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Quartz in ash, and air in a high lung cancer incidence area in China☆

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ABSTRACT

Exposure to crystalline silica (quartz) has been implicated as a potential cause of the high lung cancer rates in the neighbouring counties of Xuanwei and Fuyuan, China, where the domestic combustion of locally sourced "smoky" coal (a bituminous coal) is responsible for some of the highest lung cancer rates in the nation, irrespective of gender or smoking status. Previous studies have shown that smoky coal contains approximately twice as much quartz when compared to alternative fuels in the area, although it is unclear how the quartz in coal relates to household air pollution.

Samples of ash and fine particulate matter ($PM_{2.5}$) were collected from 163 households and analysed for quartz content by Fourier transformed infrared spectroscopy (FT-IR). Additionally, air samples from 12 further households, were analysed by scanning electron microscopy (SEM) to evaluate particle structure and silica content.

The majority (89%) of household air samples had undetectable quartz levels ($<0.2\ \mu g/m^3$) with no clear differences by fuel-type. SEM analyses indicated that there were higher amounts of silica in the smoke of smoky coal than smokeless coal ($0.27\ \mu g/m^3$ vs. $0.03\ \mu g/m^3$). We also identified fibre-like particles in a higher concentration within the smoke of smoky coal than smokeless coal ($5800\ fibres/m^3$ vs. $550\ fibres/m^3$). Ash analysis suggested that the bulk of the quartz in smoky coal went on to form part of the ash.

These findings indicate that the quartz within smoky coal does not become adequately airborne during the combustion process to cause significant lung cancer risk, instead going on to form part of the ash. The identification of fibre-like particles in air samples is an interesting finding, although the clinical relevance of this finding remains unclear.

1. Introduction

The lung cancer epidemic in Xuanwei and its neighbouring county of Fuyuan, located in Yunnan province, China, is causally linked to the domestic combustion of locally sourced "smoky" coal (a bituminous coal) (Mumford et al., 1987; He et al., 1991; Chapman et al., 1988). Users of smoky coal have, regardless of smoking status or gender, been found to experience lung cancer rates of up to one hundred times that of those using alternative fuels (Barone-Adesi et al., 2012). Smoky coal is the primary fuel in use throughout the region, being used by approximately 75% of the population for their day-to-day cooking and heating. The alternative fuels available include "smokeless" coal (an anthracite coal), wood, and various plant materials (including corn cobs and tobacco stems). (Barone-Adesi et al., 2012).

Previous epidemiological studies have provided some insight regarding which constituents of smoky coal (and its associated smoke) contribute to lung cancer risk in the area. Most notable has been the finding that smoky coal users are exposed to high levels of

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polycyclic aromatic hydrocarbons (PAHs), including the known carcinogen benzo[*a*]pyrene (BaP) (Downward et al., 2014a; Lv et al., 2009; Lan et al., 2002; Mumford et al., 1993, 1995). However, more recently, exposure to crystalline silica (quartz) has gained increasing attention as a potential contributor (Large et al., 2009; Li et al., 2013; Tian, 2005; Tian et al., 2008; Vermeulen et al., 2011; He et al., 2012). This attention is largely derived from several small studies which have identified higher amounts of quartz in samples of smoky than smokeless coal and a positive correlation between quartz content of smoky coal and lung cancer rates in the area. To date, these studies have largely been based upon small sample sizes, sourced solely from Xuanwei. A larger study, incorporating samples from Fuyuan in addition to Xuanwei did not identify any relationship between quartz and lung cancer rates (He et al., 2012). Further, no evidence of quartz related lung disease has been reported within the area.

We recently confirmed based on a large survey of coal samples (n = 146) collected from both Xuanwei and Fuyuan, that higher amounts of quartz within smoky coal exist than in smokeless coal (4.6% vs. 2.2%) (Downward et al., 2014b). However, the contribution of this quartz to household air pollution (and thus personal exposure) needs to be established. In the current paper we present the findings of quartz in household air and fuel ash from households in Xuanwei and Fuyuan. We also present the findings of field emission gun scanning electron microscopy in combination with X-ray analysis (FEG-SEM/EDX) on additional air samples collected to study the physico-chemical characteristics of the air particulate matter.

