# Results of Laboratory Tests on the Corrosion Resistance of Alloy 22 and Titanium-7

Presented to

Nuclear Waste Technical Review Board

September 10, 2001

Las Vegas, Nevada

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Department of Chemistry
The Catholic University of America

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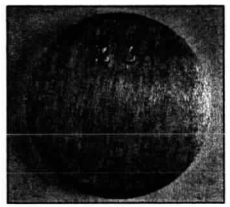
## Part 1: Testing of Alloy 22 under accelerated conditions

- Aqueous testing of Alloy 22 disks
  - Screening for aggressive elements under accelerated conditions
  - Testing with aggressive elements under progressively milder pH and temperature
- Corrosion rate (microns/year) measured by both weight loss and solution analysis

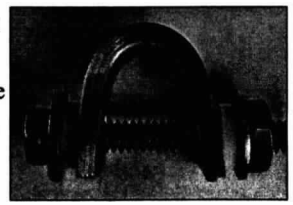


*Untreated disk*



## Testing of Alloy 22 under accelerated conditions

- Aqueous dryout testing of Alloy 22 U-bends
  - Accelerated conditions with lead as aggressive species
  - Varying pH and temperature
- Visual and metallographic inspection for signs of local corrosion



*Untreated U-bend*



## Alloy 22 Disk Tests – Screening for aggressive elements

| *Corr. rate (μM/year)* | Oxidizing Conditions | | Reducing Conditions | |
|---|---|---|---|---|
| Element | By weight | By Solution[1] | By weight | By solution[1] |
| None | 102[2] | 123 | 143 | 162 |
| Pb | 223 | 148 | 152 | 133 |
| Hg | 65 | 70 | 52 | 81 |
| Cd | 358 | 320 | 570 | 1258 |
| Sn | 486 | 431 | 460 | 382 |
| Se | | 301 | | 257 |
| $Na_2S_2O_3$ | 275 | 255 | 336 | 309 |

[1] ***Based on Nickel Data***

Simulated 1000xJ13; 5000 ppm element; pH $1_{RT}$; 160° C; 14 days

## Alloy 22 Disks Extrapolation Tests

Temperature extrapolation

| µm/year | 160° C | 120° C |
|---|---|---|
| Pb[1] | 59 | 19 |
| Hg[1] | 51 | 17 |

*Values based on Ni solution data*
*[1]30 day test*
*[2]14 day test*

pH extrapolation

| µm/year | $pH_{RT}$ 1 | $pH_{RT}$ 2-3 | $pH_{RT}$ 5 | $pH_{RT}$ 14 |
|---|---|---|---|---|
| None[1] | 53 | 18 | 0 | |
| Pb[1] | 43 | 59 | 0 | 0 |
| Hg[1] | 100 | 24 | 21 | 0 |
| Sn[2] | 431 | 63 | 49 | |
| $Na_2S_2O_3$[1] | | | | 25 |

Simulated 1000xJ13; 5000 ppm aggressive element.

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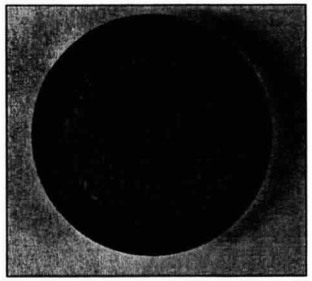
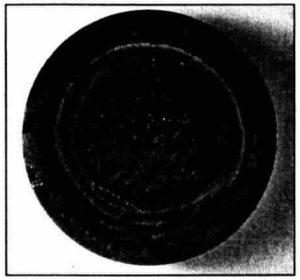
## Alloy 22 Disk Tests Thiosulfate Environment



*Before cleaning*



*After cleaning – 0.7% weight loss*

5000 ppm $Na_2S_2O_3$ (S basis), pH 14, 160°C, 14 days, oxidizing conditions.

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## Alloy 22 Disk Tests Thiosulfate environment

**pH extrapolation**

| $pH_{RT}$ | µm/year |
|---|---|
| 14 | 49* |
| 9.5 | 7 |
| 6.5 | 1 |

*Simulated 1000x J13*
*30 day test*
*Temperature 160° C*
*5000 ppm S (as $Na_2S_2O_3$)*

**Temperature Extrapolation**

| Temp. | µm/year |
|---|---|
| 160 | 49 |
| 120 | 7 |
| 105 | 3 |

*Simulated 1000x J13*
*30 day test*
*$pH_{RT}$ 14*
*5000 ppm S (as $Na_2S_2O_3$)*

**Concentration Extrapolation**

| Concentration | µm/year |
|---|---|
| 5000 ppm S | 49 |
| 1000 ppm S | 12 |
| 500 ppm S | 12 |

*Simulated 1000x J13*
*30 day test*
*$pH_{RT}$ 14*
*Temperature 160° C*

* All µm/year based on weight loss

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## Dryout Tests on Alloy 22 U-Bends

| pH | Temperature | Duration | Local Corrosion | Weight Loss (%) |
|---|---|---|---|---|
| 1 | 250 | Dryout < 6hr | Pits on edges, lines at apex | 0.1 |
| 1 | 230 | 24 hours; partial dryout | Crevice pitting | 0.25 |
| 3 | 250 | Dryout: <6 hr | Crevice pitting | 0.004 |

Simulated 1000xJ13 water with added 5000 ppm Pb.
Heated at 230° or 250° C in a partially sealed vessel until dryout.

