



Teaching-Aid

Petrographic examination of coal-combustion fly ash

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ABSTRACT

Fly ash is composed of inorganic and organic constituents, either neoformed in the boiler or flue gas from melting minerals of the charring or thermoplastic transitions in coal, primarily vitrinite, or inherited from the coal or auxiliary fuel. Chemical analyses alone are not sufficient to fully describe the complexity of fly ash. For example, the forms of carbons and their relationship to the inorganic fly ash constituents; the burn-out of coal and non-coal carbons; and the efficiency of combustion, can all be described by petrographic studies of fly ash.

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1. Introduction

Coal combustion to raise steam to generate electricity is the most important means of power production in many countries. Eight countries use more than 100 Mt coal/year, with China using >2.5 Gt/year and the United States using over 0.73 Gt/year, much of it for power production (World Coal Association, 2011). Of this coal consumption, a significant amount remains as fly ash, the portion of the coal-combustion products leaving the boiler and being largely captured by pollution-control devices rather than being emitted from the stack.¹ In 2009 in the US, 60 Mt of fly ash was produced out of over 125 Mt of coal-combustion products (American Coal Ash Association, 2011). Class F fly ash, containing relatively high SiO₂ and Al₂O₃, with <20%CaO is pozzolonic but not self-cementing (ASTM International, 2011). Class C fly ash, with >20% CaO, is both pozzolonic and self-cementing. While class F ash is often considered to be the product of the combustion of higher rank coals and class C ash is considered to result from the combustion of lower rank coals, the major oxide composition, not the age or rank of the coal, is the determining factor.

Fly ash is important as a potential substitute for Portland cement, the most common form of fly ash utilization, and other industrial and agricultural applications (American Coal Ash Association, 2011). Fly ash is also the site of deposition of trace elements such as Zn, As, Se, and Pb (Mardon and Hower, 2004) and fly ash carbons adsorb Hg

from the flue gas stream (Hower et al., 2000, 2010). Fly ash has also been considered as a source of base metals, Ga and Ge, and rare earth elements (Dai et al., 2010; Seredin, 2011).

In this paper, the classification of the microscopically identifiable constituents in coal-combustion fly ash, with mention of some of the non-coal fuels that may be co-fired with coal, is discussed. Techniques such as high-resolution transmission electron microscopy (HRTEM) (Hower et al., 2008; Silva et al., 2010) have pushed resolution down to the several-nanometer scale, but such techniques are not routinely available and results cannot be readily quantified. The use of scanning electron microscopy images as a means of characterizing fly ash, while producing esthetically interesting views of some features, tells nothing of the internal composition of particles. Rather, most of the discussion below is based on the observation of particulate samples mounted in Sudan Black-laced epoxy; prepared to a final 0.05-micron polish; and observed using oil-immersion 50×, reflected-light objectives with crossed polars and a wavelength plate. The systematics of fly ash petrographic characterization were built upon the procedures and modifications of Hower et al. (1995, 2001, 2005a) after work by Hullett et al. (1981), Bailey et al. (1990), Lester et al. (1996), and Alvarez et al. (1997).² The original material, the macerals and minerals in coal, will not be described in detail in this paper; readers can refer to ICCP (1998, 2001), Ward (2002), and Sýkorová et al. (2005) for details.

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¹ Other coal combustion products (also known as coal combustion byproducts, coal utilization byproducts, among other names) include bottom ash and boiler slag and flue gas desulfurization products, including gypsum.

² The 'Petrographic atlas of fly ash' at <http://mccoy.lib.siu.edu/projects/crelling2/atlas/>, part of John C. Crelling's *Petrographic Atlas of Coals, Cokes, Chars, Carbons, & Graphites* contains a series of fly ash images accompanied by brief explanations of the image and the source coal.

