# **Chapter 8**

# MINERALOGICAL COMPOSITION OF SOIL SAMPLES IN THE NELLIS DUNES RECREATION AREA

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## **1. Introduction**

Natural dust is primarily composed of mineral grains. A mineral is a substance having a crystalline internal structure and characteristic chemical composition or a definite range of composition that has been formed naturally and occurs in the Earth's crust (Watt, 1982). Most minerals have a characteristic crystal form and physical properties. Characterizing the types of minerals present in dust is an extremely important, but often overlooked task (Guthrie, 1992). Determining the types of minerals present in dust is important because (1) many minerals are known to accumulate in lung tissue and adversely affect health (for example: quartz, mica, gypsum, apatite, talc, rutile, pyroxene, feldspar, numerous clay and zeolite minerals, and numerous serpentine and amphibole minerals, some of which are commonly referred to as 'asbestos') (Guthrie, 1992; Klein, 1993; Ross et al., 1993); and (2) some minerals are highly chemically reactive and can pose increased risk because known carcinogens may be absorbed onto them or they may be bioreactive (Nettesheim and Griesemer, 1978; Guthrie, 1997; Plumlee et al., 2006; Duzgoren-Aydin, 2008). In order to better understand the mineralogy of dusts derived from the surfaces at NDRA, we determined the mineralogy of soil samples from the 17 surface map units and 5 parking areas using x-ray diffraction (XRD)

## 2. Potential health effects of mineralogical components

The harmful effects of some minerals on human health have been recognized for centuries. Hippocrates (460-355 BC) referred to the metal digger as "a man who breathed with difficulty" (Carretero et al., 2006). Pliny the Elder (23-79 AD) described illnesses associated with exposure to mercury (Hg) sulfide dust. Health effects caused by exposure to mineral dusts were sufficiently known by the Middle Ages to be discussed by Agricola in De Re Metallica (1556). In this publication, Agricola noted: "…Some mines are so dry that they are entirely devoid of water and this dryness causes the workmen even greater harm, for the dust, which is stirred and beaten up by digging, penetrates into the windpipe and lungs and produces difficulty in breathing… It eats away the lungs and implants consumption in the body" (Carretero et al. 2006).

Historically, research into potential health effects associated with exposures to mineral dusts has focused on workplace settings, particularly in mining operations extracting or processing asbestos, crystalline silica, coal, and toxic metals including lead (Pb) and mercury (Hg). Recently, the focus has shifted to environmental exposures to asbestos, coal or heavy metal bearing dusts that have been linked to diseases such as asbestosis, silicosis, or coal miners pneumoconiosis, as well as other earth materials such as kaolinite (a clay mineral), soil dusts, cements and other materials containing elements such as calcium (Ca), manganese (Mn), and vanadium (V) whose toxicities are not well known (Duzgoren-Aydin, 2008). Research has demonstrated that mineral dusts primarily cause damage when inhaled, and rarely by ingestion, or penetration into the skin. Several minerals have been shown to produce a variety of pathologies within the lungs including lung cancer, mesothelioma (mesothelial cancer), and pneumoconiosis (the lung loses its capacity to function; Carretero, et al. 2006). Mineral toxicity may be determined in epidemiological studies (evaluating the relationships between human exposure to a hazardous substance and the potential health effects), in vivo studies in which animal models are used to study the effects of mineral dusts on exposed populations, and in vitro studies which focus on determining the biological activity of a mineral (Guthrie, 1992).

Several characteristics are important in determining the biological activity and potential toxicity of minerals. These include particle size and shape, surface properties, dissolution behavior, ion exchange and sorptive properties (Hochella, 1993; Guthrie, 1997; Carretero et al., 2006). Particles with diameters greater than approximately 10 microns ( $\mu$ m) impact the upper reaches of the respiratory tract, and move rapidly up the bronchioles by specially adapted cells that sweep the particles towards the throat. These particles are then cleared and coughed or spit up or swallowed. Particles with diameters of one to two  $\mu$ m are capable of penetrating the deepest regions of the lung. These particles tend to remain in the alveolar walls of the lung because the body's natural clearance processes are not efficient in the deep lung.

