*Distribution of Potentially Hazardous Phases
in the Subsurface at Yucca Mountain, Nevada*

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Cover Photo: Secondary electron image of erionite in the matrix of a core from drill hole USW UZ-14 (~1364 feet). The scale is 1 cm = 1.7 μ m.

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DISTRIBUTION OF POTENTIALLY HAZARDOUS PHASES IN THE SUBSURFACE AT YUCCA MOUNTAIN, NEVADA

by

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ABSTRACT

Drilling, trenching, excavation of the Exploratory Studies Facility, and other surface- and underground-distributing activities have the potential to release minerals into the environment from tuffs at Yucca Mountain, Nevada. Some of these minerals may be potential respiratory health hazards. Therefore, an understanding of the distribution of the minerals that may potentially be liberated during site-characterization and operation of the potential repository is crucial to ensuring worker and public safety. Analysis of previously reported mineralogy of Yucca Mountain tuffs using data and criteria from the International Agency for Research on Cancer (IARC) suggests that the following minerals are of potential concern: quartz, cristobalite, tridymite, opal-CT, erionite, mordenite, and palygorskite. We have re-evaluated the three-dimensional mineral distribution at Yucca Mountain above the static water level both in bulk-rock samples and in fractures, using quantitative X-ray powder diffraction analysis. Erionite, mordenite, and palygorskite occur primarily in fractures; the crystalline-silica minerals, quartz, cristobalite, and tridymite are major bulk-rock phases. Erionite occurs in the altered zone just above the lower Topopah Spring Member vitrophyre, and an occurrence below the vitrophyre but above the Calico Hills has recently been identified. In this latter occurrence, erionite is present in the matrix at levels up to 35 wt%. Mordenite and palygorskite occur throughout the vadose zone nearly to the surface. Opal-CT is limited to zeolitic horizons.

I. INTRODUCTION

The Yucca Mountain Site Characterization Project of the U.S. Department of Energy is conducting an on-going study of Yucca Mountain, Nevada, and its surroundings to assess the suitability of the area to host the nation's first potential high-level radioactive waste repository. As efforts relating to site characterization intensify, including drilling and excavation of the Exploratory Studies Facility (ESF), a thorough knowledge of the airborne particulates generated through such activities is crucial to worker and environmental safety. It is important to identify any potential hazards related to airborne materials that could impact the safety of workers during mining, drilling, excavation, and other future activities in the area of the potential repository. These materials might be generated during drilling or excavation or released from muck piles. In this report we attempt to address this concern by evaluating potential mineral hazards in relation to mineral distributions and toxicities.

Three-dimensional information on the bulk-rock mineralogy is available from the extensive mineralogy-petrology studies conducted at Yucca Mountain. Los Alamos National Laboratory staff have worked to characterize and to understand the mineralogy and petrology of the rocks at and surrounding Yucca Mountain (Heiken and Bevier 1979; Sykes et al. 1979; Bish 1981; Bish et al. 1981; Caporuscio et al. 1982; Vaniman et al. 1984; Bish and Vaniman 1985). Bish and Chipera (1989) is the most complete and recent summary of the mineralogy of Yucca Mountain rocks obtained through quantitative X-ray powder diffraction analyses of drill core and cuttings. The mineralogical data for bulk-rock samples discussed in this paper are taken from Bish and Chipera (1989), and information on fracture mineralogy is from Chipera and Bish (1989), Bish and Chipera (1991), Carlos (1991), and recent fracture-mineralogy studies that are in press (Carlos et al., 1993). These studies serve as references for any reader interested in the overall distribution of minerals in the vicinity of Yucca Mountain.

In this report, we focus on the distribution of minerals that are present in the subsurface and that may be potential health hazards. Numerous minerals have been suggested as potentially hazardous following inhalation, and some of these occur in the subsurface at Yucca Mountain. In Section II ("Biological Data on Mineral Toxicity"), we summarize the published biological data for minerals that are known to occur at Yucca Mountain. Based on these data, the minerals at Yucca Mountain may be divided into three groups: (1) minerals that clearly represent potential health hazards; (2) minerals that do *not* represent potential health hazards; and (3) minerals that are probably not health hazards, but data on their biological activities are extremely limited. We will discuss the minerals in the first group, because these minerals are extremely important to consider in any risk assessments. We will also discuss the minerals of the third group, because they cannot be eliminated from concern as *potential* health hazards. The distributions of the minerals in the first and third groups are discussed in Section IV. However, we will not discuss the minerals of the second group in this report.

II. BIOLOGICAL DATA ON MINERAL TOXICITY

The biological activities of minerals are generally evaluated using one of three approaches: epidemiological studies, *in vivo* studies, and *in vitro* studies. Epidemiological studies evaluate an agent's health risks by determining the relationships between human exposure to the agent and observable health effects. *In vivo* studies evaluate an agent's health risks by testing the agent on living animals. *In vitro* studies evaluate an agent's activity in simplified systems, such as individual cell types. A more detailed discussion of these methods is given by Guthrie (1992; Guthrie and Mossman, 1993). Data from these three types of studies will be used below to evaluate the biological activities of minerals at Yucca Mountain. Biological activity is used as a measure of a mineral's potential to affect a biological system: A biologically active mineral may induce a response when introduced to cells or animals. However, biological activity does not necessarily imply that a mineral is carcinogenic. Some minerals appear biologically active but do not appear to be carcinogenic in humans. A carcinogenic response in humans results from complex mechanisms that are affected by numerous processes and properties, including (but not limited to) biological activity, particle size and morphology, biodurability, exposure levels and conditions, concurrent exposures to other agents, and genetic factors.

The International Agency for Research on Cancer (IARC) is part of the World Health Organization and is recognized as an authority on carcinogenic substances. Periodically, IARC publishes monographs on the evaluation of the carcinogenicity of various substances to humans. Several of these monographs (IARC, 1971, 1987a, 1987b) explicitly address minerals that occur at Yucca Mountain.

IARC classifies the biological data on an agent with respect to carcinogenicity to humans and animals, the former based on epidemiological data and the latter based on experimental data. The data on an agent's carcinogenic potential for humans or animals are classed as follows (IARC, 1987a):

Sufficient evidence of carcinogenicity—a causal relationship has been established between exposure to the agent and cancer induction;

Limited evidence of carcinogenicity—a positive association has been observed between exposure to the agent and cancer induction for which a causal relationship is possible but for which chance, bias, or confounding cannot be ruled out;

Inadequate evidence of carcinogenicity—available studies are of insufficient quality to permit a conclusion regarding the presence or absence of a causal relationship between exposure to the agent and cancer induction;

Evidence supporting a lack of carcinogenicity—adequate studies show no relationship between exposure to the agent and cancer induction.

Using these summaries, IARC groups each agent based on its carcinogenic potential. The groups indicate the following:

Group 1—the agent is carcinogenic to humans;

Group 2A—the agent is probably carcinogenic to humans;

Group 2B—the agent is possibly carcinogenic to humans;

Group 3—the agent is not classifiable as to its carcinogenicity to humans;

Group 4—the agent is probably not carcinogenic to humans.

Table I lists the minerals known to occur at Yucca Mountain and summarizes the conclusions of the IARC monographs. No minerals at Yucca Mountain are listed as Group 4. Minerals in Groups 1 & 2 should be treated as human carcinogens, and a conservative approach would be to treat minerals in Group 3 as carcinogens unless other factors (as discussed below) suggest otherwise.

While reviewing the summary of carcinogenicity data presented in Table I and in the remainder of this report, it is important to consider several factors, particularly that although a mineral may be shown to be carcinogenic under some conditions, under other conditions the same mineral may not pose a cancer risk. This is because minerals induce carcinogenic responses only under specific conditions. It is generally believed that most minerals are only of concern if they remain in contact with the respiratory tract for extended periods. Consequently, only minerals occurring as respirable particles (*i.e.*, $< \sim 10 \mu\text{m}$) can pose a potential risk. Furthermore, the respiratory tract possesses numerous defense mechanisms against inhaled particles, and most of these involve removal or isolation of a particle. These defense mechanisms can fail, however, if the particle has a fibrous shape or if the respiratory tract is overloaded with particles. (This latter condition should not result from modern mining practices.) Finally, a particle must possess specific physical and chemical properties so that it does not dissolve rapidly and it induces the biochemical responses that lead to carcinogenesis. These criteria can eliminate concern over mineral under some conditions, regardless of whether the mineral poses a risk under other conditions.

Table I: Summary of the potential risk posed by minerals at Yucca Mountain.

