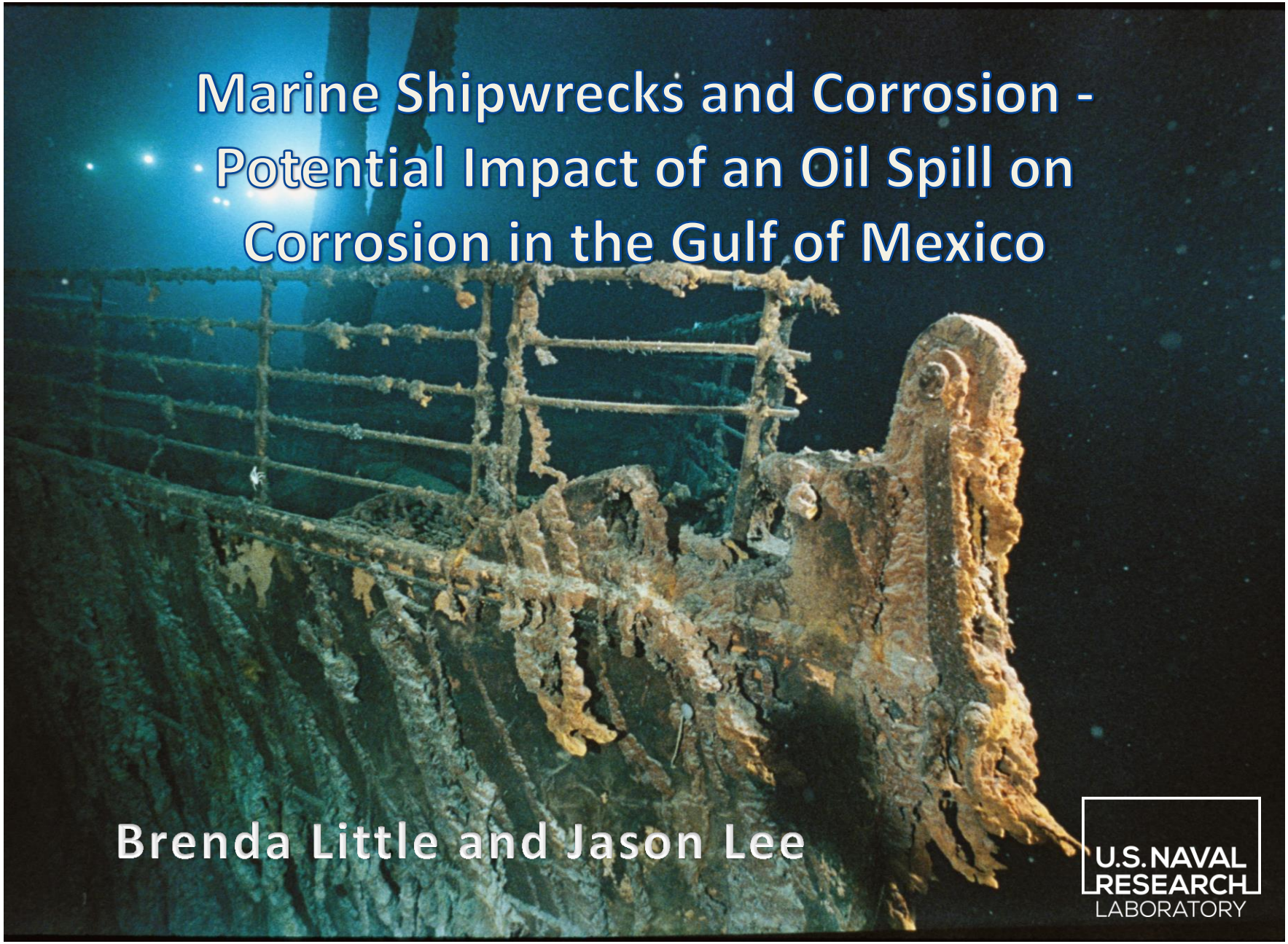
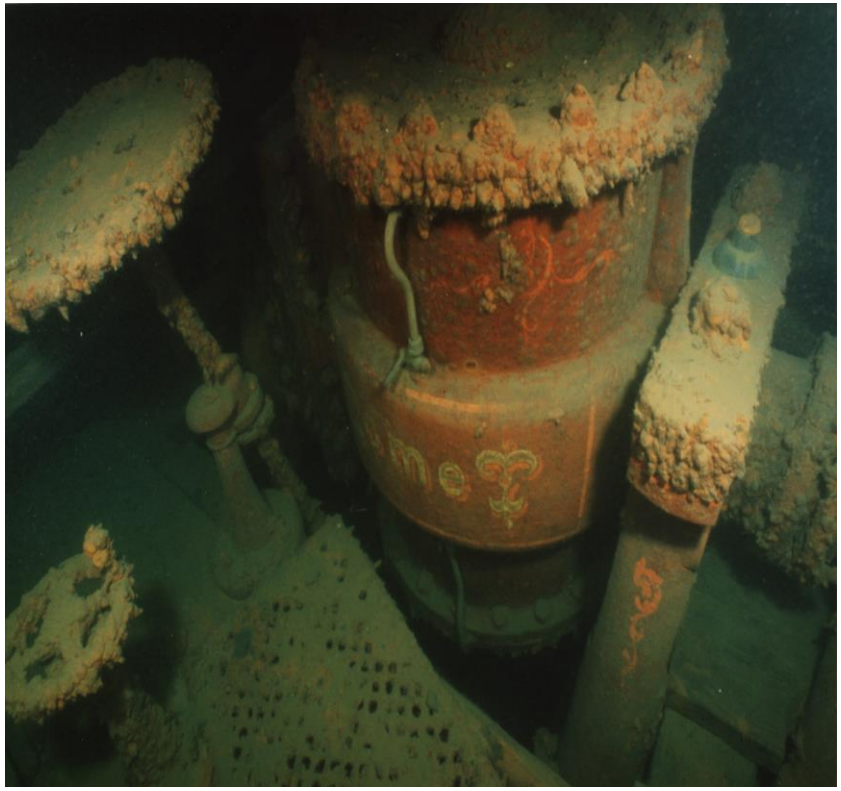

Marine Shipwrecks and Corrosion - Potential Impact of an Oil Spill on Corrosion in the Gulf of Mexico
Brenda Little and Jason Lee
U.S. NAVAL RESEARCH LABORATORY



Comet
Sank in 1875,
Lake Superior, 70 m

RMS Titanic
Sank in 1912,
North Atlantic, 3800 m

Deepwater Horizon Oil Spill

Spill occurred April 2010.

Macondo well head at 1500 m depth.

5,000,000 barrels of Louisiana sweet crude was released.