Mineral dusts are removed from the lung by multiple mechanisms including exhalation of suspended particles, sequestration of particles by macrophages, relocation through the mucocilliary escalator and lymphatic system, in situ dissolution, or some combination of these mechanisms (Lehnert, 1993; Plumlee et al., 2006). Inflammation and other immune responses to mineral particles may also play a role in disease (Plumlee et al., 2006). Since macrophages are not able to completely engulf mineral fibers that are longer than the cells themselves, phagocytosis of fibers is incomplete and irreversible cell damage and death may result. Many researchers have found that fiber length is one of the most important carceinogenic properties of inhaled minerals (Rödelsperger et al., 1987) ADSTER, 2003). Stanton et al. (1981) developed the "Stanton hypothesis" which relates a fiber's morphology to its activity for the induction of tumors. These researchers stated that the optimum dimensions for the induction of tumors is a diameter <0.25 µm and a length >8 µm. Nolan and Langer (1993) subsequently reported that the "Stanton hypothesis" has some limitations. Other investigators have defined critical fiber dimensions for lung cancer and mesothelioma as <0.3 to 0.8 µm in diameter and >10 to 100  $\mu$ m in length for lung cancer, and 0.1  $\mu$ m in diameter and >5 to 10  $\mu$ m in length for mesothelioma (Carretero et al. 2006). Pott (1989) reported that fiber pathogenicity depends not only on the fiber dimensions, but also on the persistence of the fiber in the lung.

The surface is the portion of a mineral that ultimately interacts with a fluid or cell. In some instances, the surface structure may differ significantly from the "bulk" structure. For example, a mineral undergoing dissolution often forms a precipitate at the surface with a composition and/or structure that differs from the bulk material. Differences in surface related factors relative to the bulk can result in changes in the active sites on the surface, affect binding and sorption processes, alter dissolution characteristics and impact a mineral's pathogenic potential (Guthrie, 1997).

Dissolution may play a significant role in particle clearance mechanisms and can result in the release of metals such as iron or other potentially toxic elements to the lung fluid. Dissolution characteristics are often used to differentiate nonhazardous minerals from potentially hazardous minerals. Nonhazardous minerals typically do not remain in the lung for long periods of time, whereas hazardous minerals may have long residence times in the lung (Guthrie, 1997). One of the ways in which a mineral can interact with a fluid is through exchange of an element or molecule. Most minerals have only a limited capacity for cation exchange because sorption occurs only at the surface. For these minerals, the cation exchange capacity is related to the amount of surface area, and complexation of ions or molecules with the surface may have a significant impact on the reactivity of the mineral (Guthrie, 1997). However, other minerals, including smectites and zeolites, have internal as well as external surface areas. As a result, these minerals are characterized by high cation exchange capacities (CECs) and ions can rapidly diffuse from the mineral surface to its interior.

In summary, the primary factors that influence the health hazards of minerals are: (1) point of entry into the body (skin, ingestion, inhalation); (2) type of response (irritation, fibrosis, cancer); (3) duration of exposure to the particles; (4) particle size; (5) morphology of fibers with diameters <0.25  $\mu$ m and lengths >8.0  $\mu$ m; (6) chemical composition, including high iron content; (7) low solubility at low pH; (8) surface potential; (9) hydrophobic character versus hydrophilic character; (10) in vitro activation of phagocytic leukocytes; and (11) production of hydroxyl radicals that can break the DNA strand which constitutes the first step in genotoxicity and cancer (Carretero et al. 2006; Plumlee et al., 2006). A classification scheme designating mineral particles as Category I (exceedingly dangerous) or Category II (dangerous after continuous and protracted exposure) was developed by van Oss et al. (1999) using factors (5), (7), and (10). For either category, the onset of disease in humans typically occurs after one to several decades. It is also important to note that mineral dust risks are closely associated with cigarette smoking. For the same time period of mineral dust exposure, smokers are more likely to be affected than non-smokers (Carretero et al., 2006).

