Otolith nickel and vanadium as lifetime markers of fish exposure to crude oil

Ernst Peebles, David Jones,
Elon Malkin and Steve Murawski

USF UNIVERSITY OF SOUTH FLORIDA
COLLEGE OF MARINE SCIENCE

The concern over diseased fish has been widely publicized.

"Huge red flag": Sick fish in Gulf are alarming Florida scientists — Skin lesions, fin rot, diseased livers and ovaries

MAY 12TH, 2011 AT 10:16 AM

Gulf Fish are Sick, Worse May Come

written by therockyriver.com staff

Unusually high numbers of mortally sick fish are being cau
is to blame.

scientists, fishermen alarmed at rate of sick fish in the gulf

August 19th, 2011 by Kurt Niland

Unusually high numbers of sick fish are being caught in the Gulf of Mexico - like this Red Snapper with fin rot and skin lesions - and scientists are afraid the BP oil spill is to blame.

Sick fish suggest oil spill still affecting gulf

By Craig Pittman, Times Staff Writer
In Print: Sunday, April 17, 2011

Fishermen in the Gulf of Mexico have caught red snapper with bacterial infections that have eaten through skin. Scientists say it's a sign a toxin has compromised the fish's immune system.

[Courtesy of Jim Cowan, Louisiana State University]

Is oil to blame for sick fish?

4:24 PM, Jul 8, 2011 | comments

Sick fish possibly due to oil spill

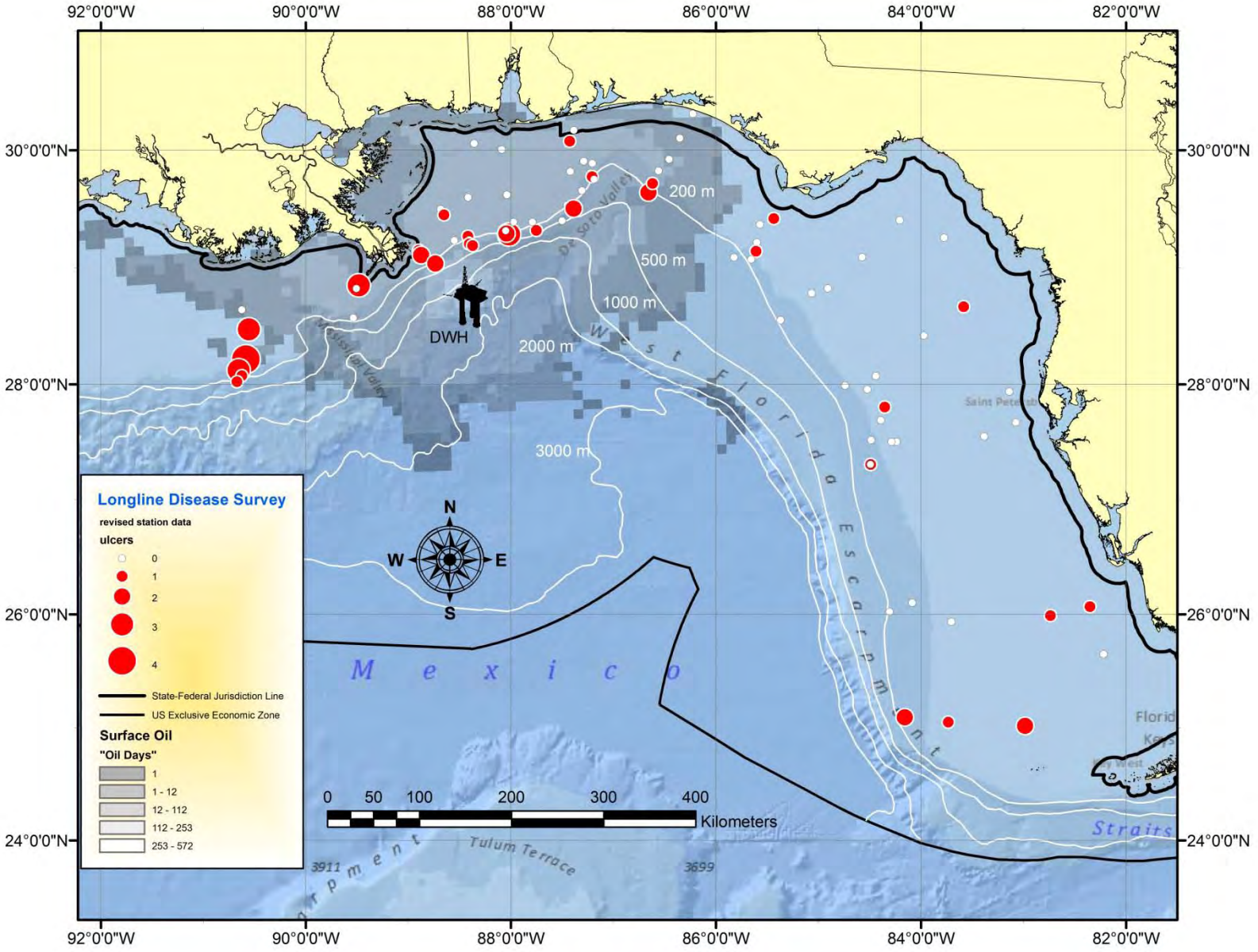
Story Created: Aug 16, 2011 at 1:36 PM America/New_York