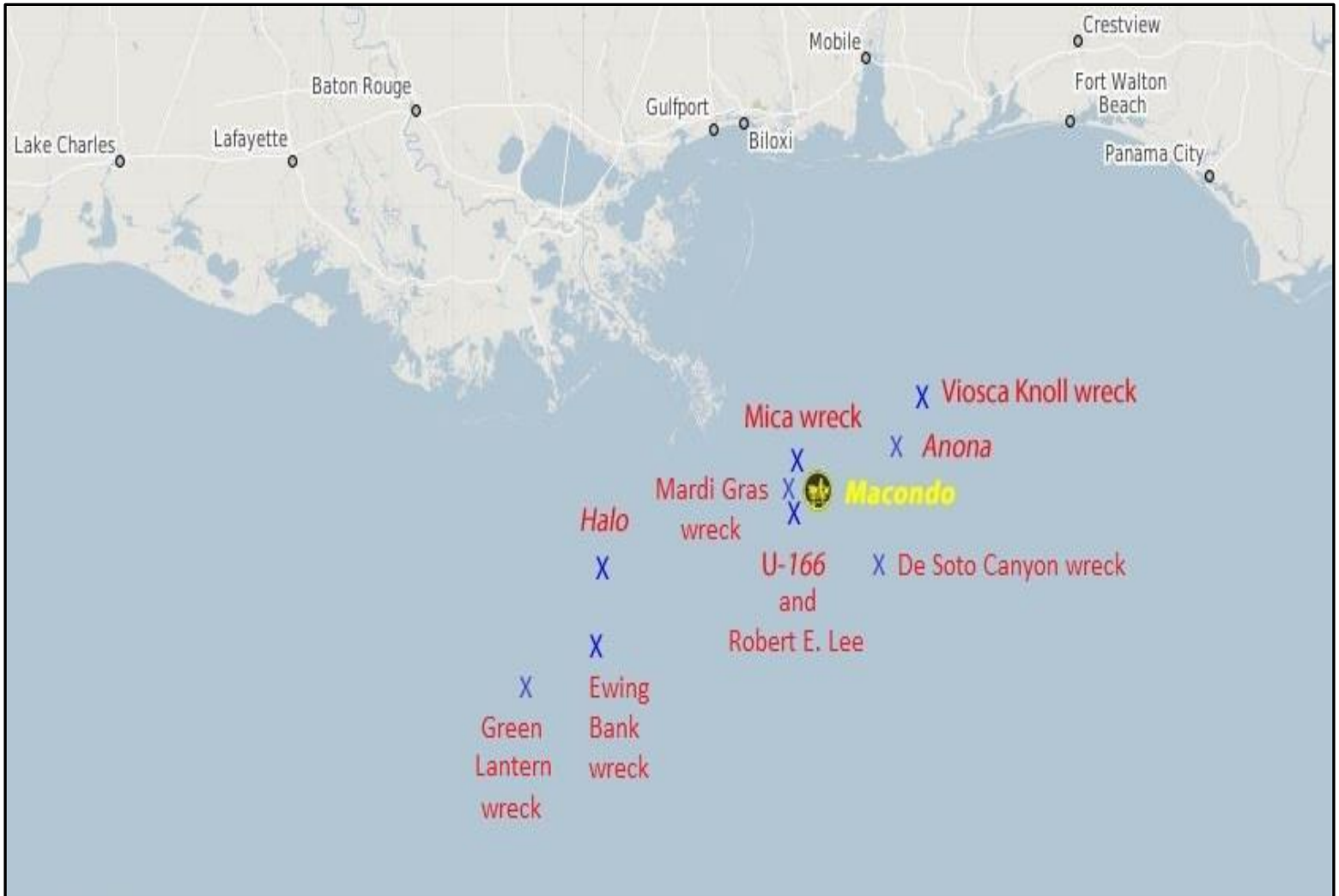
47, 000 barrels of Corexit dispersants (9500A and 9527A) containing dioctyl sodium sulfosuccinate were applied.

Hydrocarbons deposited across 2280 km^2 seafloor.

Three Methods used to Evaluate Corrosion of GOM Shipwrecks

- Comparison of rusticles on shipwrecks before (2008) and after (2014) exposure to oil spill
- Exposure racks placed next to affected and unaffected shipwrecks (17 weeks)
- Laboratory microcosms (16 weeks)

Shipwreck Locations Relative to Macondo Well Head



Gulf of Mexico Shipwreck Information

Reproduced from Church *et. al* (2009)

Structure	Depth (m)	Dates in Service	Vessel Type	Cargo	Observations
Virginia	**90**	**1941-1942**	**Tanker**	**180k barrels gasoline**	Fish and invertebrates count incomplete due to poor visibility; vermillion snapper and various corals
Halo	**150**	**1920-1942**	**Tanker**	**63k barrels crude oil**	Few brown rusticles, corals, invertebrates, reef fish
Gulfpenn	**560**	**1921-1942**	**Tanker**	**90k barrels gasoline**	Some microbial concretions; abundant *Lophelia pertusa,* high invertebrate diversity, reef fish
U-166	**1,260**	**1942-1942**	**U-Boat**	**Mines and torpedoes**	Brown and white rusticles, Venus flytrap anemones, red deep-sea crabs, squat lobsters and other deepwater demersal species
Robert E. Lee	**1,500**	**1924-1942**	**Passenger Freighter**	**Passengers**	Abundant brown rusticles, Venus flytrap anemones, red deep-sea crabs, squat lobsters and other deepwater demersal species
Alcoa Puritan	**1,970**	**1941-1942**	**Cargo Freighter**	**10k tons bauxite**	Greatest density of rusticle formations, predominant invertebrate was deep-sea crab, other demersal species

Properties of Rusticles on Marine Shipwrecks

- Distinct microbial communities (FeOB, FeRB and SRB)
- Iron oxides/hydroxides (goethite and lepidocrocite)
- Accumulation of ions from seawater

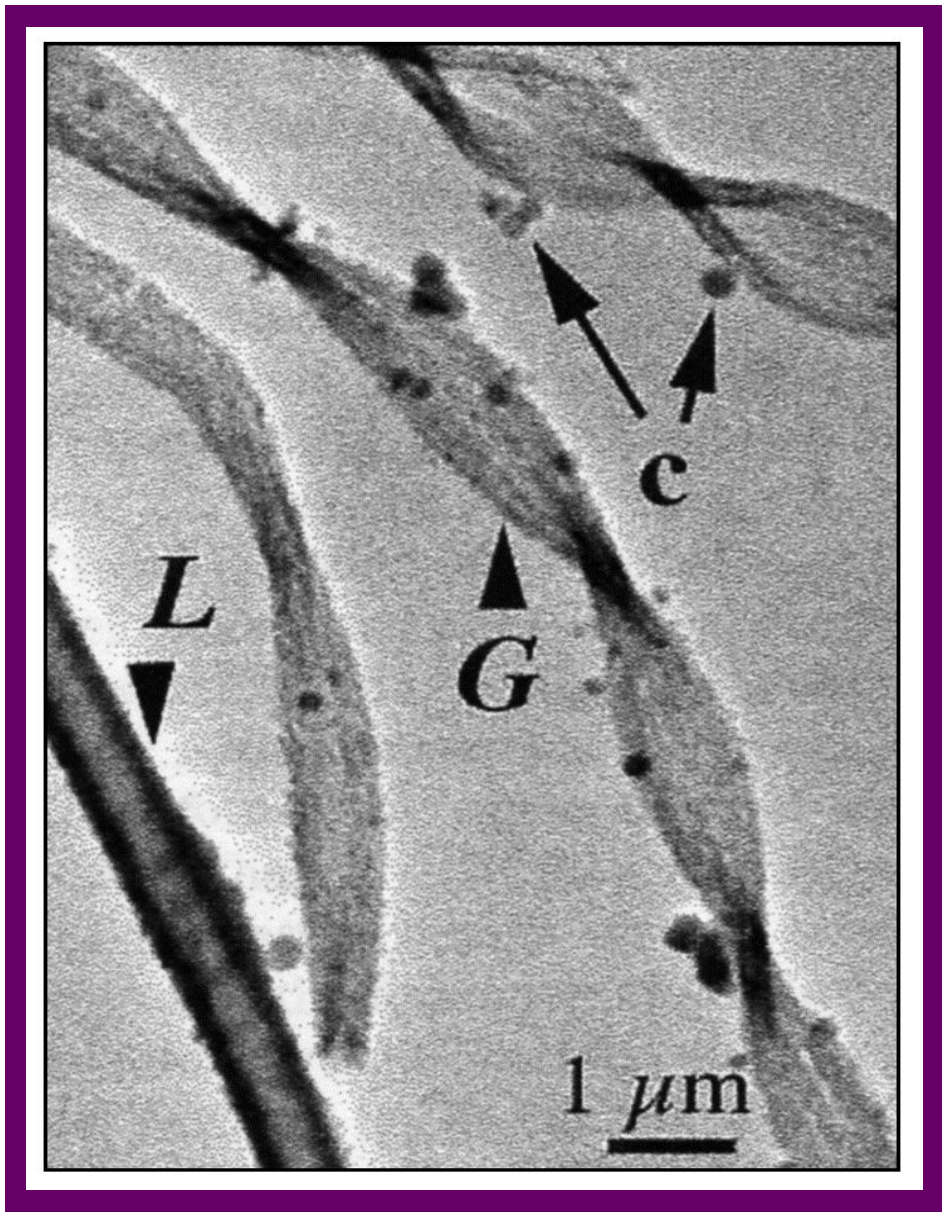
Neutrophilic, micraerophilic, stalk-forming Iron-oxidizing Bacteria (IOB), e.g., *Gallionella*

