SORPTIVE MINERALS INSTITUTE

APPENDIX A

MSHA-2023-001

MSHA Public Hearings on Proposed Rule on Lowering Miners' Exposure to Respirable Crystalline Silica and Improving Respiratory Protection

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Sorptive Minerals Institute
August 21, 2023

Sorptive Minerals Institute

- Founded in 1970
- Industry trade association representing the manufacturers and marketers of absorbent clay products
- Members' products used daily around the world in thousands of commercial, industrial and consumer applications (Cat Litter, Animal Feed, Cosmetics, Environmental Sealants, etc.)
- SMI is the scientific research arm of the sorptive clay industry

SMI History of Crystalline Silica Research

- SMI research program began in1988
- Silica research presented at scientific conferences in the U.S, (1996, 1997,1999, 2002, 2003, 2005); Germany (2006); Italy (2000 & 2002); the Netherlands (1999); and South Africa (2000, 2006 & 2008)
- Research on exposure and silica species characterization led to issuance of a Safe Use Determination (SUD) in 1999 by the California Office of Health Hazard Assessment for respirable crystalline silica in clay mineral-based cat litter
- Completed two *in vivo* studies at the Fraunhofer Institute (2003, 2008)
- Results of the 2008 *in vivo* study and a study characterizing the test samples were published as companion papers in highly regarded, international journal, *Inhalation Toxicology*

SMI History of Crystalline Silica Research

- Ongoing research with The National Center for Earth and Environmental Nanotechnology Infrastructure at Virginia Tech “NANOEARTH” in 2010, 2017, 2018 and 2020 to further characterize the surface of crystalline silica from sorptive clays

SMI’s Focus
“It’s the Surface…..”

MSHA states “Physical characteristics relevant to the toxicity of respirable crystalline silica primarily relate to its size and surface characteristics. Researchers believe that the size and surface characteristics play important roles in how respirable crystalline silica causes tissue damage. Any factor that influences or modifies these physical characteristics may alter the toxicity of respirable crystalline silica by affecting the mechanistic processes (OSHA, 2013b; ATSDR, 2019).”

My objective today is to provide MSHA with information about the unique nature of crystalline silica in sorptive clays and the critical role of the particle surface in determining toxicity.

Characteristics of Silica in Sorptive Clays

- Present as non-crystalline (amorphous) opal or crystalline quartz
- Opal is not subject to MSHA’s Proposed Rule
- This is consistent with absence of health risk associated with exposure to amorphous silica
- Quartz is subject to the Proposed Rule
- SMI is concerned about MSHA’s assessment of health risk of respirable quartz in sorptive clays

Characteristics of Crystalline Silica in Sorptive Clays

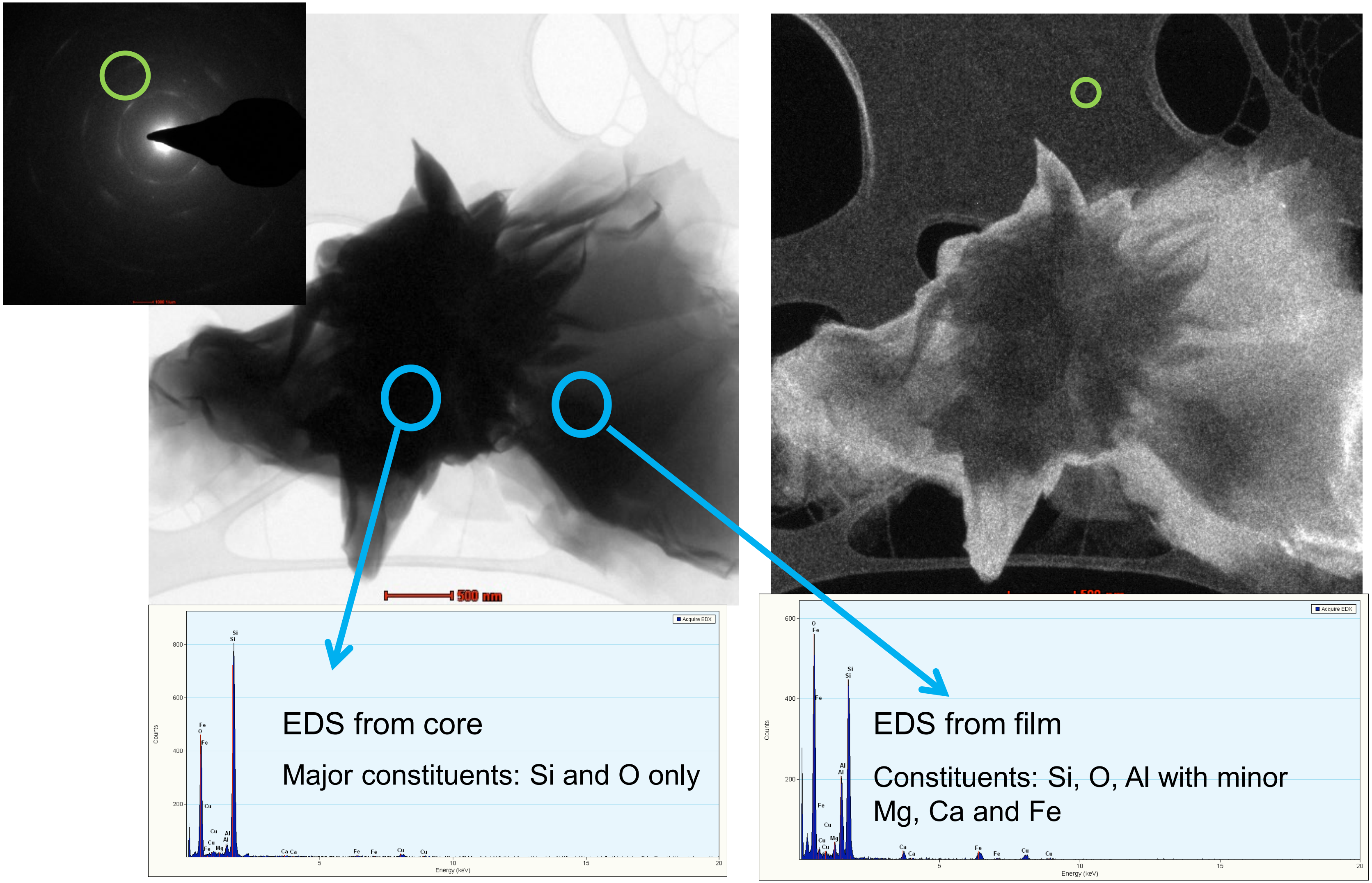
- Quartz is the only crystalline polymorph present
- Authigenic, residual or detrital in origin
- Geologically ancient
- Has been in intimate contact with surrounding clay matrix for 10 million to 110 million years
- Never subjected to high temperatures needed to create Cristobalite or Tridymite
- Different from quartz MSHA proposes to regulate

