



## ENVIS CENTRE ON BIOGEOCHEMISTRY

*(Supported by: Ministry of Environment & Forests, Govt. of India)*

SCHOOL OF ENVIRONMENTAL SCIENCES  
JAWAHARLAL NEHRU UNIVERSITY, NEW DELHI, INDIA

Vol. 17

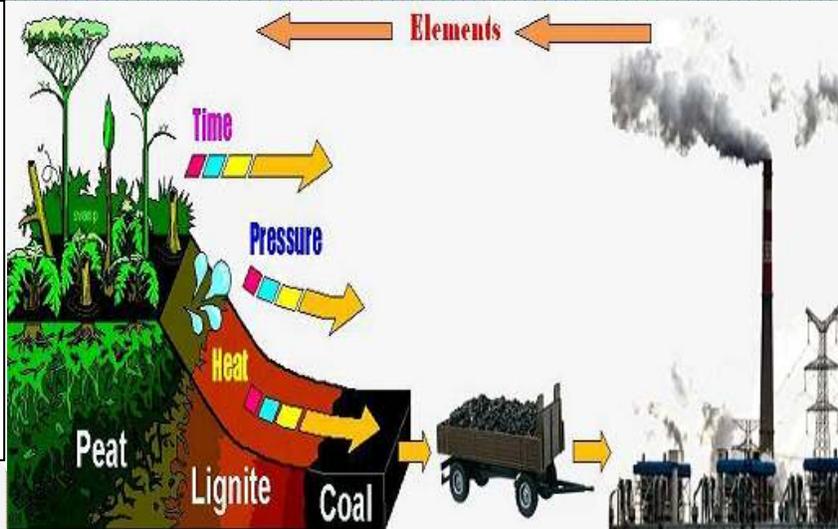
Number 1

2011-12

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From Editor's Desk



The present issue contains a lead article highlighting the role of coal in the biogeochemical cycling of various elements. Coal, an important energy resource, has been the driver of all developmental and economic activities the world has witnessed in the last 150 years and it continues to be central to the energy policies and planning of most of the developed as well as developing and emerging economies of the world. The way various elements get transferred from one subsystem of the earth to the other through its formation and subsequent utilization is a classic example of biogeochemical cycling. Various biological, chemical, physical and geological processes governing the movement through lithosphere, hydrosphere, atmosphere and biosphere are discussed in detail. In addition, this issue has extended abstracts on coal geochemistry and a list of recent publications on biogeochemistry.

This issue is also available on our website: [www.jnuenvis.nic.in](http://www.jnuenvis.nic.in). We solicit feedback and suggestions from our esteemed readers, if any, to improve our functioning further.

Prof V. K. Jain  
Editor

## Biogeochemical cycling of elements through coal

Coal formation, its exploration and usage sets a suitable example to understand the concept of biogeochemical cycling of elements among different spheres (lithosphere, atmosphere, hydrosphere and biosphere) of planet Earth. Biogeochemical cycling of elements means the flow of chemical elements and compounds between living organisms and the physical environment. Chemicals residing in plants or living organisms pass through the food chain and return to the soil, air, and water by different mechanisms which could take place at different temporal and spatial scales. As an element moves through this cycle, it often forms compounds with other elements as a result of metabolic processes in living tissues and of natural reactions in the atmosphere, hydrosphere, or lithosphere. The process of coal formation in nature and its utilization for energy production represents cyclic biogenic mass exchange among the different components of earth. Large number of elements present in the earth's crust is locked up in the biomass by the primary producers. The fixed biomass over a period of time under earth's crust undergoes a variety of biophysical and chemical changes and transformed to coal. The process of formation of coal is a long term process taking place over a geological time scale. But its exploration and usage is taking place on human scale as coal dominates the energy scenario of the world. Nearly 70% of energy demand is met by coal based thermal power plants across the world. In the absence of a reliable economical attractive alternative to energy generation by fossil fuels, coal is expected to remain as the major energy resource for decades to come. Table I provides the dependence of major countries across the world on coal energy.

**Table 1** Percentage dependence on the coal for energy production by major countries.

S. No.	Country	%age	S. No.	Country	%age
1.	Poland	93	7.	India	69
2.	South Africa	93	8.	Morocco	69
3.	Australia	80	9.	Czech Rep	59
4.	PR China	78	10.	Greece	58
5.	Israel	71	11.	USA	50
6.	Kazakhstan	70	12.	Germany	47

([www.nationmaster.com](http://www.nationmaster.com))

**Coal formation:** Coal is found in deposits called seams that originated through the accumulation of vegetation in the swampy conditions that has undergone physical and chemical changes (Miller, 2005). Coal types differ throughout the world depending upon the nature of plant materials deposited (which decided the type of coal), in the degree of metamorphism or

coalification (this process decides the rank of coal) and in the range of impurities included during such processes (Ward, 2002). Vegetation tended to grow for many generations, but with plant material settling on the swamp bottom and getting converted into peat by microbiological action (Bouska, 1981). After some time, the swamps become submerged and get covered by sedimentary deposits, and a new future coal seam is formed. When this cycle is repeated, over hundreds of thousands of years, additional coal seams were formed (Ward and Sua' rez-Ruiz, 2008). These cycles of accumulation and deposition were followed by diagenetic (i.e., biological) and tectonic (i.e., geological) actions and, depending upon the extent of temperature, time, and forces exerted, formed the different ranks of coal observed today.

Coal formation process can be broadly categorized into two stages (a) peatification and (b) coalification.

**Peat Formation:** Peat formation or Peatification is the first stage in the conversion of plant biopolymers into coal (Hatcher, 1990). Peat accumulation happened in the places where the rate of accumulation of dead biomass exceeds the rate of its microbial decay (Orem and Finkelman, 2003). These conditions are generally found in shallow, aquatic environments, such as swamps and marshes (Gleason and Stone, 1994; Taylor et al., 1998). Degradation of organic matter by fungus is limited to the near-surface zone only where oxygen is available (Tissot and Welte, 1984; Benner et al., 1984), however the less efficient anaerobic bacterial biodegradation predominates within the peat (Given et al., 1983; Yavitt and Lang, 1990; Orem and Finkelman, 2003). Over the time, loss of oxygen and nitrogen occurs whereas organic carbon content increases with depth (Orem and Hatcher, 1987).

**Coalification:** The geochemical process that transforms plant material into coal is called coalification and is often expressed as:

**Peat → Lignite → Subbituminous coal → Bituminous coal → Anthracite**

Peat formation is followed by coalification under intense lithostatic pressure caused by the thickness of the sediment overburden over a longer span of time. Coalification can be described geochemically as three step process: the microbiological degradation of the cellulose of the initial plant material, the conversion of the lignin of the plants into humic substances, and the condensation of these humic substances into larger coal molecules. Chemically, there is a decrease in moisture and volatile matter (i.e., methane, carbon dioxide) content, as well as an increase in the percentage of carbon, a gradual decrease in the percentage of oxygen (Elliott, 1981; Schobert, 1987). During the initial stages of coalification peat is transformed to brown coal and lignite (Stach et al., 1982; Tissot and Welte, 1984; Orem and Finkelman, 2003). At the later stages of coalification, the organic matter is exposed to more extreme temperatures and pressures

resulting in the formation of subbituminous coal, bituminous coal, and anthracite (Hatcher and Clifford, 1997). Oxygen is progressively lost during coalification (Venkatesan et al., 1993). Nitrogen containing compounds are also lost during early stage of coalification (Knicker et al., 1996). In addition, loss of low-molecular weight hydrocarbons from the cracking of resistant cuticular biopolymers, and algal biopolymers also reduces the H/C ratio (Elliott, 1981). In bituminous coals and anthracites, much of the oxygen present in the original plant organic matter has been lost (Tissot and Welte, 1984). The nitrogen content is also decreased. Nitrogen is formed from the thermal decomposition of nitrogen-containing organic compounds in the coal (Boudou and Espitalie, 1995).

**Types:** Coal type reflects the nature of the plant debris from which the original peat was derived, and the degree of degradation to which they were exposed before burial (Ward and Sua' rez-Ruiz, 2008). Depending upon the extent of coalification coal is broadly classified into:

- ❖ *Peat*, is considered to be a precursor of coal, rarely used as a commercial fuel.
- ❖ *Lignite*, also referred to as brown coal, is the lowest rank of coal and used exclusively as fuel for electric power generation.
- ❖ *Bituminous* coal, dense sedimentary rock, dark black in colour and is primarily as fuel in steam-electric power generation, making coke.
- ❖ *Anthracite*, the highest rank; a harder, glossy, black lustrous coal.

### **Inorganic Geochemistry of Coal:**

Coal contains almost all the elements found in the periodic table except for few extremely rare elements (Finkelman, 1994; Bragg et al., 1998). The inorganic constituents can vary in concentration from several percentage points down to parts per billion of the coal (Raask, 1985; Miller, 2005). Incorporated within the fossilized carbonaceous material are minerals from the original plant tissue (included) and silt deposited during the formation of the coal (excluded) (Senior and Flagan, 1982; Ward, 2002; Xu et al, 2003 ). On grinding, the coal breaks down into particles of quite a variable nature's - particle containing organic matter, pure mineral grains, and inorganic matter (Querol et al, 1995). Abundance of the inorganic constituents in coal varies from at every level—between coal basins, between coal beds within a basin, and within coal beds. Abundance of inorganic constituents is also influenced by the variations in the plant communities, source material, detrital influx, diagenetic processes, and epigenesis (Raymond et al., 1990). The minerals in a coal clearly reflect it's geochemical environment of deposition and diagenesis rather than the composition of the source rocks (Bouska, 1981; Swaine, 1990).

