U.S. Department of Energy
Office of Civilian Radioactive Waste Management

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Effects of Temperature on the Compositions of Soluble Salts in Dust at Yucca Mountain

Presented to:
Nuclear Waste Technical Review Board

Presented by:
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Las Vegas NV

Planning Guidance for Underground Dust Sampling (MOL.20010228.0517)

"The primary objective of this sampling and analysis program is to determine the physical and chemical composition of dust from both natural and anthropogenic sources. Sampling will focus on dust that tends to accumulate on metallic surfaces, both vertical and horizontal, throughout the ESF and cross drift. The samples will be collected in a consistent fashion, and in sufficient number, to provide a statistically significant population. Analyses will include both qualitative and quantitative methods."

John Pye, Dec. 13, 2000

Major Sources of Dust at Yucca Mountain

- **Global**
  - **Large dust clouds from Gobi Desert storms periodically cross the Pacific Ocean and the US**
- **Regional (arid southwestern US)**
  - **Ongoing USGS studies (Reheis and coworkers) have identified dry playas and alluvial fans as major sources of dust**
    - **Owens Lake, in particular**
- **Local**
  - **Surface activities**
  - **Subsurface tunneling and operational activities** ***(see supplemental slides 37 and 38 for sources of underground dust)***

Objectives of the Dust Study

- **Characterize the major and trace element compositions of underground and surface dust that may accumulate on waste canisters**
  - **Bulk dust samples (total dissolution)**
  - **Contained soluble salts (distilled water leachates)**
- **Identify the major components of dust**
  - ***Geogenic* component--rock and soil**
  - ***Technogenic* component--introduced materials (ground-up conveyor belt, organic aerosols, iron and iron oxide particles, chemicals, etc.)**
  - ***Biogenic* component—e.g. pollen**

Approach

- Sample underground, surface, and atmospheric dust
  - Underground (tunnel walls, ribs, pipes, electrical cabinets)
  - Surface dust (natural accumulations)
  - Atmospheric dust (cyclone collector)
- Analyze bulk-dust samples by conventional rock analysis methods
  - Major oxides by wavelength dispersive X-ray fluorescence (WDXRF)
  - Trace elements by inductively coupled plasma mass spectrometry (ICPMS)
  - Other methods including combustion, titration, and ion selective electrodes
  - Pb isotopes to detect atmospheric dust underground

Approach (cont'd)

- Analyze soluble fraction of dust (USGS Techniques and Methods 5-D3, 20 parts leachate to 1 part solid to avoid saturation of readily soluble constituents)
  - Anions and cations by ion chromatography (IC)
  - Trace metals by ICPMS
  - Alkalinity of leachates by IC and by titration
- Identify salt minerals
  - Scanning electron microscope (SEM)
  - Synchrotron (ANL and LLBL)—attempted but not successful
  - X-ray diffraction of bulk samples and evaporated leachates

Dust Collection from the ESF and the ECRB

- **Dust vacuumed from tunnel wall, trapped by a cyclone, and deposited in a 250 milliliter sample bottle attached to the cyclone**
- **Several square meters of surface vacuumed to yield 250 to 400 grams of dust per sample**

Drift-Scale Test (DST) Alcove Sample Collection

- **Dust brushed from heater canisters onto a tray then transferred to a sample bottle**
- **Between 4 and 65 grams of dust collected from several square meters of each canister**

Atmospheric Dust Sample Collection

- **Atmospheric dust collected using a Torit® cyclone**
- **Samples collected generally monthly with a yield of about 1.5 grams of dust per sample**

Chronology of Dust Studies

- **LANL determined mineralogy of dust in the ECRB (Dust and Wall-Rock Hazardous Mineral Distribution in the East-West Cross Drift, Yucca Mountain, Nevada, October 19, 1998)**
- **Planning guidance to the USGS for underground sampling was issued on December 13, 2000 (Slide 2)**
- **ESF-1 samples collected on February 7, 2001**
  - **27 multigram samples were collected between ESF Station 02+02 and Station 78+56 by brushing dust from flat surfaces, pipes, inverts, and tunnel walls**
  - **Initial analytical results were reported in letter reports in September 2001 and in February 2002**

Chronology of Dust Studies (cont'd)

- **Larger samples required for size classification *(see supplemental slides 38 and 39)***
  - **ESF-2 samples collected on February 12, 2002**
    - **Fifteen 250-400 gram samples were vacuumed from the tunnel walls between ESF Station 2+23 to Station 76+22 using a commercial battery-powered vacuum interfaced with a stainless steel cyclone**
  - **ECRB samples collected on October 20, 2003**
    - **Six 250-400 gram samples were vacuumed from the tunnel walls and the conveyor belt between ECRB Sta 16+90 and Sta 25+25**

Chronology of Dust Studies (cont'd)

- **Yucca Crest samples collected on June 29, 2004**
  - Ten approximately 200 gram samples were collected from dust deposits on the lee of large rocks and bushes, and from bedrock depressions
  - Analyses showed an impoverishment of soluble salts due to leaching by precipitation
- **Sheltered samples collected on February 10, 2005**
  - Four multigram samples collected from areas protected from precipitation (trailer, missile silo liner, attic of the Sample Management Facility)
- **DST samples collected on April 5, 2006**
  - Ten multigram samples collected from canister heaters

Chronology of Dust Studies (cont'd)

- **Cyclone collector started on June 29, 2005**
  - Deployed at the South Portal until March 29, 2007
  - Moved to the old batch plant and operated from June 5, 2007 to Sept. 20, 2007, and restarted on December 6, 2007
  - Samples of approximately 1.5 grams each retrieved on a monthly interval
  - USGS receives 200-300 milligrams, the rest being archived at the Sample Management Facility (SMF)

Identification of Salt Minerals in Dust

- **SEM examination**
  - Halite, sylvite, gypsum, natroalunite ($NaAl_3(SO_4)_2(OH)_6$), dolomite
  - Very sparse grains of pyrite, molybdenite, native sulfur, metallic zinc
  - Cannot use method to identify nitrates
- **XRD analyses of evaporated leachates**
  - Halite, sylvite, calcite, gypsum, and bassanite ($2CaSO_4 \cdot H_2O$)
  - Salammoniac NH_4Cl
  - Mascagnite $(NH_4)_2SO_4$
  - Biphosphammite $(NH_4,K)H_2PO_4$
  - Weddellite $CaC_2O_4 \bullet 2H_2O$ (hydrated calcium oxalate)

Underground Dust Geochemistry

ESF and ECRB

Major and Trace Element Enrichments in Bulk Underground Dust Relative to Host Rock

- **Underground dust is 90 to 95 percent host rock**
- **Major Elements**
  - **FeO (introduced as metallic iron), CO_2 and F (from fracture minerals), organic C and Cl (neoprene abraded from conveyor belt and introduced materials), and Cl (from pore water)**
- **Trace Elements**
  - **Bi, Cd, Co, Cr, Mo, Ni, Sb, V, Zn (metallic elements associated with construction and materials introduced during construction)**

(See supplemental slides 40, 42, 43, and 44)

Average Non-Rock Material in a Kilogram of Average Dust

Constituent	ESF-2 Dust Grams	ECRB Dust Grams	Sources
FeO	23.9	12.9	Steel and iron
MgO	2.9	1.9	?
CaO	17.6	13.3	Calcite
P_2O_5	2.1	0	Explosives?
Cl	1.3	0.8	Neoprene, etc.
F	0.8	0.2	Fluorite
CO_2	9.0	8.3	Calcite
Organic C	13.6	8.6	Neoprene, etc.
Bound H_2O+	22.9	14.3	Clay, zeolites, glass

Average Soluble Salt Contents and NO_3/Cl Ratios in Underground, Surface, and Atmospheric Dust

(see supplemental slide 41)

Dust	Salt (%)	NO_3/Cl
ESF-2	0.5	2.2
ECRB	0.1	1.1
Surface	0.1	3.1
Protected (4 samples)	0.2-7.0	0.5-7.7
Atmospheric (cyclone)	2.3-5.5	10
Regional (Reheis)	13	--

