# SQUID Imaging of Exfoliation and Intergranular Corrosion

**John P. Wikswo and Yu Pei Ma**

**Vanderbilt University**

Kevin Cooper, Luna Innovations, Inc.,

James Suzel, S&K Technologies

Robert Kelly, University of Virginia

November 14, 2001

# Practical Corrosion Questions

What is the instantaneous rate of corrosion?

How does it depend upon?

- Humidity
- Environment (salt, *etc.*)
- Corrosion abatement technology
- Maintenance
- Metallurgy

SQUIDs can help answer these questions.

# How do you quantify hidden corrosion?

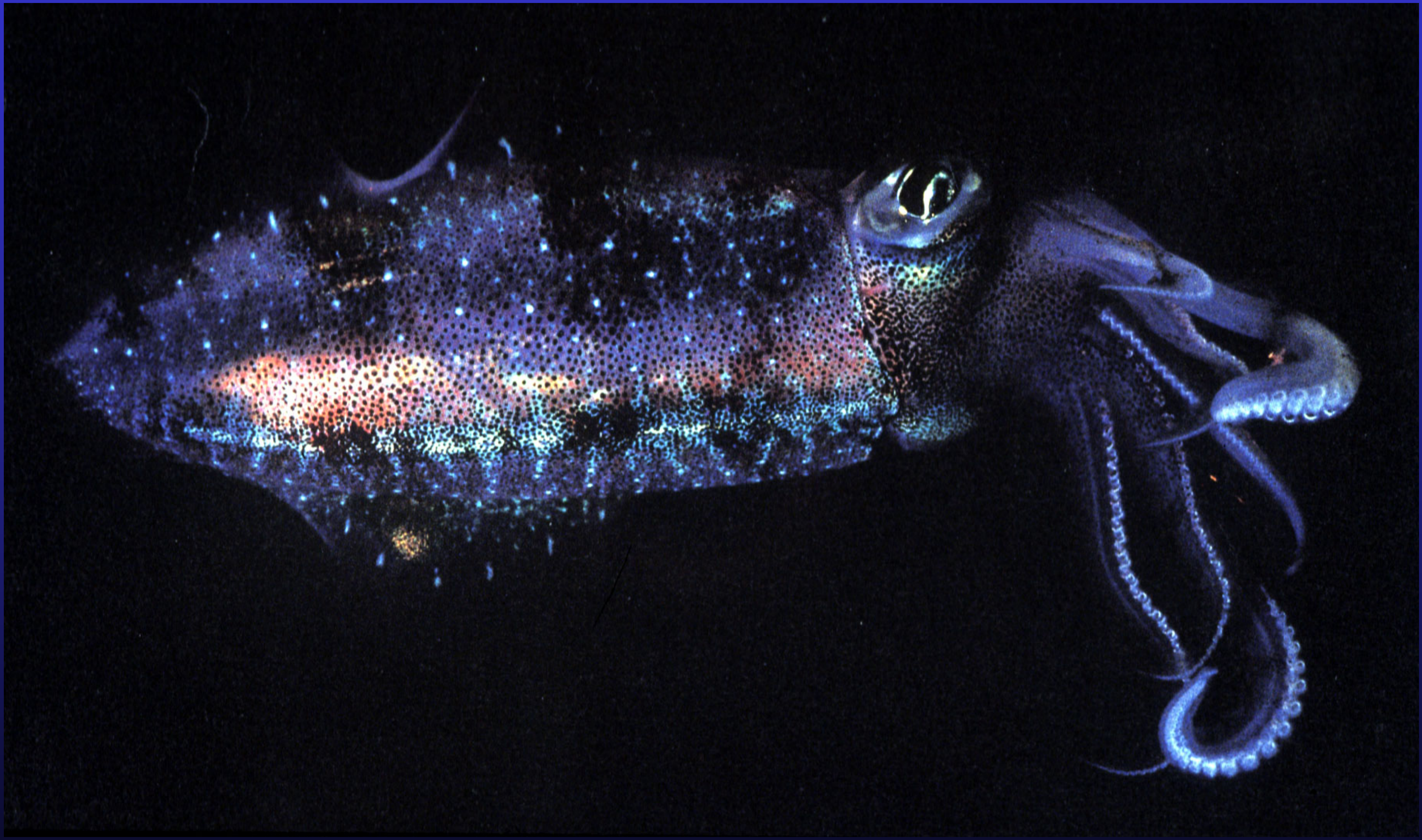
- NDI – detects corrosion damage and missing metal
  - Measurable material loss may take months
- Mass Loss – detects metal loss by weighing
  - Well-suited for determining the average rate over intervals as short as several weeks
  - Cannot be used on old lap joints or exfoliation/IGA
- Potentiometric measurements
  - Limited to exposed surfaces
- SQUIDs – detects magnetic field of corrosion currents
  - Can detect ***instantaneous*** corrosion
  - Difficult to obtain absolute calibration

# Why use a SQUID magnetometer?

- There are no established techniques that can measure the **rate** of hidden corrosion
- There is little knowledge of how corrosion **rates** are affected by environment, structural condition, flight history, or maintenance procedures.
- Standard electrochemical techniques cannot study the instantaneous rate or distribution of hidden or crevice corrosion.
- SQUIDs are ideally suited to map the distribution of **hidden** corrosion ACTIVITY in an aircraft lap joint or wing plank
- Caution: The mechanisms by which corrosion activity produces the observed magnetic fields are not fully understood

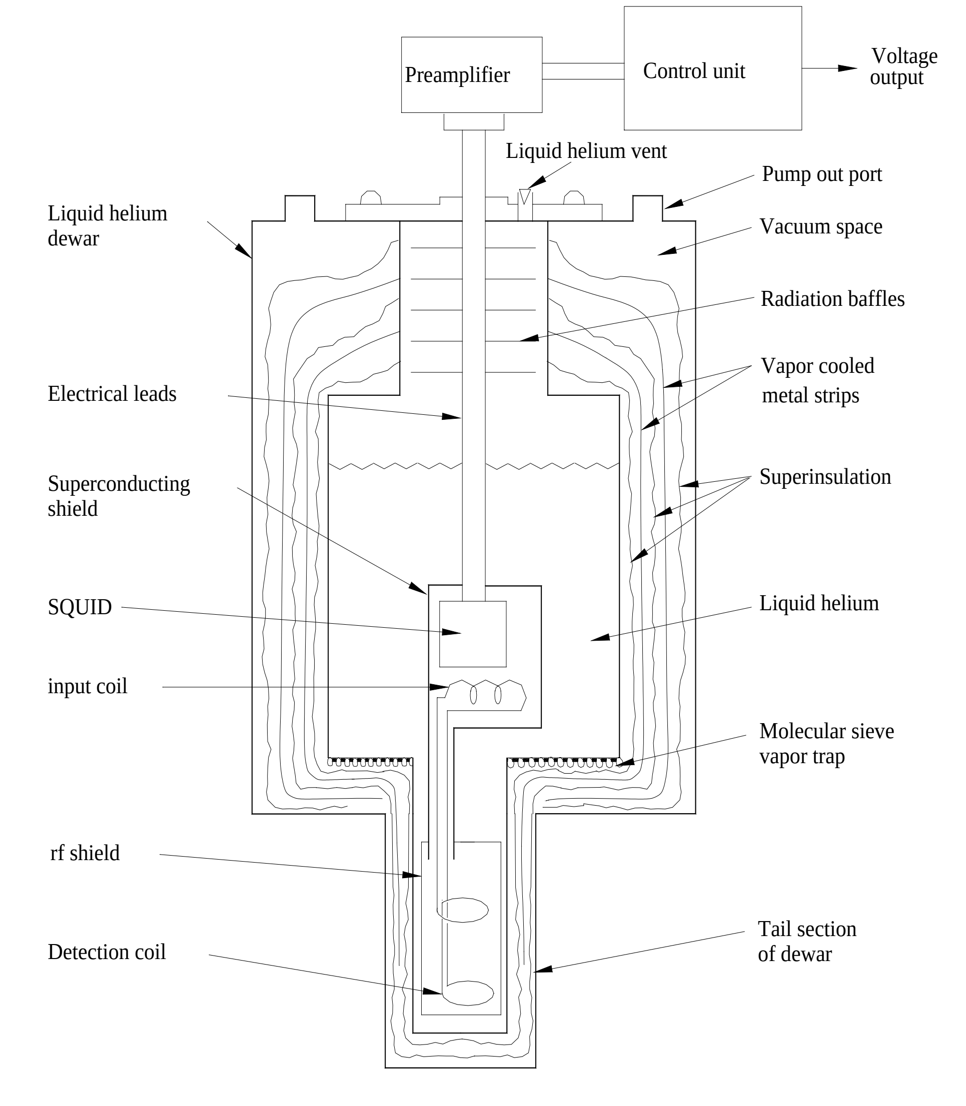
ELECTROMAGNETICS LABORATORY
DEPARTMENT OF PHYSICS AND ASTRONOMY, VANDERBILT UNIVERSITY

# What is a SQUID magnetometer?

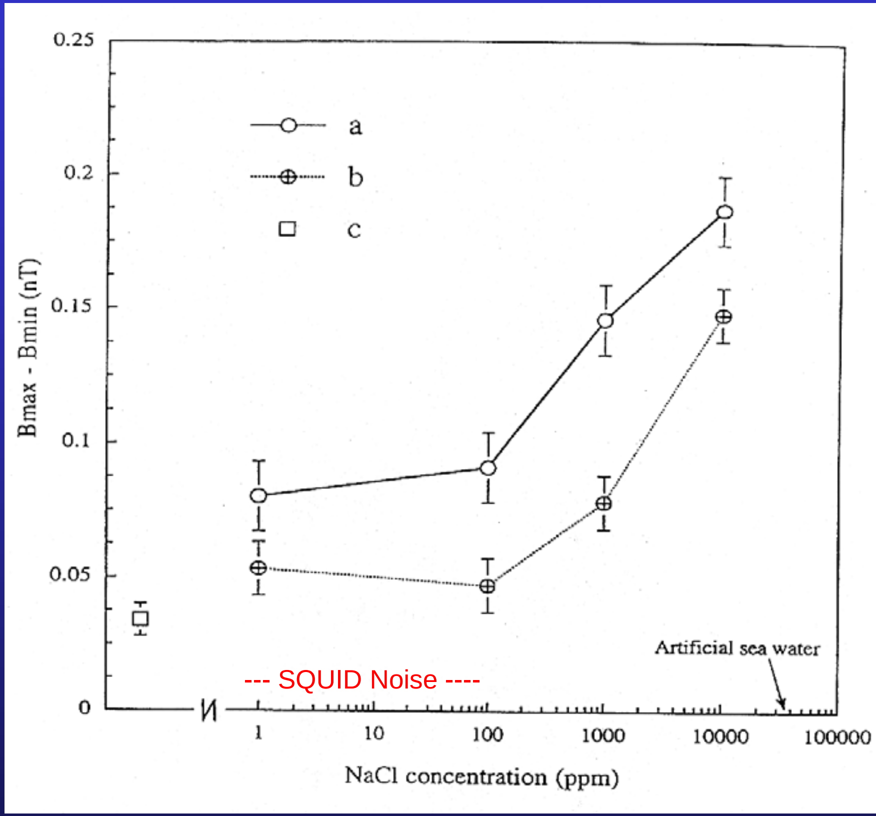


# Superconducting QUantum Interference Device (SQUID) Magnetometer

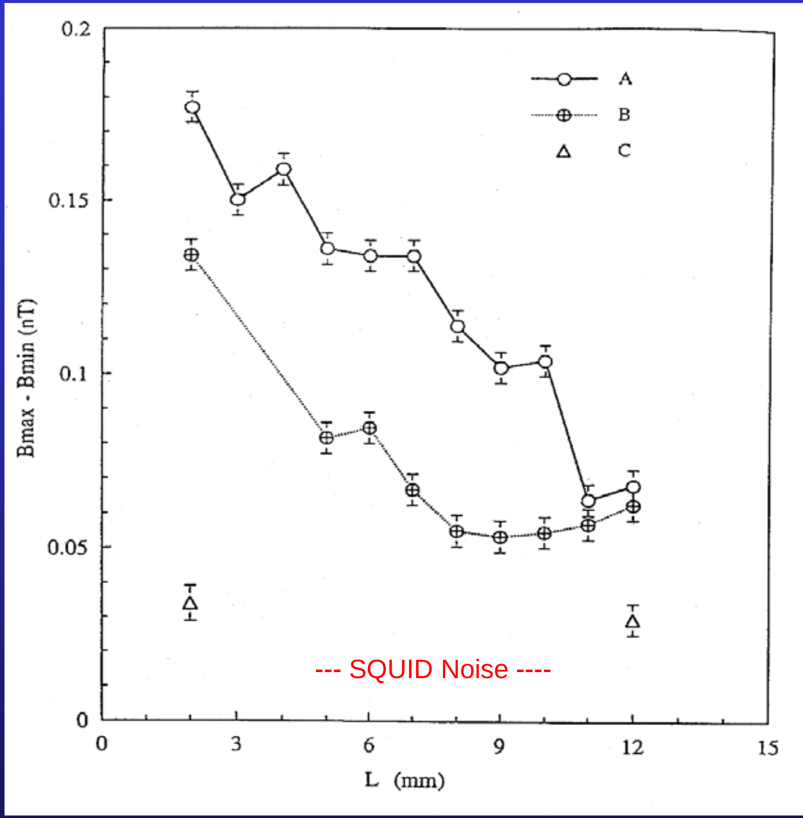
- Pickup coil coupled to a SQUID that measures the current induced in the pickup coil.
- A flux-to-voltage converter with unrivaled **sensitivity** (5-20 f T/Hz$^{1/2}$)
- Spatial **resolution**: 1 to 3 mm (20 um max)
- **Bandwidth** of DC to 10's kHz.



