SECTION 6

DUST MEASUREMENT AND EXPOSURE ASSESSMENT

PART 1

CHARACTERIZATION OF SURFACES

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ALUMINOSILICATE SURFACE CONTAMINATION OF RESPIRABLE QUARTZ PARTICLES FROM COAL MINE DUSTS AND FROM CLAY WORKS DUSTS

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Abstract—Respirable high-silica particles from four coal mines, a clay mine and a tunnelling site were analysed for silicon vs aluminum composition by performing scanning electron microscopy–energy dispersive X-ray analysis (SEM–EDS) at electron accelerating voltages of 20 kiloelectron volts (keV). The same particles were analysed at 5 keV to determine possible differences in surface vs bulk composition. In some cases high-silica particles exhibited a decrease in the ratio of silicon to aluminium K-alpha line intensities with decreasing electron beam accelerating voltage. This behaviour is consistent with aluminosilicate surface contamination or occlusion of a silica particle. Some 20 high-silica particles were analysed from each of 10 samples. Powdered aluminosilicate glass was used as a control for the behaviour of silica with a homogeneous distribution of aluminium in the particle. Significant differences were found between the control and sample means for an Illinois bituminous coal mine dust, two western and one central Pennsylvania bituminous coal mine dust low-temperature ashes, and a clay mine and mill dust sample, but not for an anthracite coal mine dust and two central Pennsylvania bituminous coal mine dust low-temperature ashes.

INTRODUCTION

RESPIRABLE dust quartz content commonly is measured on bulk samples by using i.r. spectroscopy or X-ray diffraction. For research purposes, individual particle-by-particle SEM–EDS analysis at 20–30 keV electron beam accelerating potential may be used also. Such measurements have not provided an unambiguous association of quartz content with occupational pulmonary disease prevalence in exposed workers (WALTON *et al.*, 1977). Rather, there is evidence that coal rank modifies the relationship between dust exposure and pneumoconiosis development (WALTON *et al.*, 1977; ROBOCK and BAUER, 1990; ATTFIELD and MORRING, in press). SEM–EDS analysis was performed to measure the silicon fraction, Si/(Si + Ai), at 20 and at 5 keV on high-silica particles to determine if some respirable quartz particles generated by mining exhibit heterogenous composition with depth (WALLACE *et al.*, 1990), which might affect the bioavailability of the quartz surface.

EXPERIMENTAL METHODS

SEM–EDS elemental analysis using an Hitachi S570 SEM with a Kevex 8000 EDS was performed at 20 and at 5 keV on each of some 20 randomly selected high silica-particles from each of 10 dust samples. In a randomly selected field, all particles which did not image as overlaid or agglomerated particles were analysed at 20 keV. A particle was considered to be high-silica if silicon (Si) accounted for 75% or more of the 20 keV-excited spectra line intensities for elements of atomic number equal to or greater than that of sodium; most clays associated with coal mine dusts ,e.g. kaolinite and illite, are of approximately equal atomic per cent silicon and aluminium with SEM–EDS-measured silicon fraction of spectra being in the range of 40–60%. Then five measurements were made at each voltage for each high-silica particle; each measurement used 40 s of signal accumulation at 5 keV and 25 s at 20 keV. Particles for which one or more of the five measurements at a voltage indicated beam drift were excluded from the analysis. Some additional particles were analysed at 20, 11, 9, 7 and 5 keV to examine the behaviour of measured silicon fraction with voltage. Respirable-sized particles from a powdered piece of aluminosilicate glass (designated as 'Glass' in the data) were used as the control to represent the behaviour of high-silica particles with homogeneous aluminium contamination. Respirable-sized particles from a powdered piece of quartz rock saved by the family of a victim of the New River Hawks Nest tunnel silicosis disaster provided an example of pure silica. High-silica particles were analysed in an Illinois bituminous coal mine dust sample (I), in an eastern Pennsylvania anthracite coal mine dust sample (A), in three central Pennsylvania bituminous coal mine dust low-temperature ash samples [provided by the U.S. Mine Safety and Health Administration (C1, C2, C3)], in two western Pennsylvania bituminous coal mine low-temperature ash samples [provided by MSHA (W1, W2)], and a clay mine and mill dust sample (Clay mine). The three bituminous coal regions represent different sub-ranks. The moisture- and ash-free carbon content of coals from those seams were 84% for the anthracite, 69% for the central Pennsylvania, 64% for the western Pennsylvania and 48% for the Illinois bituminous coals.

