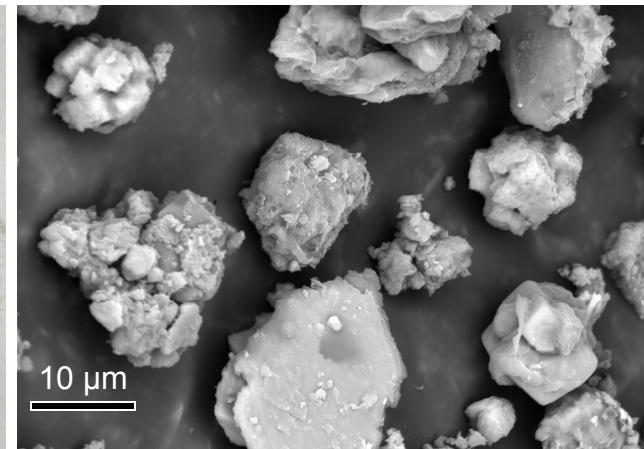


Exceptional service in the national interest



Sampling and Analysis of Dusts/Salts from In-service Storage Canisters at Calvert Cliffs, Hope Creek, and Diablo Canyon ISFSIs

Charles Bryan and David Enos, Sandia National Laboratories
SNL/BAM workshop, 8 October 2014, Albuquerque



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Overview

- **Background and ISFSI's sampled**
- **Types of samples and sampling methods**
- **Sampling issues**
- **Analysis methods**
- **Hope Creek**
- **Diablo Canyon**

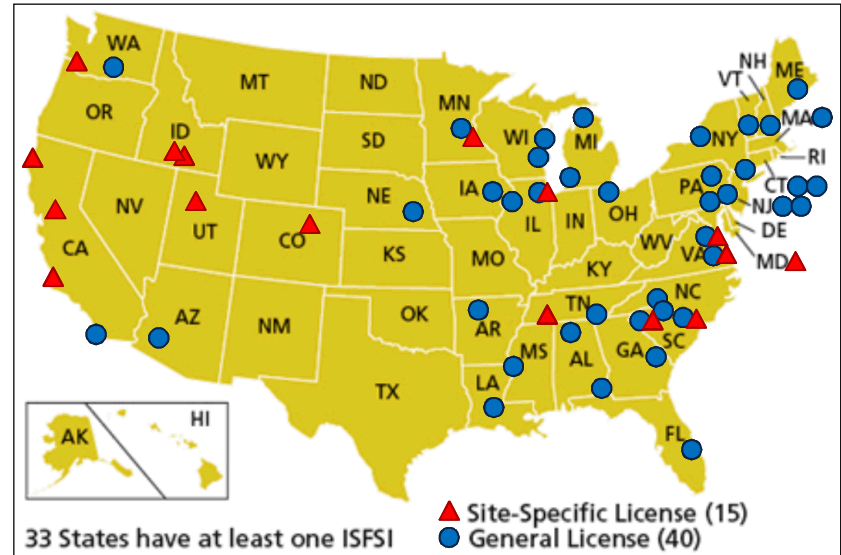
Background

- **Stress corrosion cracking (SCC) of stainless steel due to deliquescence of chloride-rich salts on the metal surface is well-known, especially in near-marine environments.**
- **Many Independent Spent Fuel Storage Installations are at coastal sites. Possible risk of SCC.**



Calvert Cliffs
NUHOMS
system

Diablo Canyon
HI-STORM
system

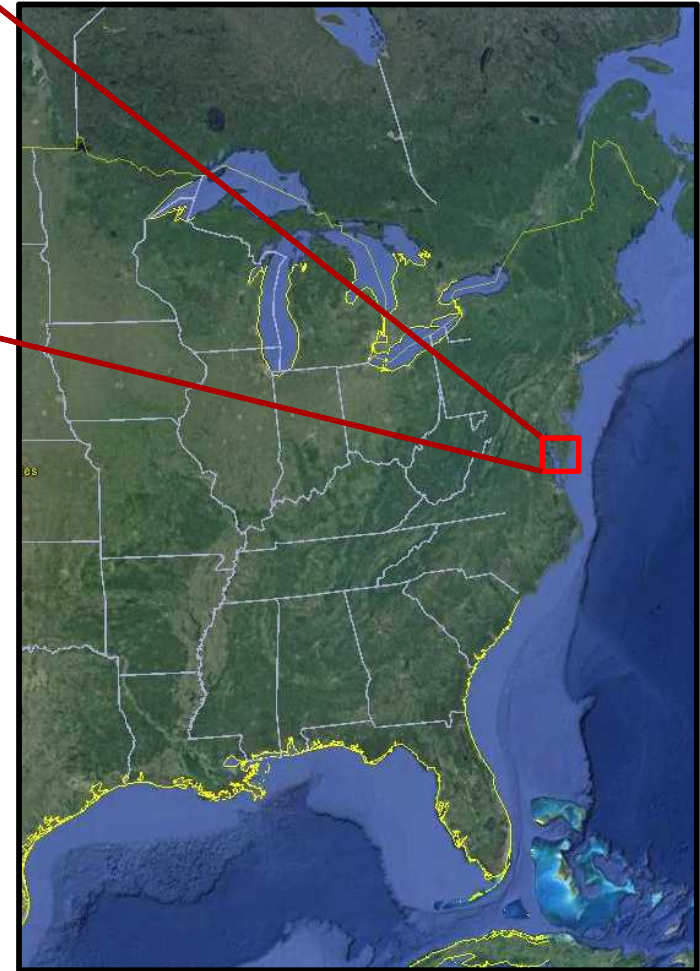


- **EPRI sampling program: Assess the composition of dust on the surface of in-service stainless steel SNF storage canisters, with emphasis on the deliquescent salts.**
- **ISFSI locations sampled:**
 - Calvert Cliffs: Transnuclear NUHOMS system, horizontal storage canister (June, 2012)
 - Hope Creek: Holtec HI-STORM system, vertical canister (Dec, 2013)
 - Diablo Canyon: Holtec HI-STORM system (Jan 2014)
- **Samples delivered to Sandia National Laboratories for analysis**

Calvert Cliffs Site



Eastern U.S.

