Fine-grained barite in coal fly ash from the Upper Silesian Industrial Region

Mariola Jablonska · Frans J.M. Rietmeijer · Janusz Janeczek

Abstract Barite nanocrystals are common and abundant in the troposphere over the Upper Silesian Industrial Region, Poland. The presence of barite nanocrystals is the result of burning Ba-enriched coals (up to 4,260 ppm Ba). ATEM, ASEM and EPMA analyses provided evidence of inefficient coal burning for domestic purposes at temperatures of 800–900 °C as the cause of emissions of barite, which survived unmelted. Much higher temperatures of coal burning for industrial purposes resulted in thermal decomposition of barite into BaO, which could react with airborne sulfuric acid to produce nanometre-sized secondary barite. Formation of both the secondary barite and gypsum in the troposphere contributes to the lowering of acidity of rain over Upper Silesia. Barite nanocrystals are often embedded in sheets of hydrocarbon materials with sizes in the range of respirable aerosols; therefore, they may enter the human respiratory system.

Keywords Barite · Coal fly ash · Environment · ATEM · ASEM

Introduction

Barite (BaSO$_4$) has widespread occurrences and often in sufficiently high concentrations to be an economically

M. Jablonska (✉)
Faculty of Earth Sciences, University of Silesia,
Będzinska 60, 41-200 Sosnowiec, Poland
E-mail: mjablons@us.edu.pl

F.J.M. Rietmeijer
Institute of Meteoritics,
Department of Earth and Planetary Sciences,
University of New Mexico,
Albuquerque, NM 87131, USA

J. Janeczek
Faculty of Earth Sciences, University of Silesia,
Będzinska 60, 41-200 Sosnowiec, Poland

viable ore deposit. Barite is much used in oil and gas drilling industries as a weighing agent in drilling fluids (Davey and others 1991; Komov and others 1994). On offshore rigs, water-treatment techniques with organic solvents are used to remove barite crusts from clogged pipelines and porous strata when the build-up of this crust threatens oil production. These activities will release barite to the local marine environment. Barite is also used in rubber and glass manufacturing and as a pigment and filler material (Komov and others 1994). In general, the anthropogenic applications may have a limited impact on the global environment. The geological occurrences of barite (Table 1) indicate that weathering can easily generate barite dust for aeolian transport with some fraction of it being deposited in the marine environments. Dissolved barium in marine environments is also derived from ice melting and fluvial input (Guay and others 1999). Barium is part of an abiotic deposition–dissolution cycle that is activated by organic materials. This association explains the observed covariation of dissolved Si and Ba in oceans and estuaries (Bishop 1988). It is perhaps not surprising that authigenic barite is commonly associated with coal deposits (Bouška 1981). The geological occurrences seem to indicate that favourable conditions for authigenic barite formation arise from the presence of 'organic' or carbon-rich matter and an influx of SO$_2$ or (SO$_4$)$^{2-}$ (Komov and others 1994). These conditions may exist in volcanogenic–sedimentary deposits. Barium is a common trace element in volcanic ejecta (Table 2). Barium minerals do not appear to be common in volcanic ejecta although this situation may reflect a sampling and analysis bias rather than prove their absence. Barite was found in fumarolic incrustations in the Valley of 10,000 Smokes, Alaska (Zies 1929). Barium also occurs in aerosol particles in the lower and upper troposphere (Murphy and others 1998). Barite dust, probably from the 1982 eruptions of the El Chichón volcano, was present in the upper stratosphere between 34–26 km altitude during May 1985 (Table 3).

Coal burning is probably the most efficient process that significantly releases barite into the environment for regional and semi-global aeolian dispersal in the troposphere. Coal burning for both domestic and industrial uses is the major source of dust and gas emissions in the Upper Silesian Industrial Region, Poland. Barium concentrations in Upper Silesian coals range from 0.2 to 4260 ppm (Ptak and Różkowska 1995) with an average concentration of

Table 1

Geological occurrences of barite

Occurrence	Reference
Gangue mineral in metalliferous hydrothermal veins	Deer and others (1962)
Sinter deposits associated with hot springs	
Veins and cavity filling concretions in limestone, sandstone, shale and clays	
Residual deposit of limestone weathering	
Common, optically 'extremely fine' authigenic grains in coal seams	Bouška (1981)
24–750 ppm Ba (dry coal) in lignites; the host is listed as 'likely barite'	Miller and Given (1987)
Suspended anthropogenic and natural barite particles in deep ocean waters	Jedwab (1980)
Barite–opal–organic carbon associations in oceanic particulate matter; in situ formation of barite particles 0.5–5 µm in size	Bishop (1988)

Table 2

Barium in distal-airfall tephra and volcanic ash collected in the troposphere and stratosphere. No identification of its host phase is available