# SQUID Sensitivity for Weak or Deep Corrosion




SQUIDs can detect corrosion of aluminum in 1 ppm NaCl



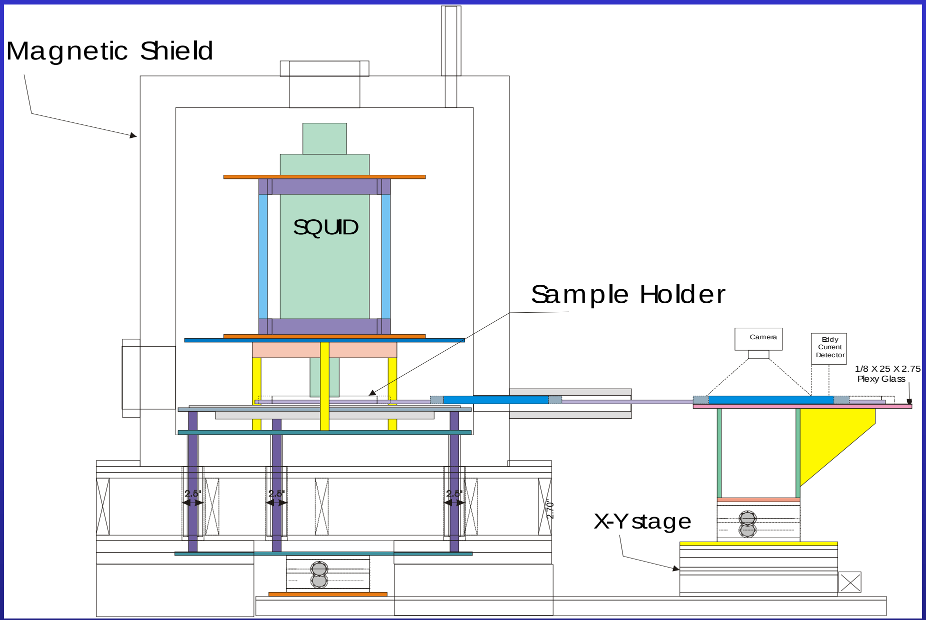

SQUIDs can detect corrosion of aluminum through 1 cm of metal or air

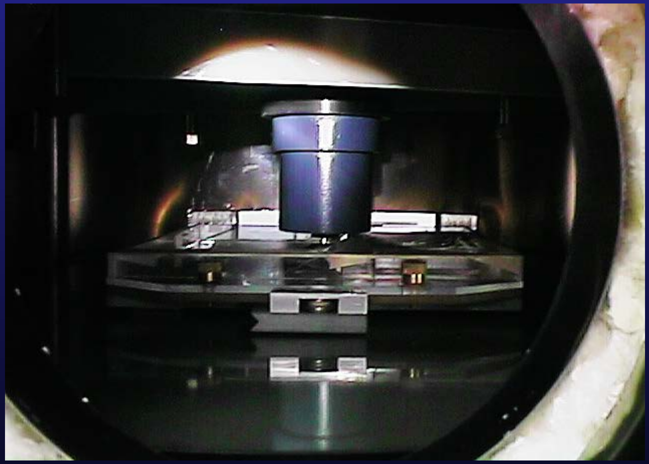
Detection of Hidden Corrosion of Aircraft Aluminum Alloys by Magnetometry Using a Superconducting Quantum Interference Device," D. Li, Y.P. Ma, W.F. Flanagan, B.D. Lichter, and J.P. Wikswo, Jr., Corrosion, 53(2): 93-98 (1997).

# Conclusions from AFOSR-URI studies

- SQUIDs are suited for the periodic, non-destructive analysis of corrosion test specimens where the corrosion activity is not directly accessible to a potentiostat, *e.g.*, corrosion that is hidden under a thick coating or one or more layers of metal.
- SQUIDs may be the only technique to detect these hidden **currents** non-destructively and instantaneously.
- **The external magnetic field does not reflect all of the internal corrosion activity, *i.e.*, there are field cancellation effects.**

# The AFCO Corrosion SQUID System



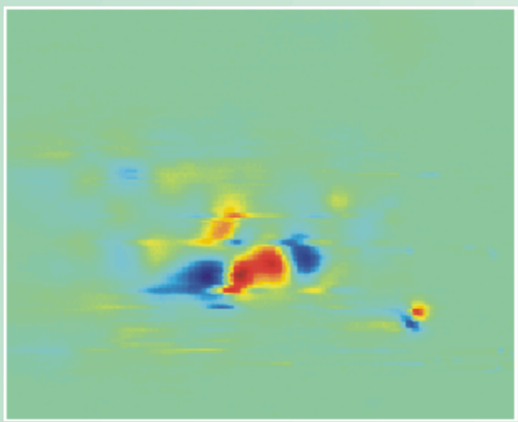
# SQUID Corrosion Measurements in the Laboratory

- This is a laboratory technique for determining the rates of hidden corrosion under different conditions.
- This is **NOT** an NDI tool!
- It is highly unlikely that this technique can be applied to intact aircraft on the flight line!

How do the SQUID data correlate with the <u>instantaneous rate</u> of corrosion?

Start with the spatially-integrated magnetic activity (SIMA)

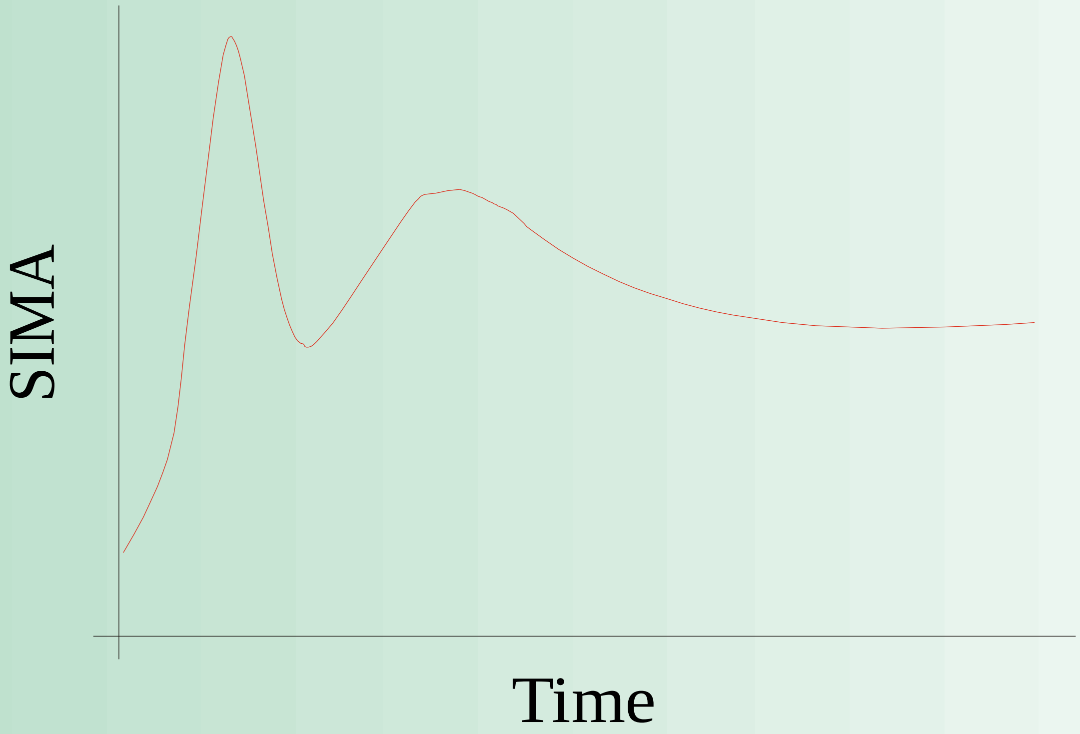
$$\int_{XY} \left| \; \right|$$



$$= \text{SIMA}$$

$$\text{SIMA}(t_j) = \Sigma_{XY} \, | \, B\,(X,Y,t_j) \, | \, \Delta X \, \Delta Y$$

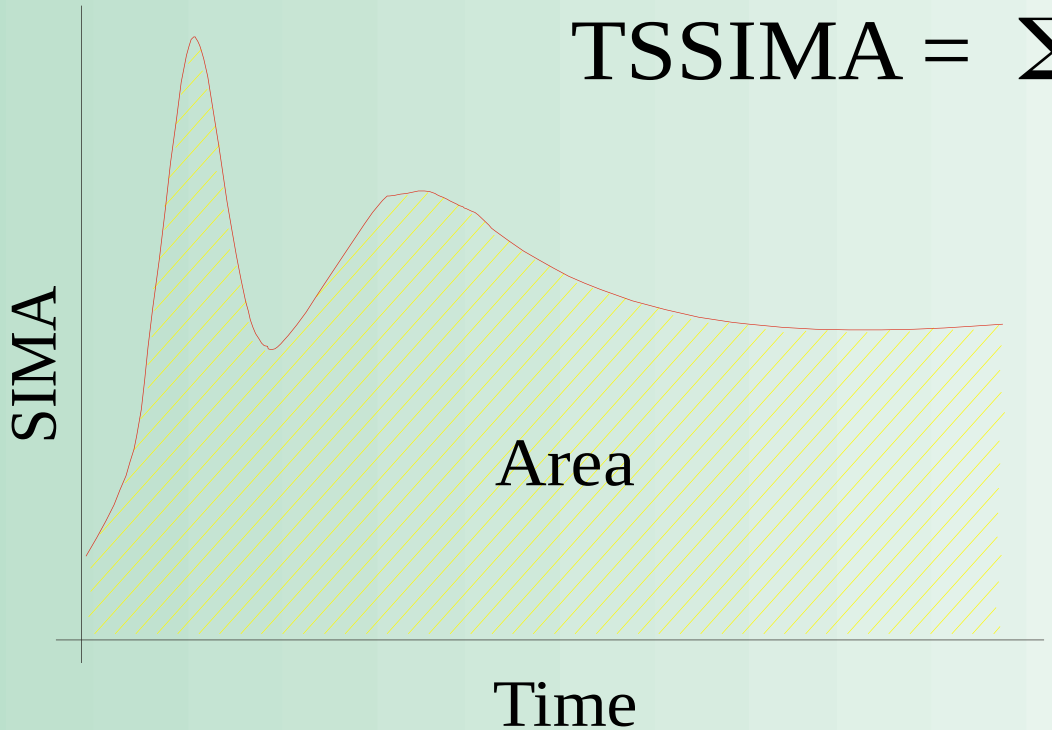
Ideally, SIMA is proportional to the instantaneous corrosion activity, i.e. corrosion rate



## How do the SQUID data correlate with mass loss?

Use the temporally-summed spatially-integrated magnetic activity (TSSIMA)

$$\text{TSSIMA} = \sum_j \text{SIMA}(t_j)\,\Delta t_j$$




TSSIMA correlates well with mass loss, but with a geometry-dependent calibration factor

# Corrosion Rates in Old Lap Joints

## Protocol 3 exposure sequence

Step 1: Humid Air (98% RH)

Step 2: Distilled Water

Step 3: 0.01 M Chloride

Step 4: 0.1 M Chloride

- Bake-out before each step
- Degauss after each bake-out
- Each step is repeated three times for all specimens

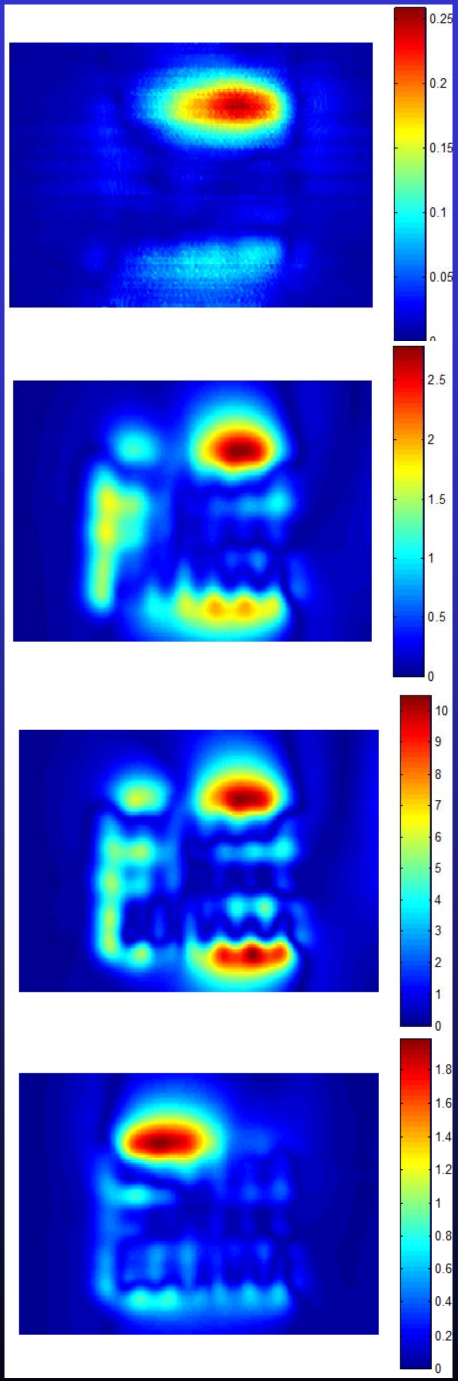
# SQUID Images

Step 1: Humid Air (98% RH)

