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Kandovan the next 'Capadoccia'? A potential public health issue for erionite related mesothelioma risk

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ABSTRACT

BACKGROUND: The Kandovan region in Iran is physically and geologically similar to the Cappadocian region in Turkey where fibrous zeolites, including erionite, have been found in volcanic tuffs. In some Cappodocian villages there is strong evidence that erionite, and possibly related minerals, are responsible for the high level of mesothelioma found there. So, although mesothelioma clusters have not been reported in Kandovan, it is a plausible hypothesis that many cases of mesothelioma in Iran may be due to naturally occurring fibrous zeolites.

METHODS: A detailed study of Iranian geology was made to determine similarities between the Kandovan region and Cappadocia, 'inter-mountain zones' in the Western US and Mexico. Areas where mesothelioma cases probably attributable to erionite exposure have been found.

RESULTS: Although there is a long history of asbestos use in Iran many cases of mesothelioma do not present with positive asbestos exposure histories. Since fibrous zeolites are so widespread, why have not more mesotheliomas attributable to them been found throughout Iran? Various possible reasons were explored including misdiagnosis, poor surveillance, a general lack of awareness that this tumor may be linked to mineral fibre exposure. There is also the analytical problem of identifying fibrous erionite in lung tissue.

CONCLUSIONS: There is every reason to believe mesotheliomas due to fibrous zeolite including erionite will be found in Iran. The most likely places to find them are the villages that look very similar to those found in Cappadocia since these are based upon similar geological formations.

Key words: Erionite, Iran, Kandovan, volcanism, mesothelioma

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INTRODUCTION

In 1972, the eminent Turkish chest physician, Professor Izzettin Baris, diagnosed pleural mesothelioma in a Kurdish herdsman from 'Karain', a small village in Capadoccia. Investigation showed that this, usually rare disease, was common in several villages in the region [1]. This sentinel observation led to an international scientific investigation sponsored by WHO IARC in 1974. A team of experts visited Karain to find people living in caves carved into the local volcanic rock formations (commonly known as 'fairy chimneys'). They discovered the rocks contained fibrous zeolites including erionite, mordenite, and phillipsite. Lung burden studies confirmed significant quantities of these fibres in the lungs of the people and the animals they raised. (reported variously by the team members e.g. [2,3]). Since the simple demonstration of the fibres in the lungs of these individuals was not adequate to identify which of these fibres was potentially responsible for the observed mesothelioma excess and sufficient quantities of each were not available for experimental testing, it was not, at that time, possible to confirm their possible carcinogenicity. However, a highly fibrous erionite from Rome, Oregon, USA, morphologically similar to that found in Turkey, was available in sufficient quantities for testing. This was tested in rats by inhalation and inoculation in the UK by Wagner et al. [4]. Those tests confirmed the extreme potency of this fibre type for the induction of mesothelioma to be 500 to 1,000 times more potent than South African crocidolite (see Ilgren et al. [5] for review). To this day, the carcinogenicity of fibrous mordenite and phillipsite has never been tested by inhalation and their potential for mesothelioma, whilst being likely, has never been confirmed.

Large amounts of fibrous erionite were first demonstrated by Deffreyes [6] in the western part of the United States and he subsequently warned that it could be a human health hazard. Later, Sheppard and his colleagues in numerous publications (e.g. [7]) confirmed this work finding large quantities of erionite in the Western US particularly within so called 'intermountain zones'. Fortunately, such regions are very sparsely populated which explains in part why erionite related mesothelioma in the western part of the United States have not been found. [8,9]

Wagner [4] (pers commun. 1990), nonetheless, still believed erionite related mesotheliomas would eventually be found in people living in these intermountain zones particularly since materials potentially contaminated with fibrous erionite had also been sold commercially [10-12]. The 'intermountain zone' of concern [13] actually extended semi-continuously from the North-west of the United States into Mexico. Twenty years elapsed before Wagner's predictions were confirmed through the discovery of an erionite related mesothelioma case in south central Mexico with clusters of other mesothelioma cases nearby [5,14]. This was the first report of erionite related mesothelioma outside of Turkey. Subsequently, other clusters of erionite related mesotheliomas were demonstrated in other parts of Mexico as well [15].