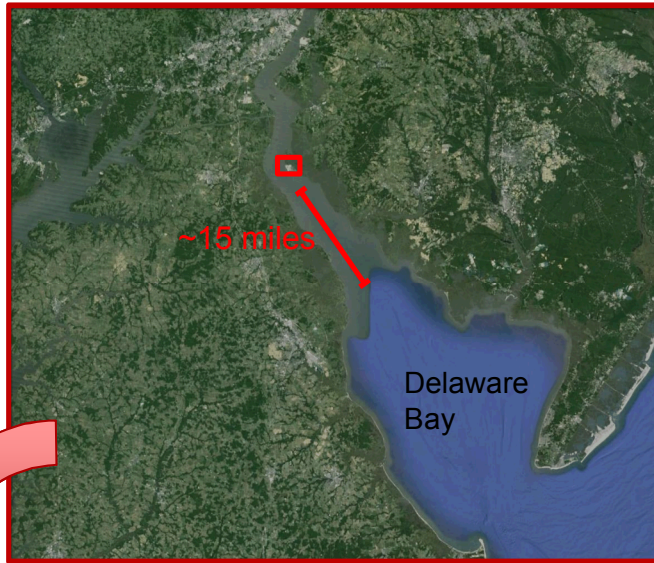


ISFSI is ~0.5 miles from Chesapeake Bay

- Sheltered bay
- Brackish water

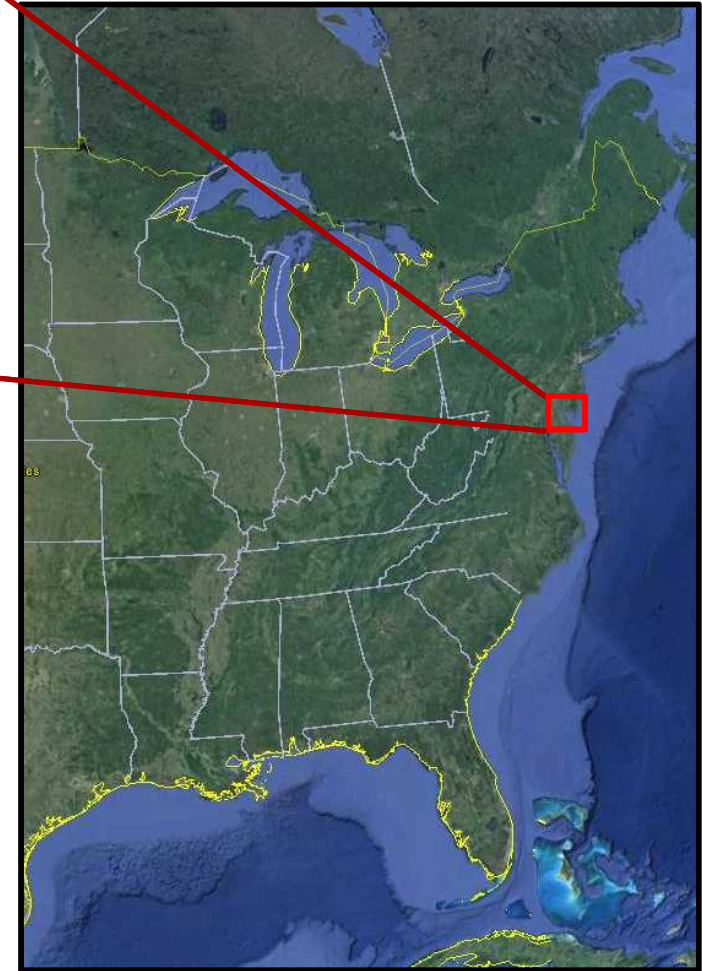
Hope Creek Site

Eastern U.S.



ISFSI is ~0.25 miles from the Delaware River, 15 miles upstream from Delaware Bay

- Brackish water
- Sheltered from open ocean



Diablo Canyon Site

Western U.S.



ISFSI is ~1/3 mile from the shoreline,
on a hill above the plant.

- Elevated (~400 feet) above sea level
- Rocky shore, breaking waves
- Open ocean



Sampling

■ Entry

- NUHOMS horizontal storage systems—entered through door, annulus around shield plug (~2.5 cm)
- HI-STORM systems—entered through upper ventilation opening



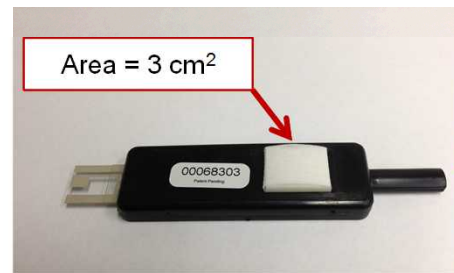
Removing the Gamma Shield



Sampling with the remote sampling tool

■ Wet sampling

- Salt-Smart™ sensors
- Used to characterize soluble salts (quantify amount per unit area)
- After use, sensor was split and captured salts were rinsed out for analysis



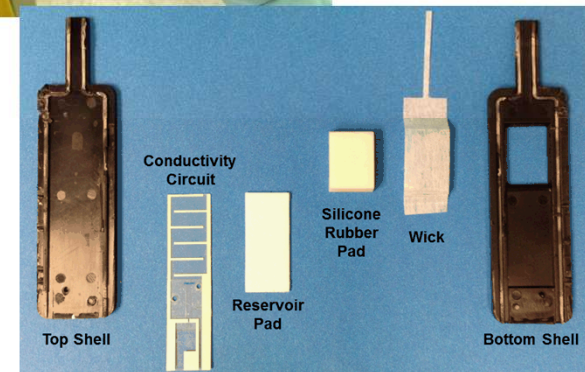
Salt-Smart™ sensor



■ Dry dust samples

- Scotch-Brite™ pads
- Used to characterize salt components (chemistry, mineralogy, texture); cannot quantify amount per unit area

Scotch-Brite™ pad



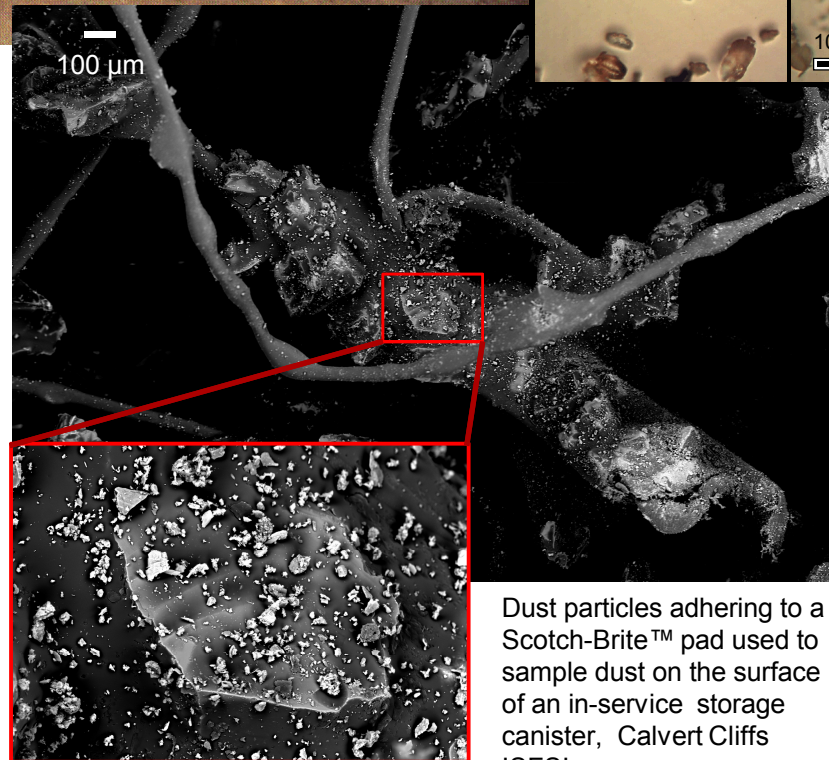
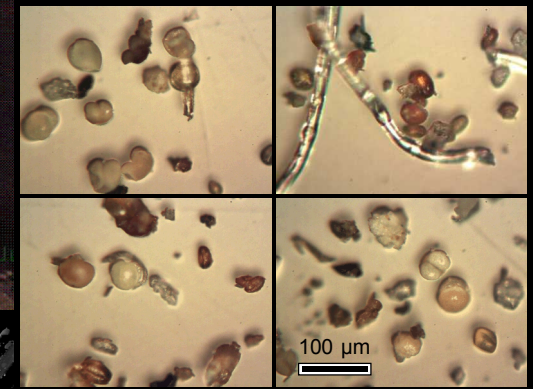
- **SEM imaging and energy dispersive system (EDS) element maps**
 - Dry samples
 - Provide textural and mineralogical information
 - Identification of floral/faunal fragments in dust
- **X-ray fluorescence**
 - Dry samples
 - Micro-analytical technique—allows chemical mapping of the dry pad surfaces with a resolution of $\sim 50 \mu\text{m}$
 - Provides semi-quantitative chemical analyses—yields element ratios that can be used in mass balance calculations
 - Cannot detect elements lighter than sodium (e.g., oxygen, nitrogen)
- **X-ray diffraction**
 - Analysis of pads for mineralogical information
- **Chemical Analysis**
 - Dry pad and Salt-smart[®] samples leached with DI water, and the leachate analyzed to determine soluble salts in the dust
 - Insoluble fractions digested and analyzed to determine bulk chemistry