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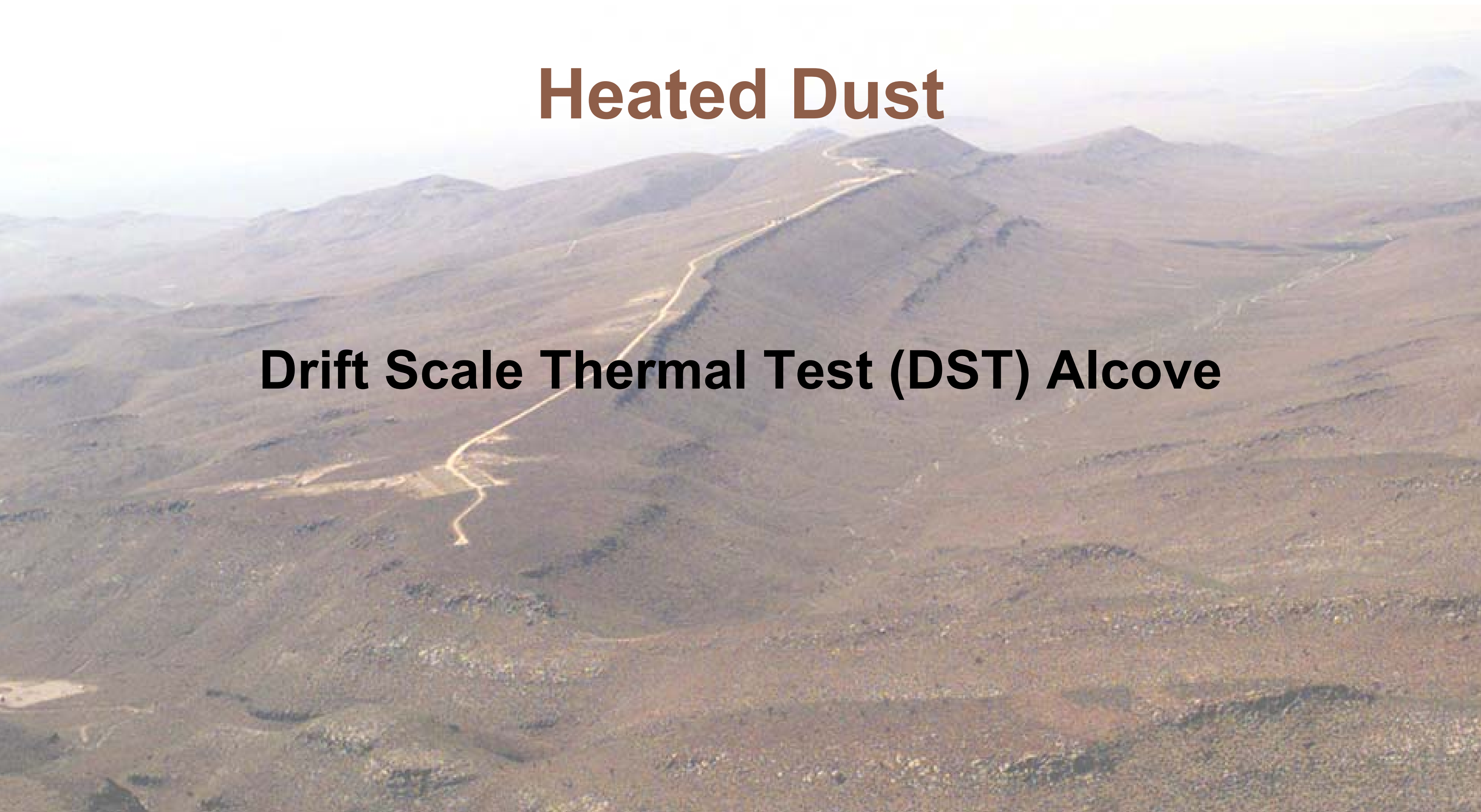
Heated Dust

Drift Scale Thermal Test (DST) Alcove

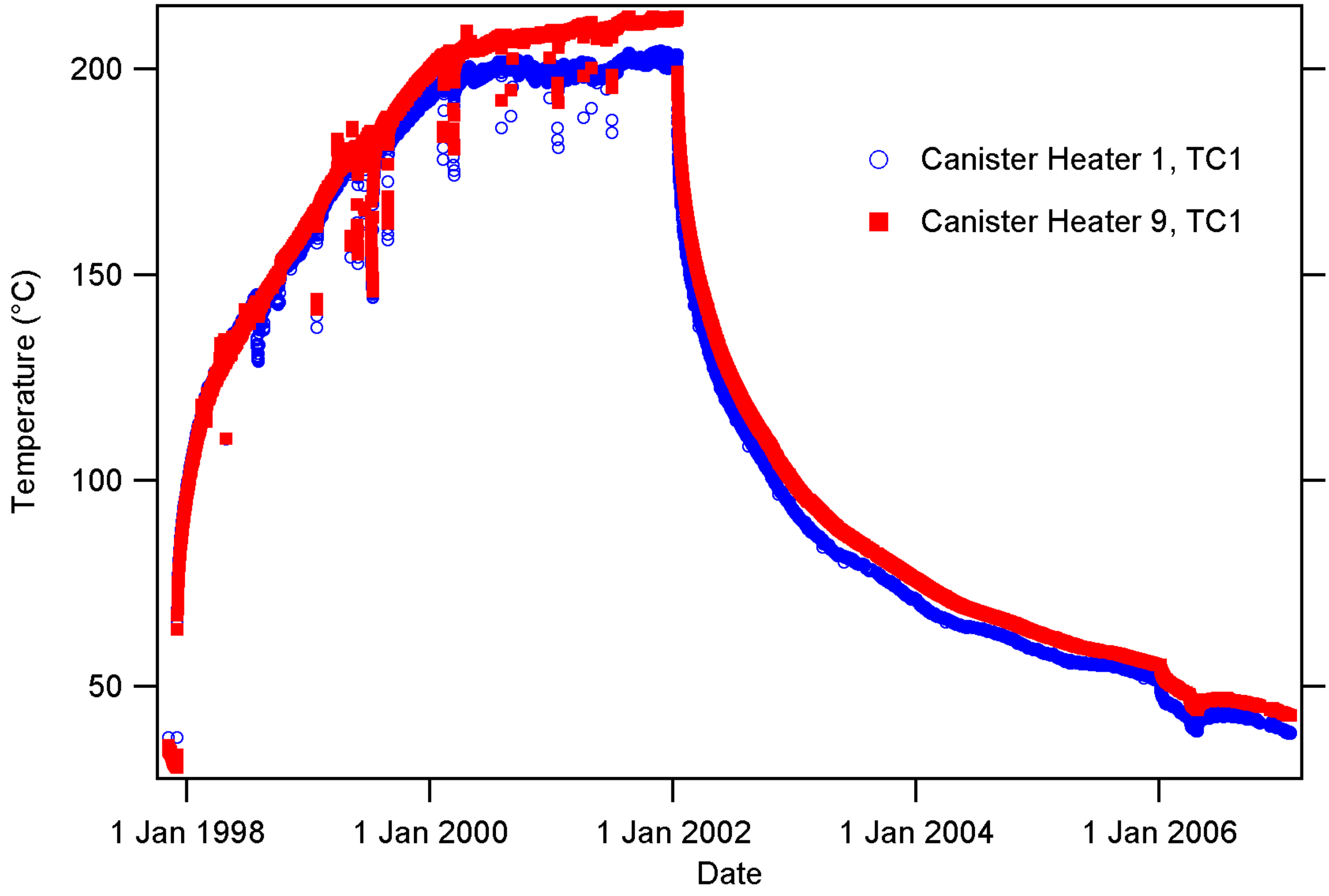


Drift Scale Thermal Test (DST) Alcove

(see supplemental slide 45)

- **Objective**
  - Evaluate coupled thermal, hydrological, chemical, and mechanical processes
- **Temperature range from ambient to ≈200 °C**
- **4 years of heating and 4 years of cooling**
  - Test began December 1997
  - Electrical heaters were turned off January, 2002
  - Entry into heated drift in April, 2006
    - Observations, specimen retrieval and sample collection

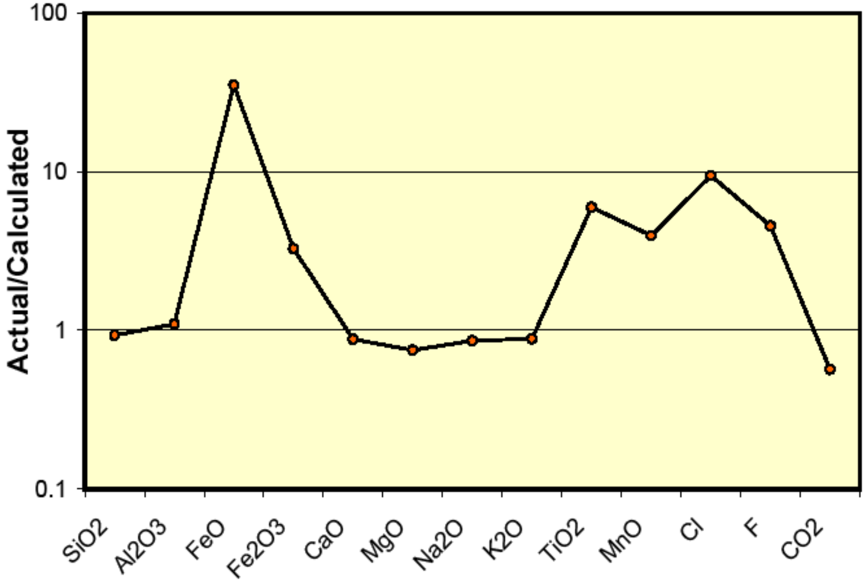
Canister Heater Temperature



Geochemistry of DST Dust

- **Relative to average composition of bulk ESF dust, bulk DST dust samples are strongly enriched in Fe (II and III), MgO, CaO, TiO_2, MnO, Cl, F, and CO_2**
  - **Enrichment in CaO and CO_2 is from limestone aggregate (no evidence of carbonation seen in thin section, *see supplemental slide 46*)**
- **Relative to average composition of ESF soluble fractions of dust, leachates of DST dust are enriched in Na, K, Ca, Cl, SO_4, F, and Br and depleted in Mg and NO_3**