The Iranian village of Kandovan, 50 km south of Tabriz, is reminiscent of Cappadocia [16]. The inhabitants live in similar 'caves' carved into 'fairy chimneys'. Geological study shows continuity between the Iranian and Turkish Anatolian volcanic plates that include Kandovan and many other areas of Iran as well. Mineralogical studies show vast amounts of natural zeolites, including different fibrous forms, in the Tabriz basin and other parts of Iran especially the province of Tehran. Erionite was found in several of these areas. Natural zeolites have been sold widely throughout Iran for decades.

Although mesothelioma clusters have not been reported in Kandovan, many cases of mesothelioma in Iran do not present with positive asbestos exposure histories. There are many cases of drug resistant TB in Iran. These were the major sources of diagnostic confusion when mesotheliomas were first recognized in South Africa by Wagner et al. [17] and by Baris and others in 1974 in Turkey [18]. Therefore, taking all of the aforementioned observations together, lung burden studies of Iranian mesothelioma cases should be done and a possible public health alert should be issued for those living in Kandovan and the other areas in Iran where people presently live in volcanic caves. We feel that many cases of mesothelioma in Iran may be due to naturally occurring fibrous zeolites and/or amphibole asbestos either at source and/or in commercial products that use such materials. Therefore, in a manner similar to the hypothesis that first queried the existence of erionite as a cause of mesothelioma in central Mexico [5] which was later confirmed to be the case one year later in this area [14]. In the light of Turkish and Mexican experience we believe a high degree of suspicion is warranted in Iran and possibly other parts of the Middle East that share geological similarities to Cappadocia.

Kandovan geology

Kandovan and Tabriz are Northwest of the Zagros geological area of Iran, whilst Tehran is in the central part. This region contains sedimentary and volcanic rocks with extensive areas of zeolite deposition [19-23] and important ophiolitic complexes containing both serpentine and amphibole [19,20,24].

Regional Geology & Potential Extent of Zeolitic Zones in the Tabriz Basin

Much of NW Iran is located within the UDMA (Urumieh-Doktar magmatic arc) volcanic zone. [25]. The two largest volcanoes in Iran, Sahand and Savalan, cover ca 10,000 sq km.[26] and encompass the entire province of Tabriz in North Eastern Azerbaijan. The area is covered by thousands of sq km of volcanic lava flows in continuity with many other volcanic belts [26]. The Savalan volcano is ca 100 km to the NW of Tabriz and the Sahand volcano is located ca 40 km south of Tabriz city [27]. Hydrogeochemical processes and chemical characteristics around Sahand Mountain indicate it is structurally part of the northern UDMA [28] which has been found to contain zeolites [29-31]. The high calcic-alkaline - SiO_2 conditions in all parts of the Sahand and Sabalan facilitate zeolite formation [25,32].

Zeolite-bearing veins in the volcanic materials tended to distribute themselves at the interflow zones of the differentiated lavas along their flow paths. Zeolites as well as tremolite have also been found in the Yengi esparan marl intrusions to the north of Tabriz [33].

Regional Zeolite Occurrences

Zeolites in the volcanic rocks of north Central Iran and Azarbaijan have been well studied [34,35]. In particular Comin-Chiaramonti et al. [36] noted "in north-eastern Azerbaijan there is mesolite, chabazite, thomsonite, analcime, stilbite, heulandite and phillipsite. Mesolite is said to constitute the bulk of the zeolites whilst chabazite is frequently associated with mesolite." (also see Lescuyer and Riou [37]). The Amirabad mine in Mianeh, ca 160 km SE of Tabriz, is a major commercial source of zeolite for many parts of Iran including Tabriz itself [38-41]

Tabriz

Tabriz (pop ca 1.7 million) is one of the most important industrial cities in Iran. Pozzolanic zeolite based cements have been used in Tabriz and other Iranian cities. As the Tabriz basin alluvial tuff aquifers contain vast amounts of zeolites and these serve as major sources of groundwater for Tabriz, it is also possible that secondary zeolitic exposure may come from this source since these are found in the pozzolanic cement conduits.

