

# Risk of Silicosis in Cohorts of Chinese Tin and Tungsten Miners and Pottery Workers (II): Workplace-Specific Silica Particle Surface Composition

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**Background** *It is hypothesized that surface occlusion by alumino-silicate affects the toxic activity of silica particles in respirable dust. In conjunction with an epidemiological investigation of silicosis disease risk in Chinese tin and tungsten mine and pottery workplaces, we analyzed respirable silica dusts using a multiple-voltage scanning electron microscopy–energy dispersive X-ray spectroscopy (MVSEM-EDS).*

**Methods** *Forty-seven samples of respirable sized dust were collected on filters from 13 worksites and were analyzed by MVSEM-EDS using high (20 keV) and low (5 keV) electron beam accelerating voltages. Changes in the silicon-to-aluminum X-ray line intensity ratio between the two voltages are compared particle-by-particle with the 90th percentile value of the same measurements for a ground glass homogeneous control sample. This provides an index that distinguishes a silica particle that is homogeneously aluminum-contaminated from a clay-coated silica particle.*

**Results** *The average sample percentages of respirable-sized silica particles alumino-silicate occlusion were: 45% for potteries, 18% for tin mines, and 13% for tungsten mines. The difference between the pottery and the metal mine worksites accounted for one third of an overall chi-square statistic for differences in change in measured silicon fraction between the samples.*

**Conclusion** *The companion epidemiological study found lower silicosis risk per unit cumulative respirable silica dust exposure for pottery workers compared to metal miners. Using these surface analysis results resolves differences in risk when exposure is normalized to cumulative respirable surface-available silica dust. Am. J. Ind. Med. 48:10–15, 2005. Published 2005 Wiley-Liss, Inc.<sup>†</sup>*

**KEY WORDS:** *silicosis; particle surface; mining*

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## INTRODUCTION

Quartz (SiO<sub>2</sub>) is often encountered in hard rock mining and can contribute a hazardous component to associated respirable dusts. It is hypothesized that alumino-silicate clay coatings (a layering of alumina and silica), decrease the bio-availability of the crystalline silica surface, which in turn modulates the disease potential of these dusts. The possibility of silicotic activity varying with surface properties of silica particles in a dust has been suggested by animal model studies of native and treated crystalline silica dusts

[LeBouffant et al., 1982]; by studies of silica dust toxicity changes with thermal treatment [Razzaboni et al., 1990; Fubini et al., 1999]; and by epidemiological investigations of silicosis risk of workers exposed to crystalline silica in mixed-composition dusts [Walton et al., 1971; Robock and Klosterkotter, 1973; Kreigseis and Scharmann, 1982; Muir et al., 1989; Attfield and Moring, 1992; Hnizdo and Sluis-Cremer, 1993; Hnizdo, 1994; Steenland and Brown, 1995; Kreiss and Zhen, 1996; Chen et al., 2001]. MVSEM-EDS analyses of silica particles in a clay-works dust [Wallace et al., 1990] and in coal mine dusts [Wallace et al., 1994; Harrison et al., 1997] have shown the presence of aluminosilicate-coated high silica particles which are not agglomerates but are occluded with a continuous coating as seen by appearance and by analyses of multiple locations on a particle. Measurements of coal mine dust silica particles by an independent technique, laser ablation of particle surfaces with mass spectroscopy analysis of vaporized constituents, independently suggests the existence of such structured particles [Tourmann and Kaufmann, 1994].

Respirable dust samples were collected from workplaces in the parallel retrospective cohort epidemiology study of the risk of silicosis in Chinese tin and tungsten miners and pottery workers [Chen et al., 2005 (this issue)].

## MATERIALS AND METHODS

Airborne dust samples were collected using the NIOSH cyclone separator - PVC filter collector for respirable dust (NIOSH Manual of Analytical Methods #7500). Sampling was performed at 2.0 L/min rather than the NIOSH protocol value of 1.7, which would result in a slightly smaller size for the 50% cut-point for filter-collected particles. Samples were available for surface analysis from 13 of the 20 worksites involved in the epidemiology study.