2. Methods

2.1. Study design

This paper forms part of a larger case-control and cross-sectional epidemiology study aimed at cataloguing the constituents of solid fuels and its associated household air pollution in Xuanwei and Fuyuan, before ultimately associating those constituents with lung cancer risks and biological effect markers among non-smoking women. The details of the study design have been discussed elsewhere (Hu et al., 2014) but briefly, households with a non-smoking female head between the ages of 20 and 80 were selected from villages throughout Xuanwei and Fuyuan (Fig. 1). Village and participant selection was aimed at representing the population present in the case-control study with regard to age, gender, and stove and fuel use. Therefore, households which were at least 10 years old and had not had any stove alterations undertaken in the prior five years were preferentially selected.

Households were measured and sketched with stoves and other pertinent features (windows, doors, etc.) documented. The female household head had her daily activities documented during each measurement period and provided biographical information including residential history, medical history, and socio-economic indicators.

The data for the current paper was collected during two study periods: a large-scale exposure assessment study undertaken in 2008 and 2009; and a follow-up study undertaken in 2013.

2.1.1. Primary study – large exposure assessment study

A total of 163 healthy (disease-free) female heads of household were recruited from 30 villages across Xuanwei and neighbouring Fuyuan. Visit 1 was conducted from August 2008 to February 2009 and 148 women were enrolled. Visit 2 was conducted between March and June of 2009 and an additional 15 participants were enrolled. Fifty-three participants were assessed at both visits. Up to five households were selected in each village based on: 1) having a stove that used solid fuel; 2) the residence was more than 10 years old; 3) use of the same cooking or heating equipment for the past 5 years; and 4) presence of a non-smoking healthy woman aged 20–80 years, who was primarily responsible for cooking.

Indoor air measurements were collected on 37 mm Teflon filters using a cyclone with an aerodynamic cut-off of 2.5 μm ($PM_{2.5}$), powered by a BGI AFC400S pump with a median flow rate of 3.3 L/min. Pumps were calibrated prior to each use and flow rates were measured pre and post-measurement. Cyclones were placed approximately 0.25 m from the wall and between one and two metres from the main stove (as allowed by the size of the room).

For analysis, filters were ashed at 600 degrees Celsius before being pressed into 13 mm potassium bromide (KBr) pellets which were analysed by Fourier transformed infrared spectroscopy (FT-IR), giving quartz levels in μg which were transformed into a mass concentration as a function of the volume of air (in m^3 (Chapman et al., 1988)) drawn through the filter. The limit of detection (LOD) of this methodology was 1 μg (approximately 0.2 μg/m^3 based on a 24 h measurement).

Approximately 5 g of each ash sample was deagglomerated in 50 mL of a standard solution containing water and sodium hexametaphosphate before being transferred to a 250 mL measuring cylinder and being topped up with standard solution. This mixture was homogenised and after a period of standing to allow for the sedimentation of the non-respirable fraction, the fluid was extracted and evaporated – with the remaining material being weighed. After weighing, a known portion of the remaining material was pressed into a KBr pellet and analysed by FT-IR for quartz content as a percentage of the ash.

2.1.2. Secondary study – follow-up exposure study

A secondary study was undertaken in 2013 to collect household air samples from a smaller sub-selection of villages within Xuanwei. Indoor air samples were collected on nickel coated track-etched polycarbonate filters (0.4 μm 25 mm, Nuclepore) using SKC airchek XR 5000 pumps set at flow rates of 2 L/min for 60 min. In total, 12 samples were collected for analysis (8 from smoky and 4 from smokeless coal using households).

The silica content of these filters was established using field emission gun scanning electron microscopy in combination with X-ray analysis (FEG-SEM/EDX) which was used for physico-chemical characterization, semi-quantitative estimation of the concentration, and determination of the particle size distribution for silica and fibre-like particles. Analysis was performed on a Tescan MIRA-LMH FEG-SEM with a Bruker AXS spectrometer and a XFlash 4010 detector. The filters were screened at magnifications between 200× - 5000×. Qualitative data was obtained about the type, size and shape of sampled particles, and the degree of agglomeration or aggregation. For identification of silica, automated particle analysis was performed using Scandium imaging software. From each particle/cluster of particles, the projected area equivalent diameter (dpa) was measured and an EDX spectrum recorded. From the EDX-spectrum, silica particles were defined as having greater than 95% silicon and oxygen in the total particle, conglomerate, or aggregate.

