.2	13.3	<3	60.9		14.0	1380.0	256.4
PR	16	26.4	907.2	44.1	5430.0	26.7	628.7	1412.6	12.6	7.1	34.9	9.9	10.0	18.8	182.7	409.1	33.9	7780.0	5.6	17.4	377.5	7.0	2.6	69.0		16.4	4400.0	211.7
PR	8	40.6	1098.3	41.0	7420.0	32.0	572.8	1103.7	12.3	6.3	12.6	14.8	11.3	10.3	139.6	312.1	31.0	9600.0	10.3	18.9	436.0	5.6	<3	73.2		16.1	1660.0	185.9
PR	4	35.6	1683.7	46.4	8050.0	24.8	434.2	1669.4	13.0	3.6	8.3	11.3	12.1	10.3	135.5	544.9	30.5	9500.0	14.7	43.7	680.7	5.5	<3	83.6		16.7	3630.0	206.7
PR	2	47.0	1461.4	47.3	8236.0	61.8	651.3	1335.0	13.1	3.1	24.6	17.2	11.8	22.3	174.2	675.6	31.7	10900.0	9.6	36.0	498.8	6.9	<3	84.2		19.1	3830.0	196.1
PR	1	51.7	1681.3	47.7	9780.0	50.5	644.3	1640.3	12.9	<3	30.0	14.2	11.5	18.2	143.8	800.2	29.7	12840.0	5.9	53.3	485.0	7.2	<3	89.7		14.6	4270.0	173.1
PR	0.5	55.7	1618.1	36.0	10120.0	56.9	697.4	1885.1	14.0	<3	20.8	13.1	10.3	19.8	179.4	802.1	27.4	14780.0	13.2	42.7	517.0	6.9	<3	78.8		13.5	5750.0	169.0
PR	0.3	58.9	1630.9	28.8	10530.0	43.7	591.7	1663.6	13.6	<3	5.6	14.5	10.3	2.0	131.7	913.2	26.6	16910.0	13.9	49.2	571.4	7.7	<3	78.3		11.9	5940.0	155.0
PR	0.2	59.2	1529.4	38.2	10960.0	43.7	621.5	1636.8	13.4	<3	14.2	13.8	10.5	18.8	134.2	980.7	25.3	17740.0	18.0	58.1	567.9	8.9	<3	77.9		11.5	6830.0	156.2
PR	0.063	73.5	1878.8	50.9	11600.0	43.1	626.8	2040.9	14.1	<3	16.4	13.8	10.4	4.9	160.3	1172.3	24.4	16420.0	14.3	90.9	572.0	9.4	<3	78.8		11.3	8740.0	142.9
PC	20																											
PC	16	38.0	1133.0	34.4	4470.0	27.0	470.0	2250.0	12.9	7.3	23.3	12.4	9.6	10.0	120.0	500.0	25.6	3670.0	7.2	41.7	314.9	<3	3.0	69.0	<3	17.0	7640.0	159.6
PC	8																											
PC	4	108.0	2512.4	74.1	14500.0	25.3	420.0	2530.0	15.9	<3	27.0	21.6	11.5	10.0	125.0	2010.0	34.6	13420.0	14.8	94.4	447.0	15.5	<3	89.0	<3	<3	3860.0	251.4
PC	2	100.0	1828.4	51.4	10900.0	42.6	420.0	2580.0	14.3	<3	24.0	18.4	12.6	3.0	193.0	1540.0	34.0	7320.0	19.3	177.2	449.5	10.7	<3	98.0	3.8	18.0	2860.0	240.5
PC	1	75.0	1659.6	57.3	17800.0	38.2	500.0	2750.0	14.9	<3	37.0	19.6	10.7	<3	146.0	1360.0	32.2	12550.0	23.4	94.2	451.6	11.8	3.0	92.0	<3	8.0	3380.0	115.7
PC	0.5	79.0	1571.6	58.0	15670.0	26.2	530.0	2770.0	15.0	2.7	17.0	17.7	11.2	19.0	155.0	1100.0	31.9	8760.0	18.2	106.4	415.9	9.9	3.0	87.0	<3	13.0	3460.0	162.4
PC	0.3	78.0	1684.9	58.5	20060.0	34.9	470.0	2700.0	15.6	<3	25.0	19.4	10.9	10.0	106.0	1310.0	30.4	10990.0	28.2	124.9	454.6	11.1	3.0	87.0	<3	10.0	3450.0	130.7
PC	0.2	80.0	1692.5	53.9	21060.0	22.7	540.0	2860.0	15.9	<3	30.0	22.2	10.5	17.0	122.0	1430.0	28.8	10780.0	13.2	144.3	453.2	11.4	3.0	87.0	<3	7.0	3690.0	129.2
TO	20	18.0	318.1	93.2	10020.0	86.6	490.0	210.0	11.8	4.1	40.6	9.5	10.5	18.0	270.0	130.0	22.6	2180.0	28.5	10.4	175.9	<3	2.8	88.0	<3	21.0	770.0	187.7
TO	16	13.0	429.8	45.7	3970.0	37.7	490.0	350.0	12.4	4.1	28.0	5.0	8.5	13.0	56.0	110.0	38.0	3920.0	23.9	21.8	204.0	<3	<3	59.0	<3	17.0	1210.0	134.2
TO	8	100.0	472.4	58.3	2880.0	36.4	510.0	310.0	14.3	<3	25.0	9.9	8.1	<3	62.0	1780.0	26.8	20120.0	12.8	67.4	227.4	13.7	2.5	73.0	<3	15.0	950.0	139.3
TO	4	23.0	759.0	53.2	5380.0	26.3	520.0	610.0	12.6	4.0	30.9	6.9	10.6	<3	114.0	270.0	37.3	7570.0	14.0	36.2	323.1	4.5	<3	72.0	<3	20.0	2450.0	258.8
TO	2	42.0	781.2	50.0	7680.0	26.1	580.0	1240.0	13.7	<3	21.9	7.1	11.2	5.0	128.0	850.0	36.1	13450.0	19.2	55.5	389.6	8.9	3.1	89.0	<3	16.0	2220.0	153.3
TO	1	32.0	719.4	47.9	8710.0	65.0	560.0	1120.0	13.8	<3	26.5	6.5	11.5	8.0	117.0	560.0	35.0	14880.0	16.6	70.0	369.8	6.0	2.6	83.0	<3	18.0	2720.0	161.6
TO	0.5	32.0	712.7	59.9	10620.0	41.6	560.0	1480.0	13.8	5.5	12.0	7.2	11.1	14.0	135.0	530.0	34.4	15110.0	7.8	62.7	390.3	5.7	2.8	88.0	14.4	25.0	3120.0	138.5
TO	0.3	34.0	741.8	37.3	12300.0	37.9	570.0	1370.0	14.2	3.6	31.4	7.6	10.9	9.0	127.0	480.0	32.6	14920.0	11.2	83.7	385.2	5.4	2.7	87.0	8.6	18.0	3590.0	131.4
TO	0.2	52.0	737.0	43.0	14340.0	38.0	650.0	1840.0	14.0	6.0	6.0	9.0	10.0	9.0	104.0	760.0	29.0	13990.0	8.0	105.0	433.0	19.0	<3	94.0	<3	11.0	5980.0	138.0
TO	0.063	46.0	801.2	40.0	16360.0	38.7	760.0	1580.0	13.9	3.9	18.9	8.1	9.2	6.0	127.0	730.0	25.7	20420.0	26.2	159.8	566.2	4.5	<3	82.0	<3	11.0	5610.0	132.9
FE	20	17.0	1014.6	51.0	6150.0	14.3	300.0	1040.0	11.5	3.0	23.0	4.8	9.7	<3	51.0	220.0	45.7	4230.0	18.8	37.1	478.5	3.9	<3	58.0	<3	20.0	840.0	158.4
FE	16	24.0	486.2	63.4	7280.0	19.1	310.0	700.0	11.8	5.5	23.0	8.0	9.6	12.0	71.0	270.0	33.3	5120.0	14.3	23.3	352.2	3.0	<3	61.0	<3	16.0	1390.0	262.7
FE	8	29.0	494.6	53.8	10410.0	20.3	520.0	1190.0	11.8	4.9	30.0	7.2	9.5	9.0	70.0	380.0	29.2	6620.0	14.2	73.6	412.9	3.0	<3	61.0	<3	18.0	1450.0	194.2
FE	4	48.0	661.2	58.1	12760.0	23.5	470.0	1780.0	12.9	<3	26.0	7.0	11.6	8.0	76.0	730.0	32.6	8620.0	19.6	57.7	531.3	5.1	<3	68.0	<3	18.0	2790.0	182.8
FE	2	54.0	672.3	35.8	12730.0	25.1	480.0	1600.0	13.4	<3	29.0	7.2	10.2	<3	77.0	910.0	32.0	12560.0	12.7	42.1	464.6	7.1	<3	72.0	<3	14.0	2610.0	154.9
FE	1	49.0	641.0	50.9	14480.0	27.2	530.0	1760.0	13.4	5.5	35.5	10.4	10.2	6.0	112.0	840.0	30.4	11460.0	5.4	86.7	476.7	5.2	<3	67.0	<3	15.0	3440.0	183.0
FE	0.5	59.0	525.5	44.6	20130.0	19.2	470.0	1710.0	14.0	<3	11.0	7.3	8.4	<3	78.0	1050.0	24.1	16240.0	14.5	117.1	547.6	6.9	<3	59.0	<3	7.0	6770.0	111.1
FE	0.3	47.0	579.8	14.3	14000.0	24.0	470.0	2090.0	12.9	3.7	9.0	6.9	9.1	6.0	94.0	770.0	29.5	9690.0	20.5	77.1	459.6	5.2	<3	62.0	<3	13.0	3870.0	147.0
FE	0.2	52.0	544.9	40.9	17970.0	16.6	420.0	1840.0	13.1	<3	5.0	8.0	8.7	<3	79.0	820.0	28.3	14610.0	24.1	87.5	497.9	5.4	<3	59.0	<3	10.0	4725.0	124.0
FE	0.063	609.5	48.9	16830.0	16.6	510.0	1750.0	14.0	<3	16.0	6.5	8.5	4.0	95.0	1480.0	21.8	16620.0	11.8	162.3	602.9	8.8	<3	57.0	<3	8.0	7658.0	112.3	
-FC	20																											
FC	16	1160.0	298.5	158.9	6870.0	25.0	3600.0	2710.0	41.9	<3	37.0	17.8	9.3	<3	71.0	26000.0	73.7	3800.0	17.4	37.8	380.8	139.2	<3	48.0	<3	<3	1040.0	191.0
FC	8	29.0	664.8	61.7	8760.0	20.3	420.0	3040.0	11.0	9.2	23.0	5.7	9.7	12.0	70.0	350.0	26.5	10230.0	18.1	58.4	390.7	<3	5.5	60.0	<3	18.0	1570.0	185.7
FC	4	57.0	550.2	48.5	10720.0	34.3	450.0	1690.0	12.7	<3	29.0	8.2	9.9	3.0	76.0	1020.0	28.0	10040.0	11.3	92.8	486.3	5.2	<3	64.0	<3	13.0	2770.0	159.6
FC	2	67.0	578.2	72.0	12360.0	37.5	440.0	2560.0	14.0	<3	23.0	6.8	10.3	4.0	77.0	1530.0	29.9	10060.0	10.2	87.0	502.6	8.2	<3	69.0	<3	14.0	3000.0	216.2
FC	1	53.0	591.6	48.2	6410.0	44.8	470.0	2670.0	12.9	4.7	14.0	6.8	10.6	10.0	112.0	910.0	28.9	8310.0	13.6	89.8	486.4	4.9	<3	66.0	<3	15.0	3380.0	175.7
FC	0.5	32.0	525.1	37.3	7890.0	39.6	470.0	2510.0	12.3	6.8	35.0	7.8	9.6	15.0	78.0	520.0	28.0	11600.0	9.1	107.7	519.7</							

APPENDIX VI

Results of leaching tests for 5 WtE plants investigated

		mg/kg									ug/l																								
WtE plants	GRAIN SIZE	Ca	Mg	Na	K	Cl-	SO ₄ ²⁻	F-	Br-	PO ₄ ³⁻	Al	As	Ba	Be	Bi	B	Cd	Cr	Co	Cu	Fe	Pb	Li	Mg	Mn	Mo	Ni	K	Se	Na	Sr	Tl	Ti	V	Zn
PR	0.2	177.7	0.2	77.4	75.8	702.9	438.1	0	0	0	51281	0	42.0	0	0	0	0	458.1	0	119.8	941.4	6.3	12.6	115.6	0	14.7	8.4	102629.2	16.8	412882.8	1077.9	0	4.2	2.1	60.9
PR	0.3	129.6	0.1	71.3	68.8	678.4	420.0	0	0	0	56447.7	0	39.5	0	0	0	0	353.5	0	87.3	704.9	0	10.4	35.4	0	0	8.3	95779.1	16.6	365640.4	877.5	0	2.1	2.1	56.1
PR	0.5	125.6	0.1	55.4	50.3	463.8	321.1	0	0	0	50792.5	0	43.1	0	0	0	0	248	0	69.0	653.5	2.2	10.8	36.7	0	0	6.5	74741.6	12.9	271989	802.3	0	2.2	2.2	62.5
PR	1	146.2	0.1	40.1	36.6	390.5	267.3	0	0	0	47347.2	0	50.4	0	0	0	0	212	0	50.4	755.6	4.2	12.6	39.9	0	0	8.4	57067.7	18.9	192625.5	789.2	0	4.2	2.1	44.1
PR	2	4.3.0	0.1	35.4	32.7	319.1	303.1	1	0	0	37331.2	0	40.9	0	0	0	0	197.8	0	43.0	711.8	2.1	10.8	38.7	0	0	4.3	52274.5	8.6	167590.6	673.1	0	2.2	2.2	51.6
PC	0.2	163.0	0.1	153.7	95.3	993.2	327.2	4.5	0	0	64668.3	0	83.1	0	0	383.3	0	119.3	0	1156.3	715.5	4.2	0	0	0	249.2	4.3	178123.2	61.8	471843.5	745.3	0	0	2.1	0
PC	0.3	138.5	0	139.6	90.7	887	314.9	0	0	0	66874.3	0	68.8	0	0	333.4	0	105.4	0	1170.2	625.9	2.1	0	0	0	176.4	2.2	164573.2	55.9	433720.1	662.5	0	2.2	2.2	0
PC	0.5	111.0	0.1	105.5	64.9	662.7	253.2	11.4	2	0	69119.9	0	63.1	0	0	248.1	0	73.6	0	889.4	552.9	2.1	0	0	0	88.3	2.1	127600.5	46.3	330012.9	548.8	0	0	2.1	0
PC	1	105.0	0.2	93.4	58.9	547.8	235.6	3	3	8	70823.9	0	81.1	0	0	199.8	0	75.2	0	953.4	682.4	59.3	0	100.9	11.9	47.5	37.6	111413	31.6	283301.4	464.8	0	7.9	2	0
PC	2	81.5	0	64.2	44.8	428.1	172.7	3.9	4	0	24859.9	0	43.2	0	0	122.3	0	30.6	0	361.8	274.1	0	0	0	0	49.5	0	86902.6	33.7	224803.6	314.2	0	0	0	0
TO	0.2	379.7	0	141.2	116.9	1165.5	755.8	0	0	0	16470.0	0	94.8	0	0	46.4	0	305.6	10.5	5319.9	1622.9	18.9	56.9	166.5	2.1	0	56.9	172064.7	14.8	608665.6	2282.7	0	6.3	4.2	109.6
TO	0.3	297.7	0.2	106.4	86.9	854.8	677	0	0	0	15626.3	0	79.7	0	0	35.6	0	228.6	6.3	4089.6	1273.0	16.8	48.2	136.3	0	0	44.0	133778.7	10.5	458593.9	1824.6	0	4.2	6.3	65.0
TO	0.5	248.1	0.2	77.5	65.4	631.9	457.2	0	0	0	13868.6	0	68.7	0	0	18.7	0	218.5	6.2	3360.0	1150.5	33.3	41.6	174.8	4.2	0	41.6	102048.8	12.5	338052.9	1460.5	0	6.2	6.2	<0
TO	1	240.8	0.2	70.7	59.2	573.7	438	4.6	0	0	10351.3	0	68.8	0	0	8.3	0	171.1	4.2	3392.0	1032.6	14.6	39.6	110.6	0	0	39.6	93228.2	12.5	310803.2	1328.9	0	4.2	8.3	70.9
TO	2	171.0	0.2	61.9	47.2	435.8	359.1	4.3	0	1	7087.3	0	60.8	0	0	6.2	0	146.8	4.2	3432.5	784.2	25.2	37.7	163.6	4.2	0	23.1	81355.3	10.5	270014.4	924.7	0	8.4	12.6	119.5
FC	0.2	585.5	0	167.6	112.4	1042.9	5.1	0	0	0	291.7	4.17	3853.2	0	0	0	0	31.3	2.0	1054.4	2466.2	12.5	133.4	0	0	108.4	18.8	235717.4	31.3	707668.6	9134.2	10.4	6.3	27.1	0
FC	0.3	647.2	0	156.3	84.8	918.9	14.5	4.6	0	0	412.6	2.08	3732.2	0	0	0	0	27.1	2.0	899.7	2657.5	12.5	108.3	0	0	0	16.7	216611.8	18.7	618146.6	7132.8	2.1	8.3	14.6	0
FC	0.5	652.1	0	126	66.6	779	13.2	15.5	0	1	0	0	2520.2	0	0	0	0	22.6	2.0	937.3	2778.2	16.4	88.4	0	0	0	18.5	167365	10.3	485398.7	5481.8	0	2.1	10.3	0
FC	1	706.3	0	111	59.7	695.4	45.1	5.1	0	3.5	0	0	1247.7	0	0	0	0	36.9	2.0	887.1	2931.3	55.3	96.3	0	0	0	20.5	139136.4	14.3	394421.7	4696.3	0	2	8.2	0
FC	2	695.4	0	94.4	51.8	607.5	46.8	5.1	0	0	0	0	800.0	0	0	0	0	41.2	2.0	740.2	2913.3	10.3	92.8	0	0	0	20.6	122164.2	14.4	368252.3	4113.3	0	2.1	6.2	0
FE	0.2	693.9	0	162.7	85.3	1063.6	58.8	1.8	0	0	486.9	0	5538.9	0	0	0	0	6.3	0	531.0	2401.0	44.0	149.0	0	0	0	14.7	215859	21	558507.8	6563.1	0	4.2	6.3	0
FE	0.3	725.6	0	139.6	68.7	807.1	30.1	3.4	0	0	0	0	4521.5	0	0	0	0	4.2	0	390.9	2702.8	33.4	106.6	0	0	0	14.6	180711.9	18.8	453322.3	5263.5	0	2.1	4.2	0
FE	0.5	733.7	0	125.1	60.1	741.4	41.7	7.7	0	0	0	0	2952.5	0	0	0	0	6.1	0	363.9	2769.5	32.5	95.6	0	0	0	16.3	162254.7	14.2	395105.8	4563	0	2.0	2.0	0
FE	1	693.7	0	96.3	43.2	584.9	19.5	3.4	0	0	0	0	1801.8	0	0	0	0	4.2	0	303.5	2891.4	35.8	73.8	0	0	0	16.9	122283.0	14.8	276132.9	3506.7	0	2.1	2.1	0
FE	2	754.7	0	91.1	46.6	528.0	18.1	6.4	0	0	0	0	1450.9	0	0	0	0	10.6	0	328.0	2630.2	29.3	70.7	0	0	0	14.7	117549.2	12.7	260027.9	3032.2	0	2.1	2.1	0