Inhalation of minerals are the greatest cause of respiratory cancer after cigarette smoking (Omenn et al., 1986). Two well-known illnesses responsible for the majority of human deaths resulting from mineral dust exposure and inhalation are silicosis and asbestosis. Silicosis (a pneumoconiosis type), is caused by exposure to quartz particles and was prevalent during the Industrial Revolution when quartz was a major component of many materials used in a variety of manufacturing processes (Carretero et al., 2006). Asbestosis is a serious illness resulting from the inhalation of asbestos. "Asbestos" is the commercial name for fibrous minerals used in industry. The dust from asbestos minerals produces lung fibrosis than can result in lung cancer or mesothelioma (Lemaire et al. 1989; Guthrie, 1992). Currently six asbestos minerals are regulated in the USA: chrysotile (a serpentine mineral), and five amphibole minerals: crocidolite (riebeckite asbestos), amosite (cummingtonite-grunerite asbestos), anthophyllite asbestos, tremolite asbestos, and actinolite asbestos (Strohmeier et al., 2010).

There is an important difference between fibrous and asbestiform morphologies in minerals. A fibrous morphology describes long, thin crystals. The asbestiform morphology is a special type of fibrous morphology in which the fibers are extremely thin and flexible and occur in aggregates in which individual fibers are aligned in parallel and can easily separate (Strohmeier et al., 2010). Asbestiform crystals typically have a length to width ratio greater than 20:1 (Strohmeier et al., 2010). There are 394 minerals that are known to occur with a fibrous morphology (Skinner et al., 1988). Only a few of these occur with an asbestiform morphology (Strohmeier et al., 2010). Palygorskite is a commonly occurring mineral in desert soils (Brock and Buck, 2009) that almost exclusively occurs in an asbestiform habit (Huggins et al., 1962; Ross et al., 2008). The 5 amphibole minerals that are regulated as 'asbestos', may or may not occur in the asbestiform morphology – only when they have the asbestiform morphology are they regulated (Strohmeier et al., 2010). There is still much disagreement about the potential negative health affects of the non-asbestiform varieties, as well as non-regulated

asbestiform minerals (e.g. Rödelsperger et al., 1987; Wylie and Verkouteren, 2000; ADSTR, 2003; Groppo et al., 2005; Turci et al., 2005; Plumlee et al., 2006; Addison and McConnell, 2008; Harper, 2008; Lee et al., 2008; Duncan et al., 2010).

## 3. Soil mineralogy at Nellis Dunes Recreation Area

### 3.1 Sampling locations

Soil samples were taken from 17 dust stations representing the 17 different surface types in the Nellis Dunes Recreation Area. Additional soil samples were collected from five parking areas. The location of the sampling spots is shown in Fig. 1. All samples were taken from the original desert surface (i.e., outside ORV trails) except for surface units 1.3 and 2.4 (disturbed sand and disturbed silt) and the parking areas, which can be classified as unit 1.3 (disturbed sand areas).



Fig. 1: Location of the sampling sites (blue dots)

### 3.2 Methodology

X-ray diffraction (XRD) analyses were made on all soil samples to determine the mineralogical composition. Four size fractions were investigated:  $<2 \mu m$ , 2-20  $\mu m$ , 20-60  $\mu m$  and 60-100  $\mu m$ . These fractions were separated by centrifugation and sedimentation following rinsing with distilled water. The distilled water rinses were necessary to remove soluble salts from the soils in order to disperse the samples prior to fractionation.

Pastes of K- and Mg-saturated clay ( $<2 \mu m$ ) and silt (2-20  $\mu m$ ) were smeared on glass slides (Theisen and Harward, 1962). The K-saturated sample slides were examined by XRD at 25°C and after heating at 350 and 550°C for two hours. The Mg-saturated samples were also analyzed at 25°C and after being placed in a desiccator containing a pool of ethylene glycol and heated at 65°C for two hours. The desiccator vent was closed upon removal from the oven and the slides stored in the desiccator at least 12 hours prior to XRD analysis. The 20-60  $\mu m$  and 60-100  $\mu m$  size fractions were dried from a water slurry onto glass slides. All samples were examined by XRD (CuK $\alpha$  radiation) using a PANalytical X'PERT Pro diffractometer, equipped with an X'Celerator detector. Additional descriptions of these methods can be found in Reid-Soukup and Ulery (2002) and Soukup et al., 2008.