Characteristics of Surfaces of Crystalline Silica in Sorptive Clays

- In chemical equilibrium with clay matrix
- Many millions of years old
- Occluded by amorphous and crystalline aluminosilicate and adventitious metal ions

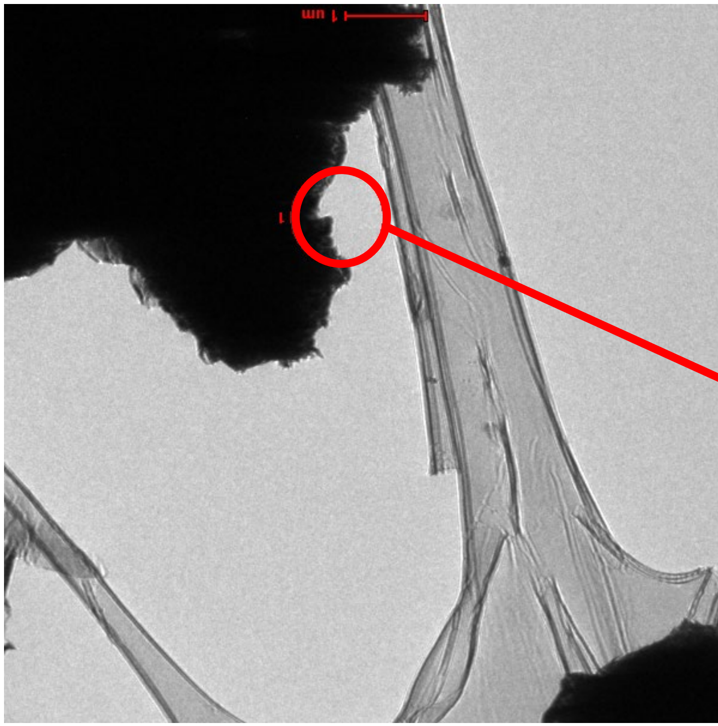
- Odom 1996 – No exposed crystalline silica surfaces for quartz particles in plant dust and products from 10 different bentonite, Fuller's Earth and Ball Clay locations (WY, SD, OK, AL, MS, IL, TN, KY) in an SEM study
- Gocmez et al 2001 – No exposed crystalline silica surfaces for quartz particles in ball clay in an SEM / XRD study
- Wendlandt et al., 2007, analyzed 100s of quartz grains from bentonite
  - Montmorillonite coatings ubiquitous, regardless of grain size
  - Clay coating resistant to removal with acid or dispersants
  - Industrial mechanical processing had no effect on surface coating
  - Concluded clay coating has potential to mitigate toxicity in the lung