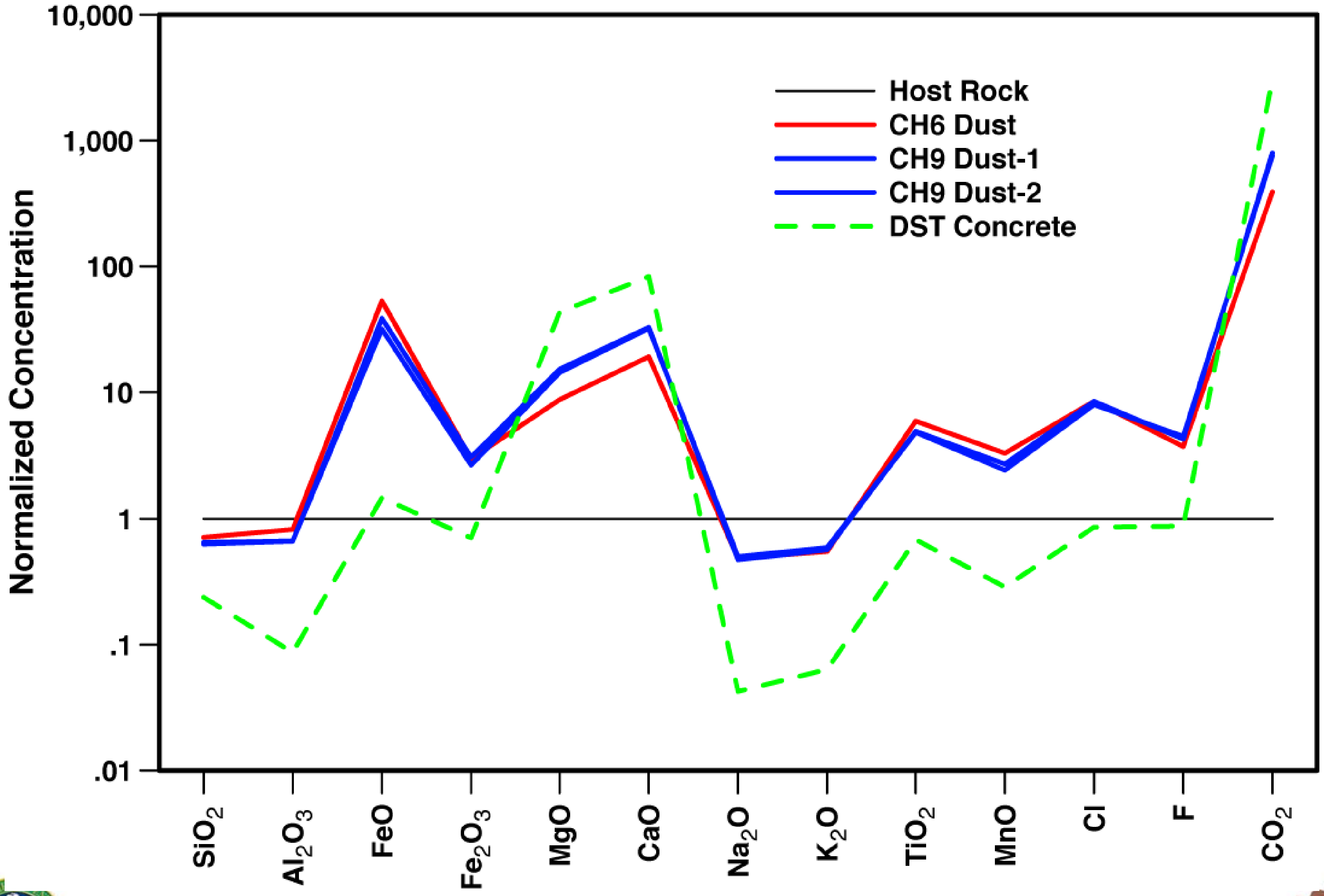
Most of DST Dust is a Mixture of Host Rock and Concrete



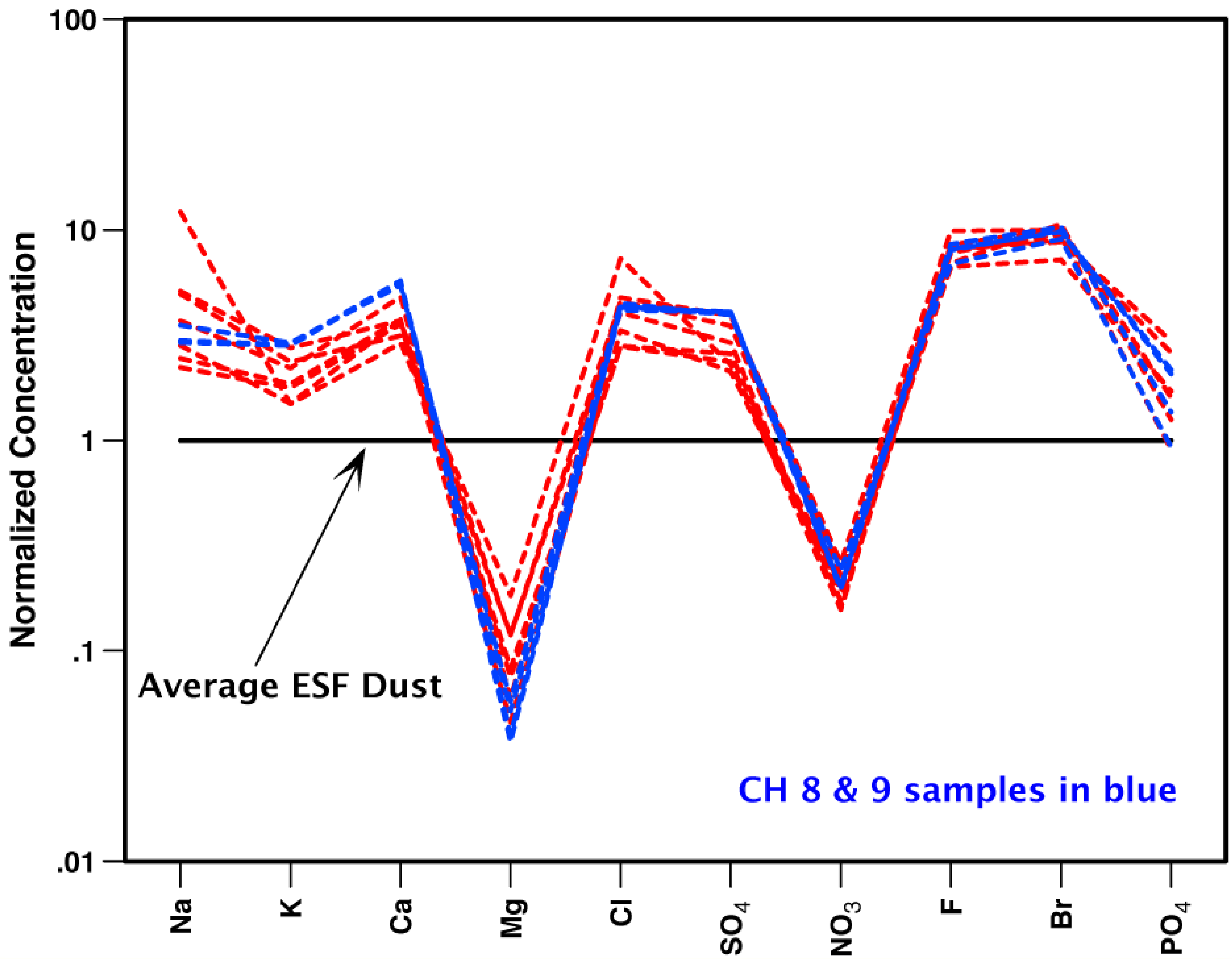
- SiO_2, Al_2O_3, CaO, MgO, Na_2O, K_2O, and CO_2 contents in DST dust are mixtures of about 0.62 rhyolite and 0.38 concrete
- Relative to this calculated mixture, actual DST dust is enriched in ferrous and ferric iron, TiO_2, MnO, Cl, and F

Iron, titanium, and manganese are probably derived from steel; chlorine and fluorine may be derived from electrical cables