APPENDIX VII

Statistical analysis between grain size and major and minor elements content; R² (lower triangle) and p value (upper triangle) for 5 WtE plants investigated

a) Parma WtE plant

PARMA	Grain size	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	As	Ba	Ce	Cl	Co	Cr	Cu	Ga	Hf	La	Mo	Nb	Nd	Ni	Pb	Rb	S	Sc	Sn	Sr	Th	V	Y	Zn	Zr
Grain size	-	9E-08	0.0078	0.528	0.096	0.498	0.050	9E-06	0.002	0.218	0.093	2E-06	0.009	0.002	0.889	2E-05	0.044	0.741	0.006	0.239	0.023	0.464	0.465	0.331	0.217	0.784	0.135	9E-05	7E-06	0.029	0.000	0.052	0.776	0.102	0.024	0.002	1E-04
SiO ₂	0.988	-	0.0075	0.476	0.095	0.488	0.028	7E-08	0.002	0.200	0.095	7E-09	0.010	0.004	0.655	7E-06	0.055	0.683	0.014	0.306	0.014	0.322	0.423	0.329	0.167	0.980	0.169	5E-05	1E-07	0.022	0.000	0.049	0.804	0.117	0.018	0.005	4E-05
TiO ₂	-0.780	-0.782	-	0.306	0.901	0.128	0.630	0.005	0.000	0.749	0.000	0.010	0.050	0.000	0.896	0.000	0.011	0.448	0.073	0.709	0.078	0.494	0.243	0.710	0.557	0.972	0.377	0.048	0.007	0.053	0.002	0.022	0.519	0.002	0.526	0.092	0.019
Al ₂ O ₃	0.227	0.255	0.361	-	0.005	0.404	0.005	0.556	0.528	0.004	0.066	0.399	0.489	0.418	0.204	0.976	0.754	0.217	0.770	0.296	0.440	0.935	0.910	0.003	0.327	0.926	0.458	0.322	0.461	0.808	0.884	0.340	0.065	0.077	0.014	0.543	0.427
Fe ₂ O ₃	0.555	0.557	0.045	0.809	-	0.360	0.003	0.157	0.850	0.000	0.460	0.101	0.167	0.684	0.542	0.347	0.791	0.728	0.181	0.159	0.147	0.420	0.877	0.063	0.134	0.610	0.131	0.029	0.132	0.564	0.236	0.596	0.095	0.434	0.000	0.135	0.148
MnO	-0.243	-0.249	0.515	0.297	0.325	-	0.924	0.380	0.178	0.853	0.287	0.424	0.221	0.340	0.551	0.252	0.164	0.998	0.797	0.445	0.953	0.982	0.057	0.612	0.954	0.918	0.764	0.566	0.500	0.585	0.559	0.800	0.571	0.301	0.834	0.675	0.360
MgO	0.632	0.689	-0.174	0.805	0.836	-0.035	-	0.031	0.446	0.001	0.772	0.020	0.044	0.568	0.167	0.128	0.671	0.535	0.292	0.298	0.049	0.345	0.583	0.039	0.165	0.463	0.192	0.008	0.025	0.436	0.255	0.691	0.136	0.590	0.000	0.242	0.042
CaO	-0.962	-0.989	0.806	-0.212	-0.483	0.312	-0.679	-	0.001	0.251	0.071	0.000	0.016	0.004	0.567	0.000	0.058	0.569	0.022	0.420	0.022	0.261	0.443	0.356	0.173	0.990	0.273	0.000	0.000	0.012	0.001	0.044	0.998	0.097	0.029	0.010	0.000
Na ₂ O	0.846	0.856	-0.963	-0.227	0.069	-0.463	0.273	-0.886	-	0.918	0.002	0.002	0.084	0.000	0.979	0.000	0.016	0.270	0.048	0.761	0.114	0.371	0.385	0.963	0.332	0.740	0.586	0.023	0.002	0.007	0.002	0.020	0.366	0.002	0.407	0.029	0.002
K ₂ O	0.427	0.443	0.116	0.819	0.907	0.067	0.879	-0.401	-0.038	-	0.320	0.192	0.118	0.940	0.533	0.496	0.607	0.484	0.386	0.245	0.263	0.454	0.936	0.059	0.201	0.400	0.180	0.044	0.251	0.887	0.455	0.870	0.067	0.214	0.000	0.510	0.257
P ₂ O ₅	-0.559	-0.557	0.909	0.601	0.265	0.374	0.105	0.593	-0.841	0.351	-	0.133	0.198	0.001	0.994	0.019	0.063	0.315	0.113	0.626	0.167	0.361	0.445	0.345	0.757	0.964	0.463	0.205	0.084	0.094	0.024	0.007	0.325	0.004	0.969	0.238	0.208
LOI	-0.975	-0.994	0.763	-0.300	-0.548	0.286	-0.716	0.989	-0.849	-0.450	0.509	-	0.013	0.008	0.619	0.000	0.047	0.722	0.024	0.376	0.021	0.369	0.400	0.257	0.161	0.918	0.232	0.000	0.000	0.024	0.002	0.091	0.832	0.129	0.018	0.007	0.000
As	-0.768	-0.765	0.633	-0.249	-0.473	0.425	-0.646	0.731	-0.572	-0.527	0.445	0.747	-	0.064	0.578	0.020	0.086	0.328	0.149	0.090	0.004	0.474	0.041	0.552	0.338	0.447	0.006	0.007	0.008	0.580	0.023	0.214	0.110	0.614	0.020	0.302	0.069
Ba	-0.842	-0.820	0.931	0.289	-0.147	0.338	-0.206	0.822	-0.932	-0.028	0.869	0.780	0.604	-	0.728	0.000	0.076	0.245	0.007	0.421	0.104	0.324	0.611	0.930	0.299	0.912	0.296	0.016	0.007	0.026	0.000	0.002	0.497	0.003	0.332	0.024	0.014
Ce	0.051	0.162	0.047	0.440	0.220	0.215	0.474	-0.206	0.009	0.224	-0.003	-0.180	-0.201	0.126	-	0.885	0.943	0.531	0.866	0.320	0.143	0.132	0.604	0.299	0.288	0.293	0.576	0.665	0.463	0.949	0.671	0.960	0.414	0.322	0.307	0.869	0.864
Cl	-0.954	-0.964	0.909	-0.011	-0.333	0.400	-0.514	0.974	-0.956	-0.244	0.721	0.955	0.717	0.914	-0.053	-	0.030	0.459	0.018	0.511	0.038	0.347	0.392	0.622	0.254	0.917	0.300	0.001	0.000	0.011	0.000	0.023	0.779	0.022	0.100	0.012	0.000
Co	-0.645	-0.621	0.756	0.114	0.096	0.477	-0.154	0.615	-0.734	0.186	0.606	0.638	0.569	0.584	-0.026	0.683	-	0.547	0.292	0.568	0.142	0.544	0.088	0.810	0.869	0.251	0.390	0.238	0.032	0.298	0.100	0.604	0.949	0.069	0.729	0.129	0.067
Cr	0.120	0.148	-0.271	-0.429	-0.126	0.001	-0.224	-0.205	0.386	-0.251	-0.354	-0.129	0.346	-0.405	-0.226	-0.265	0.217	-	0.608	0.194	0.444	0.143	0.247	0.403	0.345	0.987	0.114	0.785	0.853	0.028	0.466	0.073	0.003	0.094	0.547	0.480	0.473
Cu	-0.796	-0.743	0.589	-0.106	-0.460	-0.094	-0.370	0.710	-0.637	-0.309	0.532	0.700	0.492	0.786	0.062	0.724	0.371	-0.186	-	0.059	0.132	0.702	0.501	0.236	0.406	0.526	0.141	0.012	0.024	0.124	0.002	0.048	0.983	0.148	0.081	0.001	0.037
Ga	-0.410	-0.361	0.135	-0.368	-0.482	-0.273	-0.366	0.288	-0.110	-0.405	0.176	0.315	0.564	0.287	-0.351	0.236	0.206	0.448	0.614	-	0.066	0.730	0.861	0.141	0.383	0.965	0.004	0.215	0.287	0.752	0.270	0.508	0.075	0.647	0.080	0.283	0.670
Hf	0.704	0.741	-0.581	0.276	0.494	0.021	0.635	-0.707	0.531	0.392	-0.473	-0.711	-0.821	-0.544	0.498	-0.658	-0.499	-0.274	-0.510	-0.601	-	0.315	0.183	0.586	0.376	0.259	0.004	0.022	0.006	0.544	0.043	0.159	0.112	0.614	0.023	0.183	0.124
La	0.262	0.350	-0.246	0.030	0.288	-0.008	0.334	-0.393	0.318	0.268	-0.324	-0.319	-0.257	-0.348	0.510	-0.333	0.218	0.498	-0.139	-0.125	0.354	-	0.733	0.858	0.012	0.064	0.801	0.245	0.359	0.181	0.448	0.032	0.742	0.869	0.350	0.894	0.478
Mo	-0.262	-0.286	0.407	0.041	0.056	0.617	-0.198	0.274	-0.309	-0.029	0.273	0.300	0.651	0.184	-0.187	0.305	0.566	0.404	-0.242	0.064	-0.459	-0.124	-	0.528	0.719	0.439	0.289	0.604	0.345	0.881	0.634	0.917	0.271	0.829	0.764	0.626	0.596
Nb	0.344	0.345	0.135	0.826	0.607	0.183	0.658	-0.328	0.017	0.614	0.335	-0.396	-0.214	0.032	0.365	-0.178	-0.088	-0.298	-0.413	-0.500	0.197	-0.065	0.227	-	0.272	0.413	0.630	0.285	0.322	0.899	0.782	0.496	0.406	0.445	0.038	0.214	0.215
Nd	0.428	0.474	-0.212	0.346	0.508	-0.021	0.476	-0.468	0.343	0.442	-0.113	-0.479	-0.339	-0.366	0.374	-0.398	0.060	0.334	-0.296	-0.310	0.315	0.755	-0.131	0.385	-	0.396	0.701	0.199	0.229	0.299	0.299	0.220	0.987	0.828	0.117	0.426	0.155
Ni	-0.100	-0.009	0.013	0.034	0.184	0.037	0.263	-0.005	-0.121	0.300	-0.016	0.038	-0.272	0.040	0.370	0.038	0.401	-0.006	0.228	-0.016	0.395	0.604	-0.277	-0.292	0.302	-	0.360	0.787	0.985	0.521	0.975	0.483	0.329	0.491	0.438	0.221	0.627
Pb	-0.507	-0.471	0.314	-0.266	-0.512	-0.109	-0.450	0.385	-0.197	-0.461	0.263	0.415	0.795	0.368	-0.202	0.365	0.306	0.532	0.500	0.811	-0.820	-0.092	0.373	-0.174	-0.139	-0.325	-	0.106	0.147	0.662	0.112	0.376	0.008	0.850	0.046	0.405	0.577
Rb	0.932	0.939	-0.636	0.350	0.684	-0.207	0.777	-0.927	0.704	0.645	-0.439	-0.920	-0.790	-0.732	0.157	-0.873	-0.411	0.099	-0.754	-0.430	0.707	0.406	-0.188	0.376	0.444	0.098	-0.541	-	0.000	0.045	0.002	0.043	0.565	0.368	0.003	0.020	0.002
S	-0.964	-0.988	0.789	-0.264	-0.511	0.242	-0.698	0.984	-0.851	-0.401	0.572	0.986	0.776	0.784	-0.263	0.951	0.677	-0.067	0.702	0.374	-0.798	-0.325	0.334	-0.350	-0.419	-0.007	0.493	-0.911	-	0.034	0.002	0.075	0.720	0.137	0.021	0.009	0.000
Sc	-0.685	-0.709	0.625	0.088	-0.208	0.197	-0.279	0.753	-0.784	-0.052	0.558	0.702	0.200	0.696	-0.023	0.756	0.366	-0.687	0.519	-0.115	-0.218	-0.460	-0.055	-0.046	-0.366	0.231	-0.159	-0.642	0.669	-	0.049	0.024	0.120	0.049	0.534	0.026	0.010
Sn	-0.929	-0.896	0.843	0.053	-0.413	0.211	-0.398	0.863	-0.850	-0.267	0.702	0.855	0.703	0.946	0.154	0.919	0.549	-0.261	0.847	0.386	-0.647	-0.271	0.172	-0.101	-0.365	0.011	0.533	-0.847	0.851	0.633	-	0.008	0.992	0.027	0.097	0.006	0.005
Sr	-0.628	-0.634	0.707	0.338	-0.192	0.092	-0.144	0.645	-0.715	-0.060	0.790	0.562	0.431	0.847	-0.018	0.703	0.188	-0.590	0.637	0.238	-0																

b) Piacenza WtE plant

PIACENZA	Grain size	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	As	Ba	Ce	Cl	Co	Cr	Cu	Ga	La	Mo	Nb	Nd	Ni	Pb	Rb	S	Sc	Sn	Sr	Th	V	Y	Zn	Zr
Grain size	-	0.003	0.050	0.001	0.091	0.269	0.796	0.014	0.014	0.657	0.113	0.161	0.318	0.656	0.289	0.008	0.973	0.159	0.002	0.065	0.844	0.107	0.871	0.620	0.849	0.289	0.766	0.133	0.116	0.073	0.073	0.128	0.236	0.952	0.098	0.235
SiO ₂	0.919	-	0.049	0.000	0.009	0.744	0.675	0.000	0.012	0.657	0.066	0.105	0.295	0.447	0.154	0.001	0.910	0.212	0.004	0.014	0.373	0.036	0.974	0.824	0.572	0.183	0.690	0.028	0.107	0.168	0.045	0.078	0.248	0.486	0.141	0.169
TiO ₂	-0.755	-0.756	-	0.027	0.116	0.536	0.304	0.026	0.001	0.055	0.005	0.410	0.009	0.067	0.016	0.004	0.548	0.999	0.026	0.031	0.723	0.011	0.149	0.817	0.722	0.009	0.072	0.012	0.007	0.012	0.000	0.001	0.008	0.456	0.002	0.999
Al ₂ O ₃	-0.944	-0.972	0.812	-	0.016	0.671	0.783	0.000	0.010	0.529	0.048	0.249	0.231	0.389	0.105	0.001	0.846	0.255	0.004	0.007	0.671	0.040	0.900	0.609	0.574	0.168	0.599	0.030	0.078	0.137	0.043	0.062	0.240	0.499	0.114	0.272
Fe ₂ O ₃	0.682	0.880	-0.647	-0.848	-	0.620	0.657	0.002	0.080	0.703	0.128	0.292	0.261	0.193	0.078	0.015	0.522	0.507	0.084	0.001	0.242	0.018	0.955	0.645	0.256	0.117	0.642	0.014	0.313	0.359	0.082	0.094	0.417	0.084	0.348	0.420
MnO	-0.486	-0.152	0.285	0.198	0.230	-	0.685	0.988	0.504	0.907	0.957	0.587	0.798	0.585	0.631	0.740	0.336	0.682	0.424	0.770	0.495	0.930	0.536	0.918	0.297	0.991	0.931	0.700	0.507	0.135	0.633	0.859	0.448	0.061	0.315	0.828
MgO	0.121	0.195	0.456	-0.129	0.207	0.189	-	0.823	0.492	0.011	0.328	0.845	0.058	0.119	0.295	0.828	0.301	0.122	0.897	0.981	0.770	0.471	0.002	0.347	0.044	0.144	0.009	0.586	0.414	0.213	0.298	0.218	0.063	0.797	0.134	0.041
CaO	-0.855	-0.972	0.812	0.972	-0.930	0.007	-0.105	-	0.012	0.472	0.033	0.236	0.185	0.244	0.054	0.000	0.839	0.377	0.012	0.001	0.421	0.015	0.849	0.760	0.493	0.100	0.492	0.006	0.083	0.186	0.028	0.038	0.220	0.266	0.129	0.319
Na ₂ O	0.855	0.863	-0.948	-0.875	0.699	-0.306	-0.315	-0.865	-	0.125	0.003	0.139	0.032	0.151	0.038	0.001	0.717	0.561	0.001	0.033	0.587	0.006	0.289	0.857	0.677	0.025	0.149	0.011	0.026	0.017	0.001	0.003	0.015	0.520	0.003	0.676
K ₂ O	-0.206	-0.207	0.745	0.289	-0.177	0.055	0.872	0.328	-0.636	-	0.031	0.911	0.007	0.029	0.031	0.259	0.460	0.393	0.367	0.360	0.901	0.127	0.023	0.520	0.186	0.027	0.000	0.126	0.107	0.136	0.070	0.025	0.015	0.426	0.028	0.233
P ₂ O ₅	-0.651	-0.724	0.903	0.758	-0.632	0.025	0.436	0.793	-0.921	0.800	-	0.320	0.020	0.069	0.005	0.008	0.778	0.771	0.024	0.043	0.687	0.010	0.274	0.788	0.617	0.018	0.040	0.004	0.029	0.102	0.008	0.001	0.021	0.291	0.012	0.935
LOI	-0.592	-0.662	0.373	0.504	-0.466	0.251	-0.091	0.516	-0.618	0.052	0.442	-	0.609	0.885	0.707	0.178	0.818	0.189	0.066	0.486	0.136	0.220	0.897	0.502	0.635	0.457	0.864	0.306	0.531	0.301	0.236	0.346	0.292	0.967	0.294	0.209
As	-0.444	-0.463	0.882	0.520	-0.493	0.120	0.738	0.566	-0.798	0.894	0.832	0.237	-	0.003	0.008	0.076	0.693	0.525	0.164	0.098	0.785	0.012	0.016	0.758	0.431	0.000	0.005	0.034	0.108	0.024	0.006	0.001	0.005	0.243	0.009	0.350
Ba	-0.207	-0.346	0.722	0.388	-0.558	-0.252	0.643	0.508	-0.604	0.804	0.719	0.068	0.918	-	0.005	0.172	0.982	0.321	0.423	0.084	0.600	0.021	0.056	0.837	0.797	0.002	0.013	0.033	0.279	0.186	0.045	0.015	0.069	0.038	0.119	0.248
Ce	-0.469	-0.600	0.846	0.663	-0.703	-0.223	0.464	0.747	-0.780	0.800	0.908	0.175	0.884	0.908	-	0.032	0.921	0.799	0.144	0.015	0.709	0.006	0.216	0.963	0.960	0.005	0.026	0.002	0.104	0.184	0.019	0.002	0.068	0.057	0.066	0.660
Cl	-0.887	-0.950	0.910	0.960	-0.851	0.155	0.102	0.969	-0.962	0.495	0.884	0.574	0.707	0.580	0.795	-	0.971	0.448	0.002	0.005	0.502	0.005	0.538	0.908	0.868	0.043	0.284	0.004	0.042	0.064	0.005	0.008	0.076	0.352	0.033	0.478
Co	0.016	0.053	0.276	-0.091	0.294	0.430	0.458	-0.095	-0.169	0.337	0.132	0.108	0.184	0.011	-0.046	0.017	-	0.356	0.977	0.587	0.625	0.913	0.315	0.017	0.257	0.745	0.498	0.966	0.180	0.463	0.542	0.710	0.266	0.339	0.321	0.950
Cr	-0.595	-0.539	0.001	0.499	-0.304	0.191	-0.639	0.398	-0.268	-0.386	0.136	0.562	-0.292	-0.442	-0.119	0.345	-0.414	-	0.192	0.664	0.968	0.869	0.144	0.368	0.664	0.586	0.315	0.869	0.964	0.960	0.964	0.910	0.697	0.656	0.944	0.033
Cu	-0.941	-0.917	0.814	0.914	-0.694	0.363	0.061	0.866	-0.947	0.405	0.818	0.724	0.589	0.364	0.612	0.936	0.013	0.559	-	0.057	0.659	0.034	0.647	0.887	0.819	0.140	0.428	0.049	0.091	0.057	0.027	0.041	0.096	0.727	0.038	0.344
Ga	-0.725	-0.854	0.799	0.890	-0.947	-0.137	0.011	0.944	-0.794	0.411	0.769	0.319	0.673	0.694	0.853	0.909	-0.251	0.202	0.740	-	0.545	0.006	0.655	0.544	0.421	0.046	0.349	0.004	0.168	0.205	0.034	0.027	0.245	0.087	0.172	0.704
La	-0.092	-0.401	0.165	0.197	-0.510	-0.312	-0.137	0.365	-0.251	-0.058	0.187	0.622	0.128	0.243	0.174	0.307	0.227	-0.019	0.205	0.278	-	0.353	0.934	0.182	0.697	0.460	0.905	0.314	0.708	0.848	0.420	0.555	0.594	0.378	0.770	0.439
Mo	-0.660	-0.786	0.871	0.777	-0.839	-0.041	0.329	0.851	-0.897	0.633	0.876	0.531	0.864	0.829	0.898	0.906	-0.051	0.077	0.791	0.895	0.416	-	0.238	0.957	0.956	0.002	0.101	0.001	0.136	0.064	0.002	0.001	0.039	0.105	0.038	0.997
Nb	-0.076	-0.016	0.606	0.059	-0.027	0.285	0.936	0.089	-0.468	0.824	0.481	0.061	0.846	0.742	0.535	0.284	0.447	-0.613	0.213	0.207	0.039	0.514	-	0.389	0.123	0.046	0.016	0.387	0.317	0.059	0.118	0.106	0.022	0.668	0.061	0.085
Nd	-0.230	-0.104	-0.108	0.237	-0.214	-0.048	-0.421	0.143	0.084	-0.295	-0.126	-0.308	-0.144	-0.097	0.022	0.054	-0.845	0.404	0.067	0.279	-0.569	-0.025	-0.388	-	0.252	0.687	0.454	0.842	0.445	0.782	0.632	0.742	0.332	0.755	0.521	0.945
Ni	0.089	0.261	0.166	-0.260	0.498	0.462	0.767	-0.314	-0.194	0.565	0.232	0.220	0.358	0.120	0.024	-0.078	0.497	-0.202	0.107	-0.365	-0.181	0.026	0.638	-0.501	-	0.652	0.211	0.864	0.711	0.371	0.682	0.637	0.197	0.419	0.280	0.336
Pb	-0.468	-0.568	0.881	0.584	-0.645	-0.006	0.612	0.669	-0.818	0.810	0.840	0.339	0.971	0.941	0.909	0.770	0.152	-0.252	0.617	0.763	0.337	0.935	0.763	-0.188	0.209	-	0.016	0.008	0.109	0.041	0.002	0.000	0.009	0.130	0.018	0.525
Rb	-0.139	-0.186	0.713	0.244	-0.216	-0.041	0.879	0.315	-0.607	0.987	0.777	0.080	0.907	0.862	0.813	0.472	0.311	-0.447	0.360	0.419	0.056	0.667	0.849	-0.341	0.540	0.849	-	0.108	0.155	0.160	0.068	0.024	0.016	0.301	0.042	0.193
S	-0.625	-0.808	0.866	0.802	-0.857	-0.179	0.252	0.897	-0.870	0.634	0.916	0.455	0.792	0.794	0.930	0.915	0.020	0.077	0.757	0.911	0.448	0.954	0.390	-0.093	-0.080	0.883	0.658	-	0.065	0.163	0.006	0.002	0.066	0.084	0.059	0.813
Sc	-0.647	-0.659	0.889	0.703	-0.449	0.304	0.370	0.696	-0.813	0.659	0.805	0.288	0.658	0.477	0.664	0.772	0.572	-0.021	0.682	0.585	0.175	0.621	0.445	-0.347	0.173	0.657	0.599	0.725	-	0.090	0.023	0.037	0.036	0.836	0.014	0.709
Sn	-0.712	-0.585	0.867	0.620	-0.411	0.623	0.538	0.565	-0.845	0.621	0.667	0.459	0.820	0.565	0.567	0.727	0.335	-0.024	0.741	0.546	0.090	0.726	0.736	-0.130	0.402	0.774	0.594	0.590	0.684	-	0.010	0.030	0.008	0.918	0.003	0.801
Sr	-0.711	-0.766	0.970	0.770	-0.696	0.222	0.461	0.807	-0.950	0.716	0.887	0.515	0.898	0.766	0.835	0.905	0.281	-0.021	0.810	0.792	0.366	0.931	0.644	-0.222	0.191	0.933	0.720	0.899	0.824	0.873	-	0.000	0.004	0.354	0.002	0.994
Th	-0.632	-0.703	0.956	0.731	-0.678	0.083	0.533	0.781	-0.928	0.817	0.947	0.422	0.945	0.850	0.929	0.883	0.173	-0.053	0.773	0.810	0.272	0.949	0.661	-0.154	0.219	0.963	0.821	0.931	0.785	0.803	0.972	-	0.005	0.221	0.004	0.812
V	-0.516	-0.505	0.885	0.512	-0.368	0.346	0.729	0.531	-0.852	0.853	0.829	0.466	0.909	0.718	0.721	0.706	0.489	-0.181	0.676	0.508	0.247	0.779	0.827	-0.433	0.554	0.880	0									