Sorptive Clay Occluded Quartz Surfaces

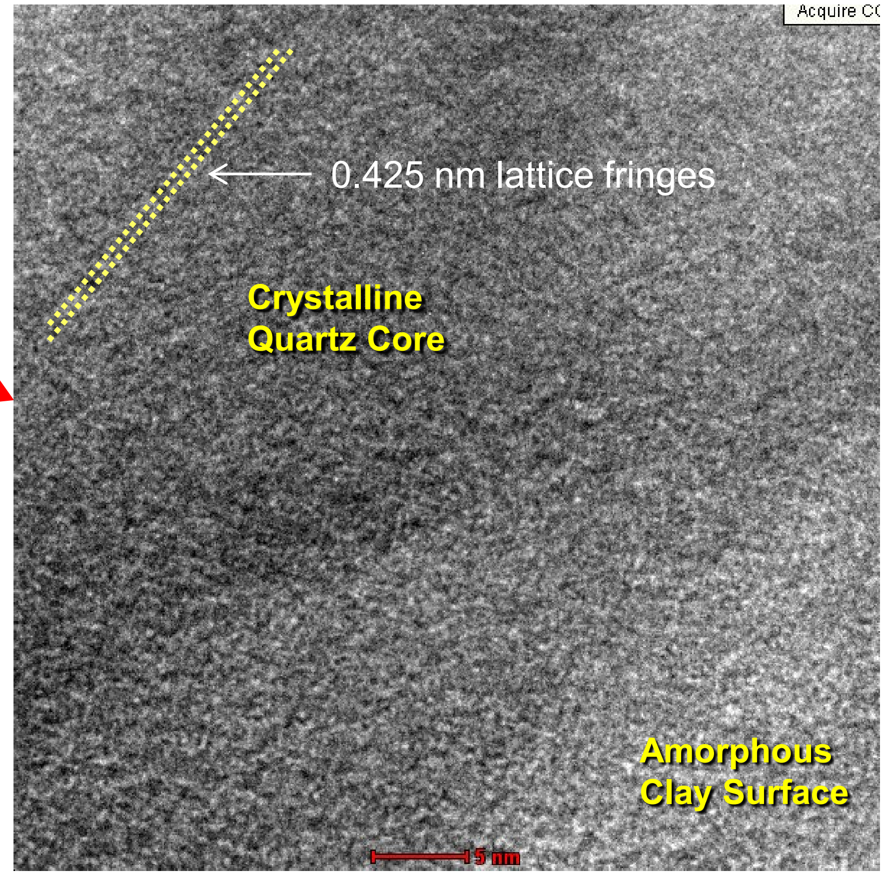


After Hochella and Muryama, 2010

Sorptive Clay Occluded Quartz Surfaces



Bright Field TEM Image



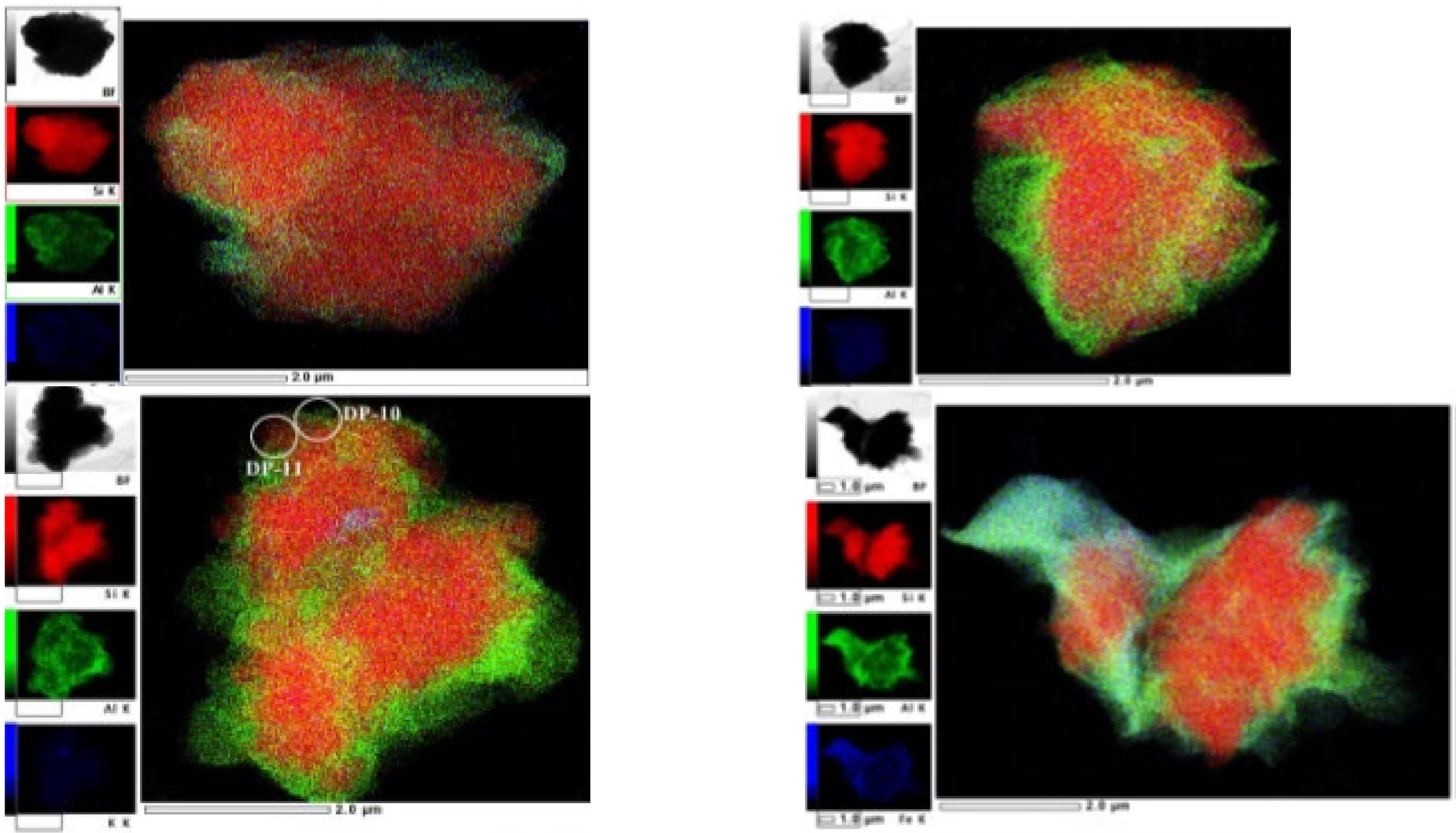
High Resolution TEM

After Hochella and Muryama, 2010

Sorptive Clay Occluded Quartz Surfaces

The aluminosilicate occlusion is both chemically and physically an intrinsic part of the quartz particle itself!