The change in silicon fraction with reduction in voltage was computed for each of the five replicates of the approximately 20 particles studied in each dust group. For presentation purposes, summary statistics (mean and SD) were derived for each particle in each dust group. In addition, box plots were tabulated by dust group for the dataset as a whole. In order to analyse formally for systematic differences between the dust groups in change in silicon fraction with reduction in voltage, an analysis of variance was performed on the complete data after omission of the New River samples (since those data were unambiguously different from the remainder and also had virtually zero variability). As a further step in the analysis, a Dunnett's test of the difference between each dust group and the control set was made. Lastly, a non-parametric test based on the hypothesis that each dust type particle distribution data was identical to that of the control group was undertaken. In this the percentage of particles in each dust group was determined, and the probability of this occuring by chance computed using the binomial distribution with parameter $P = 0.10$ and sample size equal to the number of particles.

RESULTS AND DISCUSSION

Figure 1 illustrates the difference in behaviour of SEM–EDS measurements of the change in silicon fraction of signal, Si/(Si + Al), with decreasing electron beam accelerating voltage, V, between a quartz particle which is surface-occluded by aluminosilicate of equal atomic per cent Si and Al, and a quartz particle with homogeneous aluminium occurrence throughout the particle. A one-dimensional

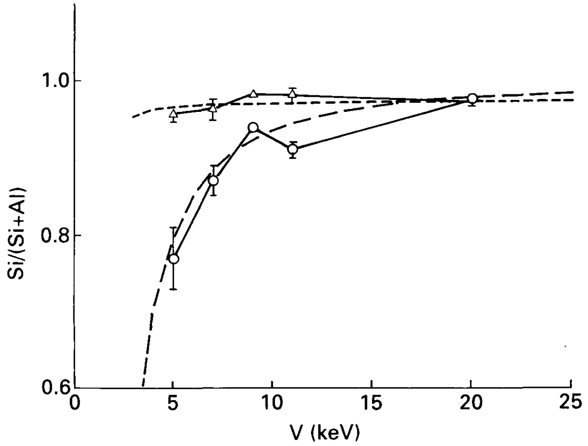

FIG. 1. Change in silicon fraction of signal with electron beam accelerating voltage for homogeneous and heterogeneous aluminium contamination of silica particles. The triangles are the experimental data points for silicon fraction measured at 5, 7, 9, 11 and 20 keV for an anthracite mine high-silica particle of 2.05 μm Wadell (area-equivalent) diameter and 0.970 silicon fraction measured at 20 keV; the dotted line is the prediction of a model for such an homogeneous particle. Circles are data points for an Illinois bituminous mine high-silica particle of 3.38 μm diameter and 0.974 silicon fraction at 20 keV; the dashed line is the model prediction for such an aluminosilicate-coated silica particle.

mathematical model (WALLACE *et al.*, 1990) using simple Beer's law expressions for the extinction of the electron energy with depth into a particle and of generated X-rays exiting the particle, with an empirical value for the cross-section for ionization of X-rays with electron energy, predicted the change in silicon fraction vs voltage for a homogeneous aluminosilicate particle of diameter 2.05 μm and 97.0% Si measured at 20 keV. That was shown as the upper dotted line in Fig. 1. The model predicts the lower dashed line behaviour for an occluded particle of 3.38 μm diameter and 97.4% Si as measured at 20 keV. Measurements on an anthracite, A, high-silica particle with the former diameter and composition are shown as triangles at the mean with SD flags. Measurements on a bituminous, I, high-silica particle, with the latter size and composition, are shown as circles with SD flags. Those particles appear to follow, respectively, the behaviour predicted for homogeneously and heterogeneously structured particles. Moreover, the behaviour shown for this anthracite high-silica particle is representative of that shown by the powdered glass control particles.

Table 1 shows the mean change and SD in measured silicon fraction for each of some 20 high-silica particles from the powdered glass control and from each of the nine worksite samples, when the electron beam accelerating voltage is changed from 20 to 5 keV.