2. Petrographic composition of fly ash

Fly ash is produced in the combustion of coal and is transported to the pollution-control devices, usually either electrostatic precipitators (ESP) or bag-house fabric filters (FF), with economizer and/or cyclone separation of ash preceding the ESPs or FFs in some power plants. The time between combustion of the coal; melting or, in the case of minerals with melting points above the combustion temperatures, liberation of the mineral matter; transport with the flue gas to the ESP or FF array; and resolidification is short, generally in the range of a few seconds. The ESPs and FFs are arranged in several rows of multiple collection devices, with a flue gas temperature drop between each of the rows. The first row of the ash-collection array collects the coarsest material. The first row also collects the most fly ash, the general assumption being that each row collects 80% of the fly ash entering that row. As an aside, we will note that the back rows of the ash-collection array, having the finest particles (therefore, greatest surface area) and the coolest flue gas temperature, can have high concentrations of volatile minor and trace elements, such as Zn and As (Mardon and Hower, 2004). As noted above, however, the back rows also are collecting significantly less fly ash than the first ESP or FF row.

Fly ash is generally composed of a mixture of inorganic and organic entities, both inherited directly from the coal and neoformed in the boiler and flue gas stream (Table 1). The following discussion will describe some of those materials.

2.1. Glass

Glass includes amorphous solid and frothy phases (Fig. 1). Glassy cenospheres (Fig. 1A), hollow glass spheres with a density $<1 \text{ g/cm}^3$, can be used as a low-density filler in a variety of industrial applications (Drozhzhin et al., 2005). The optical limits of resolution preclude the petrographic identification of fine inclusions, but the appearance of some particles (Fig. 1B) strongly suggests that either

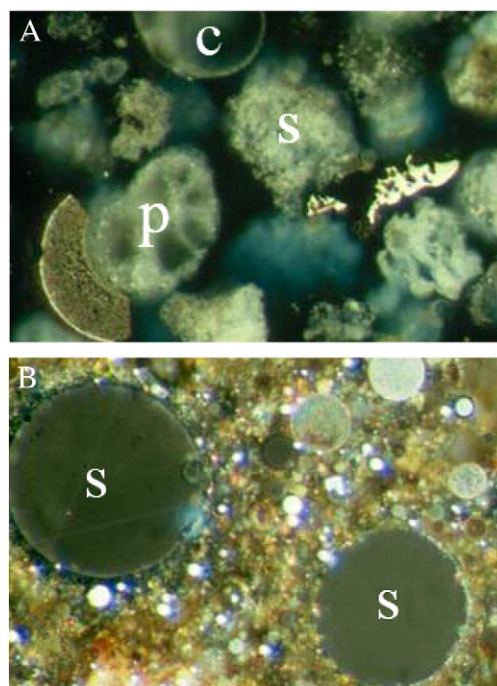


Fig. 1. A/ Glass cenospheres (c), pleiospheres (p), and solid (s) spheres. Field of view about 220 μm on long axis. B/ Solid (s) glass spheres, likely with sub-micron inclusions. Field of view about 220 μm on long axis.

fine minerals or sub-micron gas bubbles are responsible for the cloudy appearance.

2.2. Spinel (and hematite)

The spinels (Fig. 2) are a class of cubic (Isometric–Hexoctahedral) minerals with the composition $\text{Fe}_3\text{–}_x(\text{Al or metal})_x\text{O}_4$, with magnetite being among the minerals in this category. While not a spinel, hematite, as a bright mineral in reflected light, is, in practice, included in the microscopic category. Spinel is common in fly ashes derived from high-Fe coals, with some magnetite included in the feed coal in the case of coals beneficiated in magnetite-based heavy media baths or cyclones.

2.3. Mullite and other crystalline silicates

Mullite (Fig. 3), the high-temperature decomposition product of the kyanite/sillimanite/andalusite class of minerals, is an orthorhombic mineral with an ideal composition of $3(\text{Al}_2\text{O}_3) \cdot 2(\text{SiO}_2)$ with a range from $3(\text{Al}_2\text{O}_3) \cdot 2(\text{SiO}_2)$ to $2(\text{Al}_2\text{O}_3) \cdot 3(\text{SiO}_2)$. In coal-combustion fly ashes, bottom ashes, and slags, mullite can crystallize directly from the Al–Si melt. Anorthite, a triclinic mineral of composition $\text{CaAl}_2\text{Si}_2\text{O}_8$ with some substitution of Na for Ca, can form from the melts of Ca-rich ashes. Consequently, anorthite is more likely to be found in the Ca-rich class C fly ashes than in class F fly ashes.