Chemistry of Bulk DST Dust



Chemistry of DST Soluble Salts



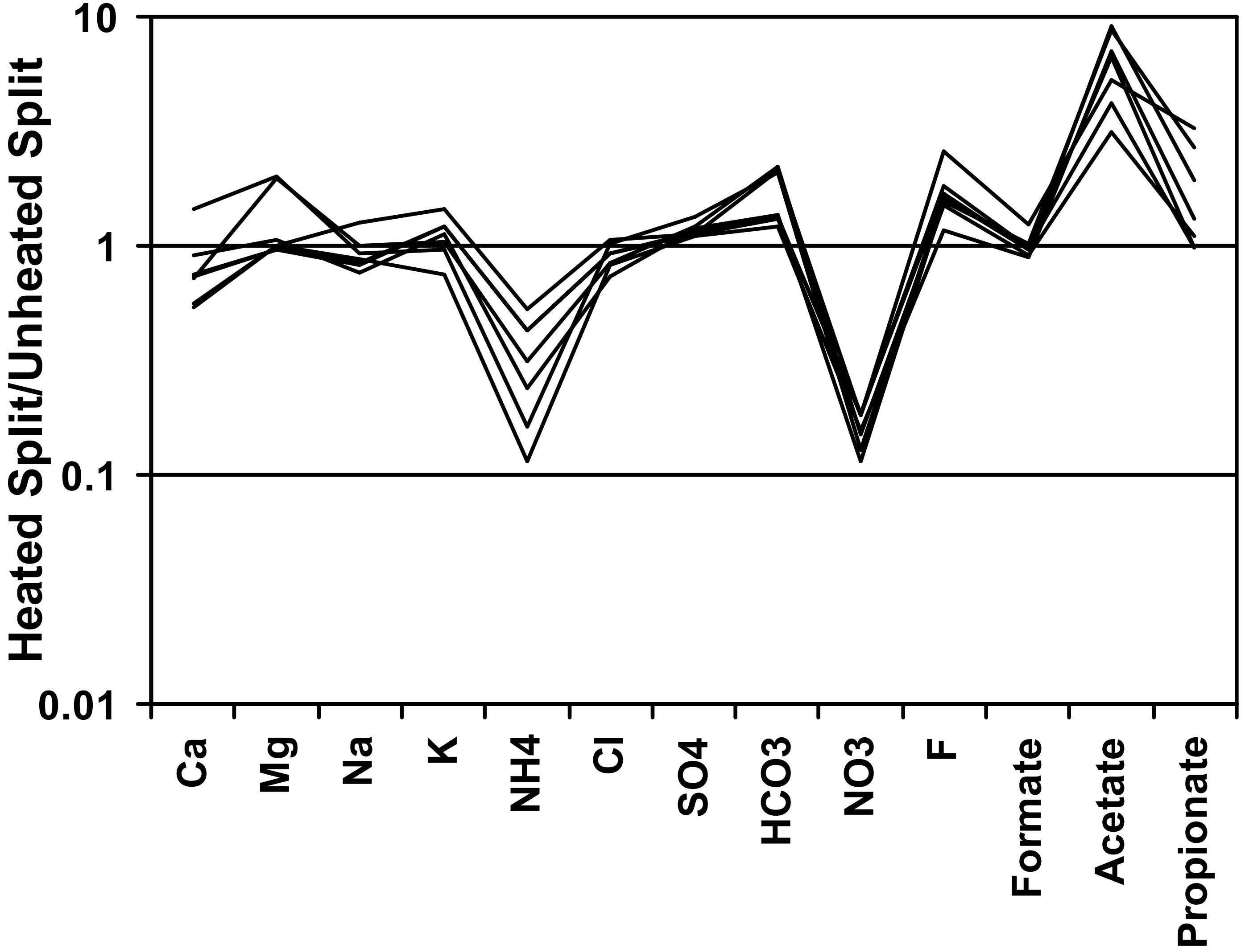
Heated Dust

Experimental Heating

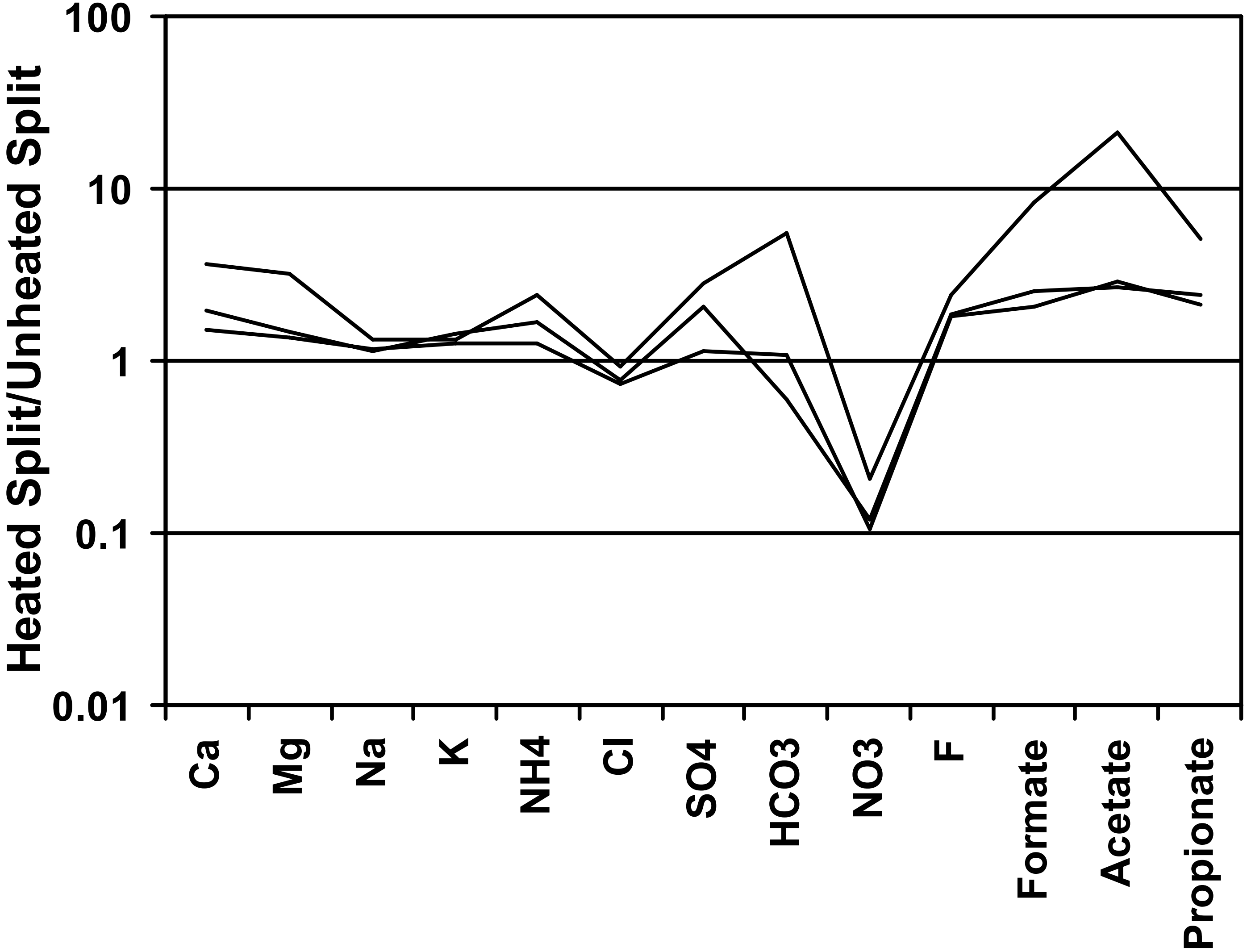
Experimental Heating of Dust

- **Aliquots of existing underground (ESF and ECRB) and atmospheric (cyclone) dust samples were split into two fractions**
- **One fraction was heated at approximately 180°C for two months at one atmosphere in an open container**
- **Unheated and heated splits were leached for soluble cations and anions and the analyses were compared**

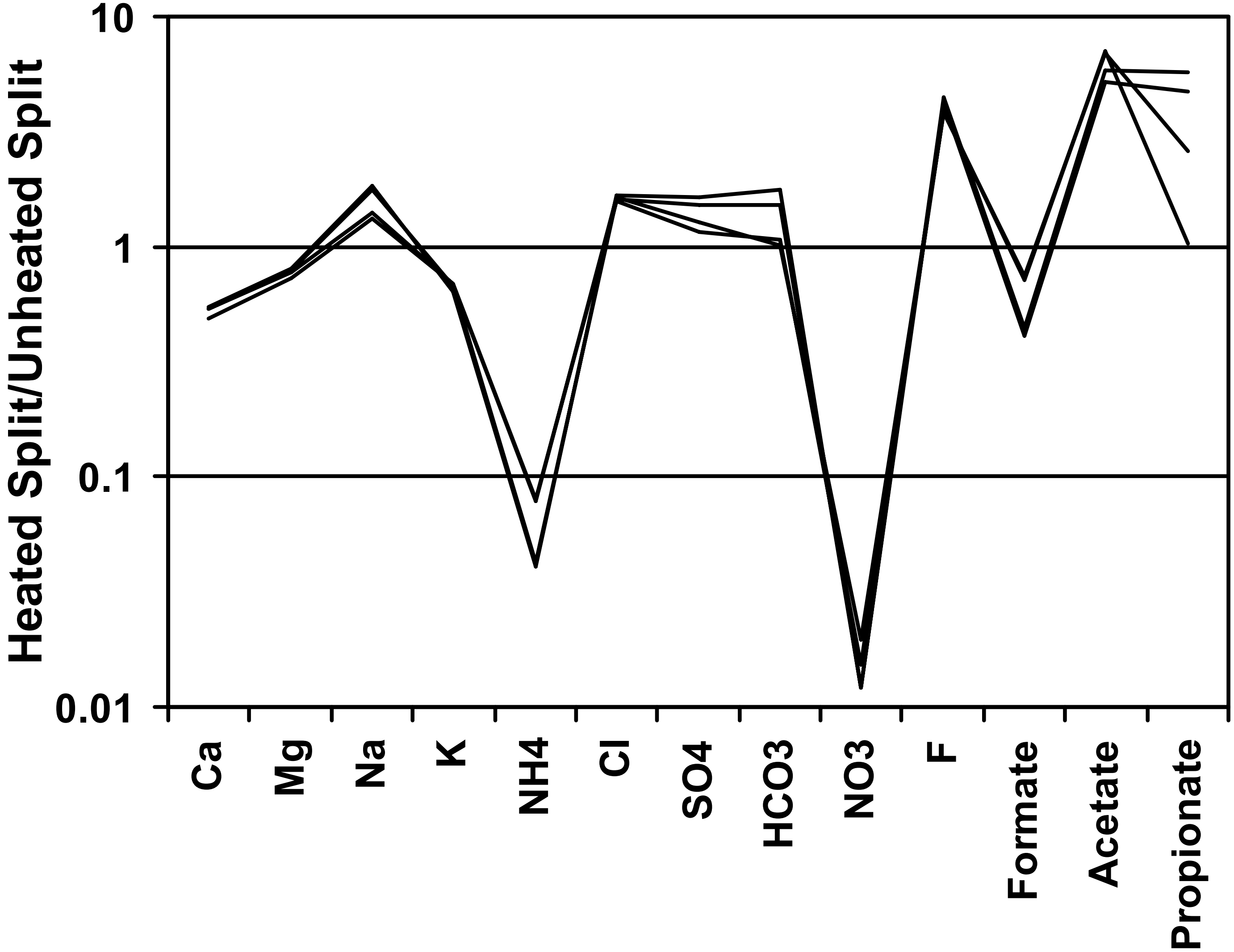
Heated ESF-2 Dust



Heated ECRB Dust



Heated Atmospheric Dust



Reduction of Nitrate by Organic Material*

- Nitrogen occurs in nature with valences of +5 in NO_3^- to -3 in NH_4^+ and a reduction series can be written as: $NO_3^- \rightarrow NO_2^- \rightarrow N_{2(g)} \rightarrow NH_4^+$
- Nitrate can be reduced by reactions of the type:

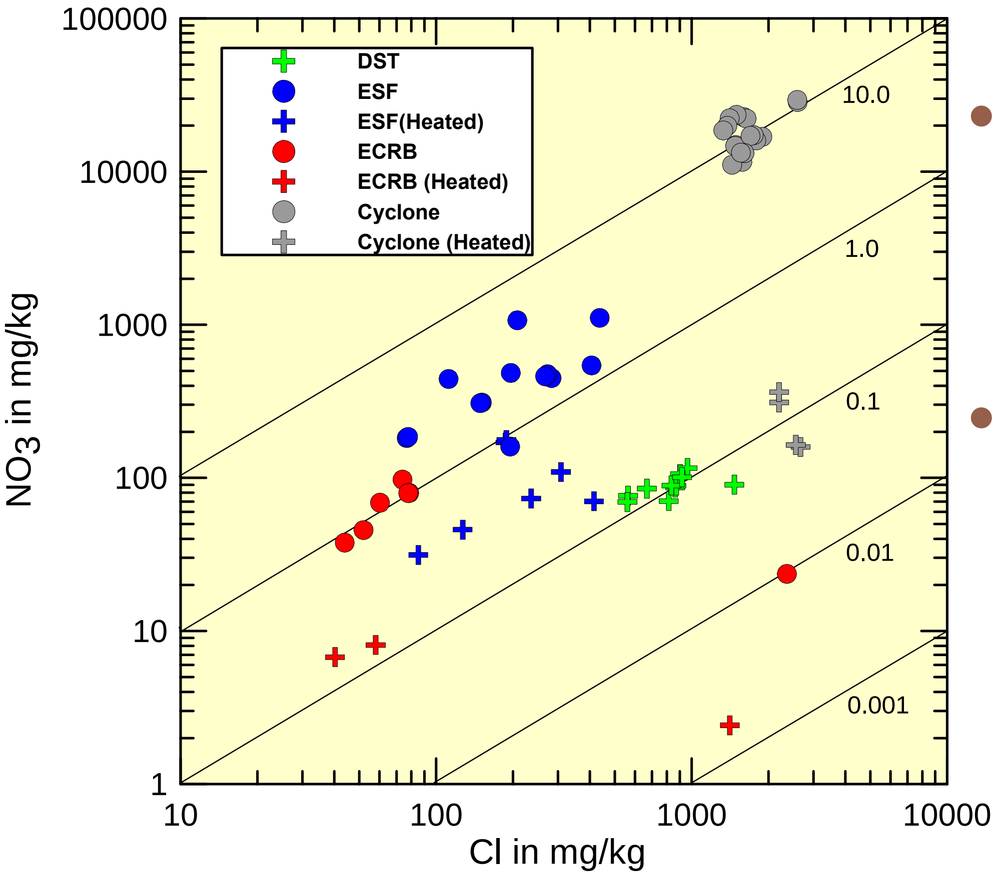
$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2\uparrow + 6H_20$$

- Reduction of nitrate by organic matter is well documented:

$$5CH_2O + 4NO_3^- \rightarrow 2N_2\uparrow + 4HCO_3^- + CO_2\uparrow + 3H_2O$$

*Appelo, C.A.J., and Postma, D., 1994, Geochemistry, Groundwater and Pollution: A.A. Balkema, Rotterdam, p. 250, 270

Nitrate-to-Chloride Relationships in Heated Dust



- **Underground and atmospheric dust typically have NO_3/Cl ratios between 1 and 10**
- **NO_3/Cl ratios are reduced 1 to 2 orders of magnitude due to loss of NO_3 upon heating to 180° to 200°C for about 2 months**

Summary

- **Underground dust**
  - Contains less than 1 percent soluble salts with NO_3/Cl ratios of 1 to 10
  - Relative to host rock, underground dust is enriched in Fe (and other metals), C, Cl, F, calcite, and bound water
- **Surface deposits of dust**
  - Where exposed, have been leached of most of their soluble salts
- **Atmospheric (cyclone) dust**
  - Contains several percent soluble salts with highest NO_3/Cl ratios (average 10)
  - Bulk analyses not yet available because of limited sample size

Summary (cont'd)

- **Low nitrate observed in DST dust relative to ESF dust**
- **Heating (2 months at 180°C) of underground and atmospheric dust substantially reduced NO_3 and NH_4 contents (except for ECRB dust) and reduced NO_3/Cl ratios by one to two orders of magnitude**
  - **Loss of NO_3 may be due to redox reactions involving organic carbon**
  - **Loss of NH_4 due to instability of ammonium salts**

Supplemental Slides

Effects of Temperature on the Compositions of Soluble Salts in Dust at Yucca Mountain

Contributors to the Dust Study

- BSC-SMF Staff
- Jon Darnell
- Robert Dickerson
- John Dinsmoor
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- Cliff Howard
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- Loretta Kwak
- Catherine Madore
- Brian Marshall
- Alan Mitchell
- Richard Moscati
- Leonid Neymark
- Thomas Oliver
- James Paces
- Connie Sorell
- Joseph Whelan

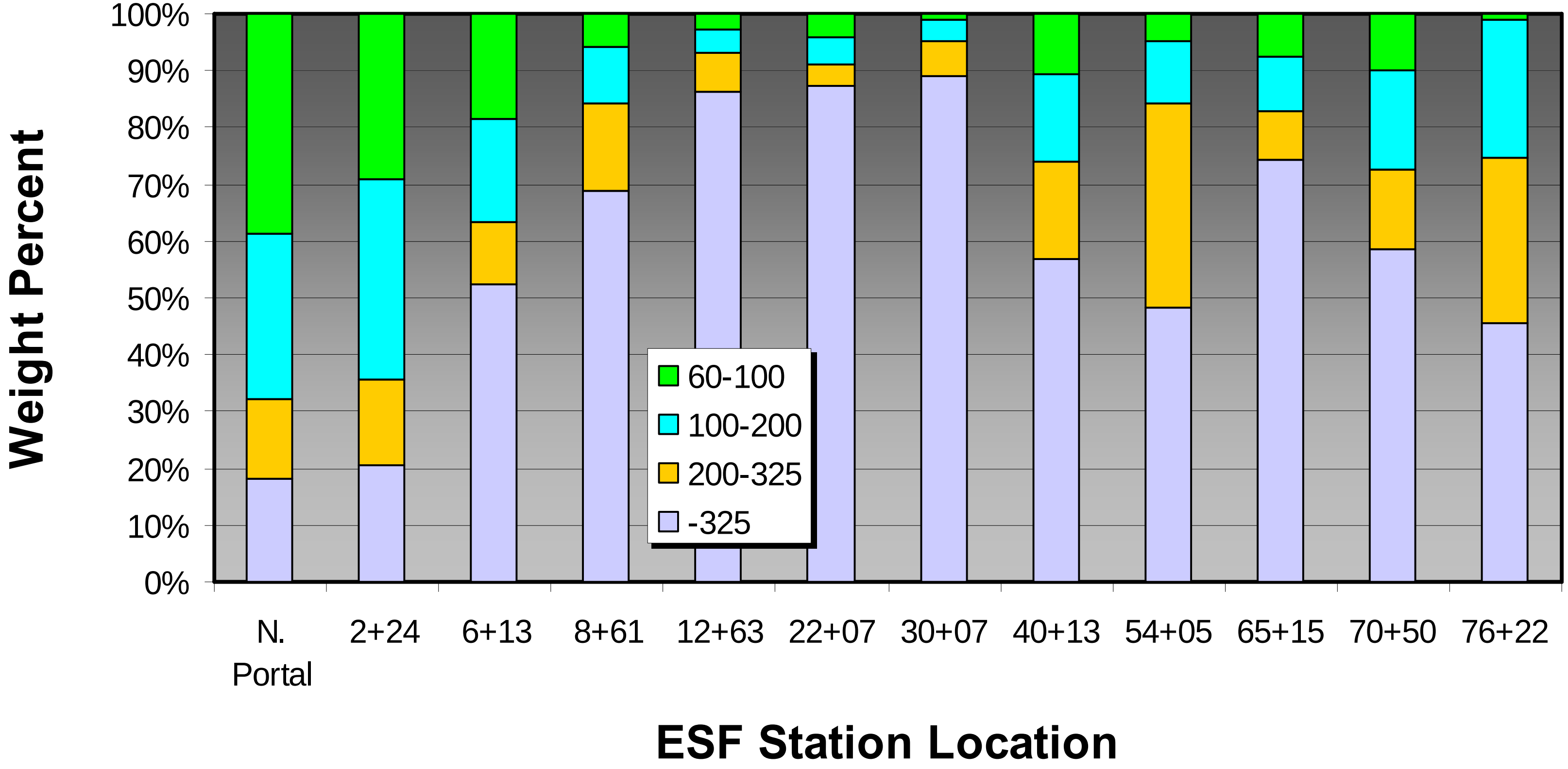
Sources of Underground Dust

- Mining (tunnel boring machine, Alpine miner, drill and blast, muck haulage)
  - Comminution of rock including fracture minerals, vapor-phase minerals, and alteration minerals (clays and zeolites)
- Particulates from diesel exhaust
- Salts from evaporated water
  - Construction water (tagged with LiBr)
  - Pore water salt halos on tunnel walls
- Abraded neoprene and fiber from conveyor belts

Sources of Underground Dust (cont'd)

- **Organic aerosols from lubricating oil, diesel oil, grease, hydraulic fluids, etc.**
- **Metal particles from a variety of sources**
- **Concrete particles from emplacement and abrasion of inverts**
- **Salts from human effluents**
- **Dust from the surface transported into the ESF and ECRB on materials and by the supply air**

Particle Size Distribution of ESF-2 Dust
(shown in mesh size)



Average Compositions of ESF-2 Dust and the Topopah Spring Tuff (rhyolite)

