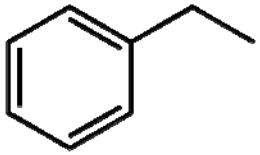
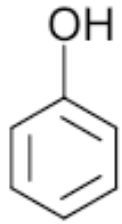
Dissolved Constituents in Water from Hydrous Retort Experiments



Carl D. Palmer and Earl Mattson
Idaho National Laboratory

Robert B. Perkins
Portand State University



28th Oil Shale Symposium
October 13-17, 2008
Colorado School of Mines
Golden, Colorado

Objective:

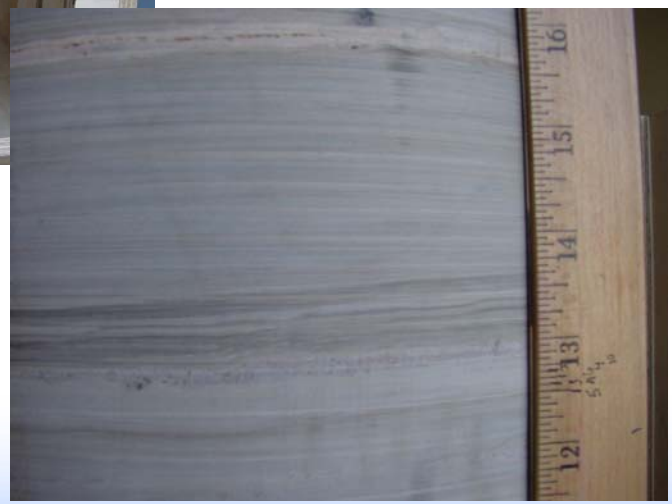
To determine the type and concentration of solutes in water in contact with heated oil shale and to gain insight into the chemical and mineralogical processes that control those concentrations.

Oil Shale Samples

Green River Formation,
Piceance Basin, CO
Rio Blanco County
Duck Creek Mine

Sample courtesy of Shell

- **TOC = 8.8%**
- **Oil Potential = 22 gal/ton**
- **Hydrogen Index = 777 mg HC/g TOC**
- **Oxygen Index = 10 mg CO_2/g TOC**



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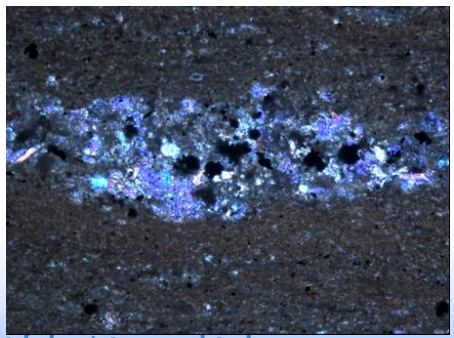
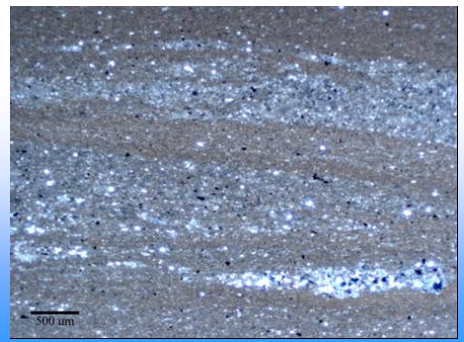
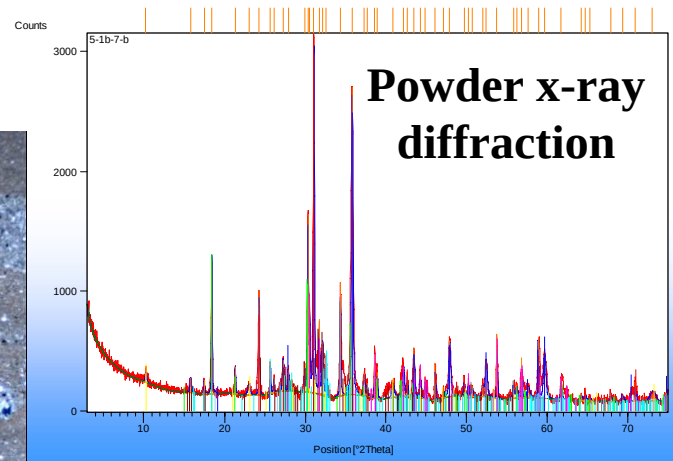
Mineralogical Composition

Mineral	Description	(wt%)
Ankerite	$Ca(Fe,Mg)(CO_3)_2$	26.5 ±1.4
Quartz	SiO_2	11.1 ±1.2
Analcime	$NaAlSi_2O_6 \cdot H_2O$ (zeolite)	14.9 ±0.9
Albite	$NaAlSi_3O_8$ (authigenic)	4.8 ±0.9
K-Feldspar	$KAlSi_3O_8$ (authigenic)	17.6 ±1.4
Calcite	$CaCO_3$	6.5 ±0.7
Aragonite	$CaCO_3$	12.6 ±0.8
Illite/musc.	$K_{0.5}(Al,Fe,Mg)_3(Si,Al)_4O_{10}(OH)_2$	6.1 ±1.6
Pyrite	FeS_2	tr







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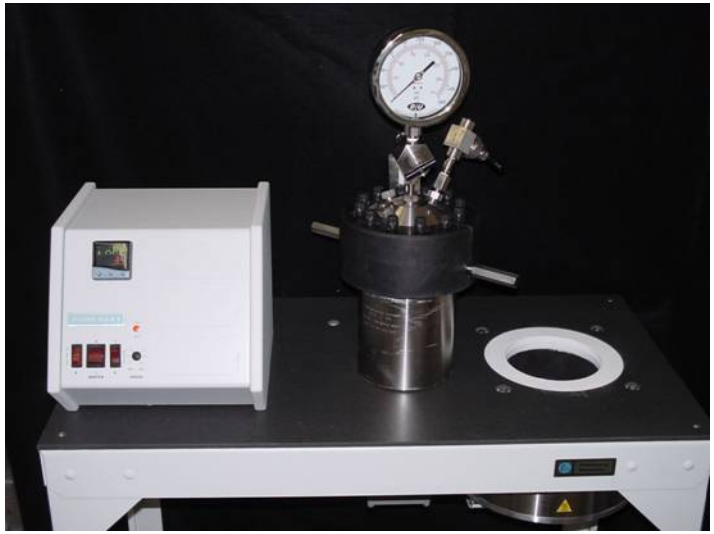
Hydrous Retorting



150 g Oil Shale
300 g Water

Air purged
from system

Oil retorted for
72 hours

Pressure released,
water/oil sampled

Sample gas

Retort cooled to
ambient T (24 hrs)