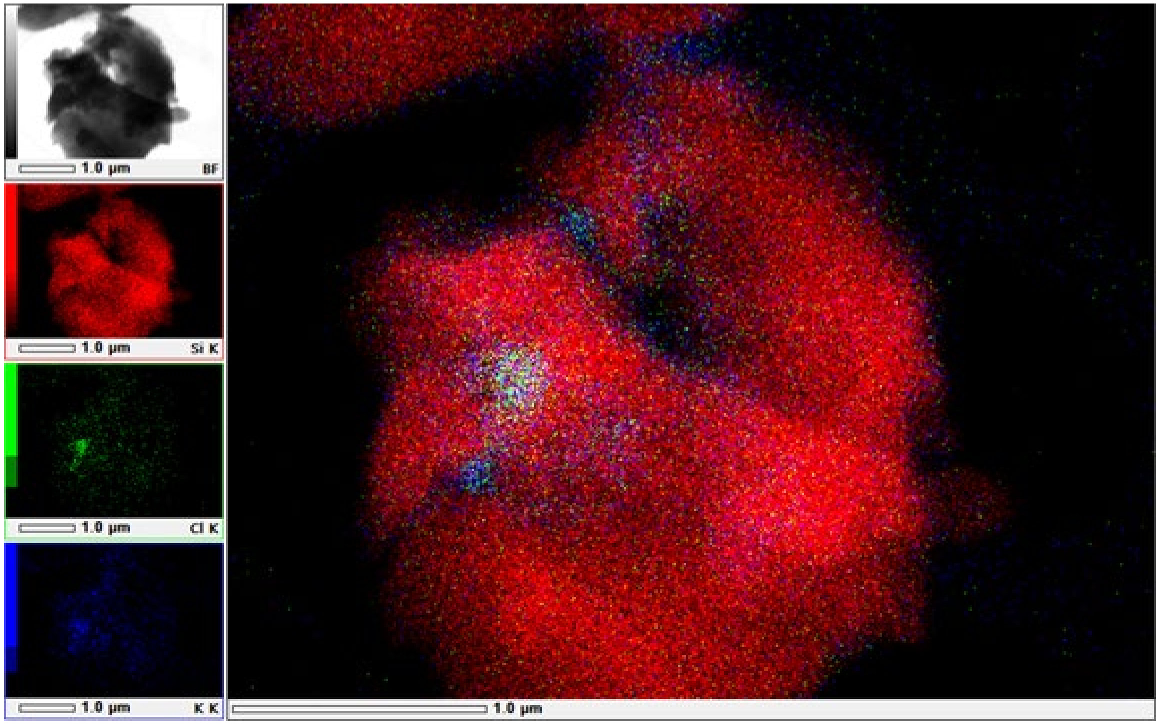
TEM / EDS Color Mapping of Quartz from Four Different Wyoming Bentonite Deposits



Red dots = Silicon atoms   Green dots = Aluminum atoms

Berti, 2018 unpublished report

TEM / EDS Color Mapping of DQ12 Middle Size Crushed Quartz



Red dots = Silicon atoms   No Aluminum atoms found

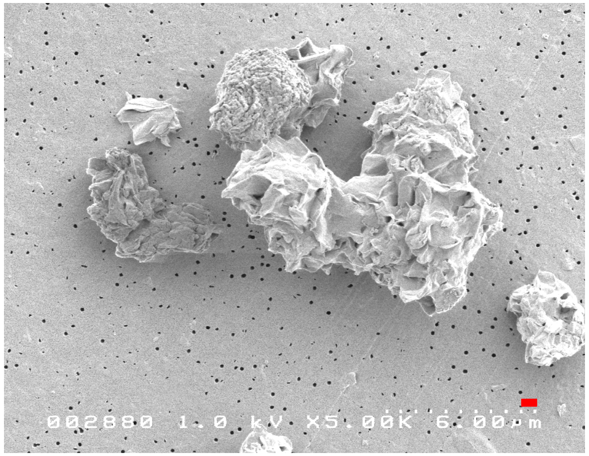
Cantando 2020 unpublished report

Characteristics of Crystalline Silica Species Known to Cause Health Hazards

- Quartz, Cristobalite, Tridymite
- Single crystal particles
- SiO_2 surface
- High degree of SiO_2 crystallinity at the surface
- “Freshly fractured”, high energy surfaces
- Generated by specific industrial circumstances that break silica particles into respirable size
  - Sand Blasting
  - Crushing, cutting and grinding stone and concrete

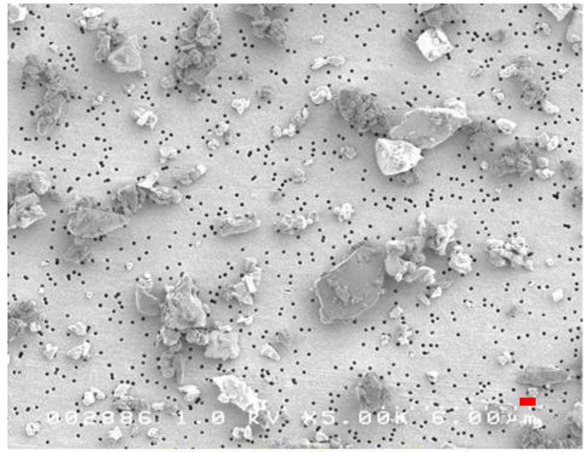
Quartz Particle Surface Morphology

Natural Occluded

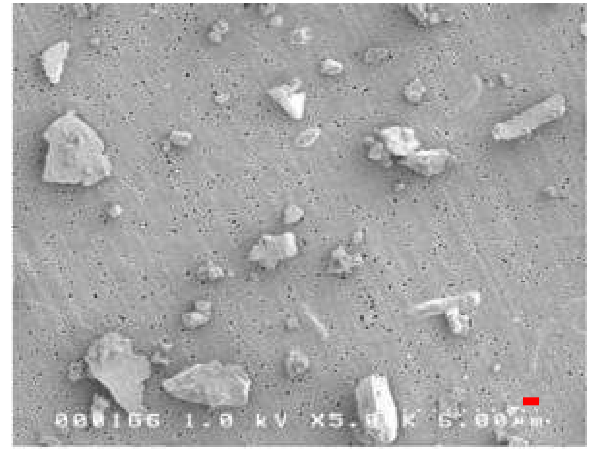


Quartz from Bentonite

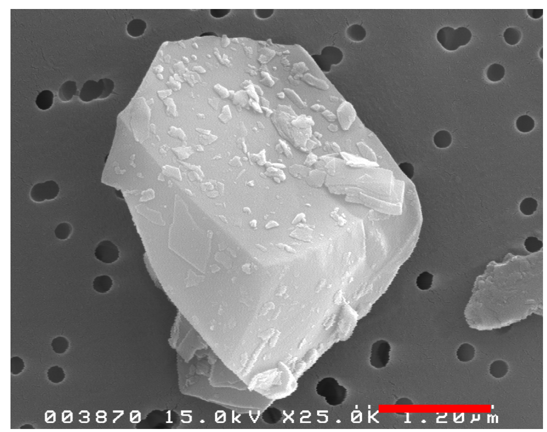
Commercially Manufactured / Occupationally Generated