## 3.3 Results

#### 3.3.1 Mineralogical components

The mineralogical composition of the 20-60  $\mu$ m and 60-100  $\mu$ m fractions of the 17 dust station and 5 parking lot samples is relatively uniform, consisting mainly of quartz and calcite, with lesser amounts of plagioclase and alkali feldspars (Table 1). Over one-half of the samples contain palygorskite; palygorskite is more commonly observed in the finer fractions of the samples. Several of the samples also contain amphiboles and a few contain a trace of kaolinite, gypsum, and mica/illite. Most of the gypsum that may have been present in these samples would have been removed during the distilled water rinses prior to fractionation.

XRD analyses reveal that the mineralogical composition of the clay ( $<2 \mu m$ ) and silt (2-20  $\mu m$ ) fractions of the soil samples at NDRA is dominated by smectite with lesser amounts of mica/illite, kaolinite, quartz, and calcite (Table 1). Nearly all of the samples also contain chlorite, palygorskite, and plagioclase and alkali feldspars. Three of the silt samples contain amphiboles and one sample contains a 1:1 interstratified illite/smectite within the clay and silt fractions. Gypsum was also identified in several samples, although it should be noted that most of the gypsum present would have been removed during the distilled water rinses prior to fractionation.

## 3.3.2 Distribution and occurrence of hazardous minerals

Potentially hazardous minerals in soils at Nellis Dunes include quartz, kaolinite, illite, smectite, and palygorskite. Quartz was identified in all of the particle size fractions analyzed, with only two exceptions (Table 1). Smectite was reported in all of the clay and

Surface	Particle	Minerals <sup>(1)</sup>										
Unit	Size (µm)	Sm	Mi/Ill	Chl	Kao	Paly	Qtz	Cal	Gyp	Fsp	Amph	1:1 Ill/Sm
Sand and Sand-Affected Areas												
1.1	<2	х	х	Х	х	х	х		х			
	2 - 20	х	х	Х	Х	х		х	х			
	20 - 60						Х	х	Х		Tr <sup>(2)</sup>	
	60 - 100						Х	х	Х		Tr	
1.2	<2	х	х	Х	Х	х	х	х	х			
	2 - 20	х	х	Х	Х	х	х	х	х			
	20 - 60					х	х	х	х	Х	Х	
	60 - 100					Tr	Х	Х	Х	Х	Х	
1.3	<2	х	Х	Х	Х	Х	Х	Х	Х			
	2 - 20	х	Х	Х	Х	Х	Х	Х	Х			
	20 - 60					Х	Х	Х	Х	Х		
	60 - 100					Tr	Х	Х	Х	Х		
1.4	<2	Х	Х	Х	Х	Х	Х			Х		Х
	2 - 20	Х	Х	Х	Х	Х	Х	Х		Х	Х	х
	20 - 60		Tr				Х	х		Х		
	60 - 100						Х	х		Х		
1.5	<2	Х	Tr		Х	Х	Х	х				
	2 - 20	Х	Tr	Х	Х	Х		х				
	20 - 60		Tr			Tr	Х	Х		Х		
	60 - 100		Tr			Tr	Х	Х		Х		
Silt/clay A	eas											
2.1	<2	NS <sup>(3)</sup>	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	2 - 20	Х	Х	Х	Х	Х	Х	х	Х	Х		
	20 - 60				Tr	Х	Х	х	Х	Х	Х	
	60 - 100				Tr	Х	Х	Х	Х	Х	Х	
2.2	<2	Х	Х		Х		Х	Х		Х		
	2 - 20	Х	Х	Tr	Х		Х	Х		Х		
	20 - 60						Х	Х		Х		
	60 - 100						Х	Х		Х		
2.3	<2	Х	Х	Tr	Х		Х	Х	Х	Х		
	2 - 20	Х	Х	Х	Х		Х		Х	Х		
	20 - 60		Tr				Х	Х	Tr	Х		
	60 - 100		Tr				Х	Х	Tr	Х		
2.4	<2	Х	Х	Х	Х	Х	Х	Х				
	2 - 20	Х	Х	Tr	Х	Х	Tr	Х				
	20 - 60					Х	Х	Х	Х	Х		
	60 - 100					Tr	Х	х	Х	Х		