Gas Generation

CO_2 1.1 – 53.6%

CO ND – 38.6%

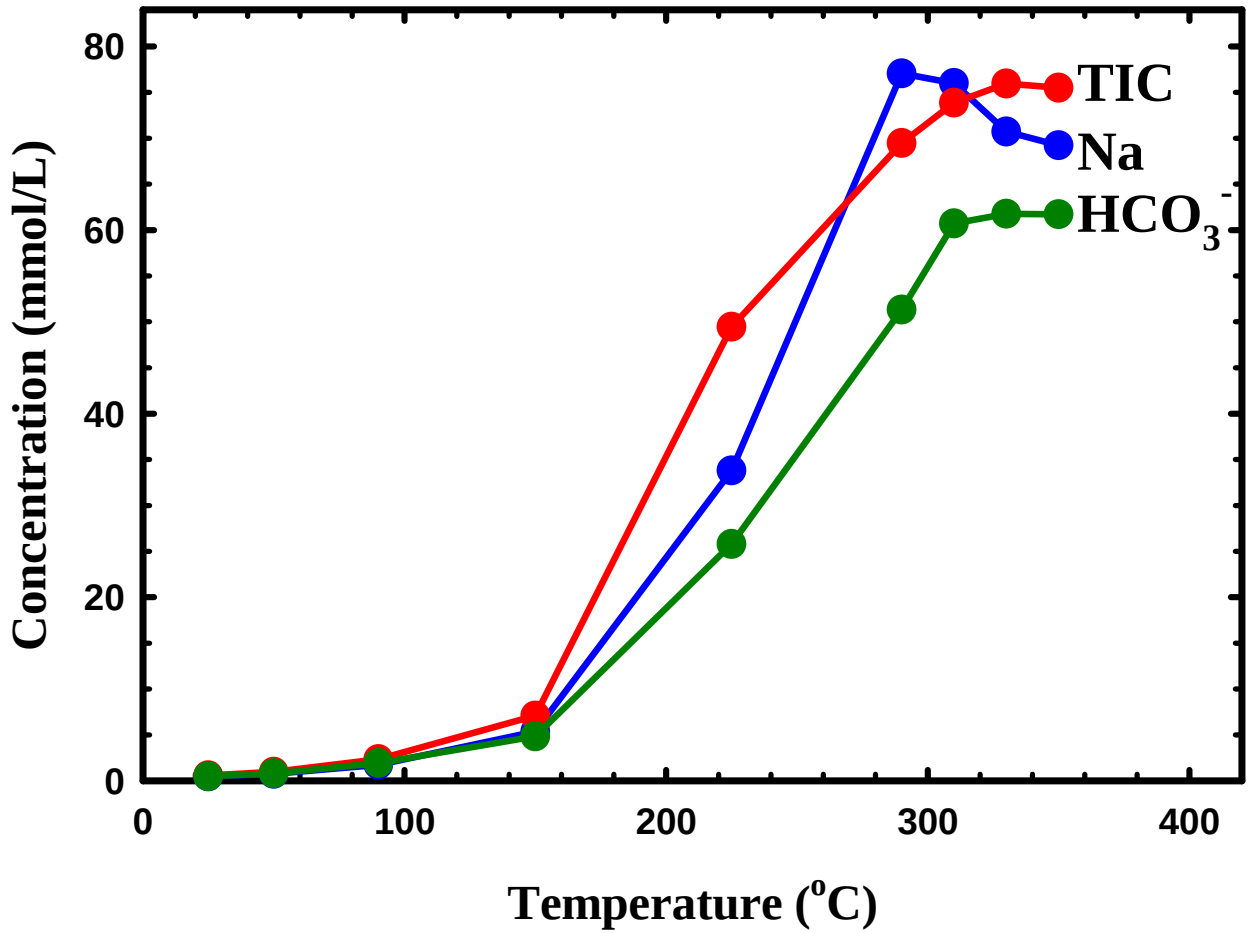
H_2 0.4 – 7.5%

CH_4 0.2 – 7.4%

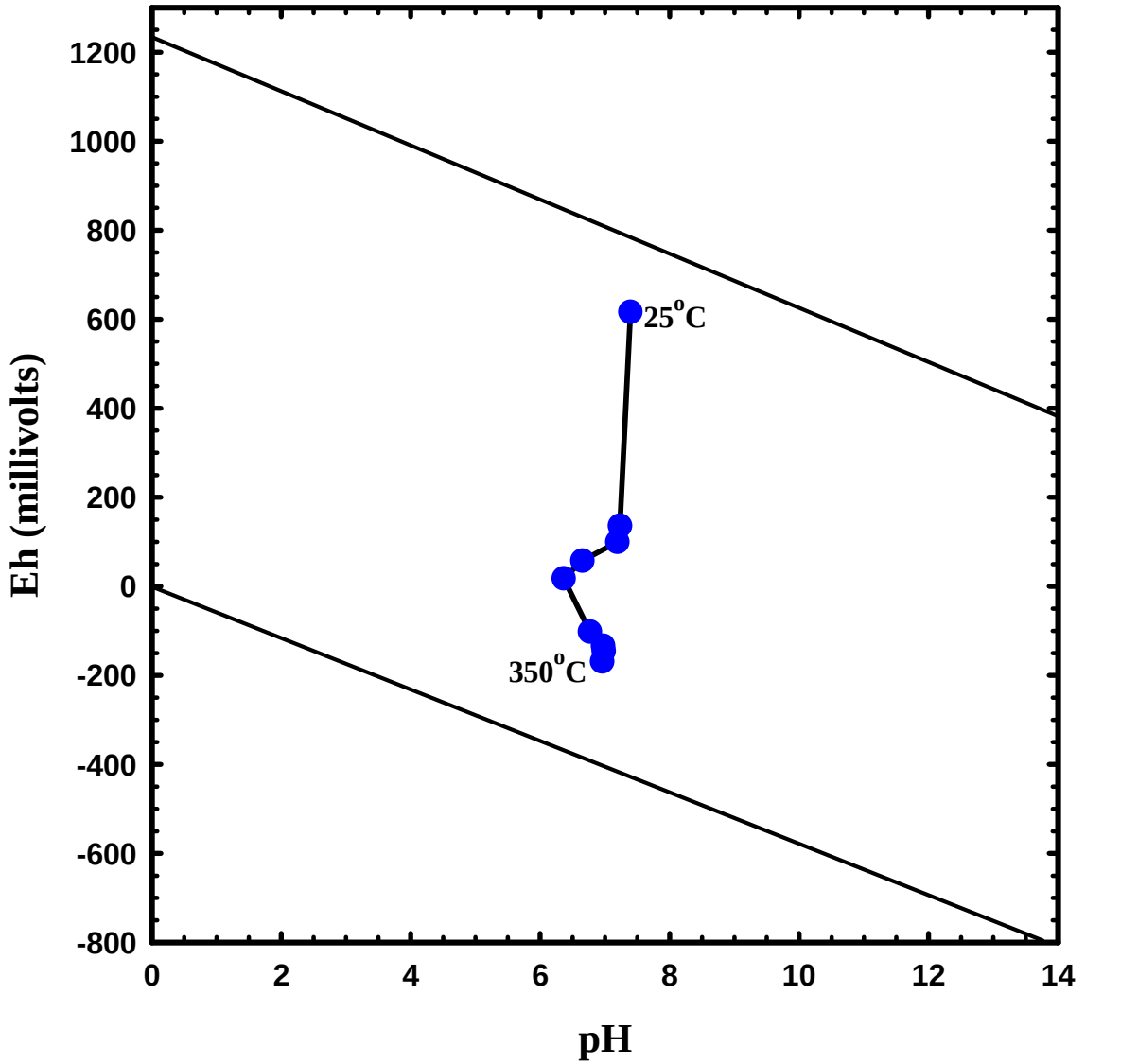
Hydrocarbons:

- Pentanes
- Hexanes
- Heptanes

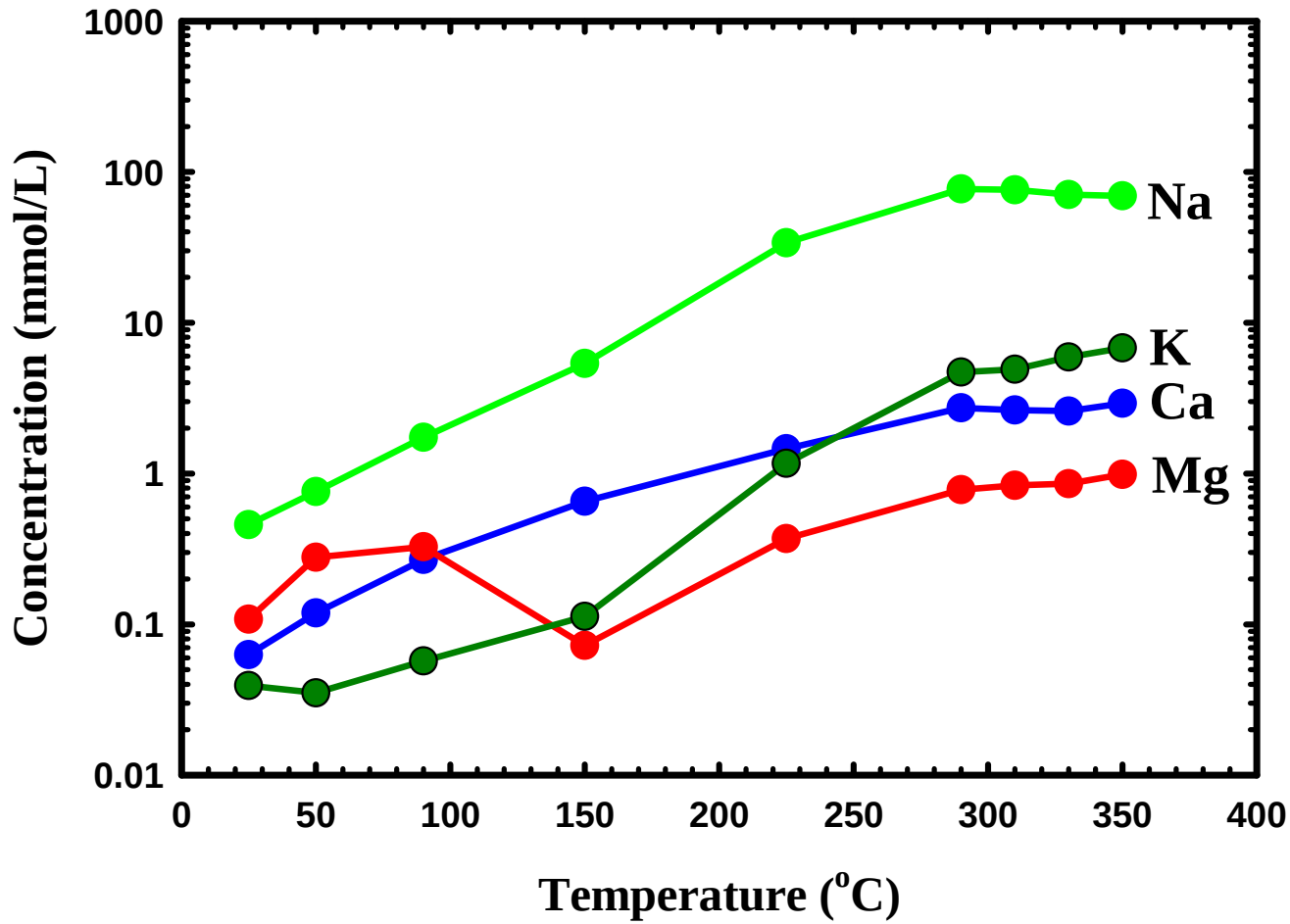
Na-HCO_3 Water



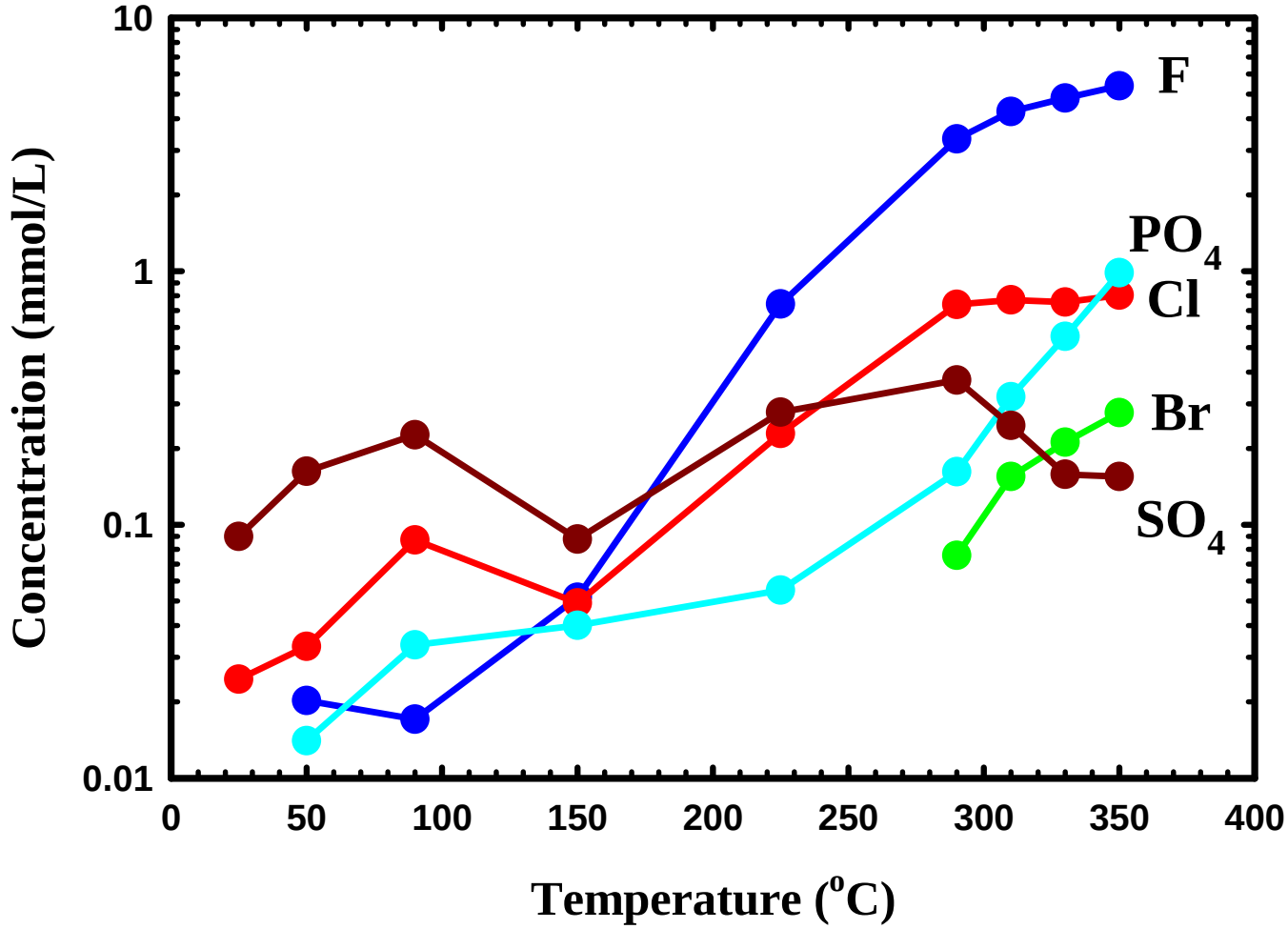
Eh-pH


Eh (millivolts)
1200
1000
800
600
400
200
0
-200
-400
-600
-800
0
2
4
6
8
10
12
14
pH
25°C
350°C