August 15, 2011 10:52 AM

PRINT

Expert: BP spill likely cause of sick Gulf fish

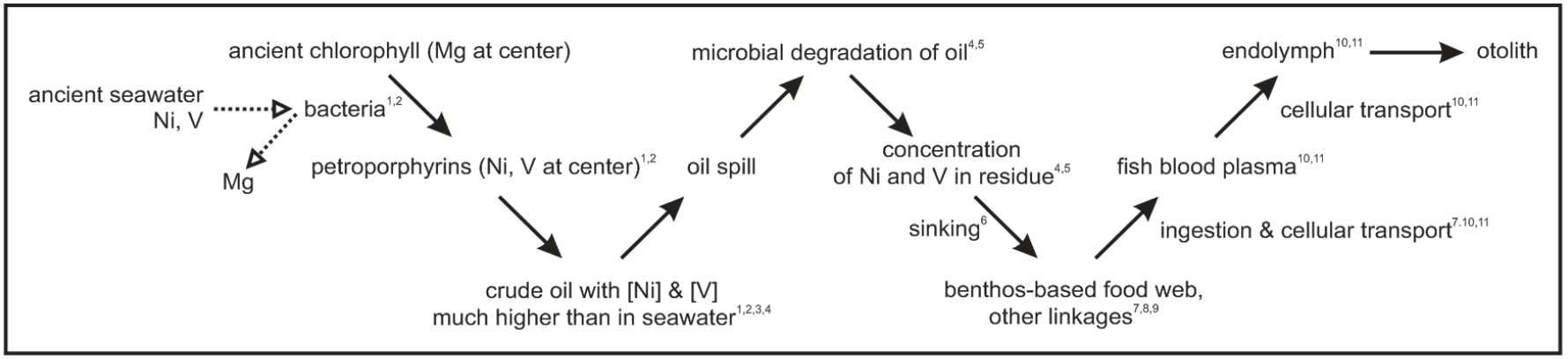
Have ulcerated fish been exposed to oil?



Oil marker pathways: Ni & V

"The metalloporphyrins, also known as **petroporphyrins**, found in crude oil are the product of the metabolism of chlorophyll by microorganisms and are usually complexed with metals they have scavenged from the environment, **predominately nickel and vanadium**." (Wang & Fingas 2003)

Suspected oil-otolith Ni and V pathways



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[2]Reynolds, J.G. 2001. Nickel in petroleum refining. *Petroleum Science and Technology*, 19:979-1007. DOI: 10.1081/LFT-100106915.

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[4]Sasaki, T., H. Maki, M. Ishihara and S. Harayama. 1998. Vanadium as an internal marker to evaluate microbial degradation of crude oil. *Environ. Sci. Technol.* 32: 3618-3621.5

[5]Christensen, J.H., A.B. Hansen, U. Karlson, J. Mortensen, and O. Andersen. 2005. Multivariate statistical methods for evaluating biodegradation of mineral oil. *Journal of Chromatography* 1090: 133–145.

[6]Alarfaj, A.A and I.A. Alam. 1993. Chemical characterization of sediments from the Gulf area after the 1991 oil-spill. *Marine Pollution Bulletin* 27: 97-101. DOI: 10.1016/0025-326x(93)90013-a.

[7]Willis, J.N. and W.G. Sunda. 1984. Relative contributions of food and water in the accumulation of zinc by two species of marine fish. *Marine Biology* 80: 273-279. DOI: 10.1007/BF00392822.

[8]Wang, W.X. 2002. Interactions of trace metals and different marine food chains. *Marine Ecology Progress Series* 243: 295-309. DOI: 10.3354/meps243295.

[9]Chiffoleau, J.F. , L. Chauvaud, D. Amouroux, A. Barats, A. Dufour, C. Pecheyran, and N. Roux. 2004. Nickel and vanadium contamination of benthic invertebrates following the "Erika" wreck. *Aquatic Living Resources* 17: 273-280. DOI: 10.1051/alr:2004032.

[10,11] References already provided by D. Jones (Campana, Thorrold, if I remember correctly)

Exposure considerations . . .