For silica and fibre-like particles the numerical concentration per particle type and size is calculated in accordance with ISO 14966 (ISO ISO 14966, 2002). Fibre-like particles are defined as particles with a length greater than 5 μm, a diameter less than 3 μm, and a length:diameter ratio greater than 3. For silica, the numerical concentration was converted into a mass concentration, using the particle size (dpa), a particle density (ρp) of 2.65 g/cm^3 and a volumetric shape factor (Sv) of 1.3. The mass of a particle is estimated as (π/6) • ρp • (dpa/Sv) (Chapman et al., 1988). The contribution of a single particle to mass concentration was calculated by multiplying the numerical concentration with the mass of the

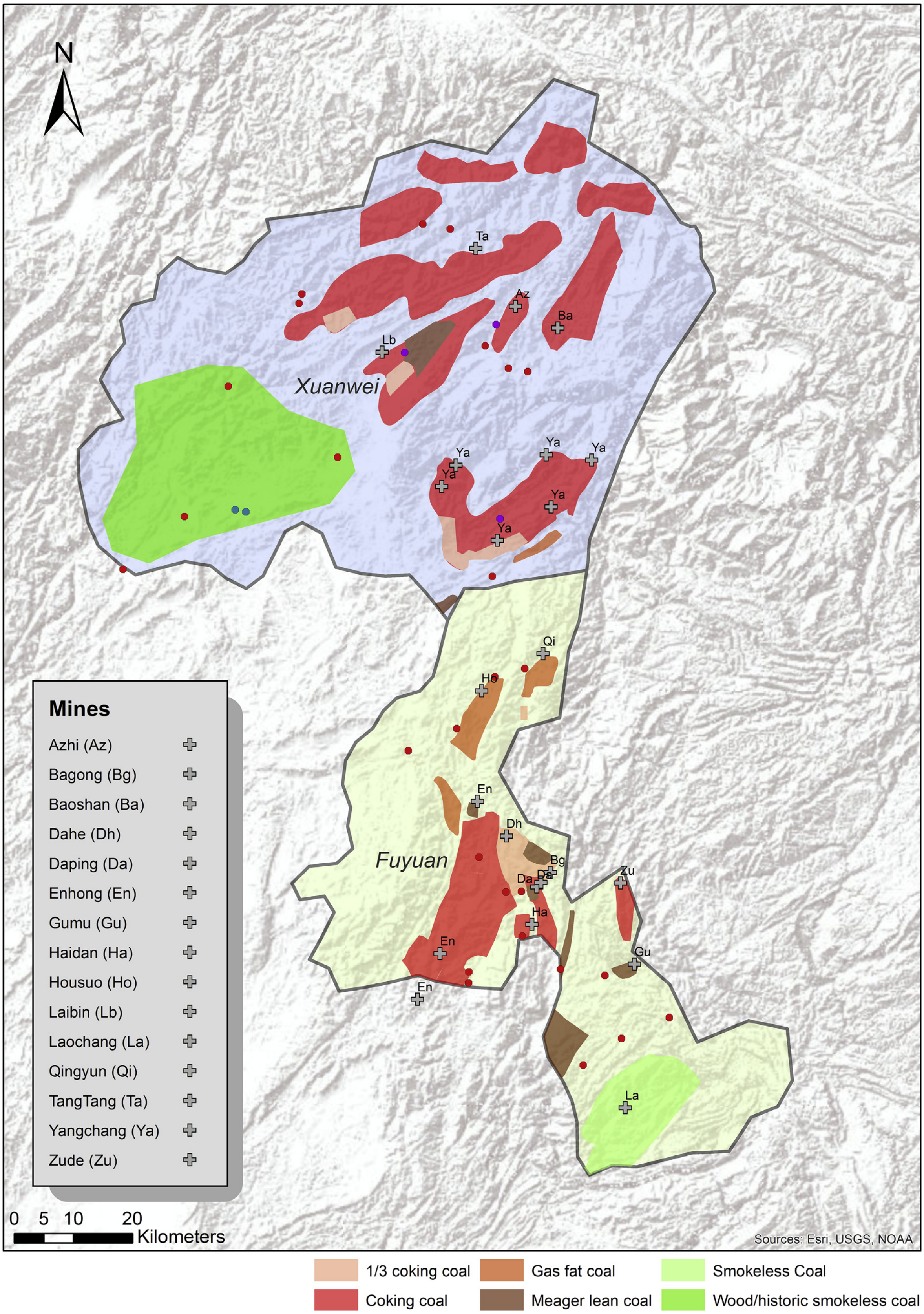

Fig. 1. Map of Xuanwei and Fuyuan counties showing approximate locations of study villages, reported coal mines and coal sub-types.
Red dots indicate villages enrolled in only the primary study.
Blue dots indicate villages enrolled in only the secondary study.
Purple dots indicate villages enrolled in both studies.
Mine locations indicate functioning mine entrances, therefore, some mines may be indicated more than once.
Only mines reported by study participants are indicated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Detects versus non-detects of airborne quartz and concentrations of detected quartz (in μg/m^3) by fuel type.

