Derby dust: geochemical characterisation of airborne inorganic particulate matter in western Derby

Hugh Rollinson, Jacob Adetunji, Graham Souch and Mike Greenwood

Abstract: We report the results of a pilot study, carried out at the University of Derby during 2010 on the nature of the inorganic particulate matter in the air in west Derby. We have found three chemically distinct groups of particles. 1: Sulphates, including Ca-sulphates (Gypsum), Na-sulphates and mixed grains in which sulphate has nucleated on a silicate host, which reflect a combination of anthropogenic and natural processes; the sulphate may be derived from industrial areas around the Bristol Channel or more locally from the A38 road adjacent to the sampling site. 2: Phosphate-silicate compounds that may be derived from fertilisers or from the local crematorium. 3: A variety of silicates, including quartz and feldspar, of natural origin but not necessarily of local provenance, and also an unusual anthropogenic iron-rich silicate. We conclude from a study of the measured compositions, grain shape and grain size that they are not harmful to human health.

Atmospheric dust affects us in a variety of ways. Within the atmosphere it exerts an influence on climate and weather patterns, and more rarely, may be a hazard to travel. Near the Earth's surface dust contributes to the transport of allogens and pathogens and is implicated in some respiratory diseases. In Britain it has been suggested that 'any air sample... will include minerals derived from rocks, soils and construction... sulphates... chlorides.....elemental and organic carbon.... biological and other organic compounds... iron compounds and a range of other metals' (Moreno *et al.*, 2004). Thus in the East Midlands we might expect dust from natural sources, such as soils, and from anthropogenic sources such as quarrying, construction, industrial processes and from traffic.

We report here the results of a pilot study, carried out at the University of Derby during 2010, on the nature of the inorganic particulate matter in the air in west Derby. Most dust studies have the particle size distribution, the mass of dust collected and the bulk composition as their primary focus. Only a few studies have focussed on the chemical composition of individual dust grains (Moreno et al., 2004). Our aim therefore was to analyse the dust particles collected, under the scanning electron microscope (SEM), with a view to understanding the chemical composition of the dust at a grain scale and to attempt to establish the origin of the dust. Only samples greater than about 2 microns in diameter were examined. Whereas smaller particles pose a potential health risk (Price et al., 2010), they are not easily analysed under the SEM and so were excluded from this study.

Thirty four air samples collected during this project were investigated on the scanning electron microscope (SEM) at the University of Derby; 106 images were recorded and 113 grains were chemically analysed. The chemical data are used to characterise the particles, make inferences about their provenance and draw some tentative conclusions about their potential consequences for human health.

Air sampling

The University of Derby has a long tradition of air sampling and has been operating spore traps on behalf of the Midlands Asthma and Allergy research Association for many years (Ryall et al., 2002). However, this study is the first attempt to quantify the composition of inorganic dust grains in Derby. Atmospheric air was collected continuously for eight hours each day on 34 selected days through the months of April to August 2010. The sampling site, now relocated from the University Mickleover site, was on the roof of the University of Derby library (SK340379), at a height of 14.5 m above the ground. This location is outside the city of Derby, in an area completely devoid of major industrial atmospheric pollution, although the A38 trunk road, which runs in a road-cutting about 7 m deep, is about 60 m away.

A Bukard air sampler was used with an intake of about 10 litres per minute (human breathing rate). Samples were collected onto a 2.5 mm diameter adhesive disc, stuck on a masked microscope slide, which moved vertically at a rate 3 mm/hr. This allowed an eight-hour sampling run normally collected between 9:00am and 7:00pm. Meteorological conditions were obtained from the University's Geographical Sciences' automatic weather station (at SK338378). This utilises a Campbell CR10X data logger and is fully compliant with UK Meteorological Office standards. Mean wind direction for each day was computed from the mean of measurements every 10 minutes during the sampling period (Table 1).