DQ12



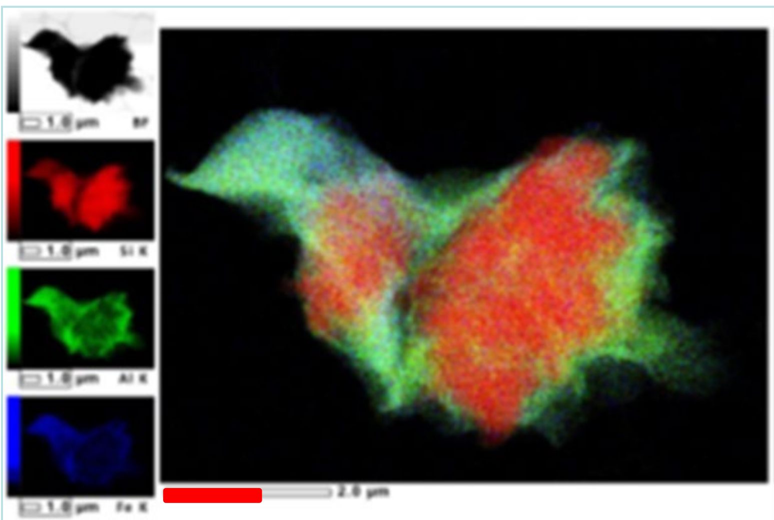
Min-U-Sil® 5



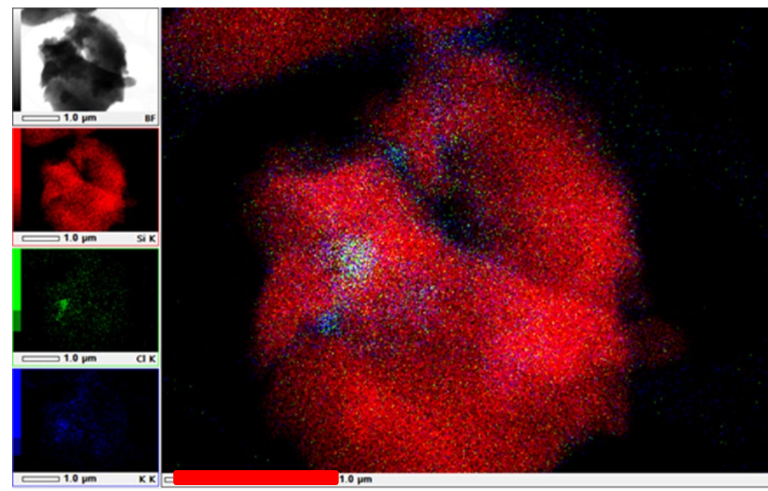
South African Gold Mine Quartz

Comparison of Quartz from Bentonite vs DQ12 Crushed Quartz

Quartz from Bentonite

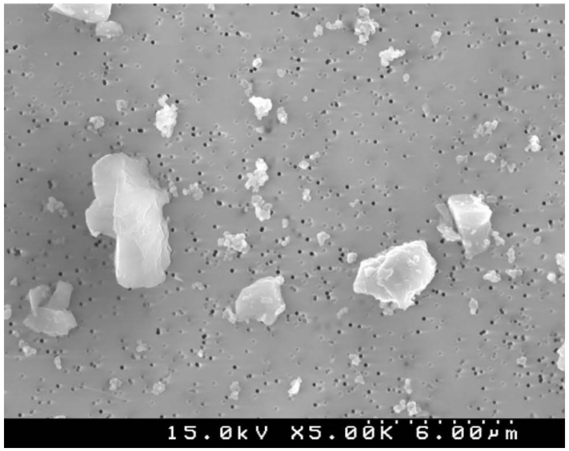


DQ12 Crushed Quartz

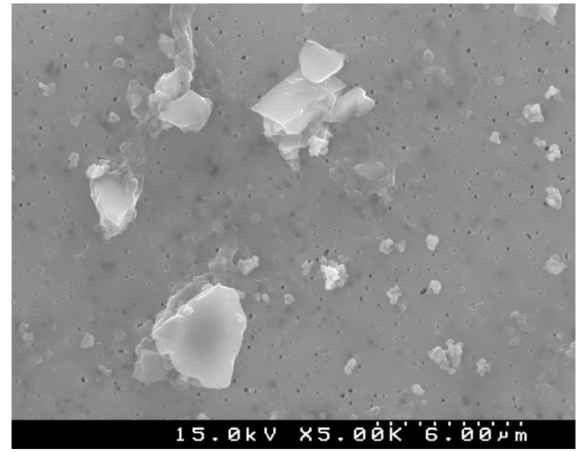


Red dots = Silicon atoms Green dots = Aluminum atoms

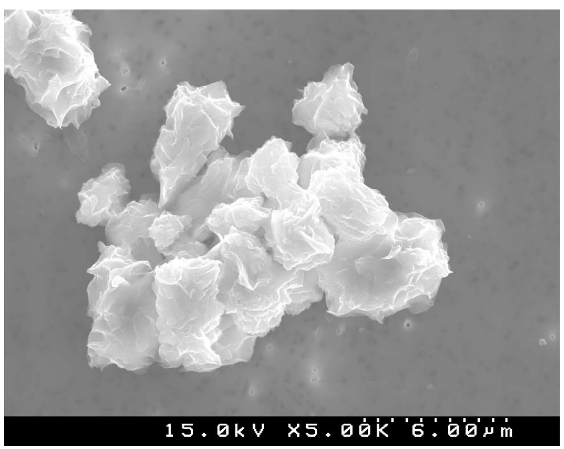
Creutzenberg et al., 2008 - 90 Day Study



