



## Notes on the occurrence of phosphate mineral relics and spheres (phosphospheres) in coal and biomass fly ash



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### ABSTRACT

The occurrence of phosphorus minerals in coal is common, and its study is mainly related with the metallurgical coke making.

Large amounts of phosphorus are emitted from coal and biomass combustion units and less direct methods, such as carbon black, are used for tracking stationary combustion sources of phosphorus.

During the study of fly ash from coal burning power plants in the state of Jharkhand, India, using XRD, SEM/EDS, XRF, ICP-MS and leaching tests, it was found that P-bearing spheres have unique visual characteristics. Therefore, this study is thought to represent the first time that P-spheres in coal fly ash are described and herein named as “phosphospheres”. To complement their characterization and how they form other fly ash types such as *Quercus suber* cork and chicken litter fly ashes were also studied using SEM.

Under the SEM the phosphospheres are brighter than the associated aluminosilicate spheres, they may show a spongy (or “punctuated”) structure, have a high P-peak in the EDS profile, and their cross-sections typically show a “pomegranate” texture resulting from immiscible silicate and phosphate melts and the segregation of the P when the glassy matrix is still in a fluid stage. Therefore, with these unique characteristics, phosphospheres are easily recognized, and may be used as a direct method for phosphorus tracking.

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### 1. Introduction

Phosphorus is an essential element for plants and it is an inherent element of the coal, and P-minerals are commonly found, although at low concentrations (<2%), by X-ray diffraction (XRD) of coal low temperature ashes, and by transmitted and scanning electron microscopy with X-ray microanalysis (TEM and SEM with EDS), including: apatite ( $\text{Ca}_5\text{F}(\text{PO}_4)_3$ ), monazite ((Ce, La, Nd, Y, Th) $\text{PO}_4$ ), xenotime ( $\text{YPO}_4$ ), vivianite ( $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ), uranium phosphate (ningyoite;  $(\text{U,Ca,Ce})_2(\text{PO}_4)_2 \cdot 1 - 2\text{H}_2\text{O}$ ), aluminophosphate minerals such as evansite ( $3\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 18\text{H}_2\text{O}$ ), wavellite ( $\text{Al}_3(\text{PO}_4)_2(\text{OH})_3 \cdot 5\text{H}_2\text{O}$ ), goyazite ( $\text{SrAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$ ), svanbergite ( $\text{SrAl}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$ ), gorceixite ( $\text{BaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$ ), crandallite ( $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$ ), and essentially amorphous phosphate gel or colophane (Alastuey et al., 2001; Bohor and Triplehorn, 1993; Creelman and Ward, 1996; Crowley et al., 1993; Dai et al., 2006, 2012, 2014, 2015a,b; Dawson et al., 2012; Diessel, 1992; Doolan et al., 1979; Finkelman and Stanton, 1978; Grieve, 1992; Hackley et al., 2005; Hill, 1988; Hower et al., 2012; Kalkreuth et al., 2006; Kokowska-Pawlowska

and Nowak, 2013; López and Ward, 2008; Mackowsky, 1968; Mahony et al., 1981; Matjie et al., 2011; Querol et al., 1997; Raask, 1985; Rao and Walsh, 1997, 1999; Reifenstein et al., 1999; Taylor et al., 1998; Vassilev and Vassileva, 1996b; Vassilev et al., 1994, 2010; Wang, 2009; Ward, 1974, 1978, 1986, 2002; Ward et al., 1996; Willett et al., 2000). However, such P-bearing minerals are rarely identified in coal by optical microscopy, since they occur mostly as particles a few micrometers in size. However, larger P-bearing crystals, petrifactions or lenses have been described in different coal samples.

Interest in phosphorus concentration in coal is mainly related to metallurgical coke production, since coals low in phosphorus are required (Mahony et al., 1981). It has been known since at least 1940 that phosphorus can cause steel to become embrittled due to segregation of phosphorus and other impurities at prior austenite grain boundaries (Stout and Doty, 1953). Phosphorus segregation effects, namely P pile-up in microelectronic materials, also occur during dopant redistribution at the silicon–silicon dioxide interface during thermal oxidation at temperatures as high as 1100 °C (Grove et al., 1964; Johannessen et al., 1978; Schwarz et al., 1981; Lau et al., 1989).

Phosphorous may also be responsible for superheater deposits in combustion and can poison catalysts of the liquefaction processes, and be leached from coal wastes and by-products (Ward et al., 1996; and

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references therein). However, P-segregation phenomena have not yet been documented to occur in fly ash from coal combustion operations.

The perturbation of the global phosphorus cycle by anthropogenic emissions, which includes the contribution of P ( $<10\ \mu\text{m}$ ) from stationary combustion sources (SCS; including fossil fuels and biomass burning units) (Graham and Duce, 1979; Wang et al., 2015), is estimated in  $1.8 \times 10^6\ \text{t P yr}^{-1}$ . This may represent over 50% of global atmospheric sources of phosphorus in regions influenced by industrialization (Mahowald et al., 2008; Wang et al., 2015), and is potentially a matter of great concern since it affects the ecosystems' nutrient cycles. Emissions of P from coal combustion are derived from volatilization of P during heating followed by its condensation within the installation on the ash particles (Meij, 1994), combined with atmospheric transportation of dust not captured by the ash collection systems (e.g., electrostatic precipitators — ESPs). The fly ash component commonly used to track the combustion source is carbon black (e.g. Mahowald et al., 2008). Therefore, finding P-bearing ash particles with unique characteristics could provide evidence of P contamination and allow the source of total phosphorous and  $\text{PO}_4$  to be traced from the SCS, instead of a less direct indicator such as carbon black.