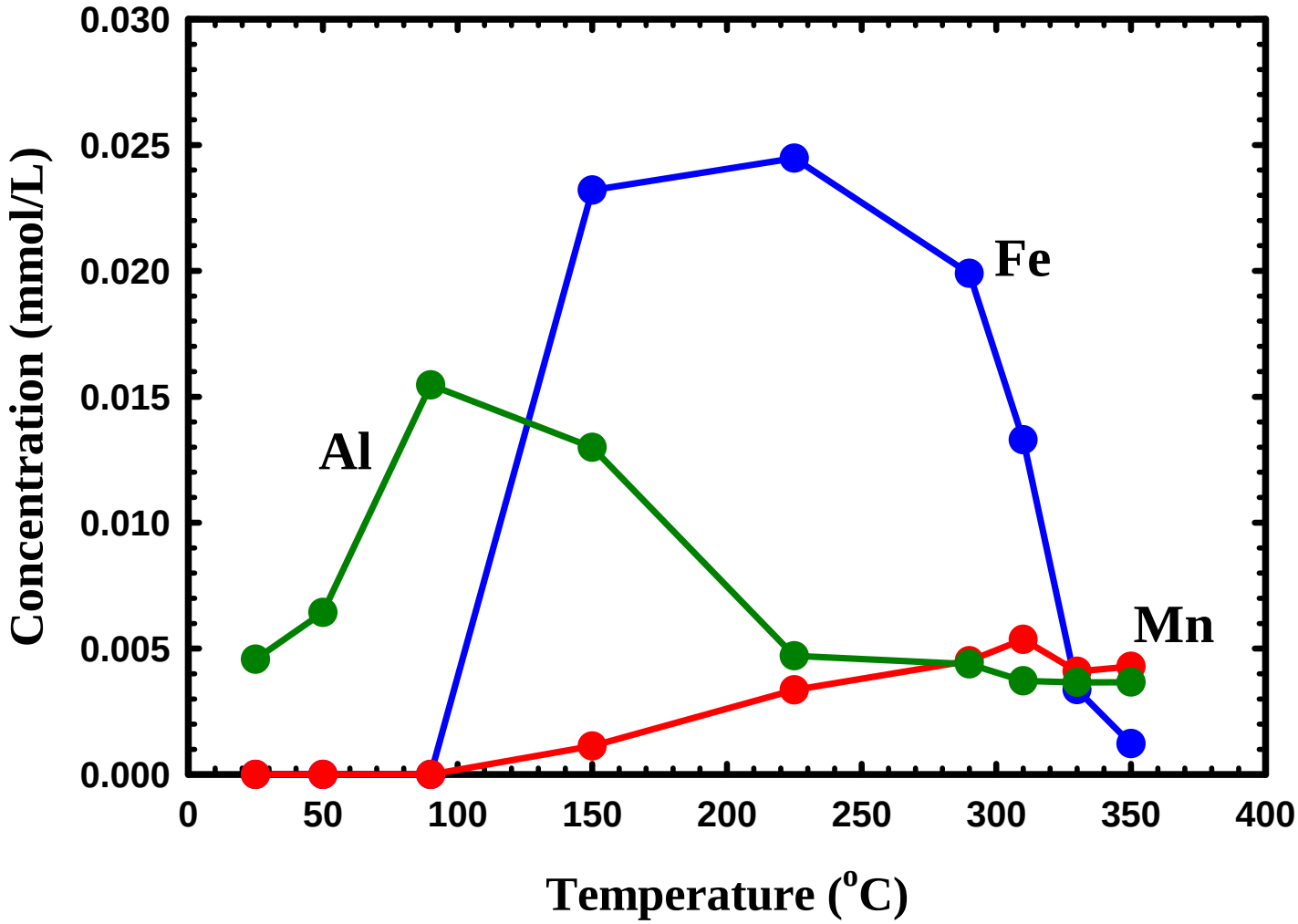
Major Cations

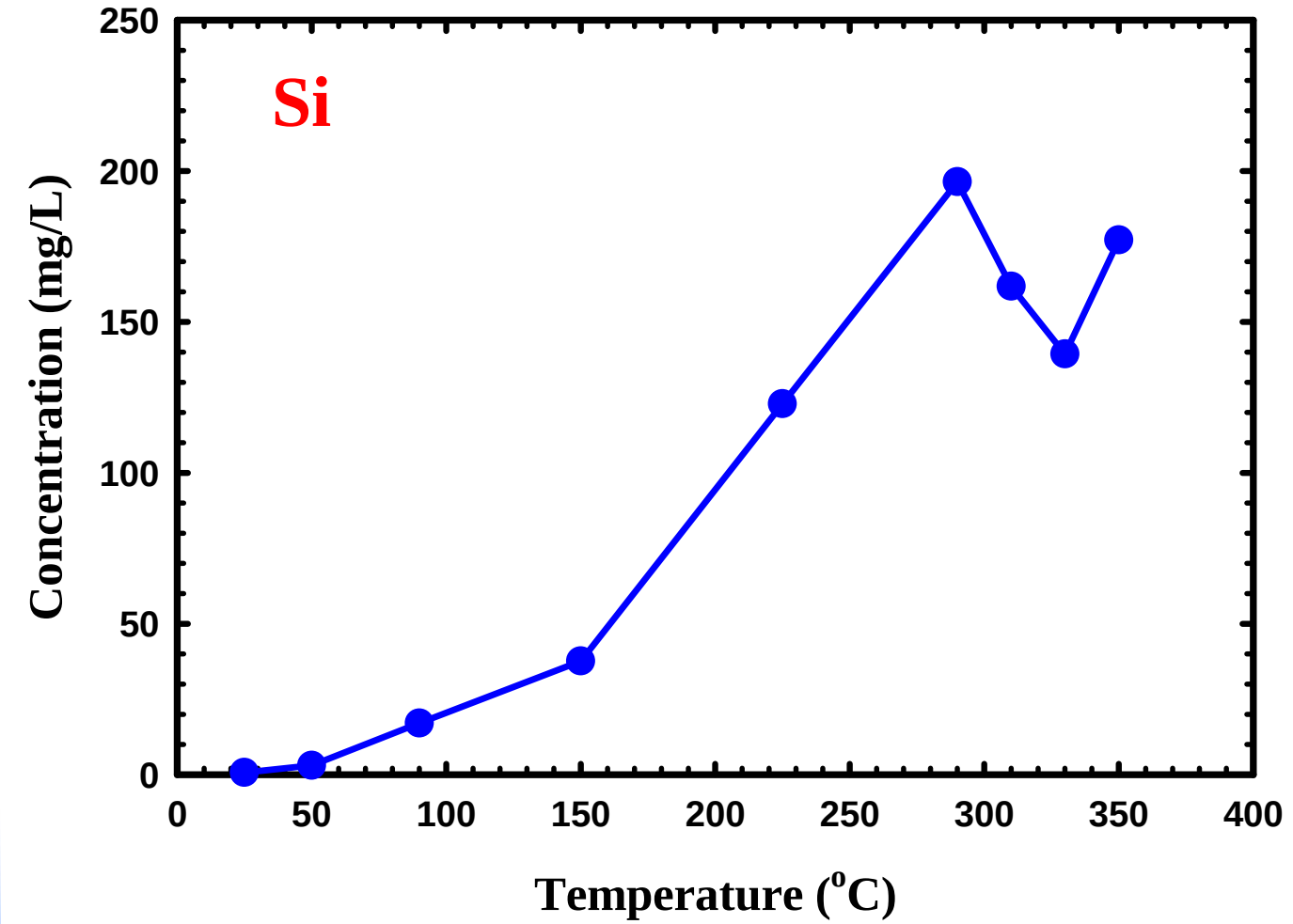


Anions

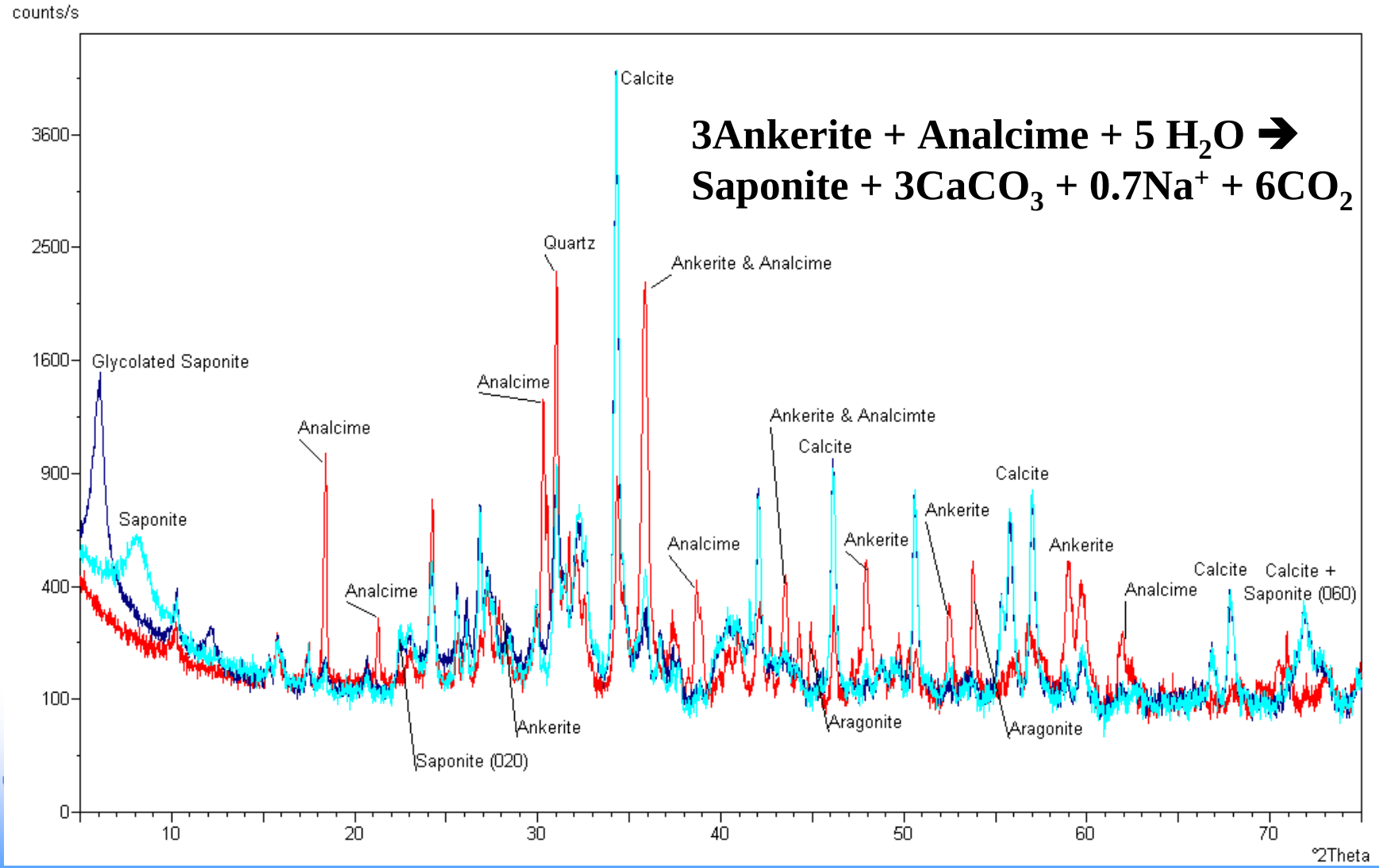

10
1
0.1
0.01
Concentration (mmol/L)
0
50
100
150
200
250
300
350
400
Temperature (°C)
F
PO4
Cl
Br
SO4