**TOO LITTLE EXPOSURE,
NO RECORD**

**TOO MUCH EXPOSURE,
FISH DIES - NO RECORD**

**INTERMEDIATE EXPOSURE,
GOOD RECORD POSSIBLE**

WHOLE OTOLITHS

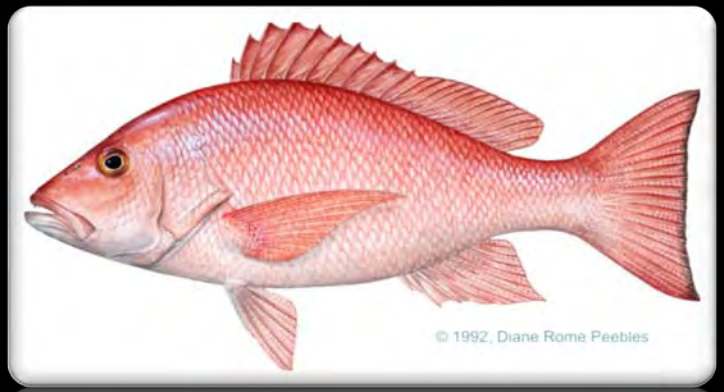
SECTIONED & POLISHED OTOLITH

ANNUAL RINGS

6 5 4 3 2 1

RED SNAPPER OTOLITHS

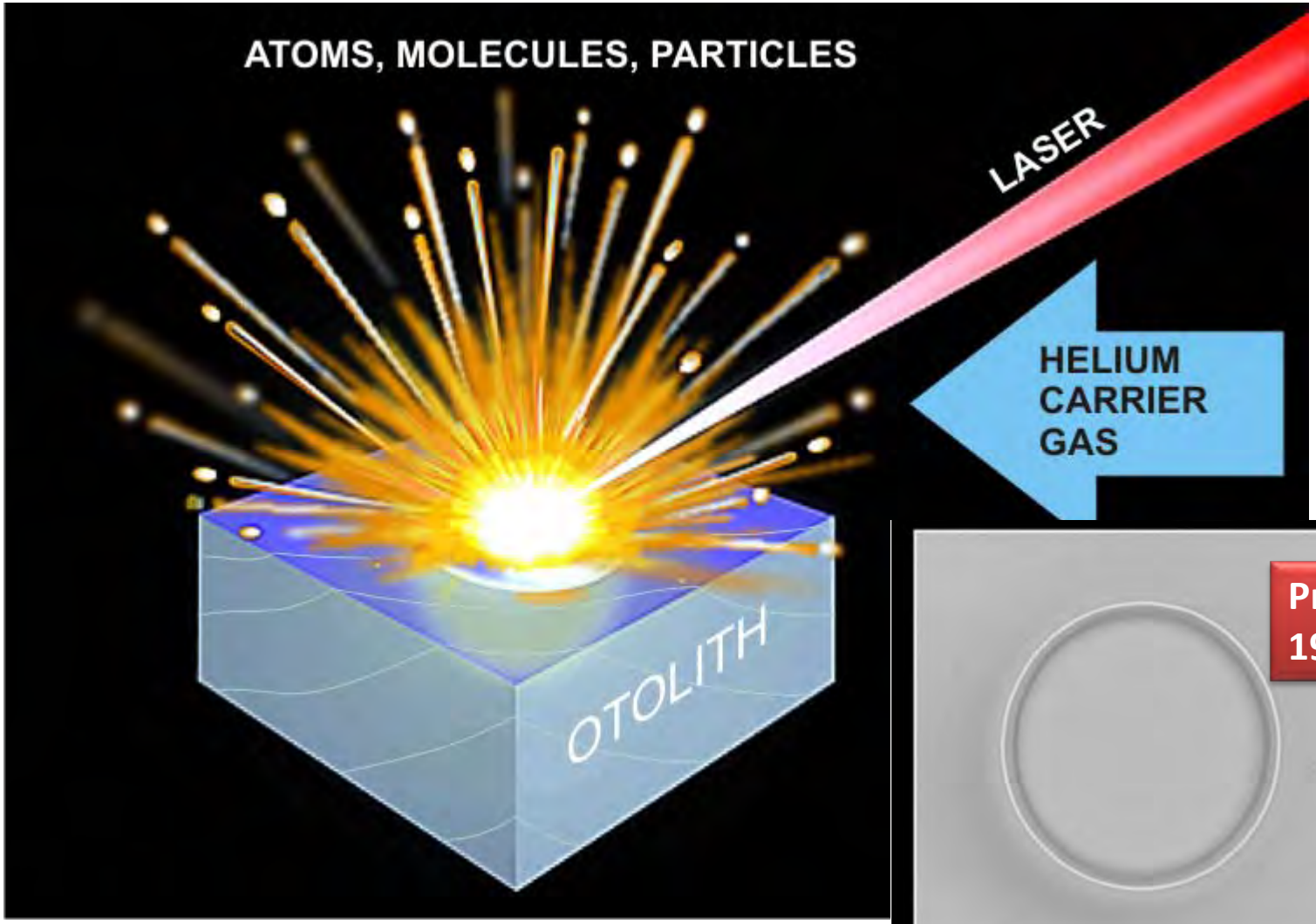
(FWRI PHOTOS)

