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Geological Epidemiology: Coal Combustion in China

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Introduction

In a recent report, the U.S. Environmental Protection Agency (EPA) has concluded that, with the possible exception of mercury, there is no compelling evidence that emissions from U.S. based coal-burning electric utility generators cause human health problems (EPA 1998). However, worldwide, the use of poor quality coal and/or the improper use of coal may cause or contribute to significant widespread human health problems. Health problems caused by impurities in coal, such as arsenic and fluorine, have been reported from the former Czechoslovakia (Bencko 1997) and from China. The World Bank (1992) estimates that between 400 and 700 million women and children are exposed to severe air pollution, generally from cooking fires. A substantial proportion of these people rely on coal for domestic cooking and heating and are thereby exposed to particulates, metal ions, gases (such as SO_x), and organic compounds causing potentially serious respiratory problems and toxic reactions.

Although addressing human health problems is the domain of biomedical and public health scientists, geoscientists have tools, skills, databases, and perspectives that may help the medical community address environmental health problems. Geoscientists are best equipped to characterize natural resources such as rocks, soils, and water. Various analytical tools used to characterize these natural materials have also been used effectively to characterize materials such as ambient dust and the products of coal combustion that cause or contribute to human health problems. In this chapter, we describe some of the geologic and geochemical tools being used to address arsenism and fluorosis caused by residential coal combustion in Guizhou Province, China.

Health Problems Caused by High Arsenic- and Fluorine-Bearing Coals

Wood had long been the primary energy source in southwest China, but by the early part of the twentieth century the forests were largely denuded and the residents were forced to use alternate sources of fuel. In southwest Guizhou Province, surface exposures of coal are plentiful and coal quickly became the primary fuel for domestic use. Unfortunately, some of these coals have undergone mineralization, causing their enrichment in potentially toxic trace elements such as arsenic, fluorine, mercury, antimony (Sb), and thallium (Tl).

Burning the mineralized coals in unvented stoves volatilizes toxic elements and exposes the local population to these emissions. The situation is exacerbated by the practice of drying crops directly over the coal fires. In the autumn, when it is commonly cool and damp in the higher elevations of Guizhou Province, the residents commonly dry their corn, chili peppers, and other foods directly over the burning coals.

Arsenic

Chronic arsenic poisoning, which affects at least 3000 people in Guizhou Province, has been described by Zheng et al. (1996). Those affected exhibit typical symptoms of arsenic poisoning including hyperpigmentation (flushed appearance, freckles), hyperkeratosis (scaly lesions on the skin, generally concentrated on the hands and feet), Bowen's disease (dark, horny, precancerous lesions of the skin: Fig. 6.1A), and squamous cell carcinoma.

Zheng et al. (1996) have shown that chili peppers dried over open coal-burning stoves may be a principal vector for the arsenic poisoning. Fresh chili peppers have less than one part-per-million (ppm) arsenic. In contrast, chili peppers dried over high-arsenic coal fires can have more than 500 ppm arsenic. Significant arsenic exposure may also come from other tainted foods, ingestion of dust (samples of kitchen dust contained as much as 3000 ppm arsenic), and from inhalation of indoor air polluted by arsenic derived from coal combustion. The arsenic content of drinking water samples was below the U.S. Environmental Protection Agency drinking water standard (1973) of 50 ppb and does not appear to be an important factor.

Figure 6.1: Extensive scaly lesions (hyperkeratosis) as evident on the hands of a resident of this region. Abundant cracks in the lesions offer access to pathogens as liver flukes, a major cause of death in this area.

Recent research on the chemical and mineralogical characterization of arsenic-bearing coal samples from Guizhou Province (Belkin et al. 1997, 1998; Finkelman et al. 1999) has added to our knowledge of this problem. Instrumental neutron activation analyses of the coal indicate arsenic concentrations as high as 35,000 ppm! The extreme magnitude of this concentration can be seen by comparison with U.S. coals, where the mean arsenic concentration in nearly 10,000 U.S commercial coal samples is approximately 22 ppm, with a maximum value of about 2000 ppm (Bragg et al. 1997).