c) Torino WtE plant

TORINO	Grain size	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	As	Ba	Ce	Cl	Co	Cr	Cu	Ga	La	Mo	Nb	Nd	Ni	Pb	Rb	S	Sc	Sn	Sr	Th	V	Y	Zn	Zr
Grain size	-	0.023	0.008	0.002	0.025	0.469	0.415	0.003	0.048	0.128	0.611	3E-07	0.235	0.006	0.036	0.009	0.612	0.000	0.000	0.014	0.068	0.771	0.563	0.928	0.727	0.143	0.899	0.019	0.261	0.001	0.000	0.263	0.098	0.165	3E-05	0.232
SiO ₂	0.704	-	0.680	0.261	0.999	0.005	0.326	0.551	0.016	0.829	0.371	0.053	0.756	0.542	0.703	0.000	0.338	0.011	0.154	0.518	0.298	0.250	0.512	0.262	0.075	0.824	0.075	0.681	0.908	0.293	0.110	0.977	0.040	0.244	0.0781	0.403
TiO ₂	-0.775	-0.149	-	0.001	0.000	0.545	0.043	0.000	0.403	0.027	0.350	0.002	0.049	0.001	0.027	0.377	0.192	0.069	0.002	0.000	0.123	0.978	0.632	0.291	0.547	0.008	0.370	0.000	0.053	0.000	0.003	0.028	0.256	0.433	0.0126	0.270
Al ₂ O ₃	-0.849	-0.393	0.866	-	0.016	0.742	0.365	0.002	0.277	0.054	0.289	0.002	0.182	0.017	0.018	0.106	0.493	0.052	0.001	0.007	0.029	0.948	0.663	0.955	0.698	0.101	0.607	0.013	0.023	0.003	0.009	0.068	0.161	0.327	0.0030	0.083
Fe ₂ O ₃	0.697	0.000	-0.910	-0.735	-	0.163	0.004	7E-06	0.495	0.002	0.068	0.010	0.268	0.000	0.009	0.583	0.052	0.096	0.003	0.009	0.178	0.338	0.745	0.202	0.324	0.090	0.081	0.004	0.133	0.003	0.003	0.145	0.738	0.498	0.0090	0.573
MnO	-0.260	-0.800	-0.218	0.120	0.478	-	0.017	0.468	0.137	0.219	0.088	0.681	0.866	0.409	0.510	0.026	0.013	0.450	0.900	0.808	0.825	0.113	0.521	0.032	0.037	0.662	0.018	0.543	0.696	0.840	0.979	0.639	0.073	0.750	0.8009	0.426
MgO	-0.291	0.347	0.647	0.321	-0.813	-0.726	-	0.043	0.718	0.011	0.222	0.245	0.539	0.005	0.192	0.795	0.027	0.642	0.135	0.115	0.733	0.372	0.350	0.034	0.541	0.269	0.029	0.108	0.263	0.187	0.106	0.289	0.980	0.888	0.1929	0.328
CaO	-0.835	-0.215	0.937	0.845	-0.965	-0.260	0.648	-	0.327	0.006	0.102	0.001	0.207	0.000	0.003	0.286	0.124	0.022	0.000	0.004	0.107	0.484	0.819	0.390	0.429	0.069	0.223	0.002	0.162	0.000	0.000	0.135	0.503	0.283	0.0015	0.258
Na ₂ O	0.635	0.733	-0.298	-0.382	0.245	-0.504	-0.131	-0.346	-	0.277	0.629	0.052	0.767	0.134	0.770	0.000	0.567	0.075	0.035	0.394	0.465	0.813	0.011	0.347	0.011	0.999	0.833	0.724	0.895	0.459	0.042	0.935	0.009	0.974	0.0497	0.879
K ₂ O	-0.515	0.079	0.690	0.624	-0.856	-0.426	0.761	0.798	-0.381	-	0.016	0.090	0.845	0.003	0.032	0.489	0.146	0.379	0.010	0.176	0.325	0.058	0.290	0.763	0.596	0.698	0.004	0.191	0.205	0.147	0.035	0.554	0.795	0.915	0.0300	0.874
P ₂ O ₅	-0.184	0.318	0.331	0.373	-0.598	-0.566	0.424	0.547	0.175	0.730	-	0.615	0.498	0.228	0.020	0.658	0.086	0.805	0.302	0.884	0.491	0.002	0.456	0.897	0.032	0.749	0.004	0.609	0.567	0.446	0.449	0.978	0.147	0.748	0.3019	0.453
LOI	-0.984	-0.625	0.839	0.846	-0.766	0.149	0.405	0.875	-0.627	0.563	0.182	-	0.152	0.001	0.047	0.019	0.439	0.000	3E-05	0.004	0.046	0.772	0.493	0.712	0.770	0.072	0.971	0.007	0.193	0.000	0.000	0.148	0.078	0.189	4E-05	0.298
As	-0.413	-0.113	0.635	0.459	-0.388	-0.062	0.221	0.437	0.108	-0.071	-0.243	0.489	-	0.314	0.515	0.986	0.428	0.210	0.359	0.005	0.233	0.070	0.560	0.082	0.523	0.000	0.363	0.004	0.227	0.023	0.252	0.002	0.295	0.133	0.452	0.310
Ba	-0.794	-0.219	0.876	0.726	-0.941	-0.294	0.801	0.929	-0.508	0.830	0.419	0.859	0.355	-	0.022	0.207	0.086	0.032	0.000	0.009	0.186	0.600	0.316	0.250	0.888	0.121	0.200	0.011	0.184	0.005	0.000	0.180	0.309	0.455	0.001	0.848
Ce	0.664	0.138	-0.690	-0.723	0.771	0.237	-0.450	-0.832	0.107	-0.675	-0.714	-0.638	-0.234	-0.709	-	0.516	0.114	0.074	0.030	0.127	0.368	0.305	0.613	0.456	0.157	0.348	0.215	0.060	0.494	0.011	0.031	0.419	0.844	0.099	0.019	0.188
Cl	-0.774	-0.919	0.314	0.542	-0.198	0.695	-0.095	0.375	-0.912	0.248	-0.160	0.718	0.006	0.437	-0.233	-	0.467	0.018	0.028	0.354	0.237	0.532	0.115	0.219	0.042	0.891	0.424	0.597	0.720	0.257	0.035	0.931	0.010	0.518	0.019	0.571
Co	0.184	-0.339	-0.450	-0.246	0.629	0.745	-0.691	-0.520	-0.207	-0.495	-0.570	-0.277	-0.283	-0.569	0.531	0.261	-	0.591	0.352	0.338	0.531	0.371	0.645	0.036	0.131	0.310	0.115	0.211	0.392	0.247	0.289	0.291	0.525	0.497	0.374	0.966
Cr	-0.912	-0.759	0.596	0.628	-0.554	0.270	0.168	0.708	-0.586	0.313	0.090	0.900	0.434	0.675	-0.588	0.722	-0.194	-	0.007	0.057	0.091	0.679	0.953	0.746	0.747	0.156	0.545	0.054	0.798	0.004	0.001	0.335	0.170	0.023	0.002	0.270
Cu	-0.917	-0.486	0.855	0.877	-0.828	0.046	0.507	0.909	-0.666	0.767	0.363	0.946	0.325	0.907	-0.683	0.686	-0.330	0.783	-	0.009	0.043	0.750	0.293	0.909	0.837	0.162	0.440	0.022	0.140	0.004	0.000	0.172	0.093	0.359	0.000	0.330
Ga	-0.743	-0.233	0.952	0.786	-0.773	-0.088	0.530	0.821	-0.303	0.465	0.053	0.818	0.805	0.774	-0.516	0.328	-0.339	0.618	0.769	-	0.134	0.476	0.642	0.231	0.794	0.000	0.862	0.000	0.082	0.000	0.008	0.008	0.111	0.345	0.040	0.279
La	0.598	0.366	-0.520	-0.683	0.463	-0.081	-0.124	-0.541	0.262	-0.347	-0.247	-0.640	-0.415	-0.455	0.319	-0.411	0.225	-0.562	-0.648	-0.508	-	0.801	0.947	0.816	0.677	0.204	0.982	0.168	0.042	0.083	0.096	0.033	0.225	0.193	0.040	0.246
Mo	-0.106	-0.402	-0.010	0.024	0.339	0.532	-0.317	-0.251	-0.086	-0.617	-0.844	0.105	0.595	-0.189	0.361	0.225	0.318	0.150	-0.116	0.256	-0.092	-	0.774	0.700	0.231	0.208	0.003	0.678	0.668	0.768	0.915	0.243	0.082	0.522	0.856	0.931
Nb	-0.209	-0.236	0.174	0.158	-0.118	0.231	0.331	0.083	-0.761	0.372	-0.267	0.246	-0.210	0.354	0.183	0.530	0.167	0.022	0.370	0.168	0.024	0.104	-	0.592	0.010	0.777	0.666	0.876	0.506	0.830	0.419	0.947	0.031	0.167	0.448	0.194
Nd	0.033	-0.392	-0.371	0.020	0.441	0.675	-0.670	-0.306	-0.333	-0.110	-0.047	-0.134	-0.575	-0.401	0.267	0.426	0.666	-0.118	-0.042	-0.417	-0.085	-0.140	0.194	-	0.253	0.075	0.681	0.132	0.808	0.264	0.541	0.187	0.582	0.388	0.839	0.396
Ni	-0.127	-0.586	-0.217	-0.141	0.348	0.662	-0.220	-0.283	-0.759	-0.192	-0.674	0.106	-0.230	-0.051	0.483	0.649	0.512	0.117	0.075	-0.095	0.151	0.417	0.766	0.399	-	0.514	0.215	0.399	0.644	0.472	0.807	0.435	0.025	0.385	0.872	0.320
Pb	-0.498	-0.081	0.775	0.549	-0.563	-0.159	0.387	0.596	0.000	0.141	-0.116	0.591	0.969	0.523	-0.332	0.050	-0.358	0.485	0.478	0.906	-0.440	0.436	-0.103	-0.586	-0.235	-	0.709	0.000	0.187	0.007	0.111	0.001	0.257	0.195	0.286	0.298
Rb	0.046	0.586	0.318	0.186	-0.576	-0.725	0.685	0.423	0.077	0.818	0.810	0.013	-0.323	0.443	-0.430	-0.285	-0.531	-0.218	0.276	0.063	0.008	-0.837	0.156	-0.149	-0.430	-0.135	-	0.774	0.509	0.887	0.663	0.941	0.301	0.374	0.650	0.758
S	-0.720	-0.149	0.942	0.750	-0.819	-0.219	0.539	0.856	-0.128	0.451	0.185	0.786	0.812	0.756	-0.611	0.191	-0.434	0.624	0.709	0.964	-0.473	0.151	-0.057	-0.510	-0.300	0.905	0.104	-	0.130	0.000	0.011	0.017	0.380	0.241	0.051	0.209
Sc	0.393	-0.042	-0.625	-0.705	0.509	0.142	-0.392	-0.478	0.048	-0.439	-0.207	-0.449	-0.420	-0.457	0.245	-0.130	0.305	-0.093	-0.501	-0.575	0.650	-0.155	-0.239	0.088	0.167	-0.455	-0.237	-0.512	-	0.191	0.320	0.031	0.302	0.819	0.195	0.649
Sn	-0.875	-0.369	0.911	0.833	-0.826	-0.074	0.454	0.912	-0.265	0.494	0.273	0.902	0.705	0.806	-0.756	0.396	-0.404	0.812	0.817	0.900	-0.573	0.107	-0.078	-0.391	-0.258	0.786	0.052	0.943	-0.450	-	0.001	0.044	0.346	0.073	0.004	0.154
Sr	-0.944	-0.536	0.831	0.771	-0.831	0.009	0.542	0.906	-0.649	0.668	0.271	0.974	0.400	0.930	-0.679	0.667	-0.373	0.885	0.954	0.780	-0.554	-0.039	0.288	-0.220	0.089	0.536	0.158	0.757	-0.351	0.871	-	0.224	0.141	0.215	0.000	0.486
Th	-0.392	0.011	0.688	0.597	-0.496	-0.170	0.373	0.506	0.030	0.213	-0.010	0.493	0.856	0.461	-0.288	0.031	-0.371	0.341	0.468	0.779	-0.673	0.407	-0.024	-0.455	-0.279	0.866	-0.027	0.729	-0.679	0.645	0.423	-	0.206	0.197	0.274	0.428
V	-0.552	-0.654	0.397	0.479	-0.122	0.590	0.009	0.241	-0.772	0.094	-0.494	0.581	0.368	0.358	0.072	0.764	0.229	0.470	0.559	0.535	-0.422	0.574	0.677	0.199	0.698	0.39										

