Risk of Silicosis in Cohorts of Chinese Tin and Tungsten Miners, and Pottery Workers (I): An Epidemiological Study

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Background *Epidemiological evaluations of the risk of silicosis in relation to exposure to crystalline silica have raised the question of whether different types of silica dust exposures vary with respect to their ability to cause silicosis. The aim of this study is to compare the risk of silicosis among cohorts of silica dust-exposed Chinese tin miners, tungsten miners, and pottery workers and to assess whether gravimetric measurements of respirable silica dust sufficiently determine the risk of silicosis or whether other factors of exposure may play a significant role.*

Methods *Cohorts were selected from 20 Chinese mines and potteries. Inclusion criteria were starting employment after January 1, 1950 and being employed for at least 1 year during 1960–1974 in one of the selected workplaces. Radiological follow-up for silicosis onset was from January 1, 1950 through December 31, 1994. Silicosis was assessed according to the Chinese radiological criteria for diagnosis of pneumoconiosis (as suspect, Stage I, II, or III). Exposure–response relationships were estimated for silicosis of Stage I or higher. Silica dust exposure was estimated in terms of cumulative total dust exposure, calculated from a workplace, job title, and calendar year exposure matrix, and individual occupational histories. Cumulative total dust exposure was converted in two steps into cumulative respirable dust exposure and cumulative respirable silica dust exposure using conversion factors estimated from side-by-side measurements conducted in 1988–89.*

Results *The male cohorts included 4,028 tin miners, 14,427 tungsten miners, and 4,547 pottery workers who had similar onset of employment and duration of follow-up. For a given exposure level, the risk of silicosis was higher for the tin and tungsten than the pottery workers.*

Conclusion *The observed differences in the risk of silicosis among the three cohorts suggest that silica dust characteristics, in addition to cumulative respirable silica dust exposure, may affect the risk of silicosis.* Am. J. Ind. Med. 48:1–9, 2005. *Published 2005 Wiley-Liss, Inc.*[†]

KEY WORDS: quartz; silica; exposure–response differences; risk assessment; cohort studies

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INTRODUCTION

Several epidemiological studies have evaluated risk of silicosis in relation to exposure to crystalline silica (silica) in hard rock miners. The reported exposure–response relationship were similar among United States gold and molybdenum miners [Steenland and Brown, 1995; Kreiss and Zhen, 1996], Chinese tin miners [Chen et al., 2001], and South African gold miners [Hnizdo and Sluis-Cremer, 1993]. However, in Canadian gold miners, the reported risk of silicosis was substantially lower, although the exposure levels were substantially higher [Muir et al., 1989]. These differences in the risk of silicosis raise the question whether different types of silica-dust exposure vary with respect to their potential to cause silicosis [Hnizdo, 1994].

Experimental studies suggest that the toxic and fibrogenic potentials of silica dusts differ depending on the innate characteristics of the silica dust [Donaldson and Borm, 1998] and the surface properties of the silica dust particles [LeBouffant et al., 1982; Vallyathan et al., 1995; Bolsaitis and Wallace, 1996; Fubini and Wallace, 2000].

Given the limited epidemiological evidence, and the experimental findings supporting differences in silica dust toxicity, it is of interest to compare the risk of silicosis in groups of workers exposed to different types of silica dust. The objective of the present study was to compare the risk of silicosis in three cohorts of Chinese workers exposed to silica dust in tin mines, tungsten mines, and potteries. In the companion study [Harrison et al., 2005 (this issue)] respirable silica particles from these three types of workplaces were analyzed for the occlusion of the silica particle surfaces to examine the potential differences in silica dust toxicity.

MATERIALS AND METHODS

Cohort Ascertainment

In this retrospective cohort study, workers were identified from 20 factories or mines that were selected out of 40 facilities. The selection of workplaces was based on availability and quality of radiographs, silicosis registry, and exposure data. Coal, iron, and copper mines were excluded from this study. Individual workers were identified from company records that included personnel files, and individual medical and occupational records. For our analysis, the cohorts included all males who started employment after January 1, 1950 and were employed for at least 1 year during 1960–1974 in the studied workplaces.

