Origin and Distribution of Dissolved Strontium in the Cambrian-Ordovician Aquifer of Northeastern Wisconsin

A Presentation to the Wisconsin Groundwater Coordinating Council

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- UW-Water Resources Institute (Project # WR12R0004),
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- UWGB Students: Joe Baeten, Mick Kiehl
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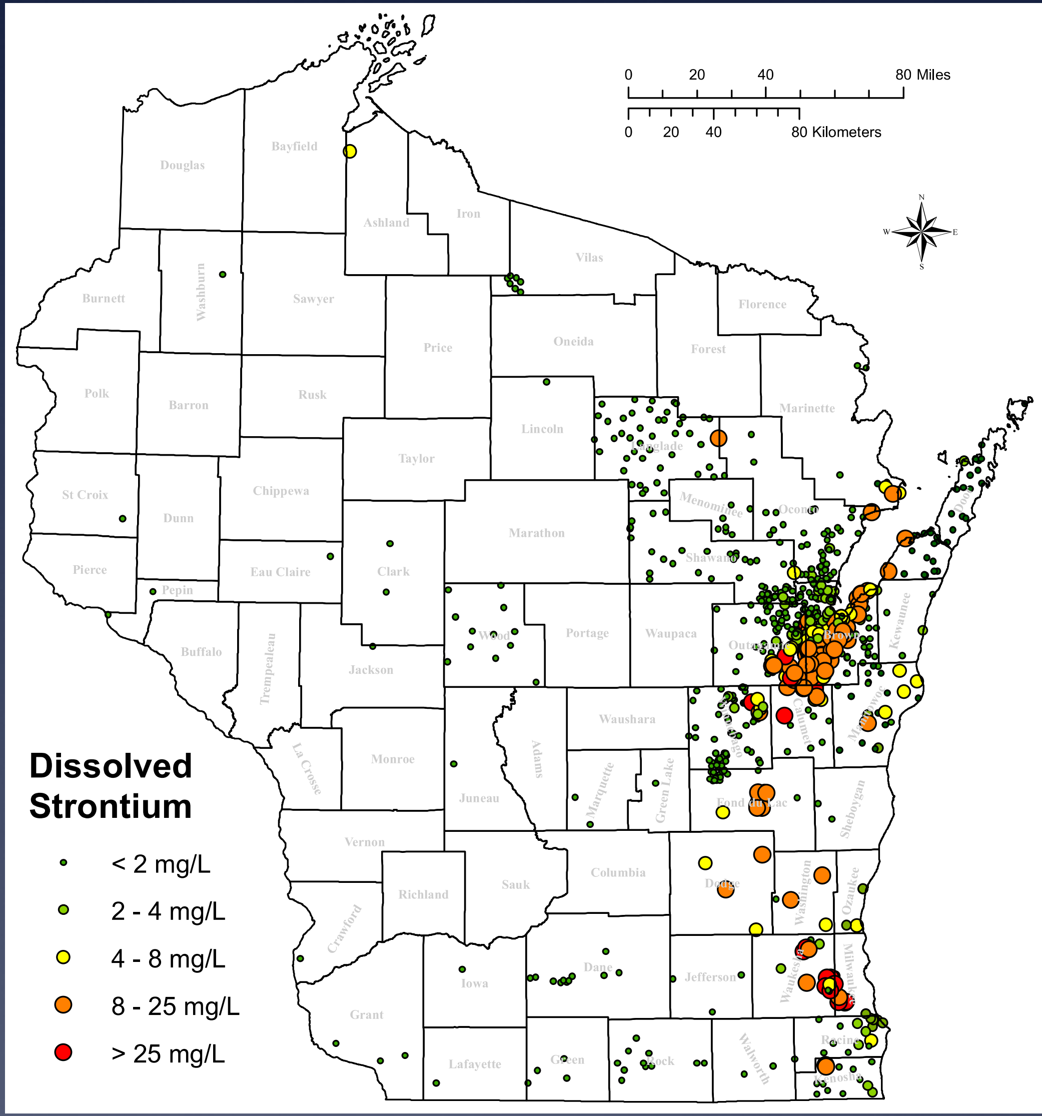
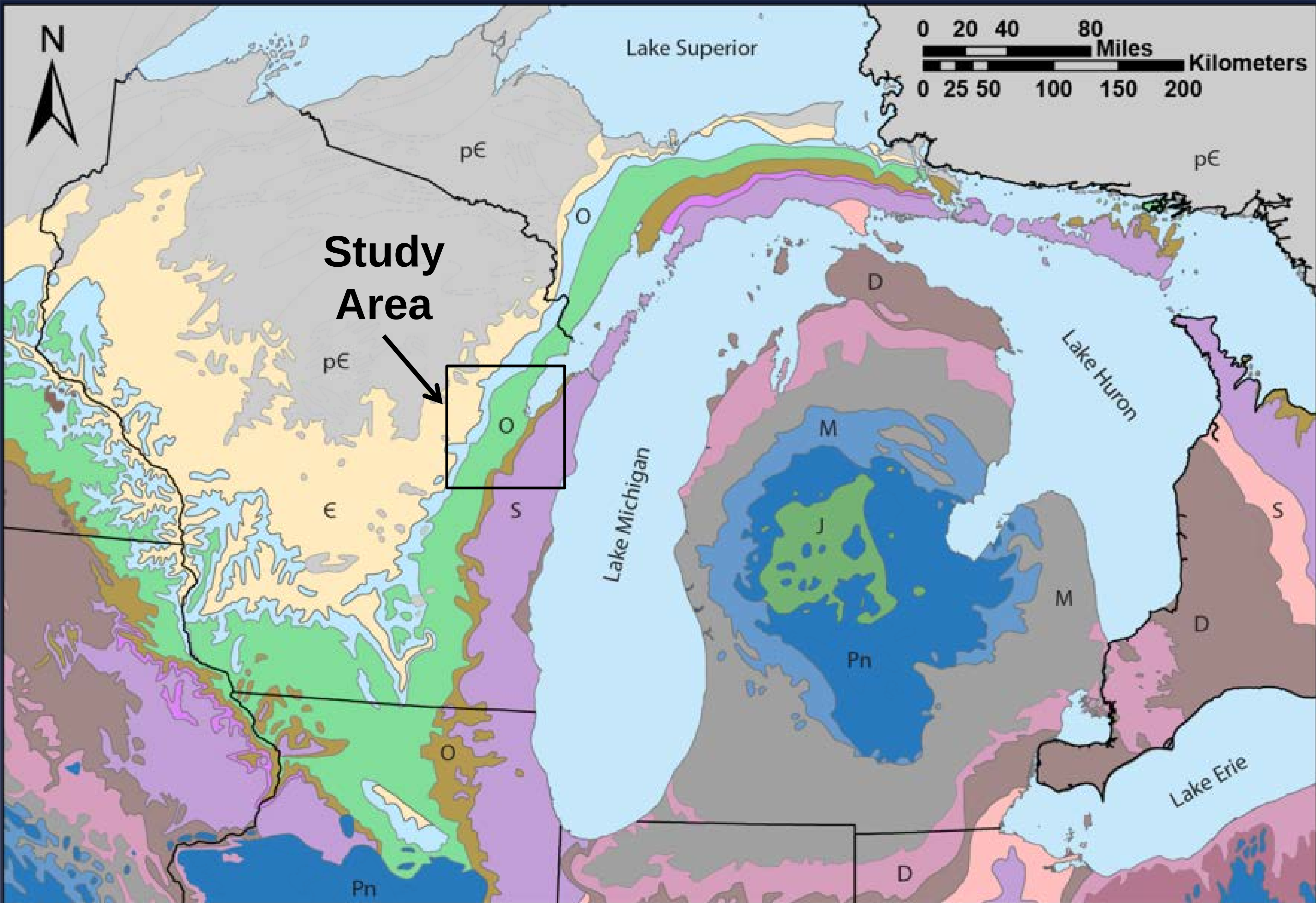
- Seymour High School: Dennis Rohr
- UWGB Faculty: Mike Zorn, Kevin Fermanich, John Lyon
- Alyssa Shiel (University of Illinois – Strontium Isotopes)

Outline:

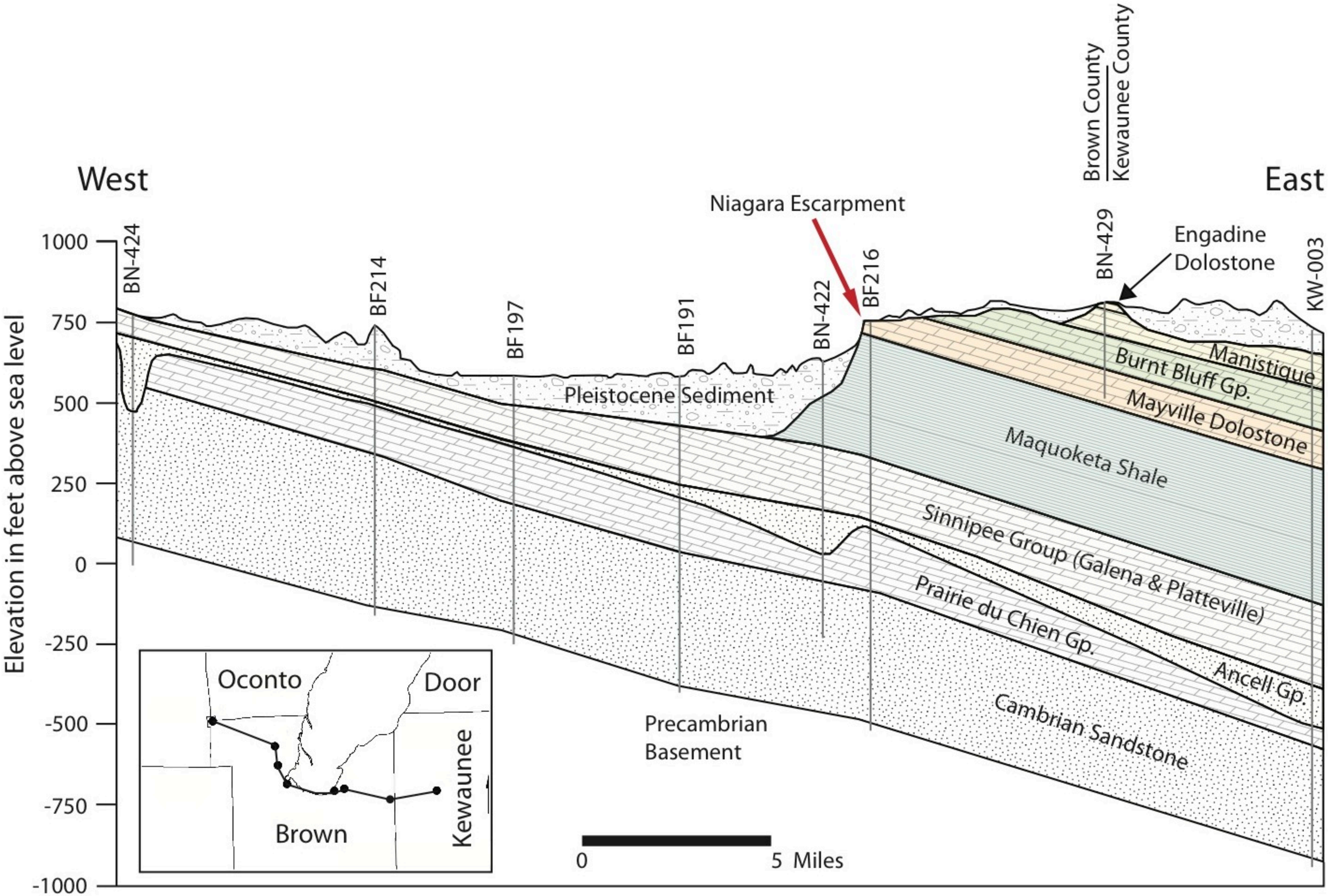
- Geology Review
- Objectives of Study
- Methods
- Results
- Recommendations





From Luczaj (2013)

Cross Section for Study Area in Northeastern Wisconsin

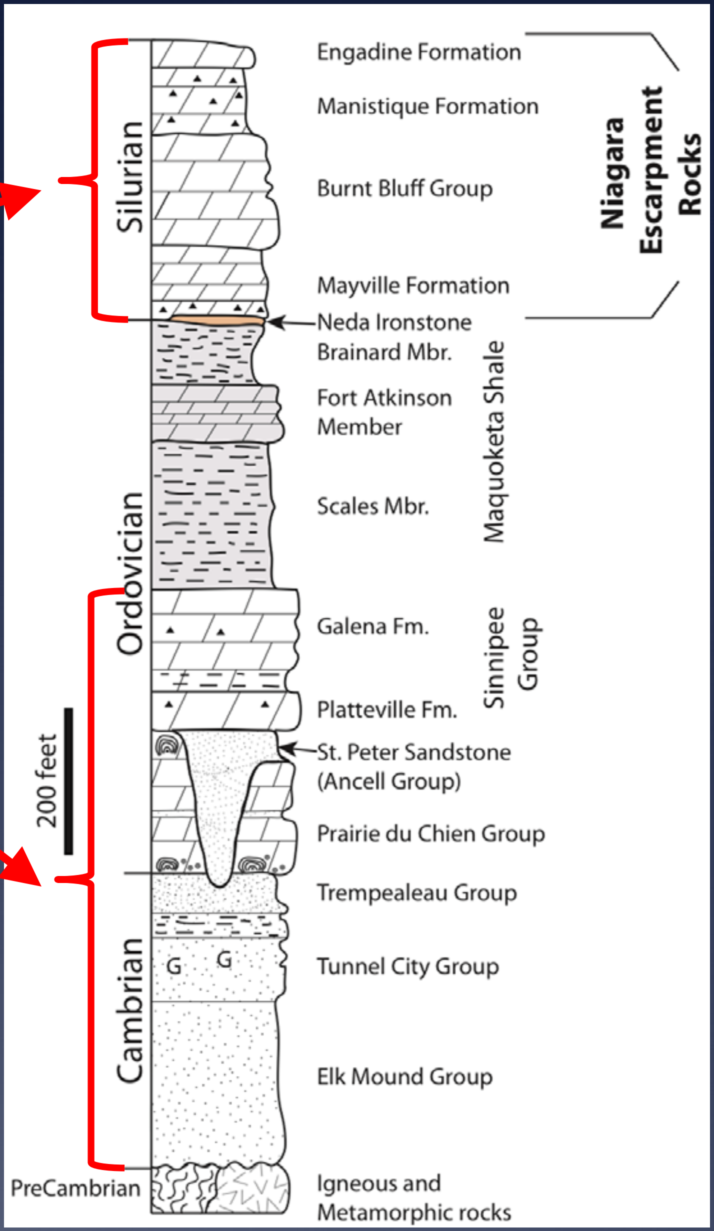


From Luczaj (in press)

Two Main Bedrock Aquifers

- Karst Aquifer
  - Vulnerable to surface activity

- Cambrian-Ordovician Aquifer
  - A confined aquifer
  - Contains Arsenic, Radium, Strontium, Fluoride, others



Stratigraphic column of northeastern Wisconsin (Luczaj, 2013)

Bedrock Chemistry Affects Groundwater Quality

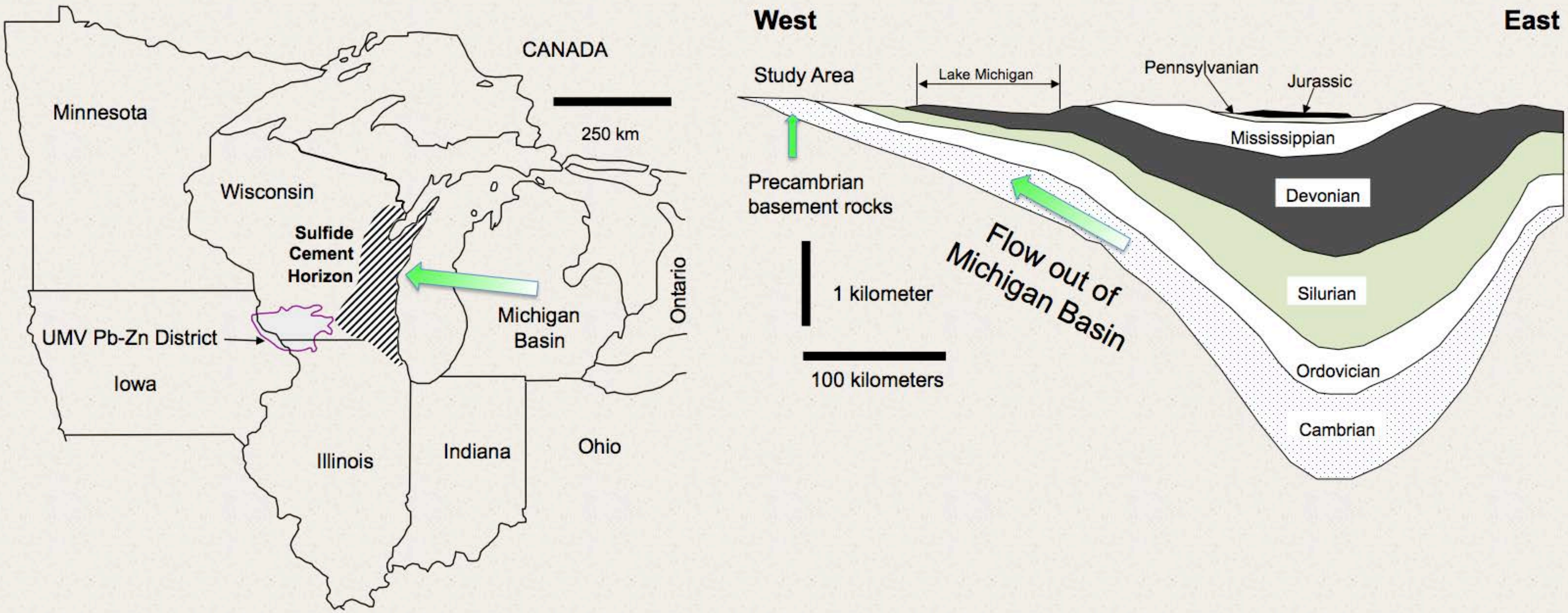
1. A regional hydrothermal system operated in eastern Wisconsin; responsible for much of the dolomite and all Mississippi Valley Type (MVT) minerals.