Kandovan

Kandovan is a village (pop ca. 700) situated on the northern slopes of Sahand Volcano ca. 50 km south of Tabriz. The people have a traditional agricultural way of life.

Many of the homes in Kandovan are in caves located in cone-shaped, naturally formed compressed volcanic ash formations that make the landscape look like a gigantic termite colony. The residents are modern-age cave dwellers. The volcanic ash and rock are efficient insulators with a reputation of being very energy efficient: cool in summer and warm in winter [42,43].

Specific geo-mineralogical information on Kandovan is surprisingly scant. Kandovan is located at ca 2,300 meters ca. 3 kms from the centre of the Sahand volcano crater. The Geological Survey of Iran map of Osku valley shows Kandovan ('Kandojan') in aerial view towards the end of a zone (PLQlp) called 'pumicic lahar'. It may overlay 'volcanic ash with block, lahar and welded breccia' (PLQash) and / or 'conglomerate with lahar, tuff, pumice, volcanic ash and fresh water limestone (PLQc), being surrounded by the latter. The transect view of Kandovan on the Osku map does not enable one to discern the geology at depth. A diagram in Qorbani's book [44] shows Kandovan village in transection and notes that in the Kandovan Period (his fig A, 1-4) at the bottom of the valley there is volcanic shear containing some ignimbrite horizons (pumice) over conglomerate ignimbrite and volcanic lava.

Alluvial tuff appears to be near the ignimbrite horizons. The mapping methods are not given so the sensitivity for excluding intrusion of zeolitic sedimentary material cannot be readily assessed. Samira et al. [42] also said the results of geologic testing of the rocks of the Kandovan region showed they are volcanic tuff.

Virta from the USGS (pers commun. 2013) noted that the GSI map of the Osku region does not exclude the possible presence of zeolites since they may form from pumice directly and also secondarily from weathering from exposure to water. The Osku valley map clearly indicates a river running through and a spring within Kandovan. Ghazi et al [25] also say the 'Sahand Volcano comprises many different geological features, such as various lithostratigraphic sections and cones developed in tuff as a result of erosive processes including crags, canyons, rivers, waterfalls and tafoni'. (Tafoni are small cave-like features found in granular rock such as sandstone, with rounded entrances and smooth concave walls. They often occur in groups that can riddle a hillside, cliff, or other rock formation.) This again emphasizes the role water erosion has played in the formation of the 'cones' in which the people live further suggesting that secondary zeolitization may have occurred therein.

Many references illustrate the similarity between Kandovan and Cappadocia in Turkey (Jamshid (Cal Tech) pers commun. 2013, ,) [16,25,42,45-47] Figures 1-3

Modes of Exposure potentially related to Mesothelioma Risk

The first exposure measurements taken in Karain [48] suggested fibre levels were very low causing some to believe erionite was not responsible for the observed disease. Subsequently, measurements were taken when the residents were conducting a series of activities that did indeed demonstrate high intermittent exposure patterns such as carving the walls, sweeping, and tending the vegetable and animal stores kept in the home (where the zeolitic materials are often used as desiccants and preservatives) (Elms pers commun. 1996). These and other activities at Kandovan and the other 'cave dwellings' would similarly place inhabitants at risk. Also, erionite may not be the only mineral fibre to produce mesothelioma. There is no reason to exonerate the other fibrous zeolites such as mordenite and phillipsite for example amongst possibly others (as discussed by Ilgren et al [5]). However, we have no epidemiological basis for doing so and the very few animal studies that have tested mordenite are not persuasive and contributory [49,50].