2.4. Quartz

Quartz (Fig. 4) does not melt at pulverized-fuel-boiler temperatures, typically 1400–1500 $^\circ\text{C}$, and, thus, passes through the boiler in crystalline form.

2.5. Rock fragments, sulfides, and incomplete coal combustion

Rock fragments (Fig. 5) represent partially vitrified portions of the rock mass of the feed coal. In general, the rock fragments have a core of baked minerals, usually derived from clays, with carbonized coal,

Table 1
Fly ash components.

Inorganic
Neoformed
Glass
Mullite
Crystalline silicates
Spinel
Lime
Sulfates
Oxidized minerals
Coal/fuel derived
Quartz
Sulfide
Rock fragments ^a
Organic
Neoformed
Isotropic char or coke
Anisotropic char or coke
Coal/fuel derived
Inertinite
Petroleum coke
Tire-derived fuel
Biomass carbons
Carbon in rock fragments ^a
Partially-burned coal ^b

^a Rock fragments generally have a glassy exterior surrounding baked mineral and (sometimes) carbon interior.

^b Partially-burned coal can have varying degrees of devolatilization features.

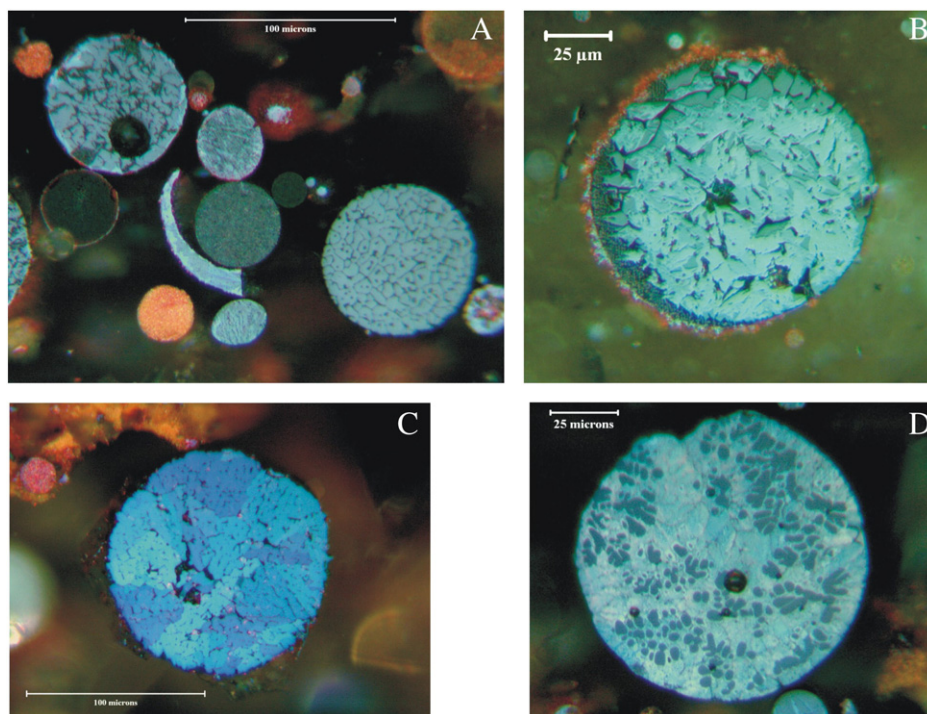


Fig. 2. A through D, spinels.

and an outer glassy rim. Sulfide minerals, another indication of incomplete combustion, are either pyrite or pyrrhotite.

2.6. Other inorganics

Lime and sulfates can be found in fly ashes, particularly ashes derived from high-Ca coals. Silva et al. (2010, 2011) found jarosite and other sulfates in fly ashes in their HRTEM studies. Oxidized minerals are among the trace constituents in some fly ashes and probably result from variations in redox conditions in the boiler and flue gas stream.

2.7. Organic-derived fly ash constituents

While most modern US boilers inherently are capable of producing low-carbon fly ashes, factors such as wear or poor tuning of pulverizers (Hower et al., 1996), conversion of boilers to low-NO_x combustion (Hower et al., 1997), and the use of hard-to-combust non-coal fuels (Hower et al., 2005b) all lead to excessive carbon in the fly ash.