d) Ferrara WtE plant

FERRARA	Grain size	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	As	Ba	Ce	Cl	Co	Cr	Cu	Ga	Hf	La	Mo	Nb	Nd	Ni	Pb	Rb	S	Sc	Sn	Sr	Th	V	Y	Zn	Zr
Grain size	-	0,902	0,602	0,851	0,977	0,770	0,852	0,857	0,888	0,786	0,522	0,894	0,323	0,250	0,276	0,213	0,224	0,270	0,216	0,240	0,364	0,653	0,201	0,209	0,750	0,267	0,383	0,184	0,254	0,141	0,388	0,269	0,361	0,219	0,203	0,350	0,208
SiO ₂	-0,045	-	1E-06	2E-10	1E-09	1E-07	2E-10	4E-10	8E-06	8E-06	2E-06	1E-09	0,004	0,020	0,014	0,046	0,034	0,013	0,043	0,024	0,043	5E-06	0,063	0,060	0,000	0,014	0,001	0,094	0,019	0,325	0,001	0,014	0,001	0,040	0,095	0,003	0,053
TiO ₂	-0,189	0,976	-	3E-06	3E-06	8E-08	5E-07	4E-06	0,000	1E-05	5E-07	8E-06	0,001	0,008	0,005	0,020	0,014	0,005	0,018	0,009	0,027	4E-06	0,028	0,027	0,000	0,005	0,000	0,045	0,007	0,191	0,000	0,005	0,000	0,017	0,046	0,001	0,024
Al ₂ O ₃	-0,068	0,997	0,972	-	8E-08	4E-07	1E-10	2E-15	2E-06	3E-06	6E-07	5E-11	0,003	0,018	0,012	0,041	0,030	0,011	0,038	0,021	0,041	2E-06	0,058	0,054	0,000	0,012	0,001	0,086	0,016	0,306	0,001	0,012	0,001	0,036	0,086	0,002	0,048
Fe ₂ O ₃	0,010	0,996	0,972	0,988	-	1E-07	1E-08	1E-07	2E-05	1E-05	1E-05	1E-07	0,005	0,024	0,017	0,052	0,039	0,016	0,048	0,028	0,044	1E-05	0,070	0,067	0,000	0,017	0,002	0,104	0,022	0,344	0,002	0,016	0,001	0,046	0,103	0,003	0,060
MnO	-0,106	0,988	0,988	0,982	0,987	-	1E-07	6E-07	0,000	2E-05	1E-06	1E-06	0,003	0,015	0,011	0,035	0,026	0,010	0,033	0,018	0,038	8E-06	0,048	0,046	0,000	0,010	0,001	0,074	0,014	0,270	0,001	0,010	0,001	0,031	0,075	0,002	0,041
MgO	-0,068	0,998	0,981	0,998	0,992	0,986	-	3E-10	8E-06	9E-07	5E-07	3E-09	0,003	0,018	0,012	0,040	0,030	0,011	0,038	0,021	0,041	3E-06	0,057	0,053	0,000	0,012	0,001	0,085	0,016	0,303	0,001	0,012	0,001	0,035	0,085	0,002	0,047
CaO	-0,066	0,997	0,969	1,000	0,987	0,980	0,997	-	2E-06	3E-06	7E-07	7E-12	0,004	0,020	0,014	0,045	0,034	0,013	0,042	0,023	0,044	4E-06	0,063	0,059	0,000	0,014	0,001	0,093	0,018	0,324	0,001	0,013	0,001	0,040	0,093	0,002	0,053
Na ₂ O	0,051	0,963	0,902	0,973	0,952	0,919	0,963	0,974	-	4E-05	0,000	3E-06	0,006	0,025	0,017	0,052	0,041	0,017	0,049	0,029	0,041	3E-05	0,073	0,067	0,001	0,017	0,002	0,102	0,023	0,333	0,002	0,017	0,002	0,046	0,099	0,004	0,060
K ₂ O	-0,099	0,962	0,960	0,971	0,957	0,953	0,978	0,971	0,945	-	2E-06	6E-06	0,004	0,017	0,012	0,037	0,028	0,011	0,035	0,019	0,043	1E-05	0,052	0,048	0,001	0,011	0,001	0,076	0,015	0,273	0,001	0,011	0,001	0,033	0,073	0,002	0,043
P ₂ O ₅	-0,230	0,972	0,982	0,981	0,958	0,978	0,981	0,980	0,929	0,976	-	2E-06	0,001	0,008	0,006	0,021	0,015	0,005	0,019	0,010	0,030	2E-06	0,031	0,029	0,001	0,005	0,000	0,048	0,008	0,201	0,000	0,005	0,000	0,018	0,049	0,001	0,025
LOI	-0,049	0,996	0,963	0,998	0,987	0,978	0,995	0,999	0,971	0,965	0,974	-	0,007	0,030	0,021	0,063	0,048	0,020	0,059	0,034	0,061	1E-05	0,086	0,081	0,001	0,021	0,002	0,123	0,027	0,392	0,002	0,020	0,002	0,056	0,124	0,004	0,073
As	-0,349	0,814	0,862	0,823	0,801	0,828	0,823	0,815	0,794	0,820	0,861	0,788	-	9E-08	9E-09	5E-06	1E-06	6E-09	4E-06	2E-07	6E-05	9E-05	2E-05	1E-05	5E-05	8E-09	1E-09	7E-05	6E-08	0,003	4E-09	7E-09	2E-08	3E-06	7E-05	2E-12	9E-06
Ba	-0,402	0,714	0,779	0,725	0,701	0,736	0,726	0,716	0,699	0,730	0,776	0,683	0,988	-	2E-12	3E-09	8E-11	5E-12	1E-09	4E-15	1E-05	0,001	7E-08	4E-08	0,000	2E-12	4E-06	8E-07	9E-18	0,000	5E-06	4E-12	1E-05	6E-10	9E-07	6E-07	1E-08
Ce	-0,382	0,741	0,801	0,752	0,728	0,761	0,752	0,743	0,726	0,755	0,799	0,711	0,993	0,999	-	4E-08	4E-09	9E-17	2E-08	4E-11	1E-05	0,001	4E-07	3E-07	0,000	8E-17	9E-07	3E-06	3E-13	0,001	2E-06	5E-17	3E-06	1E-08	4E-06	1E-07	1E-07
Cl	-0,432	0,641	0,717	0,653	0,629	0,668	0,654	0,643	0,628	0,662	0,712	0,607	0,968	0,995	0,990	-	1E-12	5E-08	8E-18	5E-10	9E-06	0,005	2E-11	2E-12	0,002	4E-08	5E-05	4E-09	5E-09	5E-05	7E-05	5E-08	0,000	2E-15	6E-09	1E-05	1E-14
Co	-0,423	0,670	0,743	0,680	0,657	0,695	0,682	0,670	0,652	0,688	0,737	0,636	0,976	0,998	0,995	0,999	-	5E-09	2E-13	6E-12	9E-06	0,003	8E-10	3E-10	0,001	4E-09	2E-05	5E-08	2E-10	0,000	3E-05	5E-09	5E-05	2E-14	6E-08	5E-06	4E-11
Cr	-0,387	0,745	0,805	0,756	0,732	0,765	0,756	0,747	0,729	0,758	0,803	0,715	0,994	0,999	1,000	0,990	0,994	-	3E-08	7E-11	2E-05	0,001	5E-07	3E-07	0,000	3E-20	8E-07	4E-06	9E-13	0,001	1E-06	2E-23	2E-06	2E-08	4E-06	7E-08	2E-07
Cu	-0,429	0,648	0,722	0,659	0,635	0,674	0,660	0,649	0,634	0,668	0,718	0,614	0,970	0,996	0,991	1,000	1,000	0,991	-	2E-10	9E-06	0,004	6E-11	8E-12	0,001	3E-08	4E-05	8E-09	3E-09	6E-05	6E-05	3E-08	8E-05	6E-18	1E-08	1E-05	2E-13
Ga	-0,410	0,702	0,769	0,713	0,689	0,725	0,713	0,703	0,686	0,718	0,765	0,670	0,985	1,000	0,998	0,997	0,999	0,998	0,997	-	1E-05	0,002	2E-08	1E-08	0,001	4E-11	6E-06	4E-07	8E-14	0,000	9E-06	6E-11	2E-05	9E-11	5E-07	1E-06	3E-09
Hf	-0,322	0,648	0,692	0,653	0,646	0,661	0,652	0,644	0,651	0,647	0,682	0,610	0,938	0,960	0,957	0,961	0,962	0,956	0,962	0,960	-	0,005	9E-06	1E-05	0,001	1E-05	2E-04	2E-05	1E-05	0,001	0,000	2E-05	0,000	9E-06	2E-05	1E-04	1E-05
La	-0,163	0,966	0,969	0,972	0,958	0,962	0,972	0,969	0,948	0,958	0,974	0,957	0,931	0,863	0,883	0,809	0,830	0,885	0,814	0,854	0,800	-	0,008	7E-03	1E-05	0,001	1E-05	0,014	0,001	0,089	7E-06	0,001	5E-06	0,004	0,014	4E-05	0,006
Mo	-0,442	0,606	0,688	0,616	0,595	0,636	0,618	0,606	0,589	0,627	0,678	0,568	0,954	0,989	0,982	0,999	0,996	0,981	0,998	0,991	0,961	0,780	-	2E-13	0,003	5E-07	0,000	9E-11	1E-07	2E-05	0,000	5E-07	0,000	1E-10	3E-10	5E-05	8E-13
Nb	-0,435	0,612	0,691	0,624	0,600	0,640	0,625	0,613	0,600	0,637	0,685	0,576	0,957	0,990	0,984	0,999	0,997	0,983	0,999	0,993	0,959	0,787	1,000	-	0,002	3E-07	0,000	1E-10	6E-08	2E-05	0,000	3E-07	0,000	3E-11	2E-10	4E-05	9E-15
Nd	-0,116	0,905	0,911	0,900	0,910	0,909	0,903	0,895	0,881	0,876	0,891	0,876	0,942	0,896	0,910	0,856	0,872	0,912	0,860	0,889	0,886	0,959	0,837	0,840	-	0,000	1E-05	0,005	0,000	0,040	1E-05	0,000	2E-05	0,001	0,0048	3E-05	0,002
Ni	-0,388	0,743	0,803	0,753	0,730	0,763	0,754	0,744	0,726	0,756	0,801	0,713	0,994	0,999	1,000	0,990	0,994	1,000	0,991	0,998	0,957	0,884	0,982	0,984	0,911	-	9E-07	4E-06	4E-13	0,001	1E-06	3E-21	3E-06	2E-08	4E-06	9E-08	1E-07
Pb	-0,310	0,863	0,900	0,872	0,851	0,873	0,871	0,865	0,844	0,865	0,901	0,841	0,996	0,969	0,978	0,940	0,952	0,980	0,943	0,965	0,916	0,960	0,923	0,927	0,958	0,979	-	0,000	3E-06	0,009	2E-16	8E-07	2E-11	4E-05	0,000	1E-11	8E-05
Rb	-0,457	0,557	0,642	0,570	0,545	0,588	0,571	0,559	0,547	0,585	0,636	0,520	0,936	0,979	0,970	0,994	0,990	0,969	0,994	0,983	0,952	0,743	0,998	0,998	0,804	0,970	0,899	-	1E-06	3E-06	0,000	4E-06	0,001	1E-08	3E-13	0,000	7E-10
S	-0,399	0,720	0,784	0,731	0,707	0,742	0,732	0,722	0,705	0,735	0,781	0,689	0,989	1,000	0,999	0,994	0,997	0,999	0,995	1,000	0,959	0,868	0,988	0,989	0,900	0,999	0,972	0,977	-	0,000	4E-06	6E-13	7E-06	1E-09	1E-06	4E-07	2E-08
Sc	-0,501	0,348	0,451	0,361	0,335	0,386	0,363	0,348	0,342	0,384	0,442	0,305	0,827	0,904	0,886	0,942	0,929	0,883	0,939	0,911	0,891	0,565	0,956	0,954	0,654	0,885	0,771	0,972	0,900	-	0,010	0,001	0,012	7E-05	3E-06	0,005	3E-05
Sn	-0,307	0,869	0,905	0,878	0,857	0,879	0,877	0,872	0,850	0,870	0,907	0,848	0,994	0,966	0,976	0,936	0,948	0,977	0,939	0,961	0,912	0,964	0,918	0,922	0,960	0,976	1,000	0,894	0,968	0,763	-	1E-06	5E-12	5E-05	0,001	9E-11	0,000
Sr	-0,387	0,744	0,804	0,754	0,731	0,764	0,755	0,746	0,728	0,757	0,802	0,714	0,994	0,999	1,000	0,990	0,994	1,000	0,991	0,998	0,956	0,885	0,982	0,984	0,911	1,000	0,979	0,969	0,999	0,884	0,977	-</					