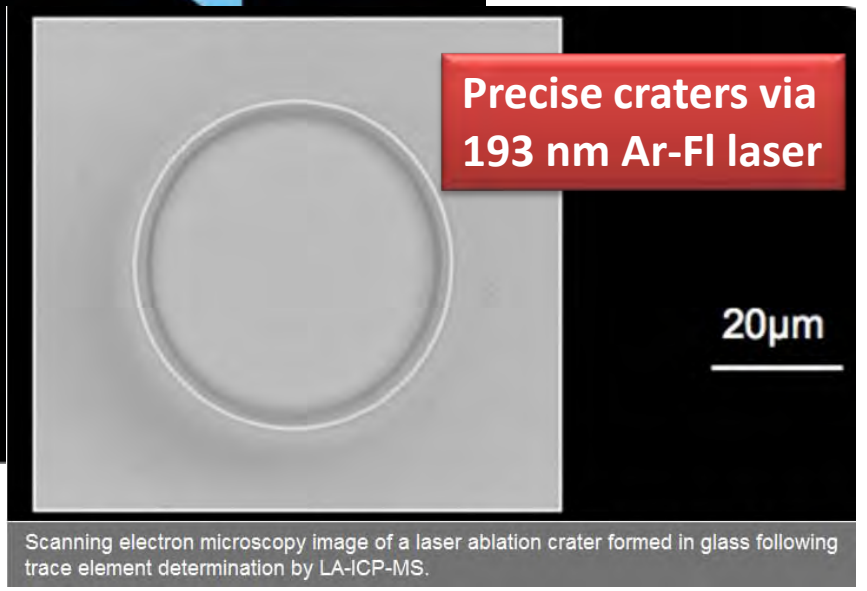


Clean Techniques Used During Otolith Preparation

Otolith microchemistry

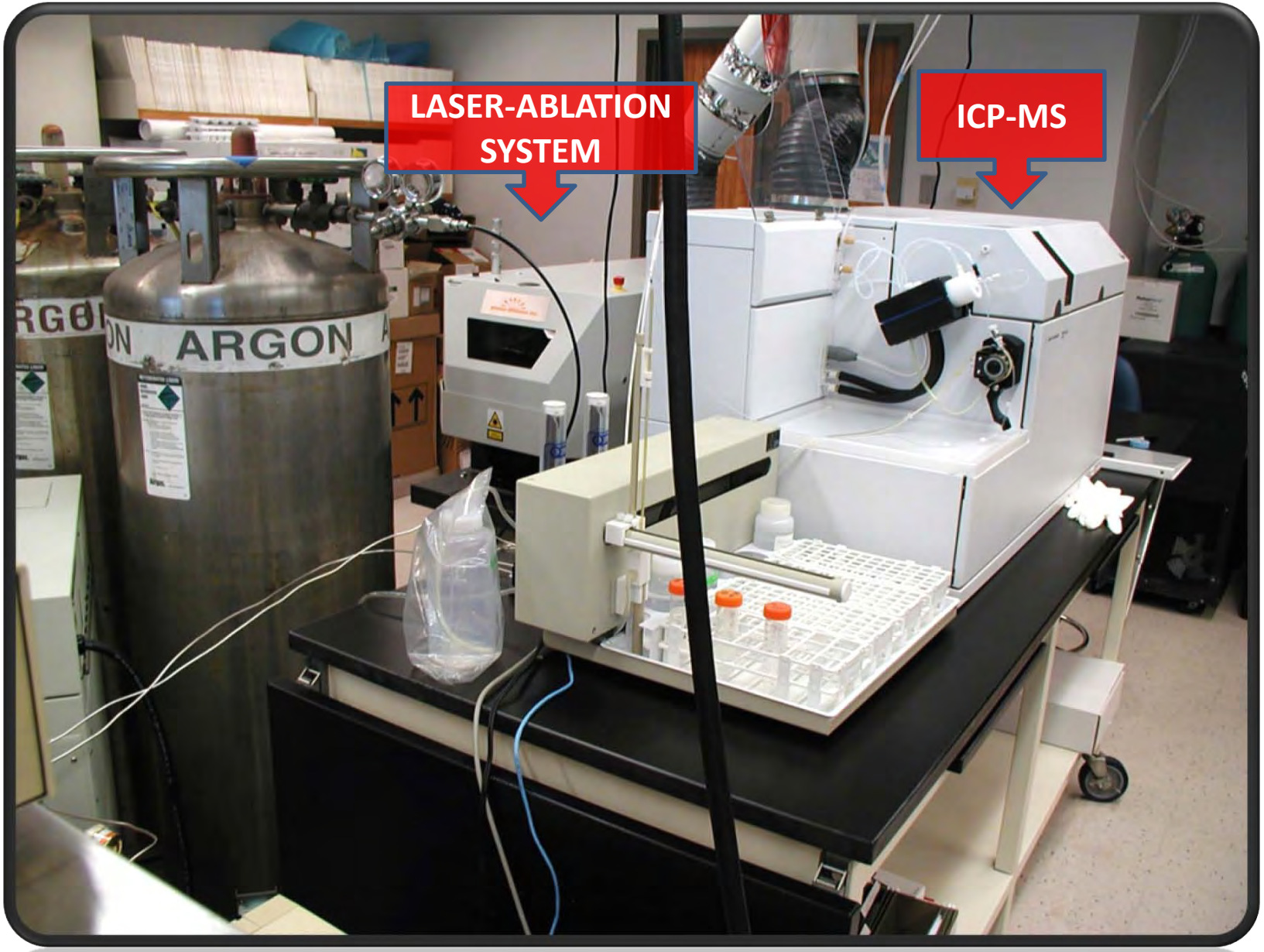
via Laser Ablation ICP-MS (LA-ICP-MS)