Mineral	Data for carcinogenicity [†]		Ranking by IARC [†]	Concern at Yucca Mountain
	humans	animals		
quartz	L	S	Group 2A	Y
cristobalite	L	S	Group 2A	Y
tridymite	L	S	Group 2A	Y
opal-CT	(L)	(S)	NL (Group 3)	Y
glass [‡]				N
amorphous silica	I	I	Group 3	
glasswool	I	S	Group 2B	
erionite	S	S	Group 1	Y
mordenite	(ND)	(I)	NL (Group 3)	Y
clinoptilolite/ heulandite	(ND)	(I)	NL (Group 3)	N
chabazite	(ND)	(ND)	NL (Group 3)	N
stellerite	(ND)	(ND)	NL (Group 3)	N
phillipsite	(ND)	(ND*)	NL (Group 3)	N
palygorskite [∞]	I	L	Group 3	Y
smectite	(I)	(I)	NL (Group 3)	N
mica	(I)	(I)	NL (Group 3)	N
kaolinite	L	L	NL (Group 3)	N
feldspar	(I)	(I)	NL (Group 3)	N
hematite	I	I/ESL [§]	Group 3 [§]	N
fluorite	(ND)	(ND)	NL (Group 3)	N
calcite	(I)	(I)	NL (Group 3)	N
Mn-oxides	(I)	(I)	NL (Group 3)	N

[†] Described in the text. Data taken from IARC monographs 1 (1971), 42 (1987), and 43 (1988) and IARC *Supplement 7* (1987). "NL" indicates that the mineral was not listed by an IARC monograph through Vol. 54 (1991). Data in parentheses represent our evaluations using the criteria outlined in IARC *Supplement 7* (1987).

[‡] "ND" indicates no data; "ESL" indicates evidence suggesting lack of carcinogenicity; "I" indicates inadequate; "L" indicates limited; "S" indicates sufficient. Data taken from IARC monographs 1 (1971), 42 (1987), and 43 (1988) and IARC *Supplement 7* (1987). Data in parentheses represent our evaluations using the criteria outlined in IARC *Supplement 7* (1987).

[§] "Glass" can be bracketed by amorphous silica and glasswool.

[∞] Palygorskite is listed as "attapulgitite" by the IARC monographs; however, "attapulgitite" is not an accepted mineral-species name.

[§] *Supplement 7* (IARC, 1987) lists hematite at "I" for animal data and lists ferric oxide as "ESL." There is no discussion regarding the difference between ferric oxide and hematite, although hematite is ferric oxide. Although hematite is listed as Group 3 in *Supplement 7* (IARC, 1987), a combined hematite+radon exposure during underground mining is listed as Group 1.

• No study has been published in the western literature on phillipsite carcinogenicity. See text.

For example, consider the risk posed by exposure to quartz. Quartz is ubiquitous at the earth's surface (*e.g.*, in beach sand, soils, and airborne dusts), so each of us is exposed to quartz daily. Cancer induction by quartz is generally believed to require high prolonged exposures and, possibly, concurrent exposure to other agents. Although quartz may be carcinogenic under some conditions, one can be exposed to quartz under most conditions and not be at risk. In other words, the typical level of precaution applied to exposures to other carcinogens may not be appropriate for quartz. This is not meant to ignore the data suggesting that quartz is carcinogenic, but rather it is to acknowledge that minerals induce a carcinogenic response by mechanisms that are very different from the mechanisms for other carcinogens, such as benzo[*a*]pyrene (a carcinogenic component of coal tar and cigarette smoke).

Finally, it is important to remember that human systems are capable of handling exposures to some levels of dusts, and risk due to exposures to minerals may be maintained at acceptable levels by minimizing (but not necessarily eliminating) dust levels. Furthermore, carcinogenic minerals induce their response by a physical contact with the respiratory tract, and a dissolved or suspended form of the mineral would not be expected to induce the same response.

III. REVIEW OF DATA

In this section, we briefly discuss the biological information available for those minerals at Yucca Mountain that represent potential health hazards, including: quartz, tridymite, cristobalite, opal-CT, glass, erionite, mordenite, clinoptilolite/heulandite, phillipsite, palygorskite, smectite, mica, feldspar, calcite, and Mn-oxides. For those minerals not listed by IARC, we use this information to develop an evaluation consistent with those in the IARC monographs, and our final analysis is given in Table I in parentheses. A more detailed discussion of the biological data on many of these minerals is given by Guthrie (1992).

A. Silica

Crystalline Silica

The biological activities of several of the crystalline silica polymorphs have been evaluated, although most of the research has focused on quartz, cristobalite, and tridymite. The data for these minerals were sufficient for IARC to list all crystalline varieties of silica as Group 2A, albeit two of the polymorphs (stishovite and coesite) exhibit at most minor biological activities (*e.g.*, Stalder and

Stöber, 1965; Brieger and Gross, 1966, 1967; Driscoll, 1993). Quartz, tridymite, and cristobalite have been the focus of numerous epidemiological, *in vitro*, and *in vivo* studies, which have demonstrated a link between the exposure to silica-bearing dusts and fibrosis and tumors in humans and laboratory animals (for reviews, see Heppleston, 1984; Holland, 1990; Saffiotti, 1992; Saffiotti et al., 1993). Generally, however, silica represents a significant risk only at high exposures, and epidemiological data suggest that, in humans, concurrent exposures to silica and other agents (*e.g.*, radon) are important determinants of actual risk (*e.g.*, McLaughlin et al., 1992). Consequently, crystalline silica minerals at Yucca Mountain would only pose a health hazard at high dust levels for prolonged periods, particularly in poorly ventilated areas.

Opal-CT

Opal-CT is not discussed explicitly in the IARC monographs, nor has it been studied extensively with respect to biological activity. As a conservative approach, we have treated opal-CT as a form of crystalline silica in Table 1. In fact, IARC defines "crystalline" as any material exhibiting structural periodicity that can be detected by X-ray diffraction, which would apply to opal-CT.

Glass

The glassy material in the tuffs at Yucca Mountain is difficult to categorize with respect to biological activity. A conservative estimate for the biological activity of this material can be derived from IARC's evaluations for amorphous silica and glasswool, because the compositions of these two categories bracket the compositions for the glassy-tuff material. This estimate would imply that the glassy-tuff material would be Group 2B, at most. However, the glassy-tuff material from Yucca Mountain is non-fibrous, particularly when compared with the material used to determine the biological activities of amorphous silica and glasswool. Consequently, we conclude that the potential cancer risk associated with the glassy material in the tuffs of Yucca Mountain is indeterminate but probably lower than Group 2B (*i.e.*, Group 3).

B. Zeolites

The biological activity of erionite (a fibrous zeolite) has been studied extensively, and all data indicate that it is extremely active in humans, *in vivo*, and *in vitro*. Limited data on other zeolites are less conclusive, particularly in light of the poor quality of the samples studied.

Erionite

Epidemiological data suggest that exposure to erionite-bearing dusts increases the risk of mesothelioma (a rare, asbestos-related cancer) in humans, even at much lower exposure levels than required for any of the asbestos minerals. Early epidemiological studies in the Cappadocian region of Turkey revealed outbreaks of asbestos-related respiratory diseases, including mesothelioma (Ross et al., 1993). The mesotheliomas were later recognized to result from non-occupational exposures to erionite (*e.g.*, Baris et al., 1987; Sébastien et al., 1984; Ross et al., 1993).

The most disturbing implication of the observations in Turkey is that erionite is capable of inducing mesothelioma in humans at low exposures. Baris et al. (1987) reported total fiber levels in the villages from 0.004–0.175 fibers/ml, and these measurements included other dusts in addition to zeolite. Simonato et al. (1989) reported newer estimates of fiber characteristics in Karain and Sarihidir (two of the affected villages) and found levels to be 0.002–0.010 fibers/ml (~80% zeolite) and 0.001–0.029 fibers/ml (~60% zeolite), respectively. The current regulatory standard for occupational asbestos exposure in the U.S. is <0.2 fibers/ml. In other words, the above studies suggest that erionite can induce mesotheliomas at exposures 1–2 orders-of-magnitude lower than the U.S. regulatory limits for occupational exposure to asbestos.

In vivo experiments have further demonstrated the high biological activity of erionite-bearing dusts (see review by Davis, 1993). For example, Wagner et al. (1985) induced mesotheliomas in 100% (40 out of 40) of the rats they exposed to Oregon erionite, with a mean survival time of 390 days. For comparison, in the same experiment, they induced mesotheliomas in 47.5% (19 in 40) of the rats exposed to chrysotile (a type of asbestos), with a mean survival time of 678 days. With respect to erionite, they stated “No other dusts we have investigated have produced this high incidence of tumours particularly following inhalation.”