Results: Calvert Cliffs

- The canister upper surface was more heavily coated with dust and salts due to gravitational settling. Samples from upper surface contained abundant pollen.
- The soluble salts are Ca- and SO₄-rich. Gypsum is the dominant salt phase present.
- Chlorides comprise a small fraction of the total salt load, and are dominantly NaCl.
- **Despite the proximity to the coast and prevailing winds from the east, the dusts sampled from in-service containers at Calvert Cliffs do not appear to have a large sea salt component. Chesapeake Bay is brackish, and may be sheltered sufficiently to limit wave-generated sea-salt aerosols.**



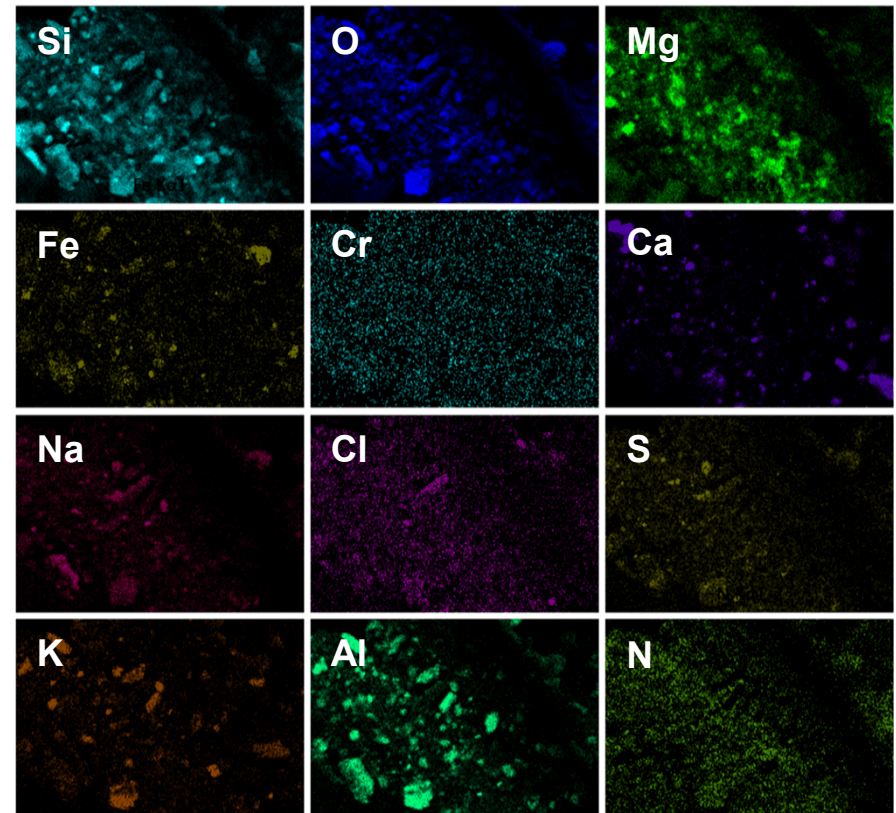
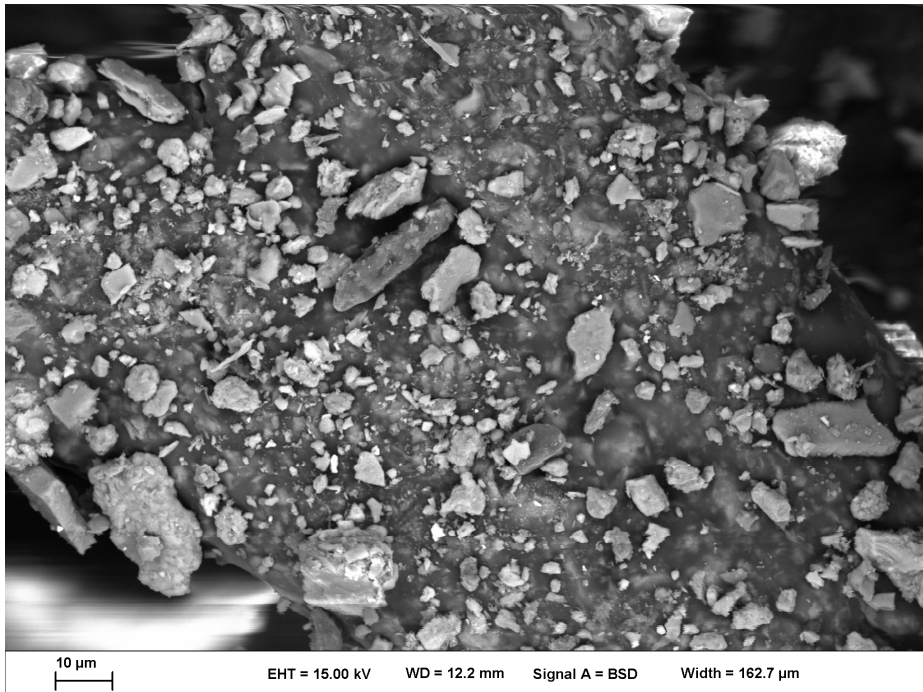
Pollen grains in dust on the upper surface of the canister.



Dust particles adhering to a Scotch-Brite™ pad used to sample dust on the surface of an in-service storage canister, Calvert Cliffs ISFSI.

Results: Hope Creek

- Flat canister top much more heavily coated than vertical sides.
- Dust dominated by insoluble minerals (quartz, clays, aluminosilicates). Soluble salts minor; dominantly gypsum, carbonates. Sparse chlorides, mostly isolated grains of NaCl.
- **Despite the proximity to the coast, the dusts sampled from in-service containers at Calvert Cliffs do not have a large sea salt component. Chesapeake Bay is brackish, and may be sheltered sufficiently to limit wave-generated sea-salt aerosols.**



Chemistry: Hope Creek Salt-Smarts[®]