Fe, Mn, Al

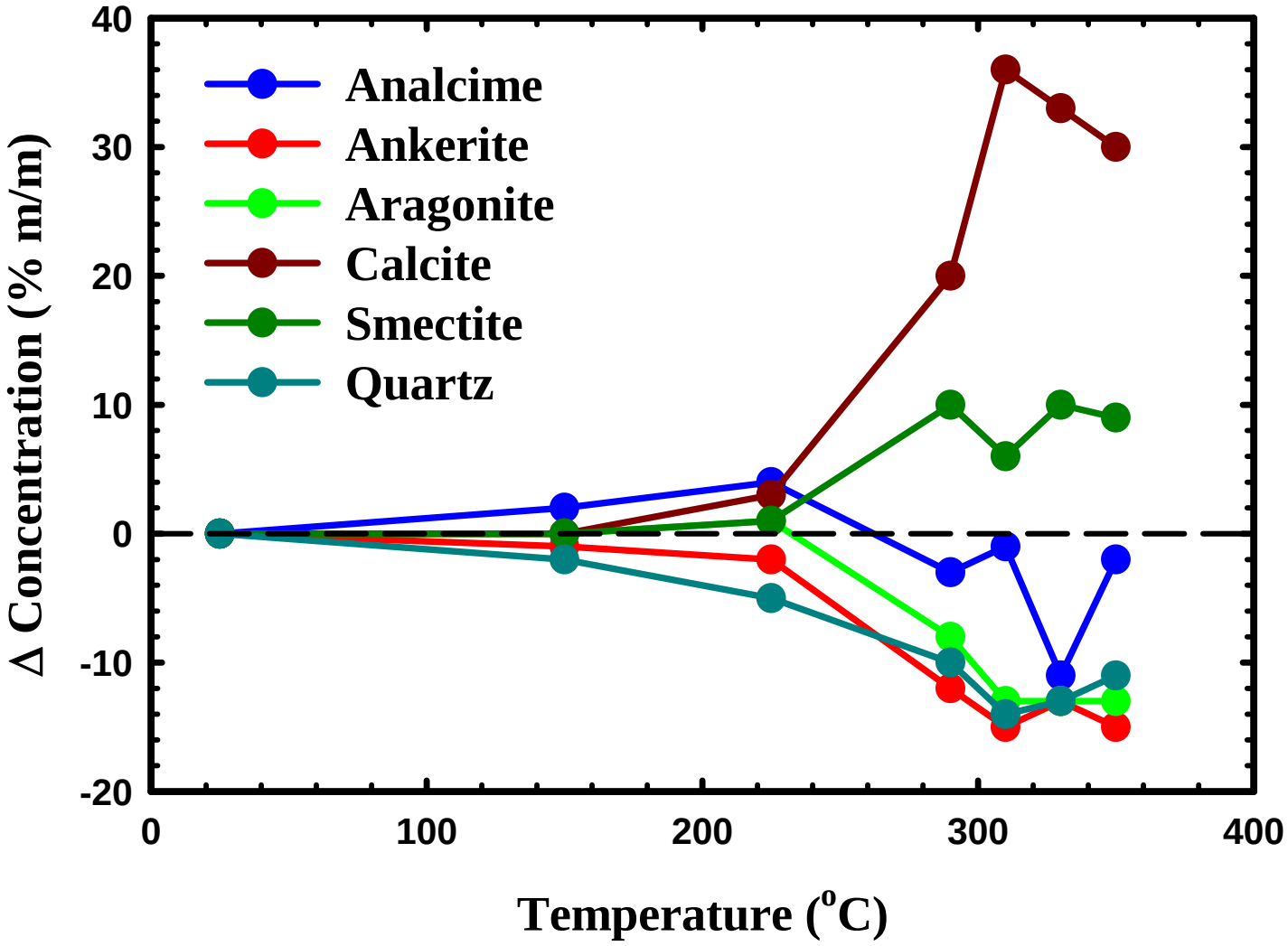

0.030
0.025
0.020
0.015
0.010
0.005
0.000
Concentration (mmol/L)
0
50
100
150
200
250
300
350
400
Temperature (°C)
Fe
Al
Mn


Si
Concentration (mg/L)
Temperature (°C)
0
50
100
150
200
250
300
350
400

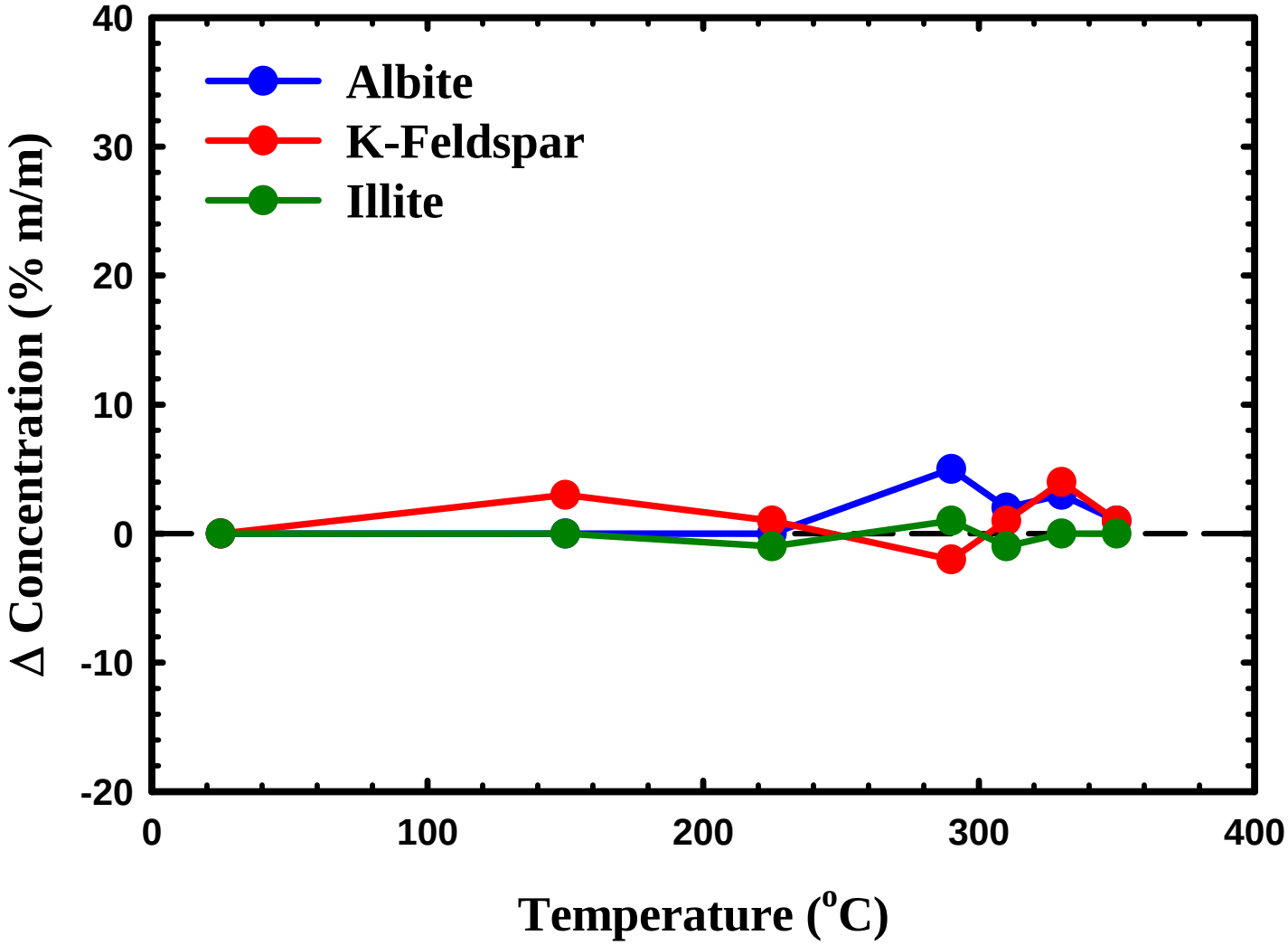
Powder X-ray Diffraction: Raw versus Spent Oil Shale



