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SURFACE COMPOSITION OF RESPIRABLE SILICA PARTICLES IN A SET OF U.S. ANTHRACITE AND BITUMINOUS COAL MINE DUSTS

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Abstract—Respirable particles of high-percentage silica content from anthracite and bituminous coal mine dust samples were analyzed for aluminosilicate clay surface coating, by measuring silicon and aluminum X-ray spectra using scanning electron microscopy–energy dispersive X-ray analysis (SEM–EDS). Silicon and aluminum elemental ratios were determined with incident electron energies of 20 and 5 keV to reveal whether surface occlusion was present. Some 20 respirable-sized, non-agglomerated particles with silicon fraction of signal of 75% or more (for elements above sodium) were analyzed for each of 12 coal mine dust samples. Mine dust samples were from U.S. anthracite and bituminous coal mining regions involved in epidemiological studies of the U.S. National Study of Coal Workers' Pneumoconiosis. Some particles of high-percentage silica content exhibited a decrease in the ratio of silicon-to-aluminum K-alpha line intensities with decreasing electron beam accelerating voltage, consistent with aluminosilicate clay surface contamination or occlusion of a silica particle. Significantly lower frequencies of particles manifesting occluded behavior were found for anthracite dusts versus all bituminous dusts. It is suggested that such occlusion alters the biological availability of the surface of those particles. This may be a factor in the results of attempts to correlate disease prevalence with conventionally measured dust composition, as in the classical failure of coal workers' pneumoconiosis disease prevalence to correlate with silica exposure while being correlated with cumulative total respirable dust exposure and with coal rank. Published by Elsevier Science Ltd.

INTRODUCTION

Workers with long-term exposures to respirable dusts generated in coal mining are at risk of developing simple coal workers pneumoconiosis (CWP) and progressive massive fibrosis (PMF) of the lungs (Hurley *et al.*, 1982, 1987). As a preventative measure, dust levels in U.S. coal mine atmospheres are limited by Federal standard to a permissible exposure limit of $2\ \mathrm{mg\,m^{-3}}$ coal mine dust as an 8 h time-weighted average exposure. Dust is collected using a personal sampler unit approved by the U.S. Mine Safety and Health Administration (MSHA). The sampler uses a pre-separator cyclone to collect "respirable"-sized particles on a membrane filter (Jacobson and Lamonica, 1969). As operated in coal mines, dust particles with aerodynamic diameters of 3–4 μm pass through the cyclone with 50% efficiency and are collected on the filter. Smaller particles pass through the cyclone with efficiencies approaching 100% and are collected on the filter. Particles larger than 10 μm aerodynamic diameter are preferentially eliminated by the cyclone and have very low probabilities of being collected on the filter. The intent is to collect and analyze as "respirable" that fraction of the airborne dust in coal mines that is capable of entering the gas exchange regions of the lung if inhaled (ATC, 1970).

Airborne dust in coal mines is composed of coal and of minerals such as quartz and clays and other inorganic minerals; the non-coal mineral dust components are generated by cutting into the rock roof or floor of the mine, or are generated from minerals within the coal seam. Respirable quartz dust is a known etiologic agent for pulmonary fibrosis (NIOSH, 1974). Therefore, the U.S. coal mine dust exposure standard is reduced as the quartz content of the dust increases, to attempt to limit respirable quartz levels to $0.1\ \mathrm{mg\,m^{-3}}$ or less. Respirable dust quartz content commonly is measured on mine dust samples by using infrared spectroscopy. In some cases, workplace dust quartz content is measured by X-ray diffractometry. Also, for research purposes, quartz content of collected dust samples can be measured by particle-by-particle analysis using scanning electron microscopy–energy dispersive X-ray analysis (SEM–EDS) at 20–30 kV electron beam energies. Interestingly, the prevalence of CWP and PMF in coal miners correlates with estimated cumulative coal mine dust exposure, rather than with silica quartz exposure (Walton *et al.*, 1977).