IARC lists erionite at Group 1: The agent is carcinogenic to humans. In light of the Turkey studies, exposure to airborne erionite should be minimized. Figure 1 shows a scanning electron microscope (SEM) secondary-electron image of erionite from a fracture in USW GU 3, illustrating the fibrous nature of erionite from Yucca Mountain.

Mordenite

No epidemiological studies have been published on the effects of human exposure to mordenite. However, several experimental studies have investigated the biological activities of this mineral. In general, these studies concluded that mordenite is much less biologically active than erionite.

Figure 1: Secondary-electron image of erionite from a fracture in sample USW GU 3 1189.3/6.

In vivo experiments by Suzuki and Kohyama (Suzuki, 1982; Suzuki and Kohyama, 1984, 1988) suggest that a mordenite-bearing dust is fibrogenic but non-carcinogenic following intraperitoneal injection in mice. (In the same experiments, Suzuki and Kohyama found erionite to be both fibrogenic and carcinogenic.) However, they described the mordenite sample as consisting of both granular and fibrous morphologies, implying that their sample contains more than one mineral species. Indeed, quantitative X-ray diffraction of this mordenite-bearing sample has shown that it contains ~63.5% impurities, including clinoptilolite, feldspar, opal-CT, and gypsum (Guthrie, 1993). Hence, the biological data published by Suzuki and Kohyama apply to an *impure* mordenite sample.

In vitro experiments by two groups suggest that mordenite-bearing dust is relatively inactive in a variety of assays (Hansen and Mossman, 1987; Mossman et al., 1989). However, the mordenite sample used in these experiments is highly impure. Quantitative X-ray diffraction of this mordenite-bearing sample has shown that it contains ~50.5% impurities, including clinoptilolite, feldspar, and opal-CT (Guthrie, 1993). Hence, the biological data on the *in vitro* activity of mordenite apply to an *impure* mordenite sample.

Figure 2: Secondary-electron images of mordenite from fractures in samples USW G4 1566 (a) and USW G4 1788 (b).

No published studies have concluded mordenite to be carcinogenic, albeit some studies have shown it to be fibrogenic and mildly biologically active. Nevertheless, because the two mordenite samples that account for all published biological data are highly impure, the biological activity and carcinogenic potential of pure samples of mordenite remain unreported. In light of the extreme biological activity of erionite, the fibrous nature of mordenite, and the uncertainties associated with pure mordenite's biological activity, we conclude that (1) the biological activity of mordenite warrants more investigation, particularly using pure samples of mordenite; (2) an evaluation of the published mordenite data using the approach followed by IARC would result in a classification of mordenite in Group 3; and (3) the potential cancer risk associated with mordenite exposure at Yucca Mountain is indeterminate. However, although mordenite at Yucca Mountain has a fibrous habit (Fig. 2), limited SEM examination of air filters obtained during the cutting of mordenite-rich Yucca Mountain tuff revealed no fibrous material (Fig. 3), despite the presence of mordenite on the filters (as determined by X-ray diffraction analysis). This suggests that the mordenite in the tuff at Yucca Mountain might be released in non-fibrous aggregates during cutting (and possibly drilling and boring), which would minimize any risk posed by mordenite exposure at Yucca Mountain.

Figure 3: Scanning electron micrographs of dust particles collected by air sampling at the SMF during the cutting of mordenite-rich rock. (a) #208; (b) #212; (c) #216. Note the absence of fibrous material, despite the presence of mordenite (as confirmed by X-ray diffraction analysis).

Clinoptilolite and Heulandite

No epidemiological studies have been published on the effects of human exposure to clinoptilolite or heulandite. Limited data have been published on the experimental investigation of the biological activities of these minerals (*e.g.*, Guthrie et al., 1992), and no *in vivo* data have been published in the western literature. Several Russian articles reported data on clinoptilolite. We are currently obtaining English translations of the articles in order to evaluate the applicability of these

studies to Yucca Mountain samples. No published studies have concluded clinoptilolite or heulandite to be carcinogenic. We are currently obtaining complete English translations for the Russian articles to evaluate the implications of these data for Yucca Mountain. However, based on our study, the biological data suggest that clinoptilolite is much less biologically active than erionite on a mass- or particle-basis, although it may be as cytotoxic as erionite on a surface-area-basis (Guthrie et al., 1992). Nevertheless, these minerals have non-fibrous morphologies. We conclude that (1) an evaluation of the published clinoptilolite/heulandite data using the approach followed by IARC would result in a classification of these minerals in Group 3 (due to the paucity of biological data); and (2) the potential cancer risk associated with clinoptilolite and heulandite exposure at Yucca Mountain is indeterminate but probably low (due to their particle morphology).

Phillipsite

No epidemiological studies have been published on the effects of human exposure to phillipsite, and no experimental data have been published in the western literature on its biological activity. One Russian article reported data on phillipsite. We are currently obtaining an English translation of the article in order to evaluate the applicability of the study to Yucca Mountain samples. The particle morphology of phillipsite is generally non-fibrous, and the abundance of this mineral at Yucca Mountain is low (only 2 known occurrences, thus far). We conclude that (1) the absence of published data on the biological activity of phillipsite would result in a classification of phillipsite in Group 3; and (2) the potential cancer risk associated with phillipsite exposure at Yucca Mountain is indeterminate but probably low (due to its particle morphology and low abundance).

C. Other Silicates

Palygorskite

Epidemiological data suggest that exposure to palygorskite-bearing dusts may increase the risk of lung cancer among some ethnic groups. Waxweiler et al. (1988) studied a cohort of 2302 miners and millers from a U.S. "attapulgit" company and reported *slight* excesses of lung cancers for whites only. Other epidemiological studies have confirmed the little-to-no risk associated with exposure to palygorskite, particularly for those with at most moderate exposures for short terms (see review by Ross et al., 1993). *In vivo* experiments have suggested that palygorskite-bearing dusts are mildly active in the lung, though some samples can be very active. For example, Wagner (1982) observed mesothelioma rates of 12.5 – 25% for palygorskite in rats compared with a rate of 22.5% for chrysotile asbestos, and Pott et al. (1974, 1990) found that palygorskite is carcinogenic at rates from 3.5 – 40% following intrapleural injection in rats. In contrast, Jaurand et al. (1987)

found that palygorskite is non-tumorigenic in rats, whereas in the same experiments, chrysotile asbestos induces tumors at a rate of 19 – 52%, depending on particle size. In other words, the biological activity of palygorskite (as determined by *in vivo* techniques) appears to vary between samples. In general, however, most studies report much lower activities for palygorskite than for asbestos. Although palygorskite appears to be carcinogenic under some conditions *in vivo*, the epidemiological data suggest that the risk of lung cancer is still relatively low, even following exposure to quantities larger than expected at Yucca Mountain. Indeed, IARC lists palygorskite as Group 3, due to the insufficient evidence implicating palygorskite as a human carcinogen. Hence, we conclude that the potential cancer risk associated with palygorskite exposure at Yucca Mountain is probably low. Nevertheless, due to the limited amount of biological data available on the biological activity of palygorskite, exposure to airborne palygorskite dust should probably be minimized. Figure 4 shows an SEM secondary-electron image of palygorskite from a fracture in USW G4.

Figure 4: Secondary-electron image of palygorskite from a fracture in sample USW G4 70.1/.5.

Smectite and Mica

Smectite and mica are common minerals at the Earth's surface, occurring in many soil and rock types. Most published studies on the biological activities of 2:1 layer silicates (including smectite and micas) suggest that these minerals can be extremely active at the cellular level. In addition, *in vivo* experiments suggest that these minerals are fibrogenic but non-carcinogenic (e.g., Pott et al., 1974, 1990; Rosmanith et al., 1990; Schyma, 1990). Epidemiological studies confirm this; however, the epidemiological studies also suggest that exposures resulting from modern mining conditions may not pose a significant risk. These minerals have tabular morphologies, so they may be cleared more rapidly from the lung than fibrous minerals. Hence, we conclude that (1) an evaluation of the published smectite/mica data using the approach followed by IARC would result in a classification of these minerals in Group 3 (due to the relatively limited epidemiological and *in vivo* data); and (2) the potential cancer risk associated with exposure to these minerals is indeterminate but probably low (due to their particle morphologies and the lack of evidence showing carcinogenicity in animals). Our evaluations for smectite and mica are consistent with IARC's evaluation for talc (another 2:1 layer silicate).