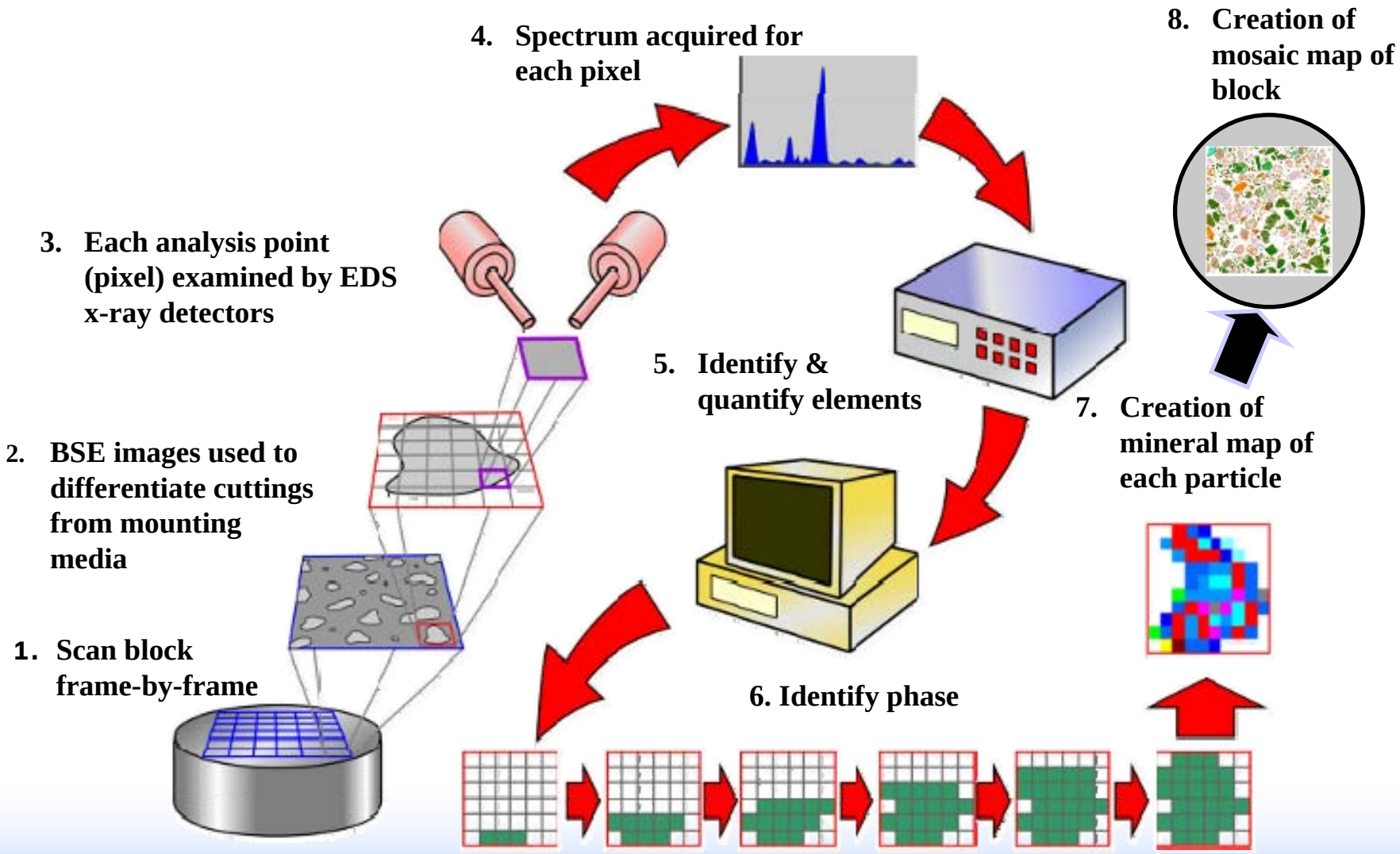
Change in Mineralogical Composition



Change in Mineralogical Composition

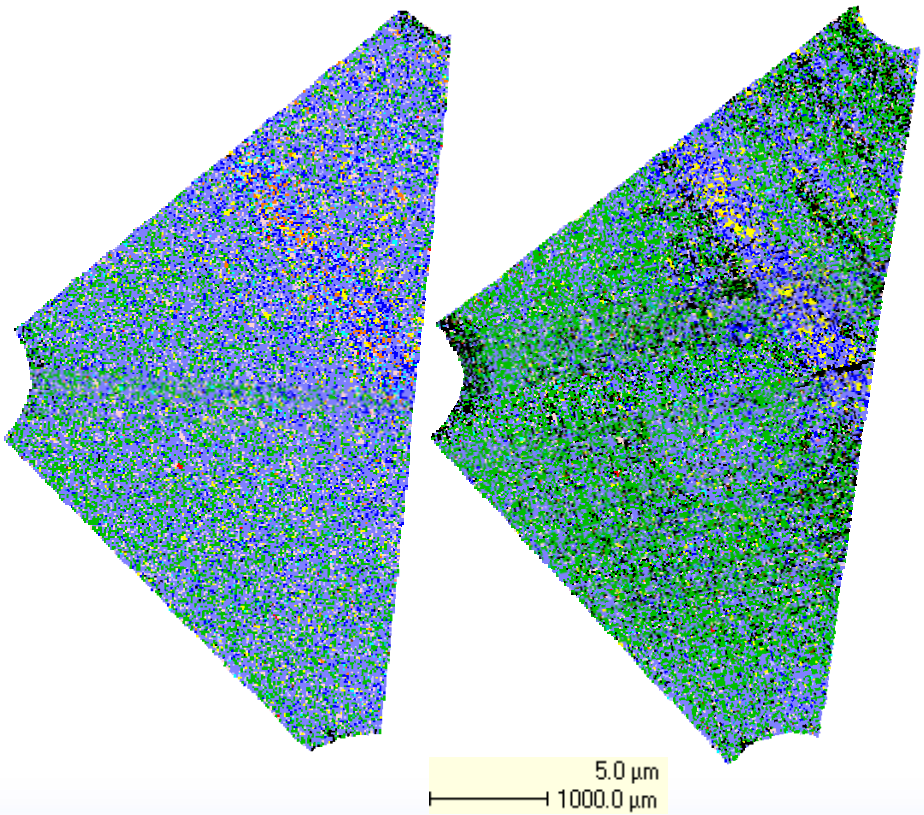


How does QEMSCAN® work?



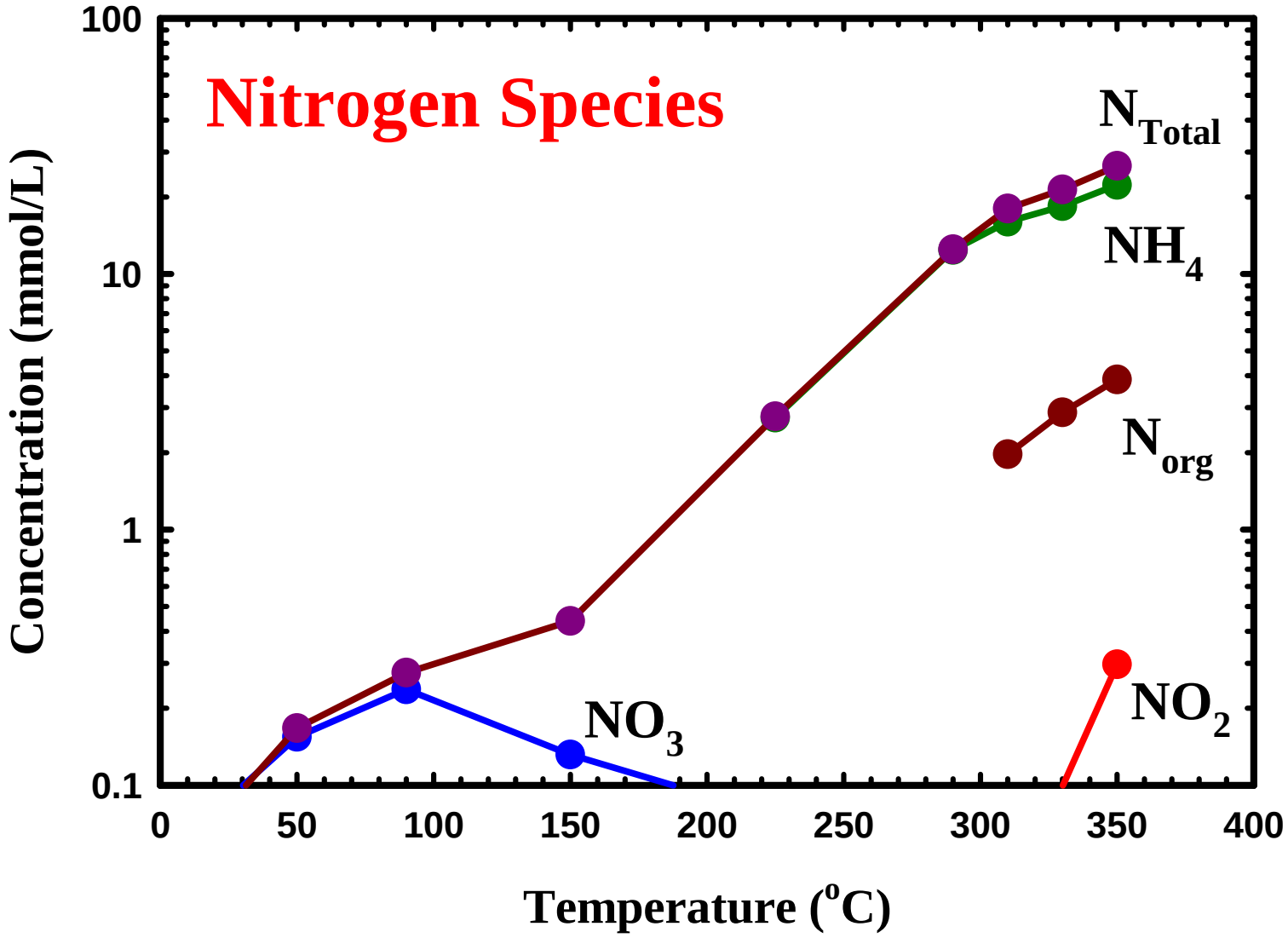
Advanced Mineralogy Research Center
Colorado School of Mines