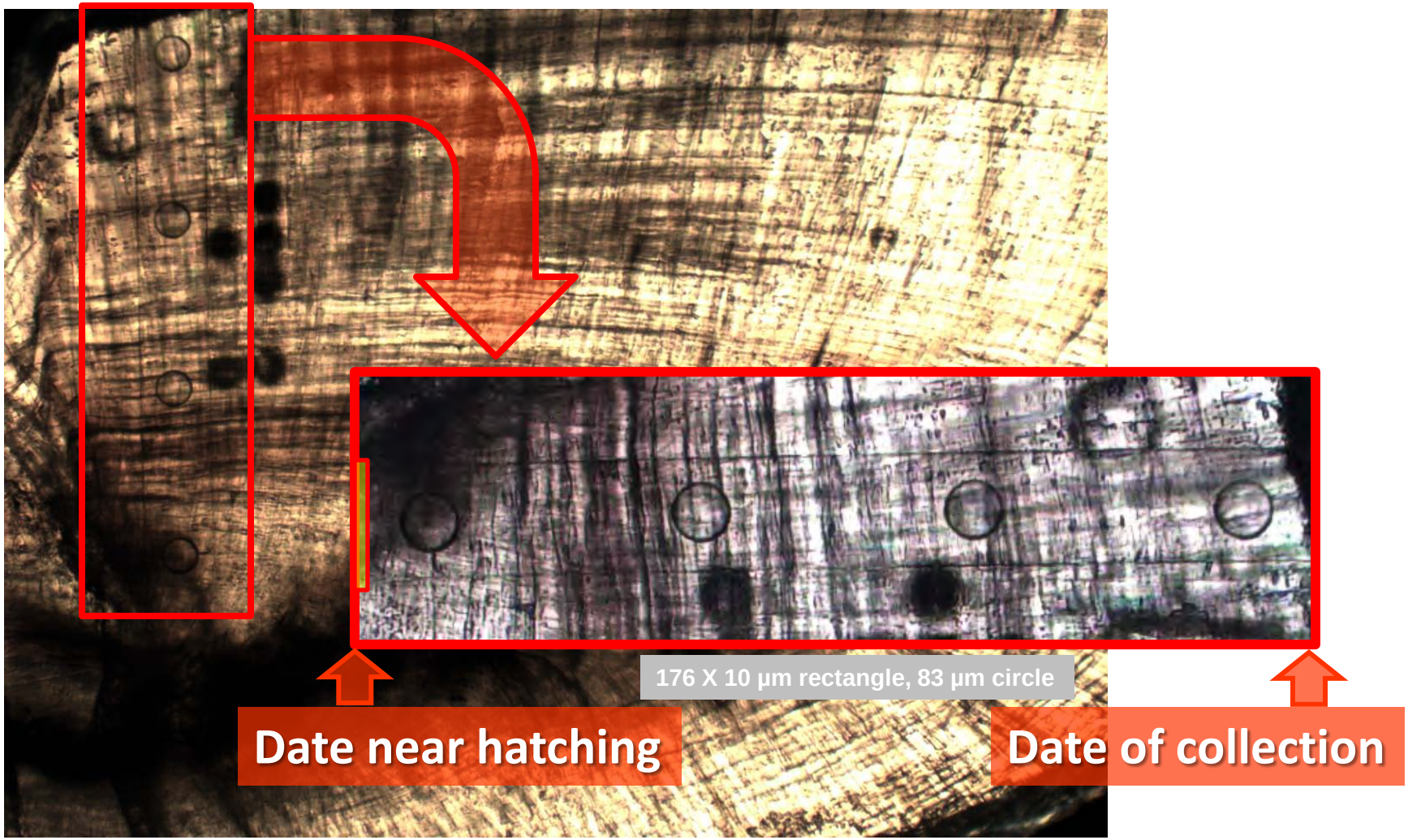


Scanning electron microscopy image of a laser ablation crater formed in glass following trace element determination by LA-ICP-MS.