Silica particles in the samples were analyzed for surface coatings of aluminosilicate clay using a multiple-voltage scanning electron microscopy-energy dispersive X-ray analytical method that compares total particle silicon-to-aluminum ratio, obtained at high energy electron beam excitation, with the composition near the particle surface, obtained by low energy electron excitation. For each of 47 samples, dust was transferred dry to an SEM carbon sample planchette; and individual non-agglomerated particles were analyzed by automated SEM-EDS at 20 kV electron beam accelerating potential to identify on the order of 100 particles for which the silicon line contributed 75% or more of the total elemental X-ray line intensities for elements above neon. These high-silicon particles were further analyzed at 5 kV beam voltage. The ratio  $\text{Si}/(\text{Si}+\text{Al})$  was computed from the data at 20 and at 5 kV for each high-silica particle; the value of the measured change in the ratio with voltage was compiled for each particle; and the distributions of these changes were statistically compared

between samples and types of workplaces. Individual particle values and sample means and medians were compared with the 90th percentile of the change in silicon fraction measured for a set of homogeneous particles in a control dust sample of respirable-sized ground glass particles. Those particles contain aluminum homogeneously distributed throughout the particle and provide the behavior of a non-occluded silica particle containing aluminum. That control material was principally silicate, with  $\text{Si}/(\text{Si}+\text{Al})$  of 0.97 measured at 20 kV (in the range of values for many workplace high-silica dust particles), and with a narrow distribution of changes in measured silicon fraction with voltage. For silicates, the depth of electron excitation of X-rays decreases from several micrometers by 20 keV electrons to the order of a tenth of a micrometer for 5 keV electrons. Then the elemental spectra ratio of  $\text{Si}/(\text{Si}+\text{Al})$  obtained at the two electron beam voltages in an SEM-EDS analysis can be compared to distinguish clay occlusion of a silica particle surface from homogeneous composition, since most clay compositions are approximately equi-atomic percent silicon and aluminum [Wallace et al., 1990, 1996; Harrison et al., 1997; Hnizdo and Wallace, 2002].

## RESULTS

The data consist of 3,982 observations of the difference in  $\text{Si}/(\text{Si}+\text{Al})$  as measured at 20 kV and at 5 kV for particles from 47 samples. Of these, 1,752 observations are from 27 samples collected at seven pottery mines, 407 observations are from 11 samples collected at three tin mines, and 1,823 observations are from nine samples collected at three tungsten mines. Table I provides the fraction and percentage of those particles with change in measured silicon fraction greater than 0.029, the 90th percentile value for the ground glass homogeneous control sample. Twenty-four of twenty-seven pottery, three of eleven tin mine, and five of nine tungsten mine dust samples had frequencies much larger than would be expected by chance alone ( $P < 0.01$ ) of particles with changes of silicon fraction greater than the 90th percentile of a homogeneous control dust, that is, of particles indicating clay surface occlusion. The averages of those sample percentages of silica particles indicating clay occlusion of their surface were 45% for potteries, 18% for tin mines, and 13% for tungsten mines.

Table II shows for each of the three types of worksite the frequencies and percentages of particles in each of four categories of change in measured silicon fraction with voltage,  $\Delta$ , from  $\Delta < 0.01$  (less than 1% change) to  $\Delta \geq 0.10$ . Table III shows the overall likelihood ratio chi-squared statistic for the frequencies for all 47 samples of particles in those four categories. A decomposition of this chi-square statistic is given in order to indicate the sources of variation. One-third of the overall chi-square statistic can be attributed to the difference between the pottery samples and the metal

**TABLE I.** The Number and Percentage of Silica Particles in Each of 27 Samples of Pottery Dust or 20 Samples of Metal Mine Dust With Changes in Measured Silicon Fraction Greater Than 0.029, the 90th Percentile for the Homogeneous Dust Control Group (Glass), Indicating Clay Occlusion of the Silica Particle Surface