Table 1: Mineralogical components in the soil samples

Notes:

(1) Sm = smectite; Mi/III = mica/illite; Chl = chlorite; Kao = kaolinite; Paly = palygorskite; Qtz = quartz; Cal = calcite; Gyp = gypsum; Fsp = feldspar; Amph = amphiboles; 1:1 Ill/Sm = 1:1 interstratified illite/smectite
(2) Tr = Trace amount of mineral detected by x-ray diffraction
(3) NS = no sample available

Surface	Particle	Minerals <sup>(1)</sup>										
Unit	Size (µm)	Sm	Mi/Ill	Chl	Kao	Paly	Qtz	Cal	Gyp	Fsp	Amph	1:1 Ill/Sm
Rock-covered Areas												
3.1	<2	х	х	Х	х	х	х		Tr	Х		
	2 - 20	х	х	Х	х	х	х	х	Х	х		
	20 - 60					Tr	Х	Х	Х	Х		
	60 - 100					Tr	Х	Х	Х	х		
3.2	<2	Х	Х	Х	х	Х	Х	Х	Х	х		Х
	2 - 20	Х	Х	Х	Х	Х	Х	х	Х	х		
	20 - 60					Tr	Х	Х	Х	Х	Х	
	60 - 100					Tr	Х	Х	Х	х		
3.3	<2	Х	Х	Х	Х	Х	Х		Х	х		
	2 - 20	Х	Х	Х	Х	Х	Х	Х	Х	х	Х	
	20 - 60		Х		Tr		Х	Х	Х	х		
	60 - 100				Tr		Х	Х	Х	Х		
3.4	<2	Х	Х	Х	х	Х	Х	Х				
	2 - 20	Х	Х	Х	х	Х	Х	Х				
	20 - 60						Х	Х	Х	Х	Х	
	60 - 100						Х	Х	Х	х		
3.5	<2	Х	Х	Х	х	Х	Х	Х	Х	х	Х	
	2 - 20	Х	Х	Х	х	Х	Х	Х	Х	х		
	20 - 60		Tr	Tr		Tr	Х	Х	Х	х	Х	
	60 - 100		Tr	Tr			Х	Х	Tr	Х		
Drainage A	reas	1										
4.1	<2	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	
	2 - 20	х	Х	Х	х		Х	Х	Tr	х		
	20 - 60					Tr	X	X	X	X		
	60 - 100					Tr	X	X	Х	х		
4.2	<2	X	X	Х	X	Tr	X	X				
	2 - 20	Х	X	Х	х	Tr	X	X				
	20 - 60		Ir			Ir	X	X	1r T	X		
4.2	60 - 100	v	V	т.	v	Τ.	X	X	Ir V	X		
4.5	2 20	X V	A V	I r v	X	11	A V	A V	л Т.	A V		
	2 - 20	л	л	л	л	Τ.,	A V	A V	v	л v	v	
	20 - 60				т.	11 T.	A V	A V	A V	л v	л	
Daubing L	60 - 100				11	11	л	л	л	Λ		
Parking LC	ot Areas											
NA <sup>(4)</sup>	<2	X	X	X	X	X	X	X	X	X		
	2 - 20	х	Х	х	х	Х	X	X	X	X	v	
	20 - 60						X	X	X	X	Х	
NA	60 - 100	v	v	v	v	v	A V	A V	A V	л v		
INA	2 20	A V	A V	л v	A V	A V	A V	A V	A V	л v		
	2 - 20	л	л	л	л	л	л V	x x	л V	x x	v	
	60 - 100						x x	x	x x	x	x x	
NΔ	<2	x	x	x	x	x	x	x	x	x	А	
14/1	2 - 20	x	x	x	x	x	x	x	x	x		
	20 - 60					Tr	x	x	x	x		
	60 - 100					Tr	x	x	x	x		
NA	<2	х	х	х	Х	x	x	x	x	x		
	2 - 20	x	x	x	X	x	x	х	x	x		
	20 - 60	-	-	-		Tr	x	х	x	x		
	60 - 100					Tr	х	х	Tr	х	х	
NA	<2	х	х	Х	Х	х	х	Х	х	Х		
	2 - 20	х	х	Х	Х	х	х	Х	х	Х		
	20 - 60						х	Х	х	Х		
	60 - 100						х	х	х	х		