The box plots in Fig. 2 characterize the distribution of the complete dataset of changes in silicon fraction with decreasing voltage in the 10 dust groups. In box plots, the central 50% of the observations (interquartile range, IQR) is contained within the boxes, with the mean being represented by a plus sign. The vertical 'whiskers' represent observations extending at most 1.5 IQRs from the boxes. The zeros and asterisks represent more extreme observations. On visual inspection it is seen that the dust groups tend to form into three clusters: the homogeneous Glass control, New River and anthracite (A) groups; the set of Clay mine, I, W1, W2 and C3, which all show little

TABLE 1. CHANGE IN SEM-EDS SILICON FRACTION OF SIGNAL WITH DECREASE IN ELECTRON BEAM ACCELERATING VOLTAGE FROM 20 TO 5 keV FOR EACH HIGH-SILICA PARTICLE

Clay mine	New River	Glass	A	C1	C2	C3	W1	W2	I
0.05 (0.07)	0 (0)	0.007 (0.02)	0.003 (0.01)	0 (0)	0 (0)	−0.01 (0.01)	−0.01 (0.05)	0.002 (0.03)	0 (0)
0.0 (0)	0 (0)	0.012 (0.01)	0 (0)	0 (0)	0 (0)	−0.004 (0.01)	0 (0.001)	0.05 (0.02)	0.003 (0.01)
0.05 (0.02)	0 (0)	0.013 (0.06)	0 (0)	0 (0)	0 (0)	0.01 (0.01)	0.009 (0.01)	0.05 (0.03)	0.01 (0.02)
0.06 (0.03)	0 (0)	0.014 (0.01)	0 (0)	0 (0)	0.007 (0.006)	0.01 (0.02)	0.01 (0.01)	0.07 (0.01)	0.016 (0.02)
0.09 (0.07)	0 (0)	0.015 (0.01)	0 (0.001)	0 (0)	0.009 (0.01)	0.02 (0.01)	0.02 (0.02)	0.07 (0.03)	0.017 (0.1)
0.13 (0.02)	0 (0)	0.015 (0.01)	0 (0.001)	0 (0)	0.015 (0.01)	0.03 (0.02)	0.05 (0.01)	0.07 (0.03)	0.019 (0.01)
0.14 (0.02)	0 (0)	0.017 (0.02)	0.002 (0.002)	0.005 (0.005)	0.016 (0.01)	0.04 (0.03)	0.06 (0.04)	0.08 (0.01)	0.03 (0.01)
0.15 (0.09)	0 (0)	0.018 (0.01)	0.003 (0.005)	0.008 (0.007)	0.016 (0.02)	0.05 (0.01)	0.06 (0.01)	0.08 (0.01)	0.03 (0.01)
0.15 (0.06)	0 (0)	0.019 (0.01)	0.007 (0.008)	0.025 (0.01)	0.03 (0.02)	0.05 (0.01)	0.06 (0.03)	0.09 (0.03)	0.06 (0.02)
0.18 (0.02)	0 (0)	0.020 (0.01)	0.009 (0.007)	0.029 (0.02)	0.05 (0.01)	0.05 (0.01)	0.06 (0.01)	0.11 (0.03)	0.06 (0.03)
0.19 (0.06)	0 (0)	0.021 (0.01)	0.009 (0.008)	0.034 (0.01)	0.05 (0.01)	0.06 (0.02)	0.07 (0.03)	0.11 (0.04)	0.08 (0.03)
0.19 (0.02)	0 (0)	0.024 (0.02)	0.01 (0.006)	0.036 (0.01)	0.06 (0.03)	0.06 (0.01)	0.07 (0.02)	0.11 (0.03)	0.08 (0.03)
0.21 (0.06)	0 (0)	0.024 (0.02)	0.011 (0.01)	0.042 (0.02)	0.07 (0.03)	0.09 (0.03)	0.07 (0.02)	0.12 (0.01)	0.08 (0.03)
0.22 (0.06)	0 (0)	0.024 (0.01)	0.012 (0.007)	0.044 (0.01)	0.07 (0.02)	0.11 (0.02)	0.10 (0.02)	0.15 (0.02)	0.09 (0.02)
0.24 (0.05)	0 (0)	0.024 (0.01)	0.013 (0.005)	0.046 (0.03)	0.07 (0.02)	0.12 (0.05)	0.13 (0.03)	0.15 (0.06)	0.12 (0.1)
0.25 (0.05)	0 (0)	0.025 (0.01)	0.02 (0.01)	0.054 (0.01)	0.10 (0.04)	0.13 (0.02)	0.16 (0.05)	0.17 (0.03)	0.13 (0.02)
0.35 (0.02)	0 (0)	0.026 (0.01)	0.022 (0.02)	0.056 (0.03)	0.195 (0.07)	0.14 (0.04)	0.20 (0.04)	0.18 (0.01)	0.14 (0.03)
	0 (0)	0.028 (0.01)	0.023 (0.01)	0.056 (0.01)			0.20 (0.02)	0.20 (0.04)	0.15 (0.01)
	0 (0)	0.028 (0.01)	0.025 (0.01)	0.068 (0.03)			0.21 (0.05)	0.24 (0.03)	0.17 (0.04)
	0 (0)	0.031 (0.01)	0.037 (0.01)	0.083 (0.03)				0.25 (0.05)	0.19 (0.05)
	0.013 (0)	0.031 (0.01)	0.306 (0.05)	0.244 (0.01)				0.37 (0.01)	0.31 (0.07)

Values shown are the means of five replicate measurements followed by the standard deviation in parentheses.