Silicosis Ascertainment

The radiological follow-up for silicosis onset was from January 1, 1950 through December 31, 1994. In China, chest radiographs have been taken of silica dust-exposed workers since the early 1950s. The radiographs were kept by each company. Radiological readings were done by a silicosis diagnosis team in each province, and most companies kept a register of workers diagnosed with silicosis. Since 1963, a new national law required that workplaces with exposure to silica dust keep a register of employees with silicosis and that yearly chest radiographs are taken from all workers. About that time, diagnostic criteria for pneumoconiosis were standardized as a suspect case, Stage I, II, or III. Most workers diagnosed with silicosis before the silicosis registry law was made effective in 1963 would be included in the silica registries. Workers continued to have radiographic examinations every 2–3 years after cessation of dust exposure.

For the purposes of this study, the quality of the radiological reading was examined in two stages. In 1986, a 5% sample of chest radiographs was selected from 40 workplaces with potential for silica dust exposure and the radiographs were read by Tongji Medical College radiologists. The purpose was to select factories and mines with well-kept radiological data for the study. In the second step, the reliability of the original diagnosis of silicosis was established by comparing the Chinese method of silicosis reading with the International Labour Office (ILO) radiological classification of pneumoconiosis [ILO, 1980]. In the comparison study, the agreement on detecting the presence of radiological silicosis using ILO major Category 1 and Stage I as minimal criteria was 89.3% [Chen et al., 2001].

In 1989, 12 Chinese professional radiologists, divided into four groups, read all prior chest radiographs. Chest radiographs obtained after 1989 were read by a panel of radiologists at a hospital affiliated to Tongji Medical College. Silicosis was defined as Stage I, II or III by at least two of three radiologists. For this study, the onset of silicosis was defined as the date when the worker's chest radiograph had reading of Stage I or higher for the first time.

Assessment of Cumulative Dust Exposure

Since the 1950s, the dust monitoring scheme in Chinese silica dust exposed workplaces involved assessment of total airborne dust concentration by a gravimetric method, a microscopic sizing method for particle size distribution, and silica content in bulk samples of settled dust [details in Gao et al., 2000; Zhuang et al., 2001]. For the purposes of this study, dust exposure was assessed in terms of cumulative total dust, and then converted to cumulative respirable dust and cumulative respirable silica dust in two separate steps.

To estimate cumulative total dust, all available industrial hygiene data were used to create an exposure matrix based on average total dust concentration by workplace, job title, and calendar year [Chen et al., 2001]. From 1950 to 1986, historical total dust concentrations were summarized for

TABLE I. Follow-Up Status for Chinese Tungsten and Tin Miners and Pottery Workers Cohorts by the End of 1994

	Pottery workers		Tin miners		Tungsten miners	
	N	Silicosis (%)	N	Silicosis (%)	N	Silicosis (%)
Follow-up status						
Working	1,440	6.6	1,547	2.3	3,578	0.5
Left industry	266	1.5	365	1.9	920	0.5
Retired	1,931	24.0	1,392	35.8	7,088	20.5
Deceased	906	21.6	712	44.2	2,759	48.5
Unknown	4	0.0	12	0.0	82	0.0
Total	4,547	17.3	4,028	21.2	14,427	19.5

each facility and job title within each facility in 3-year intervals. After 1986, total airborne dust concentrations and duration of dust exposure per shift were measured every year. Cumulative total dust exposure for individual workers was calculated as follows:

$$\mathrm{CTD} = \sum_{j=1}^{n} (\mathrm{C_J} \times \mathrm{T_J})$$

where CTD = cumulative total dust exposure in mg/m^3-years, n = the total number of job categories held by the subject during his work history, C_j = 8 hr time-weighted mean concentration of total dust in mg/m^3 for the jth job category within a facility and employment period, and T_j = duration of employment in years in the jth job and time period. CTD was calculated from the start of mining to the end of follow-up which could be one of the following: a diagnosis of silicosis of Stage I or higher; the end of radiological follow-up (if lost to follow-up or died); the end of employment; or the end of follow-up in 1994.