Occurrence	Reference
Slightly enriched (130 ng/standard cubic metre) in Soufriere plume samples of the 17 April 1979 eruption	Sedlacek and others (1982)
Slightly enriched (1.1–1.3 µg/m^3) in Mt. St. Helens plume samples of the 19 May 1980 eruption	Vossler and others (1981)
Mt. St. Helens ash-fall deposits of the 18 May 1980 eruption: 340 ± 60 ppm	Fruchter and others (1980)
Mt. St. Helens distal air-fall ash from several May 1980 eruptions: 0.02–0.04 wt% BaO	Sarna-Wojcicki and others (1981)
Ash-fall deposits of the 1982 eruptions of El Chichón volcano: average 825 ppm Ba; Ba abundances correlate with calculated glass abundances	Varekamp and others (1984)
The 1982 eruptions of El Chichón volcano: whole rock pumice 750–765 ppm Ba; phenocrysts contain 0.07–0.14 and glasses with 0.1 wt% BaO	Luhr and others (1984)

Table 3

Barium and barite aerosols and particles in the stratosphere and troposphere

Occurrence	Reference
Euhedral single-crystal particles (largest euhedral grain, 0.55×0.4×0.2 µm), small (<90 nm) particles in mono- and polymict clusters, and at the surface of silica and silicate particles	Rietmeijer (1993)
Barium in 'a high fraction' of aerosols >0.2 µm just below the tropopause mostly south of Houston, Texas, over the Gulf of Mexico and southern Mexico during April and May 1998	Murphy and others (1998)
Bull Run coal fly ash, 100–200 µm fraction: 319 ppm Ba in glass and 69 ppm Ba in crystalline mullite–quartz	Hulett and others (1980)
Oil-fired fly ash: 200–1,000 ppm Ba; coal-fired fly ash: 200–3,000 ppm Ba	Henry and Knapp (1980)
Hungarian power station burning third class brown coal; submicrometre silicate particles and particles with high Ba and high Fe content	Sándor and others (1990)

lung burdens of six out of ten deceased Roman residents that did include 'regular' cigarette smokers, but the barium host phase was not identified (Paoletti and others 1987). Coal and oil burning fly ash are likely candidates.

This paper describes the results of electron probe microanalyses (EPMA) and scanning and transmission electron microscope (SEM, TEM) analyses of barite in coal fly ash from the Upper Silesian Industrial Region (USIR) of Poland. We used the fact that barite is a chemically inert and thermally stable mineral to trace its behaviour during coal burning.

Sample collection and analyses

Samples of airborne and deposited dust were collected in 20 locations in the Upper Silesian Industrial Region (USIR) between December 1994 and July 1997 (Fig. 1). The collected atmospheric dust included suspended dust and deposited dust. The samples of airborne dust were collected at two different time scales. First, samples were collected every 24 h on fibreglass filters in the Staplex fibre apparatus. Second, samples representing the accumulated dust loading over periods of 1, 2 or 3 months were obtained on boron-silicate glass covered by Teflon filters using an automatic TEOM 1400 sampling device. Airborne dust in the village of Wielowies, located immediately to the west of the USIR (Fig. 1), was collected every 24 h using a Harvard cascade impactor. This instrument selectively traps on Teflon filters dust in the size range equivalent to aerodynamic diameters of 2.5 and 10 µm. The aerodynamic diameter is the diameter of a true particle assuming a spherical shape and a density of 1 kg/m^3, and settling velocity in air that is the same as that of a true particle. The general convention is that when the true particle density is known, and used in equation, the resulting equivalent
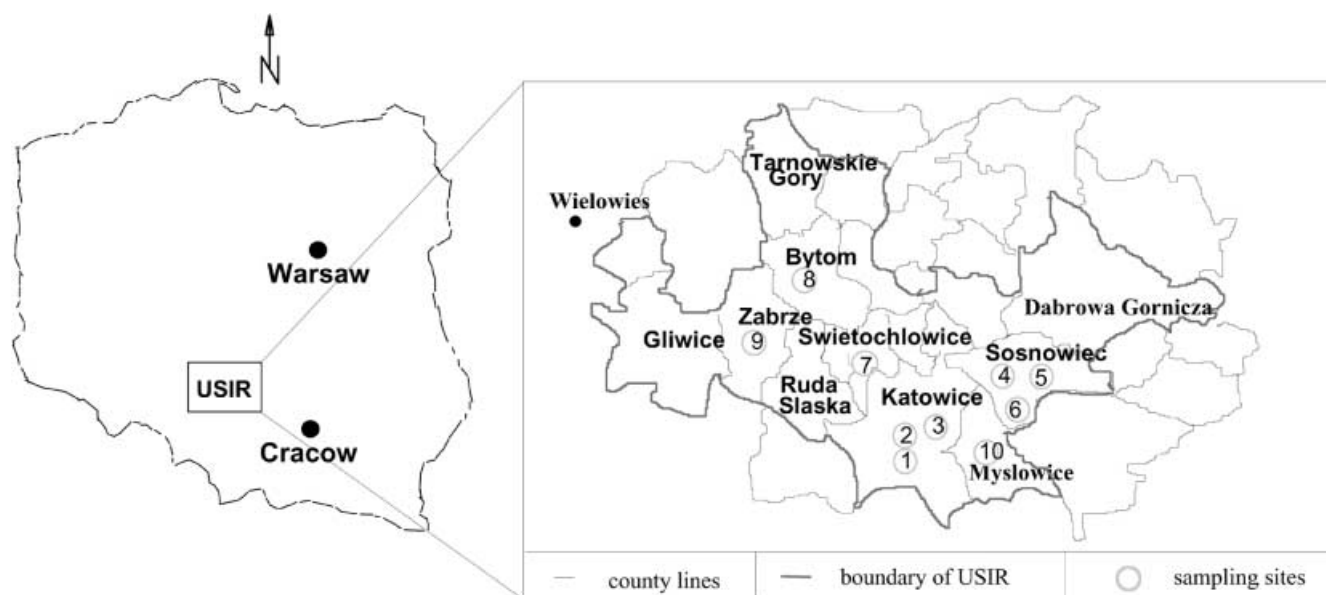
271 ppm (Różkowska and Ptak 1995). A mean value of Ba concentration in Upper Silesian coals of 176 ppm is significantly higher than the mean Ba concentration in world coals (130±19 ppm) (Różkowska and Ptak 1995). Barite crystals and veinlets were commonly observed filling fractures in coal seams in Upper Silesia. Barium concentrations were dramatically increased in fly ash resulting from burning these coals. Concentrations of Ba in fly ash ranged from 6 to 46,600 ppm Ba (Ptak and Różkowska 1995) with a mean value of 1,274 ppm. The common presence and petrographic relationships of submicrometre barite particles in coal fly ash samples from the Upper Silesian Basin may have some implications for aeolian transport of heavy metals in the environment. For example, barium and other heavy metals were reported as 'metal oxide and sulfide' particles >0.1 µm among mineral