	Detected Quartz			Quartz concentrations in measurements > LOD (11% of all measurements)			
	Detects (%)	Non-detects (%)	Total n	N	AM	GM	GSD
Smoky Coal	11 (14)	69 (86)	80	11	0.4	0.4	1.3
Smokeless Coal	0 (0)	17 (100)	17	0	–	–	–
Other Coal[a]	2 (12)	15 (88)	17	2	0.4	0.4	1.2
Wood	1 (11)	8 (89)	9	1	0.3	0.3	–
Plant[b]	1 (20)	4 (80)	5	1	0.6	0.6	–
Other Fuel[c]	3 (10)	27 (90)	30	3	0.5	0.5	1.8

Limit of detection – approximately 0.2 μg/m^3.
[a] Other coal refers to either using both smoky and smokeless coal simultaneously or the use of pre-prepared briquettes.
[b] Refers to the use of corn cobs and/or tobacco stems (sometimes in combination with wood).
[c] Refers to the use of both coal and plant materials.

particle.

2.2. Stove and fuel information

Descriptive categories for stoves were primarily developed around the presence or absence of ventilation. Therefore, the designated categories were: ventilated stoves, unventilated stoves, firepits (the traditional method of heating and cooking), portable stoves (which are designed to be lit outdoors and then carried indoors for use), mixed ventilation (use of multiple types of stoves with differing ventilation) and "unknown" (stove type either not reported or recorded). Study participants reported their fuel usage, which was used to develop descriptive categories for fuel usage. The developed categories were: smoky coal, smokeless coal, "other" coal (which refers to combinations of coal types and/or usage of processed coal products such as "beehive" briquettes), wood, plant products (includes bamboo shoots, tobacco stems and corn cobs in addition to wood being burnt in combination with other plant products) and "other" fuel (which refers to combinations of coal and plants/wood).

2.3. Statistical analysis

Normal probability plots indicated that analytical values tended towards log-normal distribution. Thus, descriptive statistics include arithmetic means (AM), geometric means (GM) and geometric standard deviations (GSD).

All statistical testing was carried out in R, version 3.0.2 (R Development Core Team R, 2014). A p value of less than 0.05 was considered to indicate statistical significance.

3. Results

3.1. Primary study

3.1.1. Quartz in air

A total of 159 $PM_{2.5}$ measurements were collected, 80 of which represented the use of smoky coal, 17 smokeless coal, 8 wood, 4 general plant products, 15 a combination of coals, and 30 a combination of multiple fuels. Of the 159 collected air samples, 141 (89%) were below the limit of detection (0.2 μg/m^3 – Table 1). There was some variation, although not statistically significant (Fisher exact test), in detection rates between different fuel types – 11 of the 80 (14%) samples from smoky coal homes had detectable quartz, compared to none of the 17 samples from smokeless coal homes. In the other fuel categories: 2 of the 17 (12%) homes burning multiple coal types, 1 of the 9 wood burning homes (11%), 1 of the 5 plant burning homes (20%), and 3 of the 30 (10%) homes burning multiples fuels had detectable quartz. Among the homes with detectable quartz, the GM of quartz from smoky coal burning homes (0.4 μg/m^3) was similar to that of other fuel types (Table 1). The highest measured concentration of quartz (0.9 μg/m^3) was derived from a household burning both wood and smokeless coal. ANOVA testing indicated that there was no significant variation in quartz concentrations between fuel or stove type.

3.1.2. Quartz in ash

A total of 146 ash samples were collected, 75 of which were from smoky coal use, 13 smokeless coal, 12 a combination of coals, 7 wood, 4 general plant products, and 35 a combination of fuels. The geometric mean for respirable quartz within smoky coal ash (0.11%) was slightly higher than that for smokeless coal ash (0.08%), however this difference was not statistically significant, although it was significantly higher than that of ash derived from wood (0.01%) and plant (0.01%) burning (Table 2). No effect of stove design or fuel source on the quartz content of ash samples was observed.

3.1.3. Comparisons of quartz in coal, ash and air

Previously, the presence of quartz in coal samples in this population has been determined via scanning electron microscopy (Downward et al., 2014b). This analysis reported that smoky coal contained approximately twice as much quartz than smokeless coal (median values: 4.6% and 2.2% respectively), extending to quartz in the respirable fraction (1.9% and 0.6%). By matching coal, ash, and air samples collected from homes on the same day, we assessed the Spearman rank correlation between these modalities (Table 3). Measurements of total and respirable quartz in coal had a low to moderate correlation to respirable quartz in ash (coefficients = 0.30 and 0.38 respectively, n = 23) and with quartz in air (coefficient = 0.31 for both total and respirable quartz, n = 12).