Belkin et al. (1997, 1998) examined polished blocks of the arsenic-rich Guizhou Province coal using a scanning electron microscope equipped with energy-dispersive X-ray analyzer (SEM–EDX), and an electron microprobe. This study also used X-ray diffraction analysis, optical microscopy, and other techniques to identify the arsenic minerals in the coal. A wide variety of As-bearing mineral phases was observed. Pyrite (FeS_2) is the most common sulfide. The range of As in pyrite determined by electron microprobe analyses is from the detection limit (~100 ppm) to about 4.5 weight percent. Arsenopyrite (FeAsS), a very rare mineral in coal in the U.S., is abundant in several of the Chinese coal samples. Other minor As-bearing minerals present include a third As-bearing sulfide, phosphates, sulfates, oxides, and silicates (clays).

The coal samples with arsenic concentrations in excess of 3 weight percent were mineralogically unusual. Although they contain small grains and framboids of pyrite, the concentration of arsenic in these forms of the iron sulfide phase is completely inadequate to account for the arsenic abundance on a bulk analysis of the coal. In SEM back-scattered electron images, a distinct banding characterized by different image brightness is observed (Figs. 6.2A, B). Semi-quantitative analysis by electron microprobe demonstrates that the bright bands contain ≈3 weight percent arsenic. No discrete As-bearing phase could be observed using electron microscopy at magnifications of 1 million times. Thus, finely-dispersed arsenopyrite, As-bearing pyrite, or any other As-mineral can be ruled out as the source of the arsenic. Using relatively new, sophisticated analytical procedures [X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS)] (Huffman et al. 1994) it was determined that most of the arsenic in these samples is present as organically bound arsenate (AsO_4^{3-}).

The chemical and mineralogical characterization of the coals in Guizhou Province has had several benefits. Commonly coals containing high ash, high sulfur, and high contents of toxic elements such as arsenic are "cleaned" to reduce the concentrations of these undesirable components. The cleaning process physically separates the inorganic constituents from the organic constituents of the coal, generally resulting in a lower ash, lower sulfur, lower arsenic fuel. Because the arsenic in these special Guizhou Province coals is largely organically bound, cleaning would have produced a fuel even richer in arsenic. Information on the arsenic mineralogy may also help predict the behavior of arsenic during coal combustion. Preliminary characterization of residual ash in coal-burning stoves indicates high retention of arsenic. Mineralogical characterization in conjunction with combustion tests may determine if one or more of the arsenic-bearing phases is primarily responsible for adsorption of arsenic on the chili peppers.

Knowledge of the concentration of arsenic in these coals could be used to systematically map the distribution of this element and identify locations of high- and low-As coals. Understanding the relationship between the arsenic content of the coals and geologic processes could help to identify areas where similar situations may exist. Knowing where these high-As coals occur could result in measures to protect local populations from exposure to arsenic and the resultant health problems in Guizhou Province.