Fig. 1
Localities of airborne and deposited dust sampling sites in the Upper Silesian Industrial Region (USIR), Poland

diameter is called the Stokes' diameter. When the particle true density is unknown, and hence unit density is assumed, the resulting computed diameter is called the equivalent aerodynamic diameter (Lodge and others 1981). Deposited dust was collected monthly in glass jars placed at 2–2.5 m above ground level. Two additional collectors of deposited dust were located on top of the Main Institute of Mining (60 m height) in Katowice and the Faculty of Earth Sciences building (95 m height) in Sosnowiec. Electron microprobe data were obtained using a JEOL 8600 EMPA that operated at an accelerating voltage of 15 kV and a sample current of 15 nA. The analyses were obtained with a probe size of 2 μm in diameter and calibrated using a barite standard. The instrument was equipped with a windowless detector that was used in the wavelength dispersive mode for barite analyses with an acquisition time of 200 s and calibrated on a natural barite standard and reduced using Tracor Northern software. Electron microscope analyses were performed using a JEOL JSM 35 SEM with a LINK 290 EDS spectrometer fitted with a Be window and a JEOL JSM 5410 SEM equipped with a VOYAGER EDS system. The accelerating voltage was 25 kV and beam current was 20 nA. Sample preparation for EMPA and SEM analyses followed standard procedures and the samples were provided with a conductive carbon coating.

A small portion of selected samples was placed on a holey-carbon thin-film supported by a standard Cu TEM mesh grid and placed in a low-background, double-tilt sample holder for analyses using a JEOL 2000FX AEM operated at an accelerating voltage of 200 keV. It is equipped with a Tracor Northern TN-5500 EDS spectrometer for in situ determination of elements with atomic number >10 using a 10–20-nm-diameter probe. Analyses were performed at the thinnest grain edges. Barite identification relied on selected area electron diffraction (SAED) with a 2–4% relative error in the single crystal interplanar spacings and on qualitative EDS analysis. Identification of small barite inclusions in carbonaceous materials is based on qualitative EDS analyses only. Particle size was measured directly on calibrated TEM micrographs with a 10% relative error.