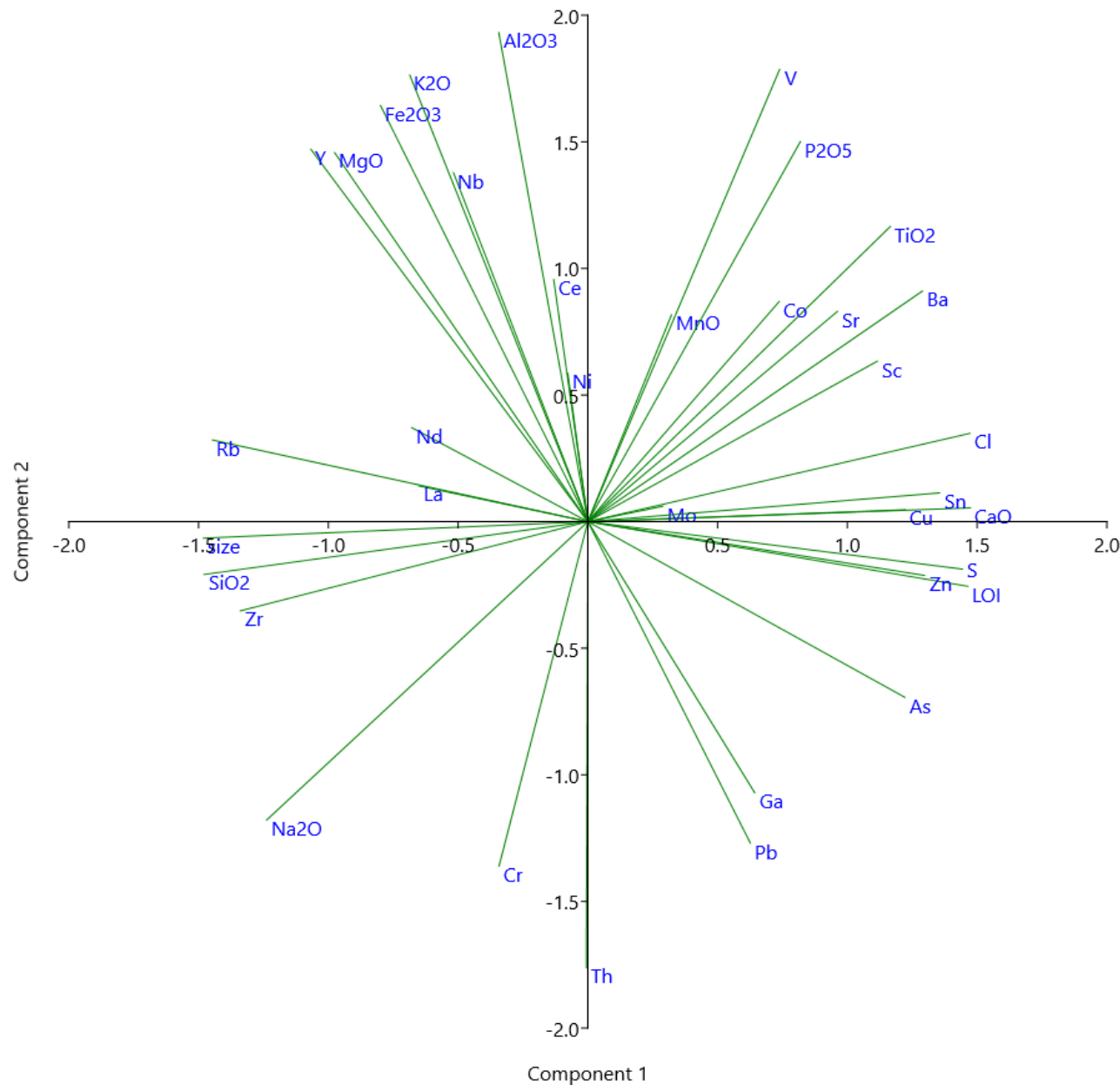
e) Forlì WtE plant

FORLÌ	Grain size	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	As	Ba	Ce	Cl	Co	Cr	Cu	Ga	Hf	La	Mo	Nb	Nd	Ni	Pb	Rb	S	Sc	Sn	Sr	Th	V	Y	Zn	Zr
Grain size	-	2E-05	0,696	0,225	0,0424	0,209	0,338	0,001	0,025	0,029	0,230	0,000	0,113	0,887	0,016	0,271	0,008	0,228	0,053	0,157	0,814	0,347	0,137	0,192	0,416	0,091	0,157	0,031	0,0052	0,208	4E-05	4E-05	0,097	0,675	0,698	0,000	0,006
SiO ₂	0,969	-	0,655	0,190	0,0443	0,153	0,273	0,000	0,022	0,011	0,201	0,000	0,080	0,815	0,012	0,179	0,024	0,175	0,014	0,117	0,722	0,371	0,087	0,150	0,465	0,180	0,111	0,013	0,0011	0,326	1E-06	1E-05	0,053	0,653	0,687	0,001	0,002
TiO ₂	-0,152	-0,173	-	0,497	0,1059	0,001	0,113	0,173	0,072	0,921	0,001	0,481	0,006	4E-06	0,138	0,571	0,620	0,000	0,776	0,002	0,206	0,206	0,008	0,081	0,233	0,513	0,008	0,031	0,1927	0,725	0,477	0,775	0,019	0,003	6E-06	0,297	0,734
Al ₂ O ₃	0,449	0,481	0,261	-	0,0670	0,919	0,100	0,334	0,830	0,002	0,806	0,447	0,831	0,638	0,947	0,873	0,718	0,913	0,213	0,731	0,499	0,487	0,519	0,015	0,569	0,820	0,842	0,434	0,3658	0,112	0,247	0,158	0,707	0,233	0,581	0,712	0,209
Fe ₂ O ₃	0,683	0,679	0,574	0,634	-	0,609	0,006	0,276	0,832	0,033	0,516	0,153	0,868	0,084	0,536	0,580	0,318	0,487	0,088	0,700	0,405	0,872	0,878	0,001	0,973	0,646	0,837	0,741	0,2869	0,637	0,104	0,046	0,936	0,009	0,119	0,254	0,011
MnO	0,464	0,518	-0,894	-0,040	-0,1983	-	0,621	0,011	0,022	0,434	0,000	0,134	1E-06	0,003	0,009	0,256	0,443	2E-06	0,626	0,000	0,207	0,191	0,001	0,473	0,165	0,522	6E-06	0,001	0,0108	0,678	0,101	0,274	5E-05	0,112	0,001	0,059	0,469
MgO	0,362	0,410	0,564	0,583	0,8289	-0,192	-	0,557	0,492	0,060	0,506	0,720	0,861	0,166	0,760	0,808	0,761	0,400	0,372	0,665	0,963	0,880	0,830	0,011	0,850	0,899	0,956	0,942	0,5009	0,756	0,484	0,430	0,882	0,001	0,153	0,824	0,046
CaO	-0,897	-0,926	0,498	-0,365	-0,4080	-0,789	-0,227	-	0,005	0,033	0,017	0,001	0,003	0,245	0,001	0,151	0,063	0,016	0,085	0,007	0,743	0,233	0,008	0,480	0,253	0,195	0,006	0,000	9E-06	0,285	0,000	0,003	0,002	0,797	0,168	0,000	0,021
Na ₂ O	0,731	0,742	-0,625	0,084	0,0832	0,741	-0,264	-0,836	-	0,332	0,023	0,002	0,021	0,171	0,008	0,080	0,018	0,010	0,100	0,019	0,706	0,199	0,037	0,971	0,747	0,171	0,049	0,007	0,0070	0,157	0,004	0,016	0,040	0,233	0,097	0,001	0,186
K ₂ O	0,718	0,791	0,039	0,879	0,7080	0,299	0,647	-0,707	0,367	-	0,560	0,083	0,253	0,999	0,239	0,519	0,365	0,488	0,043	0,252	0,758	0,990	0,152	0,028	0,346	0,534	0,259	0,069	0,0409	0,247	0,024	0,019	0,157	0,310	0,981	0,168	0,019
P ₂ O ₅	-0,445	-0,470	0,914	0,096	0,2504	-0,991	0,256	0,760	-0,740	-0,225	-	0,154	8E-06	0,002	0,009	0,306	0,414	4E-06	0,769	3E-05	0,161	0,178	0,002	0,366	0,163	0,453	0,000	0,002	0,0200	0,593	0,129	0,330	0,000	0,082	0,000	0,065	0,554
LOI	-0,940	-0,947	0,271	-0,291	-0,5180	-0,540	-0,140	0,893	-0,875	-0,607	0,517	-	0,083	0,708	0,007	0,162	0,002	0,121	0,014	0,109	0,578	0,348	0,120	0,367	0,627	0,126	0,133	0,018	0,0038	0,225	5E-06	4E-05	0,077	0,952	0,518	0,000	0,014
As	0,565	0,612	-0,828	0,084	-0,0648	0,986	-0,069	-0,858	0,745	0,426	-0,975	-0,608	-	0,009	0,004	0,289	0,358	0,000	0,503	3E-06	0,199	0,231	0,000	0,673	0,110	0,443	0,000	0,000	0,0040	0,550	0,052	0,171	2E-06	0,212	0,004	0,036	0,303
Ba	-0,056	-0,091	0,979	0,183	0,6062	-0,865	0,505	0,433	-0,499	0,000	0,878	0,146	-0,805	-	0,233	0,760	0,901	0,001	0,640	0,003	0,131	0,308	0,007	0,084	0,160	0,654	0,008	0,043	0,2687	0,781	0,648	0,973	0,022	0,006	0,000	0,503	0,619
Ce	0,766	0,788	-0,535	0,026	0,2387	0,803	0,119	-0,906	0,813	0,437	-0,801	-0,821	0,844	-0,443	-	0,109	0,110	0,017	0,149	0,015	0,538	0,113	0,052	0,865	0,493	0,211	0,007	0,006	0,0010	0,523	0,006	0,041	0,005	0,705	0,121	0,001	0,030
Cl	-0,412	-0,492	0,219	-0,063	-0,2141	-0,423	-0,095	0,521	-0,612	-0,249	0,385	0,509	-0,398	0,119	-0,570	-	0,652	0,281	0,161	0,387	0,379	0,203	0,427	0,325	0,229	0,994	0,358	0,242	0,0461	0,643	0,134	0,208	0,331	0,947	0,680	0,128	0,146
Co	-0,811	-0,734	0,192	-0,141	-0,3762	-0,294	0,119	0,641	-0,759	-0,344	0,312	0,871	-0,349	0,049	-0,569	0,175	-	0,337	0,115	0,347	0,465	0,447	0,360	0,746	0,635	0,027	0,489	0,167	0,1530	0,169	0,013	0,006	0,396	0,694	0,685	0,005	0,175
Cr	0,447	0,496	-0,931	-0,043	-0,2675	0,984	-0,321	-0,765	0,798	0,267	-0,979	-0,555	0,960	-0,893	0,762	-0,404	-0,363	-	0,591	8E-06	0,328	0,202	0,000	0,394	0,202	0,434	0,000	0,001	0,0185	0,524	0,103	0,259	0,001	0,049	0,000	0,060	0,585
Cu	0,660	0,775	0,111	0,460	0,5990	0,189	0,339	-0,604	0,582	0,682	-0,115	-0,776	0,258	0,182	0,522	-0,509	-0,563	0,208	-	0,535	0,113	0,878	0,509	0,082	0,682	0,567	0,587	0,179	0,0701	0,419	0,013	0,009	0,391	0,461	0,718	0,057	0,010
Ga	0,514	0,560	-0,871	0,134	-0,1500	0,973	-0,168	-0,819	0,752	0,427	-0,964	-0,571	0,982	-0,861	0,771	-0,329	-0,356	0,975	0,240	-	0,251	0,284	0,000	0,584	0,099	0,394	1E-05	0,000	0,0111	0,397	0,072	0,199	6E-05	0,121	0,001	0,062	0,439
Hf	0,092	0,139	0,466	0,260	0,3179	-0,465	-0,018	0,128	0,147	0,120	0,509	-0,215	-0,472	0,543	-0,238	-0,334	-0,281	-0,369	0,565	-0,428	-	0,729	0,372	0,165	0,038	0,978	0,128	0,560	0,8501	0,501	0,677	0,415	0,207	0,524	0,113	0,880	0,658
La	0,356	0,340	-0,466	-0,267	-0,0631	0,480	-0,059	-0,443	0,473	-0,005	-0,492	-0,355	0,444	-0,383	0,565	-0,469	-0,291	0,470	0,060	0,402	-0,135	-	0,257	0,676	0,797	0,052	0,249	0,270	0,2302	0,835	0,331	0,525	0,283	0,567	0,342	0,192	0,385
Mo	0,536	0,600	-0,814	0,249	-0,0601	0,915	-0,084	-0,809	0,698	0,520	-0,879	-0,556	0,925	-0,817	0,662	-0,304	-0,347	0,920	0,254	0,951	-0,339	0,422	-	0,772	0,079	0,371	0,001	9E-05	0,0125	0,526	0,067	0,151	0,000	0,172	0,012	0,081	0,444
Nb	0,479	0,521	0,610	0,772	0,8911	-0,276	0,791	-0,271	0,014	0,721	0,343	-0,343	-0,164	0,606	0,067	-0,372	-0,126	-0,325	0,608	-0,212	0,506	-0,163	-0,113	-	0,554	0,915	0,642	0,902	0,3864	0,451	0,236	0,132	0,832	0,009	0,089	0,578	0,041
Nd	-0,310	-0,280	0,442	-0,220	-0,0131	-0,505	-0,074	0,426	-0,126	-0,356	0,507	0,189	-0,568	0,511	-0,264	-0,446	0,184	-0,469	0,159	-0,583	0,695	0,100	-0,614	0,228	-	0,654	0,087	0,148	0,4389	0,859	0,528	0,603	0,083	0,503	0,157	0,551	0,979
Ni	-0,595	-0,490	0,252	-0,089	-0,1784	-0,247	0,050	0,476	-0,500	-0,240	0,288	0,549	-0,294	0,174	-0,462	-0,003	0,727	-0,299	-0,222	-0,325	-0,011	-0,662	-0,340	0,042	0,174	-	0,505	0,304	0,3942	0,321	0,149	0,168	0,508	0,711	0,598	0,118	0,308
Pb	0,514	0,567	-0,814	0,078	-0,0806	0,977	-0,022	-0,824	0,669	0,421	-0,964	-0,540	0,993	-0,809	0,821	-0,348	-0,266	0,938	0,211	0,971	-0,547	0,429	0,911	-0,181	-0,600	-0,257	-	0,000	0,0076	0,662	0,084	0,243	1E-06	0,250	0,004	0,065	0,324
Rb	0,712	0,779	-0,712	0,299	0,1291	0,911	0,028	-0,937	0,822	0,630	-0,874	-0,757	0,947	-0,682	0,829	-0,435	-0,504	0,908	0,491	0,947	-0,225	0,412	0,949	0,048	-0,524	-0,386	0,923	-	0,0005	0,374	0,007	0,034	6E-05	0,349	0,034	0,012	0,142
S	-0,834	-0,896	0,478	-0,343	-0,3994	-0,793	-0,259	0,974	-0,819	-0,687	0,750	0,849	-0,847	0,413	-0,897	0,675	0,518	-0,756	-0,628	-0,791	0,074	-0,445	-0,783	-0,330	0,296	0,325	-0,814	-0,915	-	0,386	0,001	0,007	0,003	0,877	0,198	0,002	0,018
Sc	0,464	0,371	-0,137	0,566	0,1834	0,161	-0,121	-0,401	0,513	0,431	-0,207	-0,449	0,231	-0,108	0,246	-0,180	-0,501	0,245	0,309	0,323	0,259	-0,082	0,244	0,289	-0,069	-0,374	0,170	0,338	-0,330	-	0,207	0,179	0,719	0,740	0,580	0,336	0,564
Sn	-0,961	-0,985	0,273	-0,431	-0,5762	-0,580	-0,269	0,945	-0,841	-0,737	0,545	0,978	-0,661	0,177	-0,830	0,540	0,783	-0,579	-0,779	-0,625	-0,162	-0,367	-0,634	-0,440	0,244	0,522	-0,606	-0,817	0,914	-0,465	-	1E-05	0,042	0,906	0,502	0,000	0,005
Sr	-0,959	-0,971	0,112	-0,513	-0,6762	-0,409	-0,302	0,859	-0,767	-0,755	0,368	0,960	-0,500	0,013	-0,686	0,464	0,824	-0,421	-0,805	-0,472	-0,311	-0,245	-0,520	-0,542	0,202	0											

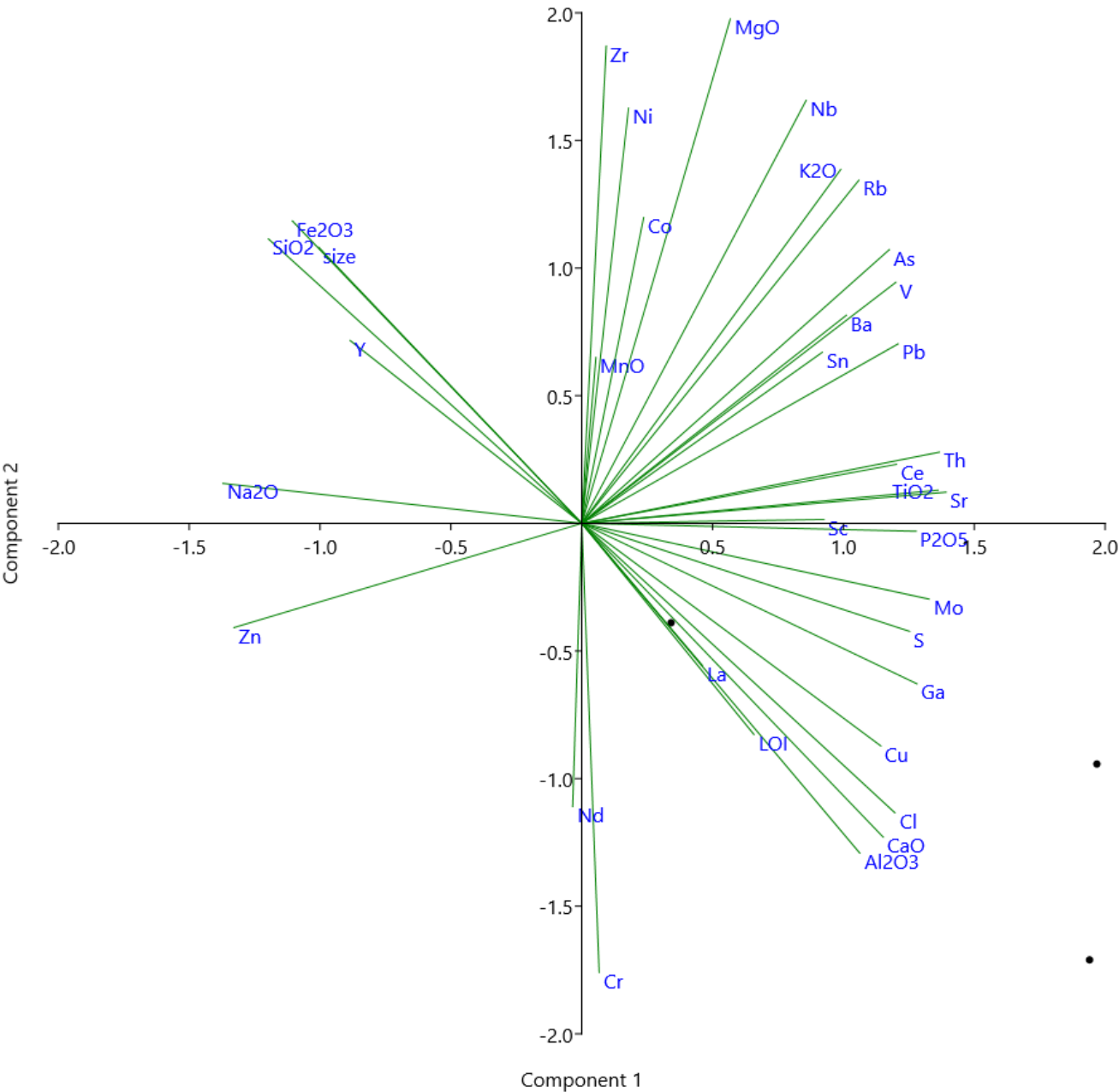
APPENDIX VIII

XRF results analysed by PCA for 5 WtE investigated.