Zeolite Occurrences in Syria

We have little information about Syrian zeolites but they are mentioned here since there is also geological contiguity of the Iranian zeolite zones into Syria. Moreover, some have observed cave dwellings of the type we find in Karain and Kandovan in parts of Syria as well (Robert Murray, 1990 pers commun.).

Zeolites associated with other types of Mineral Deposits in Iran

Zeolites in Iran have been found in association with certain types of mineralization that involve the formation of copper [28]; bentionitic clays (zeolitic-bentonitic sequences have been found in the province of Tabriz); borates (borate deposits in Iran may be associated with zeolite deposits since those formed in other parts of the world under similar conditions do contain zeolitic mineralizations.); mercury (some of the mined mercury deposits occur in hydrothermal areas also associated with zeolite formation.); perlite and pumice (Commercial pumice is a good material for forming zeolites but only if the chemistry of the water percolating through the deposit is correct (Virta per commun 2013). Qorbani [51] notes the formation of zeolites from perlite especially in Azerbaijan. Potentially zeolite contaminated sulfide, gold, silver and iron was also probably transported to different parts of Iran by train.

Commercial Uses of Natural Zeolites in Iran

Iran has many suppliers of natural zeolite both for internal use and for export to other countries both in the region and world-wide. These are used for applications ranging from agricultural to

FIGURE 1

KANDOVAN VILLAGE [46]