Kaolinite

Although this mineral may be cleared rapidly from the lung (and, hence, is not pathogenic in humans), its *in vivo* and *in vitro* activities may provide clues to the mechanisms of mineral-induced pathogenesis. Epidemiological studies suggest that kaolinite is fibrogenic only under extraordinary conditions—i.e., high dust conditions or exposure combined with another respiratory disease, such as tuberculosis (e.g., Kennedy et al., 1983; Oldham, 1983; Sepulveda et al., 1983). *In vivo* experiments reported thus far on the fibrogenic potential of kaolinite are inconclusive (see Guthrie, 1992, for reviews). Most recent *in vivo* studies of the pulmonary effects of kaolinite suggest that kaolinite is not carcinogenic (e.g., Mossman and Craighead, 1982; Wagner, 1990), although it may be mildly fibrogenic (Wastiaux and Daniel, 1990). Finally, *in vitro* experiments suggest that kaolinite can be highly active at the cellular level (e.g., Low et al., 1980; Dubes and Mack, 1988). The apparent discrepancy between the *in vivo* and *in vitro* data probably reflects kaolinite's non-fibrous morphology (i.e., kaolinite's tabular morphology may facilitate its clearance from the lung and prevent it from being highly pathogenic in humans). Hence, we conclude that an evaluation of the published data using the approach followed by IARC would result in a classification of kaolinite in Group 3. Indeed, IARC has not even listed kaolinite, despite kaolinite's widespread use in industrial settings. Furthermore, we conclude that the potential cancer risk associated with exposure to kaolinite is probably low.

Feldspar

Feldspar is the most common group of minerals at the Earth's surface. Limited data on the biological activities of feldspar (*e.g.*, Marks and Nagelschmidt, 1959; Pott and Friedrichs, 1972) suggest that this mineral is mildly active, at most. No published studies suggest that feldspar is carcinogenic in either humans or animals. If exposure to feldspar represented a major carcinogenic risk, an epidemiological link would likely have already been recognized, considering feldspar's widespread distribution. The morphology of feldspar is non-fibrous. We conclude that (1) an evaluation of the published feldspar data using the approach followed by IARC would result in a classification of this mineral group in Group 3 (due to the paucity of biological data); and (2) the potential cancer risk associated with feldspar exposure at Yucca Mountain is indeterminate but probably low (due to its particle morphology and its apparent biological inertness).

D. Other Minerals

Calcite

The paucity of published data on the biological activity of calcite makes an evaluation of its carcinogenic potential impossible. However, no published studies have suggested that calcite is carcinogenic in either humans or animals. If exposure to calcite represented a major carcinogenic risk, an epidemiological link would likely have already been recognized, considering calcite's widespread distribution the Earth's surface. The morphology of calcite is generally non-fibrous. We conclude that (1) an evaluation of carcinogenic risk due to calcite using the approach followed by IARC would result in a classification of this mineral group in Group 3 (due to the paucity of biological data); and (2) the potential cancer risk associated with calcite exposure at Yucca Mountain is indeterminate but probably low (due to its particle morphology and its apparent biological inertness).

Mn-Oxides

Most studies of oxide-bearing dusts suggest that some samples can produce fibrosis *in vivo* but are relatively inactive minerals (*e.g.*, hematite). Exceptions may include oxides containing Cr (not necessarily mineral samples). IARC does not list Mn-oxides, nor does it list any Mn compounds. The paucity of published data on the biological activity of the Mn-oxides makes an evaluation of their carcinogenic potential impossible. The abundance of these minerals at Yucca Mountain is so low that even if they were carcinogenic, their occurrence would probably present only a low risk, at most. We conclude that (1) an evaluation of carcinogenic risk due to Mn-oxides using the approach followed by IARC would result in a classification of this mineral group in

Group 3 (due to the paucity of biological data); and (2) the potential cancer risk associated with exposure to Mn-oxides at Yucca Mountain is indeterminate but probably low (due to their low abundance).

IV. ANALYTICAL METHODS

The potential hazards of a particular airborne phase hinge directly on its distribution in the rocks at Yucca Mountain, *i.e.*, whether or not it is present and, if present, what its abundances are. Thus it is important to outline how rocks are analyzed for their mineral content, how both qualitative and quantitative analyses are performed, what the detection limits are for a particular phase, and how precision and accuracy are determined. Because of the limitations inherent in sampling fractures, their mineralogy is necessarily qualitative and we report here only the presence or absence of a given mineral. These limitations include: (1) field and laboratory sampling of fracture minerals is limited and sporadic (e.g., most information is obtained from limited amounts of drill core); (2) vertical sampling of vertical fractures provides a poor statistical estimation of fracture characteristics; (3) the total amount of material along a fracture is extremely small compared with the matrix; and (4) coverage of fracture surfaces by minerals is sporadic. Consequently, quantitative estimates of a mineral's abundance would be meaningless.

The X-ray data presented in Appendix A (Bish and Chipera, 1989) were obtained primarily from core samples, with some bulk-rock data obtained from either drill-cutting or sidewall samples. The locations of the drill holes studied are shown in Fig. 5. Depths are known for both core and sidewall samples, but depths for drill cuttings are approximate within a range of about 10 ft (3.28 m). Most X-ray data were obtained on samples ground under acetone to $<5\text{ }\mu\text{m}$ in an automatic Brinkmann Micro-Rapid mill with an agate mortar and pestle. The particle size distributions of the samples were verified using a Horiba CAPA-500 centrifugal particle size distribution analyzer calibrated with glass microsphere standards. This fine crystallite size is necessary to ensure adequate particle statistics and to minimize primary extinction (Klug and Alexander 1974, pp. 365-367). A portion of most samples was mixed with a $1.0\text{-}\mu\text{m}$ corundum (Al_2O_3) internal standard in the ratio 80% sample to 20% internal standard. Powders resulting from the above preparation treatment were mounted in a cavity in a glass, aluminum, or stainless steel slide with a sample area sufficient for the sample to contain the X-ray beam at angles as low as $8.0^\circ 2\theta$. Fracture-filling samples were rarely present in amounts sufficient for quantitative analysis. Typically these samples had to be prepared by hand grinding in a small corundum mortar-and-pestle under acetone and mounting as a slurry on an off-axis-cut ("zero-background") quartz plate.

Contour Interval = 100 ft (30.5 m)
Figure 5: Location of the drill holes at Yucca Mountain from which the mineral distributions were determined.

All X-ray powder diffraction data were obtained with an automated Siemens D-500 diffractometer using Cu- $K\alpha$ radiation. Most data were collected automatically in the step-scan mode from 2.0° to $50.0^\circ 2\theta$, with a step size of $0.02^\circ 2\theta$ and count times of at least 2.0 s per step. Fracture samples were typically run overnight from 2.0° to $70.0^\circ 2\theta$, with a step size of $0.02^\circ 2\theta$ and count times of at least 16.0 s per step. Analyses for trace phases such as erionite employed count times as long as 360 s/step to improve detection limits.

Mineral identification was accomplished by comparison of observed diffraction patterns with standard patterns measured in this laboratory, by comparison with published standards from the Joint Committee on Powder Diffraction Standards (JCPDS), and by comparison with patterns calculated using the program POWD10 (Smith et al. 1982). Clay mineral standards were obtained from the Clay Minerals Society Source Clay Repository, and zeolite standards were obtained from the Minerals Research Corporation, Clarkson, New York.

A. Quantitative Analyses

Qualitative identification of the crystalline phases present in tuffs can be accomplished quickly and accurately using X-ray powder diffraction. The factors making optical identification of minerals ambiguous, such as the very fine-grained and intergrown texture of the tuffs, do not affect X-ray powder diffraction analyses. However, quantitative multicomponent analysis of rock samples is not straightforward and is complicated by numerous factors (Bish and Chipera, 1988). These factors include variations in degree of preferred orientation of crystallites, variations in crystallite size, variations in degree of crystallinity (crystal perfection), and variations in composition (solid-solution effects). In addition, the diffraction patterns from these complex mixtures of minerals often show peaks from at least six different phases. Thus the method of obtaining intensities from these complex patterns with numerous overlapping peaks can significantly affect quantitative results. Finally, because all our quantitative analyses require the use of standards, the choice of standards plays a crucial role. It is important that standards be as similar to the minerals in the rocks as possible.

Although some older analyses, and several recent analyses of samples for which amounts were insufficient, employed the external standard or adiabatic method of Chung (1974a, 1974b), most recent analyses employed the internal standard or "matrix-flushing" method of Chung (1974a, 1974b) with 1.0- μm corundum as the internal standard. Both methods require that reference intensity ratios (RIRs) be determined before quantitative analysis. We have therefore experimentally determined RIRs, the ratio of the integrated intensity of a given reflection of the phase of interest to the integrated intensity of the 113 reflection of corundum in a 1:1 mixture by

weight, for most phases found in Yucca Mountain tuffs. The 1:1 ratio of standard to sample was chosen for convenience. In practice any ratio can be used for standardization because the relative amounts of standard and sample are incorporated into the reduction of standard runs. RIR values used in our analyses are given in Bish and Chipera (1989), together with sources of materials. In the absence of sufficient pure material, RIRs for some phases (e.g., tridymite) were calculated using the program POWD10 (Smith et al., 1982); however, as pure material was obtained, experimental RIRs were determined.