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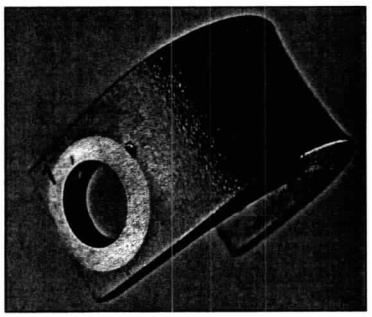
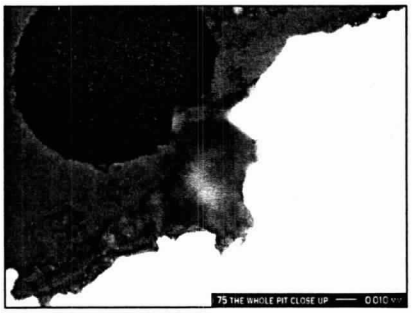
# Dryout Tests on Alloy 22 U-Bends

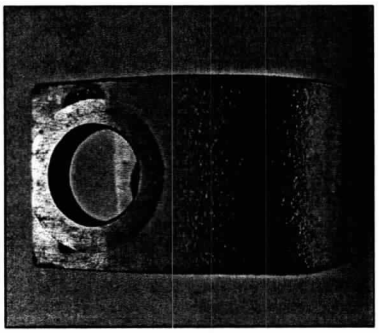


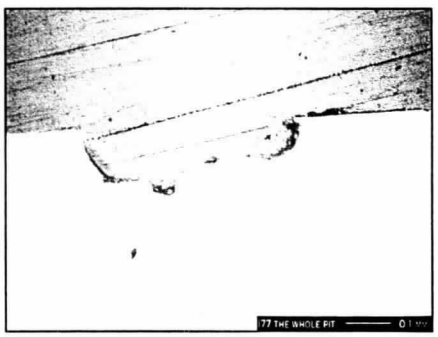



*$pH_{RT}$ 1; 250° C; Dryout < 6hr*



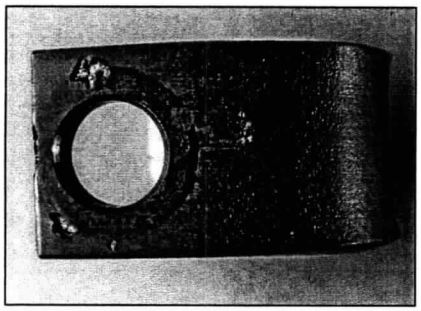
# Dryout Tests on Alloy 22 U-Bends

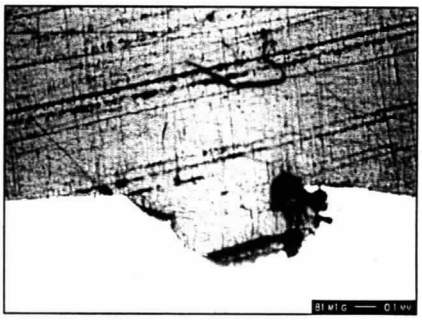





*$pH_{RT}$ 1; 230° C; Partial Dryout 24 hours*

# Dryout Tests on Alloy 22 U-Bends





*$pH_{RT}$ 3; 250° C; Dryout < 6 hours*

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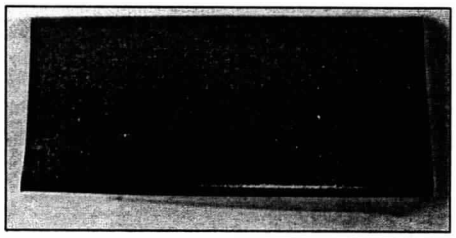
# Part 2: The Effect of Gamma Radiation on Ti-7 Preliminary Results

- Simulated 1000xJ13 excluding carbonate
- Add 1000 ppm aggressive species
- pH 7
- ~40° C
- 180 krad/hr (89 Mrad total) $\gamma$ radiation



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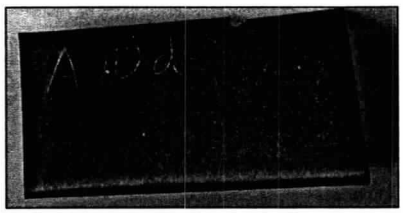
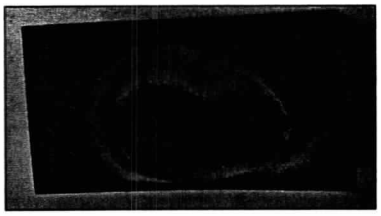
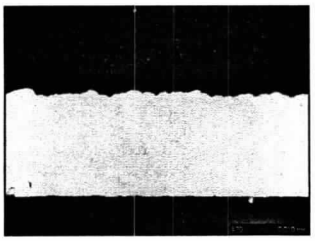
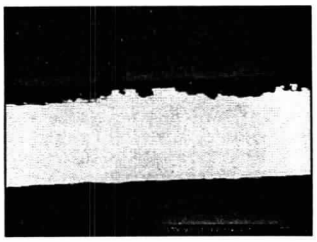
## Gamma radiation and Ti-7: $Zn^{2+}$









No gamma radiation

89 Mrad gamma radiation

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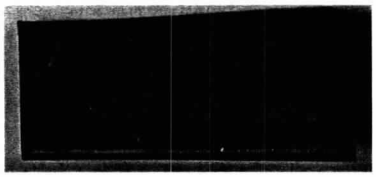
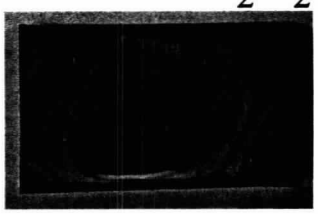
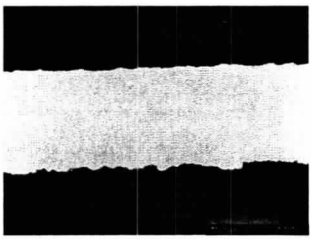
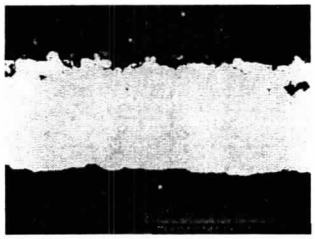
## Gamma radiation and Ti-7: $H_2O_2$









No gamma radiation

89 Mrad gamma radiation

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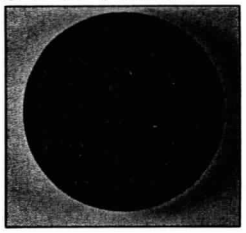
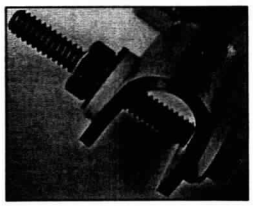
# Part 3: Tests on Ti-7 Elevated Fluoride Levels