Cumulative total dust exposure was then converted to cumulative respirable dust (CRD) and to cumulative respirable silica dust (CRSD) in two steps, using three conversion factors as follows:

$$\mathrm{CRD} = \mathrm{CF_T} \times \mathrm{CF_R} \times \mathrm{CTD} \qquad \mathrm{CRSD} = \mathrm{CF_{RS}} \times \mathrm{CRD}$$

where CF_T = conversion factor for converting Chinese total dust to US total dust, CF_R = conversion factor for converting US total dust to respirable dust, and CF_{RS} = conversion factor for converting respirable dust to respirable silica dust. Mean dust concentrations were calculated by dividing cumulative dust exposure indices by the number of net years in dusty jobs. The net years in dusty job categories was calculated by standardizing to 8-hr working shifts and 270 shifts per year. Cumulative respirable silica dust also was

TABLE II. Mean Characteristics of Chinese Cohorts of Tungsten and Tin Miners and Pottery Workers and of Those With Silicosis

	Pottery workers mean (SE)	Tin mines mean (SE)[a]	Tungsten mines mean (SE)[b]
Characteristic			
Number of subjects	4,547	4,028	14,427
Year of birth	1934.6 (0.16)	1937.3 (0.18)	1937.7 (0.08)
Age at first exposure	23.5 (0.12)	24.4 (0.10)	22.7 (0.05)
Year of first exposure	1958 (0.10)	1961 (0.12)	1960 (0.07)
Cumulative total dust (mg/m^3-years)	205.6 (2.12)	62.3 (0.92)	64.9 (0.54)
Average total dust concentration (mg/m^3)	8.2 (0.08)	3.9 (0.07)	4.0 (0.04)
Net years in dust	24.9 (0.15)	16.4 (0.13)	16.5 (0.07)
Age at leaving exposure	48.6 (0.15)	41.3 (0.15)	40.4 (0.08)
Year of leaving exposure	1983 (0.13)	1979 (0.17)	1978 (0.09)
Workers with silicosis Number (%)	785 (17.3)	855 (21.2)	2,816 (19.5)
Latency period to silicosis onset	29.4 (0.24)	20.2 (0.26)	19.0 (0.15)
Age at first diagnosis of silicosis	52.5 (0.25)	47.9 (0.33)	41.8 (0.17)
Year at first diagnosis of silicosis	1985 (0.24)	1975 (0.29)	1972 (0.16)

[a]All mean values were significantly different in comparison to pottery means at $P < 0.0001$.
[b]All mean value were significantly different in comparison to pottery and tin mine means at $P < 0.0001$.

converted to cumulative respirable surface-available silica dust, using the conversion factors developed in the companion dust surface analysis study [Harrison et al., 2005 (this issue)] for the fractions of respirable silica particles that are not surface occluded by clay and have biologically available toxic crystalline silica surfaces.

Estimation of Conversion Factors for Respirable Dust and Respirable Silica Dust

Estimation of the three conversion factors (CF_T, CF_{RD}, CF_{RS}) was based on side-by-side measurements (airborne total dust, respirable dust, and respirable silica dust, and silica content in bulk dust) done during 1988–1989 in the 20 studied facilities by Tongji Medical College (Chinese measurements) and NIOSH (US measurements) [Gao et al., 2000; Zhuang et al., 2001]. Appendix I describes the methodology for the side-by-side measurements and derivation of the conversion factors.

Statistical Methods

Analysis of variance was used (SAS Proc GLM with Dunnett's multiple comparison adjustment) to test for cohorts differences in characteristics that may affect the risk of silicosis (i.e., year of birth, year, and age of onset of exposure to dust, duration of dust exposure, levels of dust exposure, duration of radiological follow-up, and latency period from start of exposure to silicosis diagnosis). The SAS program PROC LIFETEST was used to perform the non-parametric calculation of the cumulative conditional probability of silicosis for a given exposure level by the Life Table method [SAS Institute, Inc., 1999]. To estimate exposure-response curves for cumulative respirable dust and cumulative respirable silica dust, we used the SAS program PROC LIFEREG and the Weibull distribution.