2. Invasion of Michigan basin brines occurred at elevated temperatures (> 80 - 100˚C) during the mid-late Paleozoic Era.

3. Dolomite controls first order chemistry, along with remaining saline waters. The distribution and character of MVT minerals also influence the water quality of the region.

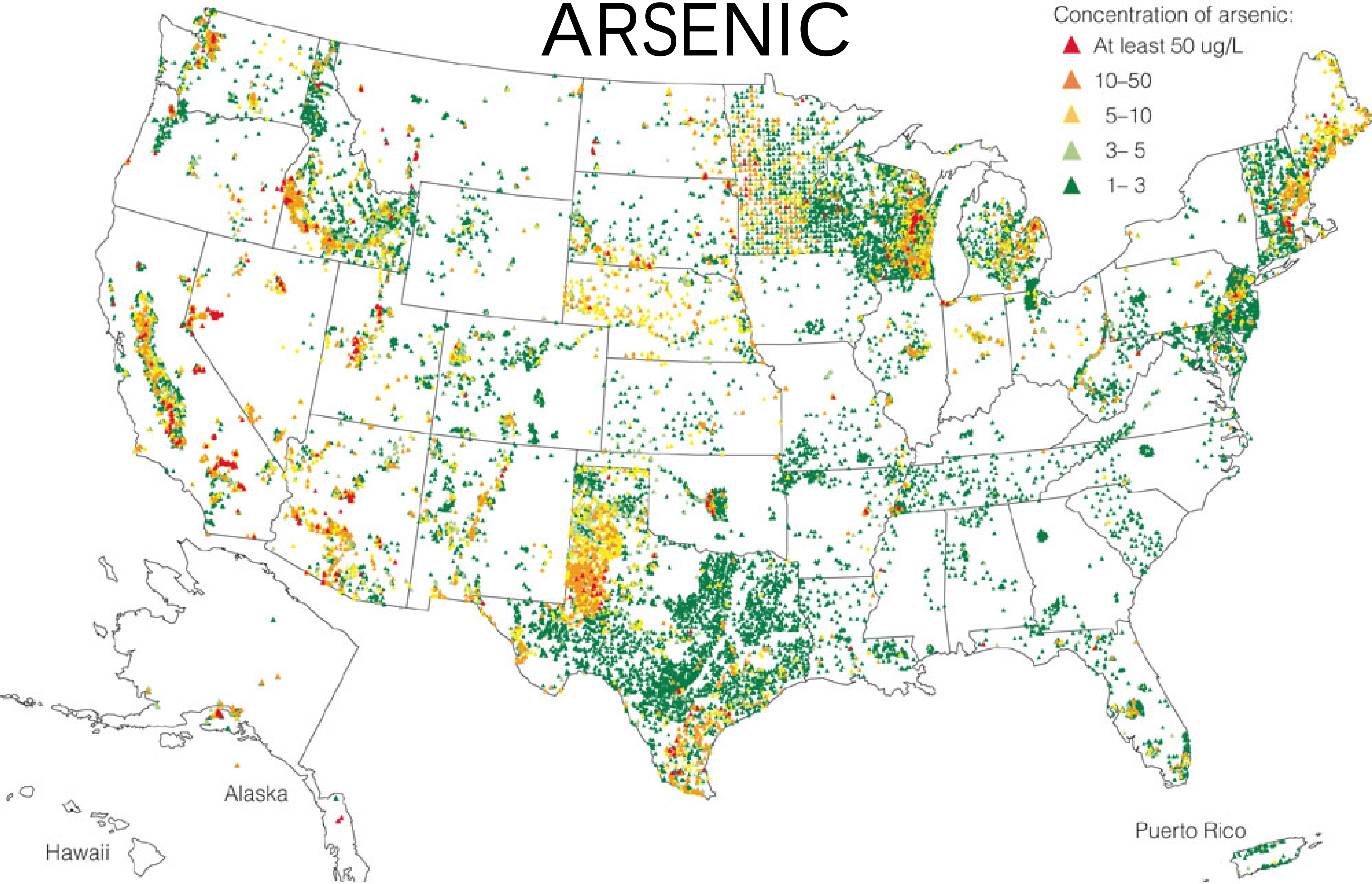
4. Arsenic, Nickel, Copper, Zinc, Lead, Cobalt, Strontium, Fluoride and other elements are related to MVT assemblage.

ORIGIN OF SULFIDE MINERALIZATION



From Luczaj (2000, 2006)

ARSENIC



10 µg/L is the current EPA Drinking Water Standard

Strontium Content of Wisconsin Municipal Waters

M. Starr Nichols and Dorothy R. McNall

A contribution to the Journal by M. Starr Nichols, Asst. Director, and Dorothy R. McNall, Chemist, both of the State Lab. of Hygiene, Univ. of Wisconsin, Madison, Wis.

1957

The occurrence of high Sr groundwater was known for over 50 years. However, no comprehensive study had been done in Wisconsin.

Community Dent. Oral Epidemiol. 1977: *5:* 243–247

(Key words: *enamel mottling; strontium*)

Enamel mottling in a high strontium area of the U.S.A.

1996

M. E. J. Curzon and P. C. Spector

Eastman Dental Center, Rochester, New York, U.S.A.

Abstract – As part of an epidemiologic study conducted in seven towns in Wisconsin,