Ferromagnesian minerals such as pyroxenes, amphiboles, and olivines are very unstable at low pH conditions and are very rare in coal; feldspars are also uncommon. Relatively more resistant minerals such as rutile, zircon, and rare-earth phosphates are relatively common in coal. When ferromagnesian minerals are dissolved in acidic swamp waters, they release metals such as nickel, copper, cobalt, chromium, and lead. The anoxic conditions in the swamp and the abundant sulfur liberated by the putrefaction of the decaying plant matter are ideal for the precipitation of sulfide minerals. Pyrite contains small amounts of chalcophile elements such as arsenic, mercury, lead, selenium, cadmium, and thallium (Orem and Finkelman, 2003). Clays are volumetrically the most abundant mineral group in coal. They can be authigenic or detrital in origin. Kaolinite is the most common clay and the most common authigenic mineral in coals. Illite and mixed layer clays in coal are almost exclusively detrital in origin. Chlorites, smectites, and other clay minerals may also be present (Vassilev and Vassileva, 2005). Quartz, one of the most common minerals in most coals, can have a detrital, authigenic, or epigenetic origin. Carbonate minerals, generally, calcite, siderite, and ankerite occur most commonly as syngenetic nodules or as epigenetic cleat and fracture fillings (Vassilev and Vassileva, 1997; Orem and Finkelman, 2003).

**Environmental Impacts:** Coal utilization for electricity production releases large quantities of waste products into the environment. Significant amounts of sulfur and nitrogen oxides, carbon dioxide, mineral and coal particulates, trace elements, and trace amounts of organic compounds are released from coal combustion in thermal power plants (Wang and Tomita, 2003).

**Carbon dioxide emissions:** The release of CO<sub>2</sub> into the atmosphere as a consequence of human activities, especially those related to fossil fuel combustion, has been reported to be linked to increased global warming and associated climate change (Ward and Sua' rez-Ruiz, 2008). *The accumulation of carbon dioxide and other "greenhouse gases" in the atmosphere affects the global climate (McCabe et al., 1993).* Of fossil fuels, coal combustion in thermal power stations result in greater amounts of carbon dioxide emissions per unit of electricity generated.

**Sulfur emissions:** Coal-fired power plants are the largest human-caused source of sulfur dioxide, a pollutant gas that contributes to the production of acid in the atmosphere and lowers the pH of rain, fog and Dew water as well. Such acidic waters have adverse implications on physical monuments, health of water bodies and soil. Sulfur in coal occurs principally as pyritic sulfur and organically bound sulfur (Vassilev and Vassileva, 1997; Orem and Finkelman, 2003). When coal is burned, the sulfur combines with oxygen to form sulfur oxides having broader environmental implications. In the atmosphere, sulfur oxides can combine with water and oxygen to form sulfurous and sulfuric acids.

**Nitrogen emissions:** Virtually all of the nitrogen in coal is organically bound. During coal combustion, nitrogen is oxidized to its higher oxides in gaseous form. However, a large part of the nitrogen oxides produced and emitted during coal combustion comes from nitrogen in the air reacting with oxygen at high temperatures. These products contribute to the formation of smog and react with oxygen in the presence of light to produce PAN that causes eye and respiratory irritation

**Emission of Fly Ash:** Ash particles of different nature and at different stages of coal combustion in power plants are formed from the inorganic matter present in coal. The ash formation process is influenced by the mode of occurrence of the inorganic matter and the combustion behavior of coal particles containing both organic and inorganic matter and the combustion conditions. Mineral matter (included and excluded) in the coal at high furnace temperatures usually melt coalesce or fragment to form particulate matter. Finer particulate matter is highly enriched with the toxic elements owing to their greater surface areas (Smith, 1979; Sarkar et al, 2003; Xiaowei et al, 2007).

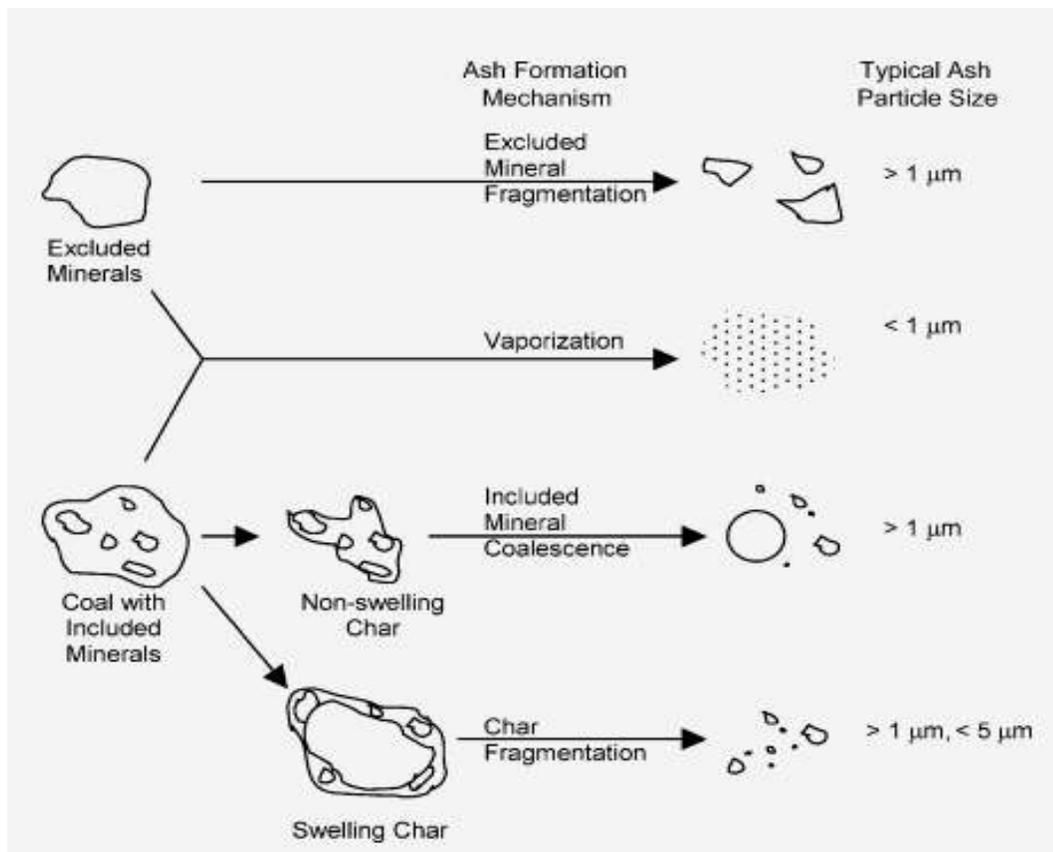


Fig 1. Mechanism of ash formation of different sizes during coal combustion

**Emission of trace elements:** Though trace elements are present in small amounts in the coal and are generally associated with the organic fraction of the coal. The partitioning of trace elements during combustion is differential in nature depending on the behavior of individual element.

Their release into the atmosphere has direct bearing on the air pollution and air quality in the region (Huang et al, 2004; Sarkar et al, 2006). The enrichment of the trace elements on the finer ash fractions is attributed to the vapourization of volatile constituents in the coal at higher furnace temperatures and subsequently the condensation or adsorption of vapours on the surface of particles at lower temperatures downstream (Senior and Flagan, 1982; Xiumin 2001; Yan 2001; Xu et al, 2003). Based on the partitioning of trace elements on various particles elements can be classified into following elemental groups (Table 1 and 2). This classification is connected to the concept of enrichment of elements on the particle surface; the relative enrichment factor (RE) (Meij and Winkel, 2007) of an element is defined as:

$$RE = \frac{\text{Element concentration in ash}}{\text{Elemental concentration in fuel}} \times \frac{\%age \text{ ash content in fuel}}{100}$$

**Table 1** Classification of elements on the basis of their relative enrichment

Class	Bottom Ash	PFA	Fly ash	Behavior in installation
I	≈1	≈1	≈1	Not volatile
IIc	<0.7	≈1	1.3 <...≤ 2	Volatile in boiler, bit complete condensation in ESP on the ash particles
IIb	<0.7	≈1	2 <...≤ 4	
IIa	<0.7	≈1	≥ 4	
III	<<1	<1	--	Very volatile, hardly any condensation

**Table 2** Elements belonging to different elemental classes

Class	Elements
I	Al, Ca, Ce, Cs, Eu, Fe, Hf, K, La, Mg, Sc, Sm, Sr, Th, and Tl
IIc	Ba, Cr, Mn, Na, and Rb
IIb	Be, Co, Cu, Ni, P, U, V and W
IIa	As, Cd, Ge, Mo, Pb, Sb, Ti and Zn
III	B, Br, C, Cl, F, Hg, I, N, S and Se