RESULTS

The respective cohorts included 4,547 male pottery workers, 4,028 male tin miners, and 14,427 male tungsten miners. Table I shows the follow-up statistics at December 31, 1994, for the three cohorts. The percentage of subjects with silicosis was highest in retired and deceased miners, especially tin and tungsten miners. Table II shows differences between the three cohorts with respect to employment characteristics and shows that the cohorts with slightly later start of exposure had higher risk of silicosis. Although the pottery workers had higher mean cumulative total dust exposure, mean concentration of total dust, and net years of exposure, they had significantly lower overall percentage of silicosis in comparison to the miners ($P < 0.0001$). Figure 1 shows, for each industry, workers frequencies according to the start of

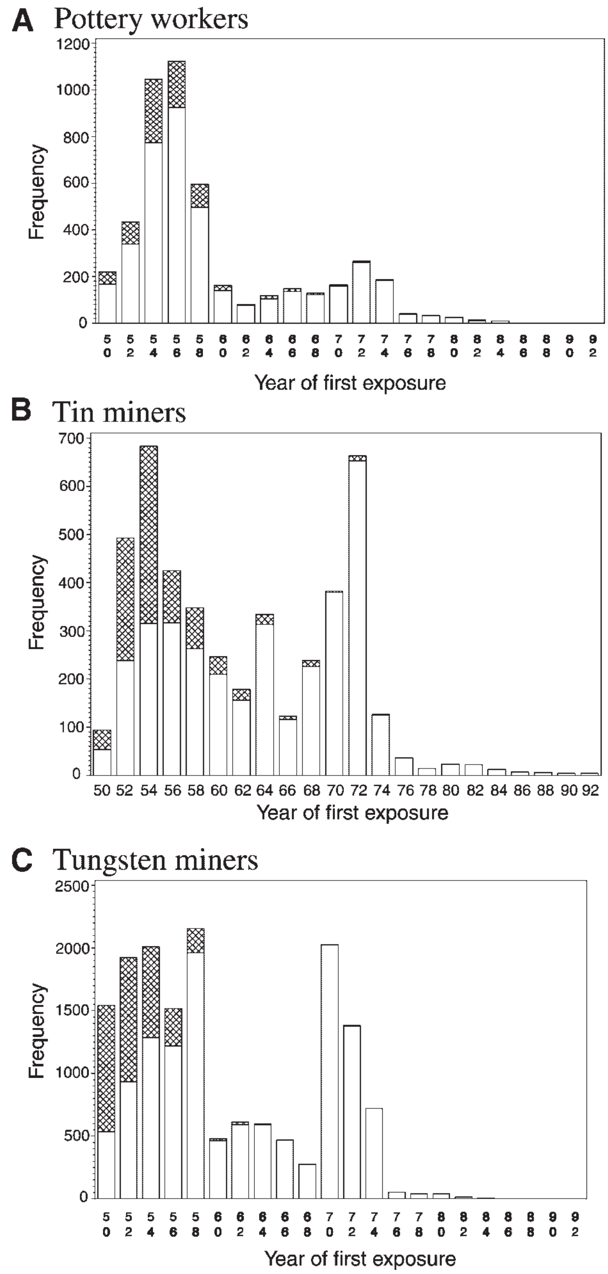

FIGURE 1. Frequency of workers according to the year when their silica dust exposure started, by industry (**A**) potteries; (**B**) tin mines; (**C**) tungsten mines. The darker shading shows frequencies for those who developed silicosis over the follow-up period 1950–1994.

employment in each industry, and the number of those workers who developed silicosis during the follow-up 1950–1994 (the hashed portion of the frequency bar).

Cumulative Risk of Silicosis According to CTD

Table III shows, for each industry and exposure level, the number of cases who developed silicosis, the number of

TABLE III. Cumulative Risk of Silicosis According to Cumulative Total Dust Levels, for Chinese Tungsten and Tin Miners and Pottery Workers Cohorts

	Pottery workers			Tin miners			Tungsten miners		
Exposure to CTD (mg/m^3-years)	Cases with silicosis (n)	Workers at risk (n)	Cumulative risk	Cases with silicosis (n)	Workers at risk (n)	Cumulative risk	Cases with silicosis (n)	Workers at risk (n)	Cumulative risk
0–24	2	4,660	0.000	37	3,468	0.000	53	11,686	0.000
25–49	23	4,247	0.001	103	2,318	0.011	185	7,625	0.005
50–74	42	3,973	0.005	89	1,480	0.055	244	5,560	0.029
75–99	48	3,651	0.016	97	1,106	0.112	320	4,325	0.071
100–149	137	3,095	0.029	309	799	0.189	708	3,179	0.140
150–199	137	2,325	0.072	157	325	0.503	773	1,791	0.332
200–249	89	1,717	0.127	29	92	0.743	411	686	0.620
250–299	80	1,266	0.172	17	39	0.825	114	149	0.848
300–349	70	897	0.225	8	18	0.901	8	10	0.964
350–399	70	611	0.285	4	9	0.945			
400–449	28	389	0.367	5	5	0.969			
450–499	14	270	0.413						
500–599	29	173	0.443						
600–850	16	56	0.537						

workers at risk, and the cumulative risk. For the same level of exposure to CTD, the pottery workers had the lowest cumulative risk, whereas there were only small differences between tin and tungsten miners.