Dust samples		Percentage of particles > 0.029	P-value
Controls	Clay mine	(15/17) = 88%	<0.0001
	Glass	(2/21) = 10%	0.64
Pottery	P1	(28/37) = 76%	<0.0001
	P2	(34/86) = 40%	<0.0001
	P3	(27/56) = 48%	<0.0001
	P4	(13/28) = 46%	<0.0001
	P5	(19/51) = 37%	<0.0001
	P6	(46/240) = 19%	<0.0001
	P7	(9/11) = 82%	<0.0001
	P8	(10/19) = 53%	<0.0001
	P9	(45/92) = 49%	<0.0001
	P10	(21/36) = 58%	<0.0001
	P11	(9/25) = 36%	<0.0001
	P12	(45/60) = 75%	<0.0001
	P13	(5/18) = 28%	0.03
	P14	(106/230) = 46%	<0.0001
	P15	(28/59) = 47%	<0.0001
	P16	(42/98) = 43%	<0.0001
	P17	(7/31) = 23%	0.03
	P18	(32/74) = 43%	<0.0001
	P19	(22/55) = 40%	<0.0001
	P20	(44/119) = 37%	<0.0001
	P21	(18/34) = 53%	<0.0001
	P22	(27/60) = 45%	<0.0001
	P23	(30/96) = 31%	<0.0001
	P24	(25/65) = 38%	<0.0001
	P25	(8/22) = 36%	0.0009
	P26	(21/40) = 53%	<0.0001
	P27	(3/10) = 30%	0.07
Tin	Sn1	(7/32) = 22%	0.04
	Sn2	(16/68) = 24%	0.0009
	Sn3	(16/88) = 18%	0.01
	Sn4	(6/48) = 13%	0.35
	Sn5	(13/34) = 38%	<0.0001
	Sn6	(5/51) = 10%	0.59
	Sn7	(2/16) = 13%	0.49
	Sn8	(5/36) = 14%	0.29
	Sn9	(0/13) = 0%	1.0
	Sn10	(3/7) = 43%	0.03
	Sn11	(0/14) = 0%	1.0
Tungsten	W1	(6/59) = 10%	0.55
	W2	(27/121) = 22%	<0.0001
	W3	(7/160) = 4%	0.997

**TABLE I.** (Continued)

Dust samples	Percentage of particles > 0.029	P-value
W4	(108/207) = 52%	<0.0001
W5	(69/419) = 16%	<0.0001
W6	(25/281) = 9%	0.76
W7	(52/339) = 15%	0.001
W8	(11/55) = 20%	0.02
W9	(38/182) = 21%	<0.0001

The binomial probability is given for obtaining that number if the true percentage were equal to 10%, the observed percentage for the homogeneous composition control group.

mine samples. There is little difference between the tin mines versus the tungsten mines. Other major sources of variation exist between some pottery worksites, between some tungsten mines, and between samples for some of the worksites or mines.

These respirable dusts were available for surface analysis from 13 of the 20 worksites involved in the companion epidemiological cohort mortality study of silicosis risk [Chen et al., 2005]. Five of the seven worksites in the epidemiology study without dust sample surface analysis were tungsten mines in the same geographic and geologic region as two of the tungsten mines that were sampled; one of the worksites was a tin mine and one a pottery. Because of the large sample of tungsten miners, recalculation of the cumulative risk of silicosis versus cumulative respirable silica dust exposure using epidemiological data from only the 13 worksites used in this dust surface analysis study resulted in an essentially identical relationship to that shown in the epidemiology report for all 20 worksites [Chen et al., 2005 (this issue)].

**DISCUSSION**

Occupational exposures to respirable crystalline silica quartz dust frequently occur in mixed dust atmospheres in

**TABLE II.** Frequencies for Four Categories of Change in Silicon Fraction With Change in Voltage, Stratified by Type of Workplace

$\Delta$ in Si fraction	Pottery factories		Tin mines		Tungsten mines	
	N	% N	N	% N	N	% N
$\Delta < 0.01$	824	47	298	73	1,348	74
$0.01 \leq \Delta < 0.05$	365	21	61	15	198	11
$0.05 \leq \Delta < 0.10$	181	10	21	5	91	5
$\Delta \geq 0.10$	382	22	27	7	186	10
Totals	1,752	100	407	100	1,823	100

The percent of the total frequency is also shown for each type of workplace.