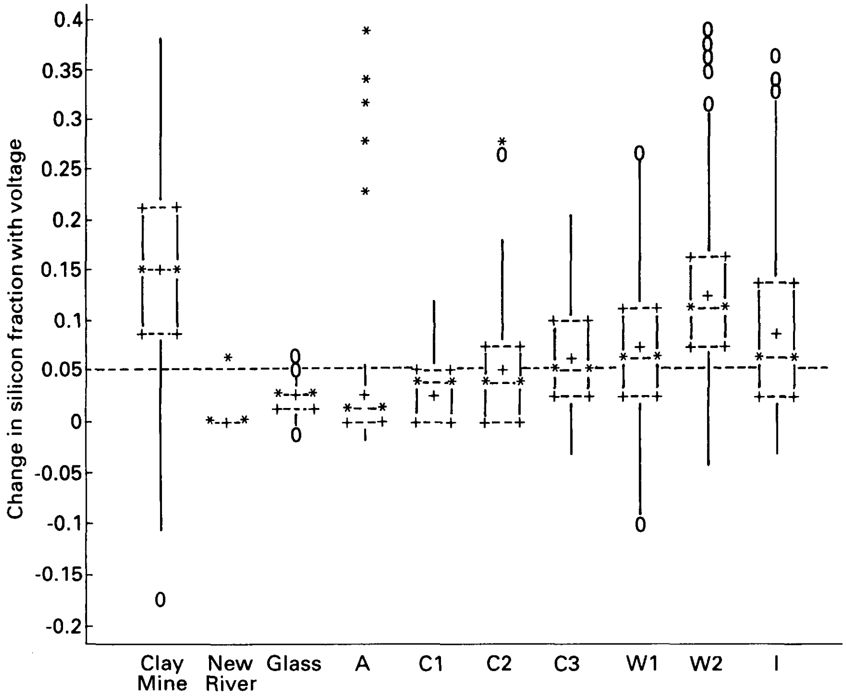

FIG. 2. Box plot for the distribution of change in silicon fraction with electron beam accelerating voltage for the control sample and nine worksite samples. Clay mine, New River = powdered tunnel quartz rock; Glass = powdered glass, A = eastern Pennsylvania anthracite; C1–C3 = central Pennsylvania bituminous samples 1–3; W1 and W2 = western Pennsylvania bituminous samples 1 and 2; I = Illinois bituminous. Boxes represent the range from first to third quartiles; crosses are the means; 'O' represent observations more extreme than 1.5 but less than 3 interquartile ranges; and '*' represents more extreme values.

overlap with the former cluster; and the remaining samples C1 and C2 which have substantial overlap with the first group even though the mean change of the two groups combined is a little greater. Most sites have but a few outliers. The anthracite sample has five observations (all the same particle) that are highly significantly different from the remaining observations. Most sites have symmetrical distributions; however, samples C1 and C3 display a positive skewness where a number of particles have a larger change in silicon fraction with voltage.

An analysis-of-variance procedure was performed to characterize formally the distribution of the change in silicon fraction with voltage for the nine locations (excluding the New River sample group). An overall *F* value of 54.18 revealed that a significant difference exists among the means, with the probability of chance occurrence of the difference being less than 0.0001. It was determined, as shown in Table 2 and indicated by the horizontal line in Fig. 1, that at the 0.001 alpha level, the following samples have mean changes in silicon fraction with voltage significantly different than the homogeneous control sample: Clay mine, W1, I, W2 and C3. There is not enough evidence to detect a difference, at the 0.05 alpha level, between the homogeneous control and each of the following: A, C1 and C2.