Geochemical analysis

The microscope slides were carbon sputter coated and examined using a LEO 1450VP SEM (Zeiss) scanning electron microscope (SEM) at the University of Derby. The electron beam was operated with an accelerating voltage of 20 kV and a beam current of 50 mA. In order to eliminate the possibility of sputtered

Sample No	Date 2010	Wind direction (deg)	Wind speed (m/s)	Atmos pressure (mbar)	Mean temp (°C)		
0	13/04	131 4.76 1012.67		1012.67	10.59		
1	19/04	88	4.21	1003.78	7.83		
2	20/04	304	7.93	1004.70	9.63		
3	21/04	209	2.85	1007.00	9.62		
5	23/04	114	4.47	1001.50	14.21		
6	26/04	293	293 5.65 1010.		15.63		
7	27/04	245	245 4.72 1012.20		16.98		
9	17/05	305	4.83 1010.20		14.80		
10	18/05	125	2.31	1014.40	16.90		
11	19/05	209	3.92 1014.80		17.71		
12	20/05	185	185 2.31 1017.80		20.77		
13	01/06	159	2.16 1002.10		13.10		
14	02/06	213	2.48	1009.00	17.52		
15	28/06	256	4.54	1005.50	22.99		
16	29/06	309	5.02 1004.7		22.34		
17	30/06	234	234 3.20 1003.90		22.32		
18	05/07	301	5.19	1008.50	18.70		
19	06/07	222	4.12	1007.33	20.08		
20	08/07	250	3.82	1003.67	20.68		
21	09/07	244	5.25	1002.00	24.00		
22	14/07	165	4.79	986.11	18.46		
23	15/07	221	7.30	988.67	19.22		
24	16/07	246	5.97	993.50	17.97		
25	19/07	214	5.13	1003.89	24.15		
26	20/07	220	2.60	993.50	22.05		
27	21/07	225	3.48	991.25	20.26		
27a	23/07	197	1.44	1008.25	17.40		
28	29/07	295	5.39	1002.89	16.60		
29	03/08	257	4.31	1000.00	19.35		
30	04/08	272	4.63	993.63	16.20		
31	06/08	198	5.52	997.13	18.94		
32	09/08	202	4.70	997.38	19.76		

Table 1. Samples' dates and weather conditions.

silicon contamination from the slide a control slide was similarly prepared. The slides were placed on the SEM stage under vacuum and grains were analysed using an Oxford Instruments Inca CS-138284 energy dispersive spectrophotometer capable of an analytical spot size of 1 micron. Most analyses were made by rastering an area within the grain a few microns across. This detector characterises the secondary Xrays from the analysed grains and converts the data into elemental concentrations. Software, typically used for the analysis of gunshot residue, was set to automatically examine a series of randomly selected areas for particles and to characterise each according to the combination of elements found. The software was set up to find particles with an inorganic composition and in particular silicates, since these are the most common substances of geological origin. The chemical composition of individual grains was re-calculated as oxides and normalised to 100%, allowing comparisons to be made with common rocks and minerals (Table 2).

Following each sample run, the software allowed relocation of specific particles or areas in order to obtain high resolution images of specific grains (Fig. 1). From these, estimates of the shape and size of individual grains were made.

Sample compositions determined from the SEM were used in combination with the size of the particles and the wind direction to assess their likely provenance. We explore the likelihood of dust grains being of natural origin; this is assessed from their composition and its correspondence to that of natural minerals and rocks. Grains with compositions that are not consistent with a mineralogical origin are thought to be anthropogenic.

Geochemical results

Three main groups of particles were identified on the basis of their chemical composition: those rich in or containing sulphur, those rich in or containing phosphorus, and those rich in silicate. There is overlap between all three groups. These three groups were identified because, whereas silicates are the most common naturally occurring materials, phosphates and sulphates are not. These latter two groups therefore are of interest because of their unusual provenance. Previous studies do not report the presence of phosphates (Moreno *et al.*, 2004; Giere and Querol, 2010).

Few particles are less than 5 μ m in diameter, and most are in the range 5-10 μ m so in terms of human health are classified as coarse particles. Typically particles of this size come to rest in the tracheo-bronchial region (Giere and Querol, 2010).