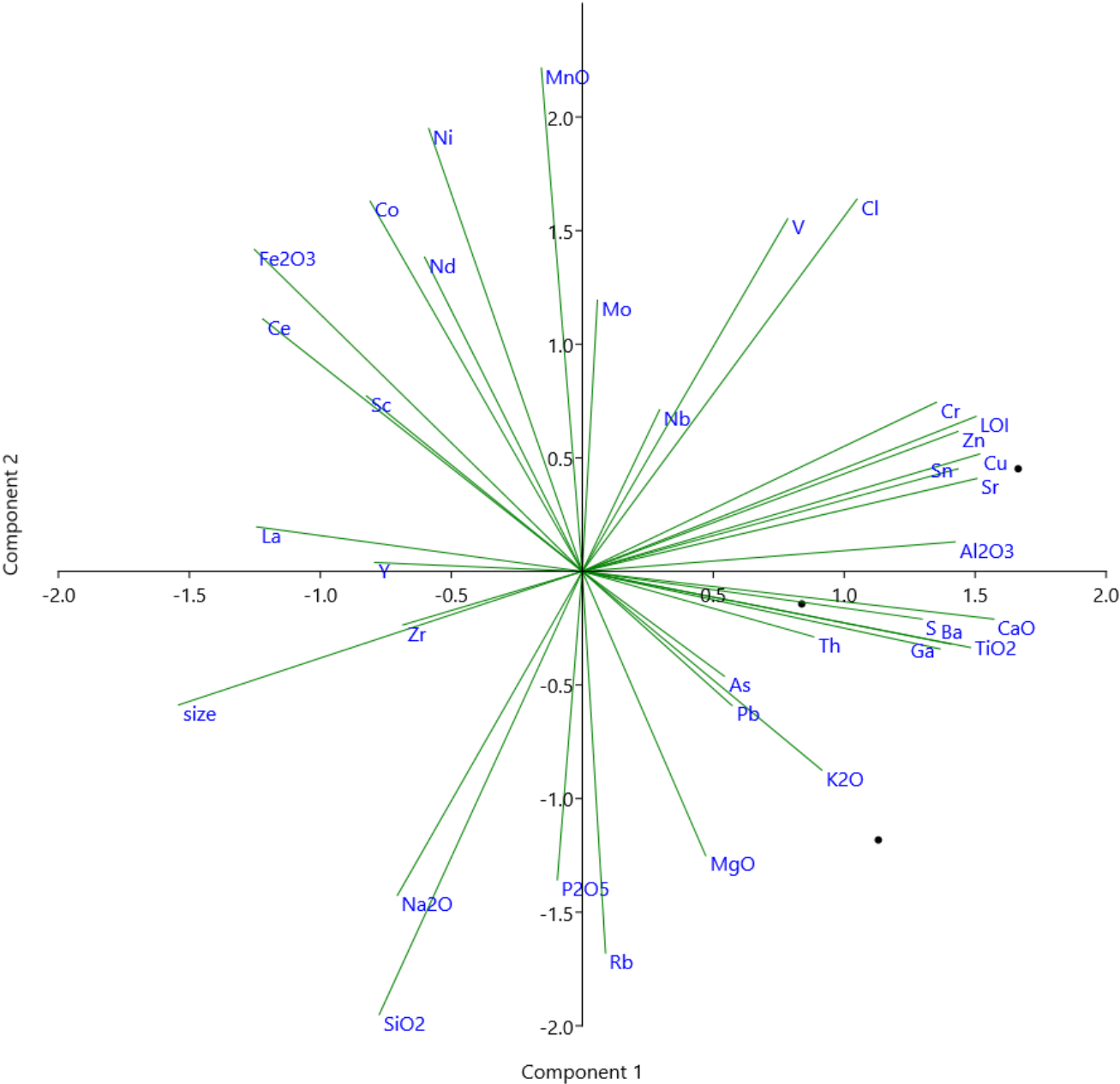
a) Parma WtE plant



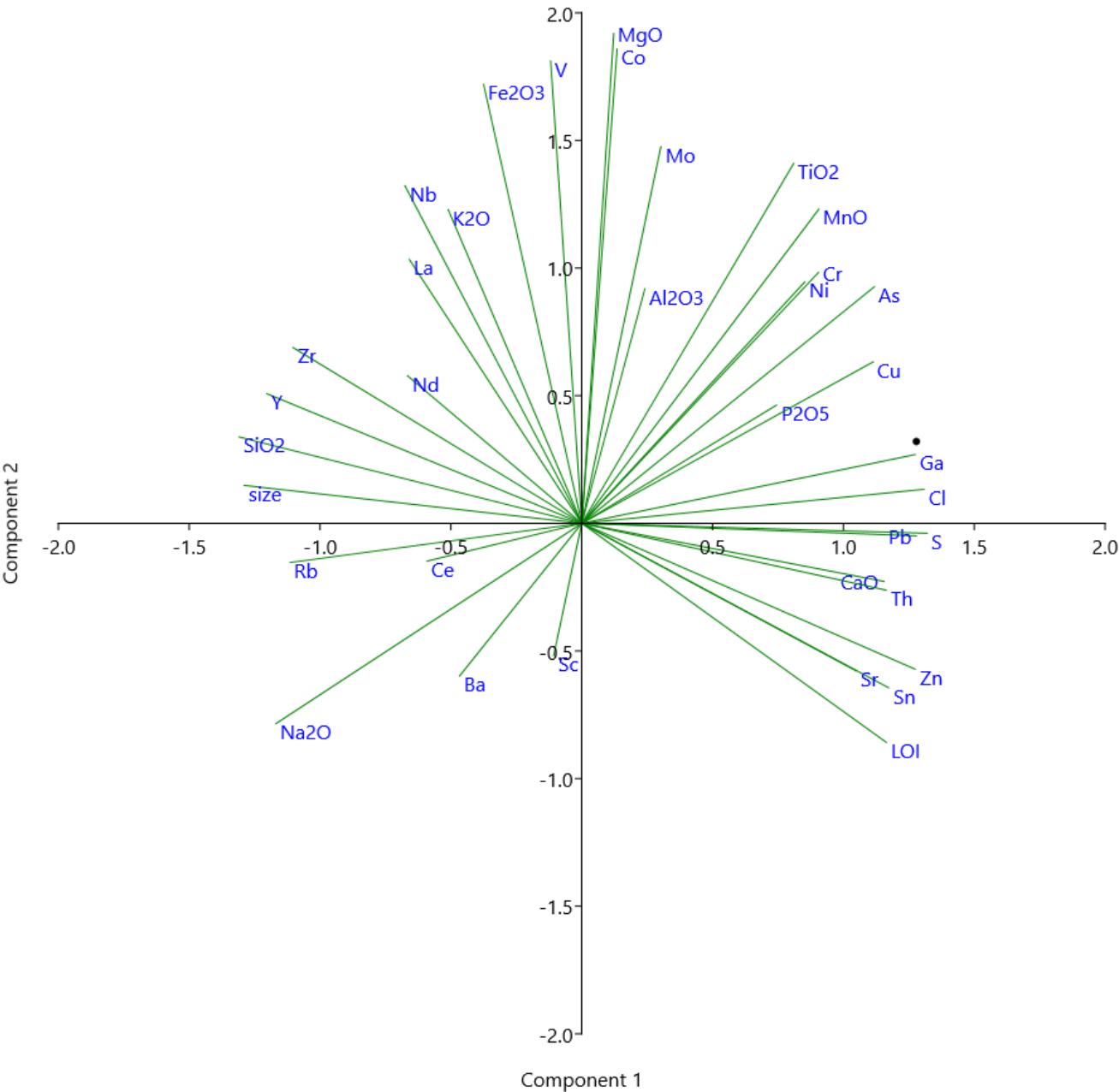
b) Piacenza WtE plant



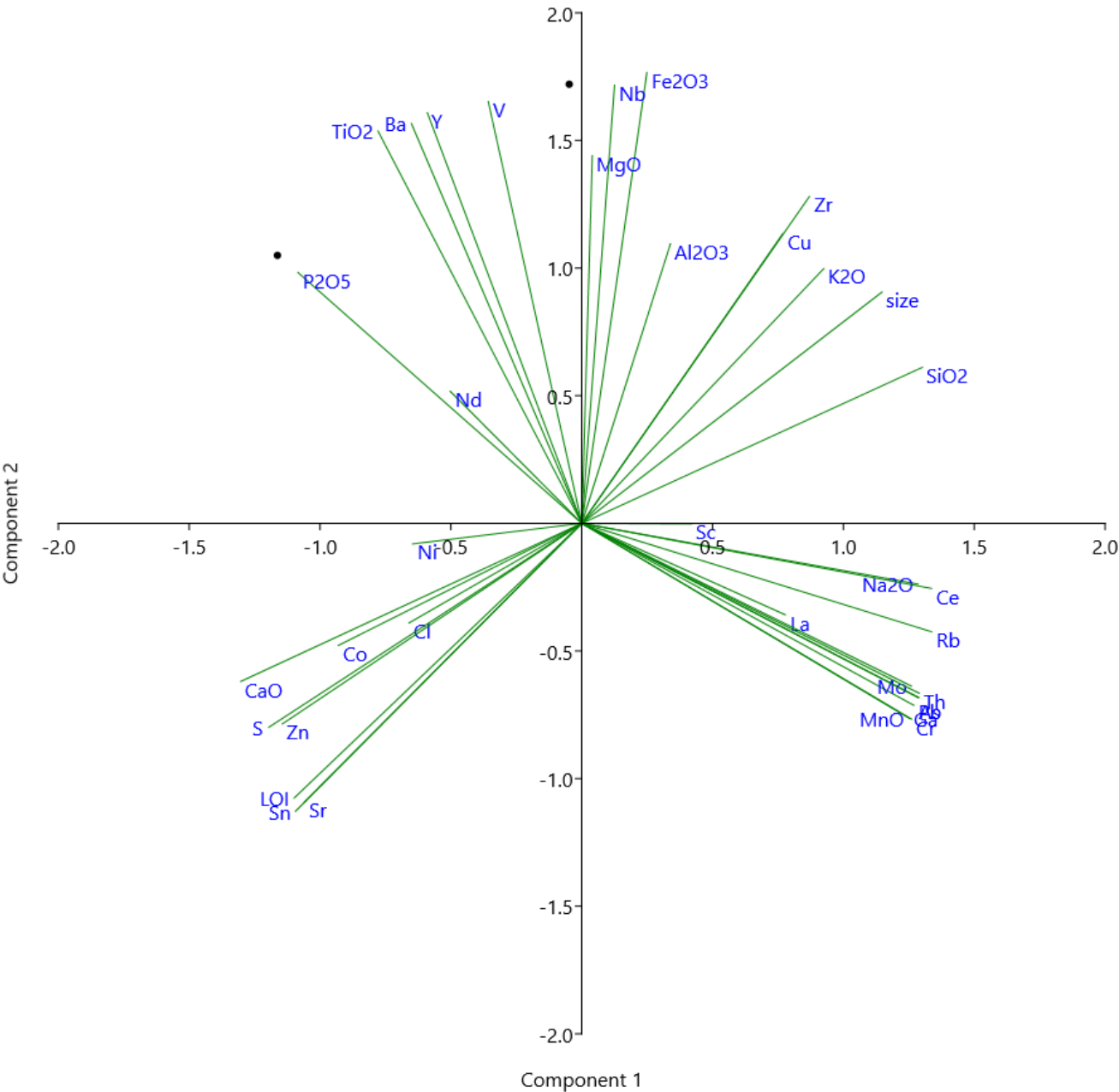
c) Torino WtE plant



d) Ferrara WtE plant



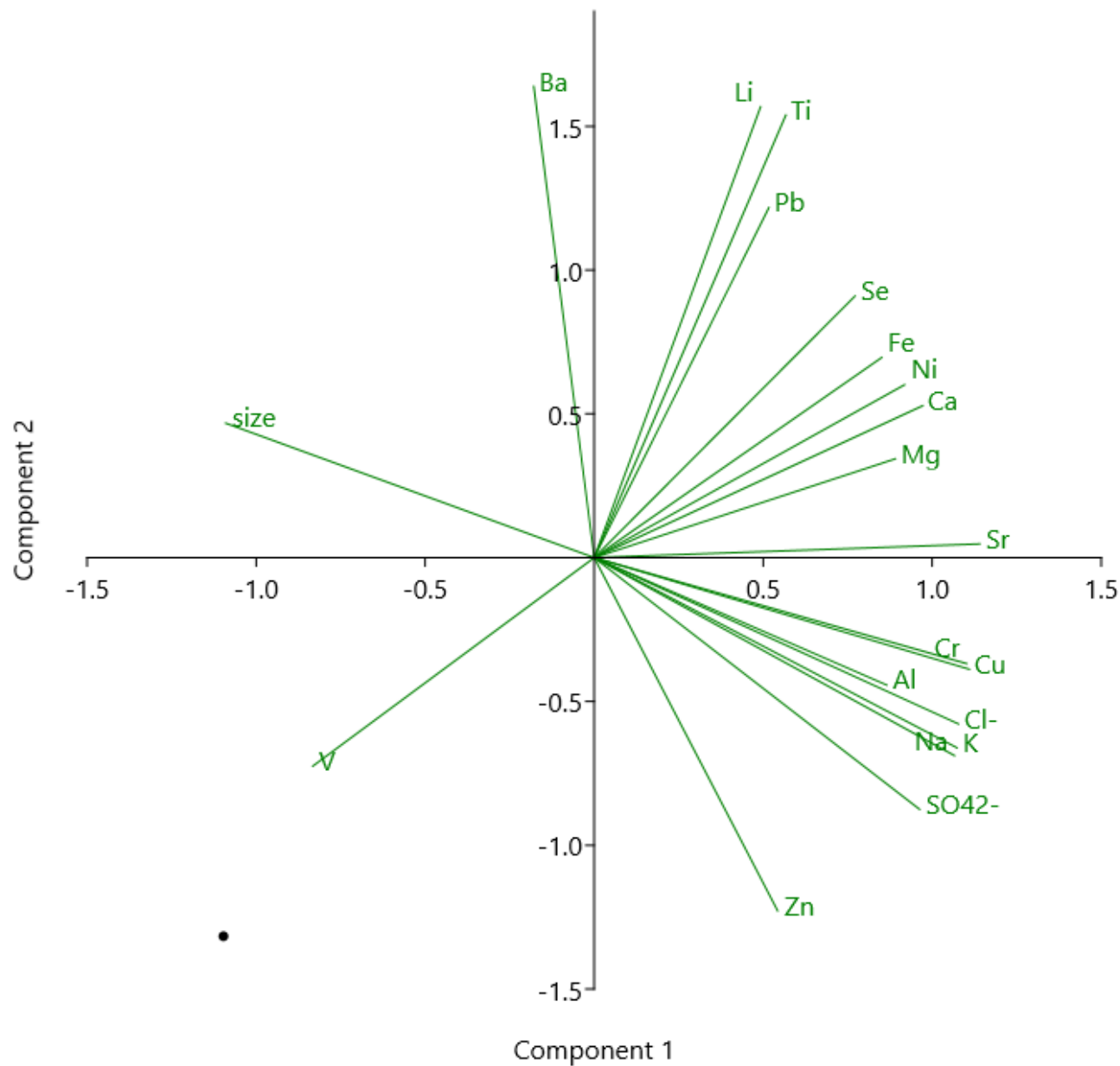
e) Forlì WtE plants



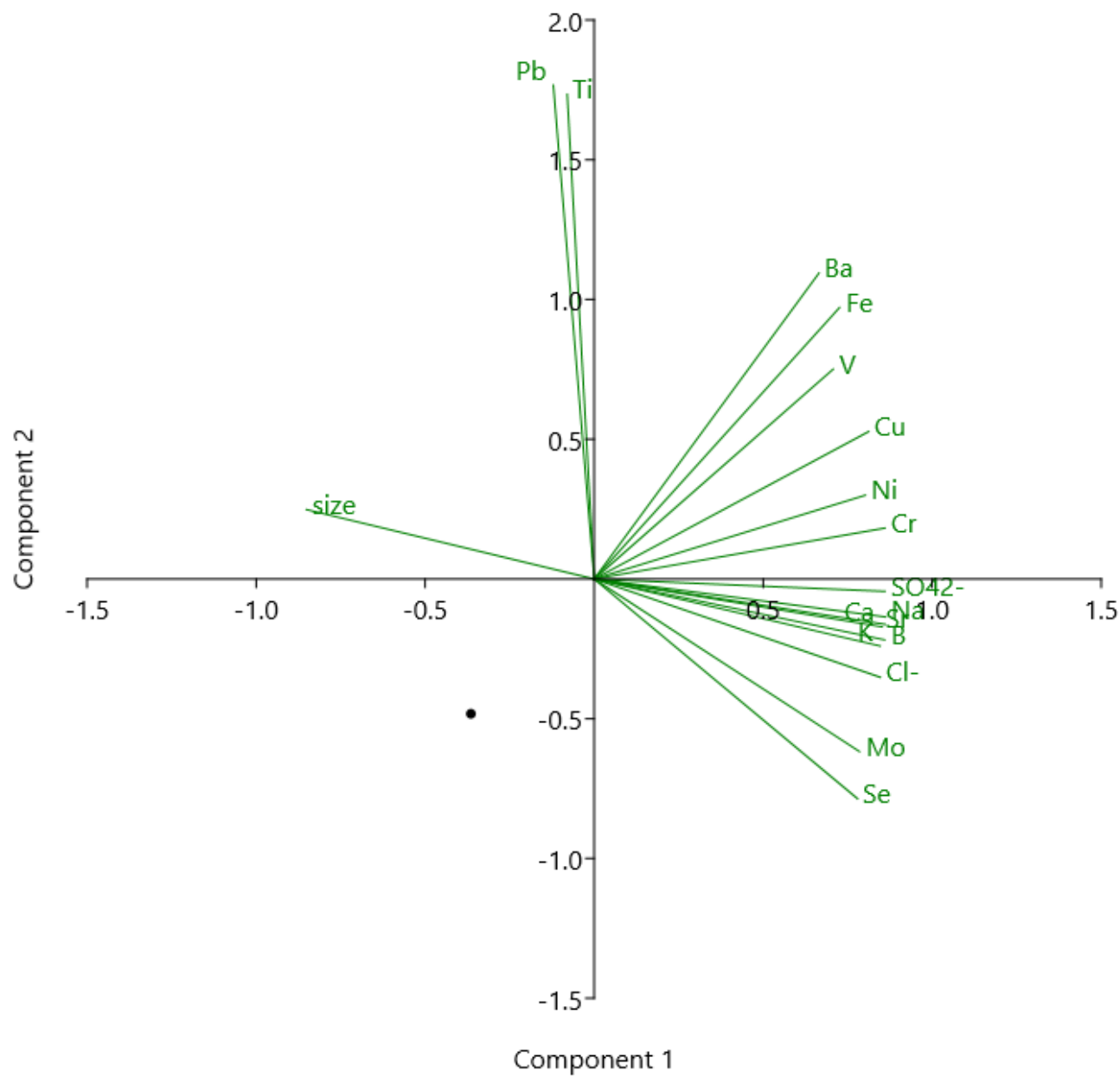
APPENDIX IX

Leaching test results analysed by PCA for 5 WtE investigated.