Incomplete coal combustion is seen in partially devolatilized, but recognizable, coal fragments. The term 'unburned carbon', often broadly applied to all fly ash carbons, is most properly descriptive of this class of fly ash fragments. The term is used in the categorization of other fly ash carbon forms, to be discussed below, but, with a few exceptions, the origins of the other carbons is quite distinct from the incompletely combusted coal particles.

Inertinite-group macerals (Fig. 6), primarily the higher reflecting forms fusinite and secretinite, with other inertinite macerals as possible contributors to fly ash carbons, are more resistant to combustion than the vitrinite-group macerals (Nandi et al., 1977; Shibaoka, 1985; Vleskens et al., 1993). Fig. 6A shows a fly ash inertinite form possibly derived from secretinite. Fig. 6B illustrates broken fusinite, while the fusinite shown on Fig. 6C is relatively intact. The partial combustion of an inertinite, shown by the brighter portions of the inertinite framework, is illustrated on Fig. 7.

The isotropic and anisotropic carbons in fly ash are derived from vitrinite group and low-reflecting inertinite-group macerals. Some variation in fly ash carbons can be attributed to the firing conditions in the boiler, but carbons also vary according to the rank of the feed coal. Vitrinites from low-rank coals do not, in general, pass through a thermoplastic stage; therefore, the consequent fly ash carbons take on a charred form of the original vitrinite. Examples of the fly ash carbon structures derived from the combustion of low-rank coals are shown on Fig. 8. Bituminous coal vitrinites are of a rank at which vitrinite is thermoplastic. While it is convenient to draw an analogy to the carbon forms observed in metallurgical coke (Gray and Champagne, 1988; Gray and DeVanney, 1986), the production of metallurgical coke differs from the pyrolysis conditions of coal combustion. Nevertheless, the anisotropy of the fly ash carbons is a function of the variation in the rank of the feed coal, with high volatile A bituminous coals resulting in anisotropic fly ash carbons. Examples of isotropic and anisotropic fly ash carbons from bituminous coal feeds are illustrated on Fig. 9. Bailey et al. (1990) distinguished between thin-walled tenuispheres and tenuinetworks (Fig. 9A) and thick-walled crassispheres and crassinetworks (Fig. 9B and C in fly ash carbons. Hower and Mastalerz (2001) and Hower et al. (2005a, 2005b) incorporated those distinctions in their classification schemes. Anthracite-derived fly ash carbons (Fig. 10) are inherently anisotropic owing to the anisotropic nature of the parent-coal vitrinites. While anthracite ranks are above the rank range for caking coals and thermoplasticity, Hower et al. (2005a) did note some vesiculated carbons among the fly ashes.

Fly ash carbons, as adsorptive materials, can limit the use of fly ash as a Portland cement substitute. ASTM 618 (US Department of Transportation Federal Highway Commission, 2011) limits fly ash carbon (as loss on ignition) to 6% and most US states have more restrictive limits. At any feed coal rank, though, if a fly ash carbon is encased in a rock fragment, glass, or any other inorganic form, the carbon is not a contributor to the carbon properties that are detrimental to the use of fly ash. Conversely, if the carbon surrounds fly ash glass, the Al-Si glass will not be a contributor to the desired properties of fly ash. Both situations are encountered in many fly ashes,