The effects of preferred orientation and chemistry on the mordenite diffraction pattern were compensated by using a procedure similar to that used for clinoptilolite (Bish and Chipera, 1989). The ratio of the mordenite 9.8° and $19.6^\circ 2\theta$ peaks was determined experimentally and an appropriate RIR was then used. However, mordenite usually coexists with clinoptilolite, making use of the $9.8^\circ 2\theta$ mordenite 200 reflection impossible because of interference with the $9.8^\circ 2\theta$ clinoptilolite 020 reflection. In these cases, we used an RIR for the $19.6^\circ 2\theta$ peak. The strong $25.6^\circ 2\theta$ mordenite reflection cannot be easily used because of interference with both feldspar and corundum internal standard reflections.

Older analyses used a calculated RIR for tridymite, but recent analyses used an RIR measured on a tridymite-rich sample from Yucca Flat, Nevada Test Site, Nevada. An RIR for tridymite was chosen that yielded a matrix-flushing-analysis total of 100% for this sample, including the other crystalline phases present in the sample. The RIR for tridymite is thus of lower precision than RIRs for other samples that can be obtained in pure form. Older analyses also included opal-CT with cristobalite, but recent analyses separated the two, using an RIR for opal-CT measured on two natural samples between 21.0° and $22.1^\circ 2\theta$.

All analyses used integrated intensities rather than peak heights. The use of integrated intensities compensates for several sample-related problems, including variations in crystallinity and crystallite size. Most integrated intensities were obtained using the Siemens first-derivative peak-search routine that yields precise intensities for resolved peaks. However, this routine divides the intensity of overlapping peaks at the midpoint between the two, which is only an approximation for most peaks. Closely overlapping or very broad peaks were measured by planimetry, and completely overlapping peaks were not decomposed. Overlapping tridymite and cristobalite peaks in samples from USW WT1 and USW WT2 were decomposed using a Siemens profile-refinement routine with a Gaussian profile function. However, more recent analyses employed manual planimetry, which we found to be superior to the profile-refinement results.

As noted above, we solved the internal standard equation of Chung (1974a) to analyze for amounts of individual phases when an internal standard was used:

$$X_i = \frac{X_c}{K_{i,n}} \frac{I_{i,n}}{I_c} \quad (1)$$

where X_i is the weight fraction of component i , $K_{i,n}$ is the RIR for line n of component i , X_c is the weight fraction of corundum in the sample (commonly 20%), $I_{i,n}$ is the integrated intensity of line n of component i , and I_c is the integrated intensity of the corundum 113 reflection. It is important to note that this method does not require that the sum of the phases be equal to 100%. Therefore, amounts of glass or other amorphous material such as opal-A can be determined by assuming that the difference between the total crystalline phases and 100% is due to amorphous components.

For older analyses and the recent analyses in which amounts of sample were insufficient for an internal standard analysis, we solved the external standard equation derived by Chung (1974b):

$$X_i = \left(\frac{K_{i,n}}{I_{i,n}} \sum_{j=1}^{j=m} \frac{I_{j,n}}{K_{j,n}} \right)^{-1} \quad (2)$$

where X_i is the unknown weight fraction of phase i in the rock, $K_{i,n}$ is the RIR for line n of phase i , $I_{i,n}$ and $I_{j,n}$ are the integrated intensities of line n for phases i and j , respectively, and m is the number of phases in the mixture. This equation differs from Eq. (1) in that it is derived using the constraint that the sum of all phase equals 100%. Both Eqs. (1) and (2) “flush” out the mass absorption coefficients by ratioing the RIRs for each phase. Both the internal- and external-standard methods of analysis have been incorporated into the program QUANT.

B. Precision of Analyses

Numerous factors affect the precision of these quantitative analyses. Some can be explicitly accommodated and others must be approximated. Factors attributable to the sample or to the sample preparation process include solid solution, other variations in composition, and preferred orientation. Errors resulting from these factors are primarily attributable to differences between samples and standards. Other potentially important errors are encountered in data analysis, such as peak overlap, peak integration, counting statistics, and peak-versus-background discrimination. Many of these errors are either canceled or can be determined during experimental measurement of RIRs. For example, errors due to preferred orientation will be compensated for if the standards exhibit the same degree of preferred orientation as the samples to be analyzed. Errors due to peak integration and peak-versus-background discrimination are typically similar for

samples and standards and thus tend to be corrected implicitly. However, errors may be significantly increased in our samples because of the presence of numerous phases with overlapping peaks. In these cases, errors due to partial or complete peak overlap, leading to problems in peak integration, are not explicitly accounted for. Therefore, we have incorporated a section of code into QUANT that can consider the presence of known combinations of phases in the tuff samples and allows for the resulting peak overlaps when calculating relative errors. We consider both the errors in RIRs and the presence of overlapping pairs of phases when calculating errors. Included among the latter are the effect of the presence of (1) smectite on the relative errors for mordenite; (2) mordenite on clinoptilolite; (3) mordenite on feldspar; (4) feldspar on mordenite; (5) feldspar on cristobalite; (6) clinoptilolite on mordenite; (7) clinoptilolite on quartz; (8) clinoptilolite on feldspar; (9) tridymite on cristobalite; (10) tridymite on feldspar; and (11) opal-CT on clinoptilolite. The resulting relative errors are thus increased by every peak overlap for the sample, and we believe the reported errors for internal-standard analyses are conservative. Errors for external-standard analyses are typically larger than those inherent in internal-standard analyses.

C. Detection Limits

Most analyses of bulk-rock or fracture mineralogy were not optimized for detection of trace phases and instead concentrated on major and minor phases. It is important to note that low detection limits are usually unimportant for some of the common minerals at Yucca Mountain, such as quartz, because these minerals occur in virtually all samples. Detection limits for most phases are <1%, and detection limits for minerals with high RIR values (e.g., quartz, cristobalite) are lower than for minerals with low RIR values (mordenite). Low detection limits are more important for minerals with a sporadic distribution, such as erionite, mordenite, and palygorskite, and in many cases, these minerals were identified in fracture samples or materials that had been manually concentrated. In addition, analysis of fracture mineralogy usually gave lower detection limits because data collection was performed overnight. Because of the documented toxicity of erionite, data-collection methods for the detection of erionite were specially optimized, giving detection limits between 100 and 500 ppm (Chipera and Bish, 1989; Bish and Chipera, 1991). These methods involved collection of X-ray diffraction data in the step-scan mode from 6 to 9° 2 θ , counting for at least 120 s every 0.02° 2 θ .

V. MINERAL DISTRIBUTIONS AT YUCCA MOUNTAIN

Quantitative mineral analyses are presented in tabular form in Bish and Chipera (1989) and are not reproduced here. However, Appendix A of this report illustrates the distribution of those phases identified above as potentially important. In addition, the occurrence of potentially

important phases in fractures is indicated on the figures. These figures illustrate the mineralogy as a function of depth in each drill hole for which we have sufficient data, and they are restricted to rock above the static water level (SWL). It is important to note, however, that analysis of fracture-filling minerals was limited by the availability of appropriate samples. The absence of a particular mineral as a fracture filling is therefore not necessarily diagnostic. The following section presents details of the distributions for those phases that we have identified as potentially important based on the biological data discussed above.

A. Silica

Crystalline Silica

Three crystalline silica polymorphs, quartz, cristobalite, and tridymite, are abundant in the rocks at Yucca Mountain. Tridymite is common only in relatively shallow rocks, often associated with devitrification features and always above the SWL. It is absent in the north end of Yucca Mountain, where mineralogical evidence suggests that a high heat flow existed in the past (Bish and Aronson, 1993). There appears to be a correlation between the loss of tridymite and the first appearance of abundant groundmass quartz with increasing depth. This transition in part reflects the passage from zones of common high-temperature vapor-phase crystallization (tridymite) to zones of lower-temperature devitrification (quartz) within the Topopah Spring Member. Tridymite occurs in many fracture samples above the SWL (Carlos, 1985).