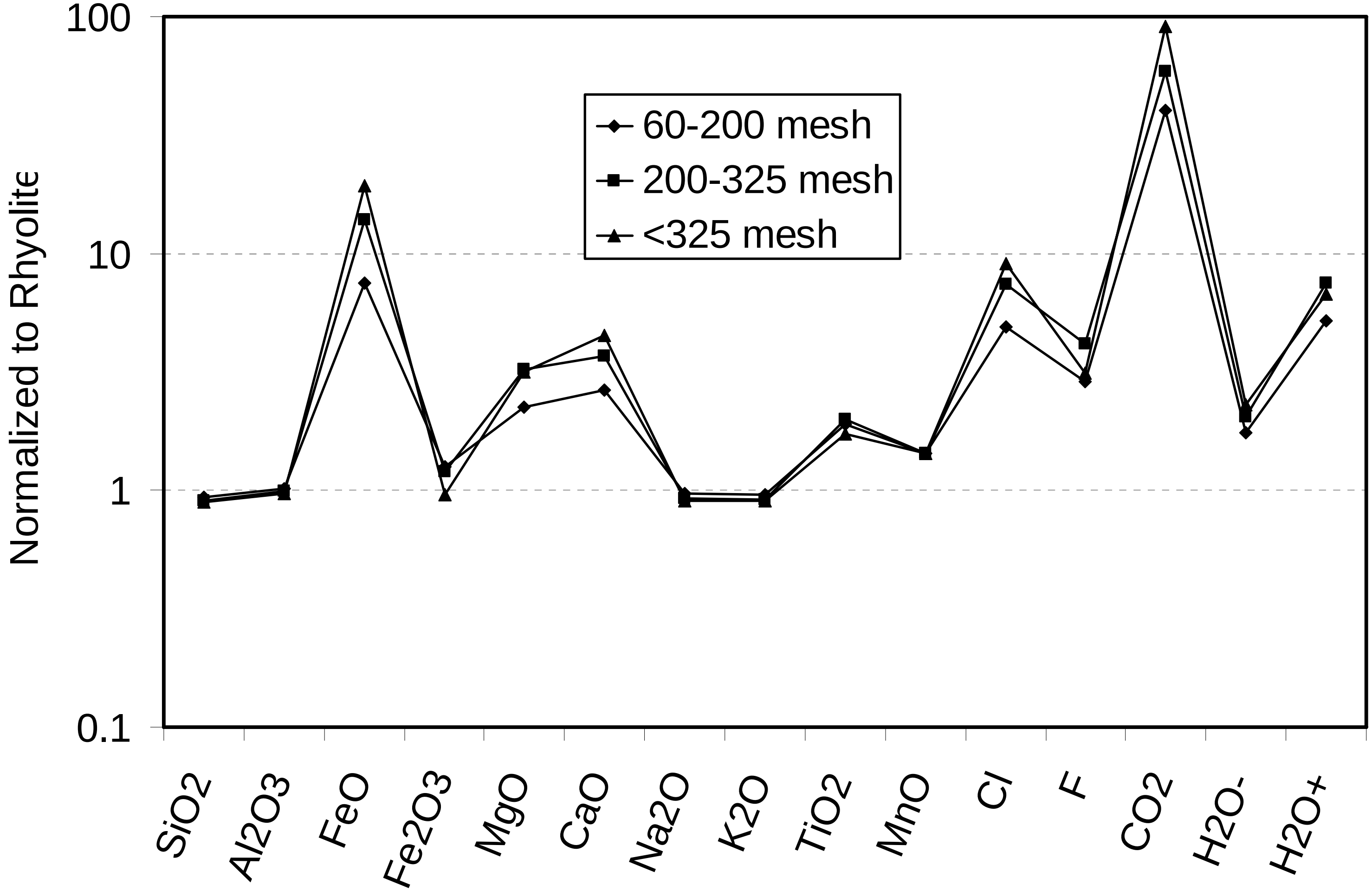
	60-200 mesh		200-325 mesh		-325 mesh		Tpt	
	Mean	*Stdev*	Mean	*Stdev*	Mean	*Stdev*	Mean	*Stdev*
SiO_2	**71.02**	*2.54*	**68.53**	*2.57*	**67.92**	*2.19*	**76.29**	*0.32*
Al_2O_3	**12.71**	*1.25*	**12.45**	*1.00*	**12.22**	*0.59*	**12.55**	*0.14*
FeO	**0.97**	*0.85*	**1.80**	*1.24*	**2.52**	*0.85*	**0.13**	*0.05*
Fe_2O_3	**1.22**	*0.51*	**1.16**	*0.63*	**0.93**	*0.44*	**0.97**	*0.07*
MgO	**0.27**	*0.21*	**0.39**	*0.23*	**0.38**	*0.21*	**0.12**	*0.02*
CaO	**1.32**	*0.57*	**1.85**	*0.65*	**2.26**	*0.65*	**0.50**	*0.03*
Na_2O	**3.40**	*0.52*	**3.25**	*0.47*	**3.18**	*0.38*	**3.52**	*0.11*
K_2O	**4.63**	*0.54*	**4.39**	*0.38*	**4.34**	*0.29*	**4.83**	*0.06*
TiO_2	**0.21**	*0.10*	**0.22**	*0.10*	**0.19**	*0.06*	**0.11**	*0.00*
P_2O_5	**0.09**	*0.16*	**0.25**	*0.54*	**0.16**	*0.27*	**<0.05**	---
MnO	**0.10**	*0.02*	**0.10**	*0.02*	**0.10**	*0.01*	**0.07**	*0.01*
Br	**0.002**	*0.002*	**0.004**	*0.003*	**0.004**	*0.002*	---	---
Cl	**0.082**	*0.050*	**0.124**	*0.071*	**0.151**	*0.061*	**0.017**	*0.004*
F	**0.110**	*0.110*	**0.159**	*0.208*	**0.119**	*0.081*	**0.038**	*0.008*
S	**0.04**	*0.03*	**0.06**	*0.06*	**0.09**	*0.05*	**<0.05**	---
CO_2	**0.40**	*0.39*	**0.59**	*0.37*	**0.91**	*0.36*	**0.01**	*0.00*
C (organic)	**0.43**	*0.31*	**0.85**	*0.52*	**1.36**	*0.64*	---	---
H_2O-	**0.42**	*0.27*	**0.49**	*0.30*	**0.55**	*0.28*	**0.24**	*0.07*
H_2O+	**2.09**	*1.27*	**2.99**	*1.29*	**2.69**	*0.78*	**0.40**	*0.09*
SUM	**99.48**	*0.42*	**99.45**	*0.99*	**100.05**	*0.52*	**99.79**	

Stdev = standard deviation, Tpt = Topopah Spring Tuff

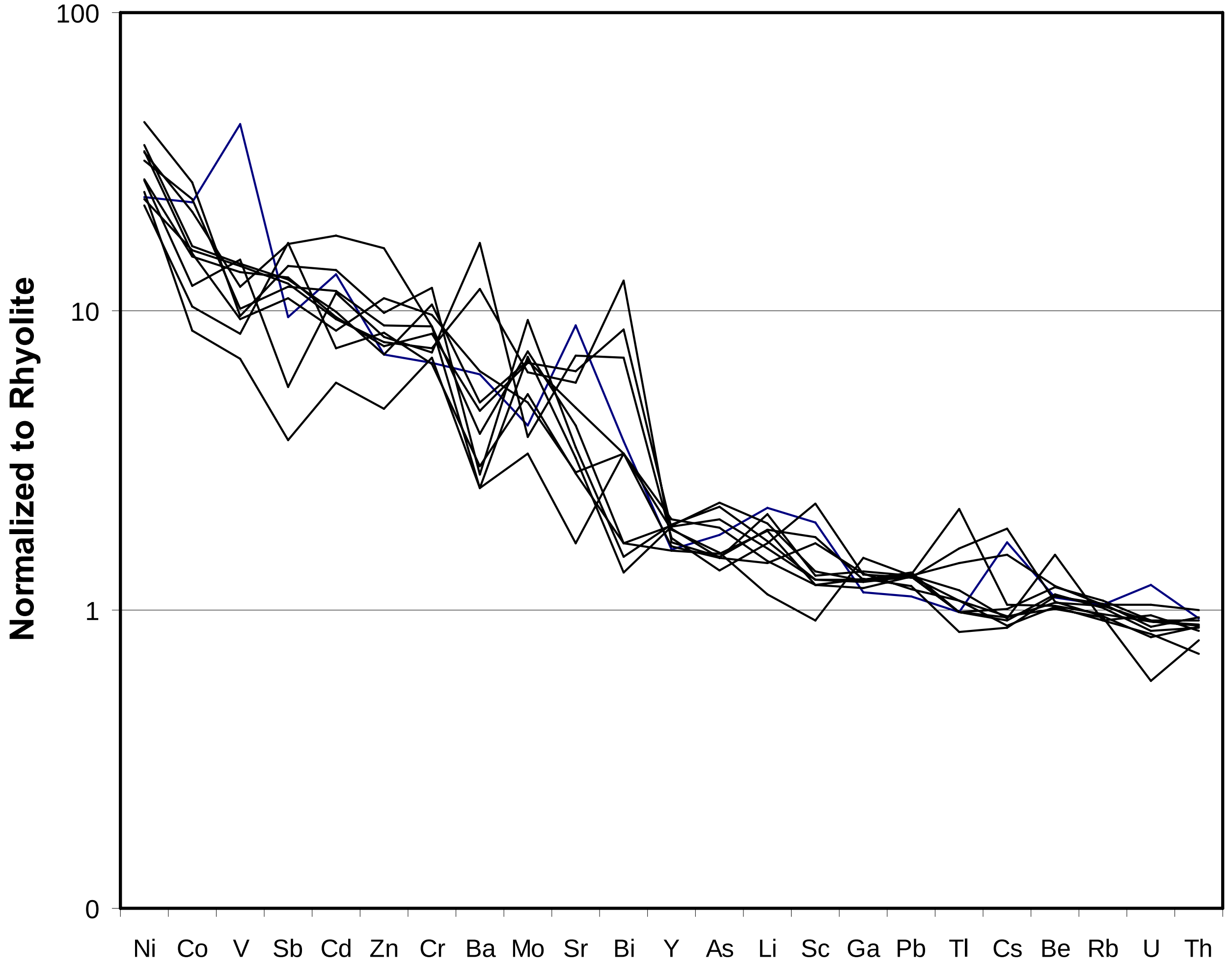
Average Compositions of Soluble Salts in mg/kg