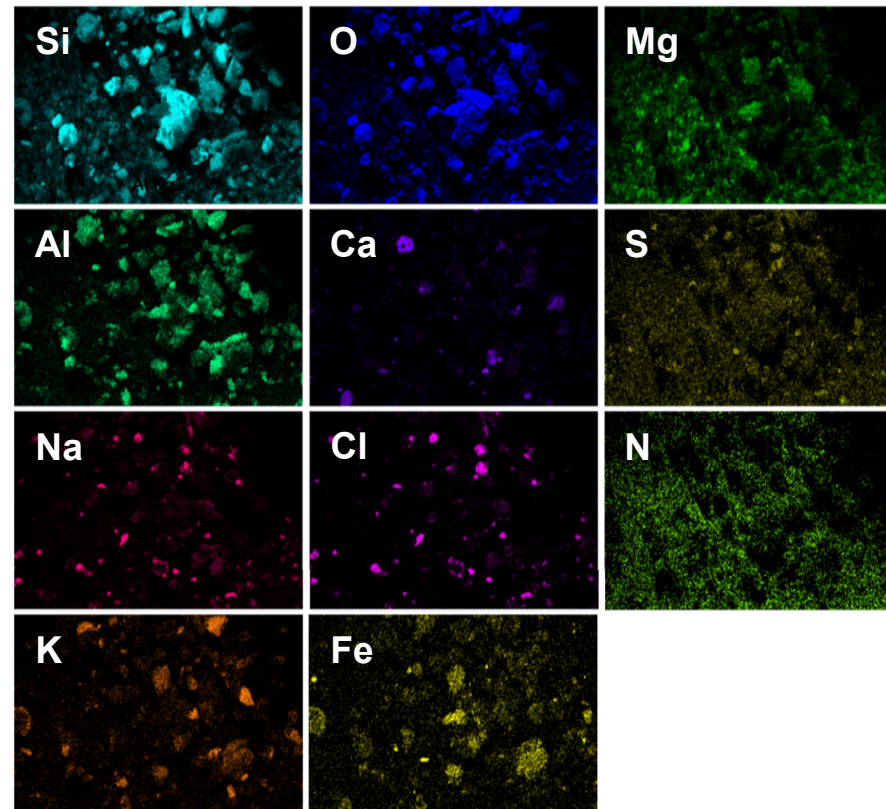
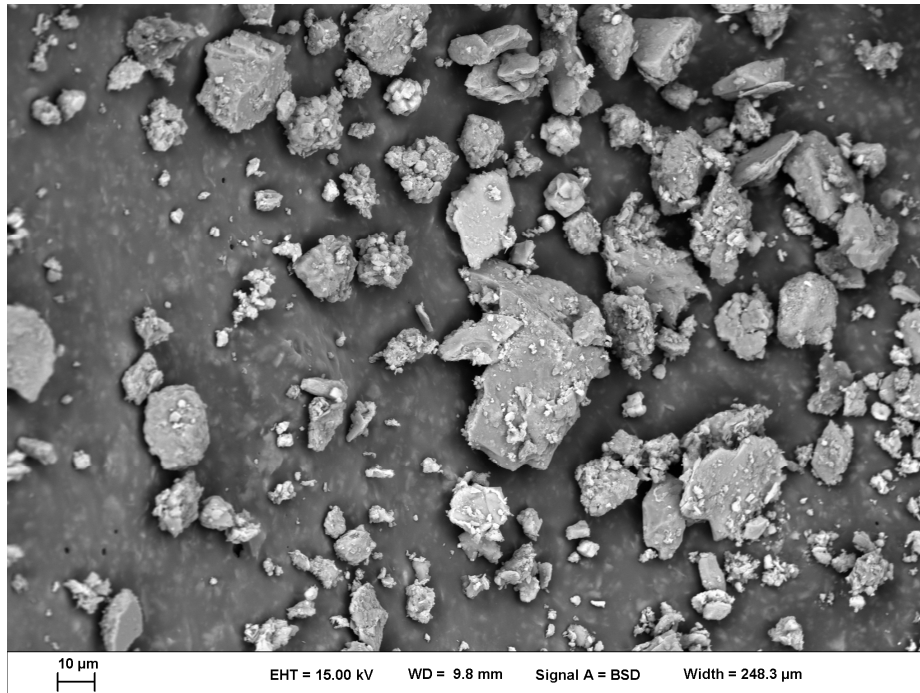
Sample	Loc.	Depth, ft	Temp, °F	Amount present, µg/sample										SUM
				K	Ca	Mg	Na	NH ₄ ⁺	F ⁻	Cl ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻	
144-008	Side	13.0	93.2	0.8	3.4	0.6	0.1	2.7		0.9	2.7		4.1	15.4
144-009	Side	7.5	116.5	1.7	4.5	0.5	0.1	2.7		0.9	6.4	1.1	6.5	24.3
144-010	Side	1.0	133.9	1.4	4.2	0.4	0.4	2.4		1.2	5.0		4.4	19.4
144-013	Top	0.0	138	18	102	33	42	2.8	0.4	4.2	19	4.8	91	317
144-014	Top	0.0	141.2	6.4	29	8.0	13.4	2.7	0.4	18	7.3	1.3	55	142
144-003				0.6	2.2	0.4		1.4		0.5	3.3	1.2	2.1	11.6
144-004				0.3	3.2	0.6		2.9		0.8	1.8	0.5	1.7	11.8
145-006*	Side	13.0	70.6	2.2	4.4	0.6	0.5	2.3		2.2	8.1		4.7	25.1
145-007	Side	7.5	100.8	1.0	2.4	0.6	0.7	2.9		2.1	2.2	0.7	5.3	17.9
145-014	Side	1.0	130.3	0.9	3.2	0.8	0.6	3.2		1.2	2.5		9.1	21.5
145-013**	Top	0.0	174.1	15	91	30	32	2.8		2.2	15	3.5	82	273
145-011**				0.2	2.3	0.3		3.0		0.7	1.3		1.7	9.6
145-002				1.2	4.8	0.5		2.7		0.7	5.9	0.8	2.0	18.5
SS-BI-8 min-1					1.3	0.2		1.1		0.4	1.6		0.6	5.1
SS-BI-8 min-2					1.2	0.2		1.5		0.7	0.9	0.5	0.2	5.2
SS-BI-15 min					1.5	0.5		5.7	0.2	0.7	1.1	1.6	1.7	12.9