Table 2
Respirable quartz as percentage of ash content.

	N	AM	GM	GSD
Smoky Coal	75	0.29	0.11	5.0
Smokeless Coal	13	0.14	0.08	4.0
Other Coal[b]	12	0.30	0.14	3.6
Wood	7	0.01	0.01[a]	1.6
Plant[c]	4	0.01	0.01[a]	1.8
Other Fuel[d]	35	0.21	0.06	7.2

[a] Significant difference ($p < 0.05$) when compared to smoky coal (via Tukey HSD).
[b] Other coal refers to either using both smoky and smokeless coal simultaneously or the use of pre-prepared briquettes.
[c] Refers to the use of corn cobs and/or tobacco stems (sometimes in combination with wood).
[d] Refers to the use of both coal and plant materials.

Table 3
Spearman correlation coefficients between quartz in coal, air, and ash.

	Respirable Quartz in Ash	Quartz in air
Quartz in Coal		
Total	0.30	0.31
Respirable	0.38	0.31
N[a]	23	12
Quartz in Air	−0.02	–
N	55	–

[a] Number of samples taken on same day contributing to correlation calculation.

Airborne quartz measurements correlated poorly with measurements of respirable quartz in ash (coefficient = −0.02, n = 55).

3.2. Secondary study

An additional 12 household air samples, measured for 1hr during normal stove operation, were collected for the secondary study – 8 from smoky coal burning homes and 4 from smokeless coal homes. Based on the particle size distribution and assumptions on the particle density and volumetric shape factor we estimated that silica concentrations (within the $PM_{2.5}$ fraction) were between 0 and 1.1 μg/m^3 for smoky coal homes (median 0.27 μg/m^3) compared to 0–0.19 μg/m^3 (median 0.03 μg/m^3) for smokeless coal homes. Semi-quantitative SEM/EDX on a limited number of samples were consisted with those findings (mean concentration for smoky coal: 0.3 μg/m^3, vs. <0.1 μg/m^3 for smokeless coal, n = 2 from each fuel group).

The observed silica generally consisted of dense particles with smooth surfaces, containing both round shapes as well as sharp edges (Fig. 2A). Material was either present as single particles or as part of larger conglomerates/aggregates together with silicate and carbonaceous particles (Fig. 2C and D). No differences in morphology of silica particles between smoky and smokeless coal burning homes was observed. However, there were clear differences in the relative percentage of silica particles relative to the total number of particles in the air samples. For $PM_{2.5}$ and, PM_{10}, the percentage of particles was 3–4 times higher in smoky coal households than smokeless. A difference was also observed in the amount of elemental silicon present in particulate matter. The mean silicon percentage was 33.1% for smokeless coal homes, compared to 41.4% for smoky coal homes.

In addition to the above identification of silica, fibre-like particles were observed via SEM/EDX. We have termed these particles "fibre-like" as they do not appear as clear crystalline fibres (e.g.