Archives of Disease in Childhood 1996;75:524–526

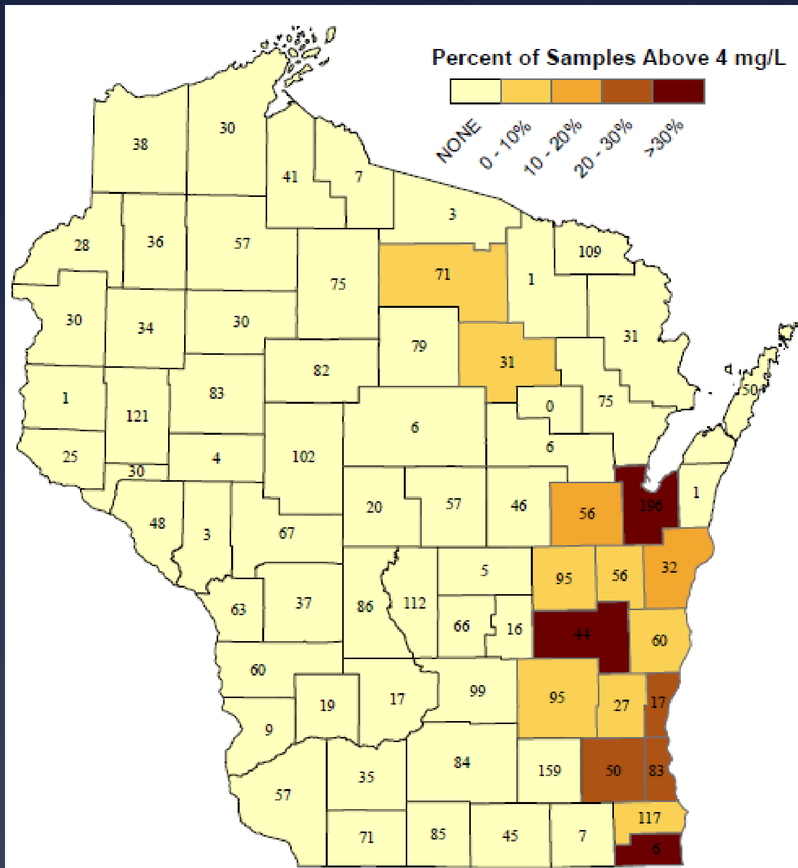
Rickets and soil strontium

Servet Özgür, Haldun Sümer, Gülay Koçoğlu

1977

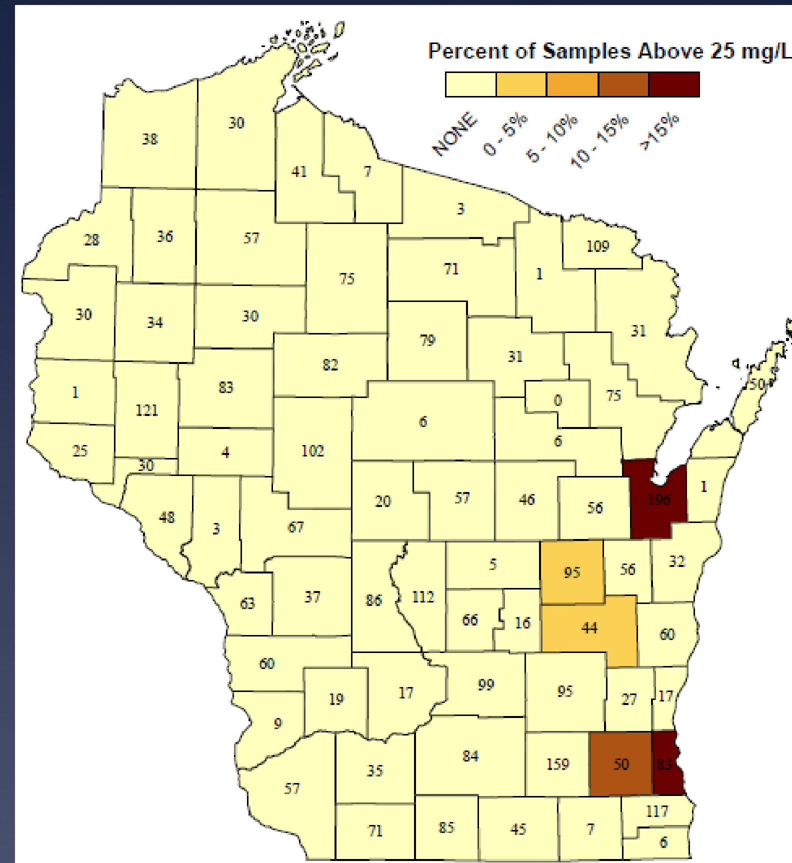
Tooth enamel mottling and rickets have been attributed to high levels of Sr ingestion

STRONTIUM IN EASTERN WISCONSIN



Exceedance of EPA's lifetime Health Advisory limit of 4 mg/L.

(From Baeten et al., 2012)



Exceedance of EPA's one-day and ten-day Health Advisory limit of 25 mg/L.

Main-Group Elements | Transition Metals | Main-Group Elements

1	Atomic number
H	Symbol
1.00794	Atomic weight

Period	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 H 1.00794																	2 He 4.002602
2	3 Li 6.941	4 Be 9.012182											5 B 10.811	6 C 12.0107	7 N 14.0067	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
3	11 Na 22.989770	12 Mg 24.3050											13 Al 26.981538	14 Si 28.0855	15 P 30.973761	16 S 32.065	17 Cl 35.453	18 Ar 39.948
4	19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 Co 58.933200	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.409	31 Ga 69.723	32 Ge 72.64	33 As 74.92160	34 Se 78.96	35 Br 79.904	36 Kr 83.798
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.293
6	55 Cs 132.90545	56 Ba 137.327	57 La* 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.96655	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.98038	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac** (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Uun (281)	111 Uuu (272)	112 Uub (285)		114 Uuq (289)		116 Uuh (292)		

Inner-Transition Metals

*Lanthanides	58 Ce 140.116	59 Pr 140.90765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.500	67 Ho 164.93032	68 Er 167.259	69 Tm 168.93421	70 Yb 173.04	71 Lu 174.967
**Actinides	90 Th 232.0381	91 Pa 231.03588	92 U 238.02891	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Metal

Metalloid

Nonmetal

Objectives

1. To determine the regional and stratigraphic distribution of dissolved strontium (Sr) in the groundwater of eastern Wisconsin, with a focus on Brown and Outagamie counties.

2. To evaluate potential sources of Sr in bedrock aquifers present in the region.

Methods Used

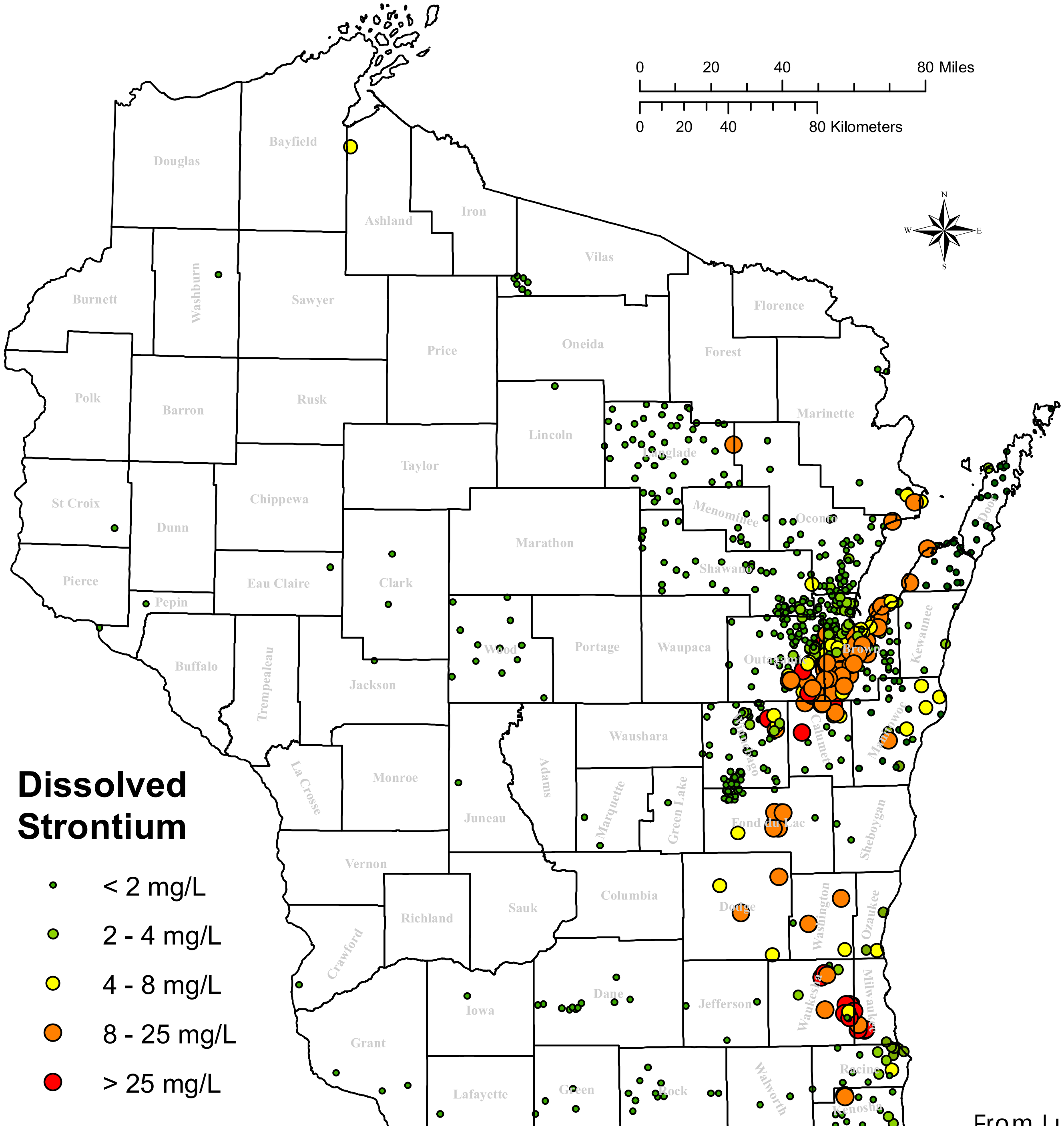
1. Major and trace element chemistry of groundwater
2. Isotopic analysis of groundwater (Sr, O, H)
3. Whole-rock chemistry of bedrock materials
4. Sr-isotopic analysis of major minerals in aquifer
5. GIS Mapping of new and existing data