TEM Image of IOB

Gallionella – G

Leptothrix – L

Colloidal aggregates - C



J. F. Banfield *et al.* Science Vol. 289, Aug. 2000. www.sciencemag.org

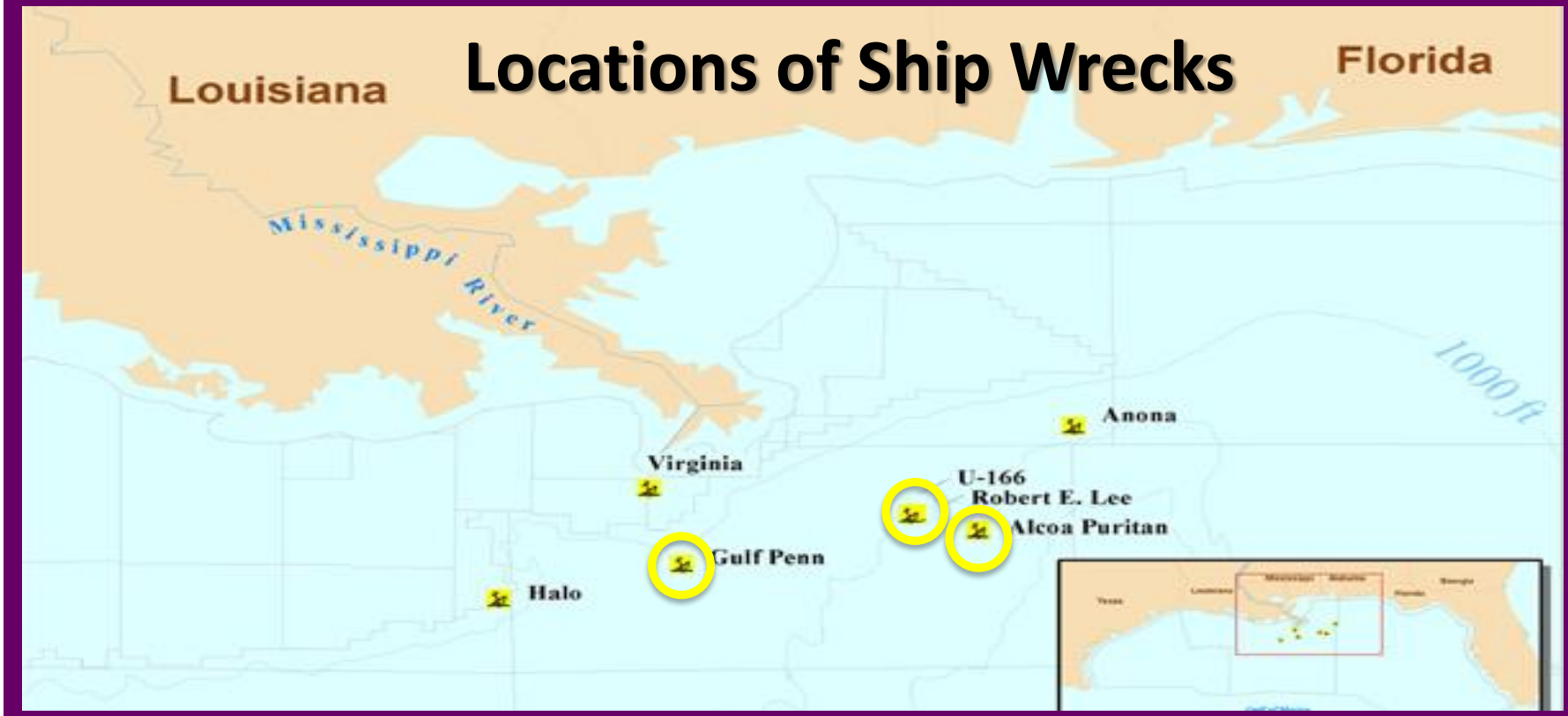
Rusticles from GOM Ship Wrecks

Gulf Penn

Robert E. Lee

ALCOA Puritan

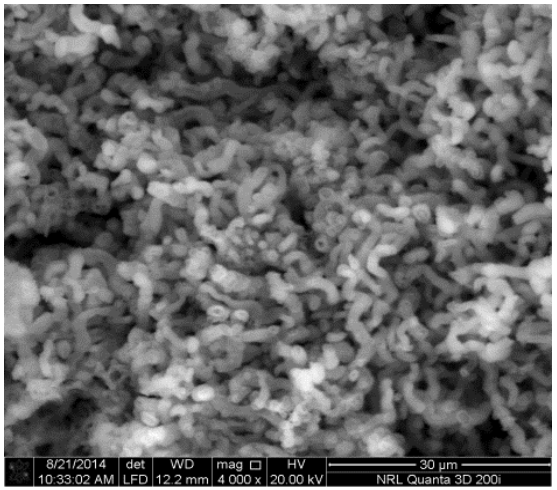
Locations of Ship Wrecks

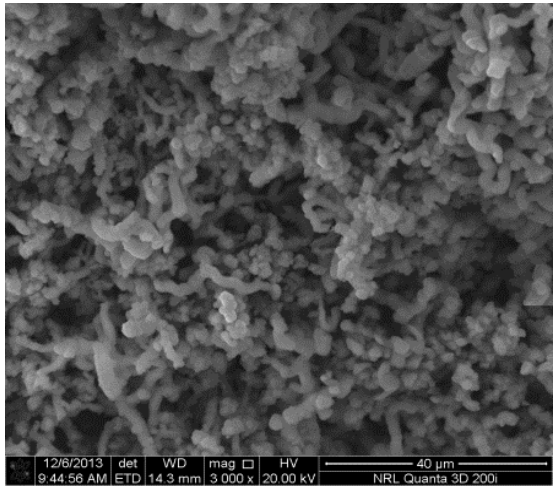


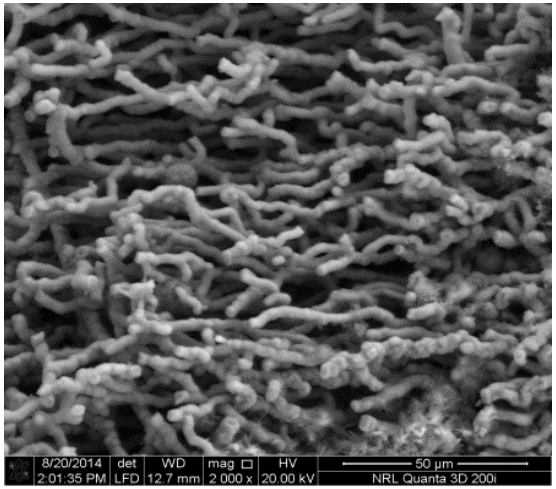
WRECK NAME	LAT/LON	DEPTH (M)	SALIN-ITY	TEMP. (C)	$[O_2]$ mL/L	PHOS-PHATE (µM)	SILICATE (µM)	NITRATE (µM)