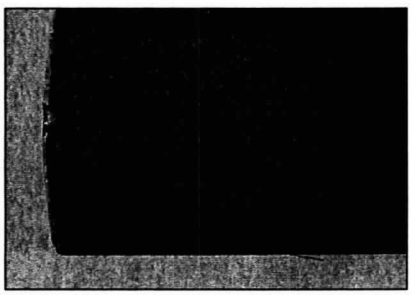
- Tests on Disks
  - 10000xJ13 at mild temperature and pH
  - 1xEJ13 with added F- and Cl- at mild temperature and pH
- Tests on U-bends
  - 1xEJ-13 with added F- and Cl- at mild temperature and pH

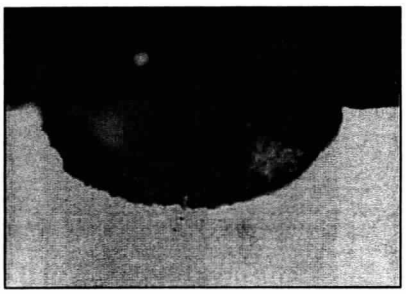






# Tests on Ti-7 Disks 10000xJ13 Environment

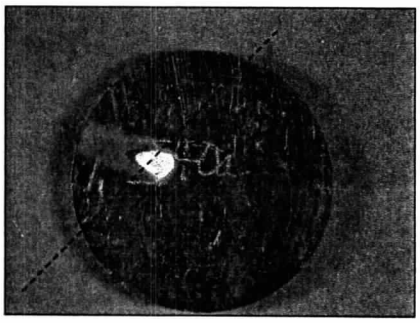




10000xJ-13; $pH_{RT}$ 4; 105$^{o}$C; 30 days

# Tests on Ti-7 Disks
## Added $F^-$ and $Cl^-$

- Sample I62b
  - 1xEJ-13 with
    - 35500 ppm $Cl^-$ (1 M)
    - and 1900 ppm $F^-$ (0.1 M)
  - $pH_{RT}$ 6.8
  - $103^{o}$ C
  - 30 days



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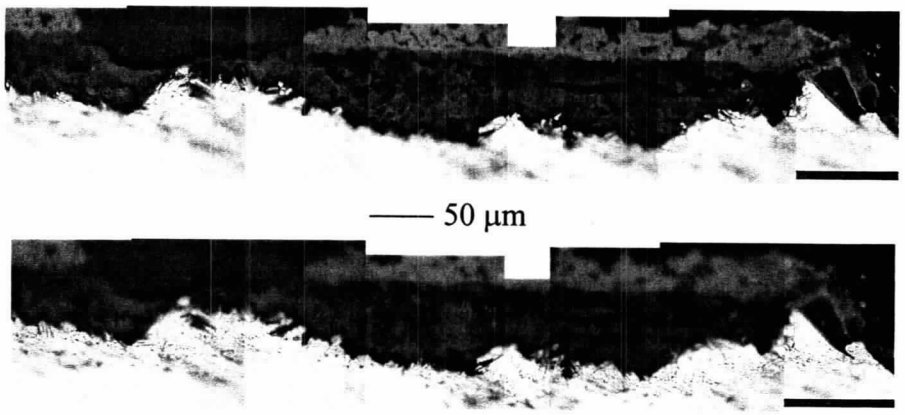
# Tests on Ti-7 Disks
## Added $Cl^-$ and $F^-$




*Metallography of I62b*

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# Tests on Ti-7 Disks
## Added $Cl^-$ and $F^-$

*Metallography of I62b*

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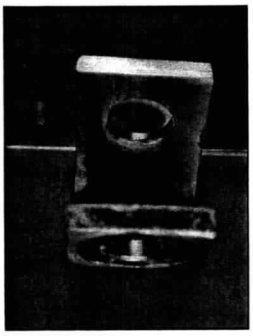
# Tests on Ti-7 U-bends
## Added $Cl^-$ and $F^-$



Sample I102: 1xEJ-13 with 35500 ppm $Cl^-$ and 1900 ppm $F^-$; $pH_{RT}$ 6.5; 105$^{O}$C; 35 days

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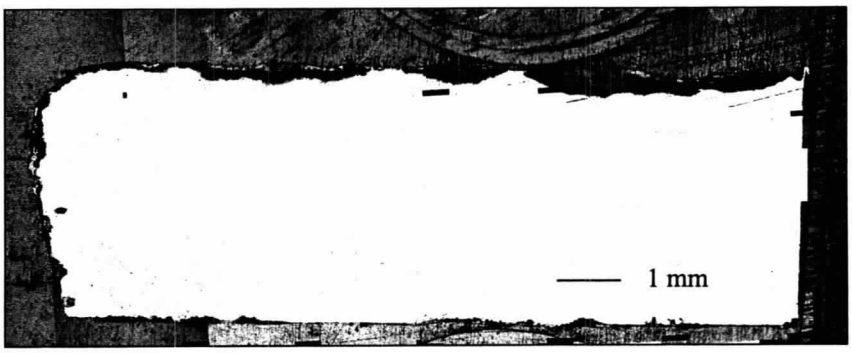
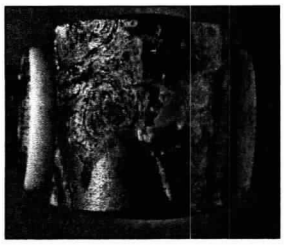
# Tests on Ti-7 U-bends
## Added $Cl^-$ and $F^-$



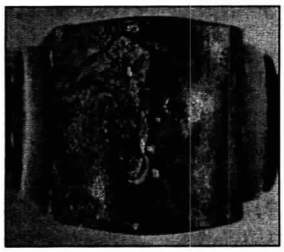

*Metallography of I102 U-Bend*



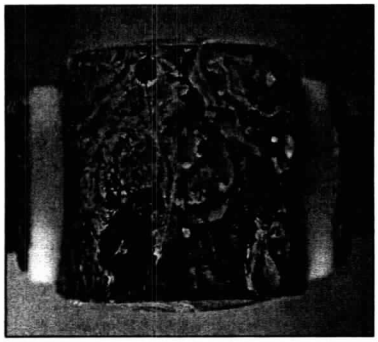
# Tests on Ti-7 U-bends
## Added $Cl^-$ and $F^-$