Project Results

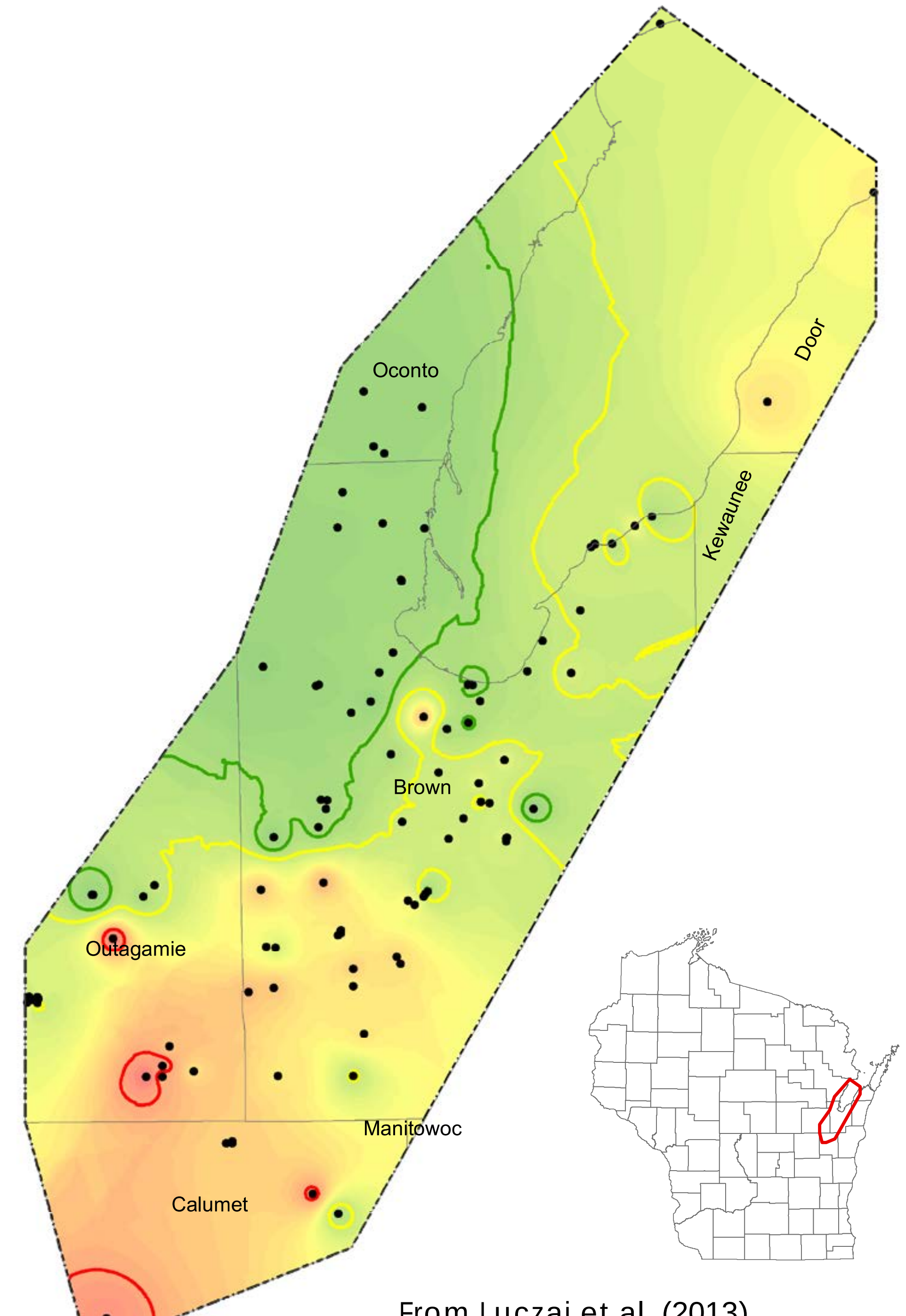
Table 1: Wisconsin Groundwater Samples with Dissolved Strontium Values			
Source	Number of Samples	Samples above 4 mg/L	Samples above 25 mg/L
UWGB Sr Project*	114	73	6
USGS (Wilson, 2012)	216	19	3
NURE Data (U. S. Geological Survey, 2004)**	4,417	5	0
Wisconsin State Lab of Hygiene	6,000	138	28
Tim Grundl (UWM) (Personal Communication)	33	13	7
Dennis Rohr, Seymour High School, WI	298	131	42
Total	11,078	379	86

**The number of samples for this project in this table does not include samples collected after water treatment. The effectiveness of strontium removal by treatment equipment will be discussed in a future publication.*

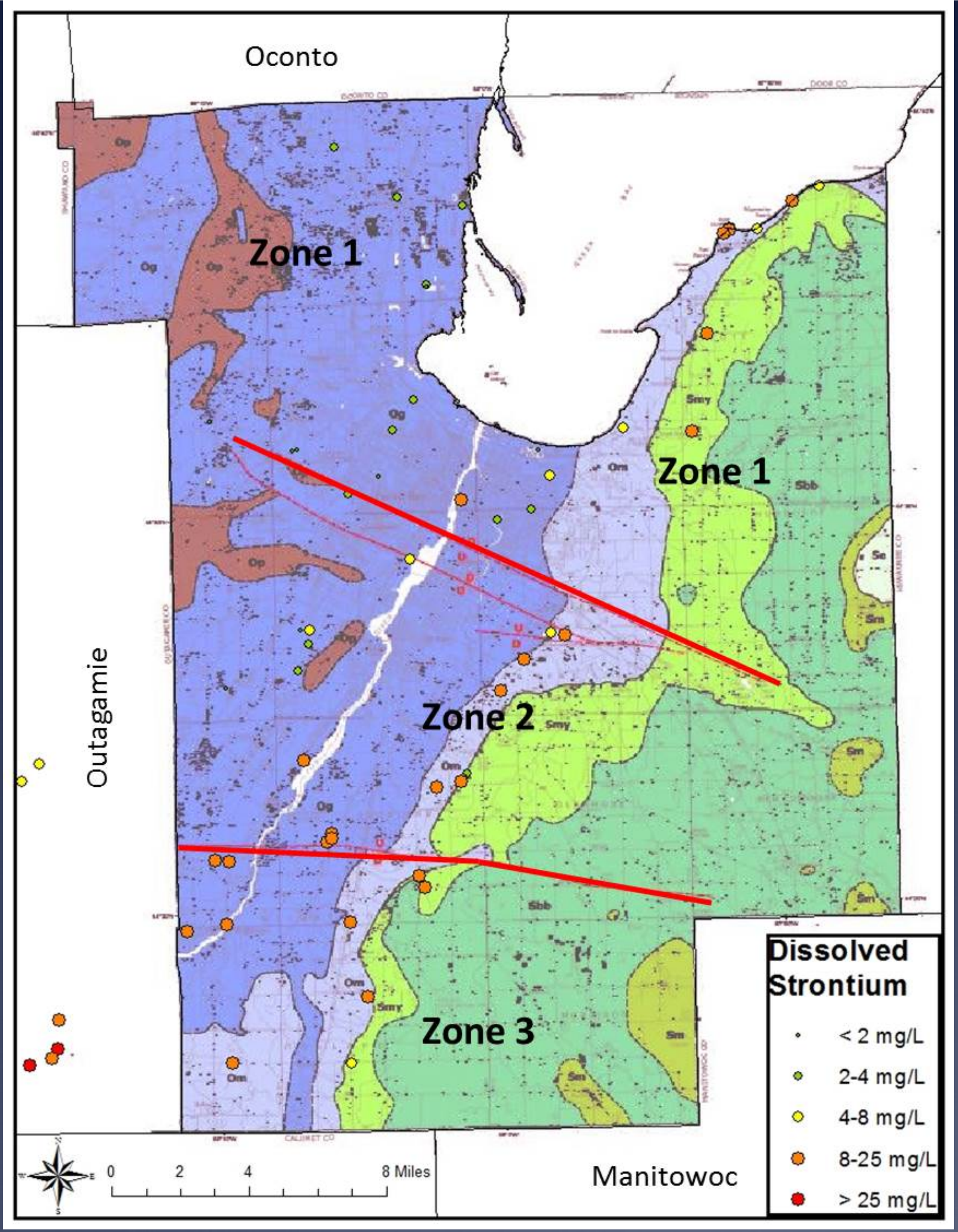
*** Many sample points from the NURE dataset were not sampled for strontium. Sampling occurred from 1975 to 1980. Not all samples in the NURE dataset are from groundwater; some samples taken from surface water sources.*



From Luczaj et al. (2013)