GULF PENN	28 29 N, 89 12 W	560	35	8	4.6	0.1	1.5	1.5
ROBERT E. LEE	28 40 N, 88 42 W	1500	34.96	4.2	3.1	0.8	5	13
ALCOA PURITAN	28 35 N, 88 22 W	1970	34.98	4.2	2.9	1.1	7	17

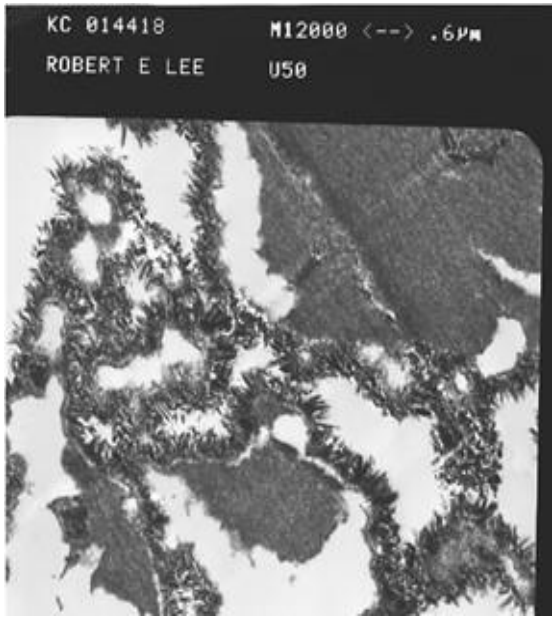
SEM Images of Iron Corrosion Products

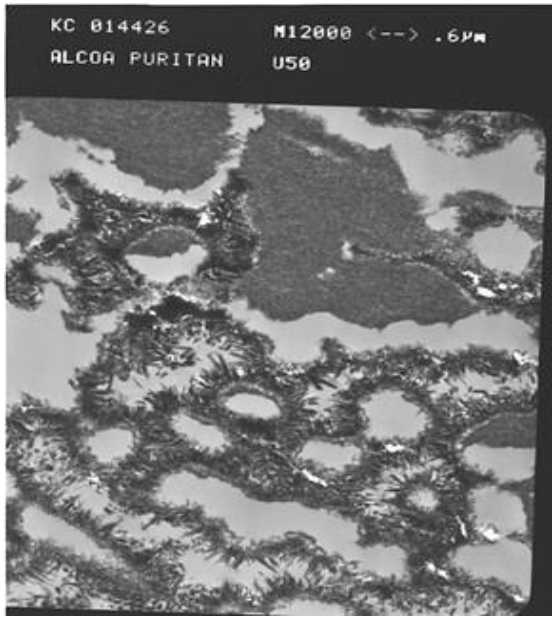
Gulf Penn *Robert E. Lee* *ALCOA Puritan*





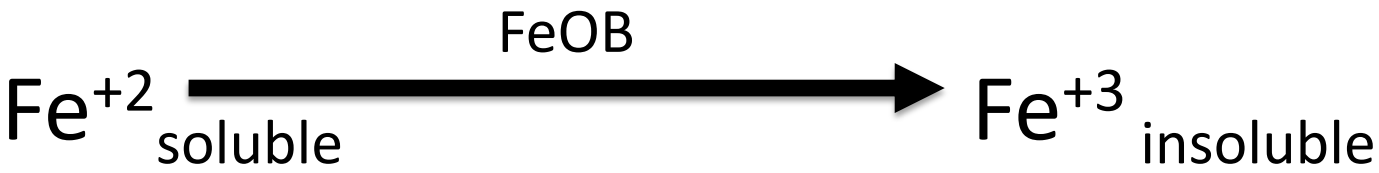






Oxidation of Fe^{+2}

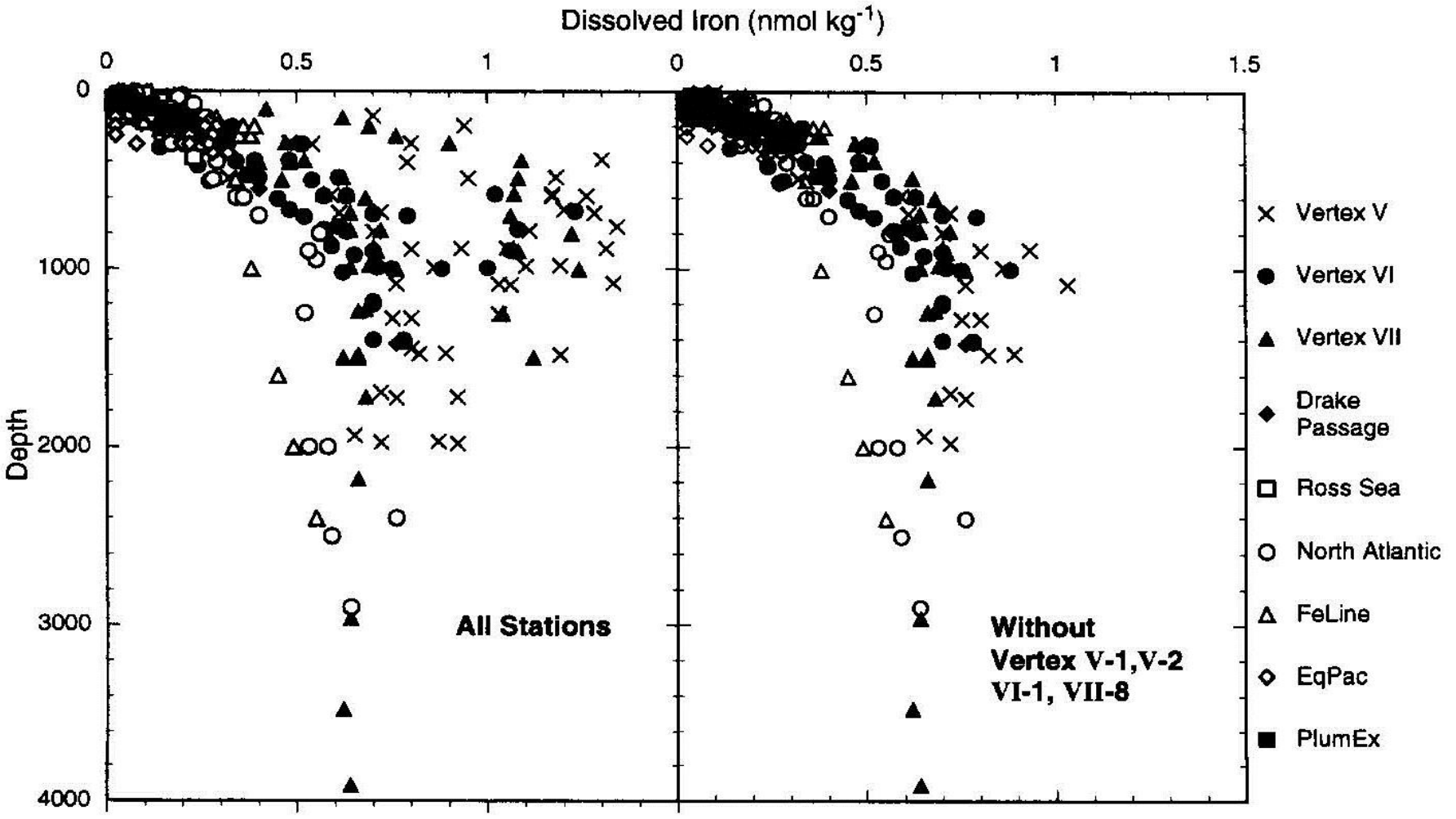
in microaerobic conditions (µM O_2)