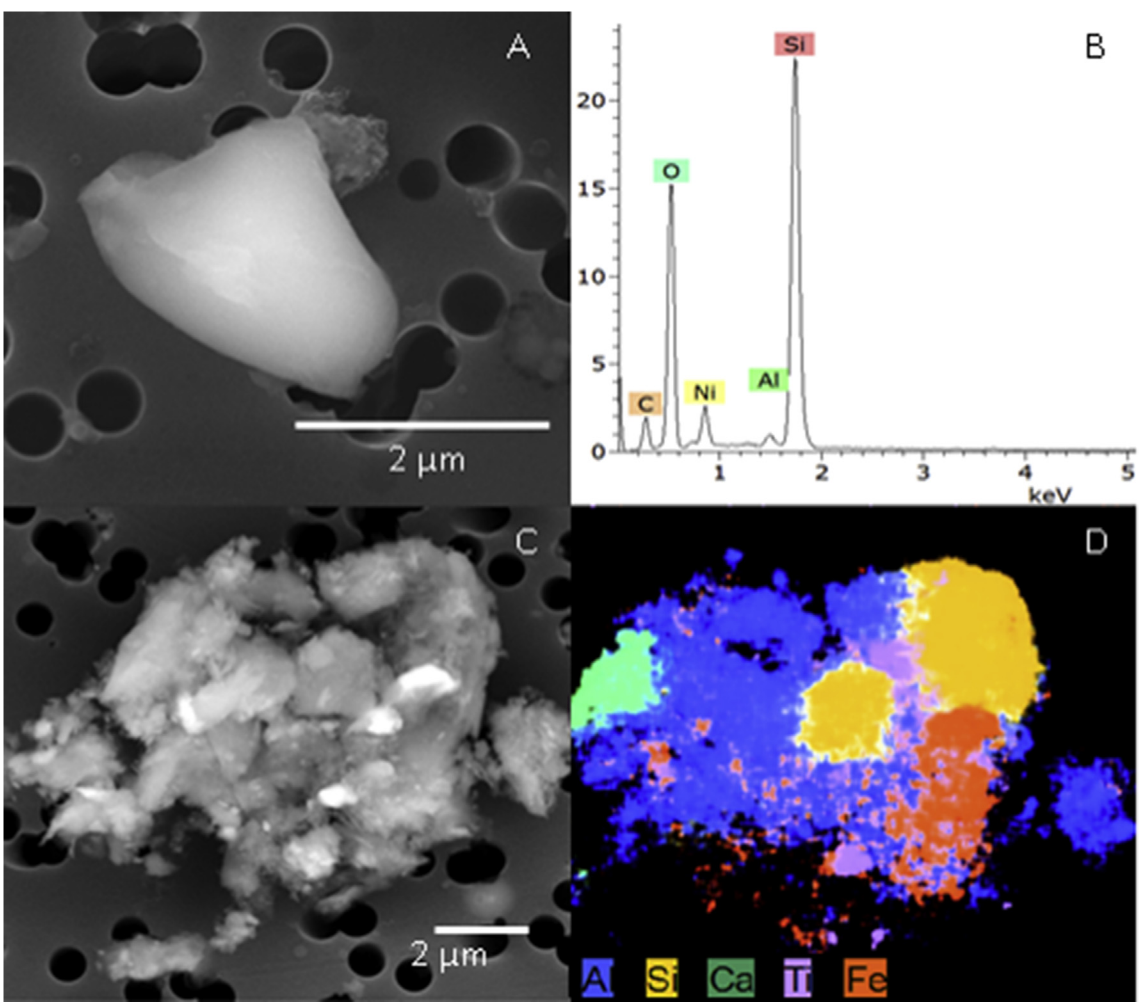

Fig. 2. SEM images and EDX analysis of two quartz structures (source: smoky coal).
SEM image of a solid quartz particle (A) and corresponding EDX spectrum (B).
SEM image of a conglomerate of alumino-silicate and quartz/SiO_2 (C) including EDX mapping (D).
The elements nickel (Ni) and carbon (C) originate from the filter.