**Indian Scenario:** Indian coal is of mostly sub-bituminous rank, followed by bituminous and lignite (brown coal). The ash content in Indian coal ranges from 35% to 50%. The calorific value of the Indian coal (~15 MJ/kg) is less than the normal range of 21 to 33 MJ/Kg (gross). In India over 75% of the total installed power generation capacity is coal-based and about 230 - 250

million MT coal is being used every year and more than 110 million MT of ash every year from the coal-fired thermal power plants and is projected to reach 170 million MT by 2010. Presently only 30% of total fly ash generated is being used in Fillings, embankments, construction, block & tiles, etc. Majority of the coal ash generated is being handled in wet form and disposed off in ash ponds which are harmful for the environment and moreover ash remains unutilized for gainful applications. Presently about 65,000 acres of land has been occupied by ash ponds. Fly Ash has a vast potential for use in High Volume fly ash concrete especially due its physico-chemical properties. As per policy decision (MOEF Gazette Notification dated Sept. 14, 1999), the existing power stations have to achieve 20% ash utilization within three years and 100% utilization in 15 years from the date of notification. New Stations have to achieve 30% ash utilization within 9 years and 10% ash utilization within 3 years and 100% utilization within 4 years and 100% annual increase. Presently, therefore thermal power stations are under great pressure to find useful applications of fly ash. The scientific community as well as industry is working hard to find avenues for utilization of fly ash on a bulk scale as our country is largely dependent on the coal based energy generation methods and it is expected to increase.

### **Conclusions:**

Coal formation in nature and its utilization is an important pathway for the geochemical cycling of matter and energy. Thus an effective use of coal as a natural resource requires a better understanding of the chemical and mineralogical characteristics of the coal that control its by-product characteristics, and environmental and human impacts.

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## Recent Extended Abstracts on Coal Geochemistry

### Mineralogy and geochemistry of Greek and Chinese coal fly ash

**Authors:** Nikolaos K. Koukouzas, Rongshu Zeng, Vassilis Perdikatsis, Wendong Xu, Emmanuel K. Kakaras

**Journal:** Fuel; Volume 85, Issue 16, November 2006, Pages 2301-2309 doi:10.1016/j.fuel.2006.02.019

**Abstract:** In this paper the mineralogy and geochemistry of Greek and Chinese coal fly ash are examined. Annual production of fly ash in China is around 160 Mt while in Greece lignite fly ash accounts around 10 Mt. Even though the mineralogical and chemical composition of the fly ashes coming from these two countries differs, there are common questions on the utilization of this material. The variation of the Greek fly ash' chemical composition, from Ca-poor to Ca-rich fly ash, has resulted to applications such as dam construction, use in cement and possibly in concrete and road construction. The Chinese fly ash, which is rich in mullite, is broadly applied for brick making.

## **Geochemistry of coals from the Elk Valley coalfield, British Columbia, Canada**

**Authors:** F. Goodarzi, D.A. Grieve, H. Sanei, T. Gentzis, N.N. Goodarzi

**Journal:** International Journal of Coal Geology; Volume 77, Issues 3-4, 31 January 2009, Pages 246-259

**Abstract:** The Elk Valley coalfield of British Columbia is one of the major coal producing areas in Canada. The coals are of Cretaceous and Jurassic–Cretaceous age and range in rank from high-volatile to low-volatile bituminous (%Romax: 0.8–1.6). Coal seams from outcrops and active mines in this coalfield were analysed for rank and maceral composition using reflected light microscopy, for geochemistry using AAS, INAA, and ICPES, and also by proximate and ultimate analyses. The Elk Valley coal seams contain low average concentrations of hazardous elements such as As, Mo, Pb, and Se. However, there are seams that contain relatively high concentrations of some of these elements, such as 8 mg/kg and 108 mg/kg of arsenic. When the geochemistry of coal seams is compared within the different parts of the coalfield, the elemental composition amongst the seams from various sections located in the central area of the coalfield is similar. Coal seams in the northern area of the coalfield have different geochemistry than coal seams in other areas of the coalfield; seams in the northern area have much higher As, Br, Cr, Cu, Fe, K, and Na content, but contain less Ca.

## **Geochemistry of trace elements in coals from the Zhuji Mine, Huainan Coalfield, Anhui, China**

**Authors:** Ruoyu Sun, Guijian Liu, Liugen Zheng, Chen-Lin Chou

**Journal:** International Journal of Coal Geology; Volume 81, Issue 2, 2010, Pages 81-96

**Abstract:** The abundances of nine major elements and thirty-eight trace elements in 520 samples of low sulfur coals from the Zhuji Mine, Huainan Coalfield, Anhui, China, were determined. Samples were mainly collected from 10 minable coal seams of 29 boreholes during exploration. The B content in coals shows that the influence of brackish water decreased toward the top of coal seams; marine transgression and regression occurred frequently in the Lower Shihezi Formation. A wide range of elemental abundances is found. Weighted means of Na, K, Fe, P, Be, B, Co, Ni, Cr, Se, Sb, Ba, and Bi abundances in Zhuji coals are higher, and the remainder elements are either lower or equal to the average values of elements in coals of northern China. Compared to the Chinese coals, the Zhuji coals are higher in Na, K, Be, B, Cr, Co, Se, Sn, Sb, and Bi, but lower in Ti, P, Li, V and Zn. The Zhuji coals are lower only in S, P, V and Zn than average U.S. and world coals. Potassium, Mg, Ca, Mn, Sr, As, Se, Sb and light rare earth elements (LREE) had a tendency to be enriched in thicker coal seams, whereas Fe, Ti, P, V, Co, Ni, Y, Mo, Pb and heavy rare earth elements (HREE) were inclined to concentrate in thinner coal seams. The enrichment of some elements in the Shanxi or Upper Shihezi Formations is related to their depositional environments. The elements are classified into three groups based on their stratigraphic distributions from coal seams 3 to 11-2, and the characteristics of each group are discussed. Lateral distributions of selected elements are also investigated. The correlation coefficients of elemental abundances with ash content show that the elements may be classified into four groups related to modes of occurrence of these elements.

## **Geochemistry of trace elements in Çan coal (Miocene), Çanakkale, Turkey**

**Author:** Gülbin Gürdal

**Journal:** International Journal of Coal Geology; Volume 74, Issue 1, 3 March 2008, Pages 28-40

**Abstract:** This study focuses on the geochemistry of trace elements and the coal quality parameters of Miocene lignite's from Çan basin. Twelve coal samples have been studied using proximate and ultimate analyses, X-ray powder diffraction, inductively coupled plasma-mass spectrometry, inductively coupled plasma-atomic emission spectrometry, scanning electron microscopy with energy-dispersive X-ray microanalysis and organic petrographic analyses. The Çan coals on an air-dried basis are characterized by broad variation of ash (ranging from 4.42% to 36.72%), high total sulphur contents (up to 8.10%) and high gross calorific values (3870–6612 kcal/kg). The mineral matter of the studied coal samples is made up of quartz, pyrite, clay minerals and gypsum. Major elements correlate positively with dry ash contents demonstrating an association with inorganic constituents. For twenty trace elements, including As, B, Ba, Be, Cd, Cu, Co, F, Hg, Mo, Ni, Pb, Sb, Se, Sn, Th, Tl, U, V and Zn received much attention

due to environmental and human health concerns. Based on statistical analyses, most of the trace elements, except for Ba, Mo, Se and U, show an affinity to ash content. Elements including As, Cu, Co and Hg appear to be associated with pyrite. The concentrations of the trace elements are within the range of world coal average. However, the V content is higher than the world coal value and some volatile elements such as As, B and U are slightly enriched in some coal samples.

#### **A preliminary study of mineralogy and geochemistry of four coal samples from northern Iran**

**Authors:** F. Goodarzi, H. Sanei, L.D. Stasiuk, H. Bagheri-Sadeghi, J. Reyes

**Journal:** International Journal of Coal Geology; Volume 65, Issues 1-2, 3 January 2006, Pages 35-50

**Abstract:** This study is related to four Jurassic-age bituminous coal (0.69–1.02 Ro%) samples collected from coal mines from the west, central and east of central, Alborz in northern Iran. Geological settings played key roles in determining the geochemistry and mineralogy of coals from the central Alborz region of northern Iran. The mineralogy of coals from the eastern part of the region is dominated by kaolinite; halloysite; and carbonates such as calcite, dolomite/ankerite, and siderite. The coals were deposited in a lacustrine environment. In the western part of the region, where the depositional setting was also lacustrine with volcanic input and tonstein deposition (glass shards present), the coal primarily contains kaolinite (68%) and fluorapatite (26%). In contrast, coal from the central part of the region, which was deposited in a terrestrial environment and on eroded limestone and dolomite rocks, is dominated by dolomite (98%) with little input by kaolinite. These coals have low sulphur (0.35–0.70 wt.%), which is mostly in the organic form (0.34–0.69 wt.%). Pyritic sulphur is detected only in one coal and in small quantities. The boron contents of these coals range from 9 to 33 mg/kg, indicating that deposition occurred in a fresh water environment. Coal with higher concentrations of Ba, Sr, and P contain fluorapatite and goyazite–gorceixite series [BaAl<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)<sub>5</sub>·H<sub>2</sub>O] minerals, which indicates volcanoclastic input. Compared to world coal averages, these coals exhibit low concentrations of elements of environmental concern, such as As (1.3–5.9 mg/kg), Cd (< 0.02–0.06 mg/kg), Hg (< 0.01–0.07 mg/kg) Mo (< 0.6–1.7 mg/kg), Pb (4.8–13 mg/kg), Th (0.5–21 mg/kg), Se (< 0.2–0.8 mg/kg) and U (0.2–4.6 mg/kg). Two of the northern Iranian coals have concentrations of Cl (2560 and 3010 mg/kg) that are higher than world coal average.