In samples in which cristobalite was distinguished from opal-CT, cristobalite is present in virtually every shallow sample examined above 400-m depth but it is very restricted in rocks below the SWL. Because of overlap of the major cristobalite peak with significant feldspar peaks in X-ray diffraction patterns, the precision of analysis of cristobalite when present in amounts below 10% is poor. Thus, the deeper samples identified as containing small amounts of cristobalite may in fact contain no cristobalite. The presence of cristobalite at shallow depths probably reflects the unsaturated nature of these rocks over much, if not all, of their history. Ernst and Calvert (1969) showed that an aqueous fluid is necessary for rapid recrystallization of cristobalite to quartz, and the recrystallization is accelerated in alkaline solutions. They concluded that conversion of the Monterey Formation porcelanite (cristobalite) to quartz in relatively pure water at 50°C would take between 4 and 5 m.y. Cristobalite occurs in most fracture samples above the SWL (Carlos, 1985).

With depth, cristobalite gives way to opal-CT in zeolitized rocks in several drill holes. Quartz is present in most samples examined at Yucca Mountain, but it is typically less abundant at shallow depths and in glass-, clinoptilolite-, and mordenite-containing samples. It generally increases in abundance below the depth where clinoptilolite and mordenite disappear (i.e., where

cristobalite and opal-CT are no longer important silica phases). Quartz is nearly ubiquitous in fracture samples above the SWL (Carlos, 1985).

Opal-CT

As noted above, early analyses of Yucca Mountain tuffs did not distinguish opal-CT from cristobalite. Our most recent analyses, however, include separate determinations of opal-CT, a disordered silica phase containing both cristobalite- and tridymite-like structural units (Jones and Segnit, 1971). Almost without exception, opal-CT occurs in samples containing clinoptilolite and/or mordenite. Thus the presence of opal-CT may be linked genetically to the formation of these two zeolites. Most of the opal-CT samples exhibit evidence for cristobalite- and tridymite-like stacking, but some more closely resemble opal-C (predominantly cristobalite-like stacking). As noted above, opal-CT was grouped with the crystalline silica polymorphs because most samples analyzed from Yucca Mountain show evidence for some three-dimensional order.

B. Zeolites

Erionite

As reported by Bish and Vaniman (1985), none of the previous reports of erionite in Yucca Mountain rocks has been verified. However, Bish and Vaniman reported that one sample of erionite has been conclusively identified in a fracture from UE-25a#1 at 1296 ft (395 m). Data from Chipera and Bish (1989) and Bish and Chipera (1991) (Appendix A) show four confirmed occurrences (and two possible occurrences) of erionite, all in the altered interface between the lower Topopah Spring Member vitrophyre and the overlying devitrified tuff. This altered zone contains a variety of zeolites that are either rare or absent in other Yucca Mountain tuffs. It appears that erionite is restricted in these samples to fractures and must have formed under unusual and very localized conditions in this altered zone. Although erionite occurs as a major phase in the UE-25a#1-1296 fracture sample, all other occurrences are as isolated trace phases. It is also noteworthy that samples adjacent (within 2-3 m) to this material in drill hole UE-25a#1 contained no detectable erionite.

Recently, we have identified in core from UZ-14 a zone (~2–3-m thick) extremely rich in erionite (containing at least 35 wt%). In this zone, erionite occurs in the matrix. The zone occurs below the Topopah Spring Member vitrophyre but above the Calico Hills. Because of its thickness and high erionite content, this zone poses a significant risk. Furthermore, the sampling interval typically used for mineral content analysis (~5–6 m) may not be sufficiently fine to allow the identification of similarly sized zones in the cores previously analyzed.

Mordenite

Several studies have emphasized the occurrence of at least four distinct zones of clinoptilolite plus mordenite beneath Yucca Mountain (Bish et al. 1984; Vaniman et al. 1984). These zones occur primarily where glassy material remained outside the zones of devitrification in the centers of ash flows. There is thus a correlation between zeolitized material and the nonwelded tops, bottoms, and distal edges of ash flows. Exceptions to this correlation occur, including the zeolitized interval at the boundary between the devitrified zone and the vitrophyre of the Topopah Spring Member. In general, however, the thicker zeolitized horizons tend to correlate with those intervals that retained glass following early tuff devitrification.

Because the significant zeolitized horizons at Yucca Mountain occur near or below the SWL, there are few matrix (bulk-rock) occurrences of mordenite above the SWL. However, mordenite occurs with or without clinoptilolite as a common fracture-filling mineral between the SWL and the surface.

C. Other Silicates

Palygorskite

The distribution of palygorskite was not described by Bish and Chipera (1989). However, this fibrous mineral has since been identified in numerous fractures above the SWL, but it has not been identified as matrix mineral. This mineral is a major constituent of fracture fillings shallower than ~80 ft depth in USW G4 and shallower than ~830 ft depth in USW GU3, and it occurs at depths between 700 and 1691 ft in USW VH1 and between 1972 and 3384 ft on USW VH2 in Crater Flat. It is not a common phase on or adjacent to Yucca Mountain but could be of concern in fractures.

VI. DISCUSSION

By combining our quantitative analyses of mineral distributions with information on mineral toxicity/carcinogenicity, we are able to evaluate potential hazards associated with airborne particles released by operations at Yucca Mountain. There are several minerals that may be of potential concern as airborne particles, but the risk posed by most of these can be minimized by safe, modern mining practices (e.g., by maintaining low dust levels and adequate ventilation). The crystalline silica minerals (quartz, tridymite, cristobalite, and opal-CT) fall into this category. These minerals are classed by IARC as probable human carcinogens, and they are ubiquitous at

Yucca Mountain. Nevertheless, the risk posed by these minerals can probably be mitigated by proper dust control. No additional "asbestos" type precautions would necessarily need to be taken to address concerns with the silica minerals.

Some minerals (e.g., palygorskite) have occurrences limited to fractures, so exposures to these minerals will likely be very small, particularly if low dust levels are maintained. Consequently, most of these minerals probably do not pose a risk at Yucca Mountain.

Erionite may pose a risk if encountered in sufficient quantity even when standard modern mining practices are followed, due to its apparently extremely high carcinogenic potential. However, erionite occurrence at Yucca Mountain appears to be restricted to zones immediately below the potential repository horizon. Consequently, it may only be a concern where the ESF workings may penetrate into the basal vitrophyre of the Topopah Spring Member.

Only limited information is available on the toxicity and carcinogenicity of mordenite, so although the published data suggest that mordenite is *not* carcinogenic, a prudent approach would be to minimize exposures to airborne mordenite, until additional biological data have been collected. These additional biological data should address the possible relationships between various mineralogical properties and biological activity, so that the biological activity of mordenite can be evaluated on a sample-by-sample basis. The precautions taken in response to the occurrence of the silica minerals may be sufficient to address mordenite occurrence at Yucca Mountain. However, the concern over erionite's extreme biological potential will probably focus attention on the potential risk posed by any fibrous zeolite, due to the poor understanding of mineralogical aspects relevant to mineral-induced diseases. If this were to occur, the approach to dealing with fibrous zeolites will probably be based on erionite's toxicity/carcinogenicity, regardless of whether or not other fibrous zeolites are as biologically active as erionite. The only way to avoid this type of blanket approach is through more extensive biological evaluations of other fibrous zeolites, provided that mineralogical and geochemical concerns are properly addressed by the experiments.

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5.1Q, the TDIF data tracking number for this record segment is LA000000000054.001. The record package containing traceability information is LA-EES-1-TIP-94-009.