**TABLE III.** The Likelihood-Ratio Chi-Square Statistics for Testing the Homogeneity of the Frequencies of Particles in Four Categories of Change in Measured Silicon Fraction With Voltage, Shown in Table II, for the 47 Pottery or Tin Mine or Tungsten Mine Dust Samples

Comparison groups	DF	Likelihood ratio $\chi^2$	P-value
Overall variation between the 47 samples	138	897.0	<0.001
Pottery versus metal mines	3	305.0	<0.001
Tin versus tungsten mines	3	9.5	0.02
Different pottery worksites, P1–P27	18	84.0	<0.001
Five guangming samples, P1–P5	12	25.5	0.01
Five Hongxing samples, P6–P10	12	87.0	<0.001
Three Jie Pai samples, P11–P13	6	43.0	<0.001
Two Jingtao samples, P14–P15	3	1.7	0.65
Five Renming samples, P16–P20	12	16.0	0.19
Three Weiming samples, P21–P23	6	13.8	0.03
Four Yu Zhou samples, P24–P27	9	9.8	0.37
Different tin mines, Sn1–Sn11	6	6.3	0.39
Five Da Chang Po samples, Sn1–Sn5	12	27.3	0.007
Five Da Chang Tong samples, Sn6–Sn11	12	15.2	0.23
Different tungsten mines, W1–W9	6	81.0	<0.001
Four Chuankou samples, W1–W4	9	155.0	<0.001
Two Xi Huashang samples, W5–W6	3	12.0	0.008
Three Xia-Long samples, W7–W9	6	5.4	0.49

The chi-square statistics below the double line represent a decomposition of the overall chi-square of 897.

which clay aluminosilicates are an additional significant mineral component. Clays are aluminosilicate minerals with ordered lattice structures of alternating layers of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) and silicon dioxide ( $\text{SiO}_2$ ), while quartz is composed entirely of  $\text{SiO}_2$  with a particular crystalline structure. Clay minerals can occur as geologic overburden or inclusions in minerals being mined, e.g., coal or metal mines. Clay powders are generated and used in addition to silica powders in pottery manufacturing. Separately, quartz dust exposures can cause lung fibrosis (silicosis); while clay exposures are not associated with significant pulmonary fibrosis disease. There have been suggestions that the risk of harm from quartz is partially diminished in mixed dust exposures involving both quartz and clay dusts, e.g., in coal mining [Walton et al., 1971]. Some respirable quartz particles in mixed dusts have aluminosilicate clay associated with the quartz particle surface, not as an agglomerate of fine clay particles on a larger respirable quartz particle. Instead, microscopy indicates a continuum clay coating or occlusion of the quartz particle surface [Wallace et al., 1990; Tourmann and Kaufmann, 1994]. Experimental studies have indicated that clay contamination of respirable crystalline silica particle surfaces can alter the cytotoxic and fibrogenic activities of the crystalline silica dust [reviewed in Bolsaitis and Wallace, 1996]. Animal model research [LeBouffant

et al., 1982] on the effect of impurities and associated minerals on quartz toxicity, found that aluminum in the form of an aluminosilicate surface coating sometimes occurred on natural silica dusts and attenuated their in vivo fibrogenic activity. An animal model instillation study using a silica dust ground from a natural sand and its endogenous trace of clay resulted in a 6 month delayed onset of lung fibrogenic activity [LeBouffant et al., 1982]. That study also found that crystalline silica dust particles extracted from coal mine dust did not initiate fibrogenic activity over the lifespan of the animal model; but those particles were promptly fibrogenic after strong acid digestion of clay from the particles surfaces.