Table 1 (ctd.): Mineralogical components in the soil samples

Notes: (1) Sm = smectite; Mi/III = mica/illite; Chl = chlorite; Kao = kaolinite; Paly = palygorskite; Qtz = quartz; Cal = calcite; Gyp = gypsum; Fsp = feldspar; Amph = amphiboles; 1:1 III/Sm = 1:1 interstratified illite/smectite (2) Tr = Trace amount of mineral detected by x-ray diffraction (3) NS = no sample available

silt-size samples that were analyzed; illite and kaolinite were also detected in most of the clay and silt-size samples (Table 1). Although palygorskite is widely distributed throughout NDRA, it is most prevalent the <2  $\mu$ m and the 2-20  $\mu$ m size fractions throughout the site.

Although XRD analysis is the standard method to identify the mineral species present, it cannot be used to measure the precise amounts of minerals present. Relative abundances among minerals can be estimated by comparing peak widths and intensities. The sharper and more intense peaks indicate either/both increased relative abundance and/or increased internal crystalline order.

Based on the relative size and sharpness of the peaks, for the grain sizes most likely to be inhaled ( $<2 \mu$ m and the 2-20  $\mu$ m), palygorskite is more abundant in the sandy areas at NDRA (units 1.1, 1.2, and 1.3) and in four of the five parking areas (PLN#1, PLN#2, PLS#1, PLS#2). As discussed previously in Chapter 6, the sandy areas are the most emissive units at the site. The amount of palygorskite in surface units 1.4, 3.2, 3.3, 3.4, and 3.5 is reduced relative to units 1.1, 1.2, 1.3 and the four parking lots. The lowest amount of palygorskite in the two finest grain size fractions was detected in surface units 1.5, 2.1, 2.4, 3.1, 4.1, 4.2, 4.3, and in PLSE#1. Palygorskite was not detected in units 2.2 and 2.3.

## 4. Harmful effects of the different minerals identified at Nellis Dunes Recreation Area

Although quartz and asbestos are the most hazardous minerals to human health identified to date, other clay minerals may be dangerous because of their limited solubility in the lung, reactivity, small particle size, and fibrous morphology. The main harmful effects of the different minerals identified at NDRA are discussed below.

## 4.1 Kaolinite

The pathogenicity of kaolinite appears to be primarily related to the presence of quartz, because kaolinite-bearing rocks typically contain other minerals, including quartz (Carretero et al., 2006). Some workers who received heavy exposures to kaolinite dust have developed pneumoconiosis, although an increased risk of lung cancer was not reported (Ross et al., 1993). Guthrie (1992) reviewed several epidemiological studies and reported that exposure to kaolinite-bearing dust is fibrogenic only when dust

concentrations are very high or exposure is combined with another respiratory disease, such as tuberculosis.

The results of *in vivo* experiments regarding the fibrogenic potential of kaolinite-bearing dusts are not conclusive. Previous investigations have indicated that kaolinite did not induce tumors in Syrian hamsters, while others indicated that a slight fibrogenic response was observed (Carretero et al., 2006). However, Wastiaux and Daniel (1990) reported that prolonged exposure of rats to high concentrations of kaolinite (300 mg m-3) was lethal. Davis (1993) suggested that differences in the kaolin dust dosages used in the experimental inhalation studies may be responsible for the different results.