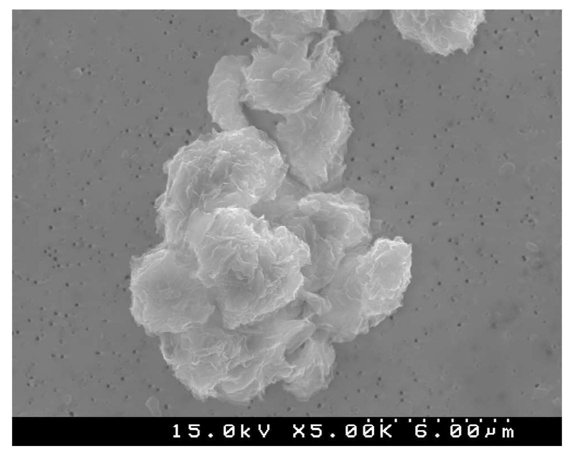
DQ12 Reference Quartz
Before Installation in Rat Lungs



DQ12 Reference Quartz
Recovered after 90 Days in Rat Lungs



Occluded Quartz from Bentonite
Before Installation in Rat Lungs



Occluded Quartz from Bentonite
Recovered after 90 Days in Rat Lungs

“Freshly Fractured” vs. “Aged” Silica

- While MSHA does not differentiate between freshly fractured and “aged” silica in its proposed silica rulemaking it does reference one study comparing these two types of silica
  - Castranova et al., 1996 – silica aged for 2 months
  - Showed freshly fractured silica is more toxic and inflammatory than “aged” silica.
  - Also showed “aged” silica still retains significant toxicity

Other Studies Comparing "Freshly Fractured" vs. "Aged" Silica

- Numerous other studies exist, that have not been referenced by MSHA, which show the toxicological difference between freshly fractured silica and silica aged for varying lengths of time.
- In its 2016 rule making OSHA cites three additional studies
  - Porter et al., 2002 – aged 14 days
  - Shoemaker et al., 1995 – aged 2 months
  - Vallyathan et al., 1995 – one aged 24 hrs and one aged 60 days

“Aged” Silica

- ”Aged” is a relative term
  - Maximum of two months following fracturing in the referenced studies
- MSHA cites a paper by Soutar et al 2004, used by OSHA in its 2016 rule making, describing the findings of a Scotish coal mine study where the authors state ”*If the effects of silica vary according to the conditions of exposure, these risks are probably towards the high end of the risk spectrum, since the silica was freshly fractured from massive sandstone, and not derived from dirt bands where the quartz grains are aged and accompanied by clay minerals*’’ (OSHA 2013b, page 336).
- MSHA states that it “*…has reviewed and agrees with OSHA’s conclusion*” (that they had a high degree of confidence of silicosis morbidity risk from the Scottish coal mine study).
- Here, MSHA acknowledges the affect of log term “aging” in concert with the presence of clay minerals in reducing the effects of silica toxicity

“Aged” vs Geologically Ancient Silica

- Silica in sorptive clays is ”Geologically Ancient” not ”Aged”
  - Has not been fractured
  - Is from 10 to 110 million years old depending on the deposit
  - Has surfaces that have been in chemical equilibrium with the clay matrix since the formation of the deposit
- The time frame difference between the geologically ancient quartz from sorptive clays and even the ”Aged” quartz referenced by MSHA and OSHA is too great to ignore
- MSHA must acknowledge the inherent differences between freshly fractured and extremely young ”Aged” quartz it proposes to regulate, and the ”Geologically Ancient” quartz from sorptive clays

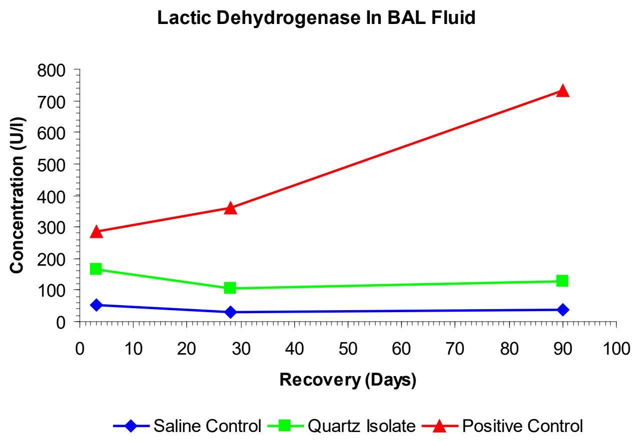
Toxicity of Occluded Quartz in Sorptive Clays

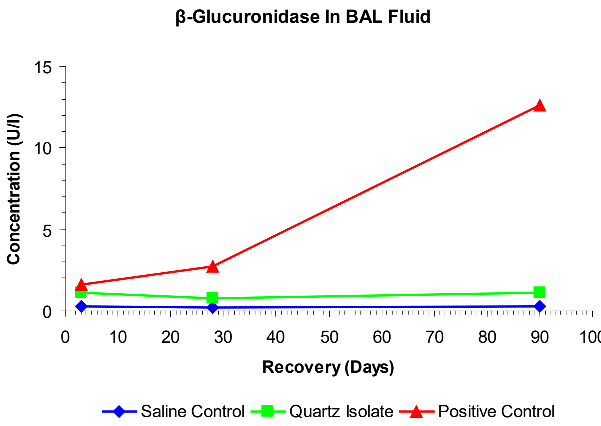
- MSHA did not consider a number of important studies assessing health effects of exposure to occluded quartz from sorptive clays
- Geh, et al., 2006 exposed human lung fibroblasts to high concentrations of bentonite with varying levels of quartz.
- Found very low levels of genotoxicity, as measured by micronucleus assays
- Creutzenberg et al., (2008) instilled respirable-size quartz isolated from bentonite in rats
- This study yielded results consistent with those from Geh et al., 2006