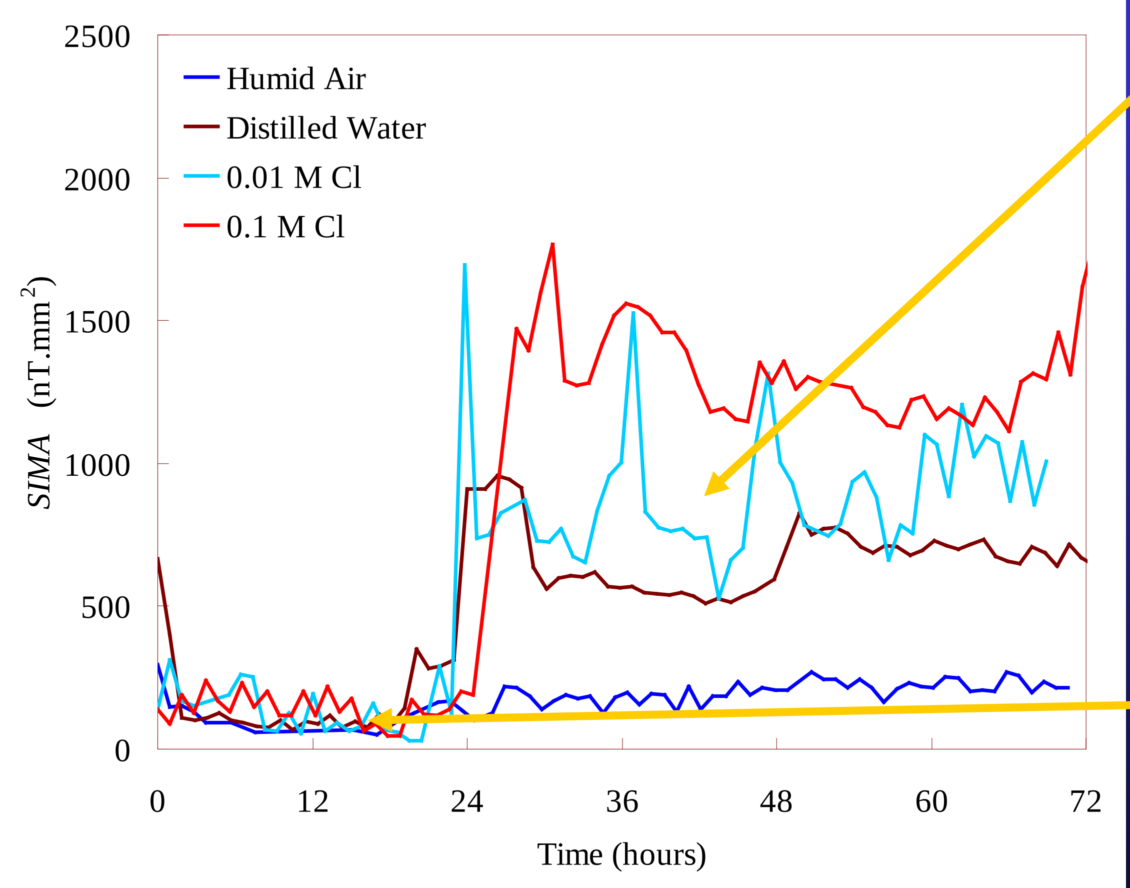
Step 2: Distilled Water

Step 3: 0.01 M Chloride

Step 4: 0.1 M Chloride

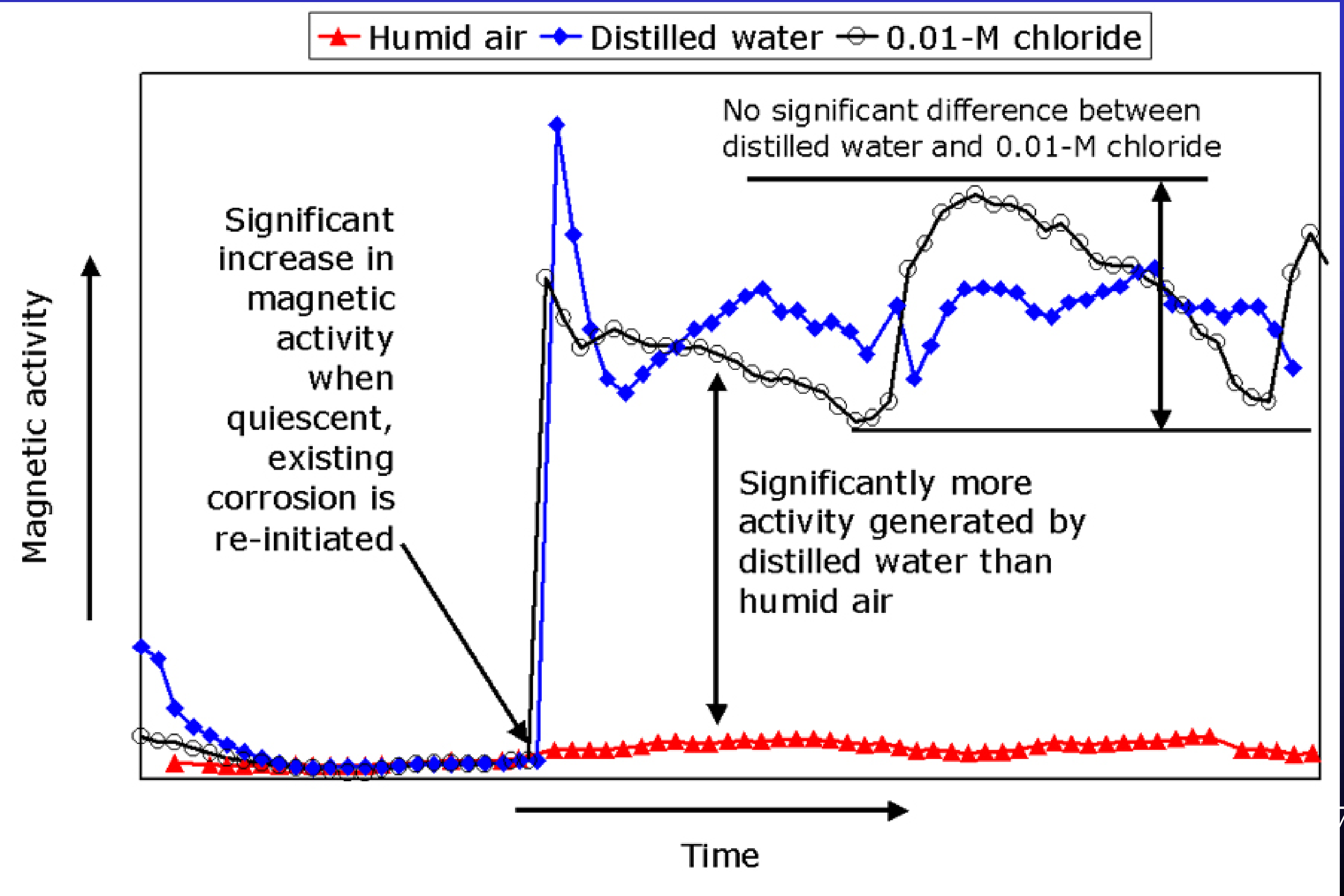


# Summed Magnetic Activity Versus Time for Old Aircraft Lap Joints

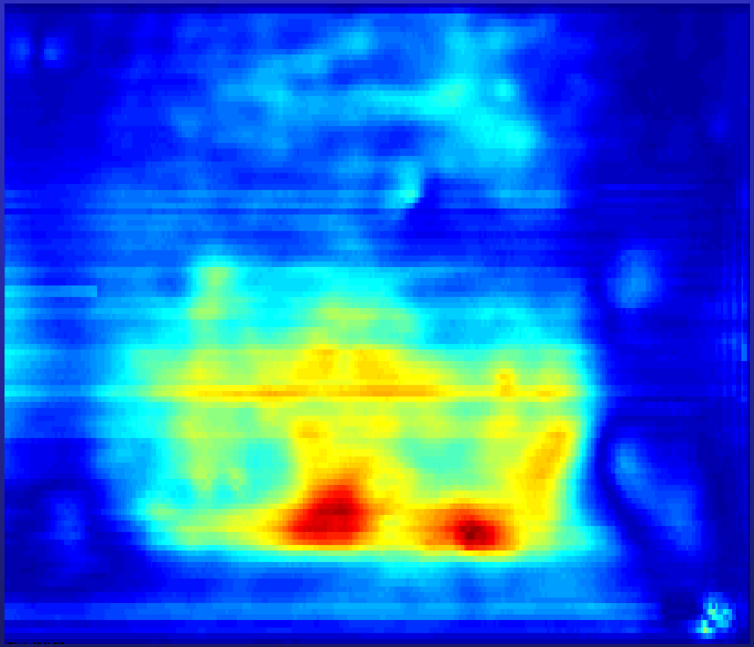


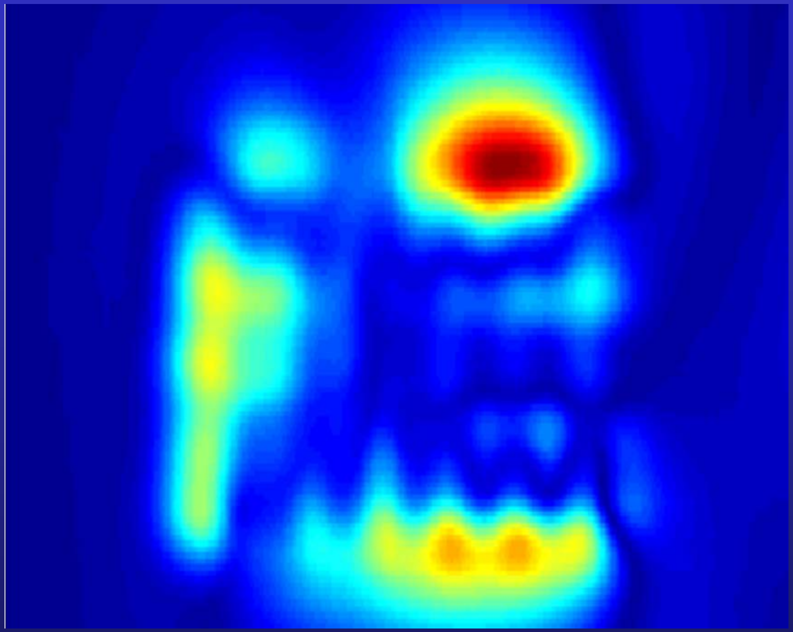

- Varied activity depending upon lap joint, corrosive solution, and time
- Reproducible dry background

# Lap Joint SIMA vs Environment



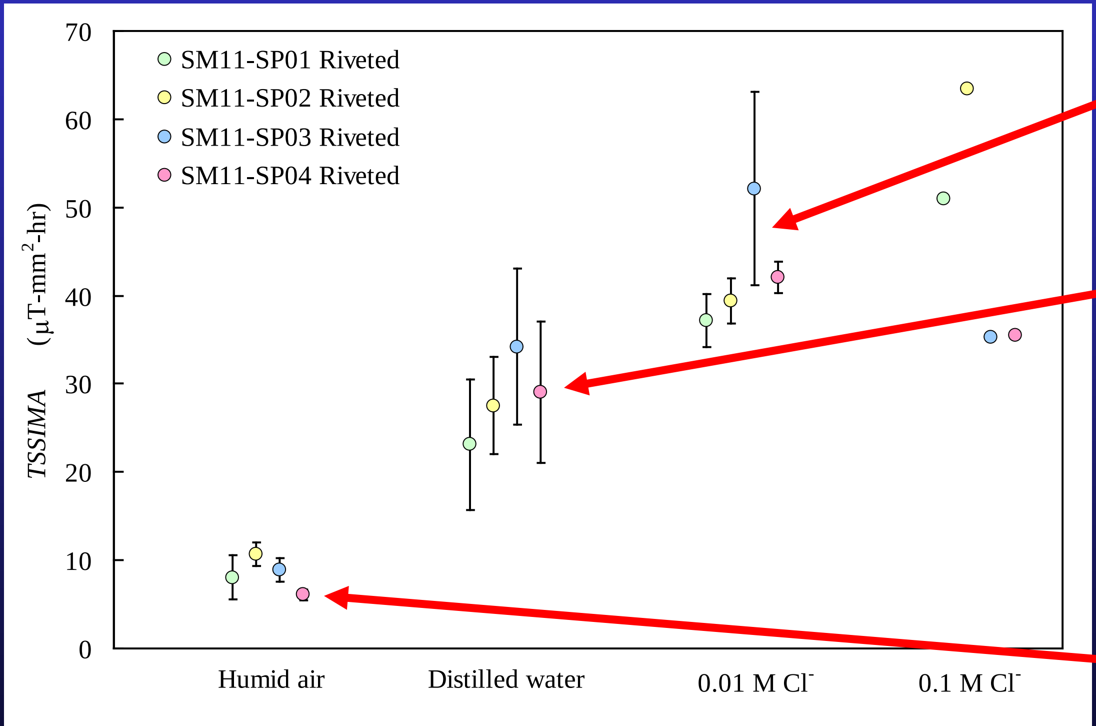
# Spot-Welded Compared with Riveted: Cumulative activity map


Riveted Specimen


Spot-welded Specimen

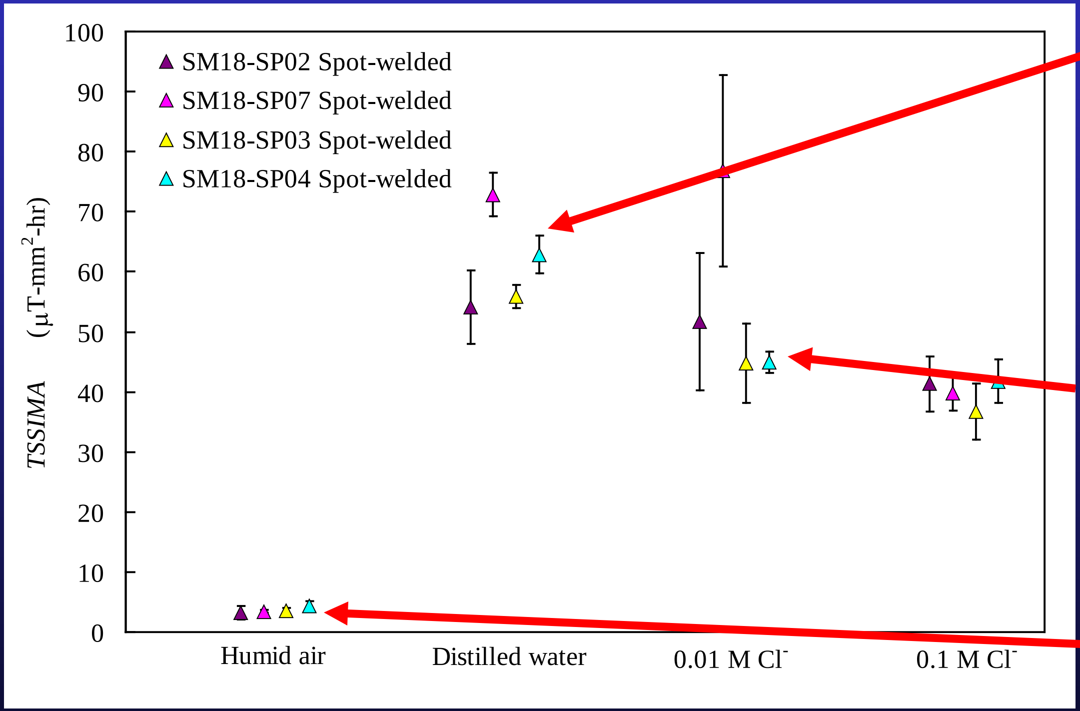
Can identify internal structure apparently associated with spot welds compared with that of rivets