Results

Major constituents of tropospheric dust over Upper Silesia include quartz, gypsum, crystalline and amorphous aluminosilicates, calcite, soot, coke, graphite, hematite, magnetite and amorphous wüstite-like iron oxides (Jablonska 1999). Many site-specific accessory phases occur, e.g. barite that is a common accessory constituent in collected airborne and deposited dust. Barite occurred in samples collected in the cities of Katowice, Bytom, Myslowice, Sosnowiec, Swietochlowice and Zabrze located in USIR (Fig. 1). In addition, barite was found in Olkusz situated immediately east of this region and in Wielowies, located immediately west of USIR (Fig. 1). Barite was not observed in other locations but probably this accessory mineral was overlooked in samples in which only the major dust constituents were examined in detail. Samples from Katowice–Centre were found to contain barite when analysed by SEM and EMPA (Fig. 2) but observations by ATEM of a small subsample did not confirm the presence of this mineral (Table 4). This observation may serve as a cautionary note when drawing conclusions on the abundance of collected multi-phase airborne dust assemblages as a function of grain size. Barite occurs mostly in the dust size fraction <3 μm mainly as idiomorphic nanocrystals 20–160 nm in size with a characteristic rhombohedral cross section. Both deposited and airborne angular barite grains in Katowice collected at a height of 60 m have a bimodal distribution with ranges
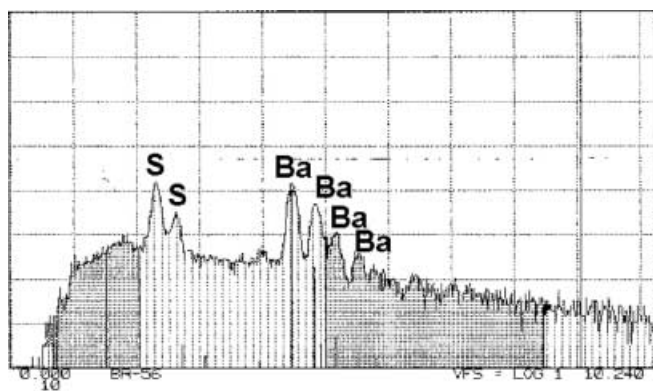
Fig. 2
EMP spectrum of a deposited barite particle collected on the roof of the Main Institute of Mining at 60 m above ground level in Katowice

1–3 μm and 5–25 μm in size (Table 4). Barite is commonly attached to hydrocarbon particles (Fig. 3), although it also is associated with amorphous aluminosilicate, quartz and Fe oxide grains (Figs. 4 and 5). The chemical compositions of collected barite particles are close to the ideal barite composition. Iron was the only detectable impurity element (Table 5).

Discussion

Transport of micrometre-sized airborne dust is typically locally or regionally limited with respect to their sources. For example, 0.5–4.5-μm-sized fly ash aerosols in a rural environment were linked to nearby power generating plants (Thomas and Buseck 1983). The origin of barite dust collected in the USIR troposphere can be explained by two mechanisms: (1) survival of coal-burning, i.e. primary barite and (2) reactions of sulfuric acid with airborne dust, i.e. neogenic barite. Angular and relatively large barite grains (1–25 μm in size) may be relicts of primary barite, whereas well-developed nanocrystals of barite may have formed by the second mechanism. Coal burning for domestic purposes is still widespread in the region, especially during winter. Barite is a chemically and heat resistant phase with a melting point at 1,580 °C. It does not thermally decompose in domestic furnaces, in which coal is burnt at temperatures between 800 and 900 °C. Thus, this activity might be able to concentrate primary barite before it is ejected into the environment. It was noted that numerous nanometre-sized barite inclusions are embedded in large carbonaceous particles collected in the village of Wielowies (Table 4). These carbonaceous particles have equivalent diameters in the range of respirable dust that can enter the human respiratory system (Lehnert 1993). The prevailing winds in this part of Poland are from the west. There is no industrial activity in the village's vicinity. The compositions of phases in the collected dust clearly show low dust emissions from domestic furnaces and the single, small, coal-fired heat-generating plant in this village that are the predominant sources of dust and gaseous

emissions (Jablonska 1999). The barite-bearing samples from this location were collected during winter at the peak of the coal-burning season that runs from 15 October to 15 April. A similar association of nanometre-sized barite grains embedded in sheets of carbonaceous materials was found in suspended dust samples collected in Sosnowiec–Pogon at 95 m above ground level (Table 4).

The possibility of neogenic barite growth in ejected dust at the points of origin and grains suspended in the local troposphere is supported by observations on fly ash trapped on electrostatic filters in two coal-fired power plants in the city of Bedzin and steel factory 'Katowice' (Smolka 1998). The EDS spectra for grains in the 20–50 μm size fraction of the fly ash showed a Ba peak but no S peak (Fig. 6). Similar EDS spectra were obtained for a few samples of suspended dust (<4 μm in diameter) collected close to the non-ferrous metal works located in Katowice (Fig. 1). These observations suggest that high-temperature industrial coal burning results in decomposition of primary barite to BaO and SO_2. The BaO grains thus produced and emitted into the troposphere could have back-reacted with sulfur dioxide and water aerosols to produce secondary barite. The laboratory experiments showed that soot-catalysed SO_2 oxidation plays a major role in the sulfate formation in air (Novakov and others 1974). This back-reaction also may be catalytically supported on carbon species. The nanometre-sized idiomorphic barite crystals are typically free of inclusions. These grains abound at the surface of glass fibres of the collection substrate suggesting they were an abundant airborne dust species in the region.