Sulphur-bearing particles

Thirty-five of the 113 analysed particles contain sulphur, and these were recorded consistently throughout the duration of the study. Concentrations vary between 3.8 and 68% sulphur expressed as SO_3 (Table 2). They are 5-50 μ m in size, with most 5-10 μ m. There is a variety of particle shapes; some grains are composite grains made of smaller particles, some are rounded and others angular or acicular (Fig. 1a and b).

From the chemical compositions samples in this group may be identified as

- pure sulphates; these grains are 5-10 μm in diameter and comprise Ca-sulphate (gypsum and anhydrite), Ca-Na-sulphates and Na-sulphates (Fig. 2a);
- mixed particles that contain a silicate and a sulphate component (Fig. 2a and b);
- mixed particles that also include a phosphatic component (5-18% phosphorus expressed as P_2O_5) and one particle that is almost exclusively sulphur and phosphorus (Fig. 2d).

The mixed silicate-sulphate particles have variable compositions, but define mixing trends on a plot of

	Sample No	size (μm)	shape	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	Total
Silicate		фііі)												
Sincute		7.00	composite	22.28.22	200212	12021012	(2000)220	5.52 S. S.	20.202	0500000	200202	02-572/92	SERVICE	0.00000
very high Fe	27a	30	rounded	29.53	0.00	26.45	31.48	12.54	0.00	0.00	0.00	0.00	0.00	100.00
very high Fe	27a	40	composite rounded	29.74	0.00	26.93	31.74	11.59	0.00	0.00	0.00	0.00	0.00	100.00
very high Fe	3	10	angular	31.73	0.00	22.34	41.14	2.94	1.84	0.00	0.00	0.00	0.00	99.99
very high Fe	12	25	elongate	33.51	0.00	21.80	27.14	17.55	0.00	0.00	0.00	0.00	0.00	100.00
very high Fe	10a	10	equant	33.79	0.00	26.29	27.76	12.17	0.00	0.00	0.00	0.00	0.00	100.01
basalt?	5b	10	elongate	45.41	0.00	20.49	17.12	14.73	2.24	0.00	0.00	0.00	0.00	99.99
basalt?	14f	10	angular	49.09	0.00	26.76	11.65	12.50	0.00	0.00	0.00	0.00	0.00	100.00
basalt?	0	20	composite	47.01	4.74	8.56	19.72	11.42	8.55	0.00	0.00	0.00	0.00	100.00
basalt?	1	5	angular	47.65	0.00	15.28	16.52	8.77	11.79	0.00	0.00	0.00	0.00	100.01
andesite	0	6	rounded	60.43	0.00	8.30	11.30	8.72	11.26	0.00	0.00	0.00	0.00	100.01
andesite	0	20	composite	62.05	0.00	11.21	10.02	7.36	9.36	0.00	0.00	0.00	0.00	100.00
granite?	11c	25	aggregate	68.73	0.00	12.08	9.51	0.00	5.54	0.00	4.13	0.00	0.00	99.99
granite?	11d		composite	70.77	0.00	18.72	6.06	0.00	4.45	0.00	0.00	0.00	0.00	100.00
K-feldspar	32b	5	irregular	57.05	0.00	30.75	0.00	0.00	0.00	0.00	12.19	0.00	0.00	99.99
K-feldspar	27a	6	angular composite	65.00	2.29	16.40	0.00	0.00	0.00	0.00	16.31	0.00	0.00	100.00
	14d	5	rounded	62.18	0.00	32.56	0.00	0.00	0.00	0.00	5.26	0.00	0.00	100.00