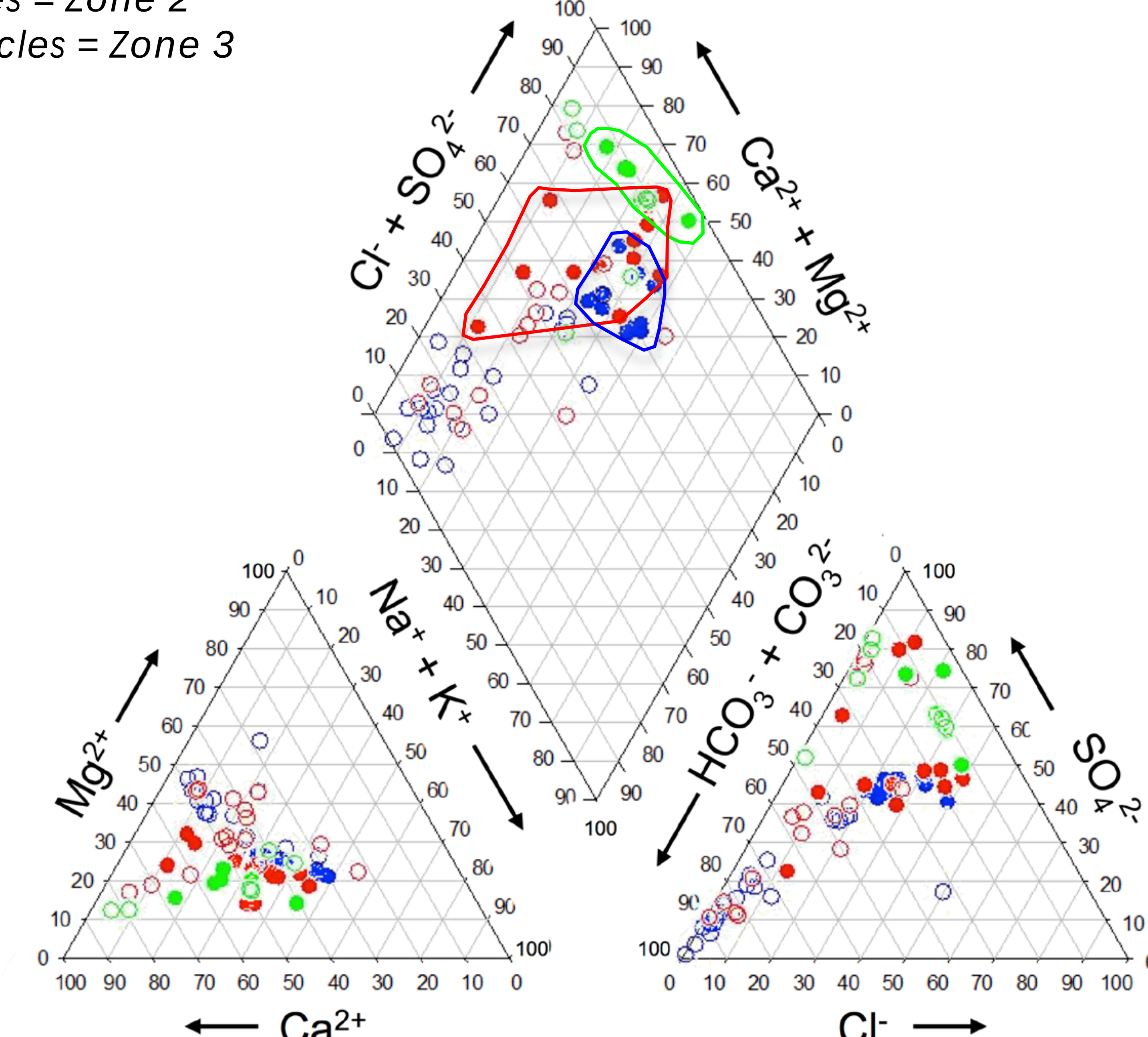


From Luczaj et al. (2013)



From Luczaj (2011) and Luczaj et al. (2013)

Blue circles = Zone 1
Red circles = Zone 2
Green circles = Zone 3



From Luczaj et al. (2013)