Similarly, the high amount of gypsum and other hydrated sulfates found among the airborne tropospheric dust in USIR could be explained by reactions of metals and metal oxides with sulfuric acid aerosols (Manecki and others 1988; Rietmeijer and Janeczek 1997). Similar reactions were observed in volcanic ejecta clouds. For example, needle-shaped Ca-sulfate crystals from the El Chichón May 1982 eruption were reported on silicate fragments in ashfall deposits (Varekamp and others 1984) and as free-floating laths in the lower stratosphere (17–19 km altitude) on 7 May 1982 (Mackinnon and others 1984). These crystals were interpreted as vapour phase condensates or reaction products after sulfuric acid reacted with Ca-bearing glass (Mackinnon and others 1984).

A distinct correlation between pH of rainfalls and concentrations of dust has been observed in the USIR. In areas with the low concentration of dust, e.g. 65 g/m^2 in Katowice during 1996, the average pH of rainfall was 4.4, whereas in areas with the high dust concentrations, e.g. 119 g/m^2 in Dabrowa Gornicza during 1996, the average pH of rainfall was 6.5 (Jablonska 1999). These observed correlations suggest that acid rainfalls are partly neutralized by the formation of gypsum, barite and hydrated sulfates from suspended dust. A decrease in the amount of both deposited and airborne dust observed in the USIR over the past decade and caused by the economic changes in the region has resulted in the increase in the acidity of rainfalls (Leśniok and Radomski 1999).

Table 4
Collector sites and heights, and collection periods of airborne and deposited dust samples containing barite, as well as the properties of barite, in the Upper Silesian Industrial Region. The Faculty of Earth Sciences building in Sosnowiec–Pogon is located 3 km from the site Sosnowiec–Centre; the site of the Katowice–Szopienice smelter works is ~5 km from the site in Katowice–City (centre)

Location	Collection		Observations
	Height	Date	
Sosnowiec–Pogon (Faculty of Earth Sciences building)	95 m	21/22 June 1994	Airborne dust; TEM: euhedral platy crystals attached to silica and aluminosilica dust and embedded in the carbonaceous sheets; size range: 46–322 nm, mean = 150 nm, mode: 112 nm. Grains, 9–24 nm (mean = 12.5 nm) are embedded in the sheets and attached to the fibres of the collection substrate
Sosnowiec–Pogon (Faculty of Earth Sciences building)	95 m	1 to 30 Sept. 1996; 1 Dec. 1996 to 2 Jan. 1997	Deposited dust; irregular grains, 2–10 μm in size associated with aluminosilica and silicate particles
Sosnowiec–Center	2.5 m	27 Oct. to 14 Dec. 1995	Airborne dust; NO data available
Katowice –Centre (Main Institute of Mining)	60 m	14 May to 17 June 1997	Deposited dust; angular grains, 5–25 μm in size, associated with angular Fe particles (Fig. 4), and angular grains, 1–3 μm in size. Smaller grains attached to silica dust
Katowice–Centre	2.5 m	25 Jan. to 7 May 1996 and 7 May to 28 Oct. 1996	Airborne dust; euhedral grains 20–160 nm are attached to aluminosilica dust and embedded in carbonaceous sheets. TEM: thin (~3 nm) euhedral plates embedded in carbonaceous sheets and attached to aluminosilica dust and fibres of the collection substrate. Size range: 24–126 nm, mean = 60 nm, standard deviation = 28.1 nm; number of grains = 16; Gaussian distribution at a 95% confidence limit
Katowice–Szopienice	2.5 m	19 Mar. to 15 Apr. 15 Apr. to 15 Sept. 1997 19 Mar. to 15 Apr. 1997	Deposited dust: angular grains, size of particles is smaller than 5 μm. Associated with aluminosilica and silica dust Airborne dust; TEM: euhedral platy grains attached to aluminosilica dust and fibres of the collection substrate. Grains are also intimately associated with soot. Size range: 21–250 nm, mean = 69 nm, mode = 22.8; standard deviation = 55.2 nm; number of grains = 20; Gaussian distribution at a 95% confidence limit. Skewness = 0.84 (owing to two large grains); otherwise this population resembles the one from Katowice–City (centre). Large grains occur near the source
Bytom	2.5 m	26 Oct. 1995 to 18 Jan. 1996	Airborne dust; small, 50–300 nm, grains attached to aluminosilica particles and embedded in carbonaceous sheets
Wielowies	2.5 m	13 to 15 Dec. 1997	Airborne dust; numerous nanocrystals embedded in carbonaceous sheets. Barite is only found associated with carbonaceous materials. Euhedral grain sizes are 21 to 135 nm (mean = 92.3; standard deviation = 43.0; number of grains = 7. Grains > 125 nm are compact aggregates of crystallites 7–20 nm in size [0.36 nm lattice fringes are the barite (201) or (021) planes (Fig. 3)], and 33–75 nm in size
Olkusz	2.5 m	30 Nov. 1996 to 2 Jan. 1997	Deposited dust; irregular grains, 2–10 μm in size including aluminosilica and silicate dust
Olkusz	2.5 m	31 Oct. 1996 to 14 Feb. 1997	Airborne dust: associated with aluminosilica substance. Lack detailed data
Swietochlowice	2.5 m	10 Apr. to 26 May 1997	Deposited dust: EMPA irregular grains < 2 μm inclusions in glassy aluminosilica materials
Zabrze (Centre)	2.5 m	1 to 30 Apr. 1996	Deposited dust: grains attached to aluminosilica particles. Lack detailed data
Myslowice	2.5 m	1 to 31 Jan. 1997	Deposited dust: angular particles, size range 1–3 μm