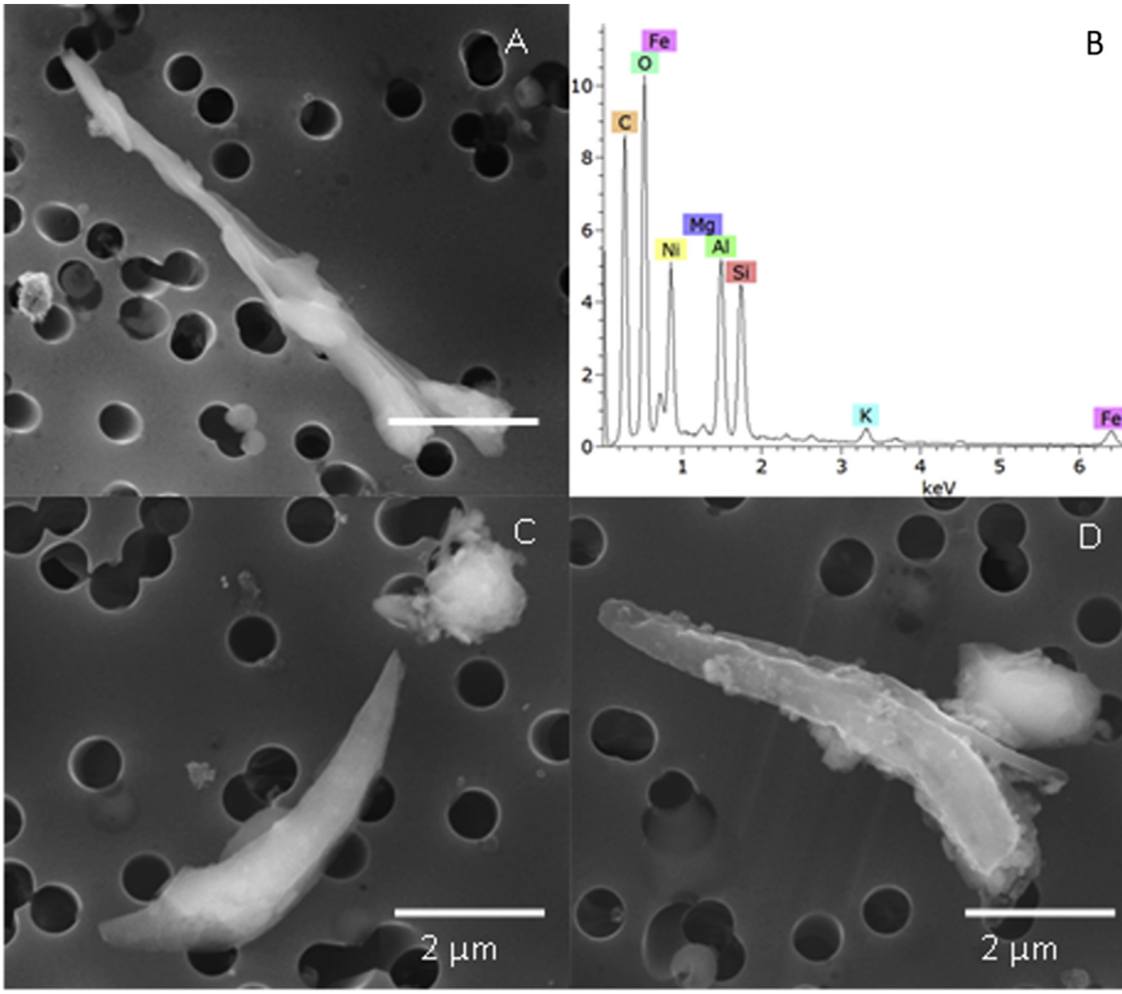

Fig. 3. SEM images (A,C,D) and EDX spectrum (B) of typical fibre-like particles (source A, B, C: smoky coal, D: smokeless coal). The element nickel (Ni) originates from the filter.

asbestos, ceramic fibres, etc.) but do meet the required definition for fibres in accordance with ISO 14966. The mean concentration of the fibre-like particles in smoky coal homes was 5800 fibres/m^3, compared to 550 fibres/m^3 for smokeless coal homes. There was heterogeneity in shape, size, and morphology observed in the fibre-like materials, both between and within air samples (Fig. 3A, C & D). Most of the fibre-like particles consisted of silicon-, aluminium, iron, magnesium, and potassium-oxides and carbon, but in varying ratios (Fig. 3B). In general, the elemental composition was similar to the elemental composition in the non-fibre-like inorganic particulate matter in the air samples.

4. Discussion

The domestic combustion of smoky coal in Xuanwei and its neighbouring county of Fuyuan, in Yunnan province, China has led to some of the highest lung cancer rates in the country (Mumford et al., 1987; He et al., 1991; Chapman et al., 1988; Barone-Adesi et al., 2012). Previous studies have suggested that exposure to quartz may be a contributing risk factor for carcinogenicity within the region, however much of this research has been limited to small sample sizes (Large et al., 2009; Li et al., 2013; Tian, 2005; Tian et al., 2008; Vermeulen et al., 2011; He et al., 2012).

In a previous study, we had demonstrated that smoky coal contains twice as much quartz as smokeless coal (Downward et al., 2014b). The current study finds that this elevated quartz does not translate to elevated concentrations within household air pollution, instead it goes on to form part of the ash. In our primary exposure assessment, we found that the majority (89%) of samples had no detectable quartz. Quartz was not detectable in any of the smokeless coal using homes compared to 14% (11 out of 80) of the smoky coal homes, 11% (1 from 9) of the wood burning homes, and 20% (1 from 5) of the plant product burning homes. However with only 17 samples from smokeless coal homes, it is difficult to determine whether this represents a true difference. To further evaluate this, the secondary study was performed wherein silica content in household air was quantitatively measured through SEM/EDX analysis, which identified that the household air pollution produced from smoky coal use, contained indeed higher amounts of silica than smokeless coal (median values 0.27 and 0.03 µg/m^3 respectively). While it should be noted that these measurements include all silicates (including crystalline and amorphous structures), even if we assume that all measured silica represented quartz (which would result in an overestimation of true quartz levels), these levels are consistent with the measurements reported in the larger exposure survey and are well within acceptable safety limits. For example, the European occupational exposure limits for quartz range from 25 µg/m^3 (Chapman et al., 1988) (Portugal) to 300 µg/m^3 (Poland) (IMA Europe Respirable Dust OELs, 2010). Further, in a pooled exposure analysis of multiple cohorts of quartz exposed workers, Steenland et al. concluded that the excess risk of lung cancer death for a worker exposed to 100 μg/m^3 for 45 years was approximately 1.5 times that of if they had not been exposed (Steenland et al., 2001). Not only are these values far in excess of what is reported in the current paper, the risk estimate associated with this level of exposure is insufficient to explain the difference in lung cancer rates between smoky and smokeless coal users (where the risk of lung cancer among smoky coal users can be up to 100 times that of smokeless coal users (Lan et al., 2008)). We should note however, that occupational exposure limits and surveys may not be fully applicable to the situation in Xuanwei and Fuyuan, as exposure is lifelong and continuous throughout much of the day, compared to occupational exposure which only occurs during working hours in adult life.