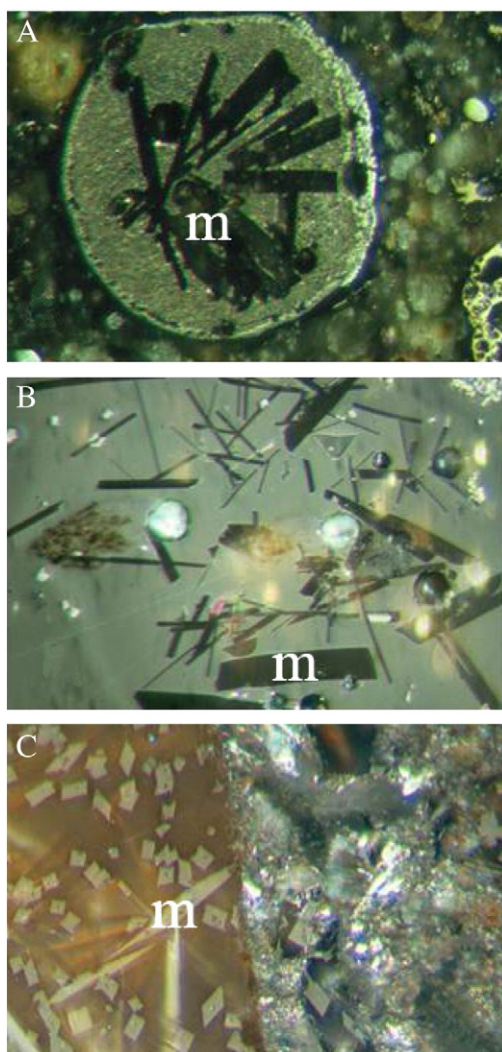


Fig. 3. A through C, mullite (m). Field of view about 220 μm on long axis.

and only petrographic examination can fully reveal the nature of the fly ash.

Fuels other than coal can contribute to the fly ash. Carbons from petroleum coke (Hower et al., 2005b), tire-derived fuel (Hower et al., 2001), and biomass are common substitutes for coal (Fig. 11A, B, C). Tires can also contribute metals from the included steel belts.

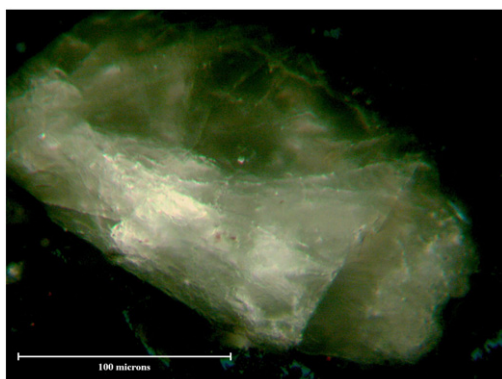


Fig. 4. Quartz. Scale = 100 μm .

3. Summary

Coal-combustion fly ash is composed of inorganic and organic constituents either newly formed in the boiler or flue gas or carried over from the coal or auxiliary fuel. The petrographic examination of fly ash can provide details unobtainable from bulk chemical analyses, such as the forms of carbons and their relationship to the inorganic fly ash constituents, important in the capture of Hg by fly ash carbons; the burnout of coal and non-coal carbons; and the efficiency of combustion, determined in part from the amount and size of carbons, including incompletely burned coal, and rock fragments.

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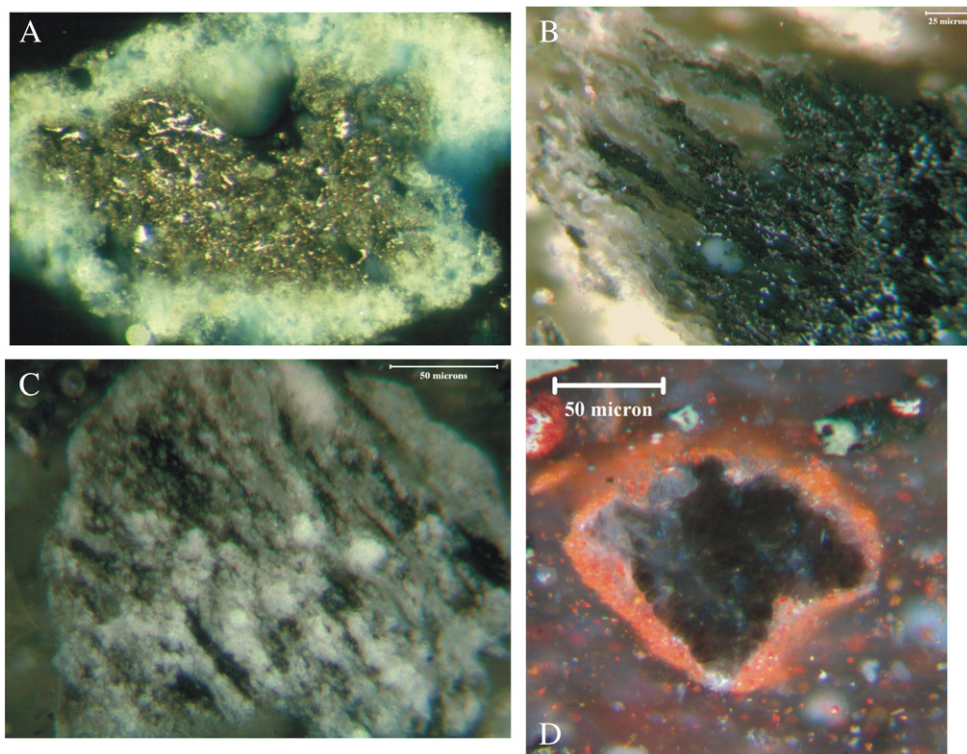