* Pad only damp

** Pad only partially saturated

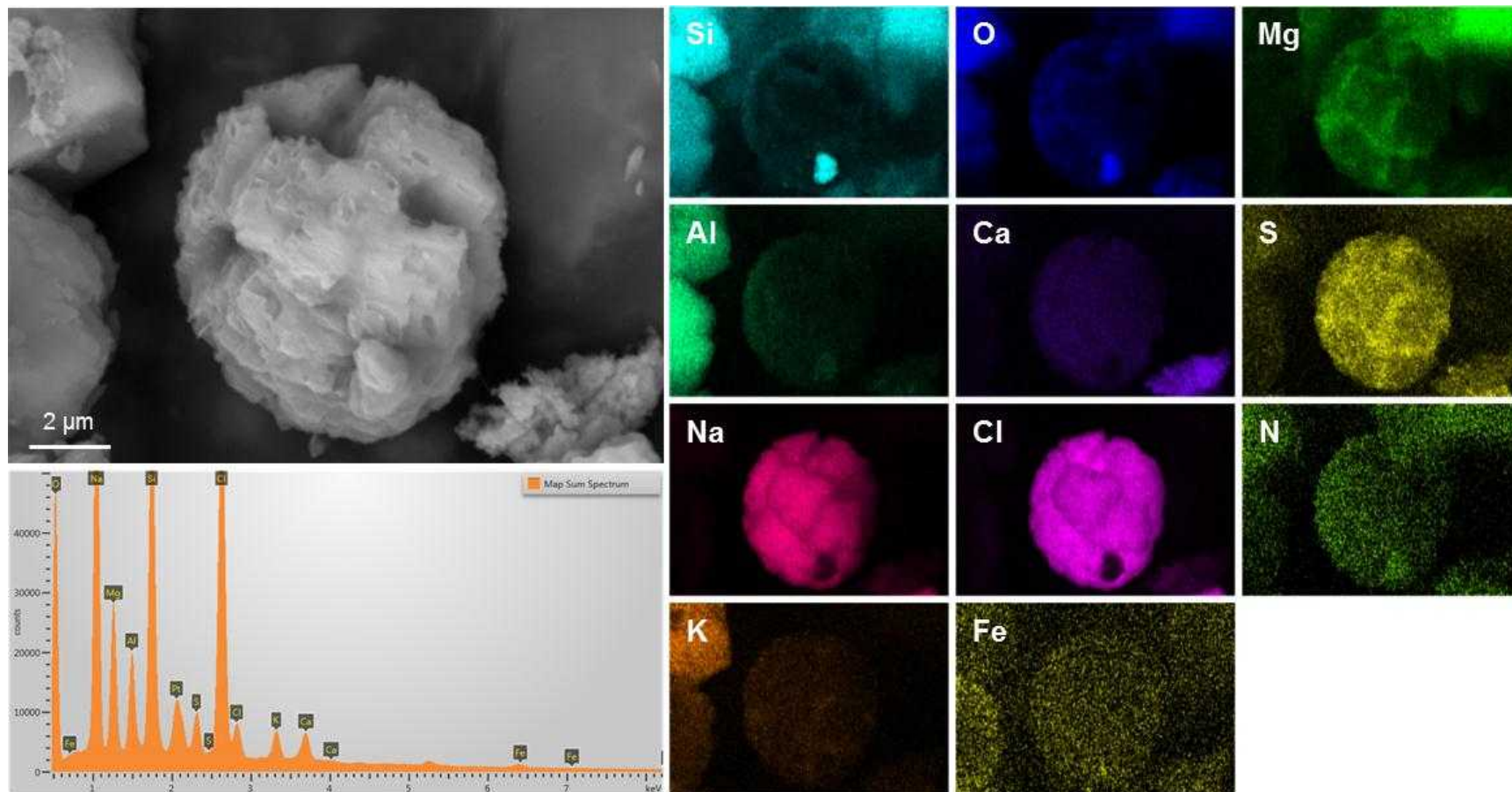
Results: Diablo Canyon

- Canister sides lightly coated, tops heavily coated.
- Dust dominated by insoluble minerals (quartz, clays, aluminosilicates), but chloride-rich soluble salts are abundant, present as sea-salt aggregates.
- **Heavy wave action at the Diablo Canyon site generates abundant sea-salt aerosols. Although 400 feet above sea level, Diablo Canyon canisters have a significant amount of sea-salts on the canister surfaces.**

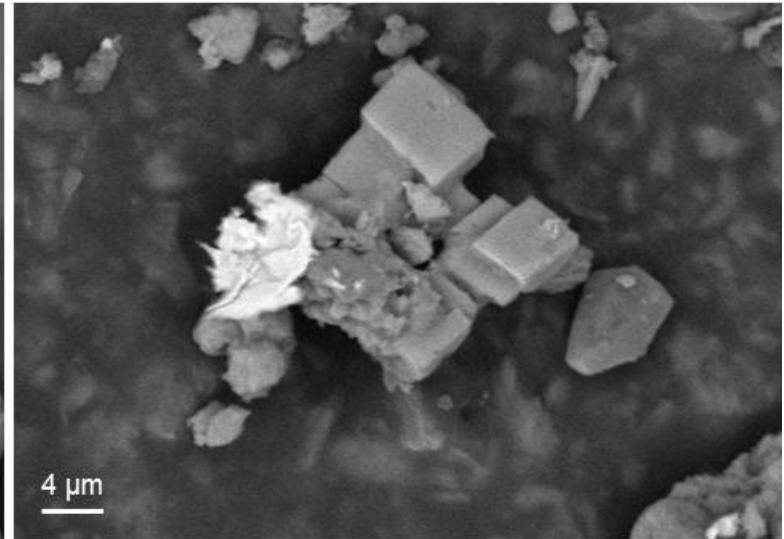
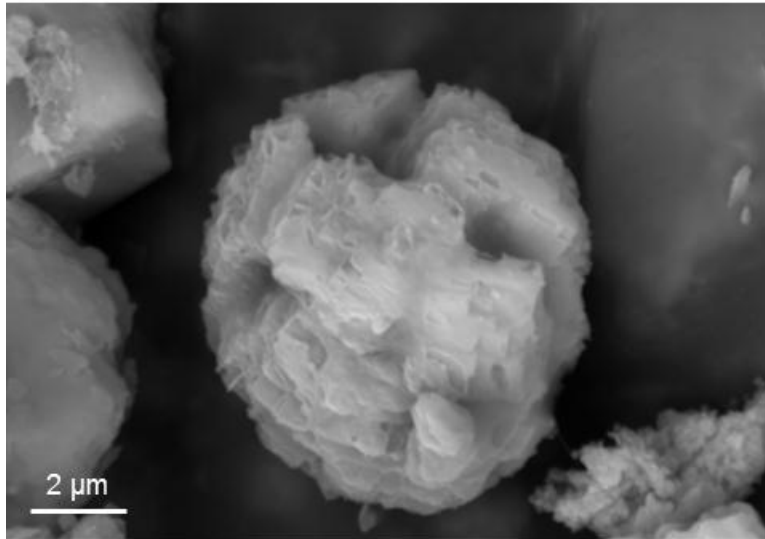
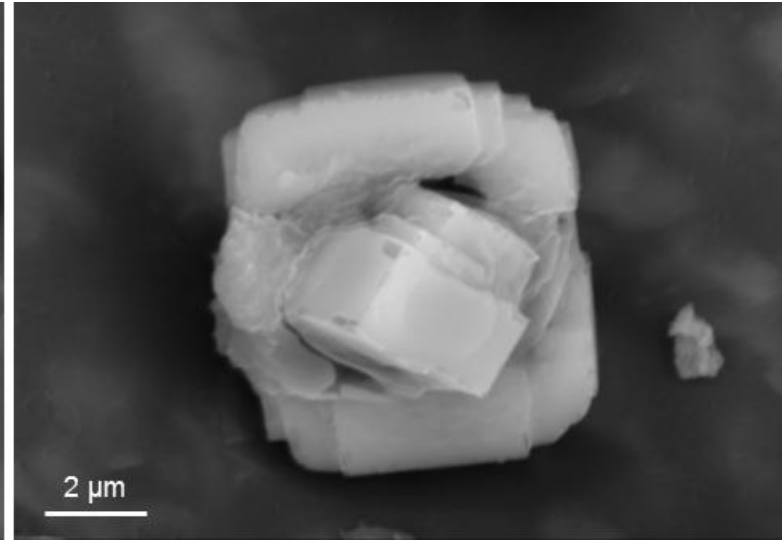
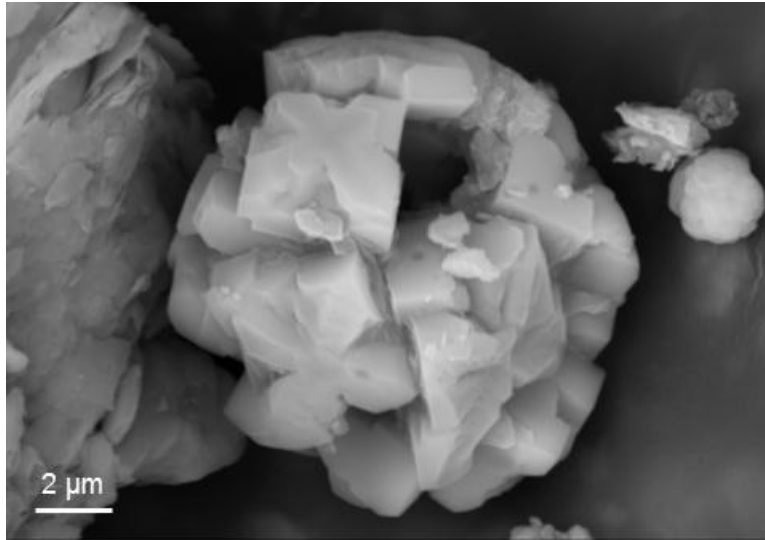