CWP and PMF have not been eliminated under the current standard (NIOSH, 1995). Estimates from epidemiological studies predict disease prevalence under the current standard, and higher disease prevalences are predicted for miners exposed to the dust in mines of higher-ranked coals. Coal rank specifically refers to the carbon-to-hydrogen ratio of a coal. Coal rank appears to be the primary modifier of the dust exposure and CWP disease relationship: it has been positively related to CWP prevalence but negatively correlated with quartz content (Walton *et al.*, 1977; Robock and Bauer, 1988; Attfield and Morring, 1991). Higher rank coals typically are those which have undergone longer or more severe conditions of geologic burial. Anthracite coals, such as those found in the U.S. in eastern Pennsylvania, are those of the highest rank. Lower in rank are bituminous coals. These can have a gradation of subranks, e.g. bituminous coals in central Pennsylvania in the Johnstown area are higher rank bituminous than those in the Pittsburgh western Pennsylvania area. Lower still in rank are sub-bituminous and lignite coals.

The seeming anomaly of a correlation of disease prevalence with coal rank but not with quartz content of dust suggests, as one hypothesis for investigation, that some unmeasured properties affecting the toxicity of the quartz content may vary between mine dusts and may vary with coal rank. This report provides additional data and analyses in our continuing investigation of the possibility that mineral surface contamination or "occlusion" of quartz particles may modify the biologically available surface area of quartz particles in some dusts (Wallace *et al.*,1990, 1994). Such mineral coating might constitute only a small fraction of the mass of a particle and not be identified by the conventional assays of quartz in mine dusts.

In this study, individual respirable silica particles in samples from a set of U.S. coal mines were analyzed for both surface and bulk composition by a scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDS) technique that compares elemental analysis of the entire depth of an individual particle with near-surface composition of the same particle to depths of fractional micrometers (Wallace *et al.*, 1990; Wallace and Keane, 1993). SEM–EDS analysis was performed to measure the silicon fraction, Si/(Si + Al), at 20 and at 5 keV on high-percentage-silica particles. This method has the ability to determine if respirable quartz particles exhibit heterogeneous aluminum composition with depth. Such a heterogeneous elemental composition would result, for instance, from a respirable particle structured of a quartz core comprising the bulk of the particle, with a thin clay coating on the surface of the particle.

Particles in a randomly selected field on an SEM carbon sample stub were screened by SEM–EDS analysis at 20 keV to select only particles with a silicon elemental fraction above 75%; those particles then were assayed for their Si : Si + Al ratio at two SEM electron beam acceleration potentials, 20 and 5 keV. Assayed particles whose measured Si/(Si + Al) ratio diminishes significantly with decreasing beam voltage are considered to be surface-occluded by aluminosilicate mineral, while those whose ratio exhibits little change are considered homogeneous. This interpretation is based on comparisons of the measured change in silicon ratio with decreasing beam voltage to the change predicted by mathematical models of the behavior of homogeneously and heterogeneously structured particles (Wallace *et al.*, 1990). Thus, analysis of a 1 μm sized particle that measured 95% Si by analysis at 20 keV and 92% by analysis at 5 keV would indicate a non-occluded particle. Such measurements would follow the prediction for a silica particle homogeneously contaminated with aluminum. Such a particle would be expected to manifest a maximum potency in interactions with biological systems, and a particle that showed a significantly reduced Si ratio by surface analysis, for example, a 1 μm particle measured 95% Si at 20 keV and 75% by analysis at 5 keV, would behave as a heterogeneously structured particle with a clay coating on a silica core.

Dust particles were so-examined from a small number of mines from a spectrum of U.S. coal mining regions that included anthracite (high rank coal) in eastern Pennsylvania, bituminous coal in central (Johnstown area) Pennsylvania, bituminous coal of a lower subrank in western (Pittsburgh area) Pennsylvania and Illinois, and Colorado sub-bituminous coal. The regions were selected to parallel regions studied in the National Study of Coal Workers' Pneumoconiosis epidemiology program of the U.S. National Institute for Occupational Safety and Health. Epidemiological studies of those mining regions have found that the prevalence of CWP, including progressive massive fibrosis, increases with coal rank: the higher the rank, the greater the disease prevalence for a given level of cumulative exposure (Attfield and Morring, 1992). The objective of the current analyses was to ascertain whether quartz particle surface occlusion by aluminosilicate minerals, such as clays, occurred in respirable coal mine dusts, and if the fraction of quartz particles occluded was different for differing coal ranks.