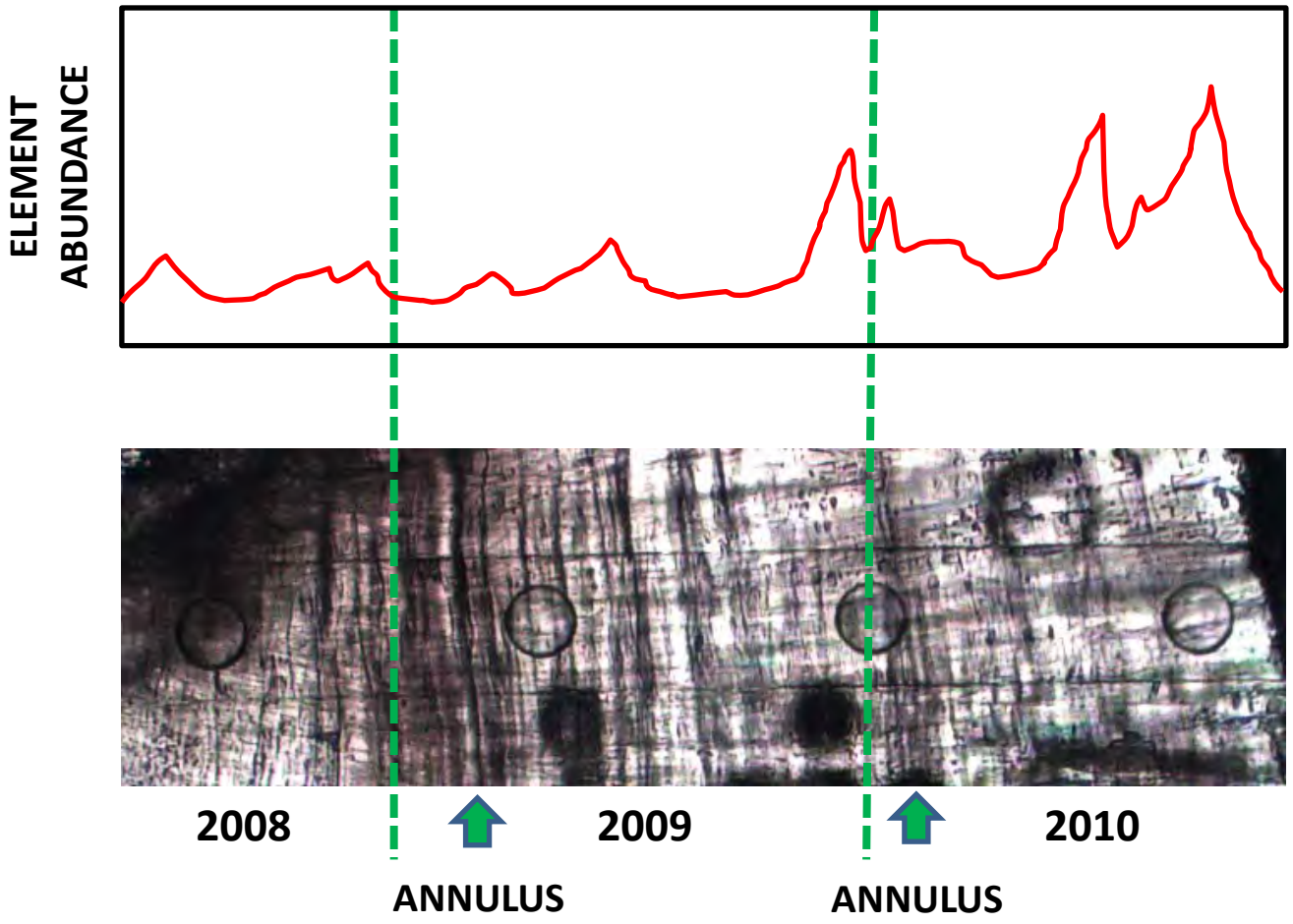
USF's LA-ICP-MS Instrumentation



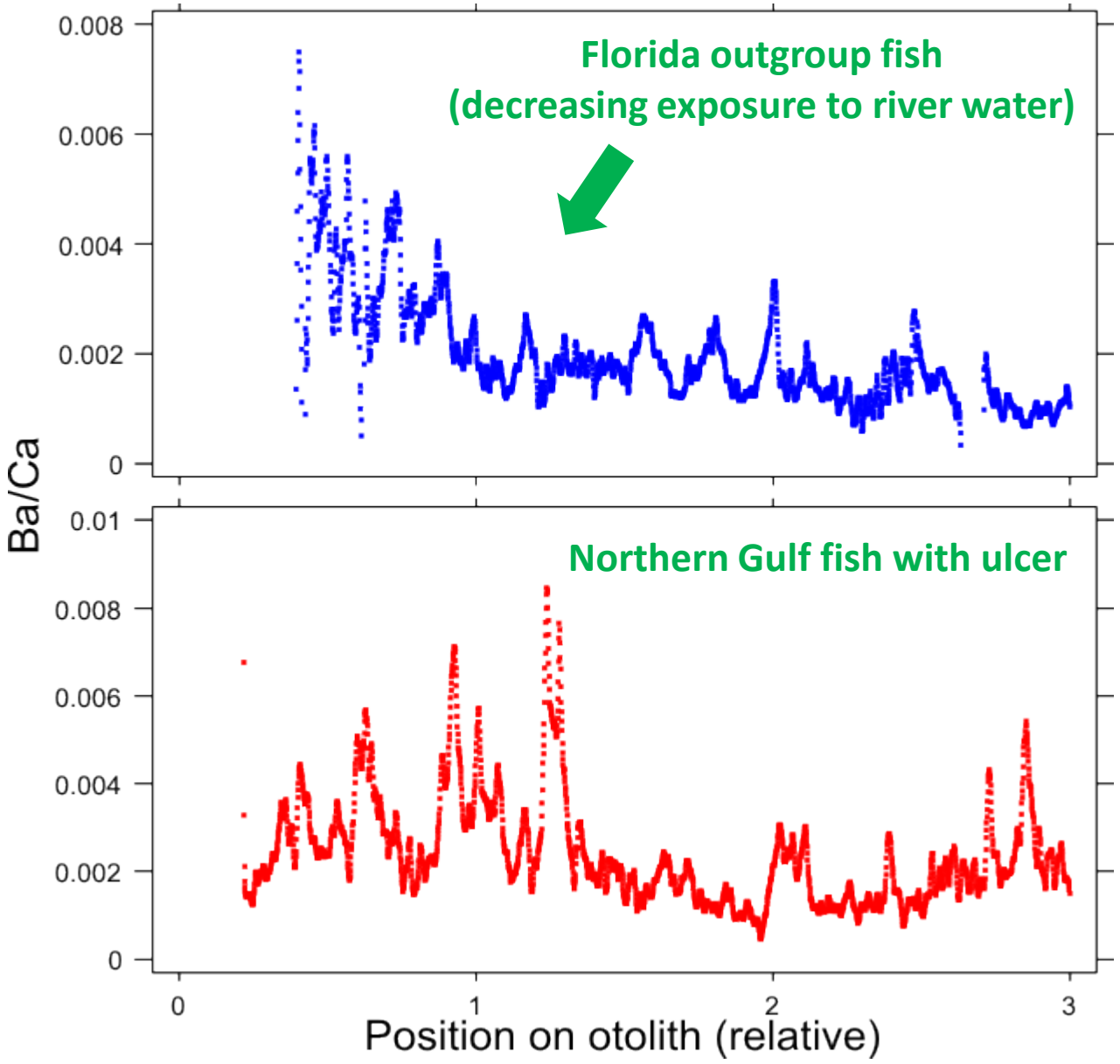
Photomicrograph of diseased red snapper otolith with “groove” visible from a rectangular laser ablation transect. Spot checks (circles) are also visible. The laser is used to clean surfaces prior to analysis (pre-ablation, another clean technique).