Ion	ESF-2	ECRB	Surface	Atmospheric	Heated Drift
Ca^{2+}	879	324	85	4450	3830
Mg^{2+}	68	30	12	1030	5
K^{+}	239	51	111	1840	550
Na^{+}	405	133	54	4200	1680
NH_4^{+}	124	24	10	352	72
SiO_2	250	52	167	301	653
Cl^{-}	202	62	24	1750	857
Br^{-}	28	5.4	<12	<5	260
F^{-}	20	8.5	4.2	21	159
HCO_3^{-}	2270	541	347	3790	3120
NO_3^{-}	442	66	75	16500	89
SO_4^{-}	914	256	42	5330	2960
PO_4^{3-}	4.4	2.7	20	136	7.6

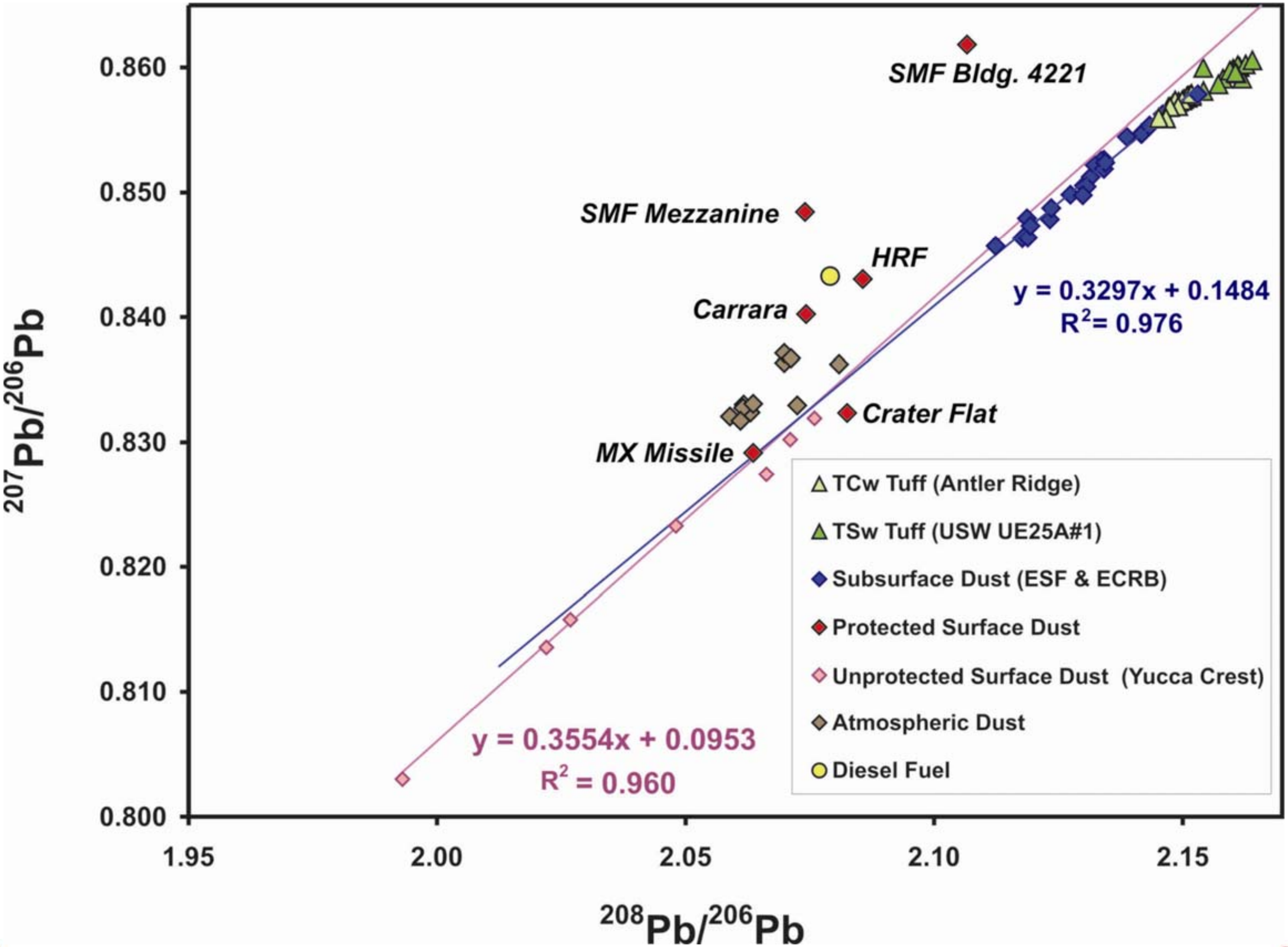
Major Elements in ESF-2 Dust Normalized to Host Rock



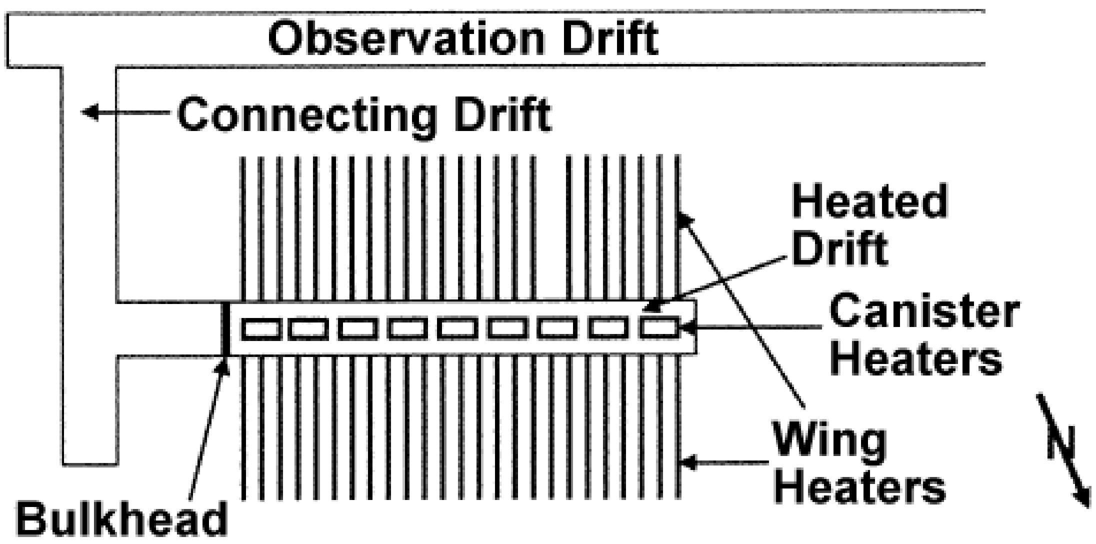
Trace Elements in ESF-2 Bulk Dust Size Fractions Normalized to Host Rock

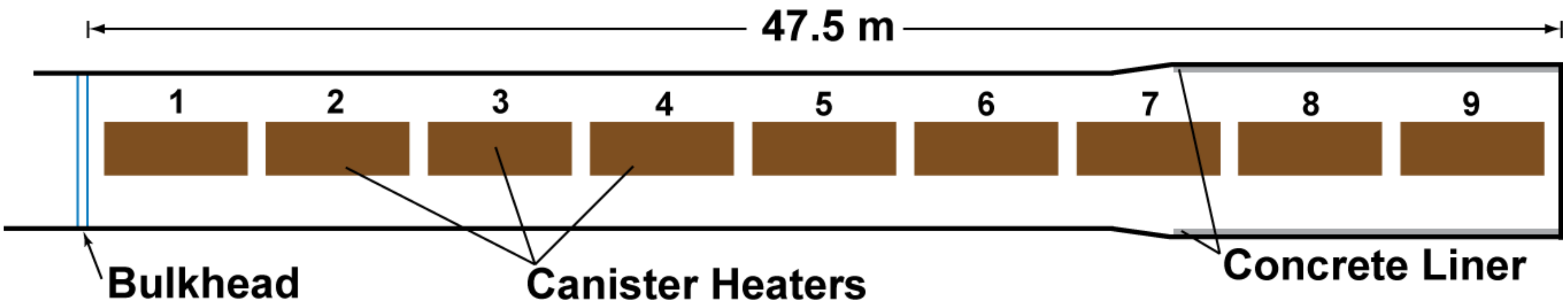


$^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ Ratios in Dust, Host Rocks, and Diesel Fuel