# Summed Magnetic Activity Versus Time for Old **Riveted** Lap Joints




- 0.01 M chloride shows higher activity
- Distilled $H_2O$ activates the chemistry within the lap joint
- Low activity in 98% relative humidity air

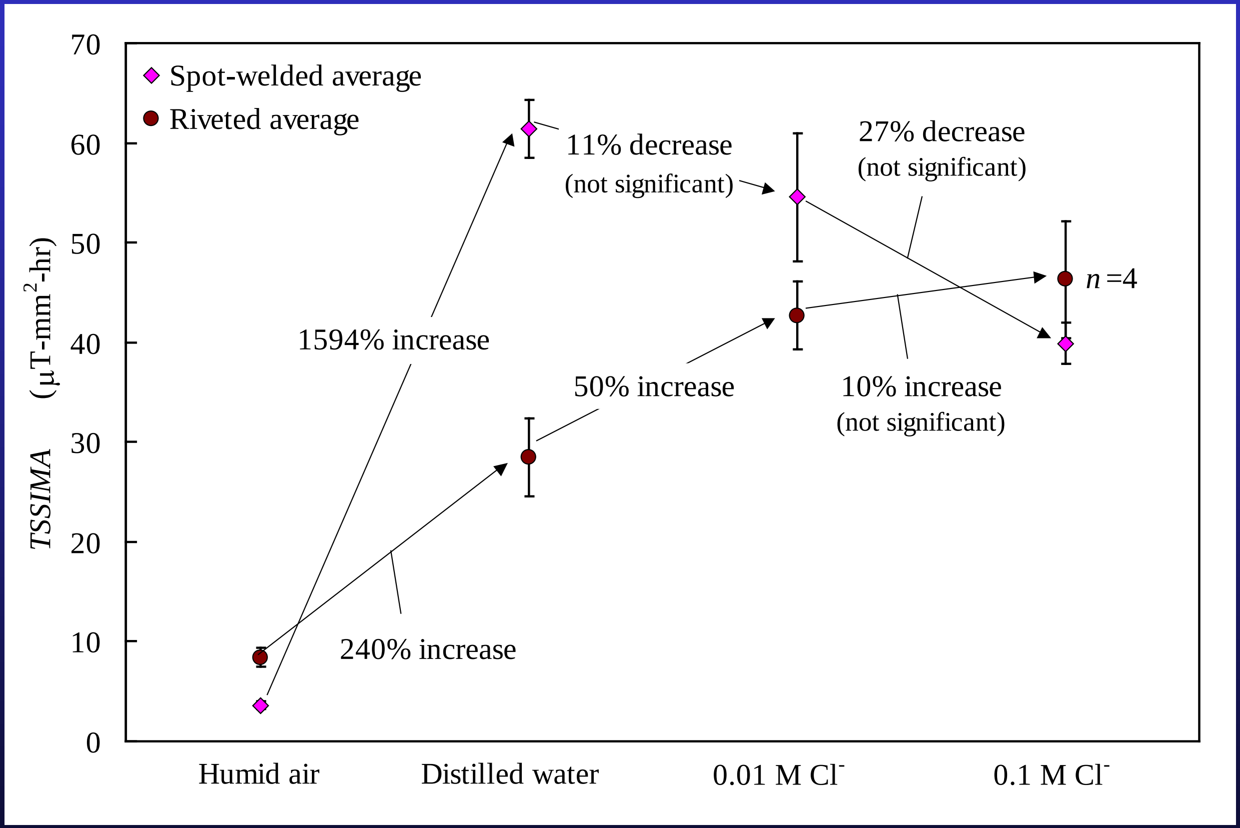
# Summed Magnetic Activity Versus Time for Old **Spot-Welded** Lap Joints




- Distilled $H_2O$ activates the chemistry within the lap joint
- 0.01 M chloride shows lower activity than distilled water
- Low activity in 98% relative humidity air

# Spot-Welded Compared With Riveted: Ratio of *TSSIMA*

- If an old lap joint is hydrated with distilled water, the chemicals already in the lap joints may be more important in the short term than what is added externally.
- **There may not be a strong dependence upon the concentration of externally-applied chloride.**



# Lap Joint Conclusions

- SQUIDs can make useful measurements of instantaneous electrochemical activity in lap joints that are not possible with any other technique.
- These data are reproducible phenomenological representations of corrosion activity.
- We can assess the effects of moisture and NaCl on old riveted and spot-welded lap joints.

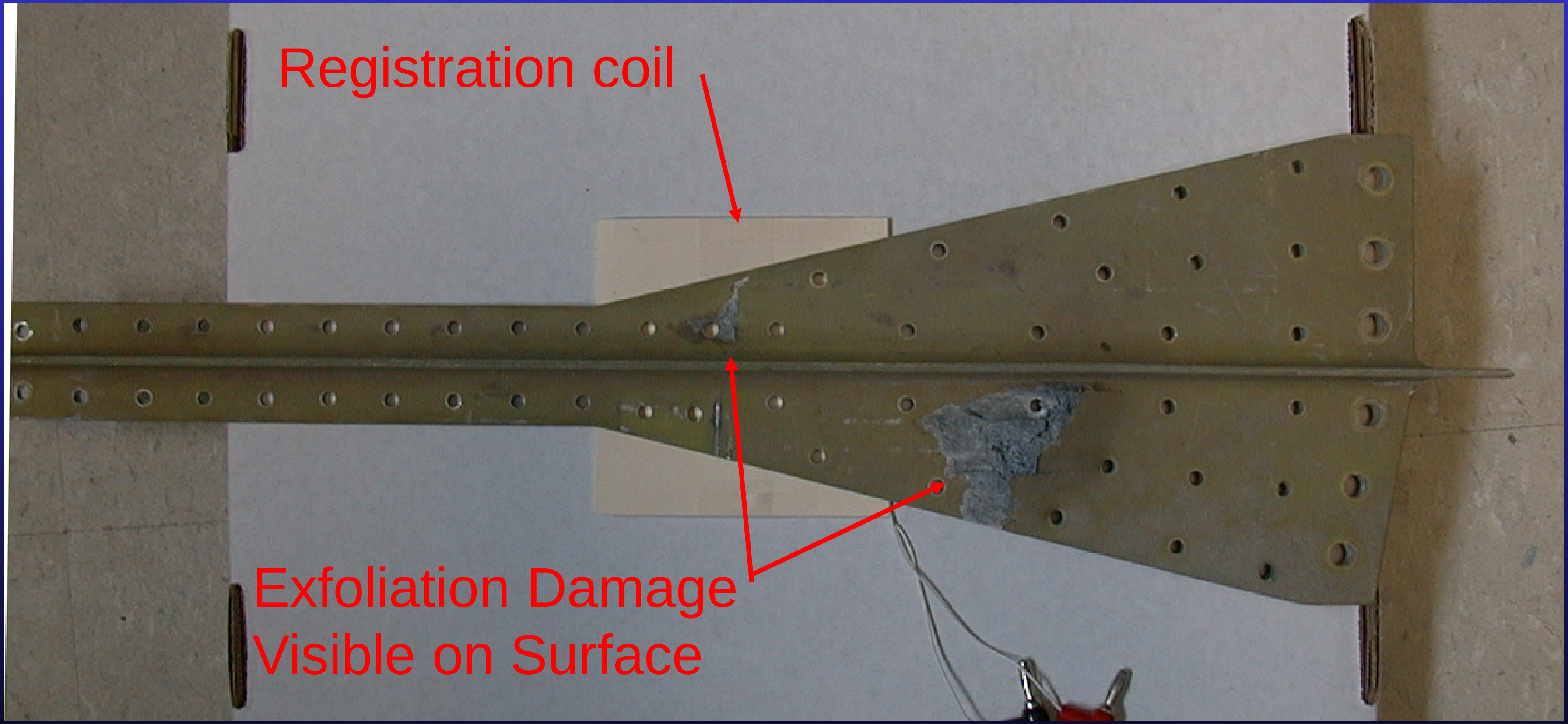
# Objective: Exfoliation/IGA

Demonstrate that SQUID magnetometry can provide information regarding the time course of exfoliation/intergranular corrosion attack in aluminum

# Preliminary Tests of SQUID Detection of Exfoliation Corrosion

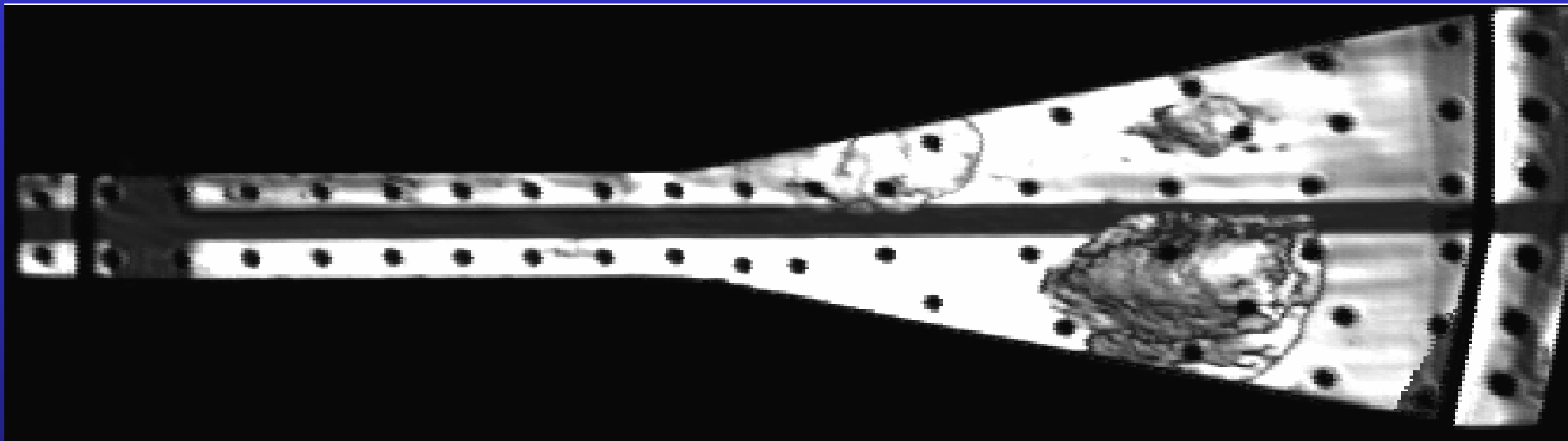
- Sample
  - Horizontal stabilizer carry through box stiffener
  - Aircraft MDS - KC-135
  - Material: 7075-T6 Forging
- Protocol
  - SQUID above flat side (side not shown)
  - Scan in air for baseline recording
  - Submerge distilled water and scan for one week

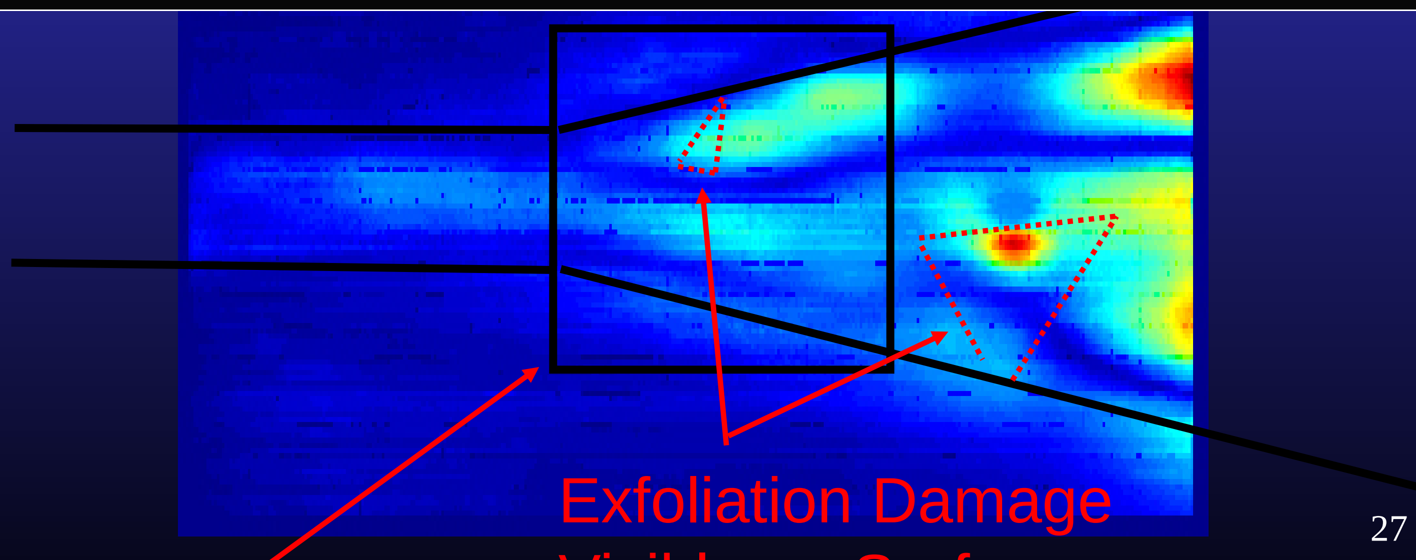
# Horizontal Stabilizer Carry Through Box Stiffener with Square Registration Coil



# Close-Ups of Exfoliation Damage

# Ultrasound and Temporally Summed Magnetic Activity (TSMA) After One Week of Exposure





# Conclusions – Box Stiffener Exfoliation

- SQUIDs can readily detect exfoliation corrosion in 7075 forgings
- Needed
  - Simpler geometry
  - Correlations of SQUID with NDE and metallography

# Luna/S&K/VU Protocol E1

- Samples: Kaiser 0.350 7075-T6 (lot 274371) 4" wide by 10" long, grain lengthwise.
- Holes" three 3/8" holes approximately 1/8" deep and 2" apart.
- Coated twice everywhere except sides of holes with XP-2000 sealant; 0.040-0.050 bare aluminum on hole sides
- Holes filled with ANCIT solution
- Anticipate 1-3 mm of penetration in 48-96 hours.