Figure 2 shows the relationships between cumulative risk of silicosis and (a) cumulative respirable dust, (b) cumulative respirable silica dust, and (c) cumulative respirable surface-available silica dust, estimated by the Weibull parametric model.

DISCUSSION

In the present study, we compared the risk of silicosis among Chinese cohorts of pottery workers, tin miners, and tungsten miners. The cohorts had similar onset of exposure from 1950 when yearly radiological examinations and measurements of total dust were introduced in workplaces with silica dust exposure in China. The cohorts had radiological follow-up for silicosis onset from 1950 to 1994 using radiographic assessment of silicosis comparable to ILO Classification.

The results show that the risk of silicosis differed between the cohorts (Table III and Fig. 2). The pottery workers, with the highest cumulative total dust exposure levels (Table II), had lowest risk of silicosis for a given exposure level. The pottery workers who developed silicosis had also longer latency period in comparison to the miners who developed silicosis. In all three cohorts the risk of silicosis was high in those who started working during the 1950s and 1960s (Fig. 1). This is consistent with the high exposure levels in the 1950s and 1960s estimated by Zhuang et al. [2001], who reported that average concentrations to respirable silica dust in the 1950s were above 0.5 mg/m^3.

To investigate whether the amount of exposure to respirable dust and respirable crystalline silica dust can account for the differences in the risk of silicosis, we converted the cumulative total dust to cumulative respirable dust and respirable silica dust using conversion coefficients derived from side-by-side measurements done in 1988–89 (see Appendix I). Figure 2 shows that the cumulative risk of silicosis for a given level of cumulative respirable silica dust is lowest in pottery workers, and is similar in the miners.

With the results of the companion surface analysis study [Harrison et al., 2005], we examined a hypothesis that thin clay surfaces, detectable by a spectroscopic surface analysis method, could diminish the biological availability of the toxic crystalline silica surfaces of some workplace-specific fractions of the silica particles and thereby diminish the disease risk. The surface analysis study indicated that 55% of the silica particles from pottery worksites, 82% from the tin mines, and 87% from the tungsten mines had surface-available, non-occluded surfaces. Figure 2C shows cumulative risk of silicosis versus cumulative respirable silica dust when the exposure is so-adjusted for silica surface biological availability by applying the above percentages as conversion factors. The figure indicates that normalizing respirable silica dust in this way for available surface resolves much of the difference in risk between the pottery workers and metal miners.

Aluminum oxide or aluminosilicate surface, or clay coatings have been observed on silica dusts from various workplaces with the suggestion of reducing the toxic effects