Major elements (% by weight) in rusticles collected in 2008

Structure	Si	S	Al	Fe	Mn	Mg	Ca	Na	K	P
Robert E Lee	0.11	0.47	0.03	52.72	0.02	0.04	0.02	0.26	0.02	0.11
Gulfpenn	0.12	0.46	0.01	64.68	0.03	0.25	0.08	1.57	0.05	0.08
Alcoa Puritan	0.06	6.31	0.01	56.90	0.02	0.18	0.11	0.65	0.03	0.00

Iron Concentrations: Ocean Water Column



(A) Dissolved (<0.4 µm) iron concentrations measured in 354 samples at stations more than 50 km from the continental coastline. (B) Dissolved <0.4) iron concentrations as in (A), but excluding the 4 stations closest to shore (VERTEX V-1, V-2,VI-1, VII-8) in the North Pacific.

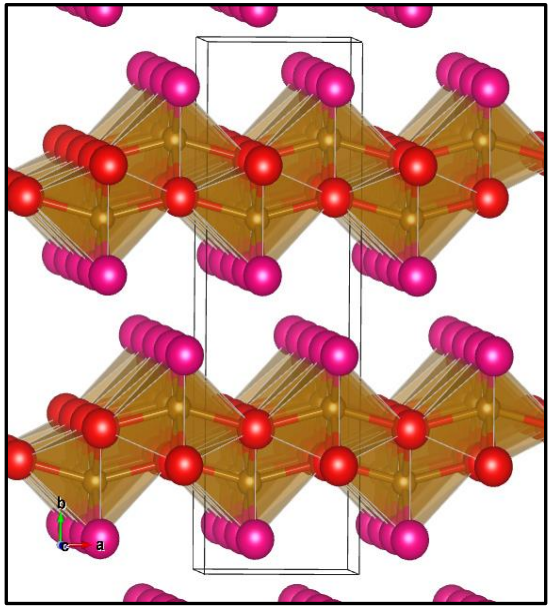
K.S. Johnson, R.M. Gordon, K.H. Coale, What controls dissolved iron concentrations in the world ocean?, Mar Chem, 57 (1997) 137-161.

Bacteriogenic Iron Oxides (BIOS)

BIOS are made up of intact and/or partly degraded remains of bacterial cells with amorphous hydrous ferric oxides.

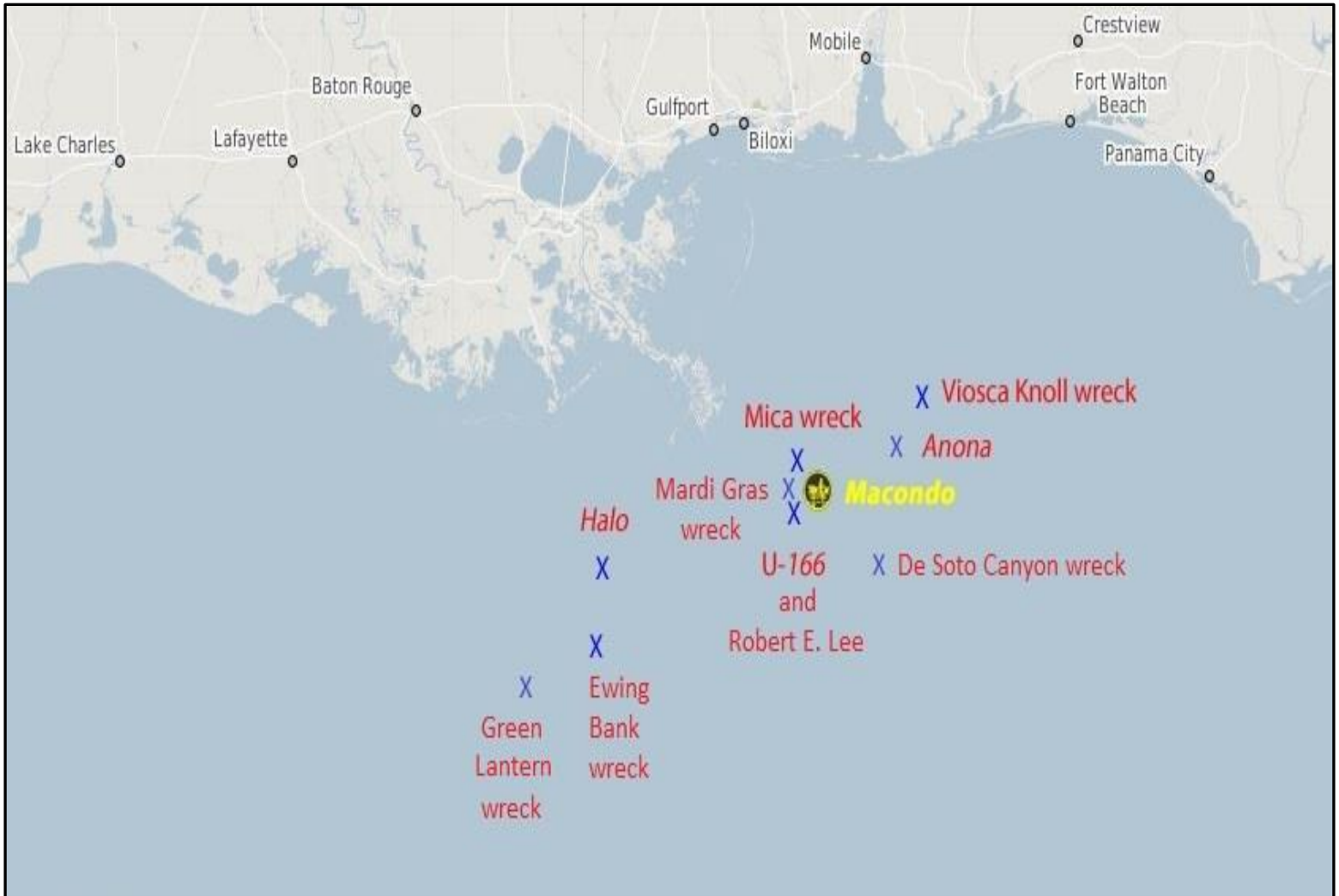
Iron Oxide/Oxyhydroxides

- 2-line Ferrihydrite $Fe_2O_3 \bullet 0.5(H_2O)$
- Lepidocrocite γ-FeO(OH)
- Goethite α-FeO(OH)
- Magnetite (Fe_3O_4) $FeO \cdot Fe_2O_3$



γ-FeO(OH) - Iron-centered oxygen octahedra joined by sharing edges into two-dimensional infinite layers ,with successive layers held together by hydrogen bonds.