REFERENCES

- Baris, I., L. Simonato, M. Artvinli, F. Pooley, R. Saracci, J. Skidmore, and C. Wagner (1987) Epidemiological and environmental evidence of the health effects of exposure to erionite fibres: a four-year study in the Cappadocian region of Turkey. *International Journal of Cancer*, **39**:10 – 17. NNA.920131.0442
- Bish, D. L. (1981) *Detailed Mineralogical Characterization of the Bullfrog and Tram Members in USW-G1, with Emphasis on Clay Mineralogy*, Los Alamos National Laboratory report LA-9021-MS. NNA.870406.0238
- Bish, D. L. and J. L. Aronson (1993) Paleogeothermal and paleohydrologic conditions in silicic tuff from Yucca Mountain, Nevada. *Clays and Clay Minerals*, **41**:148–161. NNA.940323.0290
- Bish, D. L., and S. J. Chipera (1988) Problems and solutions in quantitative analysis of complex mixtures by X-ray powder diffraction. In: *Advances in X-Ray Analysis*, Plenum Press, New York, **31**:295-308. NNA.890405.0178
- Bish, D. L. and S. J. Chipera (1989) *Revised Mineralogic Summary of Yucca Mountain, Nevada*, Los Alamos National Laboratory report LA-11497-MS. NNA.891005.0072
- Bish, D. L. and S. J. Chipera (1991) Detection of trace amounts of erionite using X-ray powder diffraction: Erionite in tuffs of Yucca Mountain, Nevada, and central Turkey. *Clays and Clay Minerals*, **39**:437–445. NNA.920319.0003
- Bish, D. L., and D. T. Vaniman (1985) *Mineralogic Summary of Yucca Mountain, Nevada*, Los Alamos National Laboratory report LA-10543-MS. NNA.870407.0330
- Bish, D. L., F. A. Caporuscio, J. F. Copp, B. M. Crowe, J. D. Purson, J. R. Smyth, and R. G. Warren, (1981) *Preliminary Stratigraphic and Petrologic Characterization of Core Samples from USW-G1, Yucca Mountain, Nevada*, Los Alamos National Laboratory report LA-8840-MS. NNA.870406.0158
- Bish, D. L., A. E. Ogard, D. T. Vaniman, and L. Benson (1984) Mineralogy-petrology and groundwater geochemistry of Yucca Mountain tuffs. In: *Scientific Basis for Nuclear Waste Management VII, Materials Research Society Symposia Proceedings*, G. L. McVay, ed., Boston, Massachusetts, p. 283-291. NNA.870406.0085
- Brieger, H. and P. Gross (1966) On the theory of silicosis: I. Coesite. *Archives of Environmental Health*, **13**:38–43. NNA.940323.0289
- Brieger, H. and P. Gross (1967) On the theory of silicosis: III. Stishovite. *Archives of Environmental Health*, **15**:751–757. NNA.940323.0288
- Caporuscio, F., D. Vaniman, D. Bish, D. Broxton, B. Arney, G. Heiken, F. Byers, R. Gooley, and E. Semarge (1982) *Petrologic Studies of Drill Cores USW-G2 and UE25b-1H, Yucca Mountain, Nevada*, Los Alamos National Laboratory report LA-9255-MS. NNA.870519.0041
- Carlos, B. A. (1985) *Minerals in Fractures of the Unsaturated Zone from Drill Core USW G-4, Yucca Mountain, Nye County, Nevada*, Los Alamos National Laboratory report LA-10415-MS. NNA.920506.0037

- Carlos, B. A. (1991) Fracture-lining minerals in the lower Topopah Spring Tuff. *High Level Radioactive Waste Management*, 486–493. NNA.910206.0039
- Carlos, B. A., S. J. Chipera, D. L. Bish, and S. J. Craven (1993) Fracture-lining manganese oxide minerals in silicic tuff, Yucca Mountain, Nevada. *Chemical Geology*, **107**:47–69. NNA.931028.0002
- Chipera, S. J. and D. L. Bish (1989) *Occurrence and Distribution of Erionite at Yucca Mountain, Nevada*, Los Alamos National Laboratory report LA-11663-MS. NNA.890412.0062
- Chung, F. H. (1974a) Quantitative interpretation of X-ray diffraction patterns of mixtures. I. Matrix-flushing method for quantitative multicomponent analysis. *Journal of Applied Crystallography* **7**:519–525. NNA.890405.0179
- Chung, F. H. (1974b) Quantitative interpretation of X-ray diffraction patterns of mixtures. II. Adiabatic principle of X-ray diffraction analysis of mixtures. *Journal of Applied Crystallography* **7**:526–531. NNA.890405.0180
- Davis, J. M. G. (1993) *In vivo* assays to evaluate the pathogenic effects of minerals in rodents. In *Health Effects of Mineral Dusts*, G. D. Guthrie Jr. and B. T. Mossman, eds., Mineralogical Society of America, Washington, 471–487. “Readily Available”
- Driscoll, K. E., Jr. (1993) *In vitro* evaluation of mineral cytotoxicity and inflammatory activity. In *Health Effects of Mineral Dusts*, G. D. Guthrie Jr. and B. T. Mossman, eds., Mineralogical Society of America, Washington, 489–511. “Readily Available”
- Dubes, G. R. and L. R. Mack (1988) Asbestos-mediated transfection of mammalian cell cultures. *In Vitro Cellular and Developmental Biology*, **24**:175 – 182. NNA.94104.0053
- Ernst, W. G. and S. E. Calvert (1969) An experimental study of the recrystallization of porcelanite and its bearing on the origin of some bedded cherts. *American Journal of Science* **267A**:114–133. NNA.900508.0013
- Guthrie, G. D., Jr. (1992) Biological effects of inhaled minerals. *American Mineralogist*, **77**:225–243. NNA.94104.0054
- Guthrie, G. D., Jr. (1993) Mineral characterization in biological studies. In *Health Effects of Mineral Dusts*, G. D. Guthrie Jr. and B. T. Mossman, eds., Mineralogical Society of America, Washington, 251–273. “Readily Available”
- Guthrie, G. D., Jr. and B. T. Mossman, eds. (1993) *Health Effects of Mineral Dusts*, Mineralogical Society of America, Washington, 584p. “Readily Available”
- Guthrie, G., D., Jr., K. McLeod, N. Johnson and D. Bish (1992) Effect of exchangeable cation on zeolite cytotoxicity. *Goldschmidt Conference Abstracts with Program*, p. A-46. NNA.94104.0056
- Hansen, K. and B. T. Mossman (1987) Generation of superoxide (O_2^-) from alveolar macrophages exposed to asbestiform and nonfibrous particles. *Cancer Research*, **47**:1681–1686. NNA.940323.0291
- Heiken, G. H. and M. L. Bevier (1979) *Petrology of Tuff Units from the J-13 Drill Site, Jackass Flats, Nevada*, Los Alamos National Laboratory report LA-7563-MS. NNA.870519.0045

- Heppleston, A. G. (1984) Pulmonary toxicology of silica, coal and asbestos. *Environmental Health Perspectives*, **55**:111-127. NNA.940104.0057
- Holland, L. M. (1990) Crystalline silica and lung cancer: A review of recent experimental evidence. *Regulatory Toxicology and Pharmacology*, **12**:224-237. NNA.940323.0298
- IARC (International Agency for Research on Cancer) (1971) *Volume 1: IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man*, World Health Organization, Lyons, France, **1**, 184p. "Readily Available"
- IARC (International Agency for Research on Cancer) (1987a) *Overall Evaluations of Carcinogenicity: An Updating of IARC Monographs Volumes 1 to 42. IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans*, World Health Organization, Lyons, France, **Supplement 7**, 440p. "Readily Available"
- IARC (International Agency for Research on Cancer) (1987b) *Silica and Some Silicates. IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans*, World Health Organization, Lyons, France, **42**, 289p.m "Readily Available"
- IARC (International Agency for Research on Cancer) (1988) *Man-made Mineral Fibres and Radon. IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans*, World Health Organization, Lyons, France, **43**, 300p. "Readily Available"
- IARC (International Agency for Research on Cancer) (1992) *Occupational Exposures to Mists and Vapors From Strong Inorganic Acids and Other Industrial Chemicals. IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans*, World Health Organization, Lyons, France, **54**, 336p. "Readily Available"
- Jaurand, M.-C., Fleury, J., Monchaux, G., Micheline, N., and Bignon, J. (1987) Pleural carcinogenic potency of mineral fibers (asbestos, attapulgite) and their cytotoxicity on cultured cells. *Journal of the National Cancer Institute*, **79**:797 – 804. MOL.19940927.0002
- Jones, J. B. and E. R. Segnit (1971) The nature of opal. I. Nomenclature and constituent phases. *Journal of the Geological Society of Australia* **18**:57-68. NNA.921103.0010
- Kennedy, T. P., W. Rawlings, Jr., M. Baser, and M. Tockman (1983) Pneumoconiosis in Georgia kaolin workers. *American Reviews of Respiratory Disease*, **127**:215 – 220. NNA.940323.0297
- Klug, H. P., and L. E. Alexander, (1974) *X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials*. John Wiley & Sons, Inc., New York. "Readily Available"
- Low, R. B., C. M. Leffingwell, and C. A. Bulman (1980) Effects of kaolinite on amino acid transport and incorporation into protein by rabbit pulmonary alveolar macrophages. *Archives of Environmental Health*, **35**:217 – 223. NNA.940104.0058
- Marks, J. and G. Nagelschmidt (1959) Study of the toxicity of dust with use of the *in vitro* dehydrogenase technique. *A. M. A. Archives of Industrial Health*, **20**:37/383-43/389. NNA.940104.0059
- McLaughlin, J. K., C. Jing-Qiong, M. Dosemeci, C. Rong-An, S. H. Rexing, W. Zhien, F. J. Hearl, M. A. McCawley, and W. J. Blot (1992) A nested case-control study of lung cancer