The collected barite aerosol particles in USIR included both 'primary' and 'secondary' barite. We suggest that the collected primary barite represents grains that were originally present in the coal deposits. They could be authigenic barite formed during coal deposition from dissolved Ba in the aqueous environments and detrital grains formed by leaching of Ba-bearing materials of fluvial and aeolian origin due to surface weathering and volcanic ejecta. Volcanogenic barium in the coal deposits will have accumulated from circumglobal volcanic activity that injected dust directly in the stratosphere. The volcanic abundances will augment a global background

Fig. 3
TEM image of an airborne, respirable polycrystalline barite particle (*arrows*) associated with hydrocarbon material collected in Wielowies. *Scale bar* is 20 nm

due to weathering of outcrops and the erosion of barite and Ba-bearing dust.

This study found nanometre-sized barite grains embedded in, and associated with, sheets of hydrocarbon materials. The sizes of these sheets collected in the location of Wielowies are within the range of respirable aerosols that can
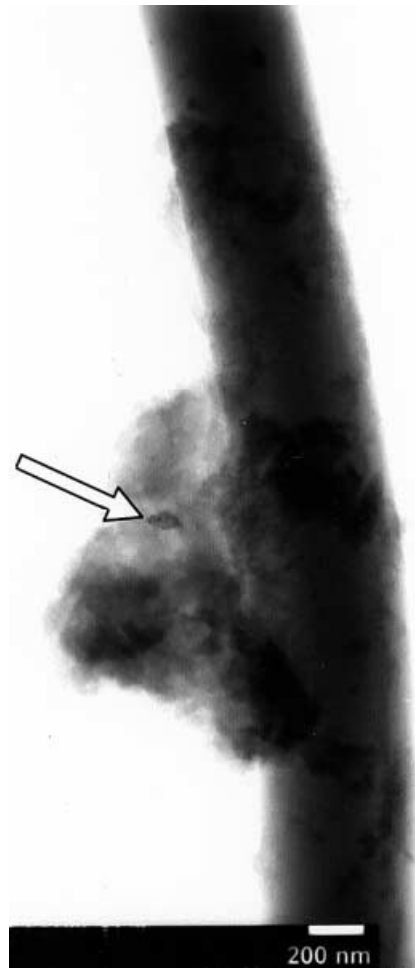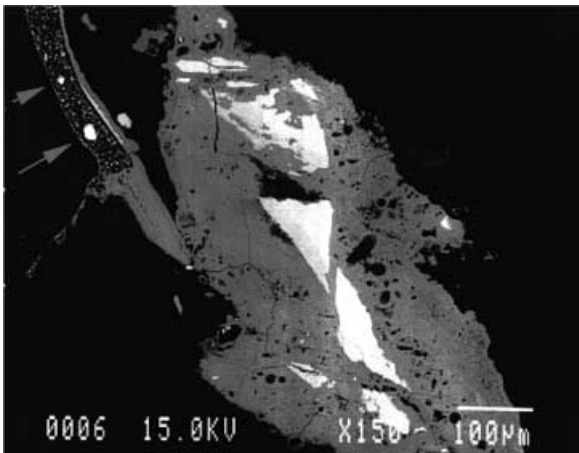

Fig. 5
TEM image of airborne barite grains attached to a silica fibre from the collection substrate. Katowice (city centre)