Shipwreck Locations Relative to Macondo Well Head



Major elements (% by weight) in rusticles

collected in 2008 before spill

Structure	Si	S	Al	Fe	Mn	Mg	Ca	Na	K	P
Robert E Lee	0.11	0.47	0.03	52.72	0.02	0.04	0.02	0.26	0.02	0.11
Gulfpenn	0.12	0.46	0.01	64.68	0.03	0.25	0.08	1.57	0.05	0.08
Alcoa Puritan	0.06	6.31	0.01	56.90	0.02	0.18	0.11	0.65	0.03	0.00

collected in 2014 after spill

Structure	Si	S	Al	Fe	Mn	Mg	Ca	Na	K	P
Surface *Anona*	0.11	12.98	0.04	50.48	0.01	0.16	0.08	1.96	0.05	0.07
Anona core	0.03	7.20	0.01	49.51	0.01	0.12	0.05	1.78	0.03	0.08

Trace elements (parts per million*) in rusticles

collected in 2008

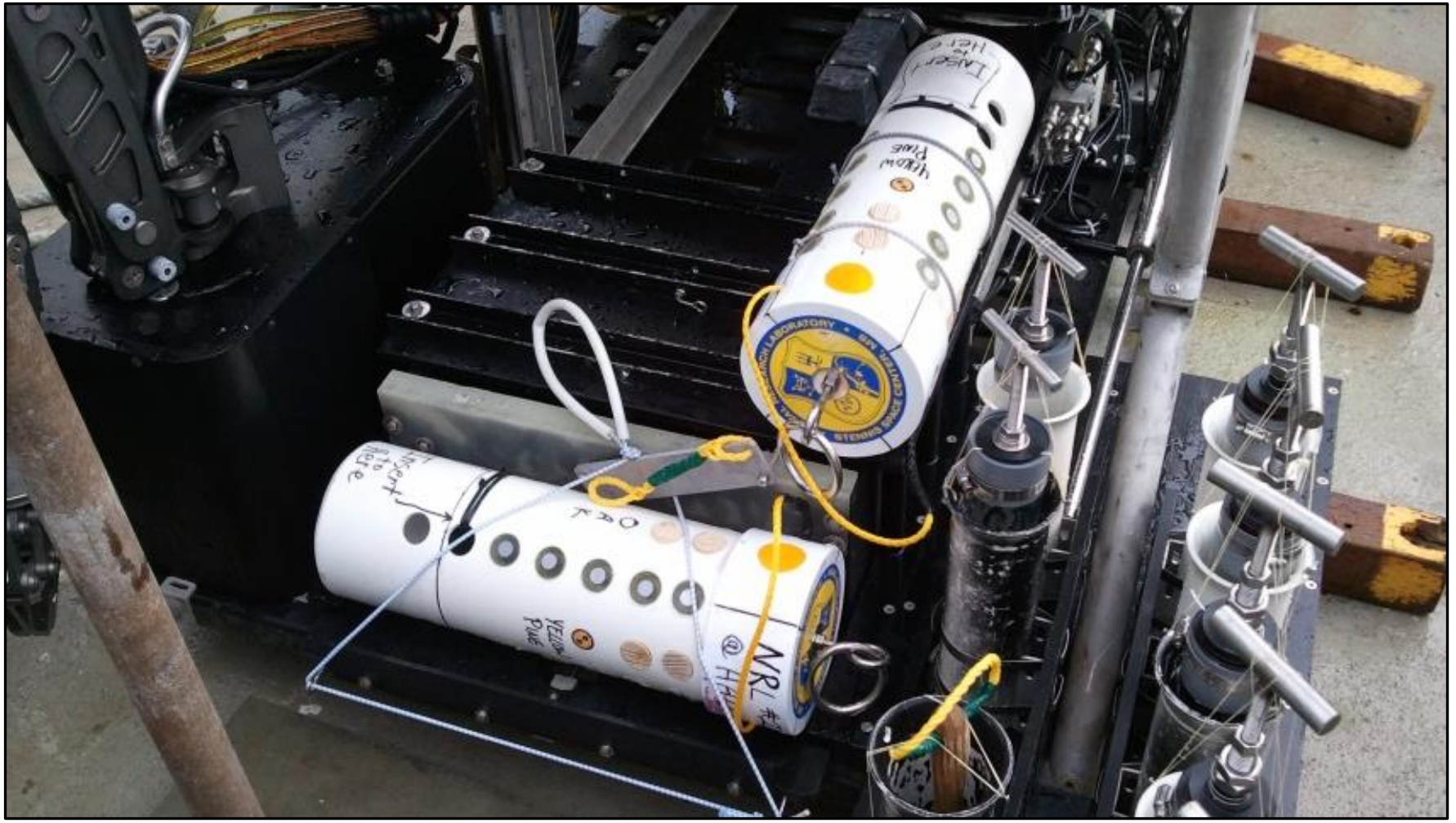
Structure	As	Ba	Co	Cr	Cu	Mo	Ni	Pb	Rb	Sn	Sr	Th	V	Zn	Zr
Robert E. Lee	33.7	8.41	3.98	9.13	5.70	58.4	4.5	11.1	21.2	7.89	6.48	N/A	101	132	14.4
Gulfpenn	38.4	2.96	7.19	11.9	0.80	97.2	2.1	16.6	67.0	3.99	33.6	5.76	63.9	72.4	14.8
Alcoa Puritan	N/A	2.07	6.83	0.64	BD	7.10	7.15	12.4	13.6	2.72	29.6	N/A	19.2	58.9	14.2