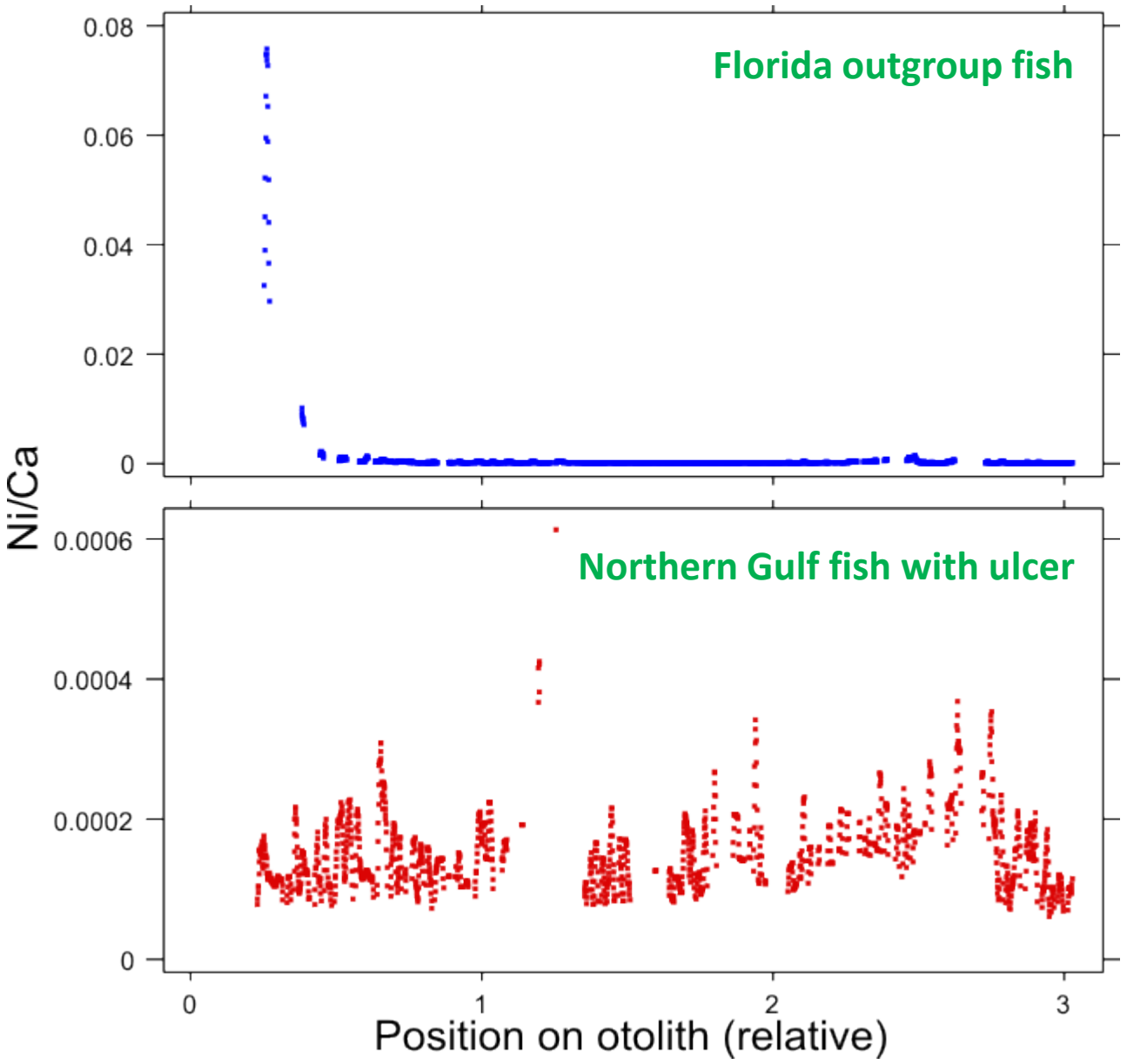
Elemental profiles can be synched with time.