EXPERIMENTAL METHODS

High-silica particles were analyzed in: two eastern Pennsylvania anthracite coal mine dust samples (A1 and A2); three central Pennsylvania bituminous coal mine dust low-temperature-ashed (LTA) samples (C1–C3) and one non-ashed sample (C4); two western Pennsylvania bituminous coal mine LTA samples (W1 and W2) and a non-ashed sample (W3); two Illinois bituminous coal mine dust samples (I1 and I2); a Colorado sub-bituminous coal mine dust (CO); and a clay mine and mill dust sample (CM). Data from the controls and samples A1, C1, C2, C3, W1, W2, and I1 were previously reported (Wallace *et al.*, 1994). The coal regions represent different coal rank or subrank. The moisture- and ash-free carbon content of coals from those seams were 84% for A1 and A2, 69% for C1–C4, 64% for W1–W3, and 48% for I1 and I2.

Samples W1 and W2 and C1–C3 were supplied by the U.S. Mine Safety and Health Administration (MSHA), U.S. Dept. of Labor. Those samples were taken of airborne dust in coal mines using the MSHA-approved sampling procedure for respirable dust, as discussed above: a cyclone preseparator removed larger particles and the sample consisted of those particles which passed through the cyclone and were collected on a filter. Samples W3, C4, I1 and I2 were supplied by J. Mutmansky from a coal mine airborne dust characterization study (Xu and Mutmansky, 1991). Sampling in that study was performed using an eight-stage Anderson sampler. The eight sequential impactor stages had 50% collection efficiencies for particles of aerodynamic diameters of 21, 15, 10, 6, 3.5, 2, 1 and 0.6 μm. Samples collected on the seventh stage, with a 50% collection efficiency at 1 μm aerodynamic diameter, were used in the current study.

SEM–EDS elemental analysis using an Hitachi S570 SEM with a Kevex 8000 EDS was performed at 20 keV and at 5 keV on each of some 20 randomly selected high-percentage silica particles from each sample. In a randomly selected field, all particles which did not image as overlaid or agglomerated particles were analyzed at 20 keV. A particle was considered to be of high-percentage silica content 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. Then five measurements were made at each voltage for each selected 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.

Respirable-sized particles from a powdered piece of aluminosilicate glass were used as the control to represent the behavior of high-percentage silica particles with aluminum contamination homogeneous throughout the particle. Dust from clay works provided a sample with a high probability of occluded silica particle occurrence. Respirable-sized particles obtained by powdering a 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.

The change in silicon fraction with reduction in voltage was computed for each of the five repeated measurements of the approximately 20 particles studied in each dust sample. The change in silicon fraction was averaged over the five repeated measurements for each particle in each dust sample, and box plots were generated from the resulting data. To test the hypothesis that each distribution of change in silicon fraction was identical to that of the control, the number of particles in each dust group with changes greater than the 90th percentile for the control group was determined. The probability of this number (or greater) occurring by chance was then computed using the binomial distribution with parameter $p = 0.10$ and sample size equal to the number of particles. The distributions of the change in silicon fraction across 12 coal mine dust samples within four ranges of change in silicon fraction (<0.01, $0.01{-}<0.05$, $0.05{-}<0.10$, $\geqslant 0.10$) resulted in a 4 × 12 table, and chi-square test of homogeneity was performed.

RESULTS

Figure 1 shows the distribution of the change in silicon fraction with reduction in voltage of the average repeated measurement per particle for each dust sample. In the box plots, the central 50% of the observations (interquartile range) is contained within the boxes, with the mean represented by a plus sign. The vertical "whiskers" represent the 95th and 5th percentiles, and the asterisks represent data points that fall outside those percentiles. The horizontal line at 0.029 represents the 90th percentile of the change in silicon fraction for the homogeneous control group (glass).

The majority of the particles within the anthracite mine group samples (A1 and A2) fall below this cut-off value, and their distributions are similar to that of the control group. The remainder of the coal mine dust samples tend to have more particles above 0.029, especially for western Pennsylvania coal mine samples. A better understanding of the number of particles for each dust sample greater than the cut-off value of 0.029 can be observed in Table 1. Comparisons of each dust sample distribution with the cut-off limit revealed that 54% of the high-silica content particles from the Illinois dust samples, 60% of the Colorado, 80% of the western Pennsylvania, and 54% from the central Pennsylvania dust samples were above the limit (p-value <0.0001 in each case); only anthracite samples (20%) and New River (0%) were compatible with the control group. Although there were significant numbers of particles which exhibited surface coating behavior, there were silica particles within each coal mine dust sample which did not exhibit surface coating behavior.