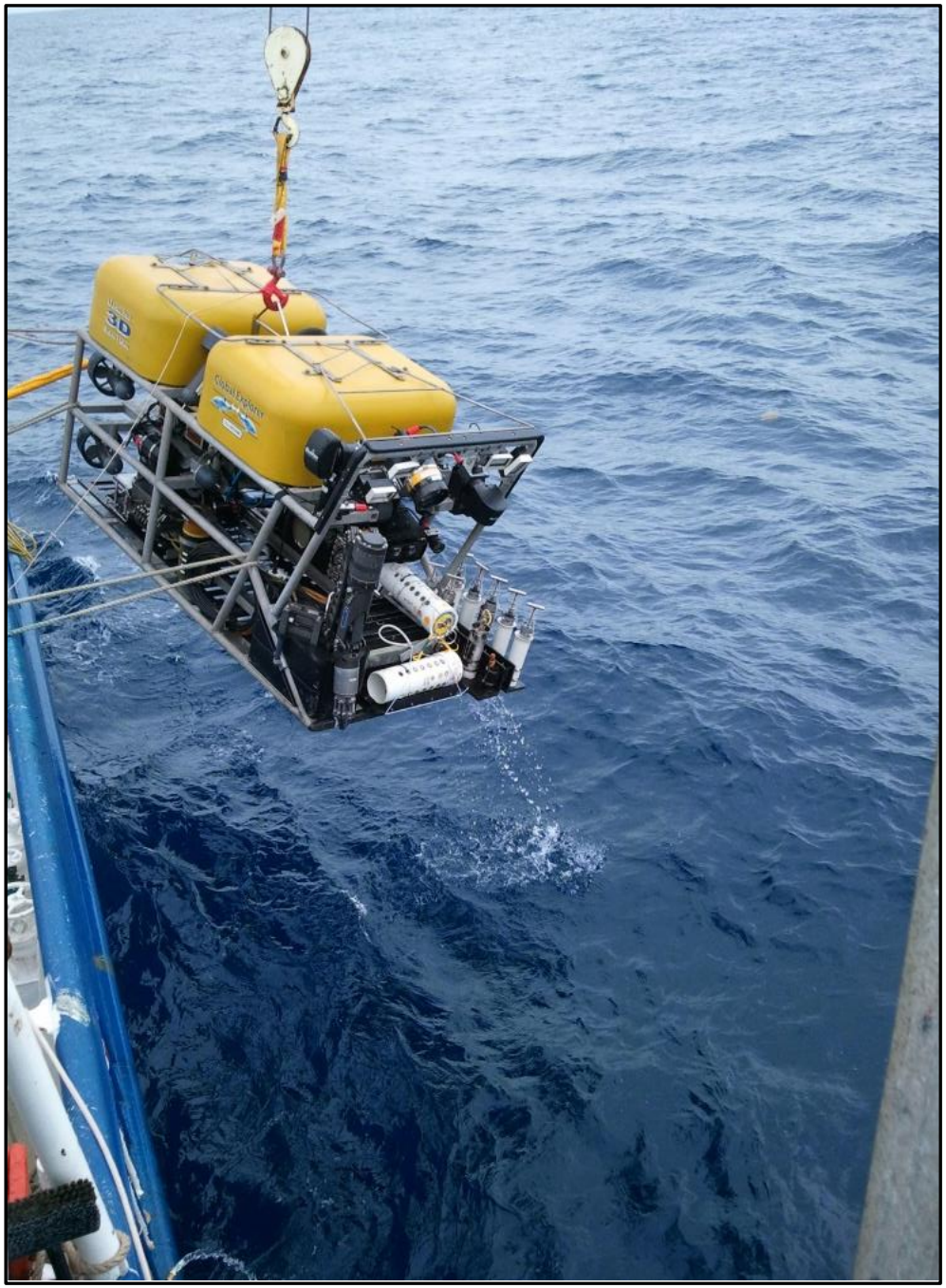
collected in 2014

Structure	As	Ba	Co	Cr	Cu	Mo	Ni	Pb	Rb	Sn	Sr	Th	V	Zn	Zr
Surface *Anona*	27.4	3.63	6.19	36.7	0.12	27.0	28.8	11.8	5.25	5.41	15.7	5.07	55.9	29183	13.4
Anona Core	6.83	0.43	19.9	2.93	0.16	17.3	2.5	18.9	29.8	2.43	11.8	3.44	15.9	141.0	12.5

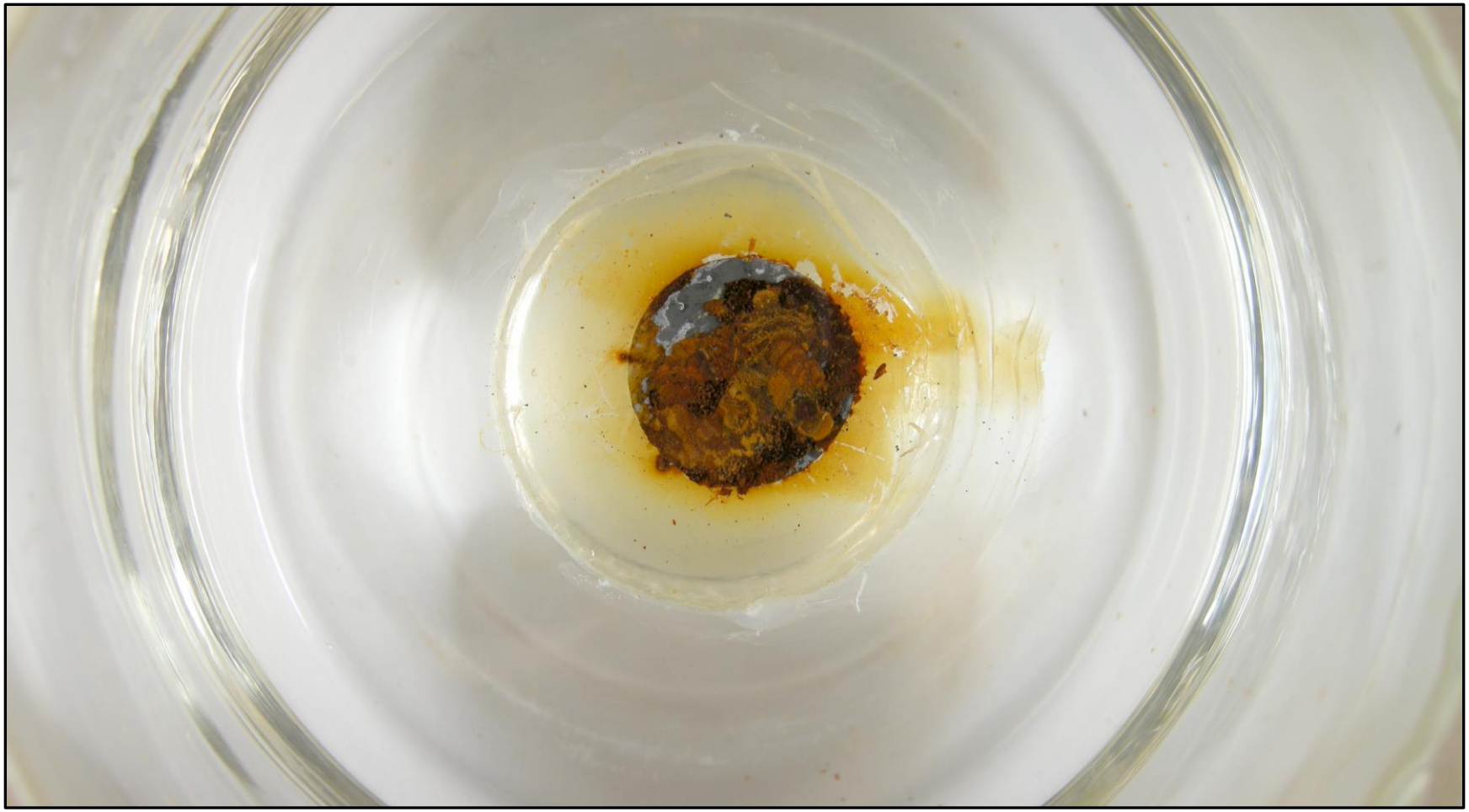
***Parts per million x 10^{-4} = % by weight**