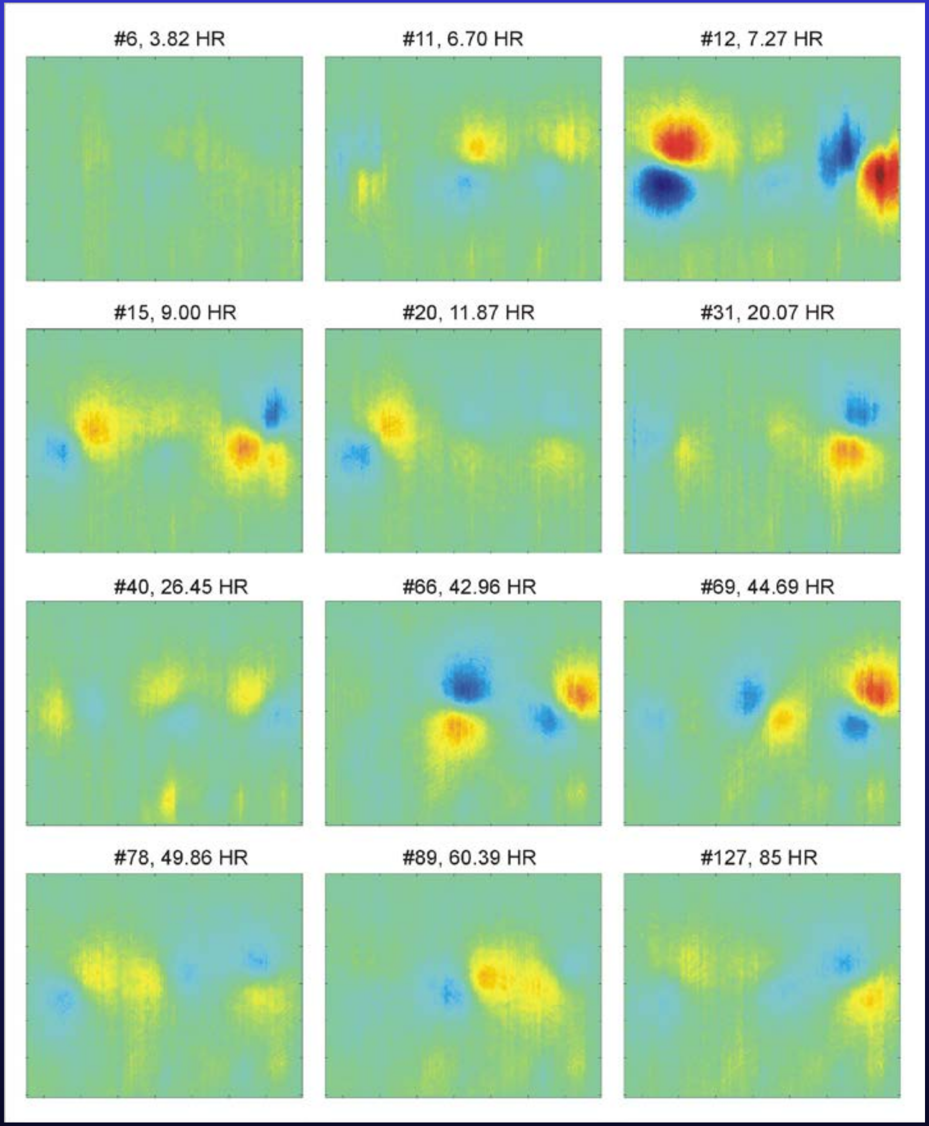
# Sample VEX001

# Exfoliation Solution

- **ANCIT** Solution:
  - 4 M NaCl
  - 0.6 M KNO3
  - 0.022 M AlCl3 (as AlCl3 · 6H2O)
  - natural pH ~ 3 to 3.3
- ASTM G34-90, in *Annual Book of ASTM Standards - Metal Test Methods and Analytical Procedures*, Vol. 03.02 Wear and Erosion; Metal Corrosion, ASTM, Philadelphia, PA, 119-124 (1990).

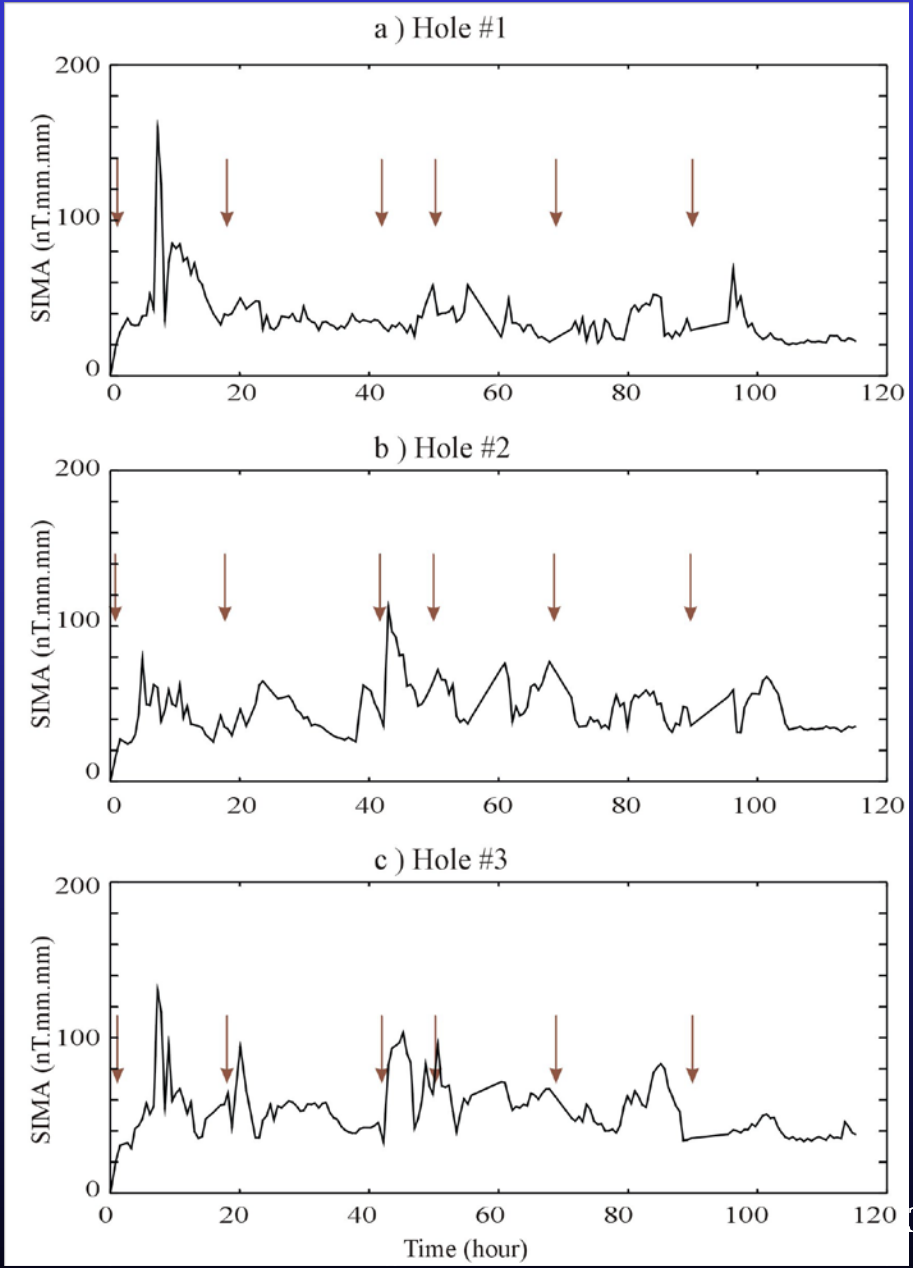
# SQUID Images During Exfoliation Corrosion Development

- Corrosion activity visible within 5 hours of exposure and reach maximum about 7.5 hours
- Time-dependence of corrosion differs from hole to hole over short time intervals (Frame #12 vs #15, and #66 vs #69)

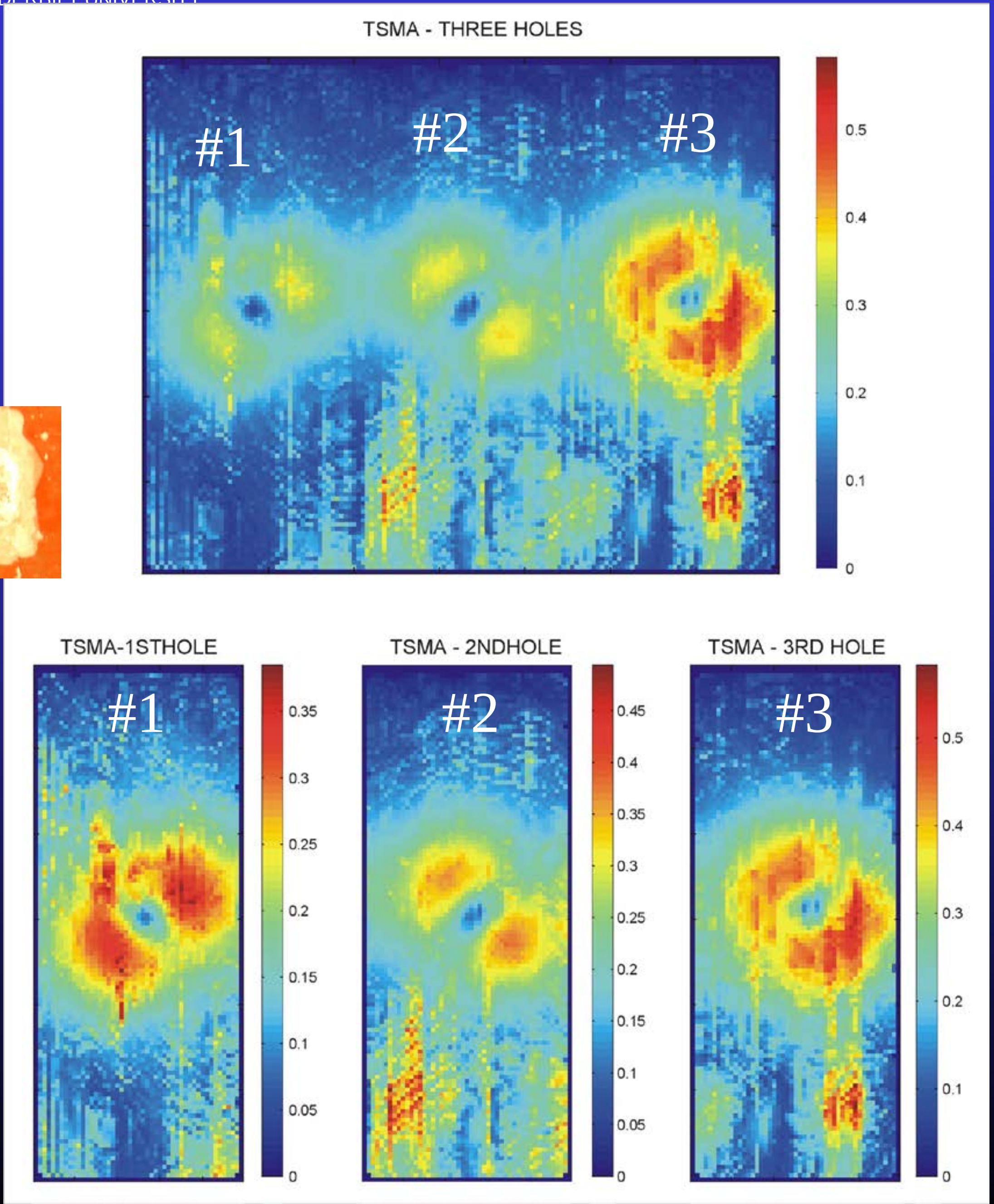


# SIMA for three holes (VEX001)

- 35 minutes/data point
- Maximum signals after 7-8 hours
- Arrows indicate time of adding solution to the holes



# TSMA for three holes (VEX001)


Holes after exposing to solution

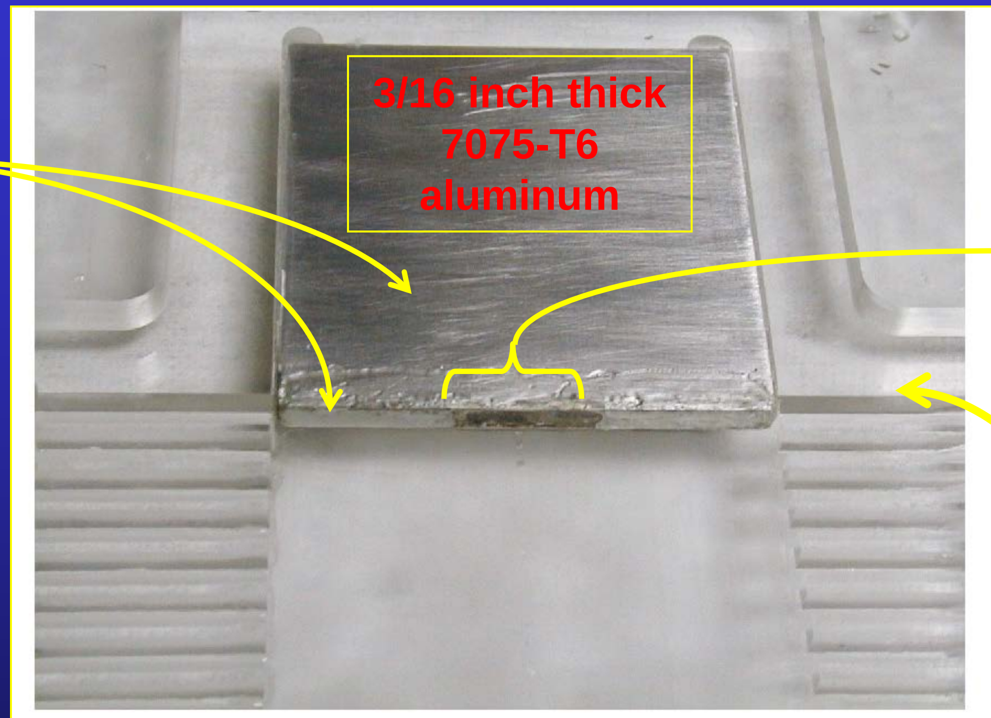
# Protocol E1 Conclusions

- SQUID can see corrosion in well sample, with clear time-dependence over 96 hours
- TSMA images of individual hole is consistent with the corrosion activity
- NDE of exfoliation damage does not show intergranular corrosion.
- The evaporation of solution in holes cause crystal accumulate around and inside the holes which may block the reaction.