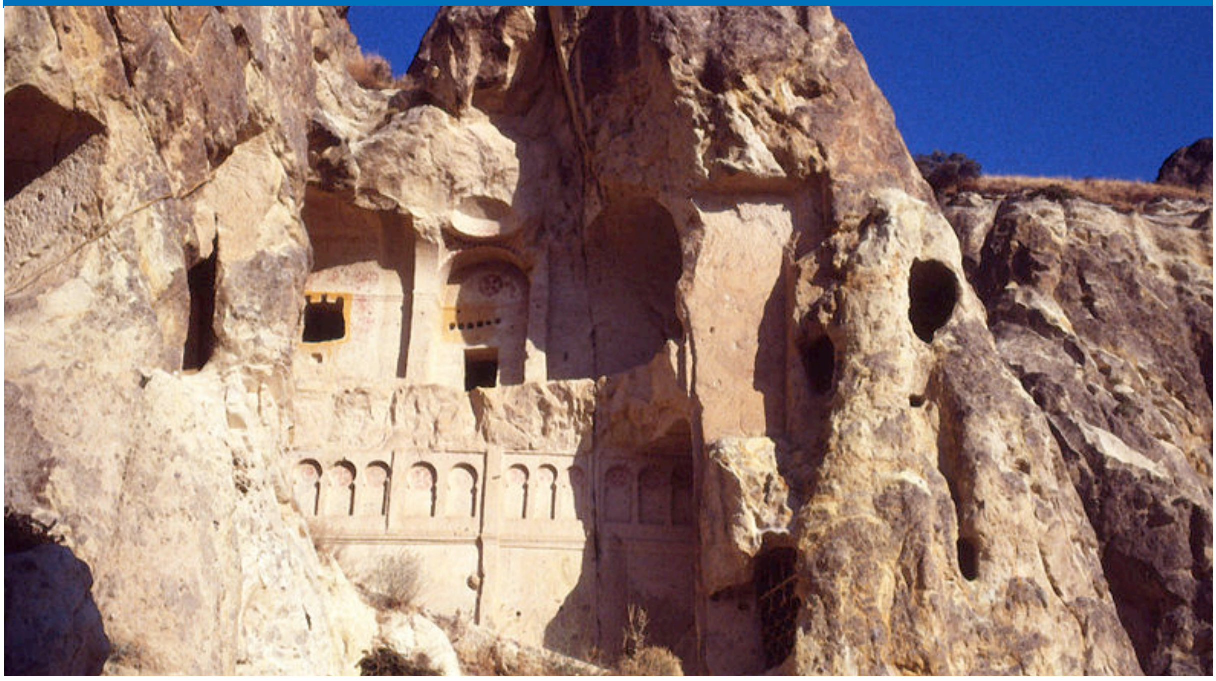
FIGURE 2

CAVE HOUSES IN KANDOVAN VILLAGE

animal husbandry to pozzolan cement, etc. There are over 60-80 different natural zeolites found in Iran of which a few are fibrous, including erionite (Nilchi, pers commun, 2013). Many of these are sold for distribution. Clinoptilolite in particular is sold widely. Although it is nonfibrous, some clinoptilolite deposits are contaminated with fibrous zeolites at source. Mianeh city near

FIGURE 3

ABANDONED COPTIC MONASTERY IN CAPODOCCIA



Tabriz is a major source of zeolites. Shojaeifard et al. [52] also said that other huge natural zeolite deposits exist in Iran but their complete and valid documentary reports on the zeolite market in Iran have never been published. They said the most dominant utilization of high quality Iranian natural zeolites is in animal husbandry, agricultural and aquacultural applications. The use of natural zeolites in Iran as ion exchanger in water treatment is also very important. Laboratory studies have investigated the utility of natural zeolites for waste water cleanup [53] and to remove a variety of materials including textile wastes [54]; radioactive materials [55,56]]; ammonium ions [57,58]; ammonia [59] and styrene [60];etc.

Natural zeolites are also sold and distributed through many cities including Tabriz today (e.g. Azer Perlite Co.) More information on the commercial uses of natural zeolites in Iran may be found in a compilation of research and industrial projects by Hossein that use natural zeolites [61] .

Apparent 'Absence' of Erionite: Chmielewská [62] said in her talk at IIZC2010

"In the 1950´s Union Carbide Corporation (at present Dow Chemicals) and some oil companies, especially Shell Development Company in USA, Canada and Mexico started to use the natural zeolites (erionite, chabazite and mordenite) as cheap molecular sieve amendments for purification and desiccation of low grade natural gas streams". Given the enormity of the Iranian gas and oil industry and its vast supplies of natural zeolites, it is difficult to believe erionite in some form has not been used in a similar fashion in Iran. Nilchi (pers commun) at the NSTRI said erionite was found in the Lurestan Province in SW of Iran, near the Iraqi and Turkish borders in the proto-Zagros foreland basin. Despite the lack of detailed documentation, we still believe erionite not only exists in Iran, but is a potentially significant cause of some of the mesotheliomas found therein in manner similar to our observations made in Mexico [5,14]

Geological relationships

Arguments for the presence of erionite in Iran can be made in the context of Iranian geology. Birsoy [63] explored the formation mechanisms, chemical characteristics and stability conditions for erionite production in Turkey and other parts of the world. She emphasized the need for high alkaline content and pH both of which are met in many of the Iranian deposits. Ilgren et al. [5] said that 'erionite is normally found with the zeolite species: clinoptilolite, chabazite and phillipsite in the western United States, Mexico, and Turkey.

Turkish connection

There is geological contiguity between Capadoccia, Kandovan and the Tabriz basin Sahand volcano area.

Intermountain West and Iran compared

The conditions in the Intermountain regions of the US are conducive to the formation of various zeolites and, in certain areas, there are large deposits of erionite. Taghipour and Mackizadeh [64] noted the geological environment of the zeolite origin in the Central Alborz Range, Northern Iran occurs in the saline environments similar to those found in the United States [13]. The Mineralogy of the zeolitic-bentonitic sequences of the Kuh-e-Arshe, north Central Iran [65] was compared to the mineralogy, chemistry and diagenesis of tuffs in the Sucker Creek formation (Miocene) in Eastern Oregon [66]. This Oregon formation is near the area where the erionite was found for use by Wagner et al. [4] for their experimental inhalation studies. Indeed, Sheppard [7] and others subsequently [9] noted the widespread presence of fibrous erionite in most of the Western US states. We believe that despite the failure to demonstrate erionite related mesotheliomas in these areas, the finding of such cancers is inevitable and only hindered by the sparse population in the areas in which large amounts of erionite are found [5].