#### **Geochemistry of radioactive elements (U, Th) in coal and peat of northern Asia (Siberia, Russian Far East, Kazakhstan, and Mongolia)**

**Authors:** S.I. Arbusov, A.V. Volostnov, L.P. Rikhvanov, A.M. Mezhibor, S.S. Ilenok

**Journal:** International Journal of Coal Geology; Volume 86, Issue 4, 1 June 2011, Pages 318-328;

**Abstract:** Geochemistry of radioactive elements in more than 5000 coal and peat samples of Northern Asia has been investigated by quantitative methods, such as the instrumental neutron-activation analysis, the method of delayed neutrons, and the X-ray-fluorescence analysis. The average U content in the coals of deposits and basins of the region ranges from 0.6 to 32.8 ppm and, for Th, from 0.8 to 9.2 ppm. Within the boundaries of basins, deposits and some coal beds lateral and vertical changes of the distribution of radioactive elements have been studied. The high concentrations of U and Th in coal deposits are spatially related to rock blocks within the basin frames, which are enriched in elements, or are connected with a volcanism of a period of coal formation. A consistent changing of the role of pyroclastic material in the radioactive elements accumulation was determined in the direction from the West to the East.

#### **Lateral variation in geochemistry, petrology, and palynology in the Elswick coal bed, Pike County, Kentucky**

**Authors:** James C. Hower, Leslie F. Ruppert, Cortland F. Eble

**Journal:** International Journal of Coal Geology; Volume 69, Issue 3, 1 February 2007, Pages 165-178

**Abstract:** The Middle Pennsylvanian/Langsettian (Westphalian A) Elswick coal bed, correlative to the Upper Banner of Virginia, is a rare example of a mined high-sulfur (> 2%) coal in Eastern Kentucky, a region known for low-sulfur coals. To characterize lateral variation in the geochemistry, petrography, and palynology of the Elswick coal bed, three sites were sampled along a southeast–northwest transect within a single mine. At the southeastern

site, the lower 101 cm of the 116-cm thick coal is dull, generally dominated by durain and dull clarain. While all benches at this site fit within the previously-defined “mixed palynoflora — moderate/low vitrinite group,” suggesting a stressed environment of deposition, the palynology of the benches of the dull interval show greater diversity than might be expected just from the petrology. Lithology is generally similar between the sites, but each site has some differences in the petrology. Overall, the coal bed shows significant lateral variation in properties at the mine scale, some of which can be attributed to the gain or loss of upper and lower lithologies, either through an actual physical merging or through the change in character of lithotypes.

Sulfur content varies between the three sites examined for this study. Site 3, located in the northwestern portion of the study area is characterized by a strikingly high sulfur zone (7.45%) in the middle of the coal bed, a feature missing at the other sites. Pyrite and marcasite, in a mid-seam lithotype at the northwestern site (site 3), show signs of overgrowths, indicating multiple generations of sulfide emplacement. The high-sulfur site 3 lithologies all have massive overgrowths of euhedral and framboidal pyrite, fracture- and cleat-fill pyrite, and sulfide emplacement in fusinite lumens. Sulfur is high throughout the mine area, but variations are evident in the extent of secondary growth of sulfides.

### **Petrology, mineralogy and geochemistry of mined coals, western Venezuela**

**Authors:** Paul C. Hackley, Peter D. Warwick, Eligio González

**Journal:** International Journal of Coal Geology; Volume 63, Issues 1-2, 20 July 2005, Pages 68-97

**Abstract:** Upper Paleocene to middle Miocene coal samples collected from active mines in the western Venezuelan States of Táchira, Mérida and Zulia have been characterized through an integrated geochemical, mineralogical and petrographic investigation. Proximate, ultimate, calorific and forms of sulfur values, major and trace element, vitrinite reflectance, maceral concentrations and mineral matter content have been determined for 16 channel samples from 14 mines. Ash yield generally is low, ranging from < 1 to 17 wt.% (mean = 5 wt.%) on a dry basis (db). Total sulfur content is low to moderate, ranging from 1 to 6 wt.%, db (average = 1.7 wt.%). Calorific value ranges from 25.21 to 37.21 MJ/kg (10,840–16,000 Btu/lb) on a moist, mineral-matter-free basis (average = 33.25 MJ/kg, 14,300 Btu/lb), placing most of the coal samples in the apparent rank classification of high-volatile bituminous. Most of the coal samples exhibit favorable characteristics on the various indices developed to predict combustion and coking behavior and concentrations of possible environmentally sensitive elements (As, Be, Cd, Cr, Co, Hg, Mn, Ni, Pb, Sb, Se, Th and U) generally are similar to the concentrations of these elements in most coals of the world, with one or two exceptions. Concentrations of the liptinite maceral group range from < 1% to 70 vol.%. Five samples contain > 20 vol.% liptinite, dominated by the macerals bituminite and sporinite. Collotelinite dominates the vitrinite group; telinite was observed in quantities of ≤ 1 vol.% despite efforts to better quantify this maceral by etching the sample pellets in potassium permanganate and also by exposure in an oxygen plasma chamber. Inertinite group macerals typically represent < 10 vol.% of the coal samples and the highest concentrations of inertinite macerals are found in distantly spaced (> 400 km) upper Paleocene coal samples from opposite sides of Lago de Maracaibo, possibly indicating tectonic controls on subsidence related to construction of the Andean orogen. Values of maximum reflectance of vitrinite in oil (Ro max) range between 0.42% and 0.85% and generally are consistent with the high-volatile bituminous rank classification obtained through ASTM methods. X-ray diffraction analyses of low-temperature ash residues indicate that kaolinite, quartz, illite and pyrite dominate the inorganic fraction of most samples; plagioclase, potassium feldspar, calcite, siderite, ankerite, marcasite, rutile, anatase and apatite are present in minor or trace concentrations. Semiquantitative values of volume percent pyrite content show a strong correlation with pyritic sulfur and some sulfide-hosted trace element concentrations (As and Hg). This work provides a modern quality dataset for the western Venezuela coal deposits currently being exploited and will serve as the foundation for an ongoing coal quality research program in Venezuela.

### **Geochemistry and mineralogy of coal in the recently explored Zhundong large coal field in the Junggar basin, Xinjiang province, China**

**Authors:** Jibin Zhou, Xinguo Zhuang, Andrés Alastuey, Xavier Querol, Jinghong Li

**Journal:** International Journal of Coal Geology; Volume 82, Issues 1-2, 1 May 2010, Pages 51-67

**Abstract:** The Zhundong coalfield is a very large coal deposit, currently under exploration, and promises to be an important coal mining resource in Western China. The coal reserves amount to 164 Gt. At Xiheishan and Wucaiwan, the coal-bearing units are the Badaowan (Lower Jurassic) and, especially, the Xishanyao formations (Middle Jurassic). These contain from one to 31 coal seams (one to 10 workable coals reaching the rank of high volatile A bituminous) with an accumulated workable coal thickness of 20–87 m. These recently explored coal reserves are of a high quality and are characterized by low ash, aluminum, iron, sulfur, and trace element contents. The minerals present in this coal are mainly quartz, kaolinite, siderite, and pyrite. The trace element contents in both Xiheishan and Wucaiwan coals are much lower when compared with the usual concentration ranges present in Chinese coals, with the exception of Ba and Sr. Thus, Ba contents in Xiheishan coal are higher than Swaine's worldwide concentration range. A large number of elements have mainly aluminosilicate affinity, and occur in clay and other detrital coal minerals. Ca and Mn have mainly carbonate affinity; Fe and S have mainly sulphide affinity in Wuchaiwan coal. In Xiheishan, Fe, Mn and Mg have mainly carbonate affinity (siderite), and probably, B, Co, Ni and S have an organic affinity.

Thus, the Zhundong coalfield contains coal with a very high quality and very low levels of impurities. The very low ash yields, S, Fe, and trace element contents may be attributed to the sedimentological setting, with intensive peat bog aggradation in a very shallow lake environment with a low detrital supply. The very low sulfur content, the relatively high Ba-sulfate (barite) content and the high siderite occurrence in Xiheishan coal (in contrast to the pyrite occurrence in Wucaiwan coal) may be attributed to the rapid aggradation of peat with the consequent oxidation and leaching of minerals, elements, and degradation of organic components. Under this scenario, sulfate is trapped by the continuous precipitation and accumulation of barium sulfate (very low soluble).