Results: Diablo Canyon

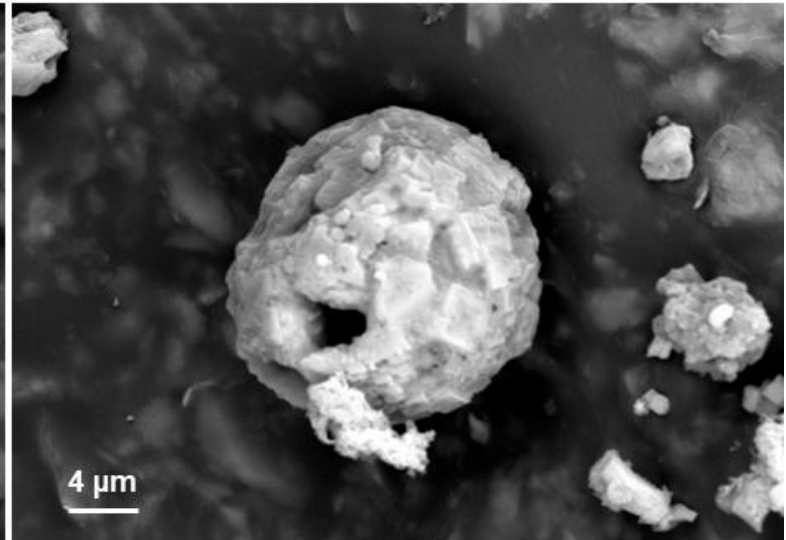
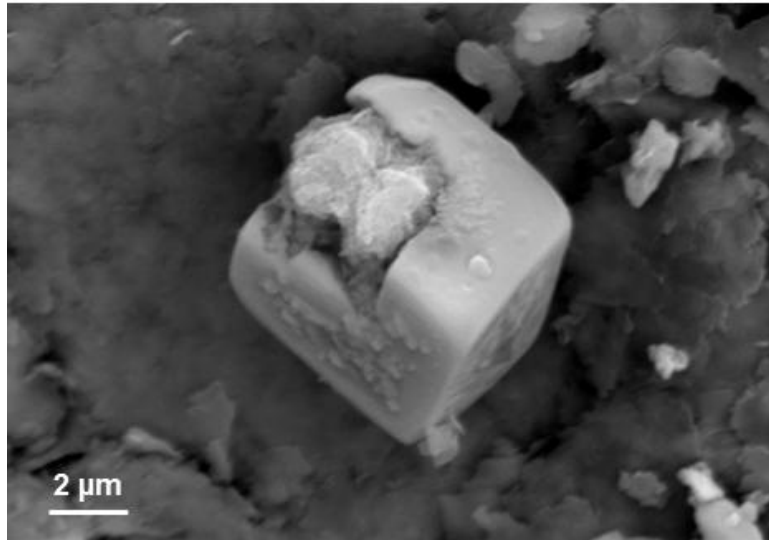
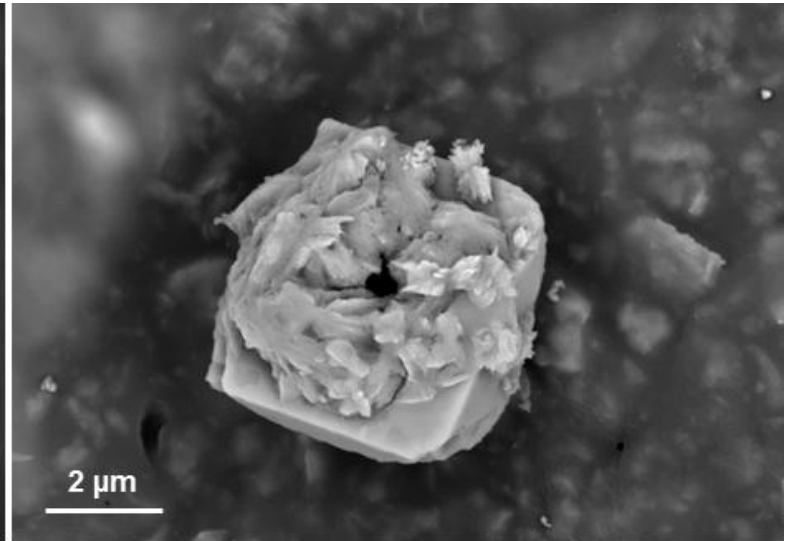
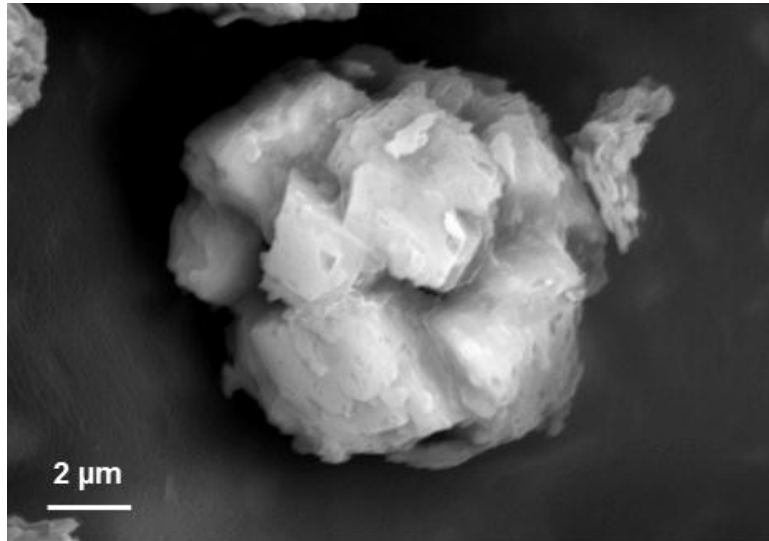
- Canister sides lightly coated, tops heavily coated.
- Dust dominated by insoluble minerals (quartz, clays, aluminosilicates), but chloride-rich soluble salts are abundant, present as sea-salt aggregates.