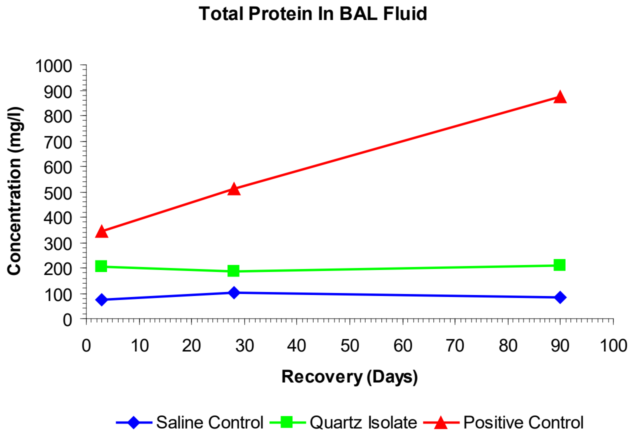
Toxicity of Occluded Quartz in Sorptive Clays

Creutzenberg et al., (2008)

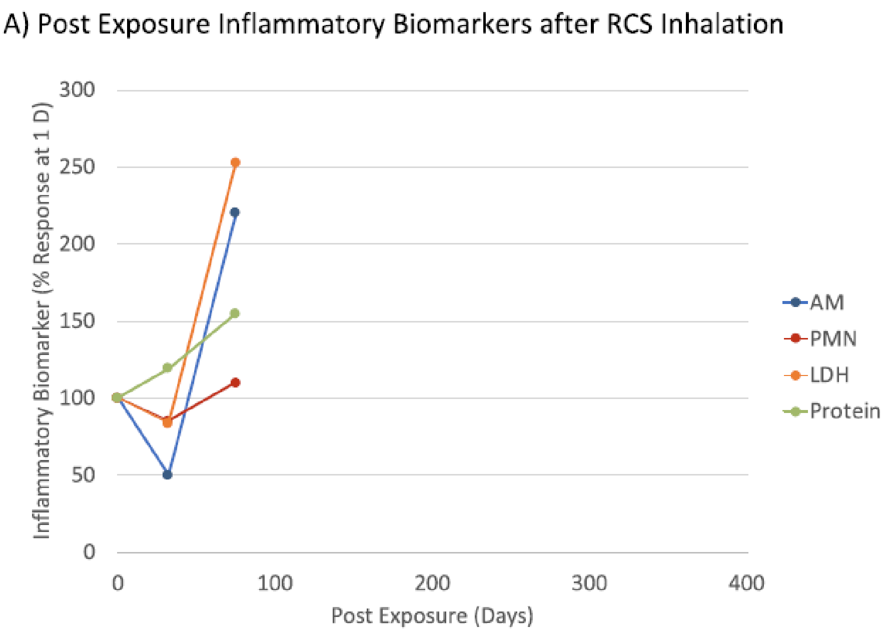
Key Indicators

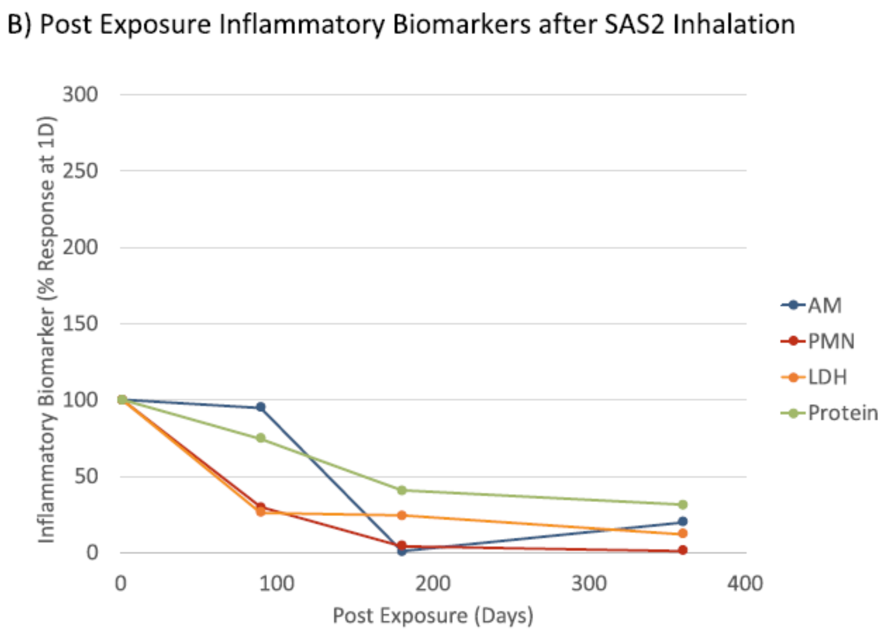






Poland et al. 2023
Pulmonary Inflammation as a Valid Predictor of Particle Induced Lung Pathology The Case of Amorphous and Crystalline Silicas





Epidemiological Studies in the Sorptive Clay Industry

- No anecdotal history of silicosis or lung cancer problems – No smoking gun!
- NIOSH retrospective cohort study – Waxweiler et al., 1988
  - Evaluated the mortality of workers in a sorptive mineral mine and processing facility in South Georgia
  - A significant deficit of nonmalignant respiratory disease was observed and no excess nonmalignant respiratory disease.
- Several reviews of worker exposures to crystalline silica have recognized that the lack of silicosis risk among clay workers with exposure to clay dust, including exposures to Fullers earth, bentonite, montmorillonite, and Attapulgite (ACGIH, 1991; USEPA 1996; IARC 2005).

Why is Crystalline Silica a Health Hazard?