Differences between the distributions of change in silicon fraction with reduction in voltage for anthracite samples (A1 and A2), central Pennsylvania samples (C1–C4), and western bituminous samples (W1–W3, I1, I2, Co) categorized into four ranges (<0.01, $0.01{-}<0.05$, $0.05{-}<0.10$, $\geqslant 0.10$) are shown in Fig. 2. The percentage of particles within the anthracite samples exhibiting particle occlusion is significantly lower than those for western bituminous coal mine dust samples. The particles within central Pennsylvania dust samples appear to show a more symmetrical distribution, with a slight shift towards non-occluded particles.

These differences between and within the distributions of the change in silicon fraction were assessed using the chi-square test of homogeneity. From Fig. 2, the change in silicon fraction was categorized into four ranges resulting in a 4 × 12 table with 33 degrees of freedom for the chi-square test. These likelihood-ratio chi-squared statistics or Wilks's statistics are given in Table 2. Across all 12 coal mine dust samples, the chi-square test showed a lack of homogeneity (p-value <0.0001) indicating a systematic difference between each coal mine sample.

An in-depth analysis resulted from partitioning the 4 × 12 table into five components, each representing a different pattern of variation. These components are: (a) difference among anthracite samples (A1 and A2); (b) differences among central Pennsylvania samples (C1–C4); (c) differences among western Pennsylvania samples (W1–W3); (d) difference

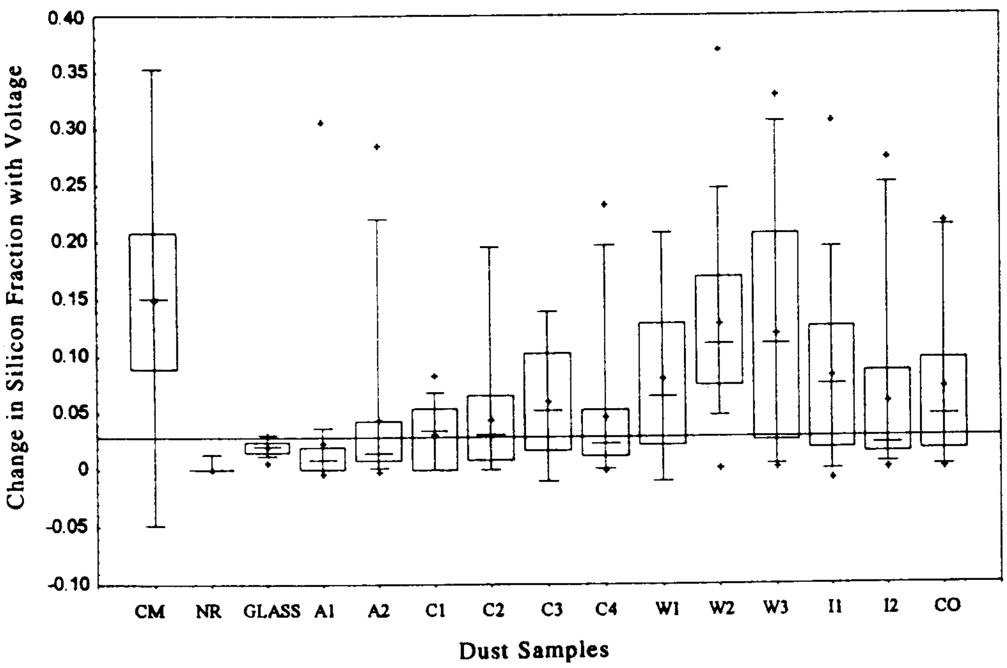

Fig. 1. Distribution of the change in measured silicon fraction with reduction in voltage of the average repeated measurement per particle for each dust sample.