### **Organic petrology of an early Paleocene coal zone, Wabamun, Alberta: palynology, petrography and geochemistry**

**Authors:** Thomas Demchuk, Alexander R. Cameron, L.V. Hills

**Journal:** Organic Geochemistry; Volume 20, Issue 2, February 1993, Pages 135-148

**Abstract:** An interdisciplinary investigation of a section through the early Paleocene Ardley coal zone at Wabamun, Alberta reveals that there are distinct vertical variations in the palynological, petrographical and geochemical properties reflecting changes in the original depositional environment. Palynological assemblages are dominated by Taxodiaceapollenites hiatus revealing that the original coal-accumulating mires were inhabited by taxodiaceous vegetation. Subordinate palynomorphs include varied gymnosperm pollen other than T. hiatus, Laevigatosporites spp (fern spores of polypodiaceous affinity), Stereisorites spp (mosses including Sphagnum) and Osmundacidites sp. (Family Osmundaceae). Coal petrography reveals that these coals are inertinite-rich. Abundant fusinite (pyrofusinite), along with semi-fusinite and inertodetrinite comprise up to 65% of the maceral assemblages. Huminite macerals are predominantly eu-ulminite B with lesser eu-ulminite A, densinite and geli-huminite (gelified huminite lacking any remnant cell structure). Liptinite macerals include resinite, sporinite and cutinite. Thinner, stratigraphically lower seams at Wabamun (seams Nos 6-3) consist predominantly of bright coal with high huminite contents. Palynofloral assemblages are comprised of T. hiatus with few abundances of other palynomorphs, suggesting that the original depositional environment was low-lying, dominated by taxodiaceous vegetation, and frequently flooded as evidenced by numerous shale partings, high ash contents and relatively high sulphur percentages. The thick No. 2 seam displays a distinct dulling-up petrographic profile resulting from increasing inertinite contents. Coupled with increased abundances of Stereisorites spp, this may be evidence of localized ombrogeny within the original Wabamun mires, and may support a genetic relationship between Stereisorites sp. and inertodetrinite. The No. 1 seam consists of abundant fibrous (fusain-rich) coal. Modes of origin of this fibrous coal include extreme oxidation due to prolonged drought and possibly forest fires. Elevated ash contents within the Nos 1 and 2 seams may be a result of this oxidation of organic matter and concentration of the inorganics, as well as airborne volcanic ash as evidenced by numerous bentonite bands within these coals. Sulphur contents are extremely low, as low as 0.05% reflecting a terrestrial depositional environment.

## **Geochemistry and mineralogy of the Cretaceous Wulantuga high-germanium coal deposit in Shengli coal field, Inner Mongolia, Northeastern China**

**Authors:** Xinguo Zhuang, Xavier Querol, Andrés Alastuey, Roberto Juan, Felicià Plana, Angel Lopez-Soler, Guang Du, Victor V. Martynov

**Journal:** International Journal of Coal Geology; Volume 66, Issues 1-2, 3 February 2006, Pages 119-136

**Abstract:** The occurrence and distribution of minerals, and major and trace elements of the coal #6-1 from the Cretaceous Wulantuga high-germanium coal deposit in Shengli coal field, Inner Mongolia are investigated. The major mineral constituents of coal #6-1 are quartz (15%), kaolinite (4–5%), illite (1%), pyrite (< 1%), feldspars (< 1%), gypsum (weathering product, < 2%) and traces of chlorite. In addition to these phases, traces of scheelite ( $\text{CaWO}_4$ ) and weddellite (an oxalate,  $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) were also detected by XRD. On the basis of chemical and mineralogical properties, a clear differentiation was found between the upper and lower coal sections: the lower section with higher sulfide mineral content, and the upper one with low sulfur content and with a higher proportion of mineral phases formed/accumulated under oxidizing conditions (quartz and dolomite). This coal seam is highly enriched in Ge, As, W, and Hg (one to two orders of magnitude higher than the usual worldwide coal concentrations), with high contents of Sb, U, Cs, and Be (one order of magnitude higher than the usual worldwide coal concentrations). The geochemical and mineralogical profile patterns of the coal seam were attributed to the development of a basal reduced marsh environment evolving towards a more oxidizing marsh environment in the upper part of the coal seam. This could be related to the evolution from a high water table low moor marsh environment to a high moor marsh into an open water body with a higher detrital influence at the top of the seam. These syngenetic geochemical characteristics are possibly modified by an unusually intensive hydrothermal alteration causing the formation of oxalate minerals and the enrichment in a series of elements such as Cs, Be, U, As, Se, and Hg.

## **Geochemistry of rare earth elements in a marine influenced coal and its organic solvent extracts from the Antaibao mining district, Shanxi, China**

**Authors:** Wenfeng Wang, Yong Qin, Shuxun Sang, Yanming Zhu, Chaoyong Wang, Dominik J. Weiss

**Journal:** International Journal of Coal Geology; Volume 76, Issue 4, 1 December 2008, Pages 309-317

**Abstract:** Twenty-six samples including roof, bottom and coal plies of a marine influenced coal bed were collected from the Antaibao mining district, Shanxi, China. The rare earth elements (REEs) were determined in solids and organic solvent extracts. The distribution pattern showed three distinct patterns: shale-like, LREE-rich and HREE-rich. This is attributed to the variable microenvironment of peat-forming swamp, the degree of marine influences and different REE sources. REEs in the coal are mainly controlled by detrital minerals but also affected by seawater. The chondrite-normalized REE patterns of the organic solvent extracts are distinctly different from those of corresponding original coal samples, which show a negative Eu anomaly, a depletion of middle REEs and an enrichment of HREEs. The LREEs in coal extracts are likely adsorbed by hydrogen-containing functional groups, and HREEs are likely bonded to carbon atoms.

## **Geochemistry of rare earth elements in Permian coals from the Huaibei Coalfield, China**

**Authors:** Liugen Zheng, Guijian Liu, Chen-Lin Chou, Cuicui Qi, Ying Zhang

**Journal:** Journal of Asian Earth Sciences; Volume 31, Issue 2, 15 October 2007, Pages 167-176

**Abstract:** The rare earth elements (REEs) in coals are important because of: (a) REE patterns can be an indicator of the nature of source rocks of the mineral matter as well as sedimentary environments; (b) REEs abundance in coal may have industrial-significance. In this study, a total of thirty-four samples of Permian coal, partings, roof, and floor were collected from the Huaibei Coalfield, Anhui Province, China. Abundances of rare earth elements (REEs) and other elements in the samples were determined by inductively coupled-plasma mass spectrometry (ICP-MS) and inductively coupled-plasma atomic emission spectrometry (ICP-AES). The results show that the REEs are enriched in coals in the Huaibei Coalfield as compared with Chinese and U.S. coals and the world coal average. Coals in the

Lower Shihezi Formation (No. 7, 5, and 4 Coals) and Upper Shihezi Formation (No. 3) have higher REE abundances than the coals in Shanxi Formation (No. 10). Magmatic intrusion resulted in high enrichment of REEs concentrations in No. 5 and 7 Coals. The REE abundances are positively correlated with the ash content. The mineral matter in these coals is mainly made up of clay minerals and carbonates. The REEs are positively correlated with lithophile elements including Si, Al, Ti, Fe, and Na, which are mainly distributed in clay minerals, indicating that REEs are contained mainly in clay minerals. The REE abundances in coals normalized by the ash are higher than that in partings. REEs abundances of coals cannot be accounted for by the REE content in the mineral matter, and some REEs associated with organic matter in coals.

### **Geochemistry and stable isotope investigation of acid mine drainage associated with abandoned coal mines in central Montana, USA**

**Authors:** Christopher H. Gammons, Terence E. Duaiame, Stephen R. Parker, S. R. Poulson, P.Kennelly

**Journal:** Chemical Geology; Volume 269, Issues 1-2, 15 January 2010, Pages 100-112

**Abstract:** The Great Falls-Lewistown Coal Field (GFLCF) in central Montana contains over 400 abandoned underground coal mines, many of which are discharging acidic water with serious environmental consequences. Areas of the mines that are completely submerged by groundwater have circum-neutral pH and relatively low concentrations of metals, whereas areas that are only partially flooded or freely draining have acidic pH (< 3) and high concentrations of metals. The pH of the mine drains either decreases or increases after discharging to the surface, depending on the initial ratio of acidity (mainly Al and Fe<sup>2+</sup>) to alkalinity (mainly HCO<sub>3</sub><sup>-</sup>). In acidic, Fe-rich waters, oxidation of Fe<sup>2+</sup> after exposure to air is microbially catalyzed and follows zero-order kinetics, with computed rate constants falling in the range of 0.97 to 1.25 mmol L<sup>-1</sup> h<sup>-1</sup>. In contrast, Fe<sup>2+</sup> oxidation in near-neutral pH waters appears to be first-order with respect to Fe<sup>2+</sup> concentration, although insufficient data were collected to constrain the rate law expression. Rates of Fe<sup>2+</sup> oxidation in the field are dependent on temperature such that lower Fe<sup>2+</sup> concentrations were measured in down-gradient waters during the day, and higher concentrations at night. Diel cycles in dissolved concentrations of Zn and other trace metals (Mn, Ni) were also noted for down-gradient waters that were net alkaline, but not in the acidic drains.