# VU Protocol E2 - Edge Test

Epoxy and Mylar coating

Flow channels for solution changes




Exposed Edge

ANCIT solution region

Lucite sample chamber

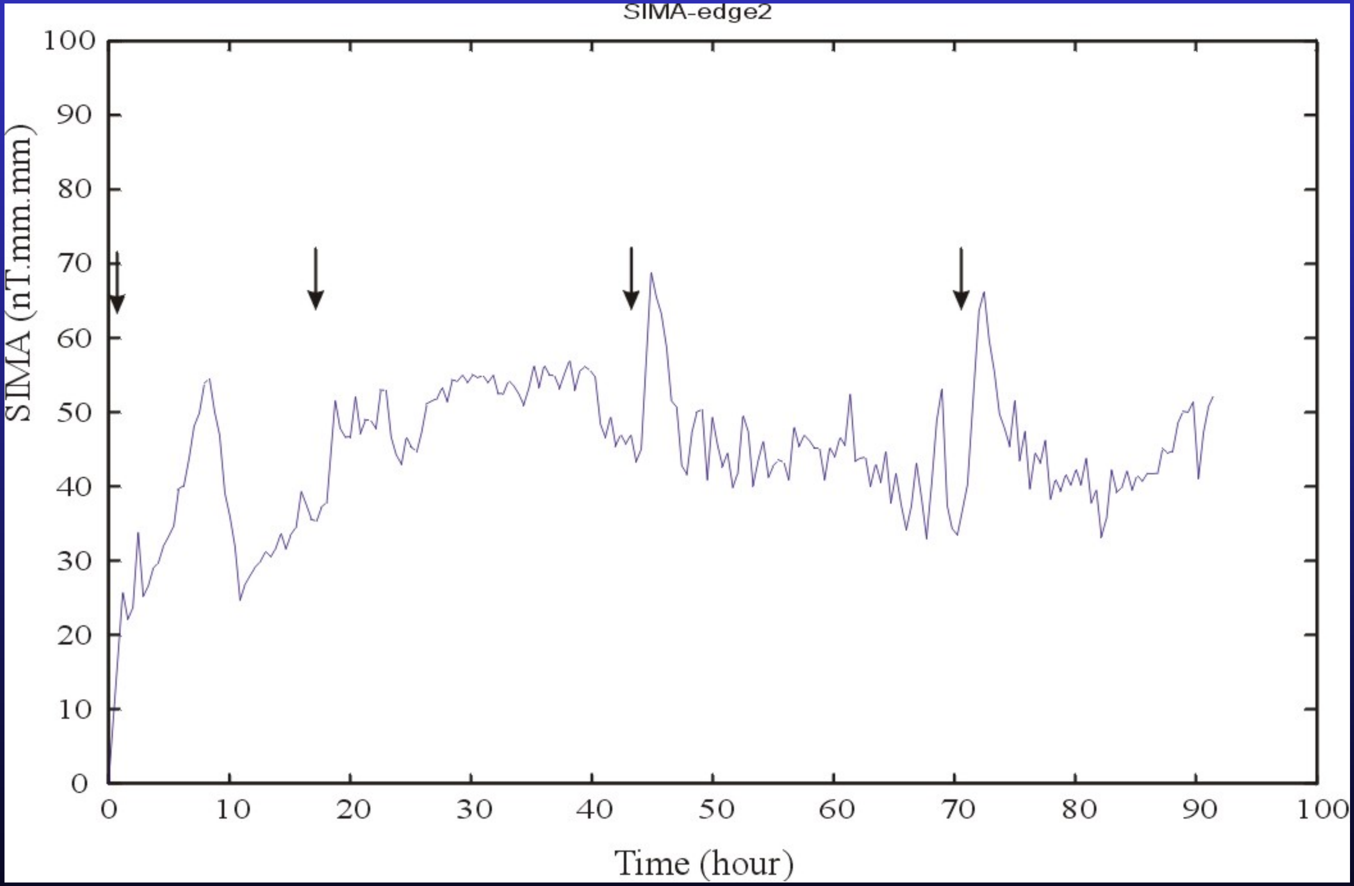
Sample: 4.8 mm thick Al 7075-T6 aluminum, 69.5 x 69.5 mm
Coated everywhere with epoxy and plastic film except 1/3 of one edge
Uncoated edge is exposed to ANCIT solution for 96 hours

# Exfoliation Solution

- ANCIT Solution:
  - 4 M NaCl
  - 0.6 M $KNO_3$
  - 0.022 M $AlCl_3$ (as $AlCl_3 \cdot 6H_2O$)
  - natural pH ~ 3 to 3.3
- ASTM G34-90, in *Annual Book of ASTM Standards - Metal Test Methods and Analytical Procedures*, Vol. 03.02 Wear and Erosion; Metal Corrosion, ASTM, Philadelphia, PA, 119-124 (1990).

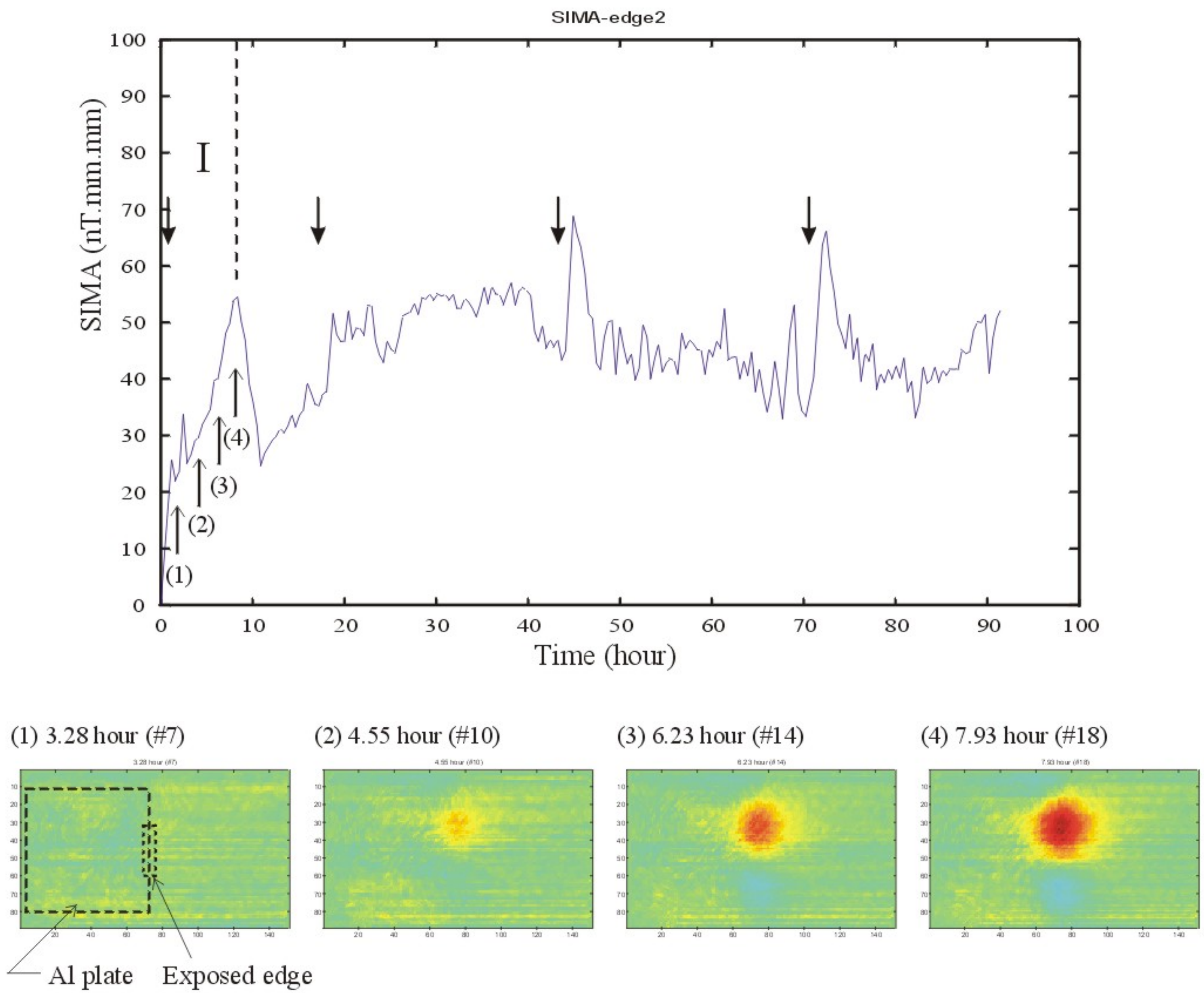
# SIMA for Al 7075

- 96 hours elapsed time for the experiment
- ~30 minutes per image and hence SIMA data point
- Maximum signal after 9-10 hours