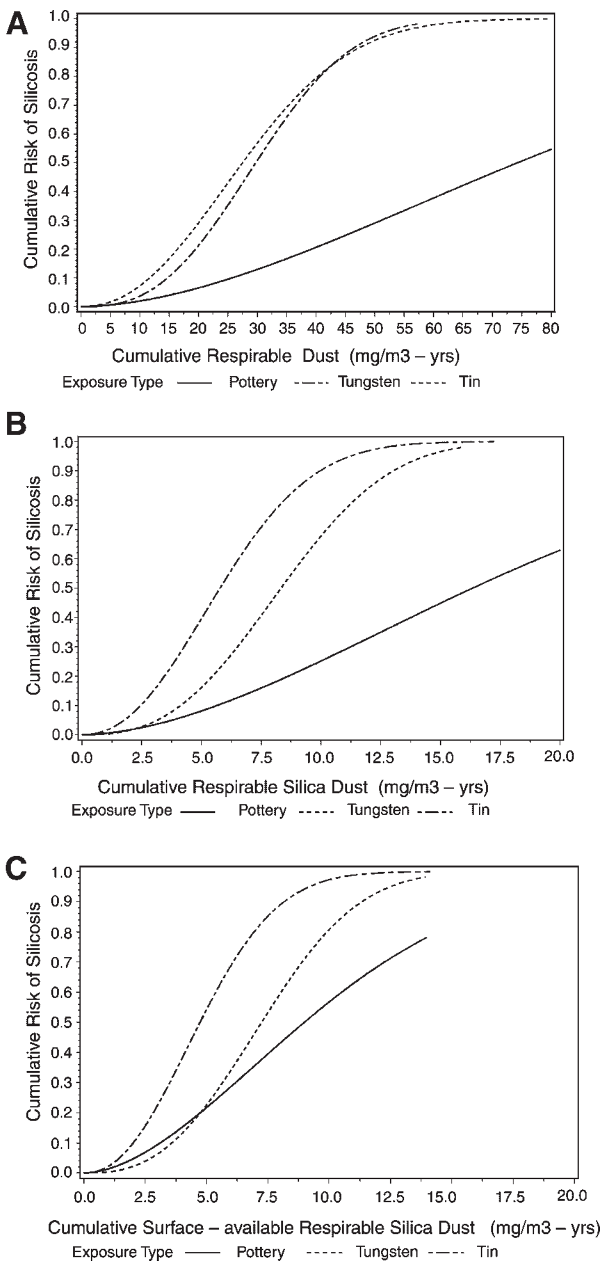

FIGURE 2. Cumulative risk of silicosis in Chinese potteries, tin and Tungsten mines in relation to (**A**) cumulative respirable dust; (**B**) cumulative respirable silica dust; and (**C**) cumulative surface-available respirable silica dust.

of the occluded silica dust particles. Experimental studies have indicated that clay and aluminum oxide or aluminosilicate surface coatings of respirable crystalline silica particle surfaces can alter the cytotoxic and fibrogenic activities of the crystalline silica dust [reviewed in LeBouffant et al., 1982; Czernichowski et al., 1987; Bolsaitis and Wallace, 1996]. The possible ameliorative effects of aluminosilicate with quartz dust for the harmfulness of mixed dust exposures has been suggested in observations of coal workers pneumoconiosis [Walton et al., 1971, 1977]. Surface occlusion of respirable silica particles by aluminosilicate has been measured on dusts from coal mines in different regions of the US, with fraction of occluded silica particles generally decreasing with increasing coal rank [Harrison et al., 1997]. Those results suggested a possible basis for the ‘‘coal-rank effect’’ of higher risk of coal workers pneumocioinsis and progressive massive fibrosis in higher rank coal seams.

Aluminum can be associated with the surfaces of silica particles in more than one manner: as an agglomerate of fine clay aluminosilicate particles on the surface of a respirable silica particle, or as a thin or monolayer aluminum oxide contaminant strongly bound on the silica surface by aluminol–silanol interactions, or as an adherent continuous and relatively thick (though sub-micrometer) aluminosilicate nano-structural coating or occlusion of the silica particle surface. Initiation of disease process could vary between the three forms of silica particle surface coating. Coal or metal mining strata typically have surrounding aluminosilicate geologic strata or mineralogical inclusions resulting in mixed composition mine dusts or complex particles [Kriegseis and Scharmann, 1982]. Pottery works typically utilize both sands and clays in the production process. Thus, a variety of types of aluminosilicate–silica particles are possible between and within industries. In the companion study [Harrison et al., 2005], we measured aluminosilicate occlusion of dusts from the studied worksites, with the fraction of occluded silica particles being much greater for pottery workplace dusts than for the metal mine dusts. Using these values for fraction of silica particles with surface occlusion by aluminosilicate, we have normalized the exposure index from cumulative respirable silica to cumulative respirable ‘‘surface-available’’ silica. The effect of this normalization on silicosis risk versus exposure is shown between Figure 2B and C.