The coal seams of the GFLCF and overlying Cretaceous sandstones form a perched aquifer that lies ~ 50 m above the regional water table situated in the underlying Madison Limestone. The δD and δ<sup>18</sup>O values of flooded mine waters suggest local derivation from meteoric water that has been partially evaporated in agricultural soils overlying the coal mines. The S and O isotopic composition of dissolved sulfate in the low pH mine drains is consistent with oxidation of biogenic pyrite in coal under aerated conditions. A clear distinction exists between the isotopic composition of sulfate in the acid mine waters and sulfate in the adjacent sedimentary aquifers, making it theoretically possible to determine if acid drainage from the coal mines has leaked into the underlying Madison aquifer.

### **Mineralogy and geochemistry of the coals from the Chongqing and Southeast Hubei coal mining districts, South China**

**Authors:** Xinguo Zhuang, X. Querol, A. Alastuey, F. Plana, N. Moreno, J.M. Andrés, Jieli Wang

**Journal:** International Journal of Coal Geology; Volume 71, Issues 2-3, 2 July 2007, Pages 263-275

**Abstract:** This paper deals with the study of the Late Permian coal deposits from Chongqing and south-eastern Hubei mining districts and of the Late Triassic coal deposits from Chongqing mining district. The Late Permian coals are characterized by relatively high amount of sulphide, sulphate and carbonate minerals and by a high total content of trace elements (with respect to the Late Triassic coals) due to the marine influence on the depositional environment. The Late Permian Chongqing and the southeastern Hubei coals showed similar geochemistry and mineralogy. However, there were some differences due to the different source rock and magmatic influence on Hubei coals. The concentrations of most trace elements in the Late Triassic coal were relatively low when compared with the usual range of the worldwide concentrations. By contrast, the contents of Ta, Se, Nb, Sc, Hf, Tl, Bi, Cu, V and Zn in the Late Permian Chongqing and Southeastern Hubei coals were higher than the usual range. Differences in occurrence of major and trace elements were found between Late Permian Hubei and Chongqing coals. Thus,

most of the trace elements investigated presented an aluminosilicate association, followed by sulphide–arsenide (Fe, S, As, Pb, Mo, Ni and Co, in most cases) and carbonate (Ca and Mg) affinities in both areas. However, there was an important phosphate and zircon association in the Chongqing coal, whereas the carbonate association was significantly influenced by magma in the coals from Hubei. In the Late Triassic coal most of the major and trace elements investigated occur in aluminosilicate associations, with the exception of S, Fe, Ca, Mn, Sr, Sn, Ba, Nb, Mo, Mg, Co and Ta, with carbonate, sulphate and sulphide affinities.

### **Geochemistry of beryllium in Bulgarian coals**

**Author:** Greta M. Eskenazy

**Journal:** International Journal of Coal Geology; Volume 66, Issue 4, 3 April 2006, Pages 305-315

**Abstract:** The beryllium content of about 3000 samples (coal, coaly shales, partings, coal lithotypes, and isolated coalified woods) from 16 Bulgarian coal deposits was determined by atomic emission spectrography. Mean Be concentrations in coal show great variability: from 0.9 to 35 ppm for the deposits studied. There was no clear-cut relationship between Be content and rank. The following mean and confidence interval Be values were measured: lignites,  $2.6 \pm 0.8$  ppm; sub-bituminous coals,  $8.2 \pm 3.3$  ppm; bituminous coals,  $3.0 \pm 1.2$  ppm; and anthracites,  $19 \pm 9.0$  ppm. The Be contents in coal and coaly shales for all deposits correlated positively suggesting a common source of the element. Many samples of the coal lithotypes vitrain and xylain proved to be richer in Be than the hosting whole coal samples as compared on ash basis. Up to tenfold increase in Be levels was routinely recorded in fusain. The ash of all isolated coalified woods was found to contain 1.1 to 50 times higher Be content relative to its global median value for coal inclusions. Indirect evidence shows that Be occurs in both organic and inorganic forms. Beryllium is predominantly organically bound in deposits with enhanced Be content, whereas the inorganic form prevails in deposits whose Be concentration approximates Clarke values. The enrichment in Be exceeding the coal Clarke value 2.4 to 14.5 times in some of the Bulgarian deposits is attributed to subsynchronous at the time of coal deposition hydrothermal and volcanic activity.

### **Geochemistry of Late Triassic coals in the Changhe Mine, Sichuan Basin, southwestern China: Evidence for authigenic lanthanide enrichment**

**Author:** Xibo Wang

**Journal:** International Journal of Coal Geology; Volume 80, Issues 3-4, 1 December 2009, Pages 167-174

**Abstract:** Five thin coals of Late Triassic age occur in the Changhe Mine, Sichuan Basin, southwestern China. Petrology and geochemistry of these coals and their roof, parting, and floor samples were studied. The results show that the Changhe coals are enriched in As (8.9–11.8  $\mu\text{g/g}$ ), W (2.2–11.2  $\mu\text{g/g}$ ), Pb (20.8–48.2  $\mu\text{g/g}$ ), and Th (7.5–18.8  $\mu\text{g/g}$ ). The source of these elements is possibly the Xuefeng old land which is an early Paleozoic source area southeast of the Sichuan Basin. Two tonsteins were found in the Changhe Mine. One is the roof (K8R) of the K8 coal which is a pure kaolinitic claystone. The other is the claystone (K9C) above the roof of the K9 coal which is mainly made up of mixed illite–smectite minerals. The REE content (287.9  $\mu\text{g/g}$ ) of the K8 coal is much higher than that of its roof (153.6  $\mu\text{g/g}$ ). SEM-EDX results show that authigenic monazite and kaolinite are the main carriers of REE in the K8 coal. On the basis of coal chemistry and occurrence of the precipitated minerals, it is likely that leaching of the K8R tonstein occurred. It is possible that trace elements including Be (8.4  $\mu\text{g/g}$ ), Zr (302  $\mu\text{g/g}$ ), Nb (26  $\mu\text{g/g}$ ), Hf (9.7  $\mu\text{g/g}$ ), Th (18.8  $\mu\text{g/g}$ ), U (5.8  $\mu\text{g/g}$ ), Ga (16.1  $\mu\text{g/g}$ ), and Pb (48.2  $\mu\text{g/g}$ ) in the K8 coal were also elevated by the leachate of its overlying tonstein (K8R). The K9C tonstein with a total thickness of 16 cm is widely distributed in the Changhe Mine and serves as a distinct marker bed for correlation of coal seams. Besides mixed illite–smectite minerals, trace amounts of euhedral zircon, anatase, apatite, and massive silica with vesicular structure were also examined, these constitute strong evidence for its felsic volcanic ash origin.

### **Mineralogy and geochemistry of the No. 6 Coal (Pennsylvanian) in the Junger Coalfield, Ordos Basin, China**

**Authors:** Shifeng Dai, Deyi Ren, Chen-Lin Chou, Shengsheng Li, Yaofa Jiang

**Journal:** International Journal of Coal Geology; Volume 66, Issue 4, 3 April 2006, Pages 253-270

**Abstract:** This paper discusses the mineralogy and geochemistry of the No. 6 Coal (Pennsylvanian) in the Junger Coalfield, Ordos Basin, China. The results show that the vitrinite reflectance (0.58%) is lowest and the proportions of inertinite and liptinite (37.4% and 7.1%, respectively) in the No. 6 Coal of the Junger Coalfield are highest among all of the Late Paleozoic coals in the Ordos Basin. The No. 6 Coal may be divided vertically into four sections based on their mineral compositions and elemental concentrations. A high boehmite content (mean 6.1%) was identified in the No. 6 Coal. The minerals associated with the boehmite in the coal include goyazite, rutile, zircon, and Pb-bearing minerals (galena, clausthalite, and selenio-galena). The boehmite is derived from weathered and oxidized bauxite in the weathered crust of the underlying Benxi Formation (Pennsylvanian). A high Pb-bearing mineral content of samples ZG6-2 and ZG6-3 is likely of hydrothermal origin. The No. 6 coal is enriched in Ga (44.8 µg/g), Se (8.2 µg/g), Sr (423 µg/g), Zr (234 µg/g), REEs (193.3 µg/g), Hg (0.35 µg/g), Pb (35.7 µg/g), and Th (17.8 µg/g). Gallium and Th in the No. 6 Coal mainly occur in boehmite, and the Pb-bearing selenide and sulfide minerals contribute not only to Se and Pb contents in the coal, but also probably to Hg content. A high Zr content is attributed to the presence of zircon, and Sr is related to goyazite. The REEs in the coal are supplied from the sediment-source region, and the REEs leached from the adjacent partings by groundwater.

### **Application of organic petrology and geochemistry to coal waste studies**

**Authors:** Magdalena Misz-Kennan, Monika J. Fabiańska

**Journal:** International Journal of Coal Geology; Volume 88, Issue 1, 1 October 2011, Pages 1-23

**Abstract:** Coal wastes produced during mining activities are commonly deposited in nearby dumps. These wastes mostly composed of minerals and variable amounts (usually 20–30%) of organic matter start to weather immediately after deposition. Oxidation of the organic matter can lead to self heating and self combustion as a result of organic and mineral matter transformations. The degree of alteration depends on the properties of the wastes, i.e., the maceral and microlithotopy composition of the organic matter and its rank.