Based on a non-parametric analysis of the particle data given in Table 1, there was

TABLE 2. MEAN CHANGE IN SILICON FRACTION OF SIGNAL WITH DECREASE IN ELECTRON BEAM ACCELERATING VOLTAGE FROM 20 TO 5 keV FOR EIGHT MINE SAMPLES

Sample	Lower confidence limit	Difference between means	Upper confidence limit
Clay mine	0.092	0.129*	0.167
W2	0.073	0.108*	0.143
I	0.026	0.062*	0.098
W1	0.023	0.059*	0.096
C3	0.002	0.039*	0.077
C2	−0.014	0.024	0.061
C1	−0.025	0.010	0.047
A	−0.032	0.003	0.039

*Significantly different from control, $P<0.001$.

evidence that all dust types except for anthracite and New River were significantly different to the control distribution. In this analysis, a cut-off value of 0.029 was used, this being derived from 90-th percentile for the control data in Table 1. Comparison of each dust type distribution with the limit revealed that between 53 and 95% of the particle values were greater than it ($P \supset 0.001$ in each case); only anthracite (10%) and New River (0%) were compatible with the control distribution.

It appears that respirable-sized high-silica particles found in some dusty workplaces can exhibit surface aluminosilicate contamination or occlusion. The multiple-voltage SEM–EDS analytical method used here, unlike Auger or X-ray photoelectron spectroscopy, does not measure the elemental composition of contaminants or surface-modifying agents which are only one or a few atomic layers thick. The surface heterogeneity measured here is on the order of 0.01–0.1 μm thick. Characterization of the mineralogical nature of the occluding material will require further research and complementary methods development. The analyses of these particular samples suggests, as a working hypothesis for investigation, that there may be some site or geologic factors, e.g. rank and sub-rank for coal mine dusts, associated with this modification of high-silica particle surfaces.

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DISCUSSION

F. GREEN: What is the diameter of the electron beam focused on the particle? Are the surface occlusions homogeneous or inhomogeneous? To what degree do inhomogeneities caused by the coating or particle shape affect the analysis? Could backscattered electron imaging (BSI) be used to study homogeneity? Does the method take into account substitution into the surface cations other than aluminium, e.g. Na, Ca, Mg?

W. E. WALLACE: The electron beam diameter, of the order of one-hundredth of a micrometre, is a function of several system parameters including the accelerating voltage and the aperture size used. In these studies it was significantly less than the lateral dimensions of the particles analysed. As the beam strikes and penetrates the sample particle it will spread within the particle and excite X-rays from a larger area which increases with increasing electron accelerating voltage. We have also acquired data by purposefully irradiating an area of a square micrometre or so, in order to obtain an area average depth profile over the full imaged surface of the particle. Second, we have examined several points across the surface of some larger particles and seen differences from point to point in the change in Si/Al with voltage, indicating coatings are not necessarily uniform. Third, I believe that alternating between secondary and backscatter imaging would not necessarily distinguish a coating, especially if the coating and substrate were of nearly the same atomic number and density. Fourth, the multiple-voltage energy dispersive X-ray analysis method we use is limited to elements with measurable line intensities at energies below the lowest electron beam energy applied. That is, using 5 keV electrons we are limited to elements with spectral lines below approximately 3 keV. For K lines, that restricts us to elements below calcium or potassium. Other systems might be able to analyse the distribution with depth of some heavier elements by using higher series spectral lines which have energies below 5 keV.

F. GREEN: There has been considerable discussion of surface protective coatings, e.g. surfactant or aluminium lactate, and their potential for etching or removal over the long term in the lung. What is known concerning the coating of particles (with organic or inorganic constituents) *in vivo* in such a way as to reduce long-term toxicity (fibrosis)?

W. E. WALLACE: There has been a significant amount of research on prophylactic coatings for respirable mineral dusts. Several research groups including our own have studied the suppression of short-term *in vitro* cytotoxicity conferred by the adsorption of phospholipid or other components of pulmonary surfactant on quartz and aluminosilicate dusts. This may model the initial event occurring upon deposition of a respired particle. We are investigating the removal of adsorbed phospholipid surfactant from quartz and clay particles by phospholipase digestion in cell-free systems and following macrophage phagocytosis *in vitro*. The digestive removal of surfactant and restoration of cytotoxicity seen in those studies suggest that such a cycle of effects may occur *in vivo*, which may or may not be mineral specific. This suggests that the *in vitro* cytotoxicity information on aluminium lactate or other organic prophylactic compounds also, should be evaluated as to the persistence of the coating under solubilization and digestive processes *in vivo*. If there is a natural inorganic occlusion of some quartz particles as by aluminosilicate coating discussed here, limiting the bioavailability of the quartz surface and consequently the pathogenic activity *in vivo*, then a similar question arises as to the persistence of the occluding surface material over time *in vivo*. As for attempts to apply inorganic coatings *in vivo*, I do not know if the information on aluminium therapy of several decades ago permits an evaluation of its effectiveness or mechanism.