enter the human respiratory system and thereby deposit embedded mineral phases such as barite in the respiratory system. Barite is known for its low solubility. However, the small size of barite nanocrystals may enhance its solubility in the fluids present in human respiratory system. Further
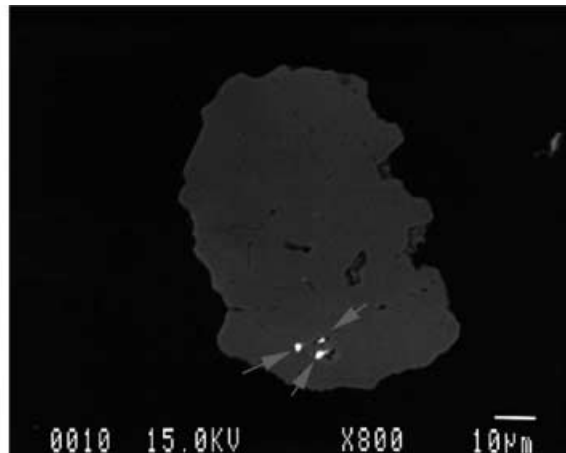
Fig. 4
Back-scattered electron images of barite particles (*arrows*) in deposited dust collected at 60 m height on top of a building located in one of the topographically highest places in the city of Katowice. The location probably also receives airborne dust from other cities in the region. The large grains on the *left image* are mostly Fe oxides (*scale bar* is 100 μm). The image on the *right* shows xenomorphic <20 nm-sized barite inclusions in a large quartz grain (*scale bar* is 10 μm)

Table 5
EMPA analyses (wt%) of individual barite particles collected in USIR (Poland) compared to ideal pure barite

Locality	BaO	SO$_3$	FeO	Total
Katowice	66.74	30.92	1.51	99.17
Katowice	65.04	33.05	1.35	99.44
Sosnowiec–Pogon	65.21	34.06	Not detected	99.27
Ideal barite	65.70	34.30	Not present	100.0
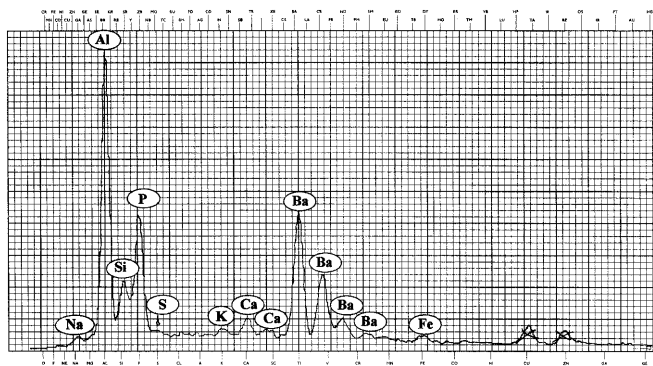
Fig. 6
EDS spectrum of the fly ash particle deposited on electrostatic filters in the coal-fired power plant in the city of Bedzin (courtesy of Smolka 1998)

study is needed to address this problem. Petrographic relationships among the various dust species are an important consideration in evaluations of potential health hazards.

Conclusions

The presence of barite nanocrystals in dust over the Upper Silesian Industrial Region is the result of burning Ba-enriched coals. Inefficient coal burning for domestic purposes will cause emissions of barite, which survived in temperatures (800–900 °C) well below its melting point. High-temperature coal burning for industrial purposes may thermally decompose barite in the coals, resulting in emissions of barium oxide, which may react with airborne sulfuric acid to produce secondary barite. Inefficient burning for domestic uses will concentrate barite that was originally present in the coals. Efficient industrial coal burning produces BaO aerosols that, together with CaO, will scavenge sulfuric acid aerosols or gaseous SO$_2$ and affect the tropospheric chemistry.

The presence of barite nanocrystals within the abundant respirable sheets of hydrocarbons raises concern about their potential health hazard to the general population of the USIR. Certainly, this issue requires further examination.

References

Bishop JKB (1988) The barite–opal–organic carbon association in oceanic particulate matter. Nature 332:341–343

Bouška W (1981) Geochemistry of coal, coal science and technology 1. Elsevier, Amsterdam

Davey RJ, Black SN, Bromley LA, Cottier D, Dobbs B, Rout JE (1991) Molecular design based on recognition at inorganic surfaces. Nature 353:549–550

Deer WA, Howie RA, Zussman J (1962) Rock-forming minerals, vol. 5, non-silicates. Wiley, New York

Fruchter JS, Robertson DE, Evans JC, Olsen KB, Lepel EA, Laul JC, Abel KH, Sanders RW, Jackson RO, Wogman NS, Perkins RW, van Tuyl HH, Beauchamp RH, Shade JW, Daniel JL, Erikson RL, Sehmel GA, Lee RN, Robinson AV, Moss OR, Briant JK, Cannon WC (1980) Mount St. Helens ash from the 18 May 1980 eruption: chemical, physical, mineralogical, and biological properties. Science 209:1116–1125

Guay CK, Klinkhammer GP, Falkner KK, Benner R, Coble PG, Whitledge TE, Black B, Bussell FJ, Wagner TA (1999) High-resolution measurements of dissolved organic carbon in the Arctic Ocean by in situ fibre-optic spectroscopy. Geophys Res Lett 26:1007–1010

Henry WM, Knapp KT (1980) Compound forms of fossil fuel fly ash emissions. Environ Sci Technol 14:450–456

Hulett LD Jr, Weinberger AJ, Northcutt KJ, Ferguson M (1980) Chemical species in fly ash from coal-burning power plants. Science 210:1356–1358