Plagioclase fel	17b	5	angular	61.09	0.00	12.15	0.00	0.00	26.77	0.00	0.00	0.00	0.00	100.01
Ca-sil	15a	15	angular composite	68.64	0.00	0.00	0.00	0.00	31.36	0.00	0.00	0.00	0.00	100.00
quartz	14c	5	rounded	100.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100.00
quartz	19a	5	angular	100.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100.00
quartz	17f	10	angular composite	88.79	0.00	6.16	2.98	0.00	0.00	0.00	0.00	2.08	0.00	100.01
Sulphate														
sulphur-silica phosphorus	30b	5	needle	14.45	0.00	0.00	3.16	0.00	29.12	0.00	0.00	8.46	44.82	100.0
sulphur-silica phosphorus	30c	5	needle	6.44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	55.70	37.86	100.0
sulphur-silica phosphorus	31a	10	composite	40.34	0.00	20.16	8.47	0.00	8.10	0.00	2.19	6.76	13.98	100.0
sulphur-silica	7	10	angular	44.82	0.00	24.95	7.16	8.04	2.76	0.00	5.91	0.00	6.37	100.0
sulphur-silica	25c	5	angular	63.19	0.00	0.00	0.00	0.00	2.48	11.24	0.00	0.00	23.10	100.0
sulphur-silica	25d	10	composite	20.45	0.00	7.43	3.21	0.00	23.88	0.00	0.00	0.00	45.02	100.0
sulphur-silica	31e	7	angular	70.25	0.00	15.09	0.00	0.00	2.74	0.00	4.74	0.00	7.18	100.0
Feldspar and gypsum	31f	7	angular	70.09	0.00	13.48	0.00	0.00	2.50	0.00	5.04	0.00	8.90	100.0
Na-sulphate	23a	6	angular	0.00	0.00	0.00	0.00	0.00	4.26	39.12	0.00	0.00	56.62	100.0
	30a	5	angular	0.00	0.00	0.00	0.00	0.00	4.75	33.57	0.00	0.00	61.68	100.0
	22(2)	5	rounded	0.00	0.00	0.00	0.00	0.00	0.00	32.05	0.00	0.00	67.95	100.0
Gypsum	14e	8	rounded	0.00	0.00	0.00	0.00	0.00	40.18	0.00	0.00	0.00	59.82	100.0
	23c	5	rounded	0.00	0.00	0.00	0.00	0.00	42.25	0.00	0.00	0.00	57.75	100.0
Phosphate														
Phosphatic	1a	8	composite	47.58	2.01	11.97	11.81	3.79	9.27	0.00	0.00	4.94	8.63	100.0
Phosphatic	12 part 2	5	rounded	81.15	0.00	9.15	0.00	0.00	0.00	0.00	0.00	9.70	0.00	100.0
Phosphatic	13 (3)	10	angular	0.00	0.00	20.84	13.18	0.00	29.37	0.00	0.00	36.60	0.00	100.0
Phosphatic	15d	5	needle	0.00	0.00	0.00	0.00	0.00	13.46	25.46	0.00	11.14	49.93	100.0
Other														
Dolomite	28b	80	angular	0.00	0.00	0.00	0.00	42.49	57.51	0.00	0.00	0.00	0.00	100.00
Fe-metal	25a	5	rounded	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00	0.00	100.00

Table 2. Representative chemical analyses (as weight percent oxides) in dust grains from west Derby. Zero values mean no detection on the SEM.

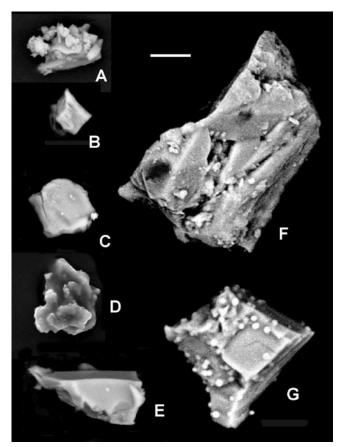


Figure 1. Secondary electron images of selected particles from the scanning electron microscope. A = silicate-sulphate; B = basalt; C = high-iron silicate; D = silicate-carbonate; E = calcium silicate; F = quartz; G = carbonate. All to same scale, bar scale is 10 microns long.