Fig. 5. A/ Partially baked rock fragment with carbon at core of particle with glassy rim. Field of view about 220 μm on long axis. B/ Partially baked rock fragment with carbon at core of particle with glassy rim. Scale = 25 μm . C/ Glass almost completely replacing rock fragment. Scale = 50 μm . D/ Partially baked rock fragment with glassy rim. Scale = 50 μm .

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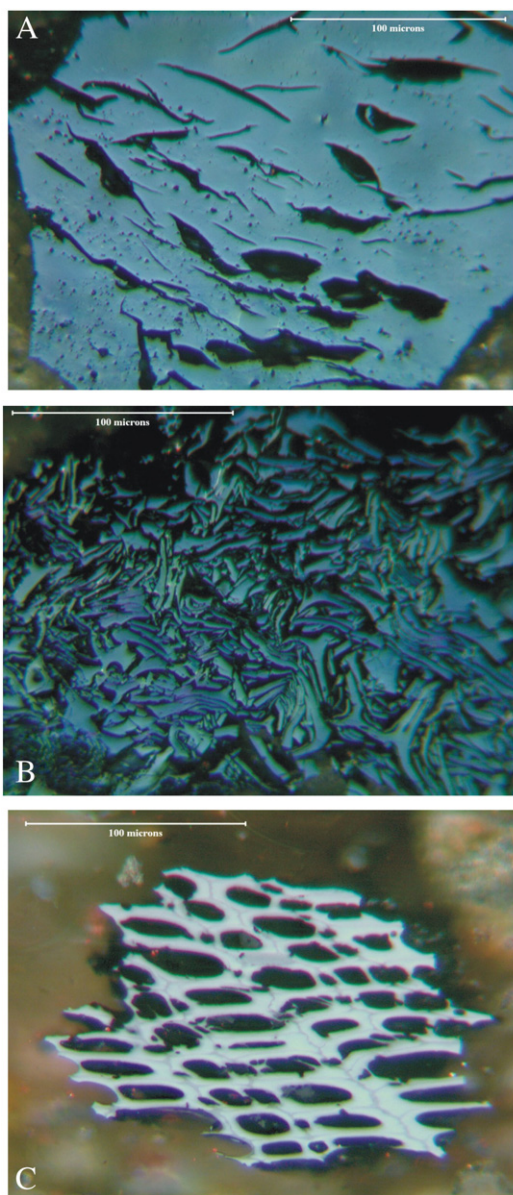


Fig. 6. A/ Inertinite (secretinite). Scale = 100 μm . B/ Broken inertinite (fusinite). Scale = 100 μm . C/ Intact inertinite (fusinite). Scale = 100 μm .