In addition to the above findings, we identified increased counts of fibre-like particles in $PM_{2.5}$ from smoky coal homes. While these particles do meet the criteria for fibres (length greater than 5 μm, diameter less than 3 μm, and length:diameter ratio greater than 3) they are heterogeneous in size and shape unlike, for example, asbestos fibres which are more uniform in nature. While they are present in far greater quantities in the smoke of smoky coal than smokeless coal (5800 fibres/m^3 vs. 550 fibres/m^3 respectively), the clinical relevance and source of these particles is unclear. The chemicals identified within the fibres (silicon-, aluminium, iron, magnesium, and potassium-oxides) are consistent with the mineral Chamosite. However, previous mineralogical analysis of uncombusted coal samples from Xuanwei has found that Chamosite levels are lower in smoky coal than smokeless coal (2.7% vs. 4.0% respectively) which would make this mineral being the source of these particles less likely (Downward et al., 2014b). Additional study, including larger sampling sizes and biological potency testing will be required to better understand what role (if any) these fibre-like particles play in carcinogenesis in the area.

A potential limitation of the reported findings is that measurements were restricted to indoor measurements and may not adequately represent personal exposure. Previous research on this population in Xuanwei and Fuyuan has identified that indoor measurements of multiple pollutants had a high degree of correlation and agreement with personal measurements. This has been demonstrated for particulate matter ($PM_{2.5}$), polycyclic aromatic hydrocarbons, and black carbon (Downward et al., 2014a, 2015; Hu et al., 2014). Therefore, on the basis of these previous findings, we are confident that the results presented in the current study are reliable approximations of personal exposure.

Measurements of ash provide, for the first time, the opportunity to explore an alternative path for the quartz identified in smoky coal. The current study has observed that ash from smoky coal contains slightly more respirable quartz (GM 0.11%) than smokeless coal (0.08%) and that there is a moderate correlation between respirable quartz in coal and ash ($r = 0.38$), which is marginally higher than that for air measurements ($r = 0.31$). These findings were further evaluated through a limited FT-IR analysis on a subset of 40 ash samples (17 smoky coal, 2 smokeless coal, and 12 from a mixture of fuels) where total quartz content was evaluated. This analysis found that smoky coal ash had approximately 9 times as much total quartz as smokeless coal (GM: 28.3% vs. 3.3%, $p < 0.05$ via paired *t*-test) and correlated strongly with the total and respirable quartz content in coal ($r = 0.79$ and 0.72 respectively). These additional findings, despite reduced sample size, suggest that the increased quartz within smoky coal goes on to form part of the ash in a non-respirable size during the combustion process. These findings indicate that exposure to quartz within the respirable fraction occurring during ash handling is likely to be similar for both smoky and smokeless coal users, meaning that this is unlikely to be a significant cause of the lung cancer rates in the area.

Overall, the findings of the current study indicate that despite smoky coal containing higher amounts of quartz than smokeless coal, very little of it becomes aerosolized during the combustion process, instead going on to form part of the coal ash, primarily within the non-respirable fraction. This finding indicates that exposure to quartz is unlikely to be the primary explanatory factor for the lung cancer rates in the area. High exposures to PAHs have previously been reported in the area, in addition to genetic studies which have identified higher lung cancer rates among individuals with variant PAH metabolism genes which together, may provide a better explanation for the high lung cancer rates (Downward et al., 2014a; Lan et al., 2000; Lan and He, 2004). The finding of fibre-like materials in household air samples has not previously been reported in this area, raising the possibility of another exposure metric of interest, however the clinical relevance (if any) of these materials has yet to be determined.

Competing financial interests

The authors declare that there is no competing financial interest in the planning, analysis or publication of this research.

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