Kaolinite-bearing dusts have been shown to be cytotoxic to most cell types in several *in vitro* experiments. The capacity of kaolin dusts to damage cells may exhibit significant variation between samples, because of variations in mineralogical characteristics between deposits and the presence of other minerals in varying quantities, particularly silica (Carretero et al., 2006).

## 4.2 Illite and Smectites

There have only been a few epidemiological studies of respiratory disease resulting from exposure to illite and smectite containing dusts. The results of some of these studies indicated that these dusts may elicit a mild fibrogenic response at high exposure levels (Carretero et al., 2006). The results, however, are complicated because of the presence of other minerals such as silica and amphiboles in the dust. For example, the silica content (including quartz and cristobalite) of Wyoming bentonite, which is composed primarily of smectites, ranges from 0 to 24% (Ross et al., 1993).

*In vivo* studies indicate that dusts containing illite and smectite are slightly fibrogenic, and *in vitro* studies suggest that they may be slightly cytotoxic (Guthrie, 1992). The variability in cytotoxicity is apparently due to SiO2 polymorphs (i.e., quartx, cristobalite, tridymite). However, a 1980 study by Daniel and Le Bouffant concluded that most smectite containing dusts were very cytotoxic *in vitro* (Carretero et al., 2006).

Oscarson et al. (1986) studied lysis of red blood cells in bovine by several silicate minerals. These investigators reported that the hemolytic activity of these minerals decreased in the following order smectites > silica > palygorskite > sepiolite > chrysotile (asbestos) > kaolinite.

More recently, Kibanova et al. (2009) studied the ability of three smectites to induce oxidative stress, a primary indicator of cell damage and toxicity. Minerals can cause cell damage because of free radicals. The cell damage is often determined as the progress of lipid peroxidation, the oxidative degradation of lipids in cell membranes. These

investigators concluded that smectites can induce oxidative stress via lipid peroxidation, and that the high concentrations of structural iron (Fe) impacts the ability of the minerals to induce this reaction. However, Kibanova et al. (2009) also indicated that there is still a lack of understanding regarding how smectites and other minerals impact processes such as proton exchange, metal complexation, and electron transfer in the body.

## 4.3 Palygorskite

Palygorskite (sometimes referred to as attapulgite) and its potential effects on human health have been studied fairly extensively, because of its fibrous morphology and use as a substitute for asbestos. The International Agency for Research on Cancer has concluded that palygorskite fibers greater than 5 microns in length are possibly carcinogenic to humans (CIR, 2003). Other studies indicate that the health risks from palygorskite are variable and depend primarily on the fiber length and diameter, and other physiochemical parameters which are controlled by the geological conditions in which it formed (Nolan et al. 1991; Galan, 1996; Carretero et al., 2006). Nolan et al. (1991) studied nine palygorskite specimens obtained from different geological locales that exhibited a range of surface characteristics and found a corresponding range in hemolytic activity. They concluded that experimental data may exhibit variable carcinogeneity for palygorskite depending on its geological origin. These investigators stated that mineral morphology is insufficient to determine a mineral's carcinogenic properties, and that fiber size distribution, surface adsorption characteristics, and stability *in vivo* must be considered when determining whether specific palygorskites will present an inhalation health hazard.

*In vivo* studies of palygorskite have shown that most palygorskite-containing dusts are mildly active in the lung, although some samples can be quite active (Guthrie, 1992). *In vitro* experiments have suggested that palygorskite is as hemolytic as chrysotile asbestos, but in other non-erythrocite cell types it is non-genotoxic, and only slightly cytotoxic (Carretero et al. 2006). Oscarson et al. (1986) studied the lysis of erythrocites by palygorskite and concluded that palygorskite was a lysing agent.

Wagner et al. (1987) performed intrapleural tests with sepiolite and palygorskite in rats, and found no increased incidence of tumors. These minerals produced an interstitial reaction similar to that caused from nuisance dust but did not produce fibrosis. However, these investigators reported mesothelioma in rats that had inhaled sepiolite and palygorskite dusts that contained a significant number of fibers more than 5 to 6  $\mu$ m in length. Similarly, Davis (1993) suggested that fibers greater than 5  $\mu$ m were harmful, whereas materials consisting primarily of short fibers were not.