Mexico

The intermountain zone of the Western United States also extends into Mexico where erionite deposits are found, some sufficient to cause mesothelioma [5,14,15]. Verdel [67] noted similarities between the Iranian arc and the western part of the central Mexican arc saying that the Mexican volcanic belt and the eastern Mediterranean region may be well-characterized, recent analogs to the Iranian Eocene volcanism.

Sampling Bias

Khalili et al. [68] said that despite the abundant occurrence of zeolite deposits in Iran, few systematic studies have been carried out. Virta (USGS 2013 per commun) points out the main difficulties: papers and maps provide general information as to where zeolites may be found but not on where they actually do occur. Zeolites are difficult to identify without the use of XRD. At present there is little economic or environmental incentive to accurately identify zeolites in Iranian deposits. The literature is sparse. Geologists who specialize in Iranian geology and who have done field work in the regions where tuffs and other potentially altered volcanic deposits are found, must be consulted. Most reports that identify altered tuffs as part of the geologic record don't mention zeolites.

ANALYSIS

Identification Issues

The identification of erionite requires special skills in so far as routine geologists may confuse fibrous zeolites with other materials, particularly fibrous clays and in the case of erionite with other fibrous zeolites (Pooley pers commun 2008). The failure to correctly identify erionite could contribute to the failure to report this fibre type to date in Iran

Sensitivity Issues

Fibrous erionite rarely occurs in pure form but tends to form focally (Virta, pers. commun, 2007) as a very minor contaminant of the host rock. This is so in many affected Turkish villages [69-71] and deposits in the western United States (e.g., Yucca Mt., Nevada [72]) and Mexico [5]. Careful searching must be done, sometimes near the limit of detection and a significant number of samples need to be assayed. Recently, Professor Hossein Kazemian, a world authority on Iranian Zeolites wrote to say that he found fibrous mordenite fibres in samples taken from a clinoptilolite deposit in the Miyaneh Region. SEM identified the fibres but they were only evaluated morphologically so the possibility of erionite could not be excluded. Moreover, the limit of detection was

1.0% and in some cases erionite can occur in very small amounts as indicated above.

Asbestos Exposure Sources in Iran

Since this paper primarily concerns a potential mesothelioma risk it is appropriate to briefly mention other minerals since there are numerous sources of natural and commercial amphibole asbestos in Iran.

Natural Asbestos Sources

The Zagros belt that extends over 2000 km from Turkey to SE Iran also contains numerous ophiolitic complexes and different forms of amphibole [19]. A paleogeographical study of the Tabriz Basin also reveals numerous ophiolites [73] and the Khoy opthiolite to the northwest of Tabriz contains very large concentrations of amphibole asbestos (Jamshid Cal Tech, 2013 pers commun). The Yengi esparan intrusions located north of Tabriz contain tremolite [33]. There are various asbestos mines in Iran including some in Azerbaijan and these have been mapped and listed by the GSI. The possibility of finding fluoro-edenite sources similar to those seen in Biancavilla, Italy that have been associated with mesotheliomas has not been excluded [74]. Various copper skarns in Iran contain tremolite and actinolite [75,76]

Commercial Use of Asbestos

In Iran, asbestos has most commonly been used for the manufacture of building materials. The Iranian asbestos cement industry for the pipe and roofing materials has operated for at least 60 years and remains today a major industry [77].

Other building materials

Plaster has been a building material in Iran for at least 4,000 years. As in Turkey, Iran may also use tremolite contaminated stuccos.