*67 days*



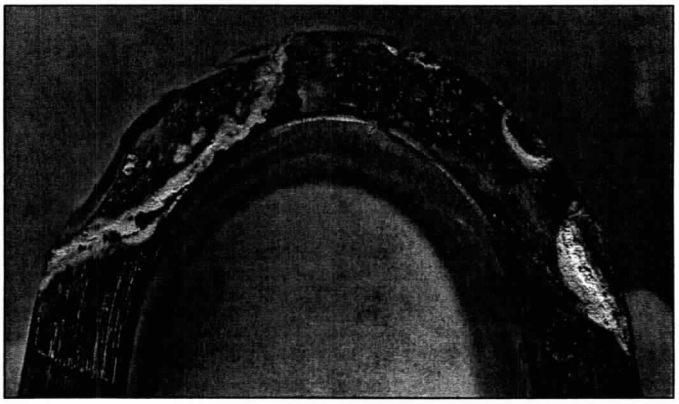
*107 days*



*164 days*

*Sample I103: Conditions identical to I102*

# Tests on Ti-7 U-bends
## Added $Cl^-$ and $F^-$



Close up of I103; 164 days

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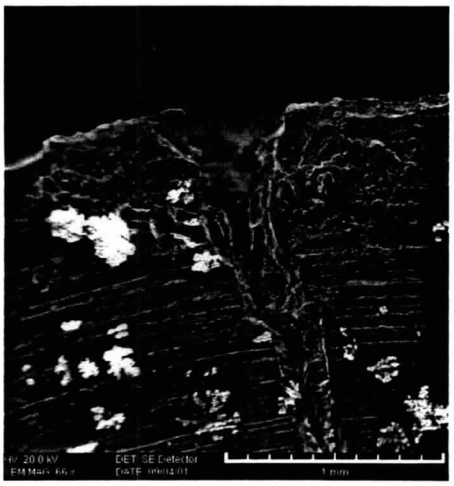
# Tests on Ti-7 U-bends
## Added $Cl^-$ and $F^-$




*Sample I103*

*SEM image*
*mouth of crack*

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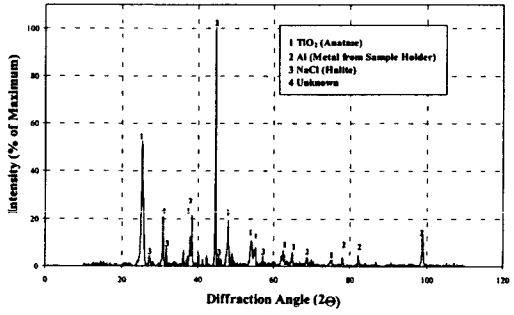
## Tests on Ti-7 U-bends
### Added $Cl^-$ and $F^-$




*X-ray diffraction of precipitate in I103 test solution.*

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## Conclusions – Alloy 22

- At 160° C, Alloy 22 exhibits general corrosion in the presence of high levels of Pb, Sn, Cd, Se, and $Na_2S_2O_3$ at low pH.
- As the temperature is lowered and the pH raised, general corrosion of Alloy 22 in the presence of Pb, Hg, and Sn is reduced but still observed within 2-4 weeks.
- At 160° C, Alloy 22 is susceptible to flaking in solutions containing thiosulfate or sulfide at high pH. Flaking still occurs at lower concentrations of thiosulfate.
- Alloy 22 is susceptible to crevice corrosion under conditions of high temperature and high concentration of Pb. Under dryout conditions, pitting is observed within 24 hours.

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## Conclusions: Ti-7

- Ti-7 is extremely susceptible to environments which contain fluoride. Disks and U-bends show marked pitting under very mild conditions.
- Ti-7 is susceptible to stress corrosion cracking in environments containing both fluoride and chloride under mild conditions.
- In the presence of gamma radiation, Ti-7 is susceptible to local corrosion in solutions containing zinc or hydrogen peroxide.

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Note: This is not a QA controlled report.