Ca+Na vs sulphate plot (Fig. 2a) and a silicate-sulphate plot (Fig. 2b) implying that silicate particles are mixed to a varying degree with Ca- and Na-sulphates. The silicate component of these particles is thought to be natural, from silicate rocks, and a variety of different silicate sources are indicated. The mixed particles including phosphorus are discussed below.

Phosphatic particles

A second group of 17 chemically distinctive particles are those containing 4-37% phosphorus expressed % P_2O_5 (Table 2). They vary in size from 5 to 20 μ m although most are between 5-10 μ m. Some are composite grains; others show an angular, rounded or acicular form. These grains are variable in composition and show the following features:

- One grain has high P_2O_5 (36.6%) and contains CaO in equal molecular proportion; Al and Fe are present in the atomic ratio 2:1. It is likely to be a chemical mixture, part of which is made up of Ca-phosphate.
- Most other samples contain silica and show a weak positive correlation between the silica content and the phosphorus content (Fig. 2d).
- Some phosphatic particles contain sulphur (as noted above). Two groups (Fig. 2c) are distinguished by sulphur that is low (<21% SO₃) or high (>40% SO₃).

Silicate particles

More than half the particles analysed are rich in SiO₂ (Table 2). Some are entirely silicate:

- Quartz: 5-30 µm in diameter, rounded or angular, some single grains, but the larger ones made up of multiple grains of quartz.
- Feldspar: 5-25 μm in diameter; both potassium feldspar and plagioclase have been identified.
- Individual grains of Ca-silicate (15 μ m across and angular), Fe-alumino silicate (5 μ m across as multicrystal aggregates), and two grains of granitic material one of which is a 25 μ m rock fragment high in SiO₂ (ca 70%) but also very high in FeO.

There is also a group of particles (5-40 µm) with variable morphologies including angular, elongate, rounded and composite. They containing very high Fe (19-41% FeO), but are low in SiO₂ (29-41%), which is less than is normal in silicate rocks. Al₂O₃ contents are high, as is MgO in most grains. Two grains with lower FeO and higher SiO₂ and more basaltic chemistry may also be part of this association. Natural silicate rocks containing more than 20% FeO are most unusual and are virtually unknown in Britain. These silicate particles show a strong negative correlation between FeO

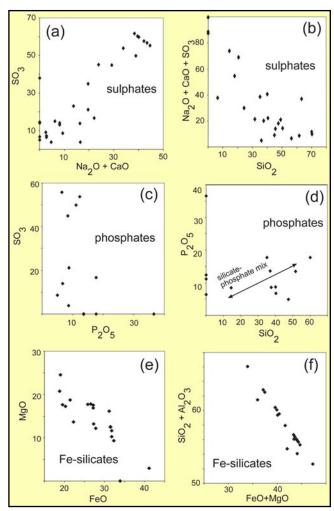


Figure 2. Geochemical plots of inter-oxide relationships in sulphate particles (a and b), phosphate particles (c and d) and silicate particles (e and f).

and MgO and a strong negative correlation between (FeO+MgO) and (SiO₂+Al₂O₃), implying substitutions between Al-Si and Mg-Fe end members (Fig. 2e and f). Mineralogically, they are closest to the composition of garnet, which does not occur naturally in this area. Price *et al.* (2010) reported particles rich in Fe and Mg in association with urban traffic in Swansea and Wang *et al.* (2003) proposed that elevated metal concentrations are related to diesel emissions. However, neither source describes these particles as silicates, and their origin remains uncertain.

We considered the possibility that these particles might be power station fly-ash; although their high SiO_2 and $\mathrm{Al}_2\mathrm{O}_3$ contents would support this view, fly-ash is not normally iron-rich, and its particles are commonly spherical, which these are not. We also considered that some silicate might be related to asbestos. However, natural asbestos is typically magnesian, not iron-rich, and there were very few fibrous particles of any type in our sample set.