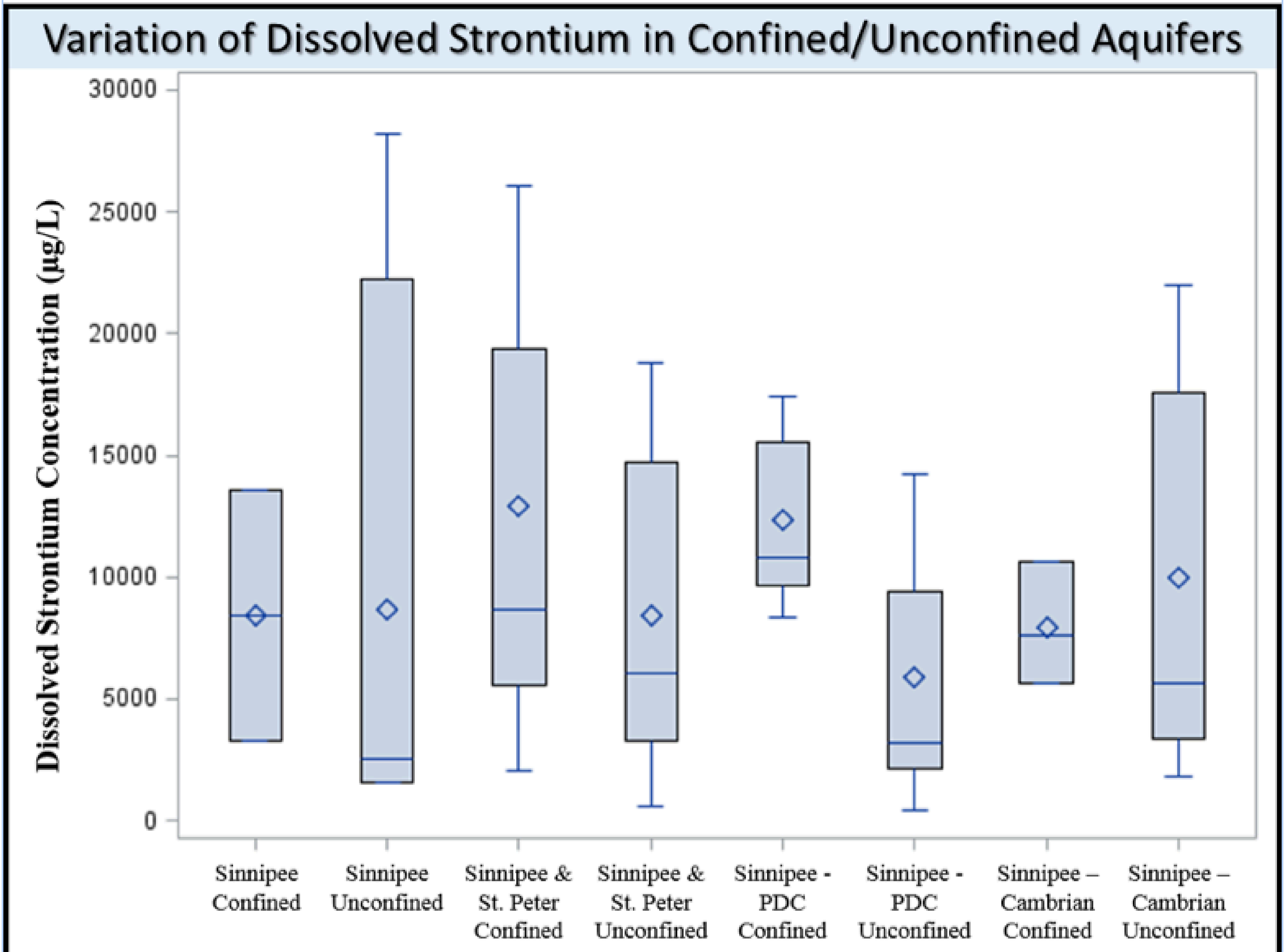


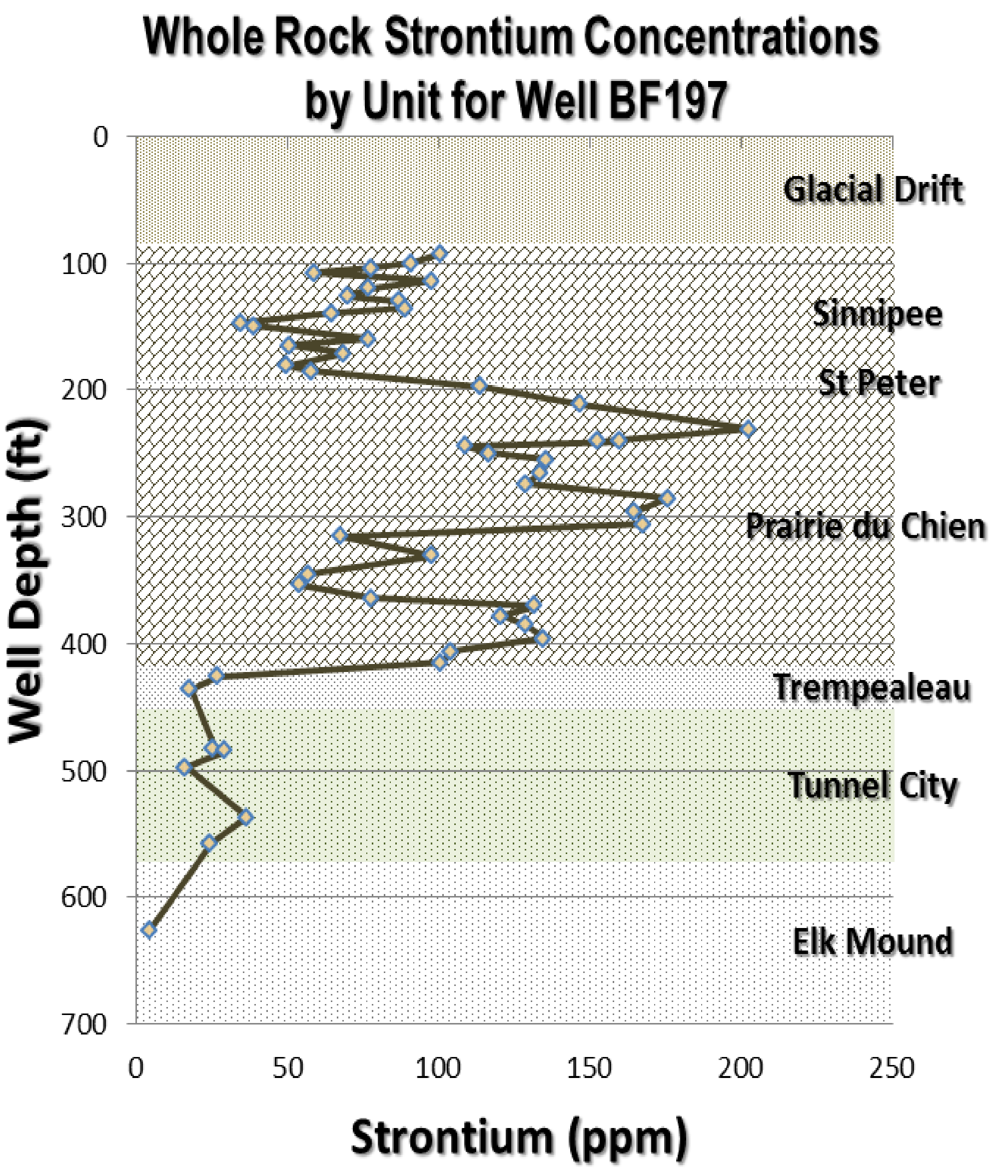
Figure 22: Boxplot showing dissolved strontium concentrations in wells open to Cambrian-Ordovician aquifer(s) and whether the well was confined (east of Maquoketa boundary) or unconfined (west of Maquoketa boundary) by the Maquoketa Shale. Top of line is the maximum, bottom of line is the minimum, top of box is the 75th percentile, bottom of box in the 25 percentile, the diamond in the box is the mean, and the line inside the rectangular box is the median. Any circle outside of the line and box is considered an outlier. This figure was created using SAS and modified using Microsoft PowerPoint.

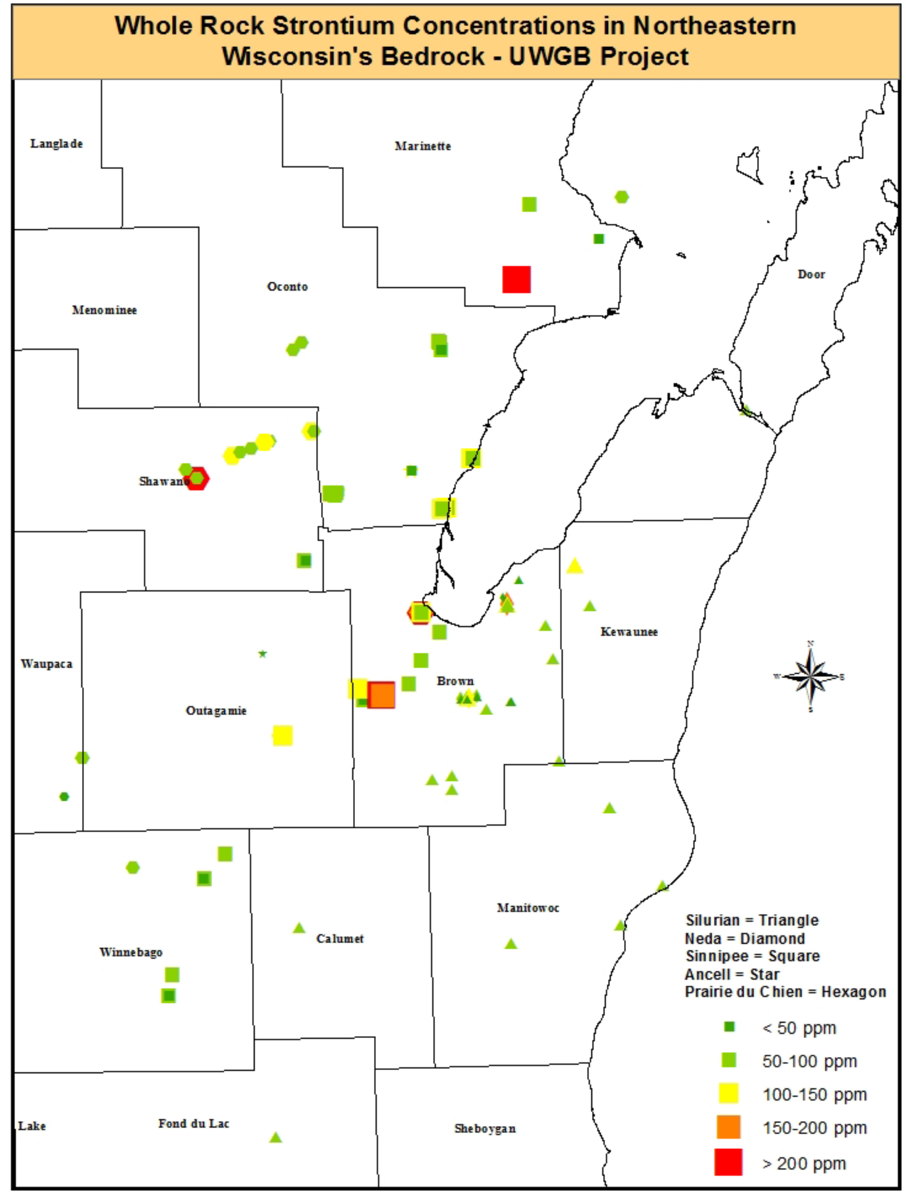
Data through March 2013

Sr Whole Rock - Luczaj & McIntire (2008)		
Rock Unit	*# Samples*	*Average (ppm)*
Silurian	36	58.9
Maquoketa – Neda	13	76.5
Sinnipee	86	78.6
St Peter (Ancell)	24	26.8
Prairie du Chien	51	106.8
Cambrian	1	87.0

Sr Whole Rock by Unit - UWGB Sr Project		
Rock Unit	*# Samples*	*Average (ppm)*
Fort Atkinson	2	93.4
Sinnipee	44	68.7
St Peter (Ancell)	10	40.1
Prairie du Chien	9	165.0
Cambrian	20	40.8
Precambrian	1	39.6

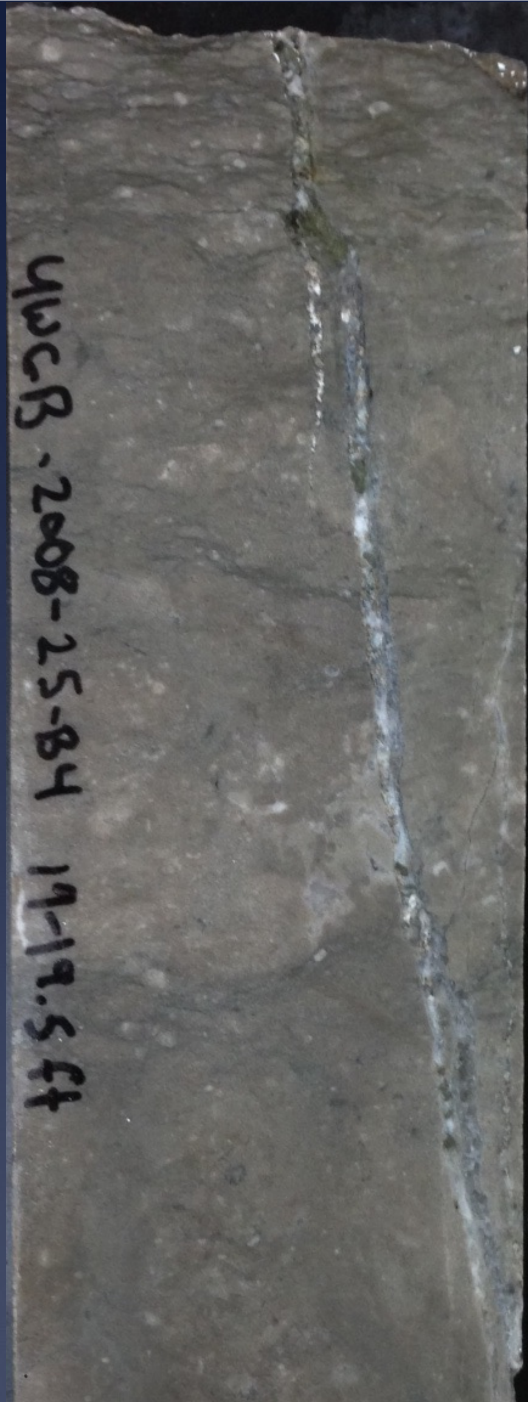
Data from this study and an ongoing study show that whole-rock Sr concentrations in dolomite and calcite are usually below 200 ppm and Always below 1,000 ppm. These whole-rock concentrations are ***not*** high enough to account for the high dissolved Strontium concentrations in eastern Wisconsin. (Sr/Ca ratios in rocks would need to be 20-6000 x higher)