# Backup Slides
# for
# Dr. April Pulvirenti
# Catholic University of America

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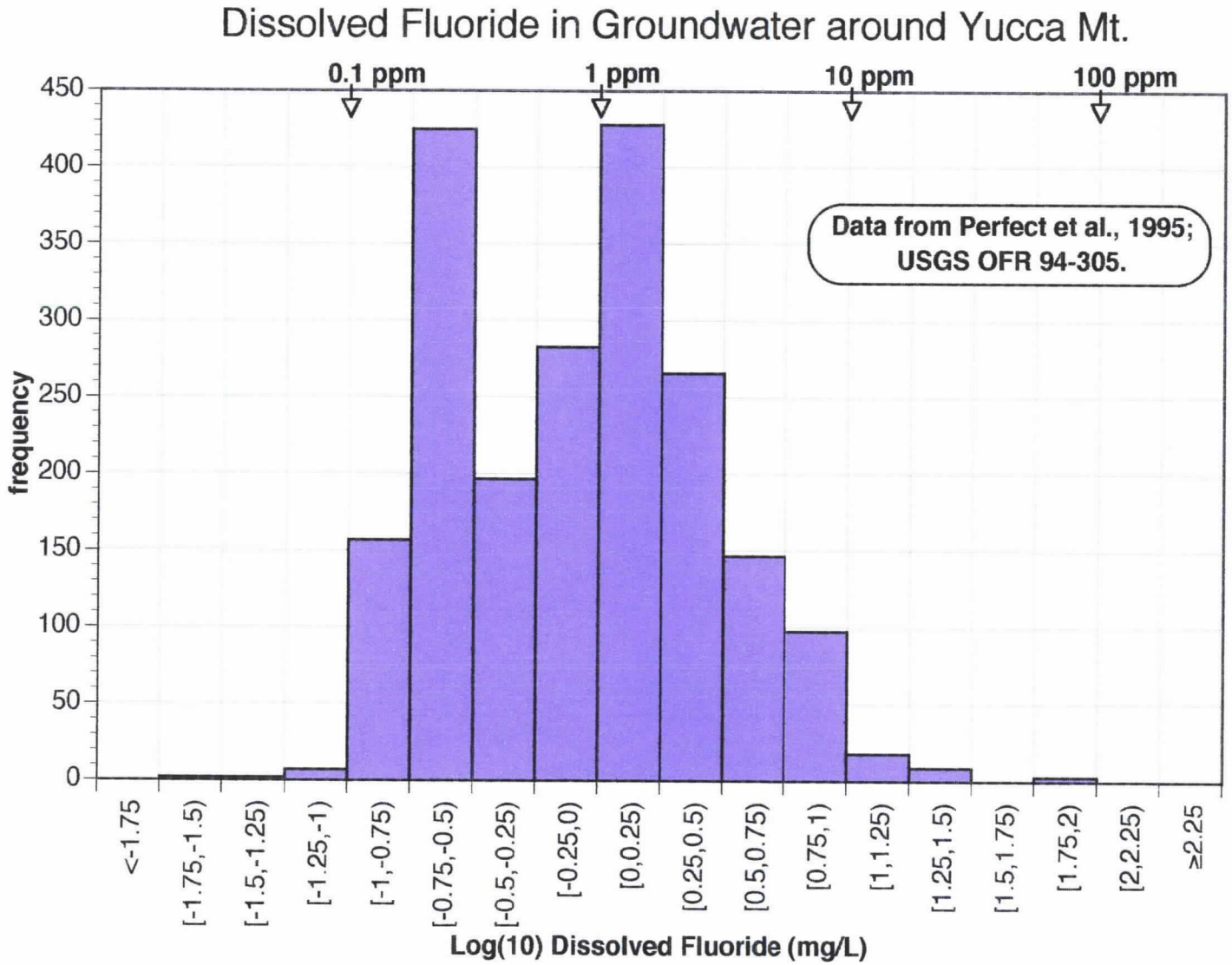
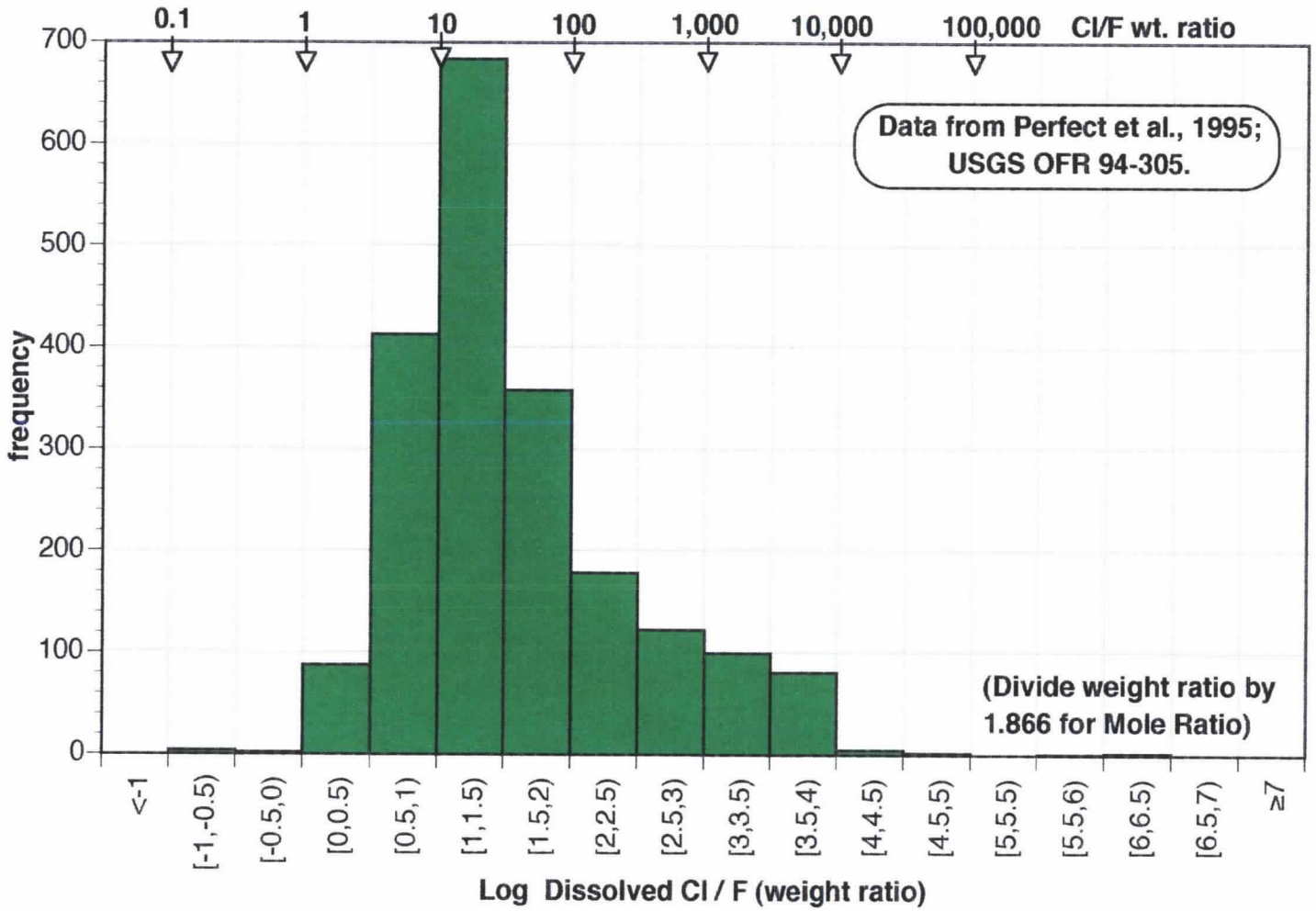
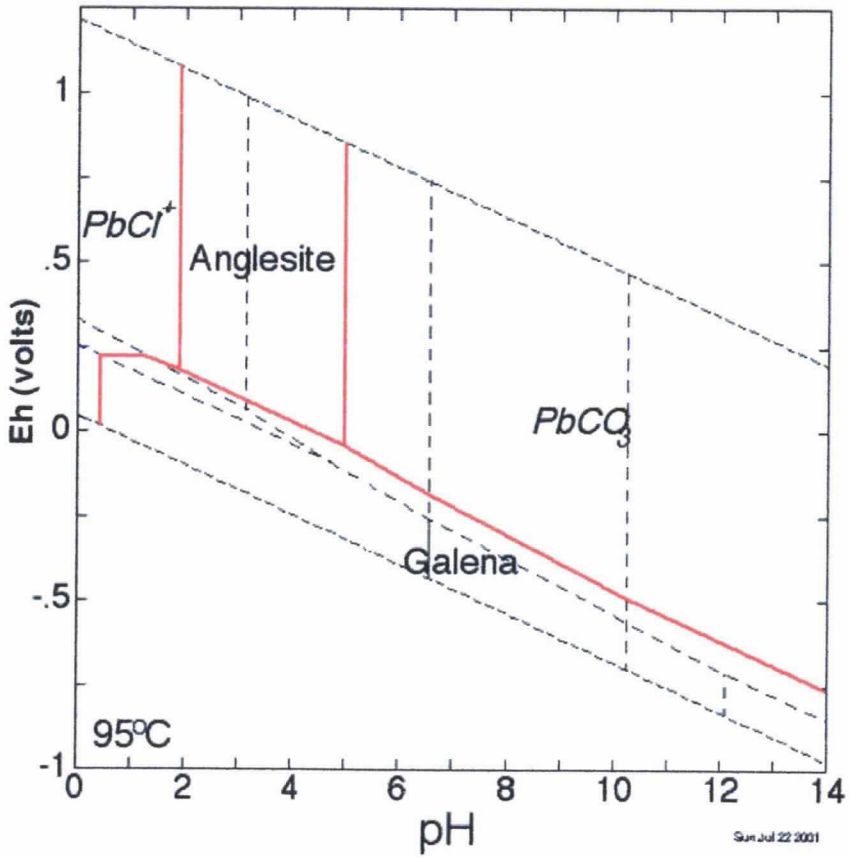
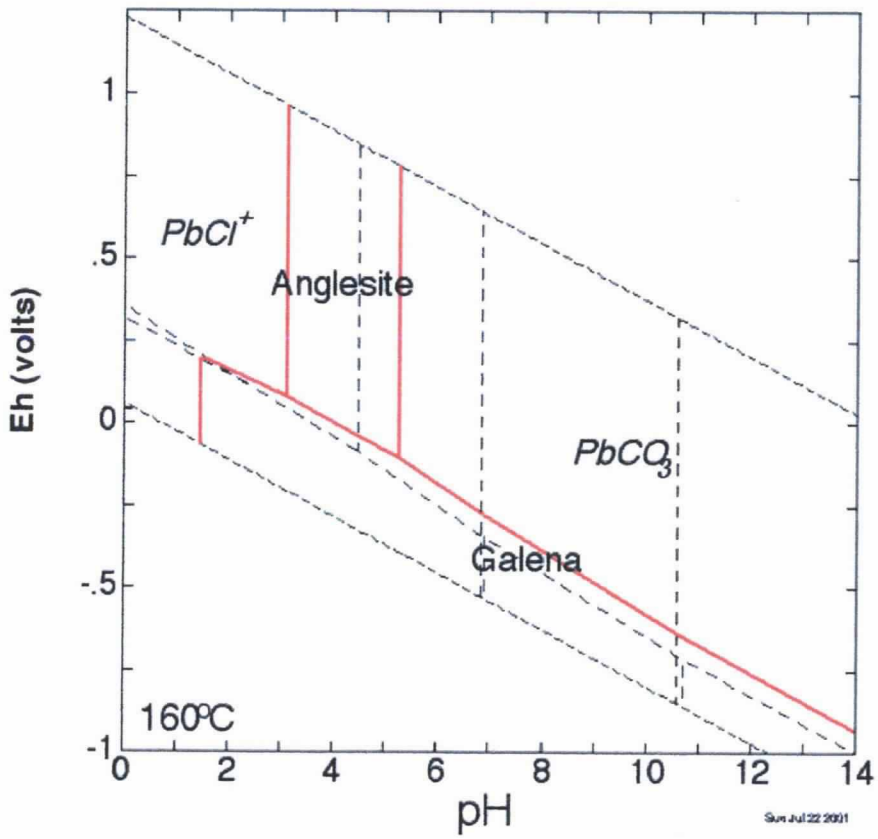