- among silica exposed workers in China. *British Journal of Industrial Medicine*, **49**:167–171. NNA.940323.301
- Mossman, B. T. and J. E. Craighead (1982) Comparative cocarcinogenic effects of crocidolite asbestos, hematite, kaolin and carbon in implanted tracheal organ cultures. *Annals of Occupational Hygiene*, **26**:553 – 567. MOL.19940927.0003
- Mossman, B. T., K. Hansen, J. P. Marsh, M. E. Brew and J. Petruska (1989) Mechanisms of fibre-induced superoxide release from alveolar macrophages and induction of superoxide dismutase in the lungs of rats inhaling crocidolite. In: *Non-Occupational Exposure to Mineral Fibres*, J. Bignon, J. Peto and R. Saracci, eds., p. 81-92. “Readily Available”
- Oldham, P. D. (1983) Pneumoconiosis in Cornish china clay workers. *British Journal of Industrial Medicine*, **40**:131 – 137. NNA.940323.0294
- Pott, F. and K. H. Friedrichs (1972) Tumoren der ratte nach i. p. -injektion faserförmiger Stäube. *Naturwissenschaften*, **59**:318. NNA.940104.0062
- Pott, F., F. Huth and K. H. Friedrichs (1974) Tumorigenic effect of fibrous dusts in experimental animals. *Environmental Health Perspectives*, **9**:313-315. NNA.940323.0293
- Pott, F., B. Bellmann, H. Muhle, K. Rödelisperger, R. M. Rippe, M. Roller and M. Rosenbruch (1990) Intraperitoneal injection studies for the evaluation of the carcinogenicity of fibrous phyllosilicates. In: *Health Related Effects of Phyllosilicates*, J. Bignon, ed., Springer-Verlag, Berlin, p. 319-329. “Readily Available”
- Rosmanith, J., W. Hilscher and S. B. Schyma (1990) The effect of the surface quality on the fibrogenicity of the phyllosilicates muscovite and kaolinite. In: *Health Related Effects of Phyllosilicates*, J. Bignon, ed., Springer-Verlag, Berlin, p. 123–128. “Readily Available”
- Ross, M., R. P. Nolan, A. M. Langer, and C. W. Cooper (1993) Health effects of mineral dusts other than asbestos. In *Health Effects of Mineral Dusts*, G. D. Guthrie Jr. and B. T. Mossman, eds., Mineralogical Society of America, Washington, 361–407. “Readily Available”
- Saffiotti, U. (1992) Lung cancer induction by crystalline silica. In: *Relevance of Animal Studies to the Evaluation of Human Cancer Risk*, 51–69. NNA.940321.0001
- Saffiotti, U., L. N. Daniel, Y. Mao, A. O. Williams, M. E. Kaighn, N. Ahmed, and A. D. Knapton (1993) Biological studies on the carcinogenic mechanisms of quartz. In *Health Effects of Mineral Dusts*, G. D. Guthrie Jr. and B. T. Mossman, eds., Mineralogical Society of America, Washington, 523–544. “Readily Available”
- Schyma, S. B. (1990) The physical characterization of muscovite and kaolinite dusts. In: *Health Related Effects of Phyllosilicates*, J. Bignon, ed., Springer-Verlag, Berlin, p. 97–105. “Readily Available”
- Sébastien, P., J. Bignon, Y. I. Barris [sic], L. Awad, and G. Petit (1984) Ferruginous bodies in sputum as an indication of exposure to airborne mineral fibers in the mesothelioma villages of Cappadocia. *Archives of Environmental Health*, **39**:18 – 23. NNA.940104.0066

- Sepulveda, M. H., V. Vallyathan, M. D. Attfield, L. Piacitelli, and J. H. Tucker (1983) Pneumoconiosis and lung function in a group of kaolin workers. *American Reviews of Respiratory Disease*, **127**:231 – 235. NNA.940323.0290
- Simonato, L., R. Baris, R. Saracci, J. Skidmore, and R. Winkelmann (1989) Relation of environmental exposure to erionite fibres to risk of respiratory cancer. In J. Bignon, J. Peto and R. Saracci, eds., *Non-Occupational Exposure to Mineral Fibres*, p. 398 – 405, International Agency for Research on Cancer, Lyon. "Readily Available"
- Smith, D. K., M. C. Nichols, and M. E. Zolensky (1982) *A FORTRAN IV Program for Calculating X-Ray Powder Diffraction Patterns - Version 10* Pennsylvania State University, College of Earth and Mineral Sciences report. NNA.890602.0030
- Stalder, K. and W. Stöber (1965) Haemolytic activity of suspensions of different silica modifications and inert dusts. *Nature*, **207**:874–875. NNA.940104.0066
- Suzuki, Y. (1982) Carcinogenic and fibrogenic effects of zeolites: preliminary observations. *Environmental Research*, **27**:433–445. NNA.940104.0068
- Suzuki, Y. and N. Kohyama (1984) Malignant mesothelioma induced by asbestos and zeolite in the mouse peritoneal cavity. *Environmental Research*, **35**:277–292. NNA.94104.0069
- Suzuki, Y. and N. Kohyama (1988) Carcinogenic and fibrogenic effects of erionite, mordenite, and synthetic zeolite 4A. In, *Occurrence, Properties and Utilization of Natural Zeolites*, D. Kalló and H. S. Sherry, eds., Akadémiai Kiadó, Budapest, p. 829-840. "Readily Available"
- Sykes, M. L., G. H. Heiken, and J. R. Smyth (1979) *Mineralogy and Petrology of Tuff Units from the UE25a-1 Drill Site, Yucca Mountain, Nevada*, Los Alamos National Laboratory report LA-8139-MS. NNA.870406.0186
- Vaniman, D., D. Bish, D. Broxton, F. Byers, G. Heiken, B. Carlos, E. Semarge, F. Caporuscio, and R. Gooley (1984) *Variations in Authigenic Mineralogy and Sorptive Zeolite Abundance at Yucca Mountain, Nevada, Based on Studies of Drill Cores USW GU-3 and G-3*, Los Alamos National Laboratory report LA-9707-MS. NNA.870519.0043
- Wagner, J. C. (1982) Health hazards of substitutes. In: *World Symposium on Asbestos*, Proceedings, May 1982, Montreal, Canadian Asbestos Information Centre, Montreal, p. 244 – 266. NNA.940323.0295
- Wagner, J. C. (1990) Review on pulmonary effects of phyllosilicates after inhalation. In: *Health Related Effects of Phyllosilicates*, J. Bignon, ed., Springer-Verlag, Berlin, p. 309 – 318. "Readily Available"
- Wagner, J. C., J. W. Skidmore, R. J. Hill, and D. M. Griffiths (1985) Erionite exposure and mesotheliomas in rats. *British Journal of Cancer*, **51**:727 – 730. "Readily Available"
- Wastiaux, A., and H. Daniel (1990) Pulmonary toxicity of kaolin in rats exposed by inhalation. In: *Health Related Effects of Phyllosilicates*, J. Bignon, ed., Springer-Verlag, Berlin, p. 405 – 414. "Readily Available"
- Waxweiler, R., Zumwalde, R. D., Ness, G. O., and Brown, D. P. (1988) A retrospective cohort mortality study of males mining and milling attapulgite clay. *American Journal of Industrial Medicine*, **13**:305 – 315. NNA.940323.0299

APPENDIX A

Graphical representation of mineralogy above the static water level (SWL), showing the relative abundances of minerals and glass in drill holes at Yucca Mountain, Nevada. The scales on individual figures can be used to estimate relative weight percentages. Modified from Bish and Chipera (1989).

USW H-4

USW H-5

USW H-6

USW WT-1

UZ-14

APPENDIX B

Quality Assurance

The following is a list of YMP logbooks and notebooks containing data presented in this report:

MAIN REPORT	<u>LOG/NOTEBOOK</u>	<u>PAGES</u>
	TWS-EES-1-1-990-1	122-1125, 132-133
	TWS-ESS-1-8/86-57	50, 51, 56
	TWS-ESS-1-7/86-35	64, 65, 70
	TWS-EES-1-2-93-6	16-21

A list of the raw-data computer files is included as part of the records package for this report.

COMPUTER SOFTWARE

Data were obtained on the LANL EES-1 Siemens D500 X-ray powder diffractometers using the commercial software package DIFFRAC5000.

LANL YMP release label = DIFFRAC5000-01-00-00.

Integrated peak intensities were obtained using the program GRAPHINT.

LANL YMP release label = GRAPHINT-01-00-00.

QUANT (version 5.04) had been qualified under the software QA requirements of the earlier QA program which included auxiliary software.

LANL YMP release label = QUANT-01-00-00.

The latest modifications to QUANT (producing version 5.05) were conducted in accordance with the QA program emplaced on 31-JAN-1994 and are documented in TWS-EES-1-1-92-03, pages 54-70.

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