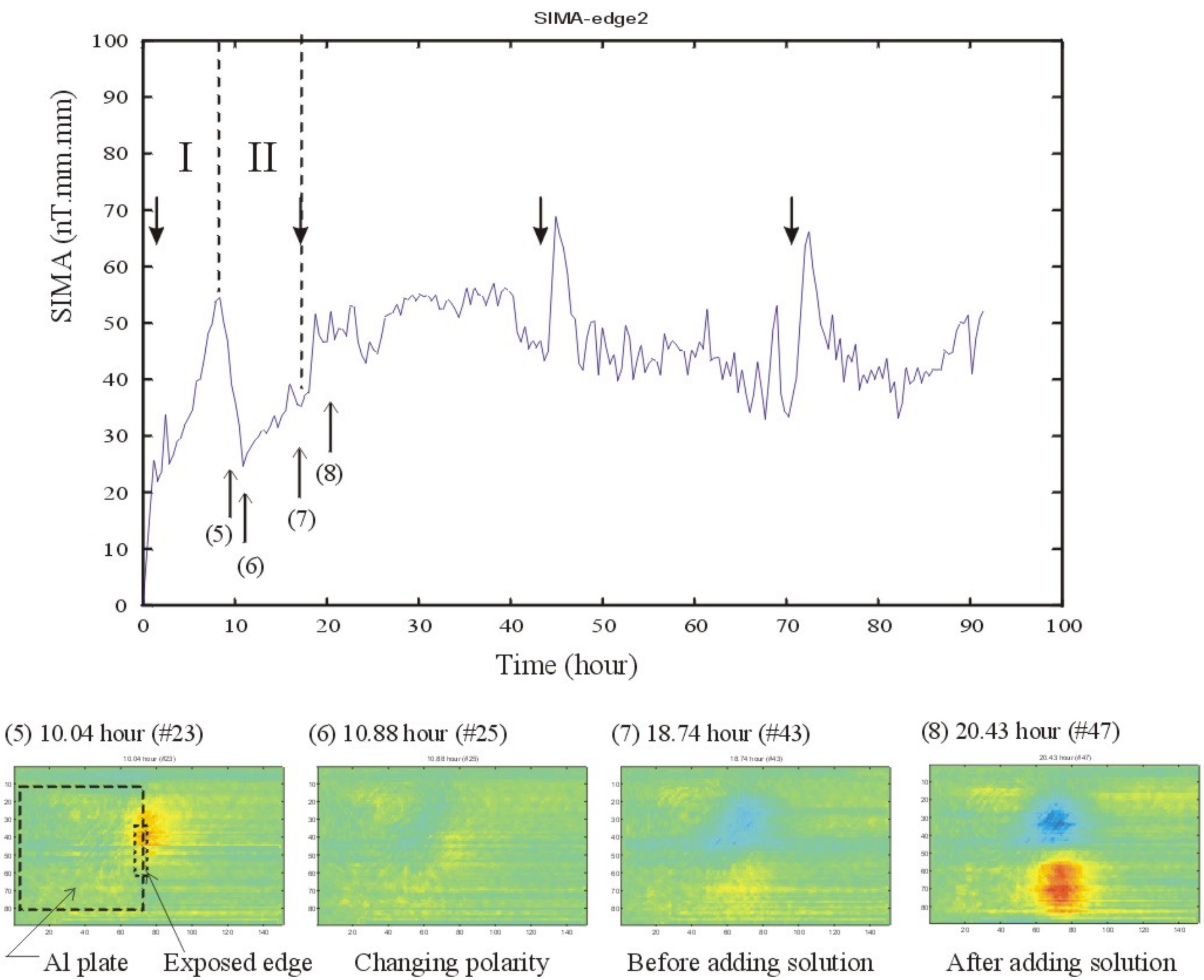

Downward arrows indicate times of adding solution to the chamber

# I. Initiating - eight hours after introducing solution



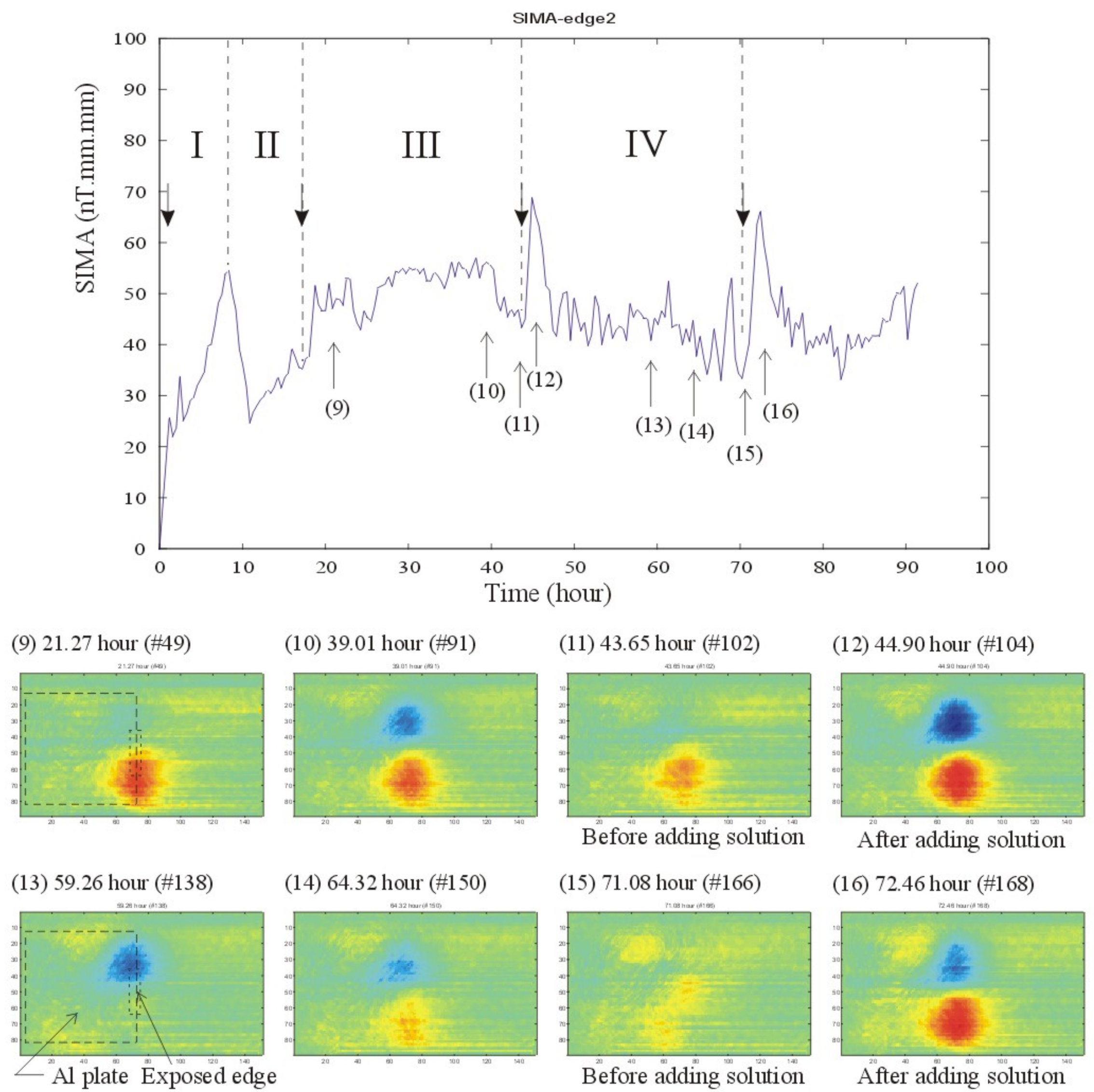

Upward arrows with (numbers) indicate times of each magnetic image

# II. Developing --- changing polarity



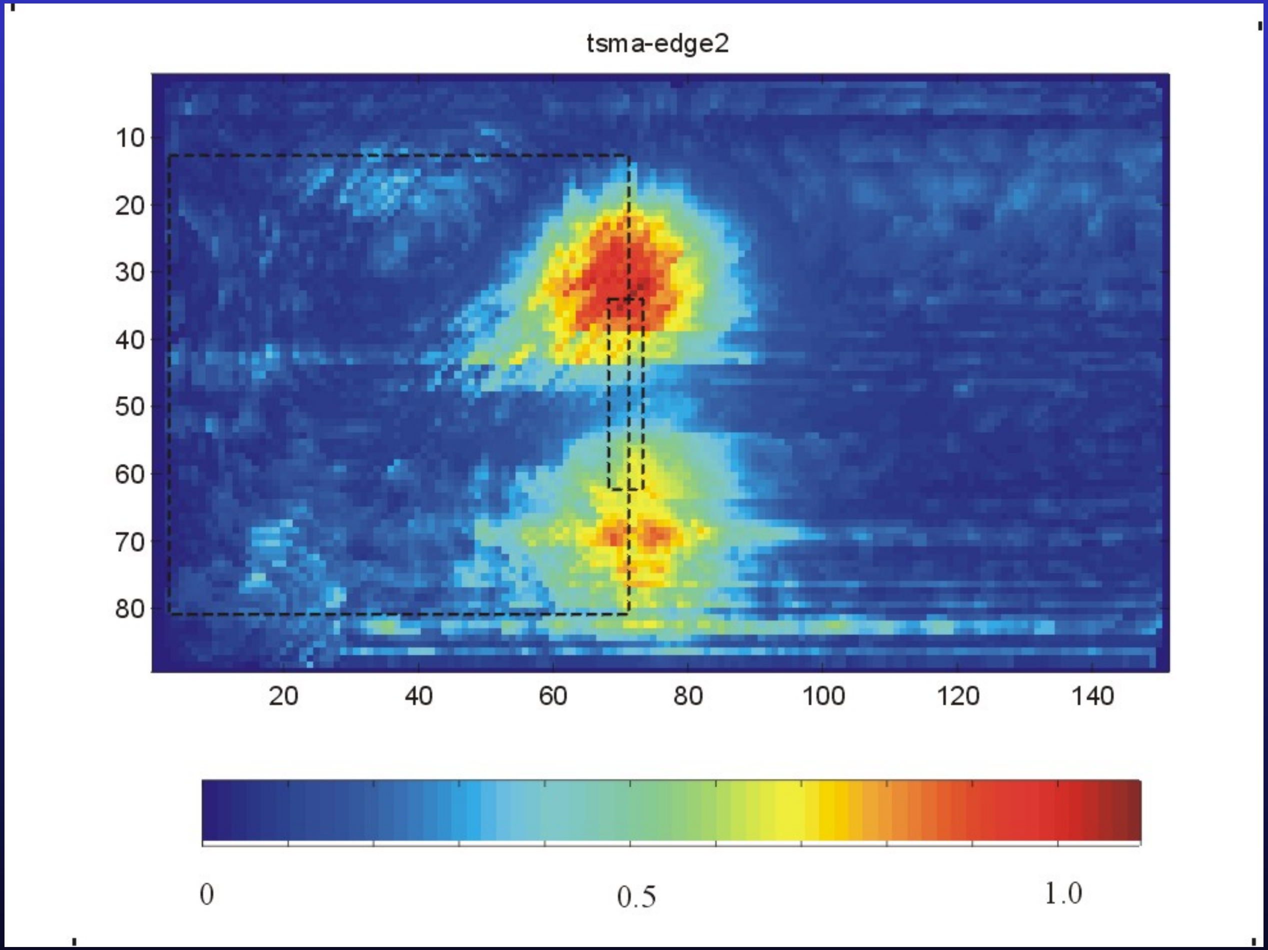

Upward arrows with (numbers) indicate times of each magnetic image

# III & IV. Adding new solution accelerates corrosion

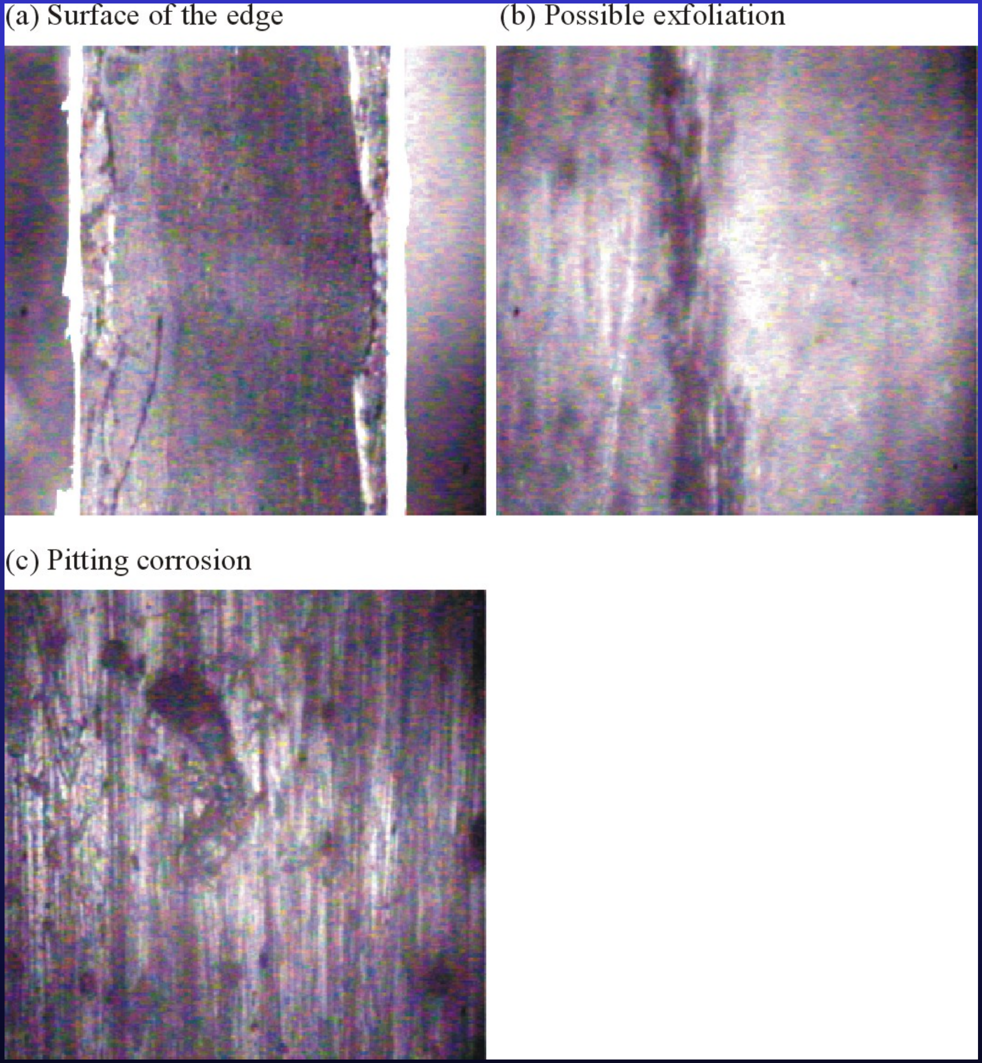



Upward arrows with (numbers) indicate times of each magnetic image

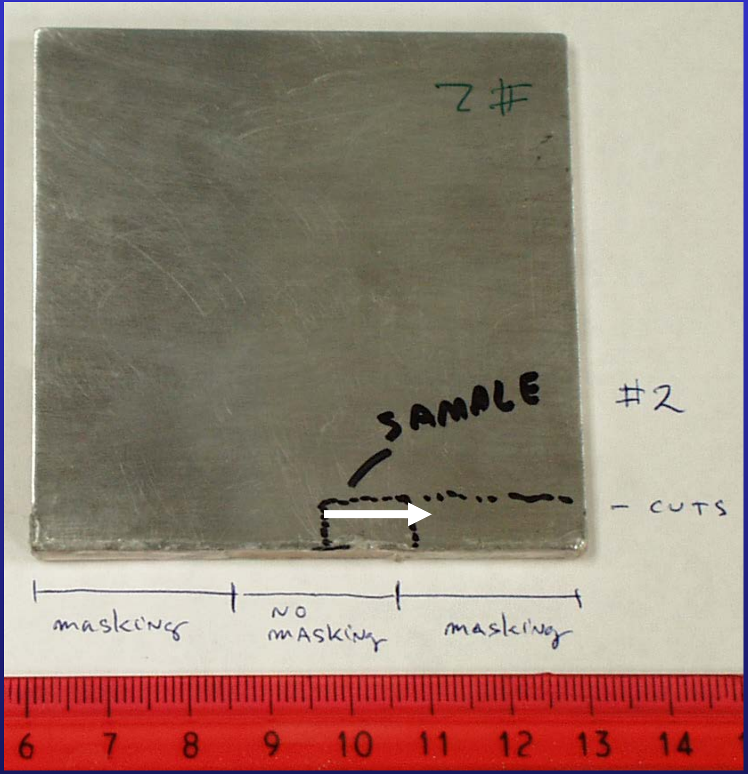
# TSMA for Al 7075



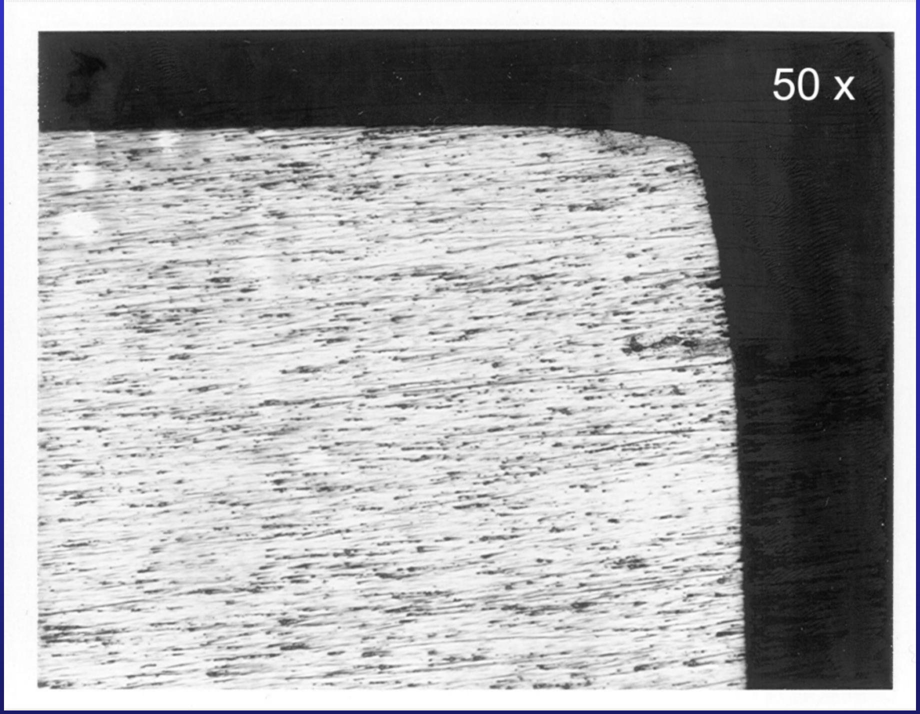
# Microscopic Photo



# Metallographic Examination




The exposed edge (non-masked) was the S-T plane.