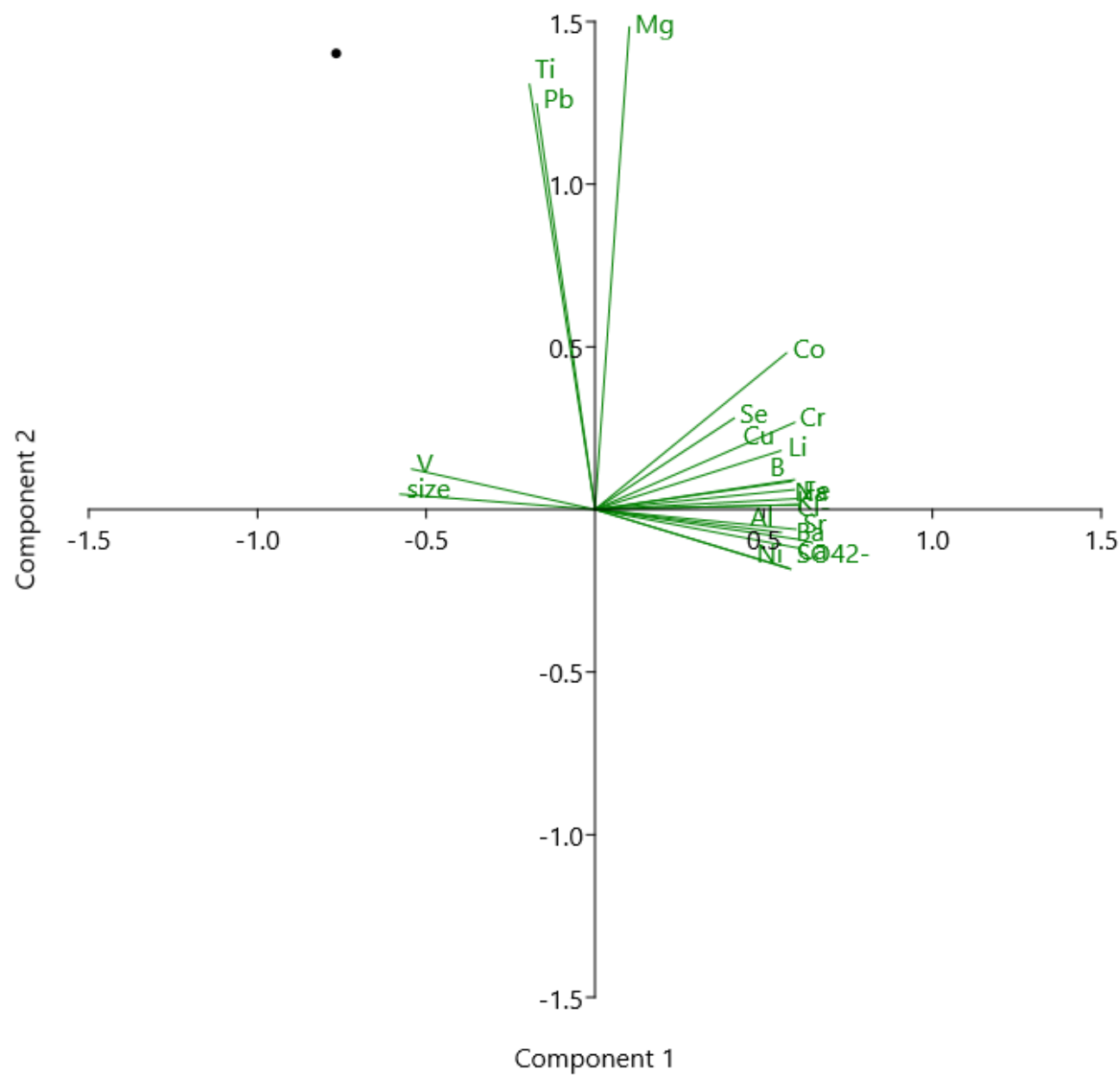
a) Parma WtE plant



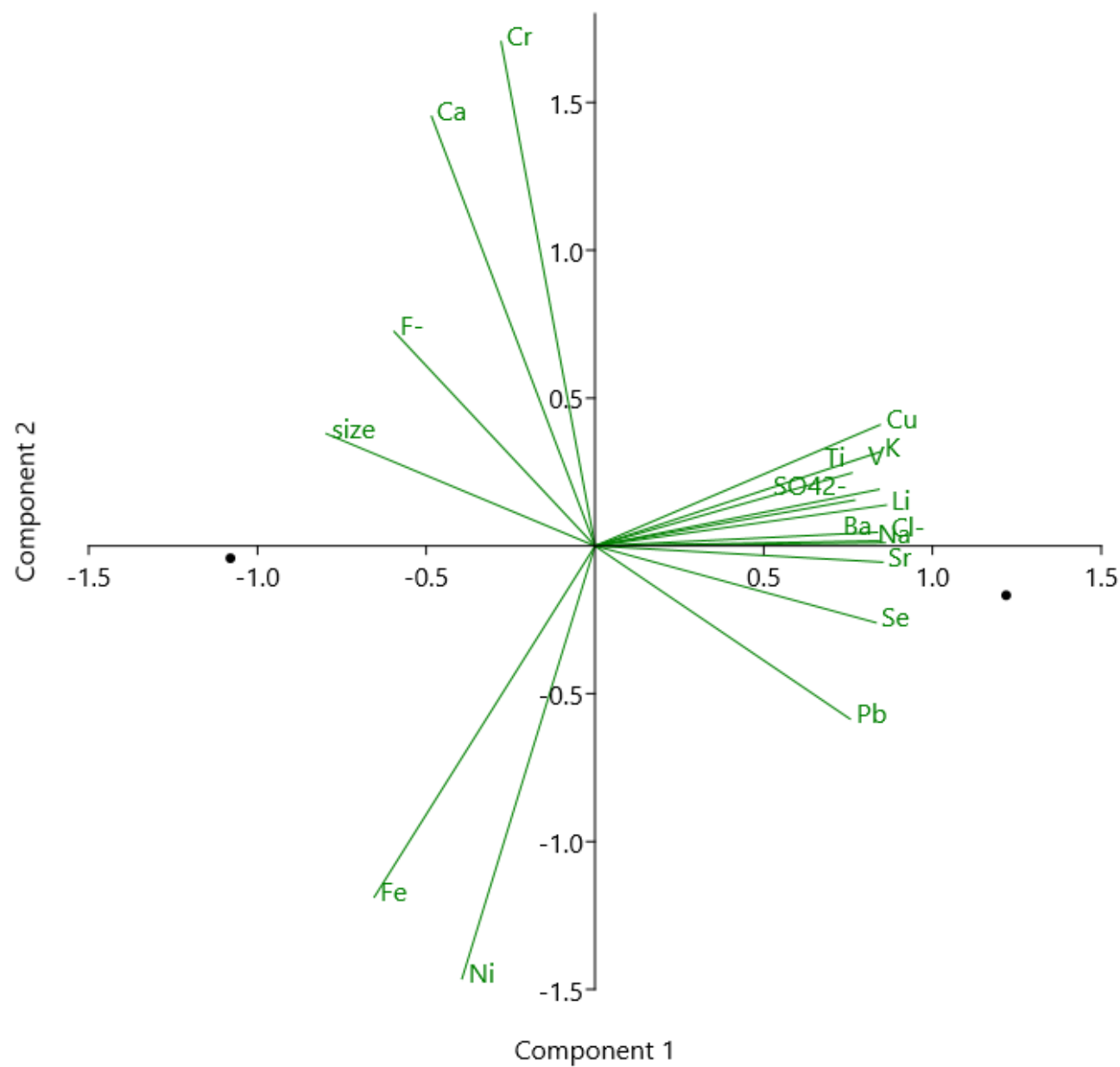
b) Piacenza WtE plant



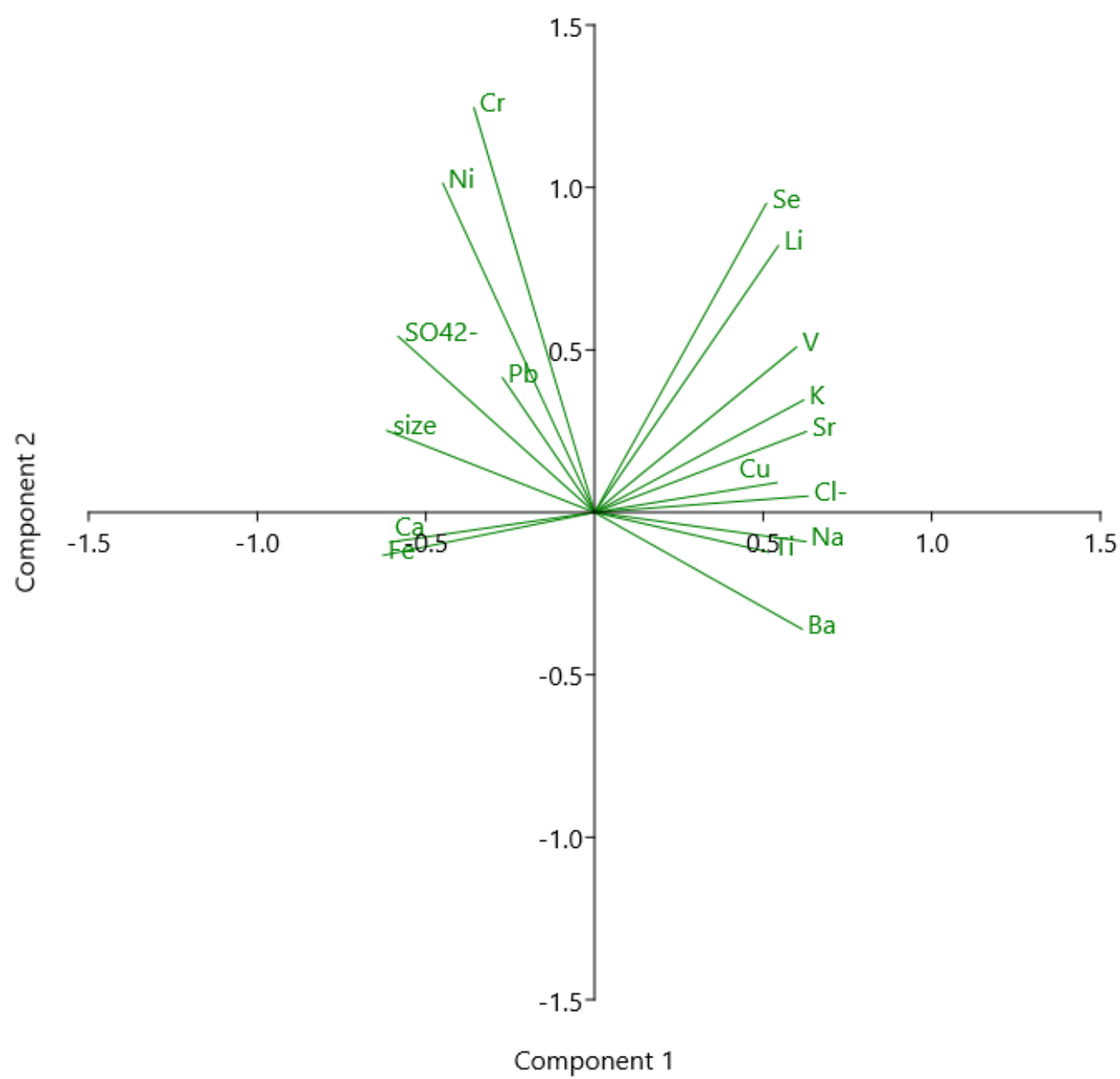
c) Torino WtE plant



d) Ferrara WtE plant

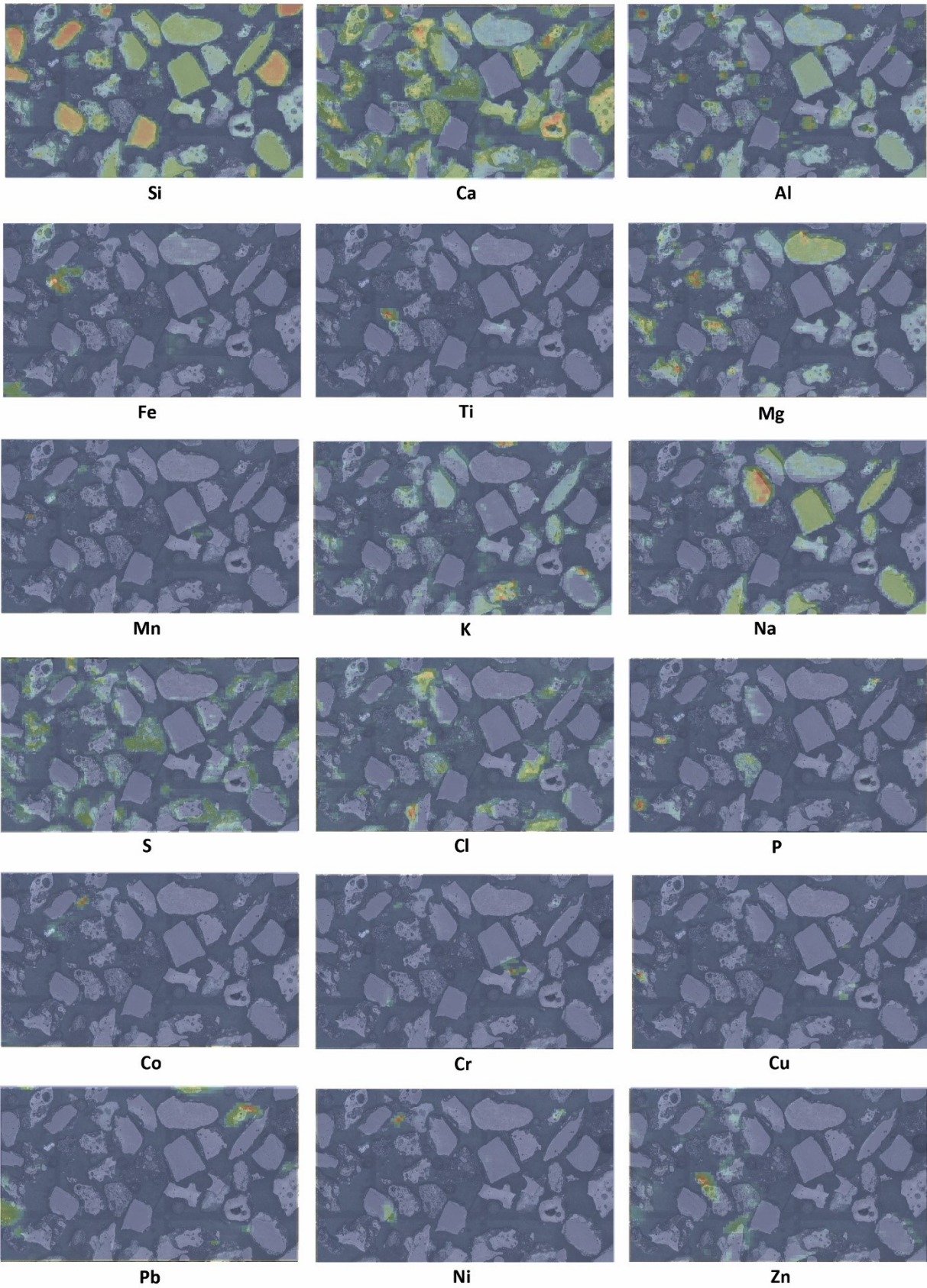


e) Forlì WtE plant

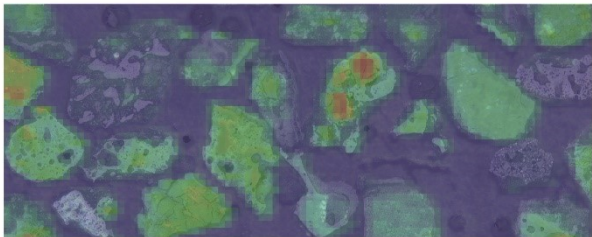


APPENDIX X

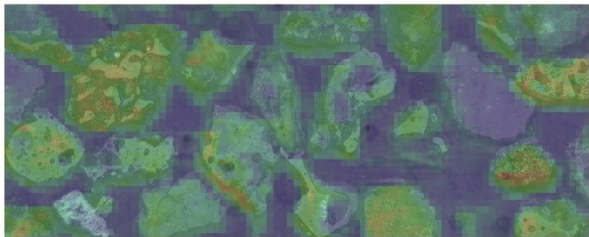
Overlay of optical images, SEM – EDS and μ - XRF map collected in **AREA 1**



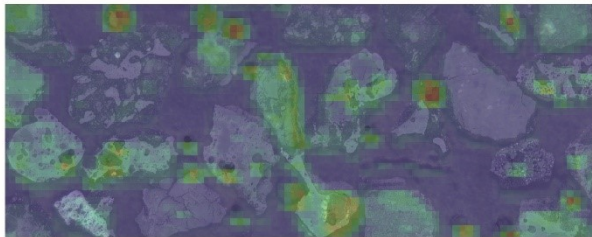
Overlay of optical images, SEM – EDS and μ - XRF map collected in **AREA 2**



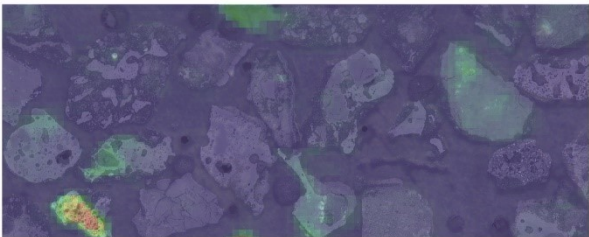
Si



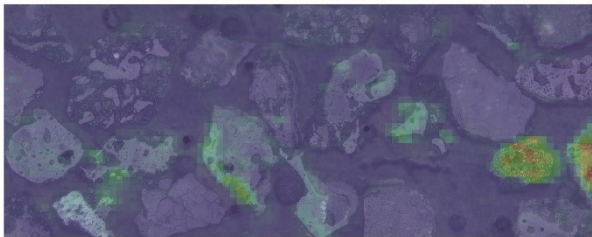
Ca



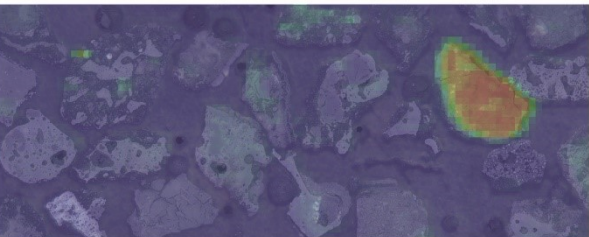
Al



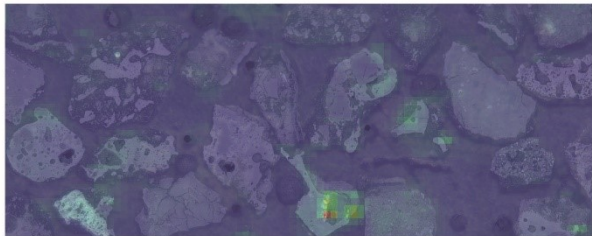
Fe



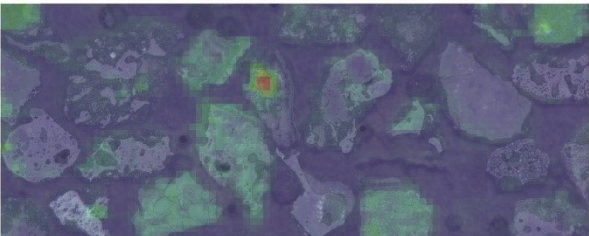
Ti



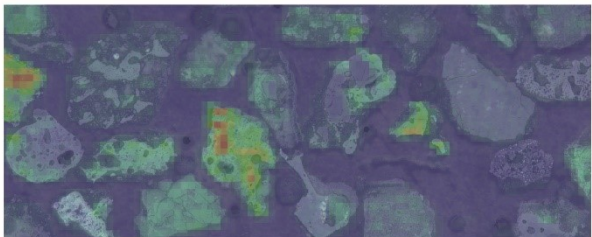
Mg



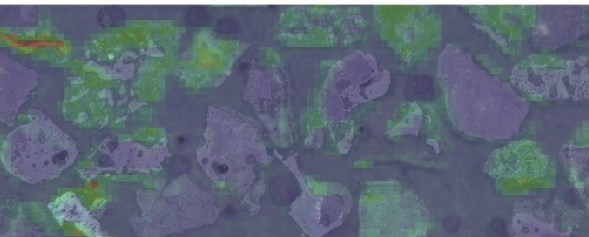
Mn



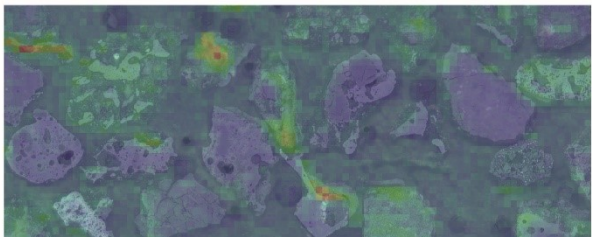
K



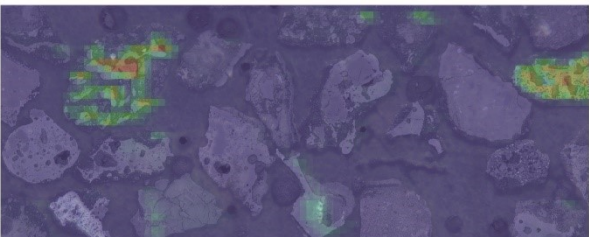
Na



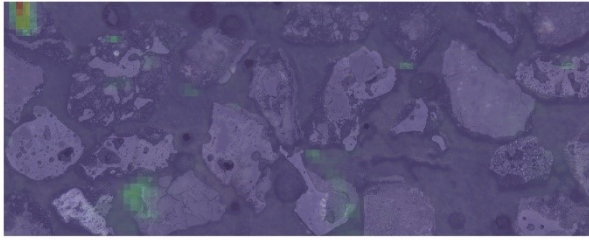
S



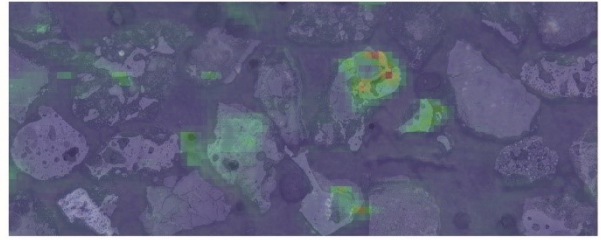
Cl



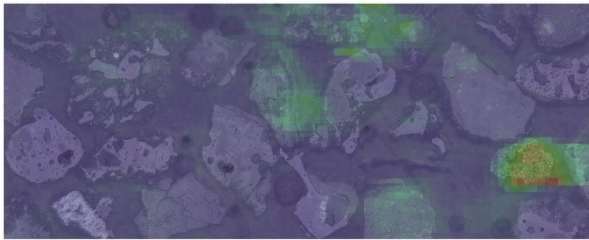
P



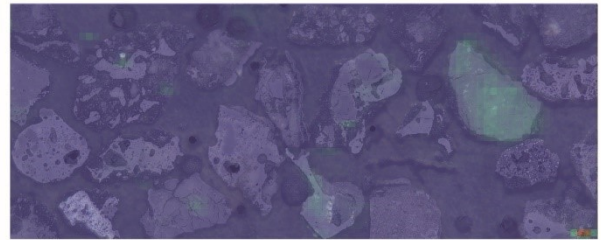
Cr



Cu



Pb

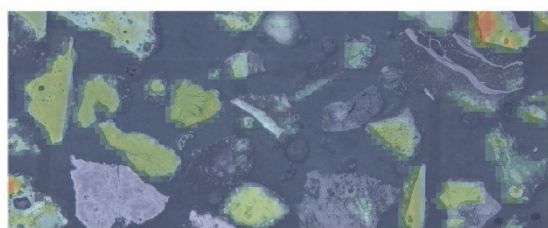


Ni

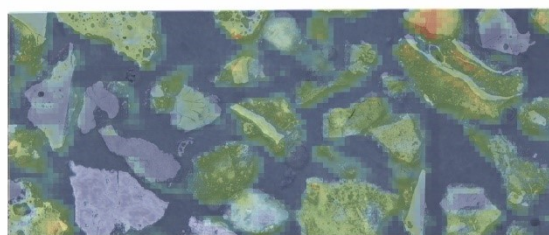


Zn

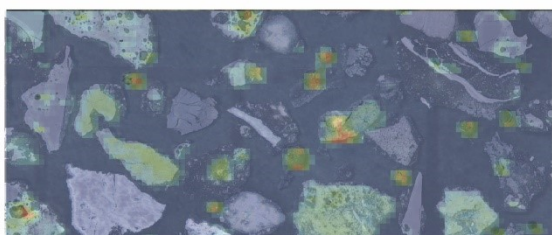
Overlay of optical images, SEM – EDS and μ - XRF map collected in **AREA 3**