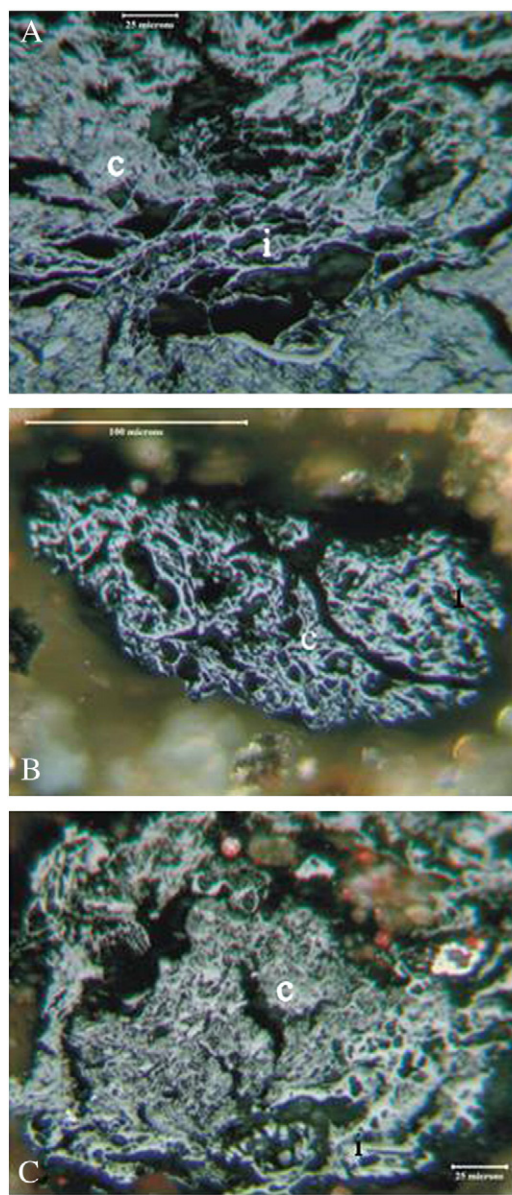


Fig. 8. A/ Charred low-rank-vitrinite-derived carbon (c) with inertinite (i). Scale = 25 μm . B/ Charred low-rank-vitrinite-derived carbon (c). Scale = 100 μm . C/ Charred low-rank-vitrinite-derived carbon (c) with inertinite (i). Scale = 25 μm .

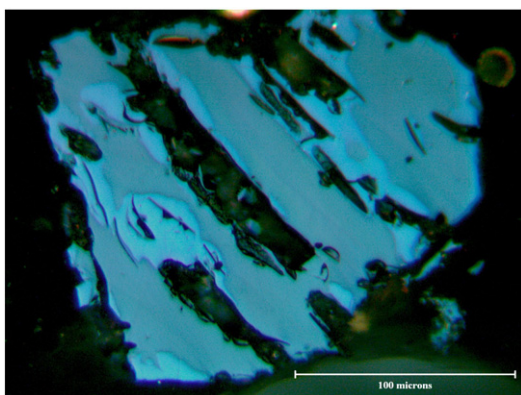


Fig. 7. Inertinite with brighter areas indicative of partial combustion. Scale = 100 μm .

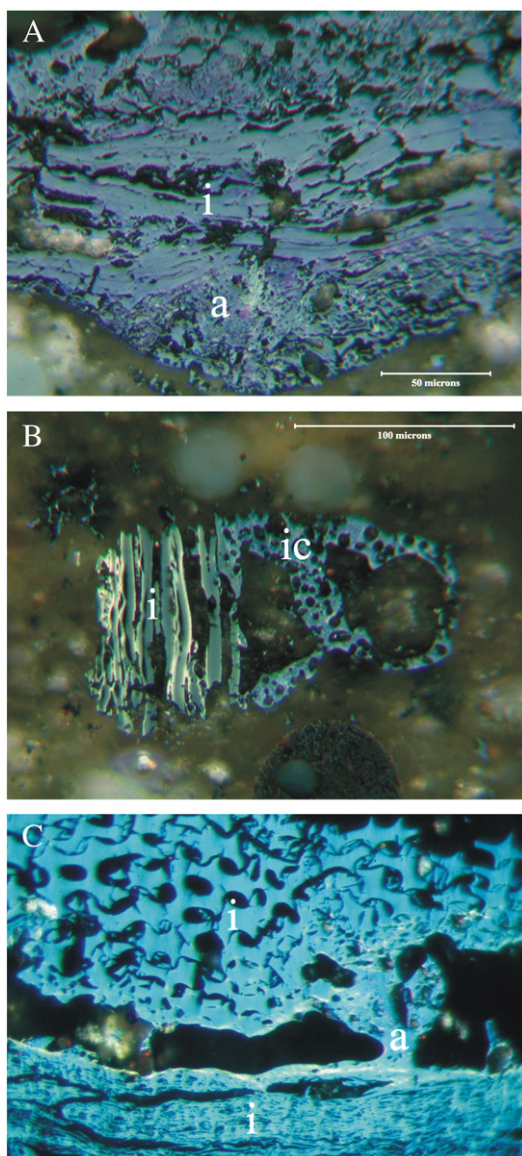


Fig. 9. A/ Anisotropic tenuinetwork carbon (a) with inertinite (i). Scale = 50 μm . B/ Isotropic crassinetwork carbon (ic) with inertinite (i). Scale = 100 μm . C/ Anisotropic crassinetwork carbon (a) with inertinite (i). Field of view about 220 μm on long axis.