Dissolved Fluoride in Groundwater around Yucca Mt.
0.1 ppm
1 ppm
10 ppm
100 ppm
Data from Perfect et al., 1995; USGS OFR 94-305.
frequency
450
400
350
300
250
200
150
100
50
0
<-1.75
[-1.75,-1.5)
[-1.5,-1.25)
[-1.25,-1)
[-1,-0.75)
[-0.75,-0.5)
[-0.5,-0.25)
[-0.25,0)
[0,0.25)
[0.25,0.5)
[0.5,0.75)
[0.75,1)
[1,1.25)
[1.25,1.5)
[1.5,1.75)
[1.75,2)
[2,2.25)
≥2.25
Log(10) Dissolved Fluoride (mg/L)

# Dissolved Cl/F Weight Ratio in Groundwater around Yucca Mt.



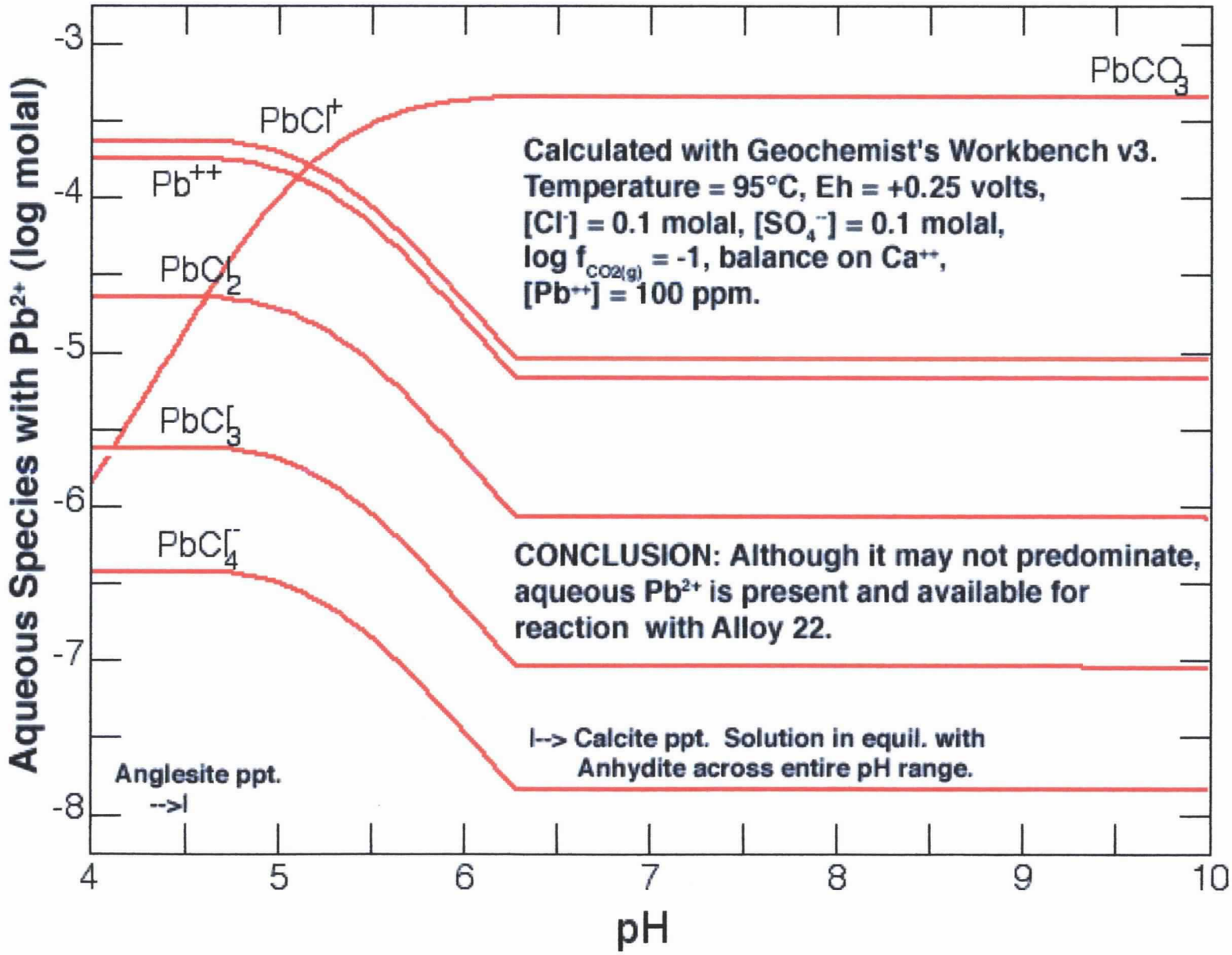
## System Pb-O-H-Cl-C-S
## [Pb++] = 10 ppm; [Cl] = 1,000 ppm
## [HCO3-] = 1,000 ppm; [SO4--] = 1,000 ppm