Alteration of wastes also depends on the heating history, i.e., the rate of heating, final heating temperature, duration of heating, and the degree of air access. Although air is probably necessary to initiate and drive the heating processes, these usually take place under relatively oxygen depleted conditions. With slow heating, color of organic matter particles changes, irregular cracks and oxidation rims develop around edges and cracks, and bitumen is expelled. As a result, massive and detritic isotropic and strongly altered organic matter forms. On the other hand, higher heating rates cause the formation of devolatilization pores, oxidation rims around these pores and along cracks, vitrinite-bands-mantling particles, and bitumen expulsions. Organic compounds generated from the wastes include n-alkanes, iso-alkanes, alkylcyclohexanes, acyclic isoprenoids, mainly pristane, phytane and, in some cases, farnesane, sesquiterpanes, tri- and tetracyclic diterpanes, tri- and pentacyclic triterpanes, and steranes, polycyclic aromatic hydrocarbons (mostly with two- to five rings, rarely six rings), and phenols. The compounds formed change during the heating history. The fact that phenols are found in dumps where heating has not yet been completed, but are absent in those where heating ceased previously suggests the presence of water washing. The organic compounds formed may migrate within the dumps. However, when they migrate out of the dumps, they become a hazard to environment. This paper is a review on transformations of organic matter (both maceral composition and reflectance and chemical composition) in coal wastes deposited in coal waste dumps. Immediately after deposition the wastes are exposed to weathering conditions and sometimes undergo self heating processes.

### **Geochemistry of trace elements in Chinese coals: A review of abundances, genetic types, impacts on human health, and industrial utilization**

**Authors:** Shifeng Dai, Deyi Ren, Chen-Lin Chou, Robert B. Finkelman, Vladimir V. Seredin, Yiping Zhou

**Journal:** International Journal of Coal Geology; In Press, doi:10.1016/j.coal.2011.02.003

**Abstract:** China will continue to be one of the largest coal producers and users in the world. The high volume of coal use in China has focused attention on the amounts of toxic trace elements released from coal combustions and also the valuable trace elements extracted or potentially utilized from coal ash. Compared to world coals, Chinese coals have normal background values for most trace elements, with the exception of higher Li (31.8 µg/g), Zr (89.5 µg/g), Nb (9.44 µg/g), Ta (0.62 µg/g), Hf (3.71 µg/g), Th (5.84 µg/g), and rare earth elements ( $\Sigma$  La-Lu + Y, 136

µg/g). This is not only due to the higher ash yields of Chinese coals but also to alkali volcanic ashes found in some southwestern coals. The background values of toxic elements of Hg (0.163 µg/g), As (3.79 µg/g), and F (130 µg/g) in Chinese coals are comparable to coals from most other countries. The genetic types for trace-element enrichment of Chinese coals include source-rock- controlled, marine-environment-controlled, hydrothermal-fluid-controlled (including magmatic-, low-temperature-hydrothermal-fluid-, and submarine-exhalation-controlled subtypes), groundwater-controlled, and volcanic-ash-controlled. The background values of trace elements were dominated by sediment source regions. Low-temperature hydrothermal fluid was one of the major factors for the local enrichment of trace elements in southwestern China.

Serious human health problems caused by indoor combustion of coal in China include endemic fluorosis, arsenosis, selenosis, and lung cancer. Endemic fluorosis, mainly occurring in western Guizhou, was mostly attributed to the high fluorine in clay that was used as a briquette binder for fine coals, in addition to a small quantity of fluorine from coal. Fluorine in the coal from endemic-fluorosis areas of western Guizhou is within the usual range found in China and the world. Endemic arsenosis in southwestern Guizhou is attributed to indoor combustion of high-As coal. Endemic selenosis in Enshi of Hubei was due to high Se in carbonaceous siliceous rocks and carbonaceous shales. Fine particles of quartz, released into air during coal combustion, are hypothesized as a possible cause for the lung cancer epidemic in Xuanwei, Yunnan, China.

Valuable elements, including Ge, Ga, U, REE (rare earth element), Nb, Zr, and Re are concentrated to levels comparable to conventional economic deposits in several coals or coal-bearing strata in China. The Ge deposits at Lincang, Yunnan province and Wulantuga, Inner Mongolia have been exploited and industrially utilized. The enrichment of Ge in the two deposits was caused by hydrothermal fluids associated with adjacent granitoids. The Ga (Al) ore deposit in the Jungar Coalfield, Inner Mongolia, was derived from the neighboring weathered and oxidized bauxite of the Benxi Formation (Pennsylvanian). The Nb(Ta)–Zr(Hf)–REE–Ga deposits in the Late Permian coal-bearing strata of eastern Yunnan and Chongqing of southwestern China were attributed to ashes of the alkali volcanic eruptions.

#### **Petrology, mineralogy and geochemistry of the Permian and Triassic coals in the Leping area, Jiangxi Province, southeast China**

**Authors:** X Querol , A Alastuey, Xinguo Zhuang, J.C Hower, A Lopez-Soler, F Plana, Rongsu Zeng

**Journal:** International Journal of Coal Geology; Volume 48, Issues 1-2, December 2001, Pages 23-45

**Abstract:** Permian and Triassic coals from a series of mines in Jiangxi Province, China, exhibit a number of unusual geochemical, mineralogical, and petrographic characteristics. The high volatile bituminous Permian coals have high concentrations of the suberinite-like maceral “barkinite.” The origin, and even the distinct character, of “barkinite” are in dispute and, consequently, it has not been recognized as a distinct maceral by the International Committee for Coal and Organic Petrology (ICCP). The Permian bituminous coals have relatively high concentrations of pyrite and marcasite. Otherwise, detrital minerals dominate their geochemistry. The Triassic coals, all from one mine complex, have higher rank (a Permian coal is also mined). Most samples straddle the low volatile bituminous/semi-anthracite boundary. The one semi-anthracite-rank Permian coal shows signs of incipient coking. A Triassic coal in the same fault block is coked by an igneous intrusions found in the mine. The coals have, in general, been dolomitized. Aside from the geochemical imprint of the dolomitization, trace element associations suggesting a contribution from a detrital mineral assemblage dominate the coals.

#### **Petrology, mineralogy, and geochemistry of submarine coals and petrified forest in the Sozopol Bay, Bulgaria**

**Authors:** Mariana G. Yossifova, Greta M. Eskenazy, Sevdalina P. Valčeva

**Journal:** International Journal of Coal Geology; Volume 87, Issues 3-4, 1 September 2011, Pages 212-225

**Abstract:** The mineralogy, petrology, and geochemistry of submarine coals and petrified tree trunks from the Sozopol Bay were investigated. The coals are lignites of Lower–Middle Miocene age. The petrified trunks are 40 cm up to 2 m high, some of which are in growth position and others are fallen. The main minerals in the coal are silicates of detrital origin (clay minerals) and authigenic pyrite. Authigenic sulfur and amber are present as well. In

the Sozopol coals stored for 30 years, a neoformed mineral assemblage comprising mainly of gypsum, iron sulfates, sulfates of varying Fe, Na, Al, K, and Mg content, and halite has been observed. The formation of the sulfates was induced by bacterial activity as well. Germanium, Li, Rb, Ti, V, Mo, Cr, Mn, Co, and Ni are enriched in the coals as compared with the Clarke values of the world brown coals. In most of the samples studied, the contents of Ga, B, Y, W, Cu, Zn, Pb, P, and Zr are elevated as well. The element distribution is influenced by the lithotype composition. Most elements have a mixed mode of occurrence. Germanium, V, Ti, Cr, B, Na, and Ni (and to a lesser extent Sr and Cu) are organically associated, while K, Li, Rb, and Fe have a distinct inorganic mode of occurrence. Molybdenum follows strictly the Fe distribution. It is suggested that the main sources of the trace elements were the volcanic rocks in the sediment source area, from which the elements were leached in the peat bog.

**Mineralogy and geochemistry of a superhigh-organic-sulfur coal, Yanshan Coalfield, Yunnan, China:  
Evidence for a volcanic ash component and influence by submarine exhalation**

**Authors:** Shifeng Dai, Deyi Ren, Yiping Zhou, Chen-Lin Chou, Xibo Wang, Lei Zhao, Xingwei Zhu

**Journal:** Chemical Geology; Volume 255, Issues 1-2, 30 September 2008, Pages 182-194

**Abstract:** The mineralogy and geochemistry of a superhigh-organic-sulfur (SHOS) coal of Late Permian age from the Yanshan Coalfield, Yunnan Province, southwestern China, have been studied using optical microscope, low-temperature ashing plus X-ray diffraction analysis, scanning electron microscope equipped with energy-dispersive X-ray spectrometer, a sequential chemical extraction procedure, and inductively coupled plasma mass spectrometry. The M9 Coal from the Yanshan Coalfield is a SHOS coal that has a total sulfur content of 10.12%–11.30% and an organic sulfur content of 8.77%–10.30%. The minerals in the coal consist mainly of high-temperature quartz, sanidine, albite, muscovite, illite, pyrite, and trace amounts of kaolinite, plagioclase, akermanite, rutile, and dawsonite. As compared with ordinary worldwide (bituminous coals and anthracite) and Chinese coals, the M9 Coal is remarkably enriched in B (268 µg/g), F (841 µg/g), V (567 µg/g), Cr (329 µg/g), Ni (73.9 µg/g), Mo (204 µg/g), and U (153 µg/g). In addition, elements including Se (25.2 µg/g), Zr (262 µg/g), Nb (20.1 µg/g), Cd (2.07 µg/g), and Tl (2.03 µg/g) are also enriched in the coal. Occurrence of high-temperature quartz, sanidine, muscovite, and illite in the M9 Coal is evidence that there is a volcanic ash component in the coal that was derived from acid volcanic ashes fallen into the swamp during peat accumulation. Occurrence of albite and dawsonite in the coal and strong enrichment of some elements, including F, S, V, Cr, Ni, Mo and U, are attributed to the influence by submarine exhalation which invaded along with seawater into the anoxic peat swamp. Abundances of lithophile elements, including rare earth elements, Nb, Y, Zr, and TiO<sub>2</sub>, indicate that the silicate minerals in the coal were derived from the northern Vietnam Upland to the south of the basin.