Diagnostic and Ascertainment Issues

If fibrous zeolites are so widespread, why have not more mesotheliomas been found throughout Iran? Misdiagnosis, poor surveillance, a general lack of awareness of this tumor being linked to mineral fibre exposure particularly outside the major cities, difficulties in identifying fibrous erionite in lung tissue, serious ascertainment bias and under-reporting are certainly probable explanations [5]. Epidemiological surveillance for mesothelioma in Tabriz appears to be inadequate [78], who provided the first report of the incidence of respiratory cancer and mesothelioma in East Azerbaijan said that "Studies on cancer epidemiology in developing countries such as Iran and information on cancer prevalence is either absent or largely unavailable…". Their study was based on the cancer registry office in Tabriz for the five year period, 2002-2008. The study was conducted by the department of surgery, the findings were based on hospital cancer case records and the diagnostic methods were not described. Of the 18 cases of mesothelioma, little historical case information was provided and the number with asbestos exposure not stated. Taheri (Nat. Inst. Lung Dis Cancer, Tehran per commun 2013) said only ca 40% of the mesothelioma cases in Iran have positive asbestos exposure histories whilst Bagheri et al. [79] in a study of 40 patients put the number at 25%. The fact that comparatively few cases have positive exposure histories could be due to recall bias and other factors or perhaps to the fact that the cause of their mesotheliomas was actually due to fibrous zeolites, not asbestos. Consistent with this is the fact that Park et al. [80] predicted the cumulative mesothelioma mortalities for Iran that suggested many more mesotheliomas should have been found on the basis of asbestos exposure alone than actually were.

The study by Hashemzadeh and Hashemzadeh [78] could be used to address some of these questions to the extent it not only included patients from Tabriz but also from other townships in Eastern Azerbajian with known zeolite deposits such as Mianeh and Ahar. Another township in their study, Maragheh, is also on the Tabriz Basin and was recently found to have underground cave complexes [78]. It would certainly be interesting to conduct lung burden studies of cases from these townships if indeed they did not have positive asbestos exposure histories.

Finally, TB appears to be a major problem in Iran (e.g. see 'Iranian Stop TB Committee'

Nat Res Inst TB and Lung Cancer (NRITLD) [81]). It is worth noting that the mesotheliomas found by Wagner et al. [15] in South Africa and by Baris in 1974 [18] in Karain Turkey were thought to be cases of resistant pleural TB. Also, diagnostic issues particularly in areas outside the major cities where populations are sparse may be limited.

CONCLUSIONS

There is every reason to believe mesotheliomas due to fibrous zeolite including erionite will be found in Iran. The most likely starting point to find them is in the villages that appear to be structurally very similar to those found in Karain, Turkey. That is so because they are derived from and based upon geological formations that are contiguous with and very similar to those found in Karain. Moreover, the mineralogical assemblages of the zeolites found in Sahand and the surrounding Tabriz basin that include such villages like Kandovan are also very similar to the ones found in Karain as well as the erionite containing areas in the intermountain zones of the Western United States and Central Mexico that have also demonstrated experimental (US) and epidemiological (Mexico) evidence for a mesothelioma risk.

Since extensive zones of fibrous zeolite containing volcanic tuff also appear in other parts of Iran, one can also expect to find attributable mesothelioma risk outside of the province of Tabriz. The robust natural zeolite industry and the distribution of zeolites for commercial use in a variety of industries may also create attendant risks.

The mineralogical characteristics of the cave dwellings in Iran should be studied and their residents carefully assessed clinically. Lung burden studies of mesothelioma cases with no asbestos exposure histories should be conducted. Consideration should be given to alerting certain populations to participate in a health screening study.

This report thus proposes that areas of high mesothelioma risk due to naturally occurring and possibly commercially used fibrous zeolites similar to those formally found in Cappadocia (Turkey) may exist along the continuation of the same geological volcanic belts found along the Anatolian – Iranian plate. Discontinuous zones of high risk may even extend from Armenia to Syria as well as straight through Iran where a series of cave like villages reminiscent of Karain appear to exist.

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