The sample collection period overlapped with the eruption in April 2010 of the Icelandic volcano Eyjafjallajökull. Samples 0, 1 and 2 (collected between April 13 and 20) are of basaltic and andesitic composition, and so may be volcanic ash from Iceland. A positive identification of Icelandic ash in Loughborough was made at the British Geological Survey in dust collected on 20th April 2010 (www. bgs.ac.uk/research/volcanoes/icelandic ash) and there are some chemical similarities between one grain of 'basaltic composition' in this study and tephra reported from Iceland (Sigmarsson et al., 2010). An indicator of these distinctive compositions is measurable TiO, in some grains. However, our imaging does not show characteristic tephra morphologies. Single grain and multi-grain aggregates are up to 20 µm in length.

Other compositions

A small number of other particles included iron oxide (three 5 μ m grains of 100% FeO) and dolomite (two 50-80 μ m grains with equal proportions of MgO and CaO).

Provenance of the particles

The dust particles' provenance may be local or distant, anthropogenic or natural. Our analysis is governed by the prevailing wind direction during the sampling period, which was predominantly from the SW (Table 1), coupled with consideration of the geology of the English Midlands.

Sulphates

Sulphur dioxide is a common constituent of atmospheric gases. It is the product of combustion in car engines and in power stations, and may also be carried inland with sea-spray. These sources give rise to the formation of Ca-sulphates (Giere and Querol, 2010) and also Na-sulphates. Evidence for mixing between

silicate materials and sulphates suggests that Ca- and Na-sulphates may nucleate on silicate particles in the atmosphere. Thus, the sulphur-bearing silicate particles are produced through a combination of anthropogenic processes (combustion of fossil fuels) and natural ones (silicate nuclei). It is not possible to identify the source of the sulphur, though the prevailing wind direction comes from industrial areas around the Bristol Channel. A more local source, the A38 road, is also possible. The mixing trend in Figure 2b points to end-member silicates with 50-70% SiO₂; these cover the range of igneous rock compositions from basalt to granite. There are, however, few local sources.

Phosphates

Naturally occurring phosphates are very rare. However, they are contained in fertilisers, where they are often associated with sulphur. In this study the phosphatic particles were mostly derived from between the west and south. The other possible source of Caphosphates is bone, and it is worthy of note that Derby Crematorium lies 1 km due west of the sampling site. Given the comparative rarity of phosphates in the natural environment, this very local source may be the origin of these particles.

Silicates

A plot of (Mg+Fe+Al+Si)/Si vs Al/Si plot subdivides the silicate mineral grains into felsic and mafic groups (Fig. 3). Our data are more representative of the rural sample set from Cornwall (Moreno *et al.*, 2004), with fewer intermediate compositions and more mafic compositions than is found in the urban data set from Port Talbot, Birmingham, London and Sheffield.

Quartz is a very common natural material. It is present in the rocks and surficial deposits of the Midlands and might be released in local quarrying operations. However, Saharan dust is also well known in Britain (Ryall *et al.*, 2002), so for very small grains (<10 µm) the provenance is not necessarily local.

Potassium feldspar would indicate a granitic provenance. Local sources are found southeast of

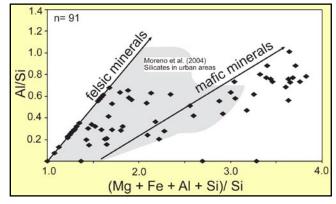


Figure 3. (Mg+Fe+Al+Si)/Si vs Al/Si plot for silicate grains compared with silicate in other urban areas (grey shaded area) (after Moreno et al., 2004).

Derby in the Charnwood Forest area, where there is active quarrying. However, the wind directions suggest a more westerly source, which is difficult to identify.

Individual grains of a Ca-silicate and a Fe-alumino silicate could be natural. The grains of granite material do not match precisely the felsic rocks from the Charnwood area, which are granodiorites and quartz diorites where high FeO is atypical. The origin of the Fe-Mg rich alumino-silicates is a puzzle. They are abundant and derive from the west and south. Mineralogically they are close to the composition of garnet, but garnet does not occur naturally in this area. These particles are most probably the product of diesel emissions, or are related to an unknown industrial process. The conclusion that these particles are not of natural origin is consistent with their distribution on the mineral composition diagram in Figure 3, where they plot at relatively high levels of Al/Si but with very high (Mg+Fe+Al+Si)/Si values and are more Fe-Mg rich than typical mafic minerals.