Jablonska M (1999) Phase composition of atmospheric dust from selected cities of the Upper Silesian Industrial Region (in Polish). PhD Thesis, University of Silesia

Jedwab J (1980) Rare anthropogenic and natural particles suspended in deep ocean waters. Earth Planet Sci Lett 49:551–654

Komov IL, Lukashev AN, Koplus AV (1994) Geochemical methods of prospecting for non-metallic minerals. VSP, Utrecht

Lehnert BE (1993) Defense mechanisms against inhaled particles and associated particle–cell interactions. In: Guthrie GD Jr, Mossman BT (eds) Health effects of mineral dust. Reviews in Mineralogy, vol 28, pp 427–469

Leśniok M, Radomski J (1999) The variability of atmospheric dust concentrations and acidity of rainfalls in the Silesian Upland (in Polish). Pols Tow Mineral – Prace Spec 15:73-82

Lodge J, Waggoner A, Klodt D, Crains C (1981) Non health effects of airborne particulate matter. Atmos Environ15:431–482

Luhr JF, Carmichael ISE, Varekamp JC (1984) The 1982 eruptions of El Chichón volcano, Chiapas, Mexico: mineralogy and petrology of the anhydrite-bearing pumices. J Volcanol Geotherm Res 23:69–108

Mackinnon IDR, Gooding JL, McKay DS, Clanton US (1984) The El Chichón stratospheric cloud: solid particulates and settling rates. J Volcanol Geotherm Res 23:125–146

Manecki A, Schejbal-Chwastek M, Tarkowski J (1988) Mineralogical and chemical characteristics of airborne dust pollutants from areas affected by short and long-range industrial emissions. Res Mineral (Pol Acad Sci) 78:27–45

Miller RN, Given PH (1987) The association of major, minor and trace inorganic elements with lignites. II. Minerals, and major and minor element profiles, in four seams. Geochim Cosmochim Acta 51:1311–1322

Murphy DM, Thomson DS, Mahoney MJ (1998) In situ measurements of organics, meteoritic material, mercury, and other elements in aerosols at 5 and 19 kilometers. Science 282:1664–1669

Novakov T, Chang SG, Harker AB (1974) Sulfates as pollution particulates: catalytic formation on carbon (soot) particles. Science 186:259–261

Paoletti L, Batisti D, Caiazza S, Petrelli MG, Taggi F, de Zorzi L, Dina MA, Donelli G (1987) Mineral particles in the lungs of subjects resident in the Rome area and not occupationally exposed to mineral dust. Environ Res 44:18–28

Ptak B, Różkowska A (1995) Geochemical atlas of coal deposits in the Upper Silesian coal basin (in Polish). National Institute of Geology, Warsaw

Rietmeijer FJM (1993) Volcanic dust in the stratosphere between 34 and 36 km altitude during May, 1985. J Volcanol Geotherm Res 55:69–83

Rietmeijer FJM, Janeczek J (1997) An analytical electron microscope study of airborne industrial particles in Sosnowiec, Poland. Atmos Environ 31:1941–1951

Różkowska A, Ptak B (1995) Barium in coals from Upper Silesia (in Polish). Przegl Geol 43(3):223-226

Sándor S, Torok S, Xhoffer C, Grieken R (1990) Individual coal flyash particles analysis by EPMA. Proc XIIth Int Congr Electron Microscopy. San Francisco Press, San Francisco, pp 254–255

Sarna-Wojcicki AM, Meyer CE, Woodward MJ, Lamothe PJ (1981) Composition of air-fall ash erupted on May 18, May 25, June 12, July 22, and August 7. In: Lipman PW, Mullineaux DR (eds) The 1980 eruptions of Mount St. Helens, Washington. Geol Surv Prof Pap 1250, pp 667–681

Sedlacek WA, Heiken G, Zoller WH, Germani MS (1982) Aerosols from the Soufriere eruption plume of 17 April 1979. Science 216:1119–1121

Smolka D (1998) Geochemical and mineralogical investigations of fly-ash from selected power plants (in Polish). PhD Thesis, University of Silesia

Thomas E, Buseck PR (1983) Characterization of a rural aerosol from Eastern Arizona. Atmos Environ 17:2299–2301

Varekamp JC, Luhr JF, Prestegaard KL (1984) The 1982 eruptions of El Chichón volcano (Chiapas, Mexico): character of the eruptions, ash-fall deposits, and gasphase. J Volcanol Geotherm Res 23:39–68

Vossler T, Anderson DL, Aras NK, Phelan JM, Zoller WH (1981) Trace element composition of the Mount St. Helens plume: stratospheric samples from the 18 May eruption. Science 211:827–830

Zies EG (1929) The Valley of 10,000 Smokes, the fumarolic incrustations and their bearing on ore deposition. Nat Geogr Soc Tech Pap 1(4):61–79