There is, however, uncertainty in the estimated exposure-response relationships presented in Figure 2 due to potential errors in the estimated dust conversion factors. The overall conversion factors for converting Chinese total dust to respirable silica dust were estimated as 0.031 for potteries, 0.039 for tin mines, and 0.050 for tungsten mines (Appendix I, Table III). Previously, Zhuang et al. [2001] used the same side-by-side data to convert Chinese total dust directly to respirable silica dust without considering the intermediate steps (i.e., conversion to US total dust and to respirable dust). The conversion factors estimated by weighted means method by Zhuang et al. [2001] were similar for potteries (0.0355) and for tin mines (0.0429), but the estimate for tungsten mines (0.0861) was substantially higher and, when applied to the data, resulted in very low risk for a given exposure level. The two-stage conversion we used provides more insight into the dust levels and associated risks at different stages. For example, our conversion factors for converting US total dust to respirable dust were comparable to the conversion factor of 0.26 for all industries combined, derived by Gao et al. [2000]. Figure 2 shows that for cumulative respirable dust, the differences between the cohorts remain similar to that observed for cumulative total dust. The conversion factors for converting respirable dust to respirable silica dust show that the average percentages of respirable silica in respirable dust were about 28% in tungsten mines, 21% in tin mines, and 22% in potteries (Appendix I, Table III).

Major limitations of the study include (i) the conversion of total dust concentrations measured over short sampling intervals to 8-hr average equivalent of respirable silica dust concentrations; and (ii) a relatively small number of side-by-side measurements on which estimation of the conversion factors was based. The greater variability in total dust measurements in potteries than in mines (Appendix I, Table AI) indicates that there is a potential for a greater error in cumulative exposure in potteries than in mines. The high cumulative risk in mines appears to be realistic for the mining sub-cohorts who started mining in the 1950s. Figure 1 shows that over 50% of those who started mining in the early 1950s developed silicosis. Based on exposure levels estimated by Zhuang et al. [2001], 15 years of mining at 0.5 mg/m^3-years of respirable silica dust during the 1950s and early 1960s would correspond to 7.5 mg/m^3-years of cumulative respirable silica dust. Because of high exposure levels during the 1950s and 1960s, the cohorts accumulated high cumulative exposure levels over a relatively short period of time and this may have resulted in lower risk per cumulative exposure in comparison to other cohorts.

In conclusion, it appears from our study that the silica dust in hard rock mines is more fibrogenic than the silica dust to which pottery workers are exposed. Including a measure of worksite-specific differences in the fraction of respirable silica particles with available silica surface suggests that differences in clay occlusion of silica particles can be a factor in the differences in disease risk [Harrison et al., 2005].

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APPENDIX I

Estimation of Conversion Factors for Respirable Dust and Respirable Silica Dust

In 1988–1989, side-by-side measurements were done in 20 mines or potteries by a special sampling survey conducted by Tongi Medical College, China, and NIOSH, USA [Zhuang et al., 2001]. Estimation of conversion factors for converting Chinese total dust to US total dust (CF_T), US total dust to respirable dust (CF_R), and respirable dust to respirable silica dust (CF_{RS}) was based on side-by-side measurements of total dust and percent silica content by Chinese methods, and measurements of total dust, respirable dust, respirable silica dust, and bulk dust silica content by US methods. The sampling methods have been described in detail previously [Gao et al., 2000; Zhuang et al., 2001]. In brief, three sampling sites were selected at each facility to be representative of distinct exposure zones. Preference was given to sampling sites previously sampled by the Chinese dust monitoring program and to those sites that were representative of high, medium, and low dust levels. Dust concentrations were obtained gravimetrically from 10-mm nylon cyclone samples collected over 8-hr shifts. Cyclones were operated at 1.7 L/min to collect full-shift time-weighted average respirable dust samples. The cyclone samples were then analyzed gravimetrically to determine respirable dust concentrations. Respirable silica dust concentrations were determined by X-ray diffraction. Percentage of silica in bulk dust (settled dust treated by phosphoric acid) was available for each industry from historical Chinese measurements done since 1950 and Chinese measurements done during the side-by-side study.

Table AI presents the mean values of side-by-side measurements for total dust, respirable dust, respirable silica, and percentage of silica in total dust and bulk dust samples and shows that the Chinese mean total dust measurements are higher than the US means. The reason for this has been previously described and is mainly due to differences in length of sampling and sampling instruments. The linear regression model with an intercept value of zero was used to estimate the specific conversion factors. Based on this estimation, approximately 71% of Chinese total dust was equivalent to US total dust (i.e., $CF_T = 0.71$). Table AII summarizes the estimated regression coefficients (i.e., the conversion factors) for the relationships between US total dust and respirable dust measurements, and between respirable dust and respirable silica dust measurements, by industry. The final conversion factors for converting Chinese total dust to US respirable silica dust were 0.031 for potteries, 0.039 for tin mines, and 0.050 for tungsten mines.