Other compositions

Dust associated with limestone quarrying is produced northwest of Derby. Some of the grains recorded may be thus derived. Other grains appear to have come from the south and are not locally derived.

Implications for respiratory pathology

All but one of the particles examined in this study was less than 50 μm in diameter and so will be removed in either the naso-pharyngeal or tracheobronchial region. Most are 10 μm or less and so the majority will be removed in the tracheobronchial region. These include the Na- and Ca-sulphates, the mixed sulphate-silicate grains, phosphorus-bearing silicates, quartz, feldspars and the high-Fe silicates. Our analysis of grain shape shows that only a small number are acicular or angular and so potentially harmful to the lungs. The majority of grains are rounded or composite in nature, and are therefore benign.

Although phosphate is commonly involved in pathological tissue mineralization, its health implications are not well known (Heaney and Banfield, 1999). However, there is very little evidence to suggest that it is a serious health hazard, and there is no legislation to control its emission into the atmosphere. Similarly there are no known toxic effects from gypsum. Silica (SiO₂) and silicates, on the other hand can cause silicosis if there is exposure to very high concentrations (Ross *et al.*,, 1999) although the abundances noted here are very low.

Acknowledgements

This study was funded by a grant from the Midlands Asthma and Allergy Research Association, which is gratefully acknowledged; two anonymous reviewers are thanked for their comments.

References

Giere, R and Querol, 2010. Solid particulate matter in the atmosphere. *Elements*, **6**, 215-221.

Groberty, B., Giere, R., Dietze, V. and Stille, P., 2010. Airborne particles in the urban environment. *Elements*, **6**, 229-235.

Heaney P.J. and Banfield J.A., 1999. Structure and chemistry of silica, metal oxides and phosphates. *Reviews in Mineralogy*, 28, 222-224.

Moreno, T., Gibbons, W., Jones, T. and Richards, R., 2004. Geochemical and size variations in inhalable UK airborne particles: the limitations of mass measurements. *J. Geol. Soc.*, **161**, 899-902.

Price, H., Arthur, R., Sexton, K., Gregory, C., Hoogendoorn, B., Matthews, I., Jones, T. and Berube, K., 2010. Airborne particles in Swansea, UK: their collection and characterisation. *J. Toxicology* and Environ. Health, 73, 355-367.

Ross M., Nolan R.P, Langer A.M. and Cooper E.C., 1999. Health effects of mineral dusts other than asbestos. *Reviews in Mineralogy*, 28, 361-408.

Ryall, D.B., Derwent, R.G., Manning, A.J., Redington, A.L., Corden, J., Millington, W., Simmonds, P.G., O'Doherty, S., Carslaw, N. and Fuller, G.W. 2002. The origin of high particulate concentrations over the United Kingdom, March 2000. *Atmos. Environ.*, 36, 1363-1378.

Sigmarsson, O., Oskarsson, N., Poroarson, P. Larson, G. and Hoskildsson, 2010. Preliminary interpretations of chemical analysis of tephra from Eyjafjallajokull volcano. www.earthice. hi.is/Apps/WebObjects/HI.woa/swdocument

Wang Y.F., Huang K.L., Li C.H., Mi H.H., Luo J.H. and Tsai P.J., 2003. Emissions of fuel metals content from a diesel vehicle engine. *Atmos. Environ.*, **37**, 4637-4643.

Hugh Rollinson and Jacob Adetunji, Geographical, Earth and Environmental Sciences; h.rollinson@derby.ac.uk Graham Souch, Electron Microscope Unit; Mike Greenwood, Biological and Forensic Sciences; all at University of Derby, DE22 1GB.