Diablo Canyon Sea-salt Aerosols



Diablo Canyon Sea-salt Aerosols



Chemistry: Diablo Canyon Salt Smarts

Sample	Location	Depth, ft	Temp, °F	Concentration, µg/sample									Sum, µg/sample
				Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	F ⁻	Cl ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻	
123-003	Side	14.0	119.7	0.3	0.6	2.4	0.6	0.3	1.2	1.5	0.4	4.3	11.6
123-004	Side	11.5	173.4	0.2	1.2	2.6	0.4	0.1	0.9	3.7	0.1	2.1	11.4
123-005*	Side	10.5	187.0	n.a.	0.3	3.6	0.2	0.3	0.5	0.6	0.5	1.4	7.2
123-002	—	—	—	14.4	0.9	6.0	0.9	0.9	14.1	11.3	n.a.	10.4	58.8
123-010	—	—	—	3.3	1.9	2.2	0.5	1.0	6.2	1.3	0.8	1.6	18.8
170-007*	Side	10.5	177.5	1.0	0.3	2.0	0.3	0.3	1.0	1.9	n.a.	1.4	8.2
170-008*	Side	9.5	182.8	0.2	0.5	2.4	0.2	0.3	0.7	2.3	0.6	0.6	7.9
170-009*	Side	9.0	188.2	0.3	2.3	3.2	0.2	0.2	0.6	9.3	0.6	0.9	17.7
170-002	—	—	—	7.3	1.3	5.9	1.3	0.2	3.2	21.0	0.8	6.2	47.3
B1-6	—	—	—	0.7	0.9	1.8	0.2	0.1	1.0	—	0.7	0.4	8.8
B1-8(1)	—	—	—	n.a.	0.2	1.0	0.1	0.4	0.3	0.2	0.3	0.2	2.8
B1-10	—	—	—	n.a.	0.3	1.3	0.2	0.3	0.6	1.9	0.8	0.3	5.6
B1-12	—	—	—	0.3	0.8	1.1	0.2	0.2	0.9	1.8	0.7	0.3	6.3
B1-14	—	—	—	n.a.	0.1	0.9	0.1	0.3	0.4	0.7	1.0	0.2	3.7
B1-8(2)	—	—	—	n.a.	0.2	1.2	0.2	0.3	0.3	1.0	n.a.	0.4	3.7

* Wick adhered to silicon pressure pad, and/or reservoir pad was only partially saturated

Summary

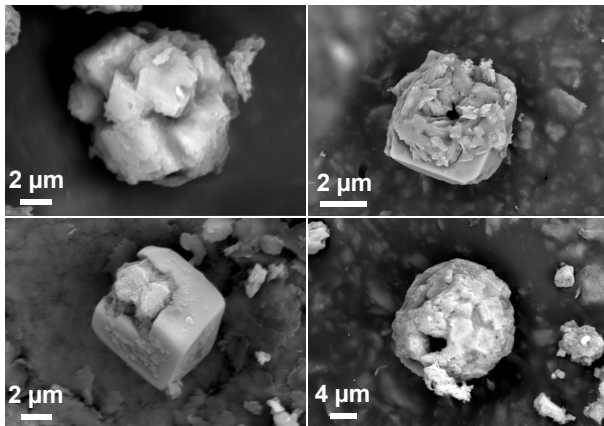
- **Dusts on Calvert Cliffs and Hope Creek canisters are largely insoluble minerals; salts are limited, and are salts are largely Ca-sulfate and nitrate-rich. NaCl was observed as rare isolated grains.**
- **Dusts on Diablo Canyon canisters are sea-salt rich. Sea-salts are present are present in both the fine (<2.5 μm) and coarse (>2.5 μm fraction). Larger grains are spherical aggregates or euhedral crystals of halite, with associated Mg-sulfate, and lesser amounts of Ca and K.**

Field data indicate that in at least some near-marine ISFSI locations, chloride-rich sea-salt aerosols comprise a large fraction of dusts deposited on canister surfaces. Once deliquescence occurs, SCC may be possible.

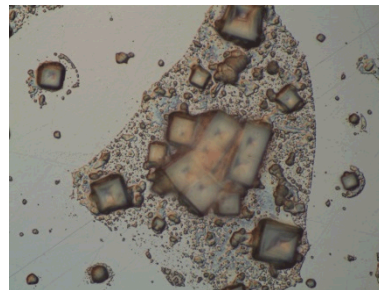
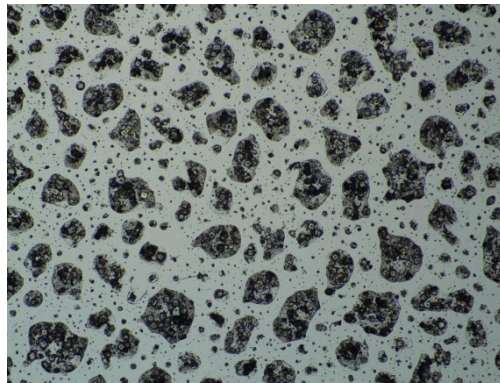
Implications

Experimental data suggest that SCC will occur when sea-salts deliquesce. But, are experimental conditions typical of field conditions?

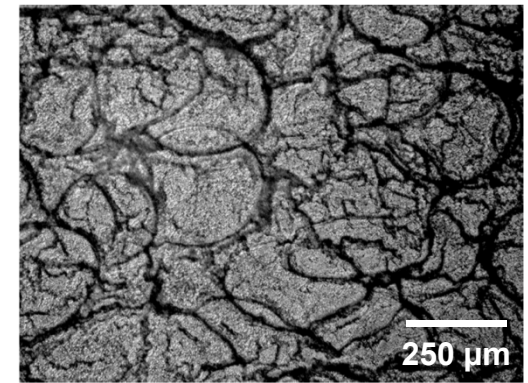
Salts on waste package surface:



Aqueous solution deposited by airbrush:



Salts in ethanol deposited by airbrush.