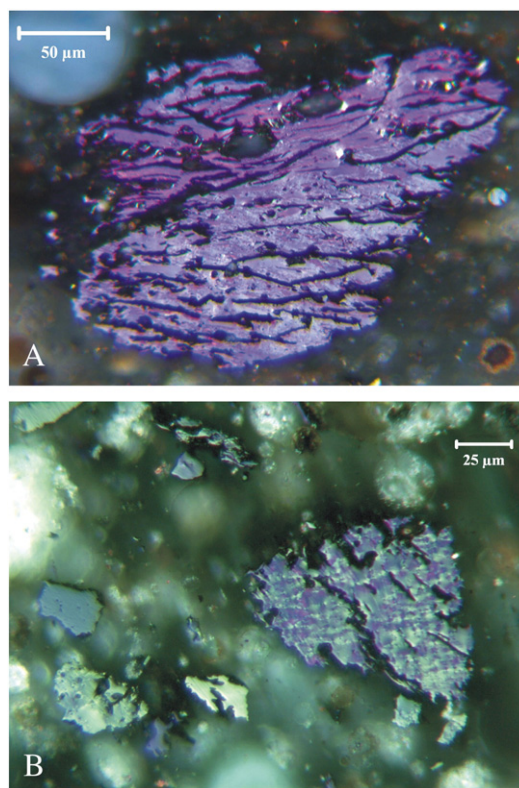


Fig. 10. A/ Anthracite-derived carbon. Scale = 50 μm . B/ Anthracite-derived carbons. Scale = 25 μm .

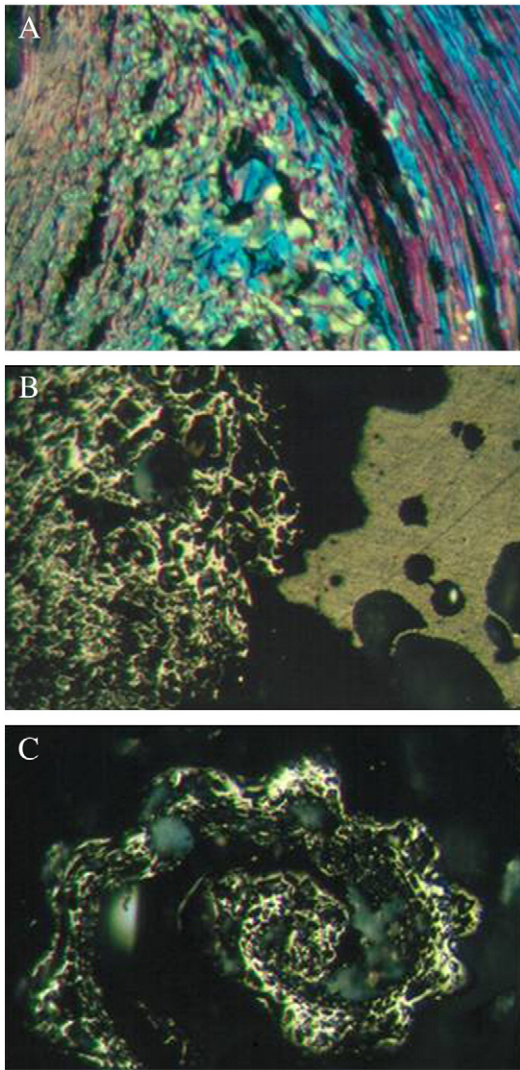


Fig. 11. A/ Petroleum coke. Field of view about 220 μm on long axis. B/ Tire-derived carbon on right with isotropic coal-derived carbon on left. Field of view about 220 μm on long axis. C/ Rice hull ash. Field of view about 220 μm on long axis.