For tin mines, we made use of side-by-side measurements of percentage of silica in total dust and in bulk dust in the three industries (see Table AI) to calculate the ratio between the percentage of respirable silica in respirable dust and the percentage of silica in the total dust or bulk dust. Bulk dust data on silica percent from potteries and tungsten mines (Table AI), based on a larger number of samples, suggest that between 56% and 68% of silica in total dust (and bulk dust) is respirable. For potteries, the estimated fraction of respirable silica in respirable dust is 0.22 (Table AII)

TABLE AI. Mean Values for-Side-by-Side Measurements Done During 1988—1989 in Chinese Potteries, and Tin and Tungsten Mines for Total Dust, Respirable Dust and Respirable Silica Dust

	Industry								
	Pottery			Tin mines			Tungsten mines		
Dust measurement	n	Mean	SD	n	Mean	SD	n	Mean	SD
By US method									
Total dust (mg/m^3)	44	2.9	2.6	10	2.8	1.8	34	1.5	0.8
Respirable dust (mg/m^3)	55	0.70	1.20	13	1.02	1.33	50	0.38	0.36
Resp. silica dust (mg/m^3)	55	0.10	0.20	13	0.10	0.16	50	0.10	0.14
By Chinese method									
Total dust (mg/m^3)	54	4.6	9.7	13	3.6	4.0	57	2.0	2.6
Total dust silica (mg/m^3)	29	1.6	3.1	9	1.3	1.8	29	0.9	0.9
Total dust silica (%)	29	35.1	8.9	9	27.5	15.4	29	49.7	16.9
Bulk dust silica (%)	19	37.4	9.1	5	29.5	13.4	17	50.4	18.3
Bulk dust silica (%) His.[a]	134	35.1	13.0	48	34.8	16.1	165	40.7	17.9

[a]Percent silica content in bulk dust samples from side-by-side measurements and from historical measurements are tabulated also.

TABLE AII. Conversion Factors From Chinese Total Dust to US Total Dust, US Total Dust to Respirable Dust, and Respirable Dust to Respirable Silica Dust, by Industry

Industry	Chinese total dust to US total dust: CF_T (SE)	US total dust to respirable dust: CF_R (SE)[a]	Respirable dust to respirable silica: CF_{RS} (SE)[a]	Chinese total dust to respirable silica dust: $CF_T \times CF_R \times CF_{RS}$
Potteries	0.71 (0.06)	0.20 (0.03)	0.22 (0.01)	0.031
Tin mines	0.71 (0.06)	0.26 (0.03)	0.21 (0.01)	0.039
Tungsten mines	0.71 (0.06)	0.25 (0.04)	0.28 (0.03)	0.050

[a]SE of the estimated regression coefficient.

and the measured fraction of silica in total dust is about 0.35 (Table AI), this results in a ratio of $0.22/0.35 = 0.63$. For tungsten mines, the respective ratios are $0.28/0.41 = 0.68$ for bulk dust and $0.28/0.50 = 0.56$ for total dust. The data from tungsten mines suggest that, on average, approximately 62% of silica in total dust or bulk dust is respirable, in potteries this is approximately 63%. Based on these ratios and the 34.8% silica content in bulk dust collected historically in tin mines (Table AI), we estimated that for tin mines, on average, the fraction of respirable silica in respirable dust is approximately $0.60/0.35 = 0.21$ (Table AII).

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.*[†]

KEY WORDS: silicosis; particle surface; mining

INTRODUCTION

Quartz (SiO_2) 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

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[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 Morring, 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 alumino-silicate-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 Si/(Si+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 Si/(Si+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 Si/(Si+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 Si/(Si+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, Δ, 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
	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

	Pottery factories		Tin mines		Tungsten mines	
Δ in Si fraction	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 χ^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 (Al_2O_3) and silicon dioxide (SiO_2), while quartz is composed entirely of 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 bioavailable (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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