Changes in Mineralogical Composition Using QEMSCAN©



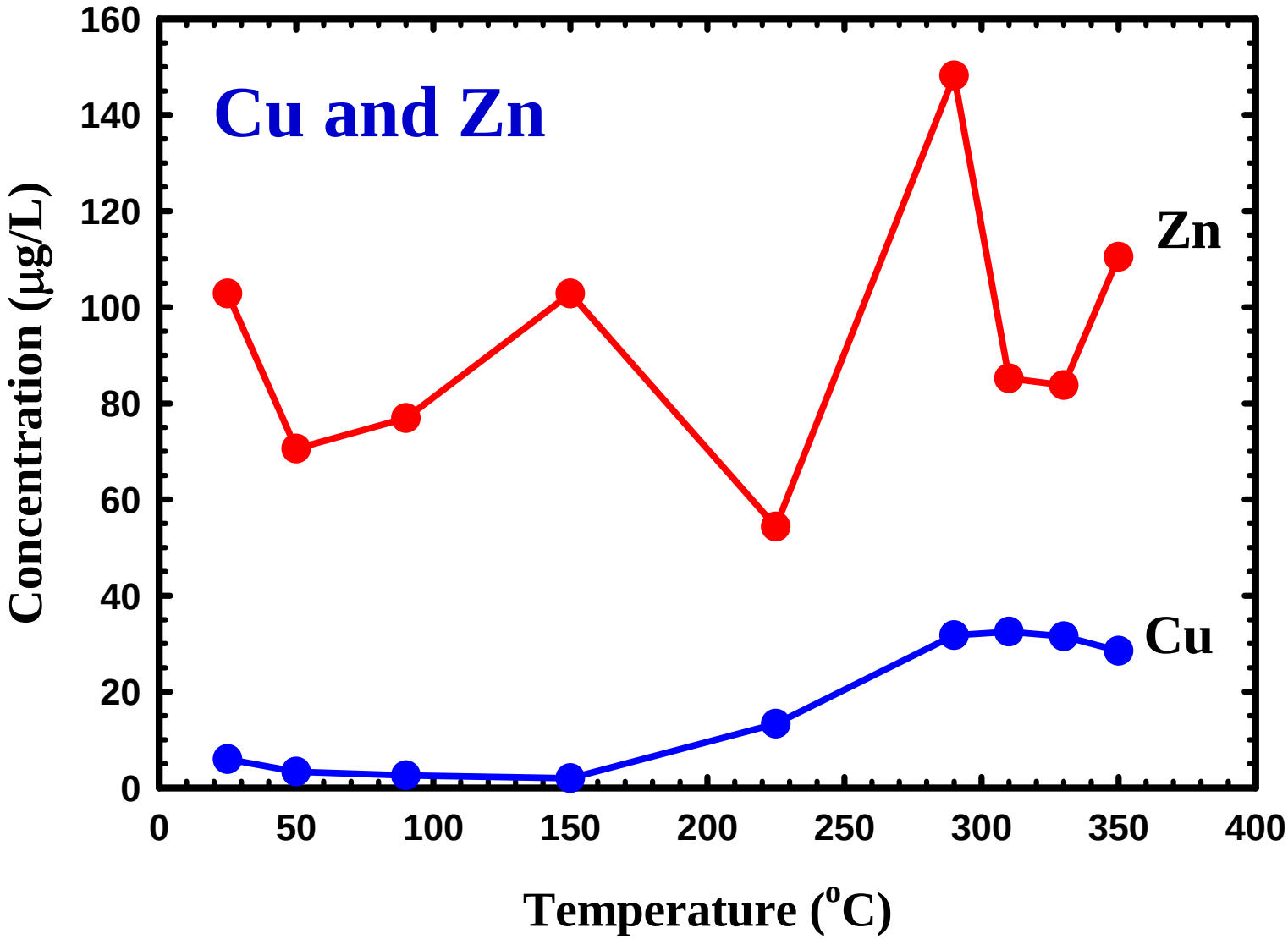
- Micrite
- Illite/Muscovite
- Dolomite
- Quartz
- Calcite
- Pyrite
- Kaolinite
- K_Feldspar
- Ankerite/Siderite
- Plagioclase
- Others
- Ti-minerals
- Apatite
- Talc
- pores

Results by Karin Hoal and Jane Stammer
Advanced Mineralogy Research Center
Colorado School of Mines


Nitrogen Species
N_{Total}
NH_4
N_{org}
NO_3
NO_2
Concentration (mmol/L)
100
10
1
0.1
0
50
100
150
200
250
300
350
400
Temperature (^oC)

Metals

- Co < 50 μg/L
- Ni < 50 μg/L
- Cd < 50 μg/L
- Pb < 5 μg/L
- Mo: 0-270 μg/L (decreased w/ increasing T)
- V < 5 μg/L except at 90°C (9.2 μg/L)

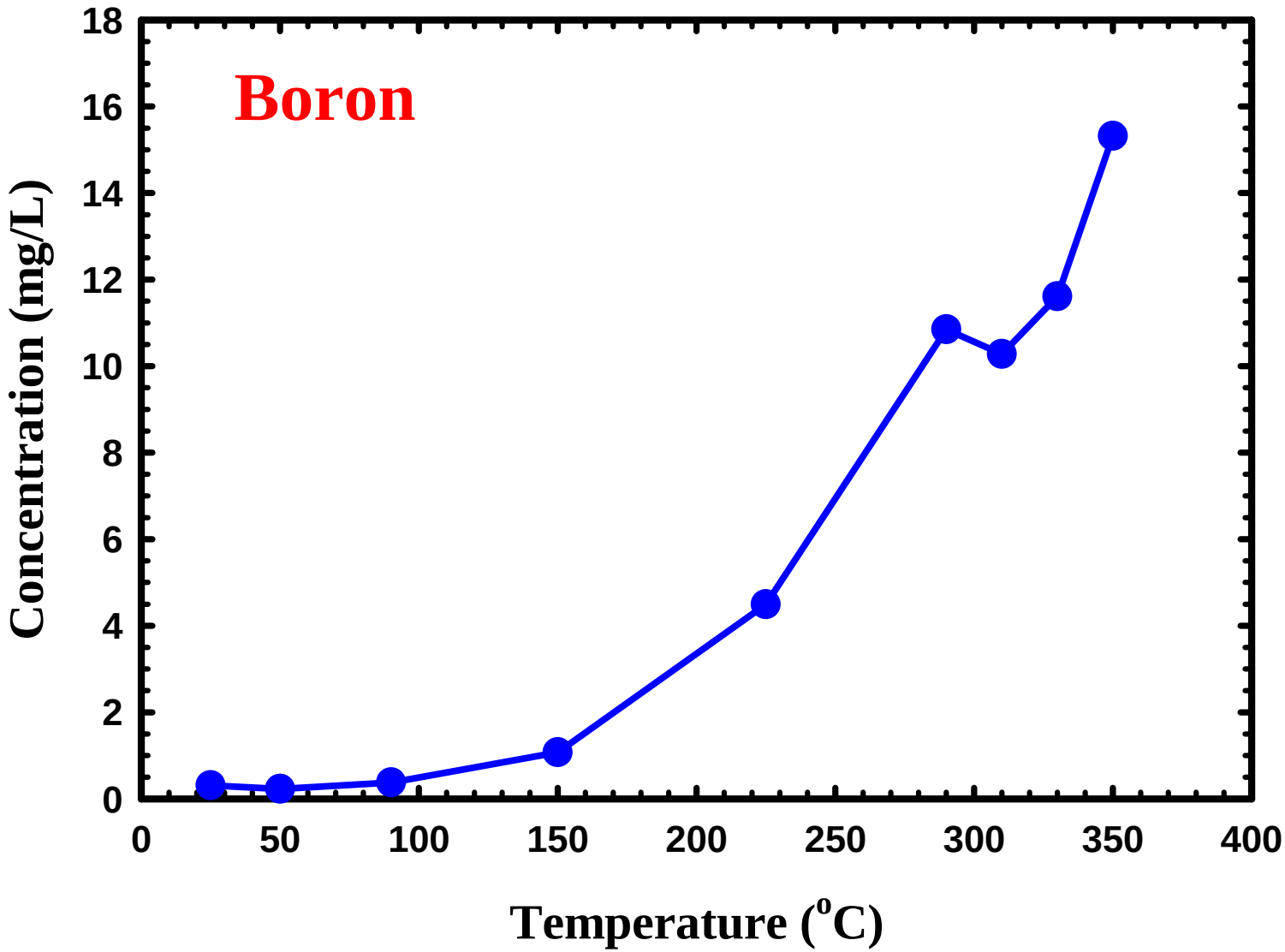

Cu and Zn
Zn
Cu
Concentration (µg/L)
Temperature (°C)
0
20
40
60
80
100
120
140
160
0
50
100
150
200
250
300
350
400