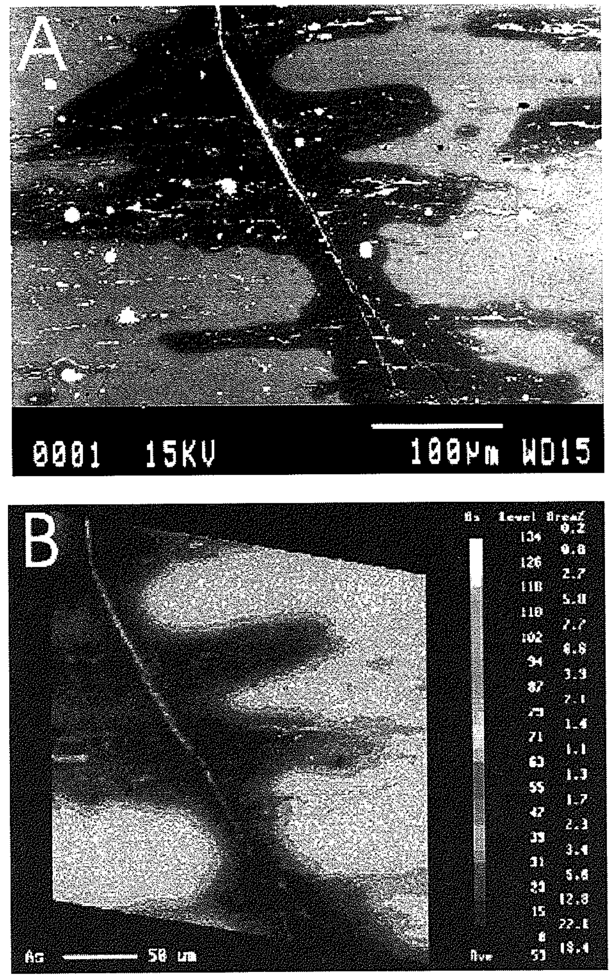

Figure 6.2:
A. SEM back-scattered electron image of polished block of arsenic-rich coal. Dark areas are coal, bright areas are mainly pyrite, milky area is coal containing organically bound arsenate. Fluids moving through the fracture in the coal appears to have removed arsenic from the organic matrix.
B. X-ray map depicting the distribution of arsenic in the coal. Light areas are high concentrations, and dark areas are low concentrations. Compare distribution of arsenic to the outline of the milky area in Figure 6.2A.

The tools and techniques employed to characterize the distribution of arsenic in these coals could be used to better understand the forms and behavior of other potentially toxic elements such as fluorine.

Fluorine

The health problems caused by fluorine volatilized during domestic coal use are far more extensive than those caused by arsenic. More than 10 million people in Guizhou Province and surrounding areas suffer from various forms of fluorosis (Zhang and Cao