Si



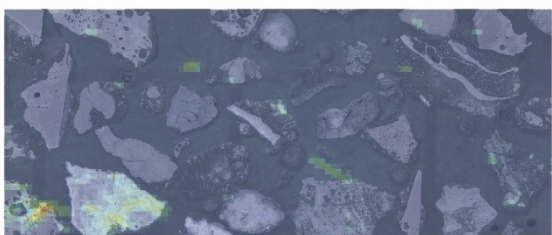
Ca



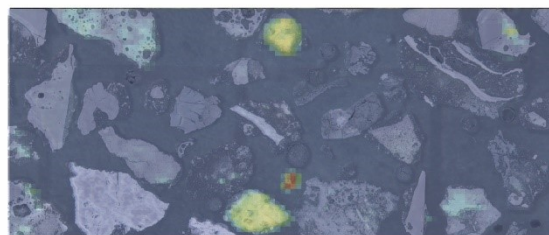
Al



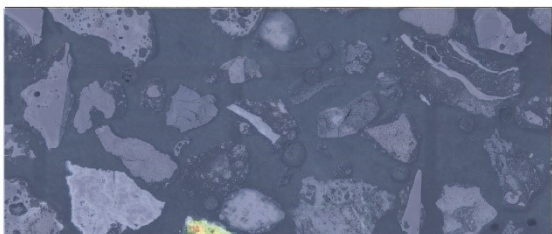
Fe



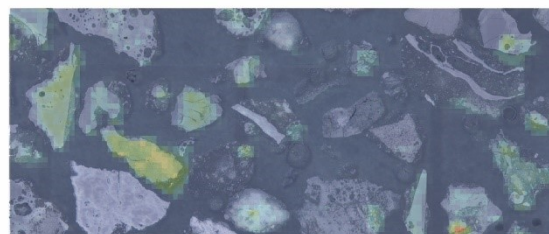
Ti



Mg



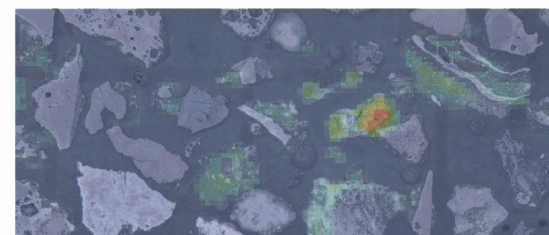
Mn



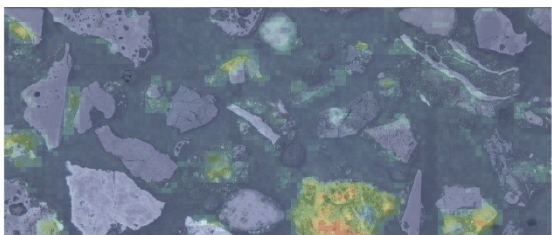
K



Na



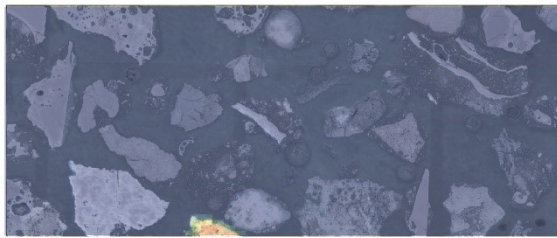
S



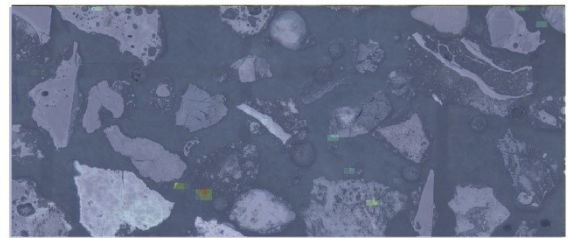
Cl



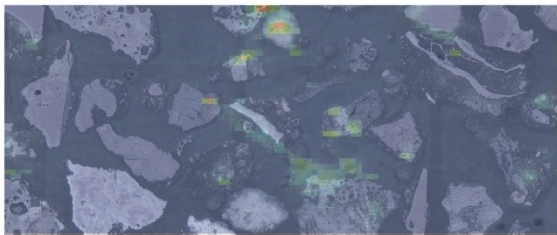
P



Co



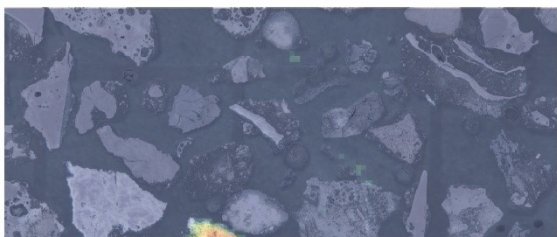
Cr



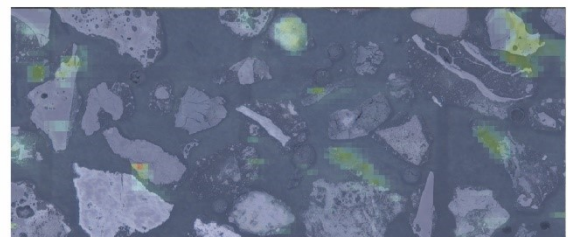
Cu



Pb



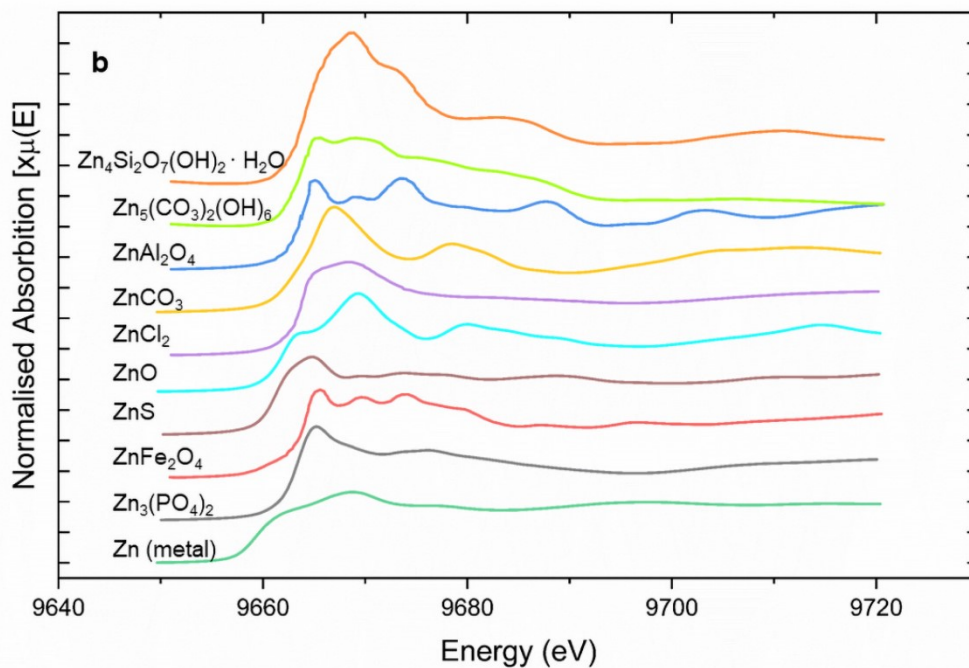
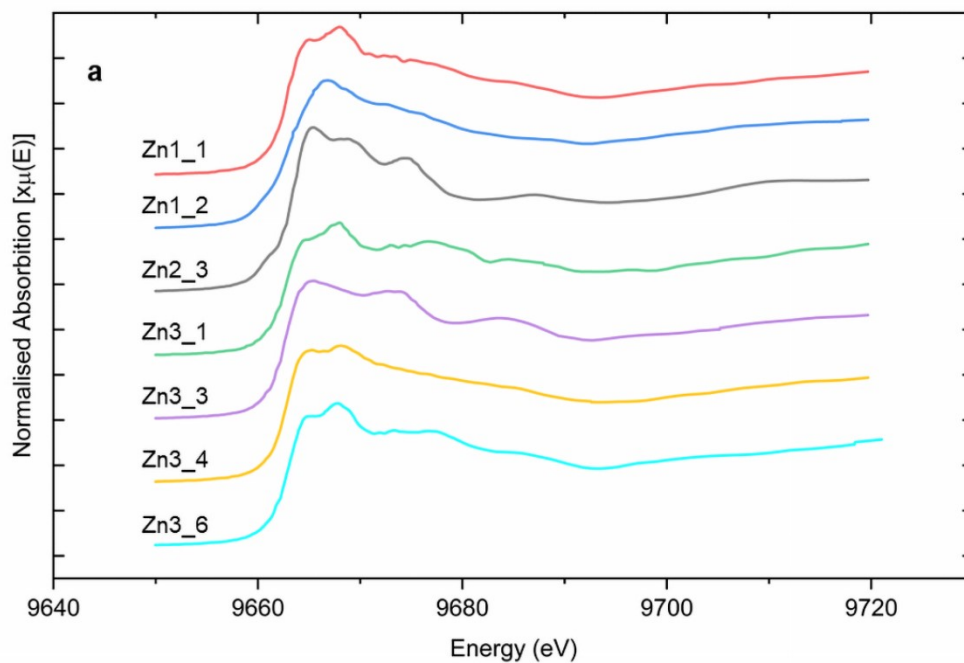
Ni



Zn

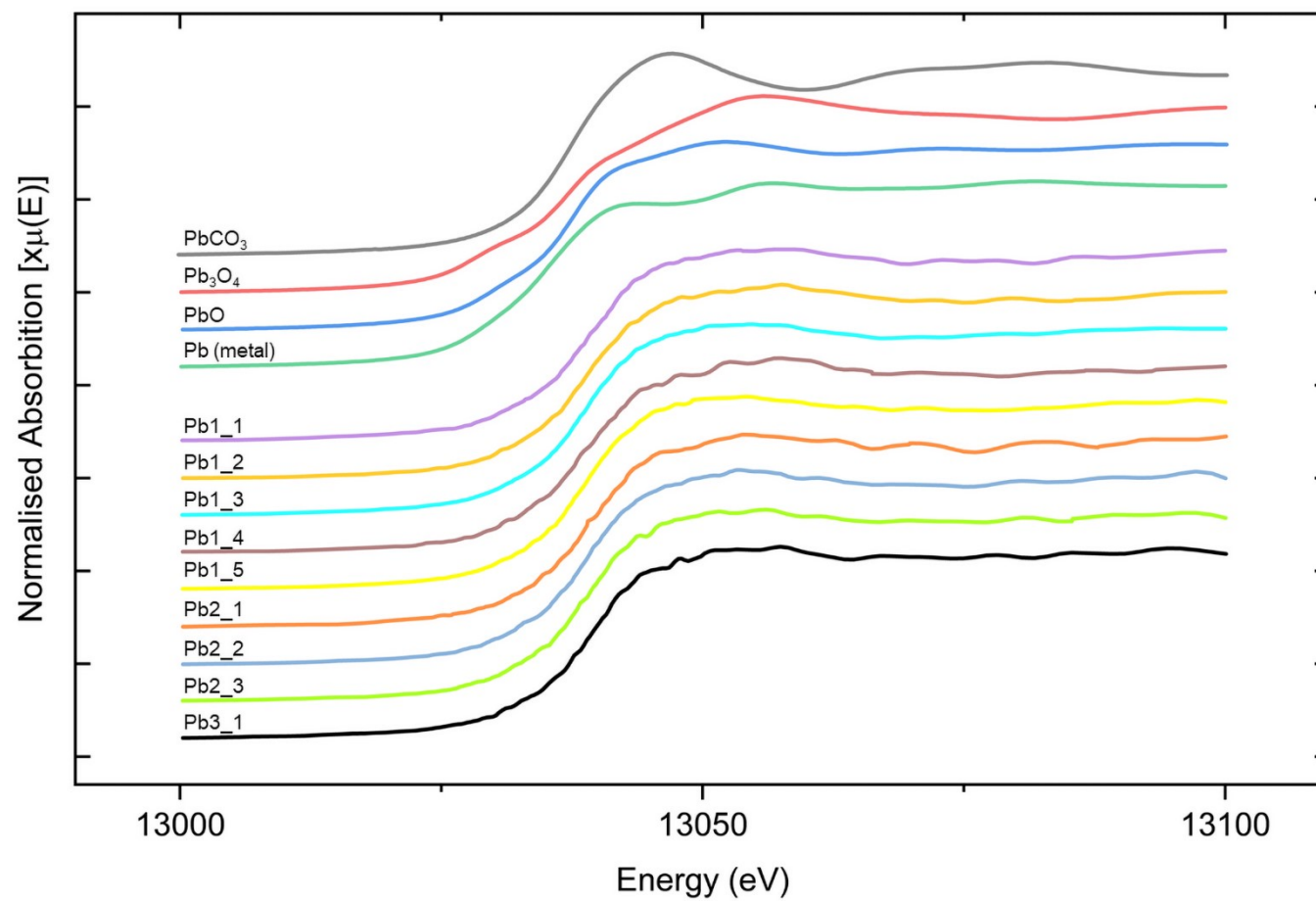
APPENDIX XI

Normalized Zn XANES spectra of reference materials (b) and seven selected spectra of BA samples (a). $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$, ZnAl_2O_4 , ZnCl_2 and ZnFe_2O_4 spectra have been extracted from Rissler et al. (2020).



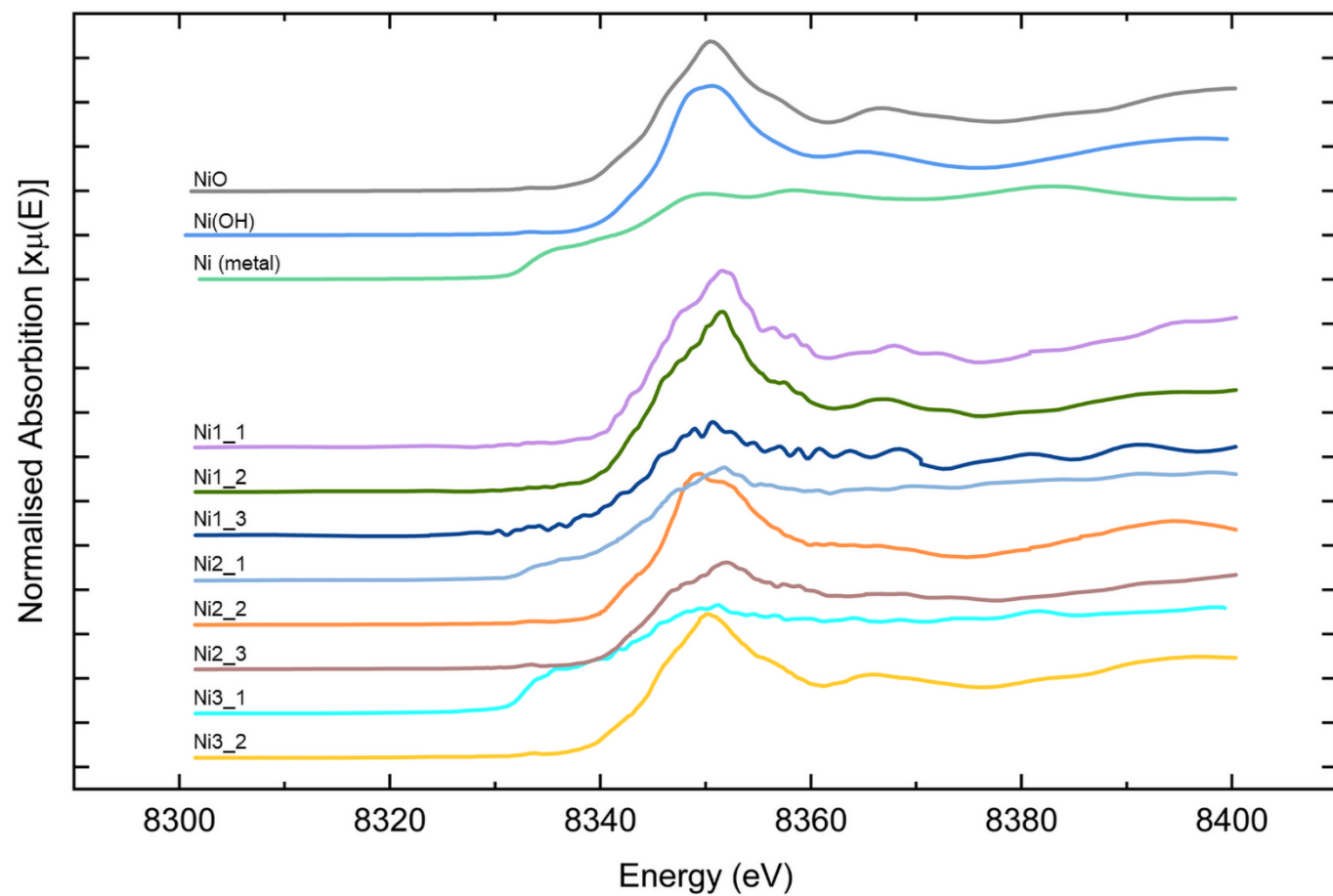
APPENDIX XII

Normalized Pb XANES spectra of reference materials (top) and collected on various clasts of the BA samples (bottom).



APPENDIX XIII

Normalized Ni XANES spectra of reference materials (top) and collected on various clasts of the BA samples (bottom).



APPENDIX XIV

Results of the LCF analysis performed on the spectra collected at the Cr K-edge on BA clasts (reported quantities are %; sigmas in brackets).

Compounds	<i>Cr1_1</i>	<i>Cr2_1</i>	<i>Cr2_2</i>	<i>Cr3_1</i>
<i>Metal Cr</i>	23 (3)	27 (1)		24 (2)
<i>FeCr₂O₄</i>	77 (3)	73 (1)	60 (4)	
<i>Cr₂O₃</i>			40 (4)	76 (1)

APPENDIX XV

Results of the LCF analysis performed on the spectra collected at the Pb L₃-edge on BA clasts (reported quantities are %; sigmas in brackets).

Compounds	<i>Pb1_1</i>	<i>Pb1_2</i>	<i>Pb1_3</i>	<i>Pb1_4</i>	<i>Pb1_5</i>	<i>Pb2_1</i>	<i>Pb2_2</i>	<i>Pb2_3</i>	<i>Pb3_1</i>
<i>PbCO₃</i>	31 (5)	29 (5)	40 (4)	25 (5)	43 (4)	29 (5)	38 (5)	37 (5)	29 (5)
<i>Pb₃O₄</i>	69 (5)	71 (5)	60 (4)	75 (5)	57 (4)	71 (5)	62 (5)	63 (5)	71 (5)

APPENDIX XVI

Results of the LCF analysis performed on the spectra collected at the Ni K-edge on BA clasts (reported quantities are %; sigmas in brackets).

Compounds	<i>Ni1_1</i>	<i>Ni1_2</i>	<i>Ni1_3</i>	<i>Ni2_1</i>	<i>Ni2_2</i>	<i>Ni2_3</i>	<i>Ni3_1</i>	<i>Ni3_2</i>
<i>Metal Ni</i>			35 (3)	66 (2)		28 (11)	84 (5)	
<i>NiO</i>	17 (10)	40 (16)	13 (10)	34 (16)		49 (9)	16 (20)	67 (7)
<i>Ni(OH)₂</i>	83 (10)	60 (12)	52 (14)		100	23 (8)		33 (4)

APPENDIX XVII

Sequential extraction procedure XRF results from Parma WtE plants samples

SAMPLE	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	As	Mo	Nb	Pb	Rb	Sb	Se	Sr	Th	U	Y	Zr	Br	Ba	Ce	Co	Cr	Cu	Ga	La	Ni	S	Sc	V	Zn
BULK <4 S0	34,57	1,09	13,29	4,71	0,11	3,51	26,72	3,13	1,73	1,83	9,30	8	13	<3	410	4	<3	<3	434	10	<3	<3	33	26	524	51	8	489	830	5	30	177	23200	<3	42	5360
BULK <4 S1	34,83	1,00	15,29	4,04	0,10	3,62	24,51	2,46	1,37	1,61	11,17	8	18	<3	1970	6	142	<3	301	6	<3	<3	37	4	1269	95	31	559	790	5	23	108	18840	<3	38	4710
BULK <4 S2	53,41	1,38	14,51	7,89	0,12	3,48	9,24	4,78	1,55	1,39	2,27	<3	18	6	140	10	66	<3	253	9	<3	11	29	4	1138	26	27	764	2630	6	33	237	1940	<3	66	5380
BULK <4 S3	55,79	1,16	15,31	6,08	0,09	3,68	7,68	3,69	1,46	1,15	3,92	<3	17	5	180	12	168	<3	182	11	<3	3	33	3	654	41	22	850	700	11	13	149	1120	<3	58	1830
BULK <4 S4	53,33	1,71	15,85	8,88	0,15	3,09	7,91	3,44	1,87	1,34	2,41	<3	21	7	230	16	180	<3	171	12	6	6	28	<3	815	61	40	639	740	12	16	152	550	<3	83	2390
0.063-0.2 S0	19,38	0,98	11,60	2,71	0,10	2,96	32,93	2,38	1,30	1,91	23,76	10	18	<3	850	<3	269	<3	501	11	<3	<3	30	54	411	56	4	569	870	<3	19	122	39030	<3	42	6830
0.063-0.2 S1	21,15	0,98	13,54	2,76	0,10	3,26	33,31	1,16	0,88	1,98	20,88	12	14	<3	1020	<3	332	<3	464	11	5	<3	31	9	546	26	5	512	900	<3	<3	160	34240	<3	40	7350
0.063-0.2 S2	33,73	3,28	21,92	6,93	0,12	2,26	8,70	1,38	1,22	3,53	16,93	24	28	10	800	13	408	<3	340	14	3	<3	33	9	2054	46	46	1638	940	11	36	397	3440	<3	151	3810
0.063-0.2 S3	34,61	3,41	22,56	7,09	0,14	2,27	7,45	1,51	1,41	3,04	16,52	28	29	14	750	13	535	<3	183	16	3	<3	33	13	1376	41	54	1758	700	11	23	329	650	<3	142	3730
0.063-0.2 S4	40,13	3,83	24,52	8,30	0,12	2,38	4,43	1,54	1,47	1,85	11,42	17	21	12	470	16	497	<3	128	15	<3	<3	33	5	2247	17	42	1473	830	11	23	291	13770	<3	132	3670
0.3-0.5 S0	31,36	0,97	14,20	4,07	0,11	3,16	25,15	3,57	1,65	1,75	14,00	10	9	<3	720	<3	218	<3	292	6	<3	<3	42	26	690	21	10	552	1250	<3	13	153	21750	<3	37	6560
0.3-0.5 S1	31,86	0,99	15,25	4,04	0,12	3,44	25,87	2,17	1,40	1,84	13,02	15	7	<3	530	<3	282	<3	293	6	3	<3	40	7	631	26	12	552	690	<3	16	147	19880	<3	53	7170
0.3-0.5 S2	44,74	2,41	20,36	7,07	0,14	2,59	8,09	2,48	1,88	2,43	7,81	19	17	<3	380	10	471	<3	160	11	3	3	40	3	1892	31	39	1442	1210	10	30	301	3580	<3	104	3050
0.3-0.5 S3	46,89	2,21	20,01	7,48	0,12	2,52	6,22	2,67	1,79	2,18	7,91	27	8	<3	390	4	282	<3	78	6	<3	<3	54	<3	1417	17	38	1208	1220	11	30	370	2020	<3	101	2690
0.3-0.5 S4	51,10	2,19	19,24	7,88	0,11	2,60	4,62	2,88	1,81	1,50	6,08	21	7	3	190	6	282	<3	73	4	<3	4	52	<3	990	61	59	1407	850	10	30	401	650	<3	102	2750
2-4 S0	48,01	0,69	10,83	4,89	0,10	3,35	16,97	5,32	1,76	1,09	6,99	<3	14	<3	330	16	41	<3	294	8	<3	<3	31	13	573	7	10	907	390	11	23	373	8350	<3	42	4760
2-4 S1	52,16	0,77	11,57	4,49	0,14	3,45	15,33	4,95	1,57	0,78	4,78	12	19	<3	5140	6	41	<3	133	10	<3	<3	41	<3	564	125	14	429	610	17	6	116	2950	<3	40	2150
2-4 S2	58,51	1,24	10,71	4,38	0,11	3,22	10,80	5,51	1,87	1,59	2,05	18	16	5	110	22	41	<3	205	9	<3	7	35	<3	793	<3	14	516	460	15	23	141	2980	<3	59	1470
2-4 S3	58,39	1,21	10,75	4,25	0,11	3,20	10,35	5,41	1,80	1,61	2,05	31	11	<3	90	19	117	<3	183	8	3	7	41	<3	797	<3	13	492	450	11	33	133	3110	<3	58	1430
2-4 S4	55,85	1,14	13,76	7,97	0,11	4,29	7,75	4,58	1,79	0,99	2,92	11	21	8	90	8	180	<3	93	8	<3	<3	44	<3	1049	105	34	1261	330	13	57	335	890	<3	63	1490
2-4 S5	62,70	1,26	11,93	6,56	0,09	2,81	7,33	4,46	1,70	1,17	1,77	34	<3	<3	30	<3	358	<3	85	<3	<3	8	61	<3	788	90	38	1447	140	8	40	307	680	<3	69	1580