The effect of silica particle surface composition on silicosis disease risk has been investigated in the companion paper [Chen et al., 2005]. Silicosis disease risk and respirable silica dust surface composition were compared between metal mines and pottery workplaces in China for which a large medical registry for silicosis was available and for which representative samples of workplace dusts could be obtained. Significant differences were observed between the miners and pottery workers for silicosis risk versus cumulative respirable silica dust exposure [Fig. II-B, in Chen et al., 2005]. The surface analysis of associated respirable particles reported in this study may be interpreted in terms of surface occlusion by clay of 45% of the respirable crystalline

silica particles from the potteries, 18% from tin mines, and 13% from the tungsten mines. This would result in an associated decrease in biological availability of the underlying crystalline silica surface, and therefore in a possible transient or permanent diminution of the expression of crystalline silica surface toxicity [Wallace et al., 1990; Fubini and Wallace, 2000]. The sample averages of the percentages of silica particles indicating clay occlusion suggest, conversely, that the percentages of respirable silica particles with biologically available crystalline silica surface are 55% for pottery, 82% for tin, and 87% for tungsten. These factors were used to convert exposure measured as cumulative respirable silica dust to exposure measured as cumulative respirable “surface-available” silica dust. Chen et al. [2005] found that cumulative risk of silicosis was significantly greater for tin and tungsten miners compared to pottery workers for any given cumulative respirable silica dust exposure level (Fig. II-A and B). However, if the dust exposures are normalized with respect to the fraction of bio-available (non-surface-occluded) crystalline silica, using these conversion factors of 0.55 for potteries, 0.82 for tin mines, and 0.87 for tungsten mines, then risk to pottery workers approaches the risk to metal miners and approximates the risk to tungsten miners. This is seen in the relationship between cumulative risk of silicosis and cumulative surface-available respirable silica dust as presented (Fig. II-C) in the companion epidemiology paper [Chen et al., 2005 (this issue)].

We suggest that silica particle surface occlusion by aluminosilicate clay may have partially but substantially diminished fibrogenic activity of pottery workplace silica dusts. It is possible that other unmeasured exposure factors could be involved in the observed differences in lung fibrosis risk, e.g., other mineral components of the dusts of unrecognized toxicity, unrecognized nano-particulate mineral content. Such clay occlusion of respirable silica has been observed in US coal mine dusts and suggested as a basis for the “coal-rank anomaly” in coal workers pneumoconiosis and progressive massive fibrosis disease risk. There, the fraction of clay occluded silica particles was associated with the nature of the rock strata surrounding the coal seam; e.g., lower frequency of particle occlusion was seen from higher rank coal seams with associated quartzitic rock; while greater fractions of the silica particles were clay-occluded in lower rank coal seams, associated with sedimentary silica rock strata [Harrison et al., 1997]. That frequency of silica particle surface occlusion generally followed the coal-rank effect in which greater pneumoconiosis and progressive massive fibrosis disease risk is seen with increasing coal rank.

## CONCLUSIONS

These studies suggest that prophylaxis is associated with aluminum as aluminosilicate occlusion of the surface of

some silica particles. That is, while the clay coating persists on a quartz particle, the biological interactions will be those of a clay particle, even though the mass fraction of the particle may be only a few percent clay. Greater structural stability was observed for such clay occluded particles from a clay works than would be expected of an agglomerate of ultrafine clay particles on a silica particle core [Wallace et al., 1990]. Those clay-occluded crystalline silica particles were found not to dissociate over a period of hours of incubation in dispersion in physiological saline of dipalmitoyl phosphatidylcholine (DPPC). That incubation with DPPC, a major component of pulmonary surfactant, was to model possible solubilization or disassociation of agglomerated particles after their deposition on the surfactant coating of the lung respiratory bronchioles and alveoli [Wallace et al., 1990]. The question arises of the longer term durability or bio-persistence of such clay coatings on respirable silica particles in vivo and the duration of associated prophylaxis, e.g., over decades. In the companion study there appears to be a several year lag in the time to disease onset in the pottery workers compared to the metal miners [Chen et al., 2005]. Longer term durability of prophylactic surface occlusion of particles sequestered in the lung remains an open question.

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