Table 1. The distribution of the number of particles in each dust group with changes in silicon fraction greater than the 90th percentile for the control group (glass)

Coal mine dust samples	Number of particles >0.029	p-value*
Control (Glass)	2/21 = 0.10	0.635
Clay mine	15/17 = 0.88	0.00
New River	0/19 = 0.0	1.00
Anthracite		
A1	2/21 = 0.10	0.635
A2	6/20 = 0.30	0.011
Central Pennsylvania		
C1	11/21 = 0.52	0.000
C2	9/17 = 0.53	0.000
C3	13/18 = 0.72	0.000
C4	8/20 = 0.40	0.000
Western		
W1	14/19 = 0.74	0.000
W2	21/22 = 0.95	0.000
W3	14/20 = 0.70	0.000
IL1	15/21 = 0.71	0.000
IL2	7/20 = 0.35	0.002
Co	12/20 = 0.60	0.000

*p-value based on the binomial distribution with parameter $p = 0.10$ and sample sizes n = 17–22.

among Illinois samples (I1, I2); (e) differences between anthracite samples (A1 and A2) and all bituminous samples (C1–C4, W1–W3, I1, I2, Co); (f) differences between central Pennsylvania samples (C1–C4) and western bituminous samples (W1–W3, I1, I2, Co); (g) differences between western Pennsylvania and Illinois and Colorado samples (I1, I2, Co); and (h)

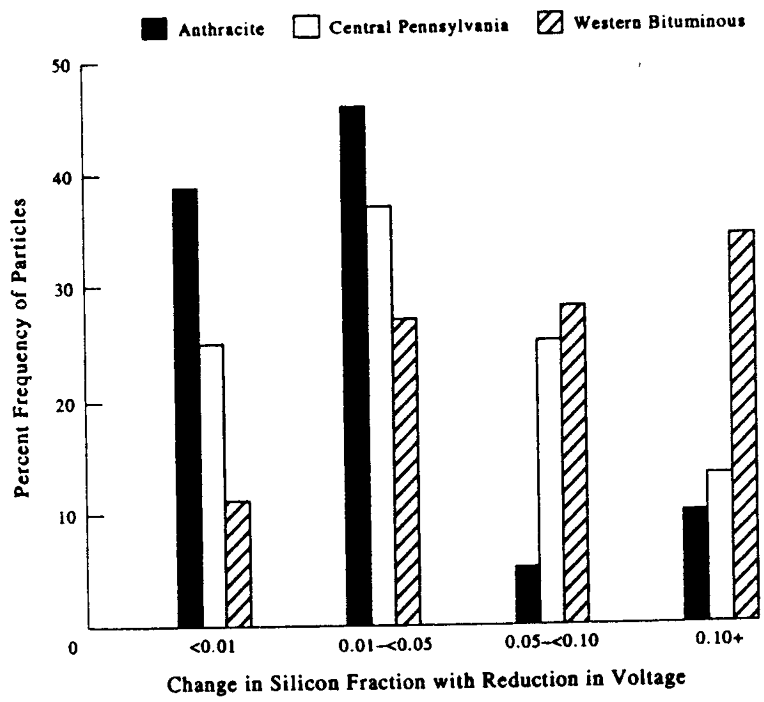

Fig. 2. Distribution of change in measured silicon fraction with reduction in voltage for anthracite, central Pennsylvania, and western bituminous coal mine dust samples.

Table 2. The likelihood-ratio chi-squared statistics for testing homogeneity of change in silicon fraction with reduction in voltage for dust sample groups

Comparison group	Df	Likelihood-ratio χ^2	p-value[†]
Overall test between 12 samples	33	91.5	***
Anthracite (A1 and A2) samples	3	6.2	
Central Pennsylvania samples (C1, C2, C3, C4)	9	16.5	
Western Pennsylvania samples (W1, W2, W3)	6	10.1	
Illinois (I1 and I2) samples	3	7.7	
Anthracite and all bituminous samples (C + W + I + Co)	3	23.4	***
Central Pennsylvania and western bituminous samples (W + I + Co)	3	14.7	**
Western Pennsylvania and (I + Co) samples	3	12.5	**
Between Illinois and Colorado samples	3	0.39	

[†] p-values represent the probability of homogeneity by chance alone, where blank = $p > 0.10$, *** = $p < 0.0001$, ** = $p < 0.01$.

differences between Illinois and Colorado samples. The first four components represent the within dust group variation, while the remaining components represent regional (coal rank) variation.