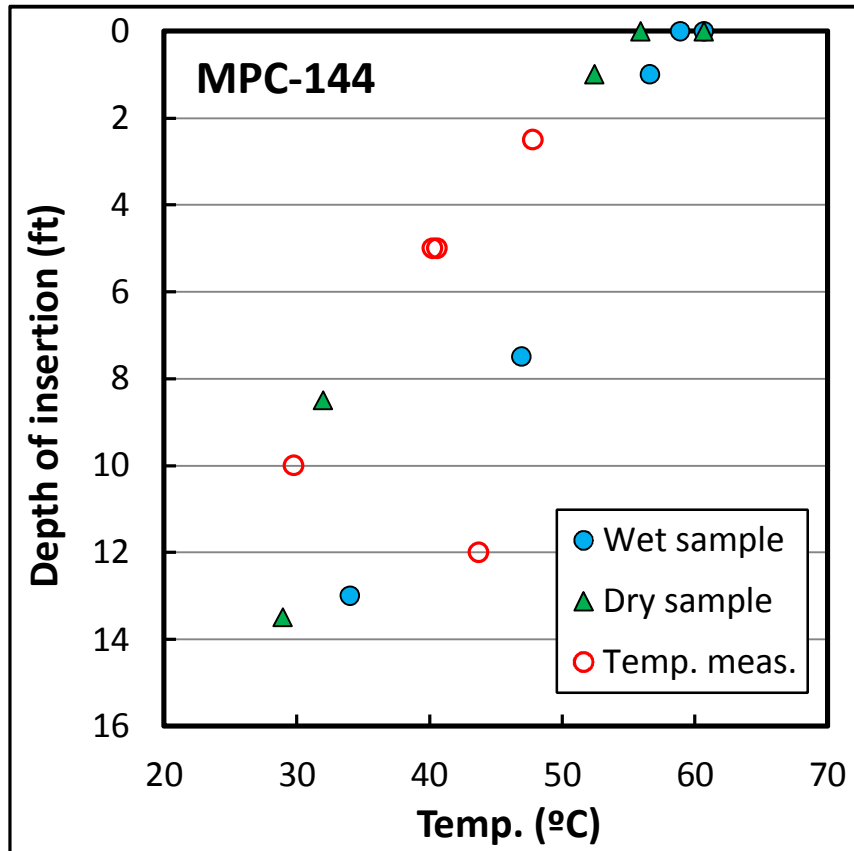


120 $\mu\text{g}/\text{cm}^2$

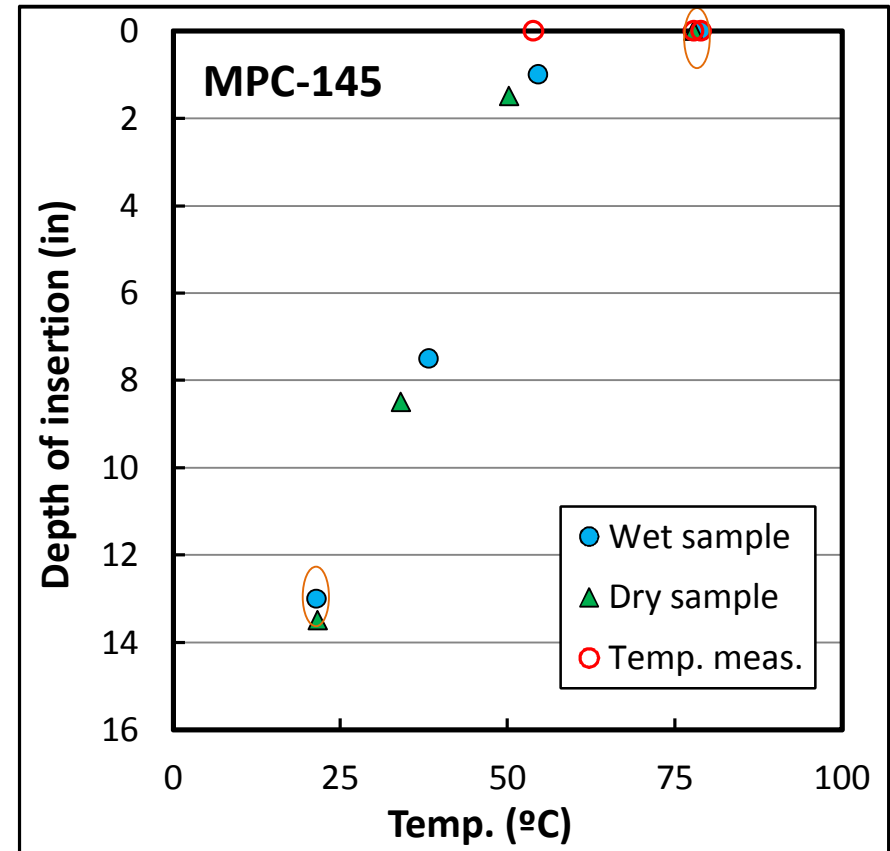
Extra slides

Samples Collected — Hope Creek

MPC-144



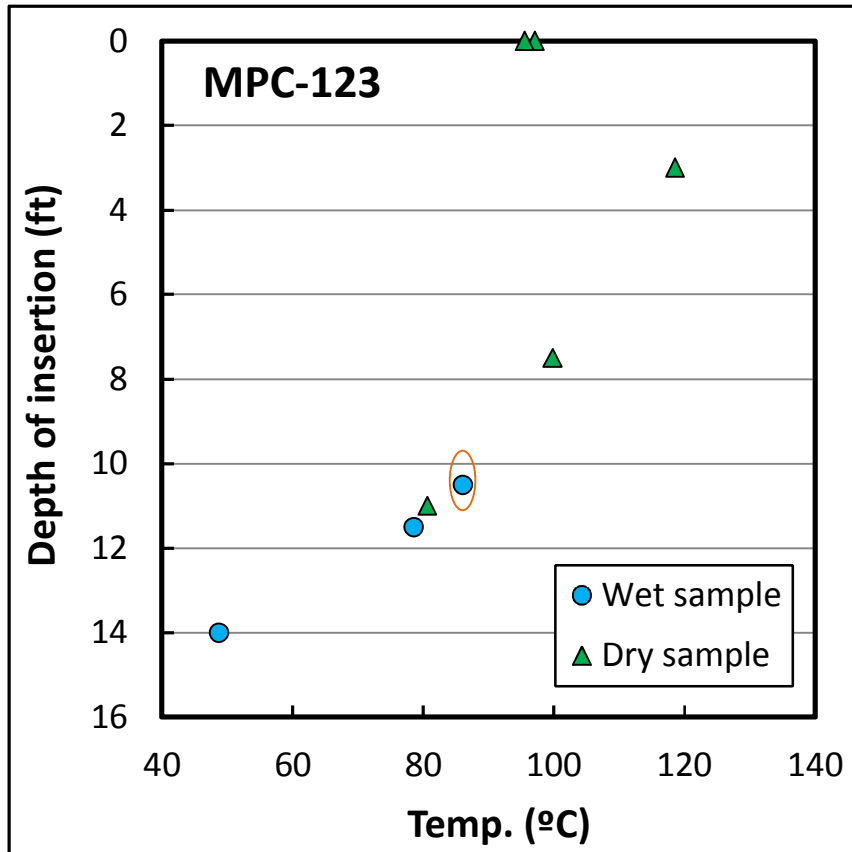
MPC-145



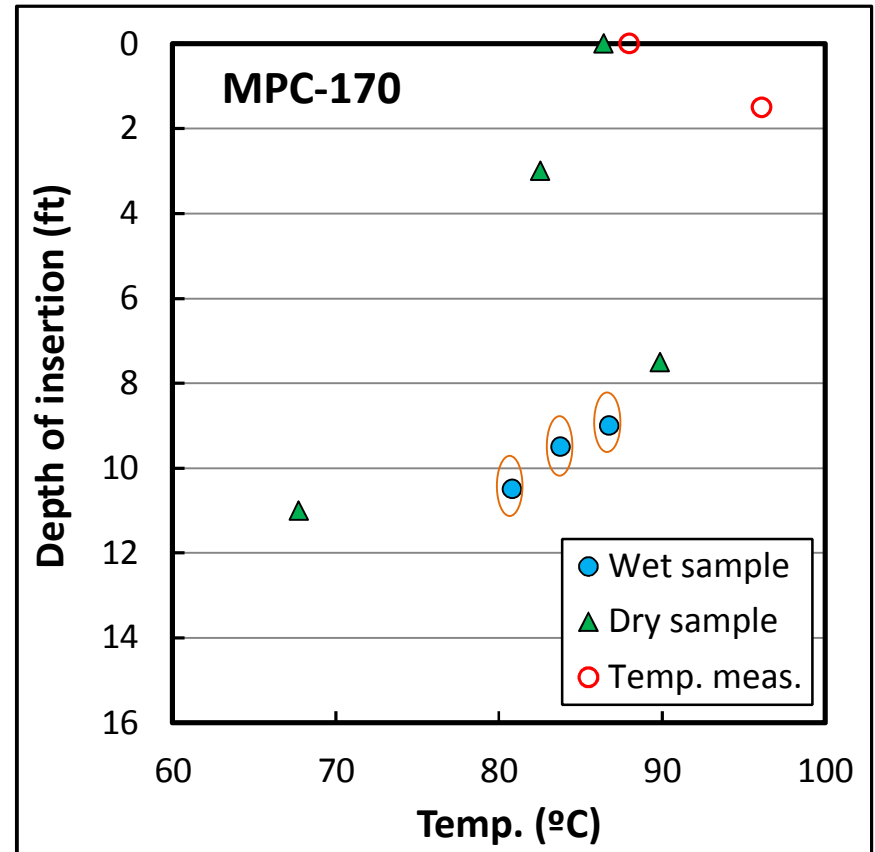
Wick stuck to silicone pressure pad, and/or reservoir pad was only partially wetted


Samples Collected — Diablo Canyon

MPC-123



MPC-170



 Wick stuck to silicone pressure pad, and/or reservoir pad was only partially wetted

Sample photographs

Samples collected from Hope Creek MPC-144