Lemaire (1991) and Lemaire et al. (1989) studied the reactivity of rat lungs to palygorskite, chrysotile, xonotlite, and some man-made fibrous silicates. The palygorskite

used was less than 1  $\mu$ m in length. Lemaire (1991) found that single intratracheal administration of palygorskite in rates produced granulomas and multinucleated giant macrophages and enhanced IL-1-like activity. Lemaire et al., (1989) found that palygorskite induces some of the histologic and cellular features of asbestos-induced fibrosis. However, they cautioned that their results could not be extrapolated to human exposure conditions.

In desert environments such as NDRA, palygorskite most commonly forms as a pedogenic mineral in petrocalcic horizons, which are colloquially termed 'caliche' (Watts, 1980; Monger and Daugherty, 1991; Brock, 2007; Robins, 2010; Brock and Buck, 2009). It also commonly occurs in less well-developed soils containing calcic pendants (Brock and Buck, 2005; Singer et al., 1995). In arid climates, palygorskite can also precipitate in highly alkaline lake environments, some hydrothermal systems, and from alkaline groundwaters (Callen, 1984; Singer, 1989).



Fig. 2: SEM image of asbestiform palygorskite from Mormon Mesa, NV (from Brock, 2007).

SEM analyses of pedogenic palygorskite from areas near NDRA, show that it has an asbestiform habit, with crystals that often exceed 8  $\mu$ m in length (Fig. 2) (Brock and Buck, 2005; Brock, 2007; Robins, 2010; and Buck, unpublished data). Because the geological and pedological conditions at NDRA are similar to those studied by Brock and

Buck (2005, 2009), Brock (2007) and Robins (2010), this suggests that the palygorskite at NDRA may pose a potential health risk if inhaled. However, determining the morphology and length of the palygorskite at NDRA was beyond the scope of this study. Future research, should characterize the palygorskite present in dusts at NDRA, including its concentration in air, the length to width ratio, and how these characteristics vary across the different map units.



Fig. 3. Epidemiological map of national age-adjusted rates of asbestosis-related mortality by county for U.S. residents age 15+, 1970-1999. (From NIOSH WoRLD, 2006).

An epidemiological map showing age-adjusted rates of asbestosis-related mortality indicates that Clark County has one of the higher national rates (NIOSH WoRLD, 2006; see Fig. 3). There are no known asbestos mines or mineral resources in Clark County (Van Gosen, 2008), which suggests that our high rates of asbestosis-related mortalities may occur from (1) occupational exposures, (2) human exposures prior to people moving here, and/or (3) exposures to non-regulated asbestiform minerals that cause health effects similar to those by regulated asbestos minerals (i.e. Rom et al., 1983). Much more

extensive research is needed to determine whether palygorskite plays a role in pulmonary disease in this region.

## 5. Summary of conclusions

Several minerals including quartz, kaolinite, illite, smectite, and palygorskite are present at NDRA, and are known to have adverse effects on human health when inhaled in large amounts or over a long time period. These minerals can result in different pathologies in the lung including cancer, mesothelioma, or pneumoconiosis. Of special concern at NDRA is the common occurrence of palygorskite, especially in the finest fractions. Because palygorskite is an asbestiform mineral, it has the potential to have health effects similar to the regulated asbestos minerals that are known to cause severe health problems. Future research is needed to determine the morphology of the palygorskite crystals (i.e. length:width ratios), and their airborne concentrations across the many different surface types at NDRA. This information needs to be combined with an assessment of the human exposure to palygorskite at NDRA during different activities (ORV and bystander), on different surface types, and under different wind conditions. Additionally, information concerning the toxicity of dust with mixed mineralogy such as that in the Nellis Dunes is not available. Future research to measure the toxicity of NDRA dust would require the use of animal models, human exposure, and/or epidemiology studies.

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