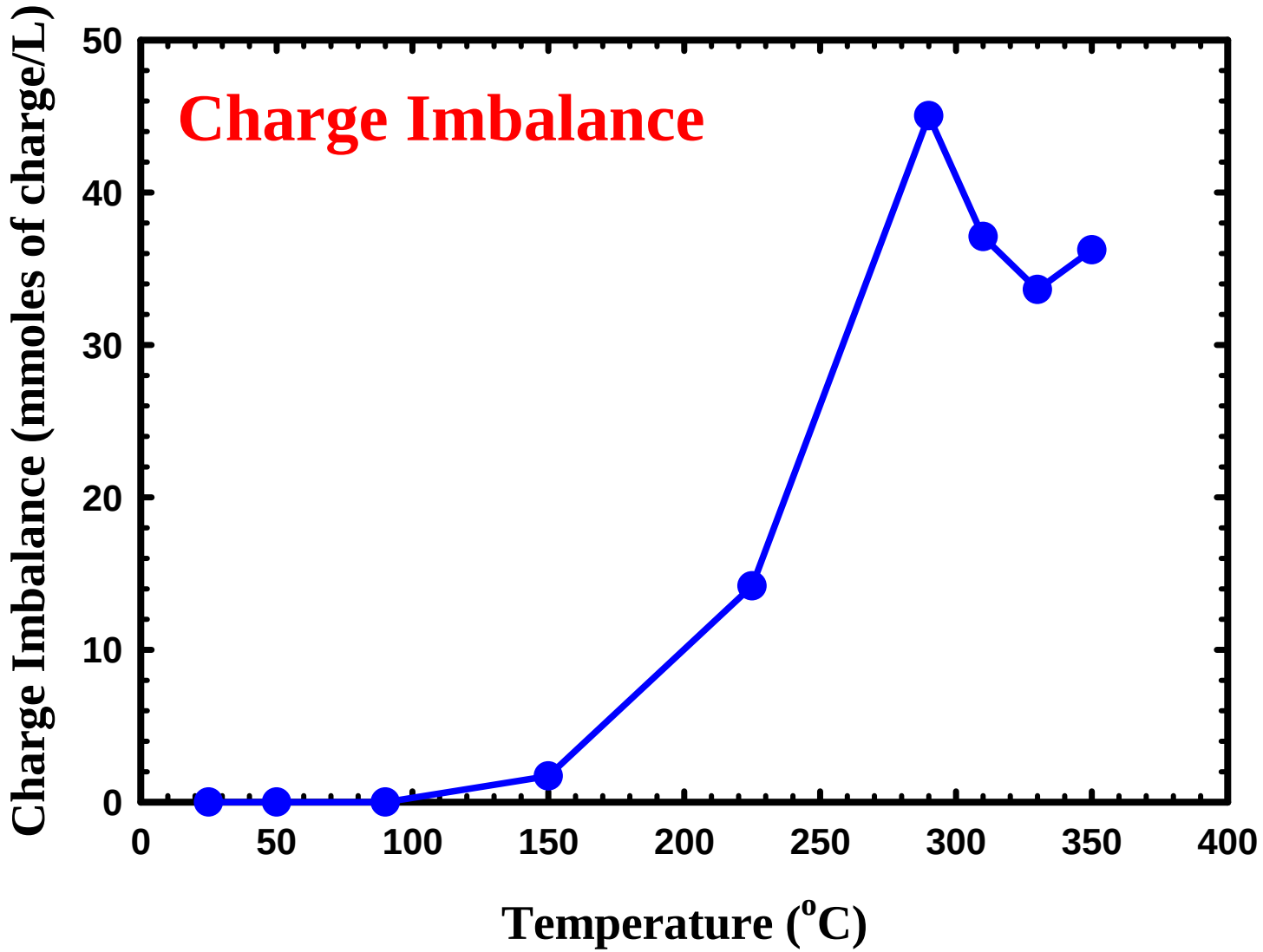
As, Se, Hg

As: no trend but values as high as 6.4 mg/L

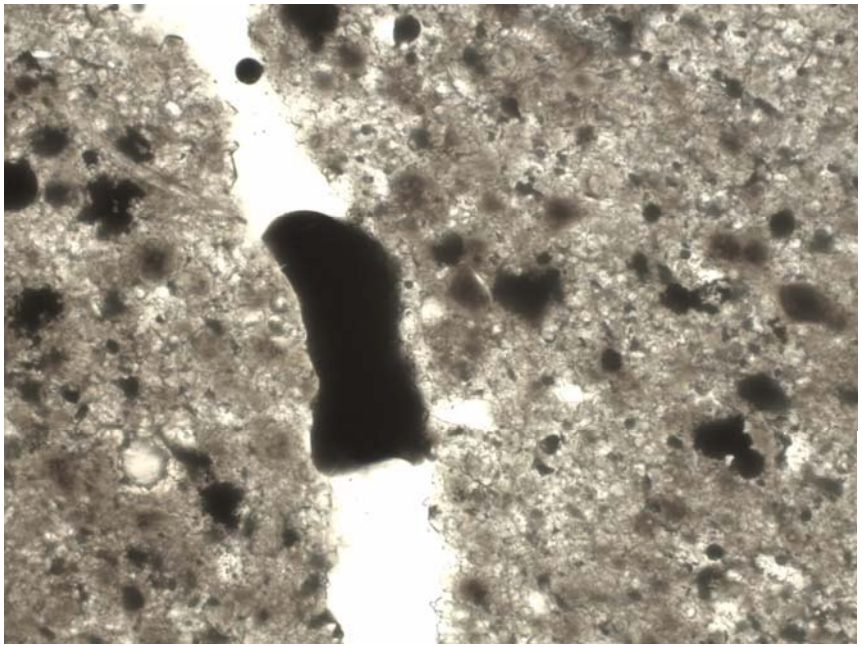
Se: detect 19-23 μg/L in preliminary tests (310 - 350ºC)

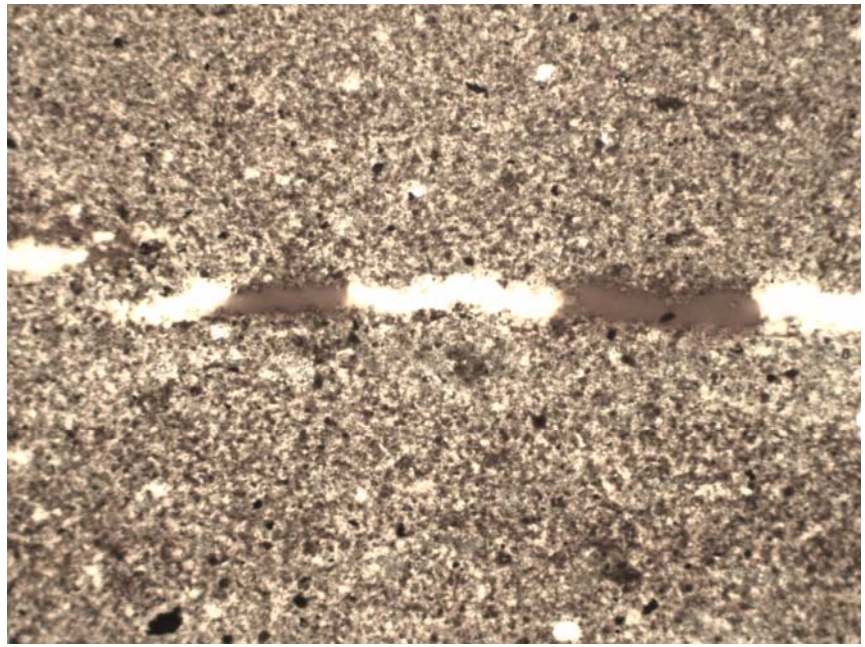
Hg: values up to 15 μg/L in preliminary tests (310 - 350ºC)


Boron
Concentration (mg/L)
0
2
4
6
8
10
12
14
16
18
0
50
100
150
200
250
300
350
400
Temperature (°C)


Charge Imbalance
Charge Imbalance (mmoles of charge/L)
50
40
30
20
10
0
0
50
100
150
200
250
300
350
400
Temperature (°C)

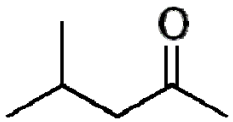
Residual Carbon

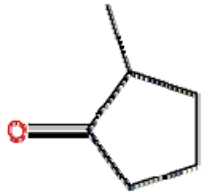


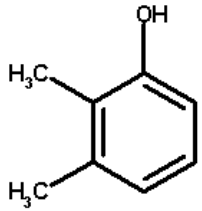


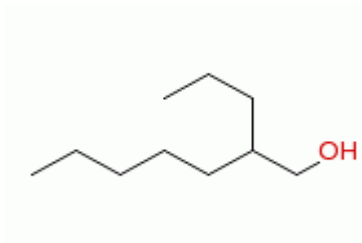
Organic Solutes in Retort Water

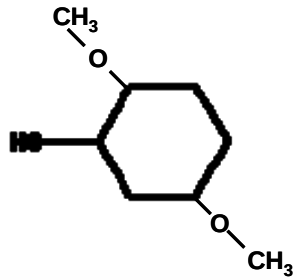
Organics:

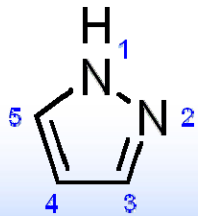
- Ketones 

- Cycloketones 

- Phenols 

- 2-propyl 1-heptanol 

- 2,5-dimethyl-aceta cyclohexanethiol 

- pyrazole 

Summary

- Clear trends in water chemistry with retort temperature
- Retort water predominantly a Na-HCO_3 type water
- Indication of silicate reactions including
  - dissolution and re-precipitation of quartz
  - dissolution of analcime
  - formation of smectite (saponite)
- Carbonates re-precipitated as calcite

Summary

- Indication of dissolved organic nitrogen
- Inorganic constituents of concern: As, Hg, B, F
- Charge imbalance suggests other anions, possibly organic acid anions
- Organic solutes include
  - ketones
  - cycloketones
  - phenols
  - alcohol
  - thiol