Biomass is richer than coal in P, and large amounts of biomass, including chicken litter, are burned daily and may also be an important source of phosphorus (Graham and Duce, 1979; Wang et al., 2015). Therefore, biomass ash is relevant to this study. Phosphorus occurs in biomass as ionic salt (phosphate-3ion), organically bound to the carbonaceous matrix in nucleic acids, as minerals included in the biomass structure as internally precipitated phytate (phosphate), or as adventitious minerals from the harvesting processes (Doshi et al., 2009; and references therein). Despite being a very complex phenomenon, biomass ash formation reactions, which include phosphorus and other inorganic elements, were simplified by Doshi et al. (2009) as a three stage process including vaporization, condensation and coagulation/agglomeration, and further simplified by Boström et al. (2012) as a result from:

- (i) Primary reactions, during the thermochemical conversion of the biomass the oxide stability for the major ash forming elements is presented as function of the temperature and oxygen partial pressures); and,
- (ii) Secondary reactions between condensed and gaseous components where compounds compete with each other according to their reactivity (as function of kinetic factors and conditions, such as the aggregation state, mass transport, and dispersion of solids) forming for example K-phosphates and later K-silicates.

After an extensive revision on the occurrence of phase-minerals (including phosphates) in biomass and biomass ash made by Vassilev et al. (2013a), later proposed a four step process for biomass ash transformations based also on an extensive revision of literature (Vassilev et al., 2013b): as temperature increases (i) devolatilization and formation of intermediate and less stable compounds, and inorganic amorphous (non-glass) material; (ii) formation of more stable silicates, phosphates and oxides; (iii) melting accompanied by dissolution of the refractory minerals; (iv) during cooling, crystallization of melt and formation of glass accompanied by some salt condensation and hydroxylation, hydration and carbonation of newly formed phases. Tertiary phases of these minerals and phases may also form due to post-combustion transformations.

Therefore, phosphate phases in coal and biomass fly have been suggested to be relics of primary minerals, others formed during the interaction between P and other elements (e.g., K and Ca) released by the decomposed organic matter and some unstable Ca- and P-bearing minerals (Boström et al., 2012; Vassilev and Vassileva, 1996a,b; Vassilev et al., 1999, 2003, 2013b). However, with the exception of the mention

to probable secondary phosphate species occurring attached to the surface of glassy spheres (Booher et al., 1994; Vassilev and Vassileva, 1996a), and to lesser amounts of P occurring in glassy spheres (Vassilev et al., 2013b).

The aim of the present study is to investigate the occurrence of P-morphotypes in coal fly ash. Although fly ash has been characterized for a long time, including both its bulk composition and specific morphotype characteristics (e.g. Vassilev and Vassileva, 2005), e.g., spheres and spheroids are a result of softening, partial and complete melting, and vitrification of coal minerals such as clay minerals, chlorite, mica, feldspars, quartz and other mainly fluxing minerals and phases which have a lower melting point (Vassilev and Vassileva, 1996a), there is no mention to the occurrence of phosphorous spheres in a similar way, for example, to ferrospheres (Lauf, 1982; Lauf et al., 1982). Nevertheless, in a study of fly ashes produced by coals from the Bokaro and Jharia coal-fields of India, several P-bearing mineral particles were identified in the coal and glassy spheres with lesser amounts of P in the associated fly ash by X-ray diffraction (XRD) and SEM/EDS (2015). This study is therefore thought to represent the first time that fly ash P-morphotypes with a characteristic texture, described herein as “phosphospheres”, have been specifically identified in fly ash samples.

For this purpose, XRD and SEM/EDS analyses have been combined to provide a basis for assessing the genesis and formation process of these P-morphotypes. The results were complemented by X-ray fluorescence (XRF) analysis for phosphate, and inductively-coupled plasma mass spectrometry (ICP-MS) for P in both the fly ash and ash leachate materials.

Phosphospheres generated from combustion of *Quercus suber* cork and chicken litter were also studied for comparison with those in coal fly ash phosphospheres, to obtain better definition of their characteristics and a better understanding of their genesis.

## 2. Materials and methods

The three fly ash samples are identified in this paper as Bokaro, Chandrapura and Jharia, based on the location of the power stations from which they were derived. The Bokaro and Chandrapura samples were collected directly from the hopper of the No. 4 electrostatic precipitators (ESPs) of the respective pulverized coal power plants, and the Jharia sample from the ESP hopper of the relevant fluidized bed combustion (FBC) power plant, in 25th and 26th of June 2013, respectively.

The Bokaro pulverized fuel (p.f.) thermal power plant, with an installed capacity of 630 MW, is located at Bokaro in Jharkhand state (Shreya et al., 2015; Valentim et al., 2016). The Chandrapura p.f. thermal power plant, with an installed capacity of 890 MW, is located in the same district on the banks of Damodar River (Shreya et al., 2015; Valentim et al., 2016). Both these thermal power plants burn coal supplied from the Bokaro Coalfield, the maximum temperature inside the furnace zone is usually between 1150 °C and 1200 °C (Shreya et al., 2015; Valentim et al., 2016).

The Jharia fluidized bed combustion (FBC) power plant is located on the northern bank of the Damodar River, with an installed capacity of 10 MW. The temperature inside the boiler is 1000 °C, and the feed coal is supplied from the Jharia Coalfields (Shreya et al., 2015; Valentim et al., 2016).

The *Quercus suber* cork is burned in the company “RELVAS II” located in the north of Portugal; the fly ash was directly collected from the cyclone hopper of a 1000 °C boiler burning cork powder, from the surface of stack built up over a two-month period, and slag was collected from a wet hopper at the bottom of the furnace. The chicken litter fly ash, resulting from the combustion of rice husk with chicken feces, was collected from the cyclone hopper and the bottom ash wet collector of a boiler operated at 1000 °C

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