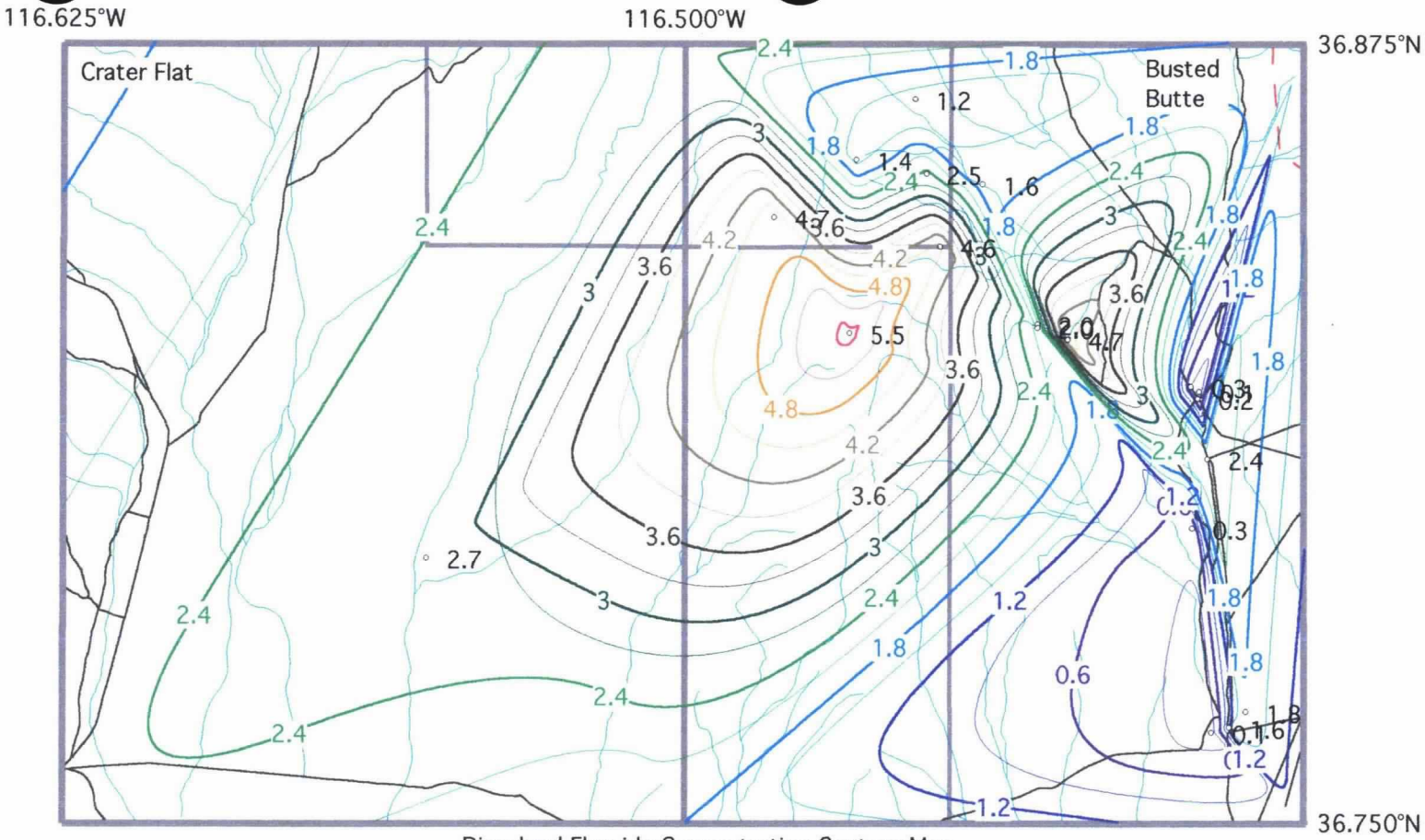




**NOTE: Fields of predominance for solid phases have mineral names; chemical formulae are for the predominant aqueous specie. Solid red lines separate fields of predominance. Long dashed lines are aqueous subspecies (C and S) boundaries. Short dashed lines are boundaries for the stability of water. Diagrams were calculated with Geochemist's Workbench v3.0.**

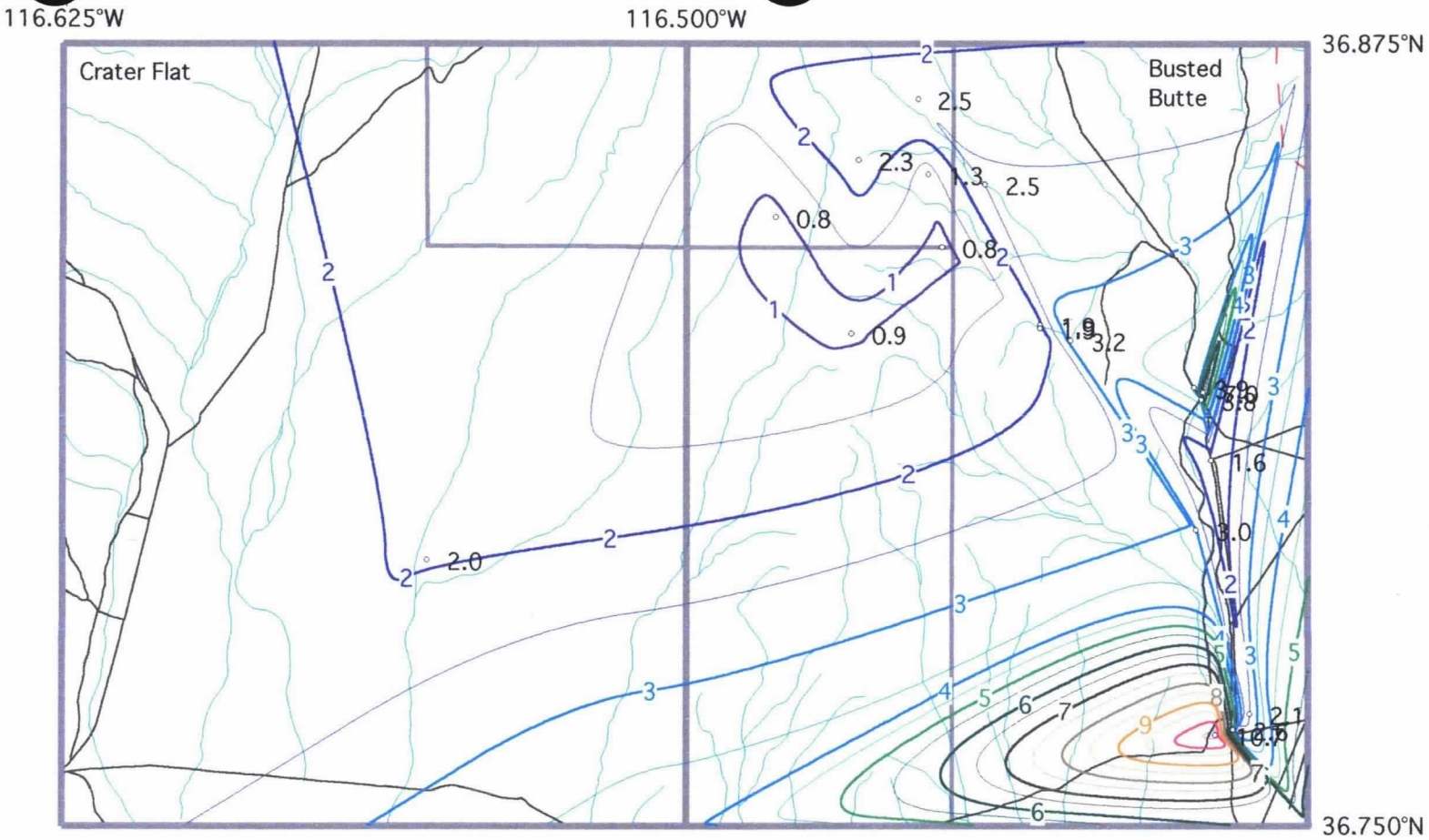
*Shettel/GMII*




Don Shevel Fri Sep 07 2001




Dissolved Fluoride Concentration Contour Map




Dissolved Chloride/Fluoride Mole Ratio Contour Map
Data from Perfect et al. (1995, USGS OFR 94-305)