**Petrography, carbonate mineralogy and geochemistry of thermally altered coal in Permian coal measures,  
Hunter Valley, Australia**

**Authors:** Alexandra N. Golab, Adrian C. Hutton, David French

**Journal:** International Journal of Coal Geology; Volume 70, Issues 1-3, 2 April 2007, Pages 150-165

**Abstract:** Carbonate minerals commonly occur in coals of many ages and from a utilisation viewpoint can be deleterious. Several studies have been undertaken of the carbonates in the Permian coals of the Hunter Valley, Australia, but few studies use a multi-technique approach. For this study, a combined petrographic, geochemical and mineralogical approach was used to determine the distribution and residence of carbonate minerals in coal that had been intruded by a dyke. The dominant carbonate assemblages comprise primary siderite in inertinite-rich microlithotypes and secondary calcite(–ankerite–dolomite)–dawsonite in vitrinite-rich microlithotypes. The secondary carbonates were found in both the aureole of heated coal and also in an unheated mine-face sample. It is believed that the secondary carbonate minerals precipitated from magma-derived fluids percolating through the coal following the emplacement of the intrusions. The textures and distribution of the secondary carbonate minerals suggest that the temperature and pressure of the fluids may be just as important in developing fractures near dykes (particularly those that have multiple phases of geometries), cleat mineralogy and coal textures as direct heating from the intrusion. The partitioning of primary siderite with inertinite and secondary carbonates with vitrinite indicates that it can be reasonably expected that there would be a partitioning of minerals in various density fractions derived from float–sink tests and consequently a partitioning of elements with inertinite-rich fractions containing

elevated Fe levels and vitrinite-rich fractions containing elevated Ca, Mg and Al. This partitioning has implications for the behaviour of the coal during washing and combustion, and the composition of combustion products.

**The geochemistry of rare earth elements (REE) in acid mine drainage from the Sitai coal mine, Shanxi Province, North China**

**Authors:** Fenghua Zhao, Zhiyuan Cong, Hongfu Sun, Deyi Ren

**Journal:** International Journal of Coal Geology; Volume 70, Issues 1-3, 2 April 2007

**Abstract:** In this paper, geochemical characteristics of rare earth elements (REE) in acid mine drainage (AMD) from the Sitai coal mine of Shanxi Province, North China were investigated by determining concentrations of dissolved REEs and major solutes in the AMD samples, concentrations of REEs in the AMD precipitate samples and country rock samples (mudstone and coal), and modeling REEs species in the AMD. The results show that AMD in the Sitai coal mine have high REEs and SO<sub>4</sub><sup>2-</sup> concentrations in comparison with several terrestrial waters worldwide. The REE speciation modeling indicates that sulfate complexes (LnSO<sub>4</sub><sup>+</sup>, > 60%) and free metal species (Ln<sup>3+</sup>, 20%–40%) are dominant REEs species in the AMD. AMD of the Sitai coal mine also shows a middle REE-enriched NASC (North American Shale Composite)-normalized pattern. The authors suggest that both REE sulfates (LnSO<sub>4</sub><sup>+</sup>) in the AMD and country rock of coal measures are possible reasons for middle REE-enriched NASC-normalized pattern of the Sitai coal mine AMD. Further work on the AMD precipitates is needed to obtain more information on the origin of the middle REE-enriched NASC-normalized patterns.

**The geochemistry of environmentally important trace elements in UK coals, with special reference to the Parkgate coal in the Yorkshire–Nottinghamshire Coalfield, UK**

**Authors:** D.A. Spears, S.J. Tewalt

**Journal:** International Journal of Coal Geology; Volume 80, Issues 3-4, Pages 157-166

**Abstract:** The Parkgate coal of Langsettian age in the Yorkshire–Nottinghamshire coalfield is typical of many coals in the UK in that it has a high sulphur (S) content. Detailed information on the distribution of the forms of S, both laterally and vertically through the seam, was known from previous investigations. In the present work, 38 interval samples from five measured sections of the coal were comprehensively analysed for major, minor and trace elements and the significance of the relationships established using both raw and centered log transformed data. The major elements are used to quantify the variations in the inorganic and organic coal components and determine the trace element associations. Pyrite contains nearly all of the Hg, As, Se, Tl and Pb and is also the major source of the Mo, Ni, Cd and Sb. The clays contain the following elements in decreasing order of association: Rb, Cs, Li, Ga, U, Cr, V, Sc, Y, Bi, Cu, Nb, Sn, Te and Th. Nearly all of the Rb is present in the clay fraction, whereas for elements such as V, Cu and U, a significant amount is thought to be present in the organic matter, based on the K vs trace element regression equations. Only Ge, and possibly Be, would appear to have a dominant organic source. The trace element concentrations are calculated for pyrite, the clay fraction and organic matter. For pyrite it is noted that concentrations agree with published data from the Yorkshire–Nottinghamshire coalfield and also that Tl concentrations (median of 0.33 ppm) in the pyrite are greater than either Hg or Cd. Unlike these elements, Tl has attracted less attention and possibly more information is needed on its anthropogenic distribution and impacts on man and the environment. A seawater source is thought to be responsible for the high concentrations of S, Cl and the non-detrital trace elements in the Parkgate coal. Indicative of the seawater control is the Th/U ratio, which expresses the detrital to non-detrital element contributions. Using other elements, similar ratios can be calculated, which in combination offer greater interpretative value.

**Petrography and geochemistry of Oligocene bituminous coal from the Jiu Valley, Petroșani basin (southern Carpathian Mountains), Romania**

**Authors:** Harvey E. Belkin, Susan J. Tewalt, James C. Hower, J.D. Stucker, Jennifer M.K. O'Keefe, Calin A. Tatu, Grigore Buia

**Journal:** International Journal of Coal Geology; Volume 82, Issues 1-2, Pages 68-80

**Abstract:** Belt samples of Oligocene (Chattian) bituminous coal from 10 underground mines located in the Jiu Valley, Hunedoara County, Petroșani basin, Romania, have been examined and analyzed for proximate and ultimate analysis, major-, minor- and trace-element chemistry, organic petrography, and vitrinite reflectance. The mineral chemistry and mode of occurrence of trace elements also have been investigated using SEM and electron microprobe techniques. Twenty coal beds occur in the Jiu Valley and most of the samples are from bed no. 3, the most productive bed of the Dilja–Uricani Formation of Oligocene age. The Petroșani basin, oriented SW–NE, is 48-km long, 10-km wide at the eastern part and 2-km wide at the western part. The coal mines are distributed along the center of the valley generally following the Jiu de Vest River. Reflectance measurements indicate that the rank of the coals ranges from high-volatile B to high-volatile A bituminous. Overall, rank decreases from the southwest to the northeast. In bed no. 3, R<sub>max</sub> varies from 0.75% in the northeast to 0.93% in the southwest. Although, most Oligocene coals in Romania and adjacent countries are lignite in rank, the Jiu Valley bituminous coals have been affected by regional metamorphism and attending hydrothermal fluids related to the Alpine orogenic event. The coals are all dominated by vitrinite; resinite and funginite are important minor macerals in most of the coals. Pyrite and carbonate generally dominate the mineral assemblages with carbonate more abundant in the northwest. Siderite occurs as nodules and masses within the macerals (generally vitrinite). Dolomite and calcite occur as fracture fillings, plant-cell fillings, and in other authigenic forms. Late-stage fracture fillings are siderite, dolomite, calcite, and ankerite. In one instance, two populations of siderite (~ 35 and ~ 45 wt.% FeO) plus ankerite fill a large fracture. Late-stage pyrite framboid alteration is Ni- and Cu-bearing, with Ni-rich pyrite, hydrated Ni, Fe sulfate, chalcopyrite and rare pentlandite and clausthalite. Some of the mines sampled in 2001 have been closed as Romania has undergone severe economic and environmental reforms in preparation for its 2007 entry into the European Union (EU). Romania's continued efforts to adapt to a market economy within the environmental and economic constraints of the EU make this collection of data valuable as the eventual fate of the other mines in Jiu Valley is unknown.

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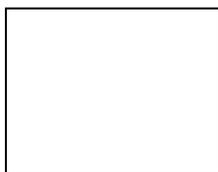
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