Map of Heated Drift and Location of Samples



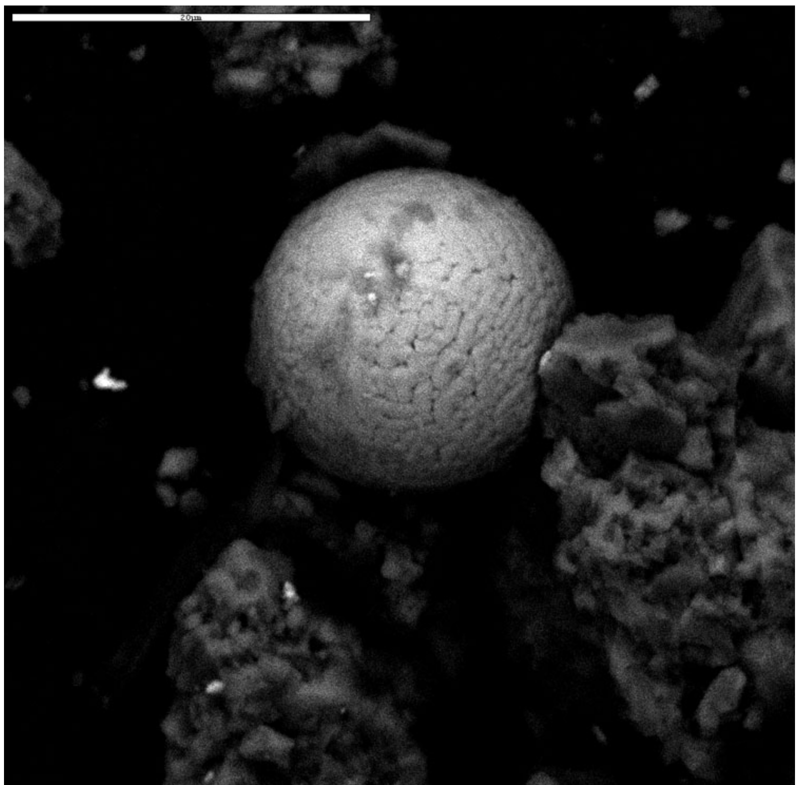


Concrete Used in the DST

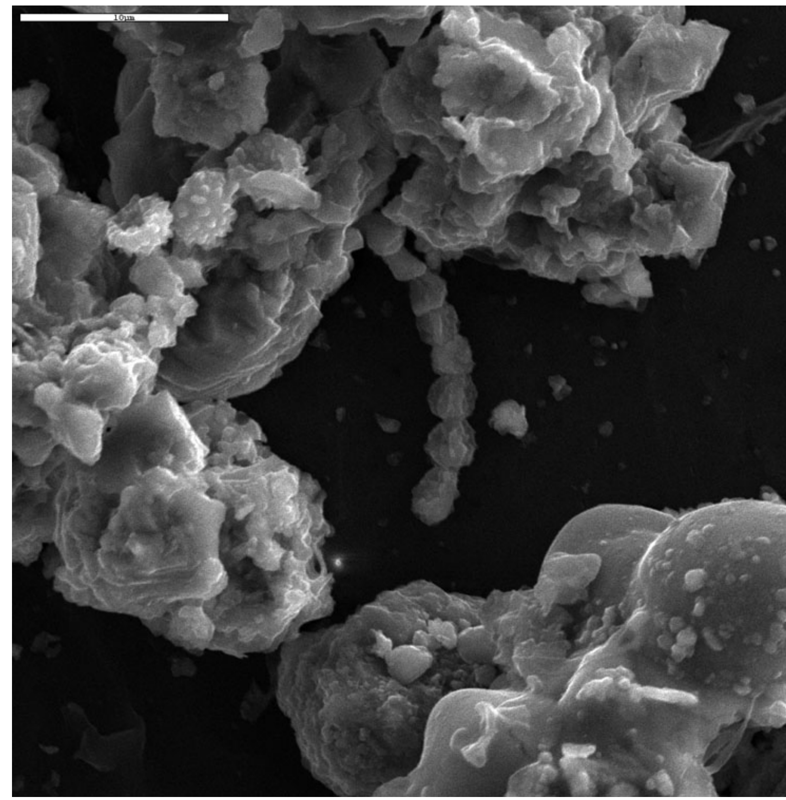
- Aggregate consists mostly of limestone and dolomite with sparse fragments of siltstone or argillite
- Slide was stained for calcite
  - Limestone clasts are pink to red
  - Dolomite clasts are gray to white
  - Cement matrix is deep red
  - Porosity is blue

SEM Images ECRB Dust

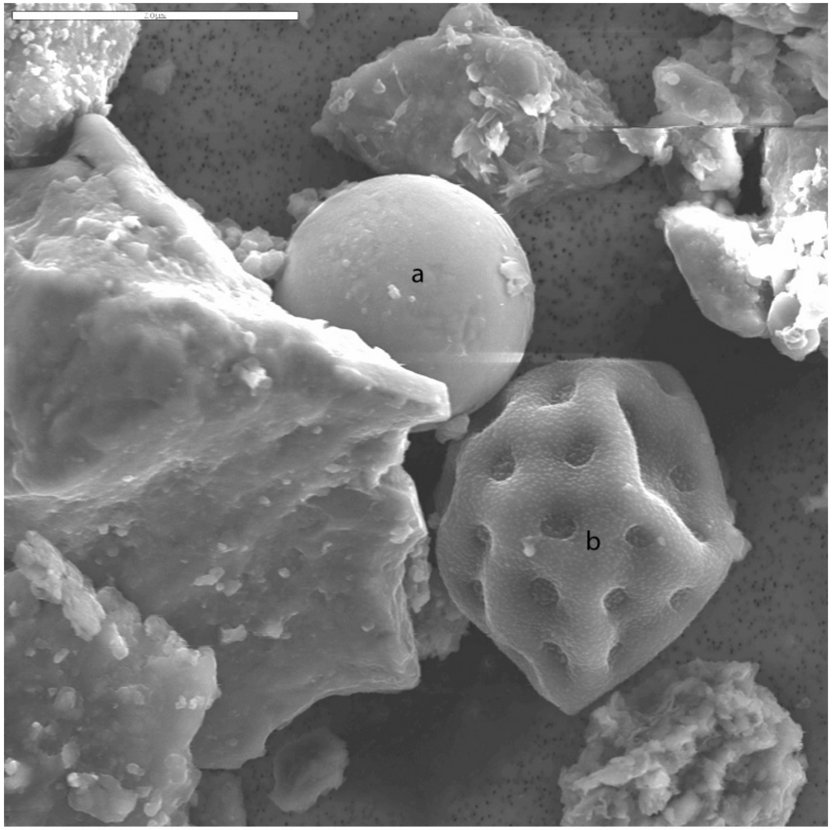
Fe-rich sphere may be fly ash or welding droplet



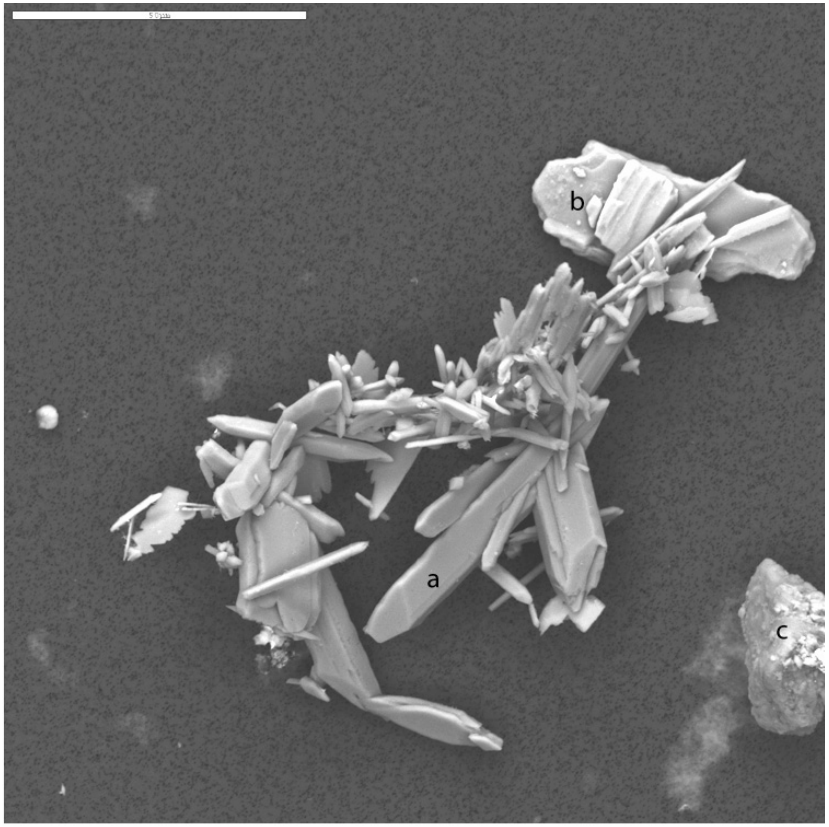
Pollen grains with dust particles and opal spheres



SEM Images SMF Attic Dust



4506a - Fly ash with pollen
a (Fe, O)
b (organic)



4506a - Sand crystal agglomeration of Na, S, O crystals
a (Na, S, O)
b (Si, Al, O, K, (Mg, Fe))
c (Si, O, Al, Mg, (K, Ca, Fe)

Information Products

- Peterman, Zell E., 2001. Letter Report on Dust Geochemistry, September 7, 2001, ACC# MOL.20011004.0234.
- Peterman, Zell E., 2002. Supplement to Letter Report on Dust Geochemistry (9/7/01), February 26, 2002, ACC# MOL.20031110.0319.
- Peterman, Z. E., Paces, J. B., Neymark, L. A., and Hudson, D., 2003, *Geochemistry of Dust in the Exploratory Studies Facility:* International High Level Radioactive Waste Management Conference, March 30—April 2, 2003, p.637-645.
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- Wolery, Thomas, Peterman, Zell, Carroll, Susan, Jove-Colon, Carlos, Sutton, Mark, Rard, Joseph, and Wijesinghe, Ananda, 2005. *Dust Salts and Deliquescence on Waste Packages in an Unsaturated-Zone Repository (abs), in* Proceedings of the 15th Annual Goldschmidt Conference: A Voyage of Discovery, Moscow, Idaho, USA, May 20-25, 2005, p. A413.
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