Exposure racks placed next to affected and unaffected shipwrecks

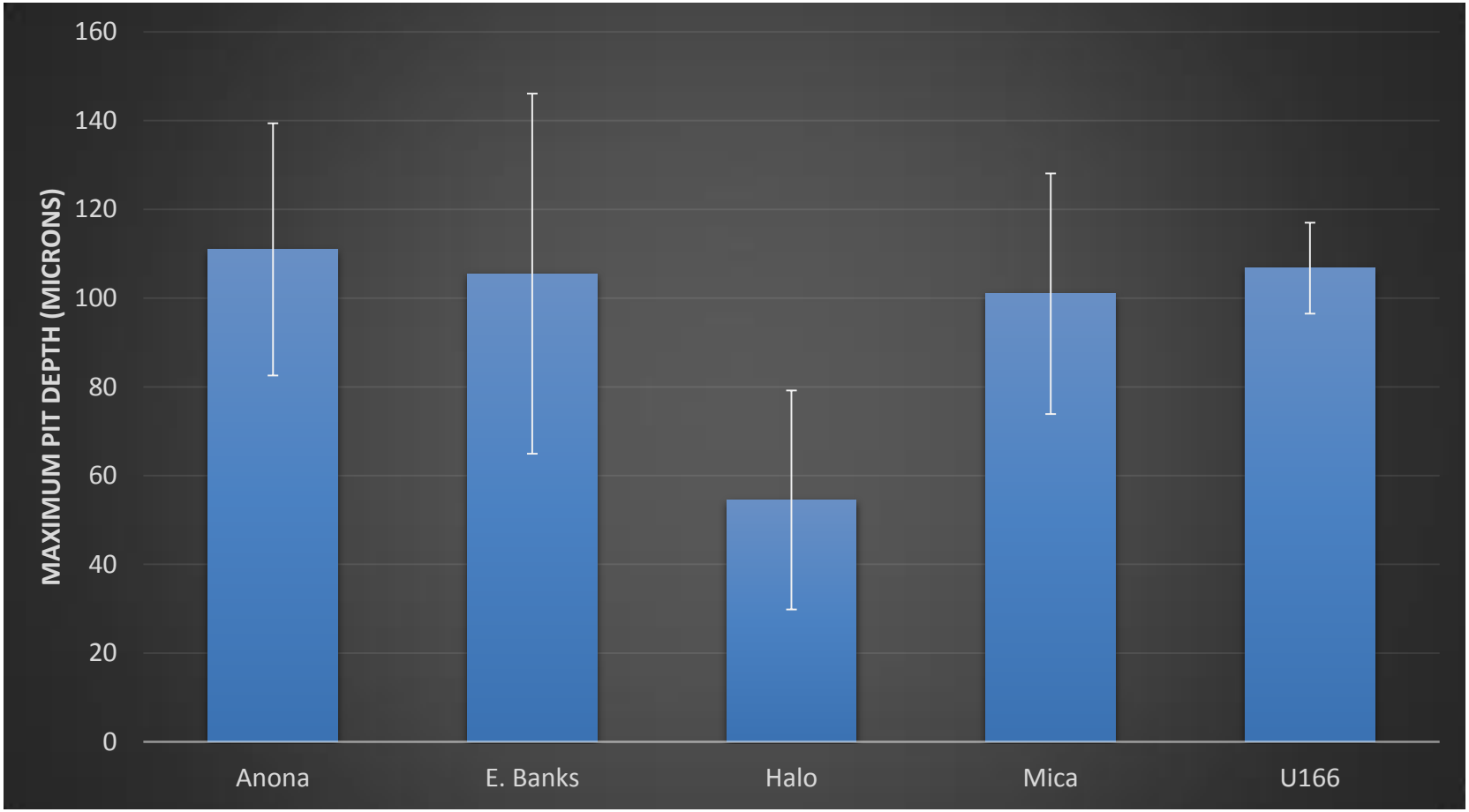




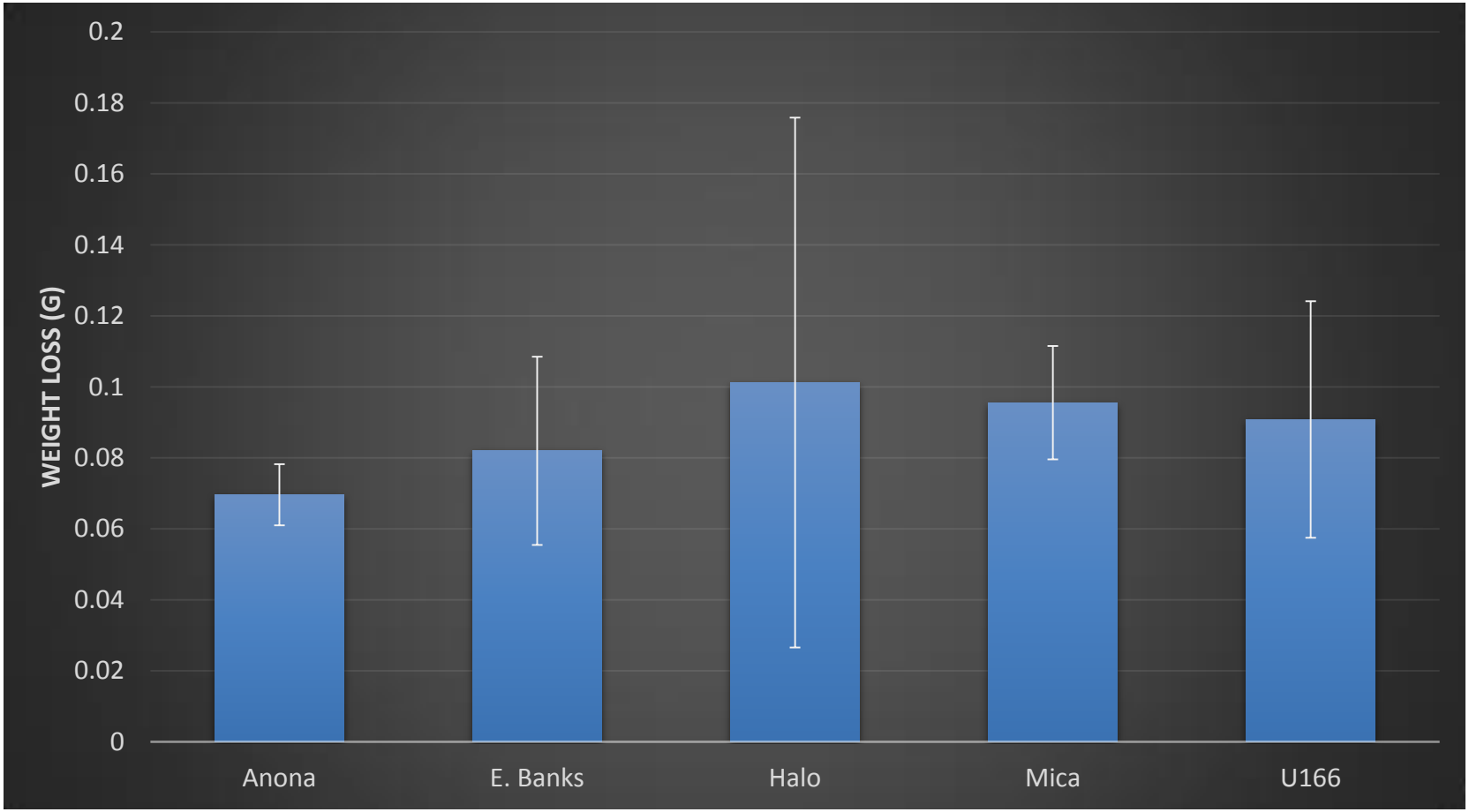
Epoxy-mounted CS coupon removed from platform at *Anona* site



Maximum Pit Depth (17 weeks)



Weight Loss (17 weeks)



Conclusions

Concentrations of sulfur with iron oxides may be related to exposure to oil and/or dispersant

Pit depths and weight loss for newly exposed carbon steel coupons cannot be used to predict hull degradation of existing shipwrecks

Sponsors

- **Office of Naval Research (Program manager Linda Chrisey - Role of FeOB in Marine Corrosion FY 10-12)**
- **Collaboration with NRL Code 6100 funded by the Bureau of Energy Management (Effects of Deep horizon Oil Spill on GOM Shipwreck Corrosion FY 14-Present)**