A comparison between anthracite samples and all bituminous dust samples contributed heavily to the overall chi-square value (23.4; p-value <0.0001), therefore representing most of the variation between the coal mine samples. However, within each group the likelihood-ratio chi-squared statistic was not statistically significant (p-value >0.05 for each case), indicating homogeneous groups. For the remaining components representing regional (coal rank) variation, there was a significant systematic difference between central Pennsylvania higher subrank bituminous dust samples and western bituminous dust samples (p-value = 0.002). In addition, there was a significant difference between western Pennsylvania bituminous dust samples and midwest (Illinois and Colorado) bituminous dust samples (p-value = 0.006), but with western Pennsylvania dusts expressing a greater fractional occlusion.

DISCUSSION

Aluminosilicate clay surface coatings of the order of 0.01–0.1 μm thickness on a respirable-sized silica particle can be demonstrated using SEM–EDS measurements of elemental composition at two or more electron beam energies (5–20 keV or higher) (Wallace *et al.*, 1990). Changes in the measured silicon fraction with voltage are distinct for the two cases of aluminosilicate clay occlusion of a pure silica core and of a silica particle with a homogeneous aluminum composition, both particles having the same size and overall composition. The change in measured silicon fraction with voltage is well-described for each case by a mathematical model using Beer's law expressions for attenuation of electron beam and induced X-ray intensities in a homogeneous or layered structure.

Respirable coal mine dusts analyzed here, supplementing those previously reported (Wallace *et al.*, 1994), were from a selection of mining areas involved in the U.S. National Study of Coal Workers' Pneumoconiosis (NSCWP). That study found a clear indication that miners who work in regions where high rank coal is mined may be at higher risk of disease for a given level of cumulative dust exposure. This also has been the finding of European studies of CWP; studies in which quartz has not been found to be a major correlate with disease prevalence. This seemingly is an anomaly, since respirable quartz is an independent pathogenic agent for pulmonary fibrosis.

Application of this method found that two categories of dust samples, New River powdered rock and anthracite mine dusts, were similar to the control powdered aluminosilicate glass, that is, they did not manifest significant fractions of aluminosilicate-coated silica particles. Other categories of mine dusts (clay, central Pennsylvania, western Pennsylvania, Illinois and Colorado) were significantly different from the control glass dust, indicating possible occlusion of significant fractions of the high-percentage silica mine dust particles. Within the same coal mine region, e.g. central Pennsylvania, the dust samples were homogeneous, that is, the fractions of particles displaying occluded behavior were not significantly different between the individual samples. The dust samples were not homogeneous when compared between regions, that is, there were statistically significant differences in the fraction of high-silica particles showing occlusion between some categories of samples. Central Pennsylvania coal mine dust samples were different to western coal mine dust samples. Anthracite dust samples were not homogeneous with all bituminous coal mine dust samples. In particular, the frequency of occluded silica particles increases from anthracite to central Pennsylvania high subrank bituminous to western Pennsylvania bituminous coal mine dusts. However, the parallel betweeen frequency of particle occlusion and decreasing coal rank or subrank is not perfect: western Pennsylvania samples exhibit a higher value than the more western and lower subrank samples from Illinois and Colorado.

These results show that respirable-sized high-percentage silica particles found in some mines can exhibit surface aluminosilicate contamination or occlusion. The analyses of this limited set of samples suggest but do not prove that there may be some site or geologic factors, e.g. rank and subrank for coal mine dusts and the depositional environment, associated with this modification of high-silica particle surfaces in coal mine dusts. Other sample variations may contribute to the differences observed. For instance, the distribution of particles of different surface properties in a mine atmosphere at the time of sample acquisition might vary in the same mine with different operating conditions, e.g. cutting surrounding mineral rock in addition to cutting coal.

The greater disease prevalence per unit cumulative exposure seen for anthracite coal regions in the NSCWP might be due to one or more factors. These include the biologic availablity of quartz particle surfaces, or currently unrecognized pathogenic activities of other components of mine dust. Clearly, additional dusts representative of the range of generation and exposure situations must be surface-analyzed for different coal rank and region to determine if frequency of occlusion and coal subrank are related. This research also could seek to identify mining situations which result in enhanced exposure to surface-bioavailable respirable quartz particles. To the extent that aluminosilicate clay surface occlusion, as measured here, is indicative of diminished biological availability of the silica particle surface, these data suggest a possible explanation for the lack of a strong correlation between mass-per cent quartz assayed exposures with CWP prevalence, and, as a working hypothesis, they suggest an etiologic role for biologically available silica surface in CWP.

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