Arrow indicates direction of observation for metallography samples.

There is not a significant amount of attack of either of the two specimens. Low magnification visual observations are suggestive of only slight surface attack of the exposed region (*i.e.*, non-epoxyed area). Cross-sectional metallographic examination also did not reveal visible attack, despite successive grinding, polishing and examination. Neither exfoliation nor intergranular corrosion was observed. Samples were wet polished to 1200 grit.

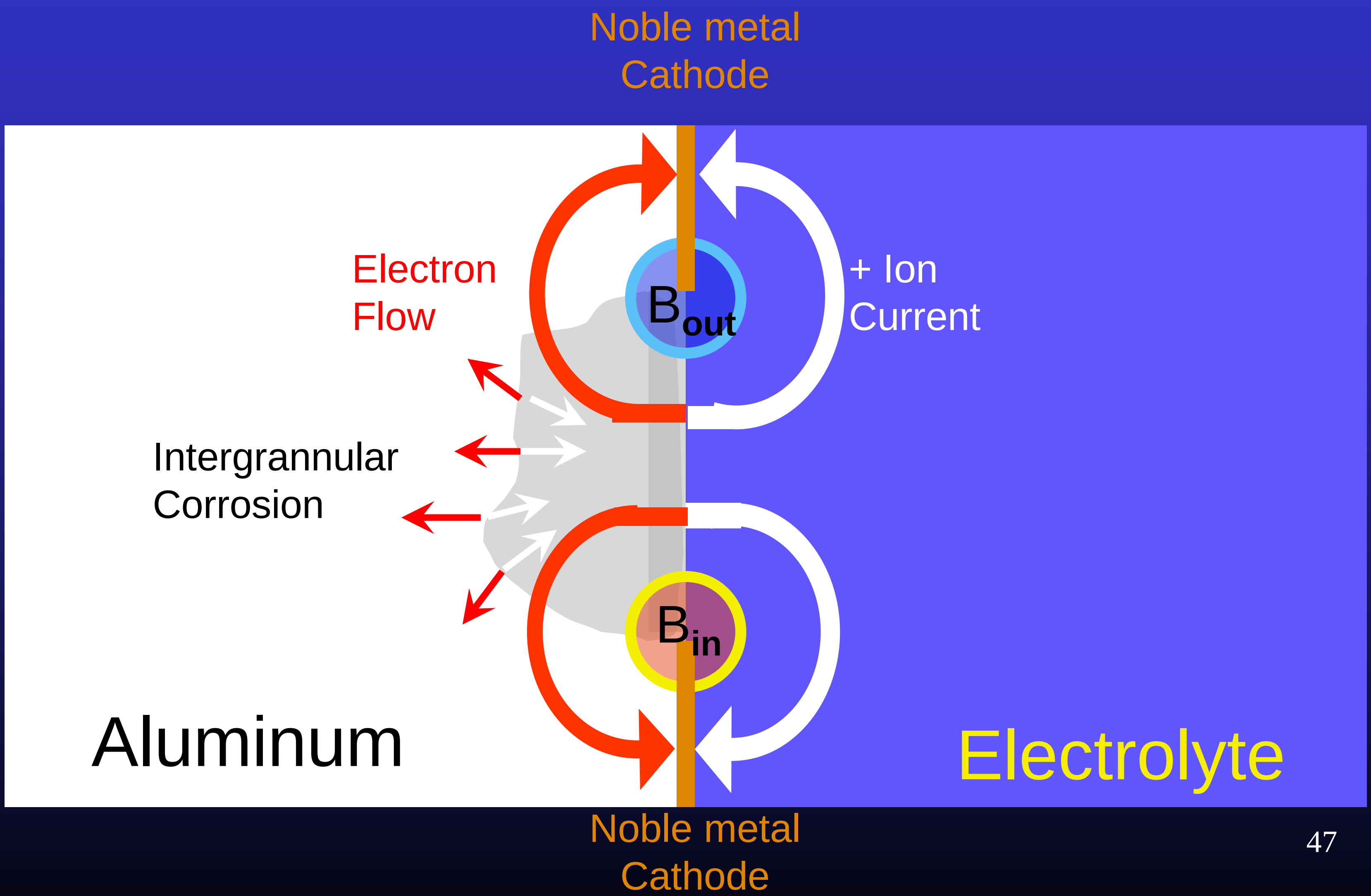
# Protocol E2 Conclusions

- Edge-exposed square sample with square fluid reservoir
  - Simple geometry will allow quantitative analysis
  - Readily accessible corrosion face for damage characterization
  - Epoxy-Mylar coating more effective than red paint
    - Mechanically robust
    - Blocks corrosion
    - Can be removed chemically
- Distinct magnetic signature from corrosion
  - Field distribution correlates with exposed corrosion edge
  - Temporal fluctuations in activity correlate with addition of solution
  - Corrosion activity reaches steady state in approximately 24 hours
  - Ideal for tracking response to environmental change

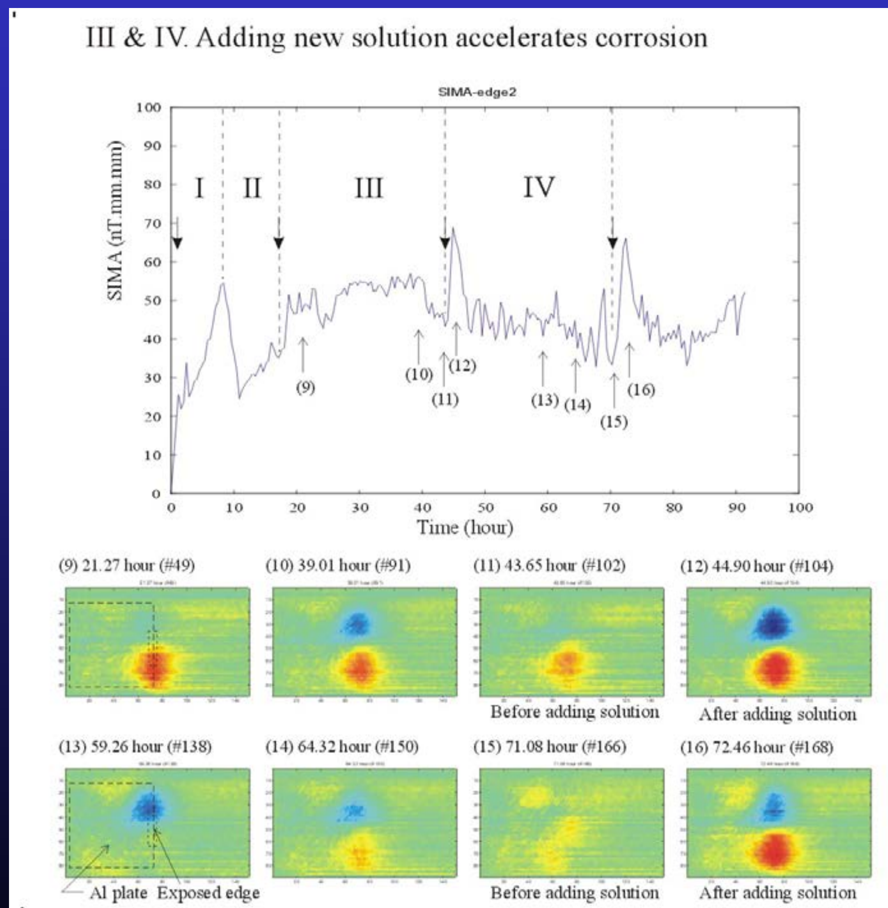
# Future Studies

- Noble metal cathode to drive exfoliation/intergranular corrosion
- Correlate SQUID data with corrosion damage
- Examine factors that affect intergranular corrosion rate
  - Temperature
  - Solution chemistry
  - Corrosion prevention compounds
  - Alloy preparation
  - Sample thickness and rolling direction
- Examine samples with long-term corrosion
  - Signals from deep penetration
  - Dependence on deep corrosion rate on external environment and baking
  - Spatial correlation between TSMA and extended corrosion damage
- Current imaging instead of TSMA
- Higher spatial resolution SQUID images with SQUID microscope

# Proposed SQUID Exfoliation Test Geometry

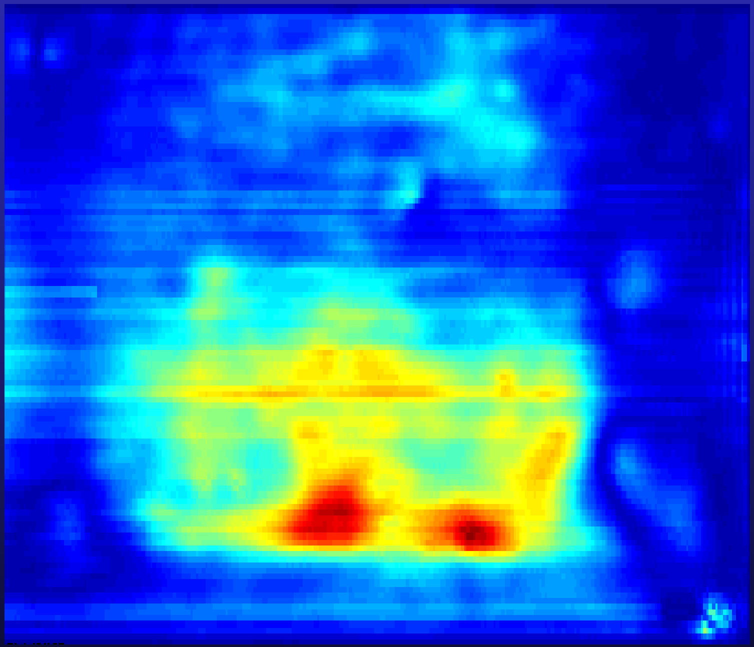


# We will see the time course of exfoliation/intergranular corrosion

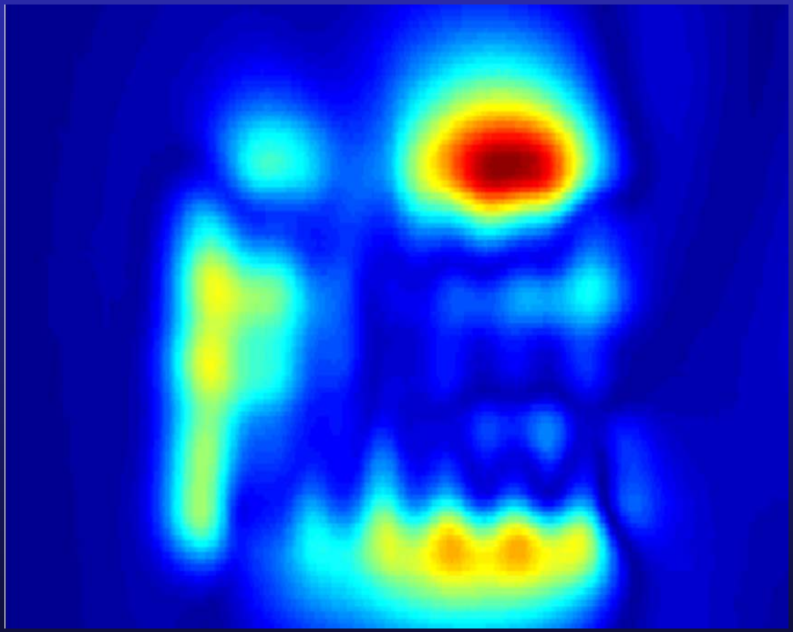



Upward arrows with (numbers) indicate times of each magnetic image

# From the Lap-Joint and Box Stiffener studies, we anticipate spatially resolving exfoliation/intergrannular corrosion activity!



Riveted Specimen



Spot-welded Specimen

# Future Studies

- Noble metal cathode to drive exfoliation/intergranular corrosion
- Correlate SQUID data with corrosion damage
- Examine factors that affect intergranular corrosion rate
  - Solution chemistry
  - Corrosion prevention compounds
  - Alloy preparation
  - Sample thickness and rolling direction
  - Temperature
- Examine samples with long-term corrosion
  - Signals from deep penetration
  - Dependence on deep corrosion rate on external environment and baking
  - Spatial correlation between TSMA and extended corrosion damage
- Current imaging instead of TSMA
- Higher spatial resolution SQUID images with SQUID microscope

# What Will We Learn?

- Transient driving forces for intergranular/exfoliation corrosion
- External modulation of corrosion rate
- Comparisons to address Critical Unknowns
  - Metallurgy
  - Preexisting damage
  - Onset/offset rates
  - ….