- MSHA references many epidemiological studies that document the hazard posed by some types of crystalline silica.
- MSHA has not provided any studies that explain **how** crystalline silica causes health hazards
- MSHA must understand the mechanism by which crystalline silica causes human health hazard:
  - to successfully mitigate the hazard
  - to regulate the material actually responsible for the hazard

Crystalline Silica Research

- Many researchers have published on the relationship between CS particle surface characteristics and particle toxicology
- A well recognized CS researcher, B. Fubini, has published at least 40 papers related to this subject since 1987

Fubini, B. et al 1987
The surface chemistry of crushed quartz dust in relation to its pathogenicity

- Investigated the surface chemistry of finely divided quartz dust focusing on its fibrogenicity
- Found that cleavage of Si-O-Si bonds on the surface of mechanically ground quartz, more than the crystallinity of the quartz, was the primary cause of SiO_2 toxicity

Fubini, B. et al 1987
The surface chemistry of crushed quartz dust in relation to its pathogenicity

- “Surface radicals are formed, which upon contact with oxygen yield several partially reduced oxygen surface species of different stabilities, potentially dangerous to the organism. Strained bridges capable of dissociating water with an extremely high heat are also formed, which may also react with other biological molecules, causing structure modifications. Both these findings can be regarded as a possible hypothesis for a molecular interpretation of the fibrogenicity of quartz dusts.”

Fubini, B. et al 1995
Physiochemical properties of crystalline silica dusts and their possible implication in various biological responses

- Found that freshly ground silicas show a higher degree of toxicity due to the reactivity of newly created surfaces.
- Grinding cleaves the silicon-oxygen bond forming dangling bonds and surface charges (surface radicals)
- Some surface radicals rapidly decayed within a few hours after grinding which was related to acute damage in workers involved in mining, drilling, or sandblasting that were exposed to freshly ground dusts in the respirable range.

Fubini, B. et al 1995
Physiochemical properties of crystalline silica dusts and their possible implication in various biological responses

- Found that differences in the pathogenic potential of dusts are a function of their mechanical history and that grinding, heating, and etching strongly influence surface properties of silica dusts.
- Also found that contaminants and the presence of water and other ions alter surface properties mitigating adverse effects

Pavan, C. et al (17) 2019
The puzzling issue of silica toxicity: are silanols bridging the gaps between surface states and pathogenicity?

- Report on results of a workshop on silica toxicity
- Found that the pathogenic activity of silica is variable, depending on the physico-chemical features of the particles.
- Noted that in the last 50 years, crystallinity and capacity to generate free radicals have been recognized as relevant features for silica toxicity.
- Also noted that the ‘surface’ of particles also plays an important role in silica toxicity though how chemical features (e.g., silanols and siloxanes) and configuration of the silica surface can trigger toxic responses remains incompletely understood.”

Pavan, C. et al (17) 2019
The puzzling issue of silica toxicity: are silanols bridging the gaps between surface states and pathogenicity?

- Has an extensive reference section
  - contains 66 published papers by 60 principal authors
- This represented the best science available on this subject in 2019.
- MSHA has cited only two of these papers in its rulemaking references (IARC, 1997 and Shi et al, 2010).
- Minimally, MSHA **must** evaluate this body of research and use it to guide its crystalline silica rulemaking.

Pavan, C. et al 2020
Nearly free surface silanols are the critical molecular moieties that initiate the toxicity of silica particles

- Defined a new group of silanols they referred to as Nearly Free Surface Silanols (NFS).
- They showed that **the local density of silanols, not their total amount or average density, determines the toxic activity of silica dusts**."
- Stated "Surface NFS emerge as the elusive element that reconciles the enigmatic inflammatory responses observed with both crystalline and amorphous silica in several experimental studies."

Pavan, C. et al 2020
Nearly free surface silanols are the critical molecular moieties that initiate the toxicity of silica particles

- Their data indicated that crystalline and amorphous silicas exist as a continuum of forms with variable toxic activity depending on surface NFS content.
- Found that biopersistence of inhaled particles is another important determinant of their toxicity.
  - Crystalline silica particles persist in the lung
  - Amorphous silica particles are, in general, rapidly cleared through dissolution and macrophage removal.

Pavan, C. et al 2023
Nearly free silanols drive the interaction of crystalline silica polymorphs with membranes: Implications for mineral toxicity

- "…. demonstrated that the diverse crystal packing of the CS polymorphs creates different silanol networks on the surfaces, characterized by different amount of NFS."
- **"Overall, we showed that the specific family of NFS is responsible for the membranolytic activity of all CS polymorph**."

Pavan, C. et al 2023
Nearly free silanols drive the interaction of crystalline silica polymorphs with membranes: Implications for mineral toxicity

- “By modulating the amount of NFS with thermal treatments, we demonstrated that the silica membranolytic activity positively correlates with the amount of NFS for all CS polymorph, including stishovite and amorphous silica resulting from lattice collapsing. We suggest here that, for CS polymorphs whose toxic activity is well established ….the membranolytic activity is NFS-mediated.”
- This solved the “Puzzling” issue Pavan noted in 2019

Pavan, C. et al 2023
Nearly free silanols drive the interaction of crystalline silica polymorphs with membranes: Implications for mineral toxicity

- “Overall, these findings contribute to the molecular understanding of the toxicity mechanism of silica-based minerals, and might be helpful for predicting and controlling the hazard associated to quartz and cristobalite, which are included in the IARC classification of human carcinogens….”

Occluded Quartz
Summary

- Occluded quartz from sorptive clays is significantly and demonstrably different from freshly fractured quartz that causes health hazards:
  - Physically (Aluminosilicate occlusion; Not fractured)
  - Chemically (No free surface radicals resulting from fracturing)
  - Toxicologically (Non-progressive, resolving inflammatory response)
- Historically both MSHA and OSHA have distinguished between silica species for the purposes of regulation.
- Occluded Quartz from Sorptive Clays is clearly a different species and should be regulated separately from non-occluded Quartz

The Sorptive Minerals Institute thanks MSHA for this opportunity to present testimony on MSHA's Proposed Rule on Lowering Miner's Exposure to Respirable Crystalline Silica and Improving Respiratory Protection

QUESTIONS?