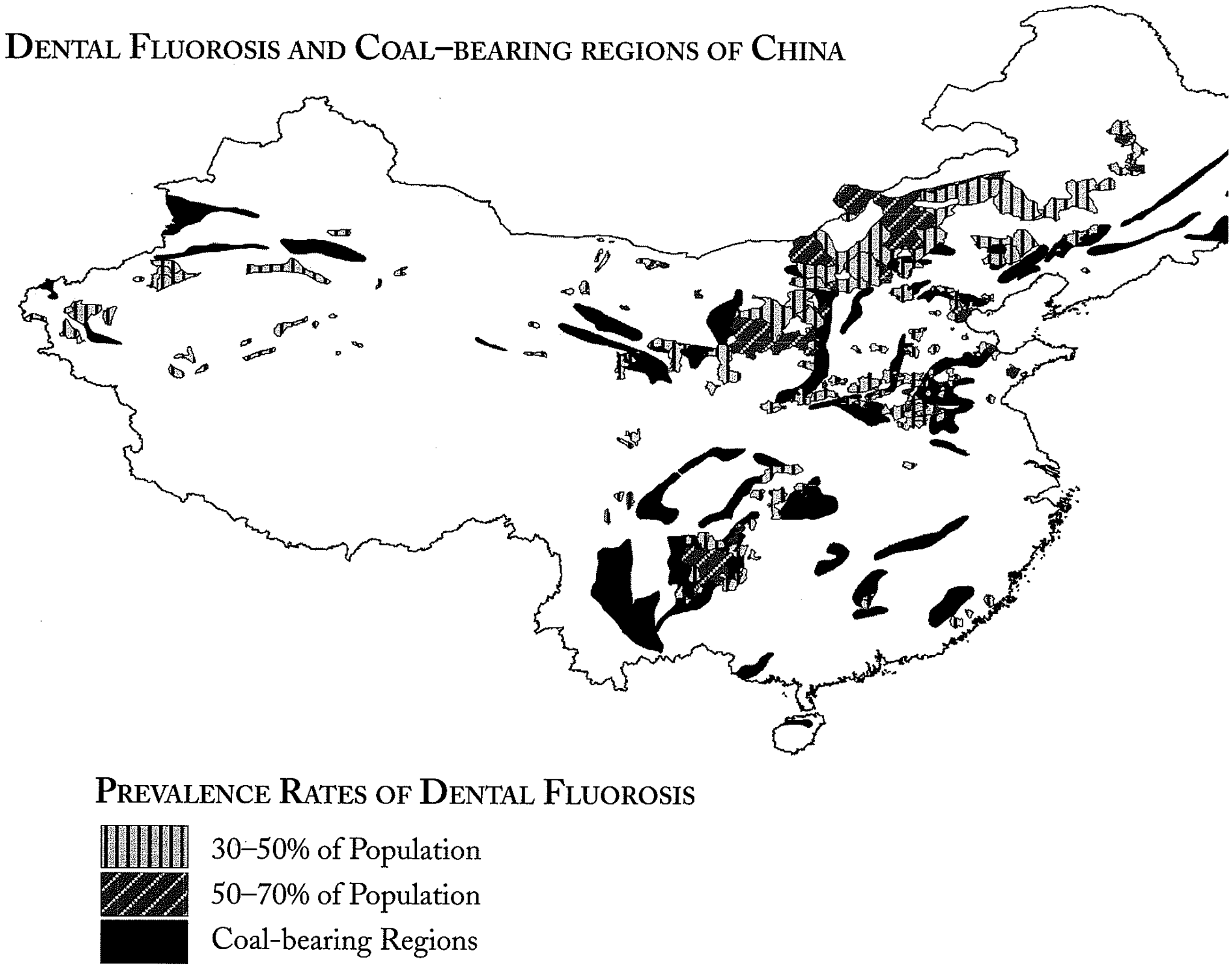

Figure 6.3: Map of China produced by GIS techniques showing the distribution of coal-bearing regions. Superimposed on this are the areas of high incidence of dental fluorosis. The coincidence of dental fluorosis with Paleozoic coal-bearing rocks in the Guizhou Province and surrounding area is compatible with domestic coal combustion as the source of fluorine. The population burns coal briquettes composed of high F-bearing coal bound with high F-bearing clay as domestic fuel, compounding F exposure from high-F water in these areas. From the Open File Report #01-318 U.S. Geological Survey compiled by A.W. Karlsen, A.C. Schultz, P.D. Warwick, S.M. Podwysocki and V. S. Lovern, with permission.

1996, Zheng and Huang 1989). Fluorosis has also been reported in 13 other provinces, autonomous regions, and municipalities in China (Ando et al. 1998).

Typical symptoms of fluorosis include mottling of tooth enamel (dental fluorosis) and various forms of skeletal fluorosis including osteosclerosis, limited movement of the joints, and outward manifestations such as knock-knees, bow legs, and spinal curvature. Fluorosis combined with nutritional deficiencies in children can result in severe bone deformation (Fig. 6.4).

The etiology of fluorosis is similar to that of arsenism in that the disease is derived from foods dried over coal-burning stoves. Ando et al. (1998) estimate that 97% of the fluoride exposure came from food consumption and 2% from direct inhalation.

Zheng and Huang (1989) have demonstrated that adsorption of fluorine by corn dried over unvented ovens burning high (>200 ppm) fluorine coal is the probable cause of the extensive dental and skeletal fluorosis in southwest China. The fluorine in the coal is primarily in the clay minerals (Belkin et al. 1999). However, the fluorosis is compounded by the use of clay as a binder for making briquettes. The clay used is a high-fluorine (mean value of 903 ppm) residue formed by intense leaching of a limestone substrate. Chemical analysis can help to identify sources of low-fluorine coals and clays in the region so that low-fluorine briquettes can be produced.

Conclusion

Domestic coal use in developing countries can cause serious health problems because of the inclusion of potentially toxic elements in this fuel source. Geoscientists from other countries have the tools and the expertise to analyze, and forecast, the concentrations, distributions, and behavior of the harmful species. Collaboration between countries generating such immediate and useful information for a variety of circumstances would go a long way toward mitigating present and future health impacts on an unsuspecting public.

Figure 6.4: Bone and joint deformation due to nutritional deficiency combined with exposure to high levels of fluorine from residential coal combustion.

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