Barium – indicator of river discharge



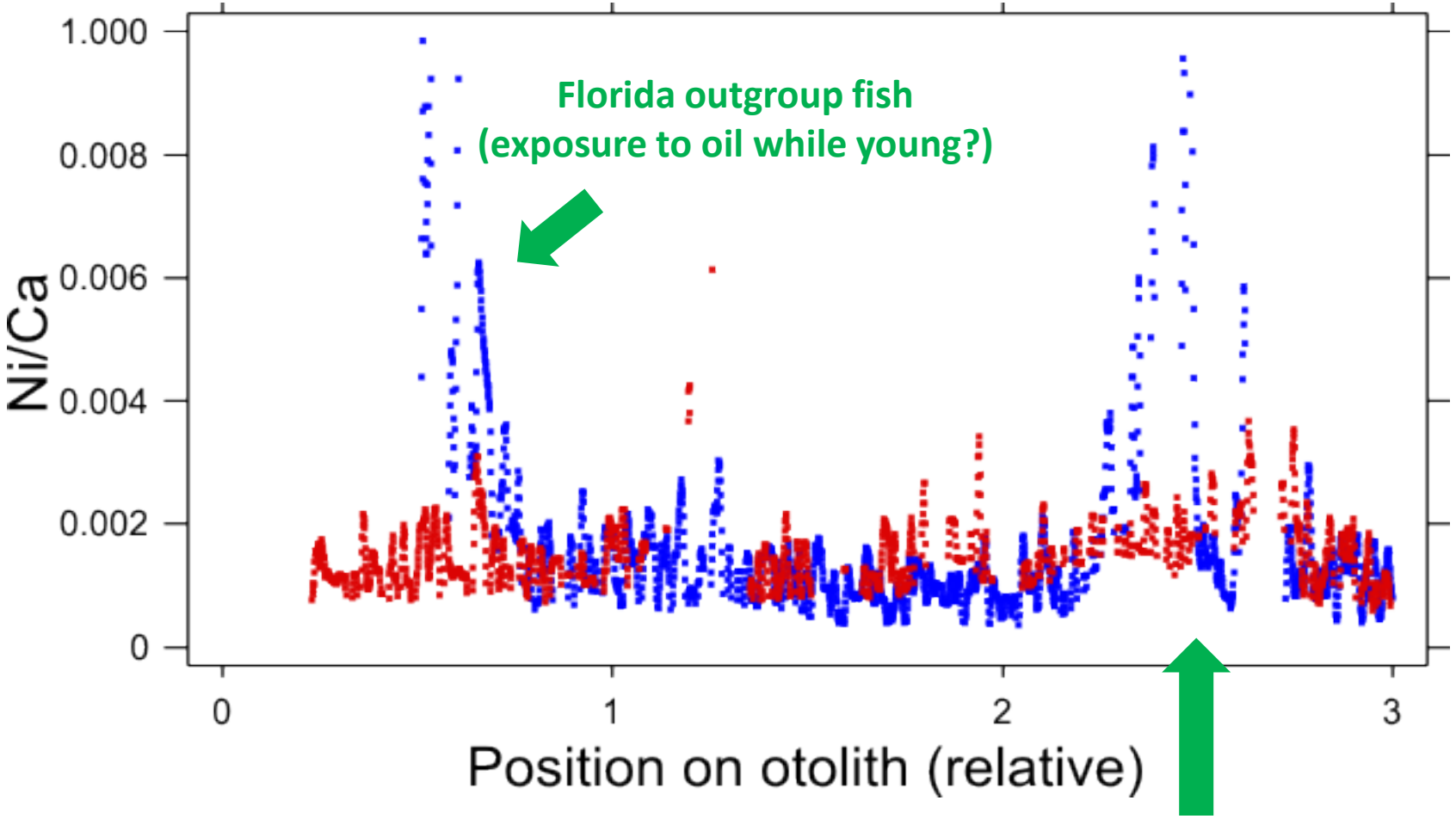
Nickel – indicator of oil exposure



Vanadium was below detection limits in these two specimens.

(Assay parameters are being optimized in an effort to correct this.)

Nickel – same-scale comparison



Where we are now . . .

- We have hundreds of discrete laser spot samples for gag, snook and red drum from Florida's west coast that serve as baselines for Ni and V.
- Profile comparisons of diseased and non-diseased fish (as shown here) started upon completion of the disease survey in August 2011.
- We do not yet know if elevated disease rates are associated with oil exposure, but should be able to determine this in coming months.
- We will continue to optimize our microchemical assay methods to improve resolution on both Ni and V.
- In the future, any fish that was alive during the BP oil spill can be analyzed.
- Note: Trace amounts of Ni & V in otoliths do not present a hazard to public health.