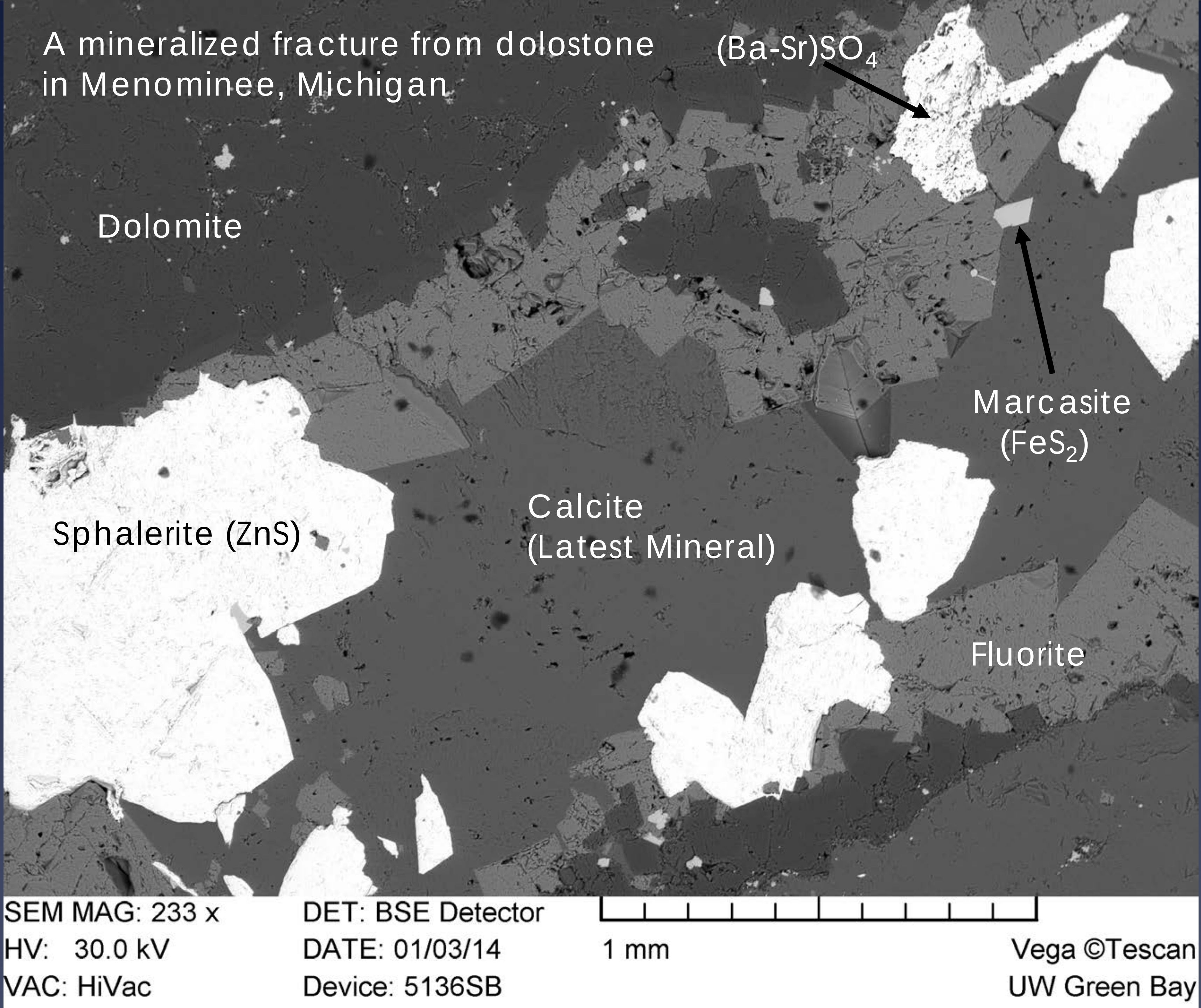
Data from Luczaj & McIntire (2008) and this study.

From Joe Baeten's Thesis (in progress)

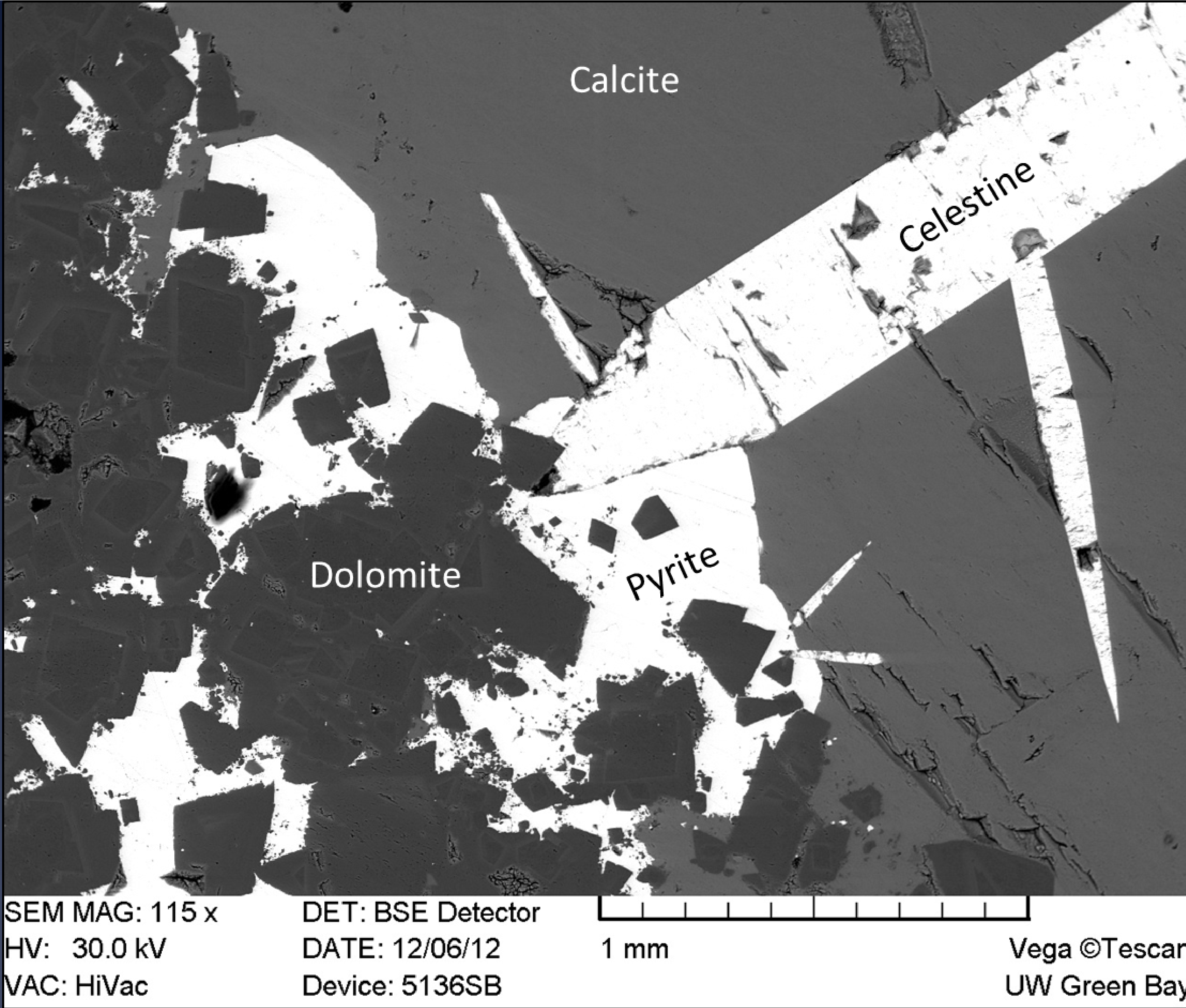


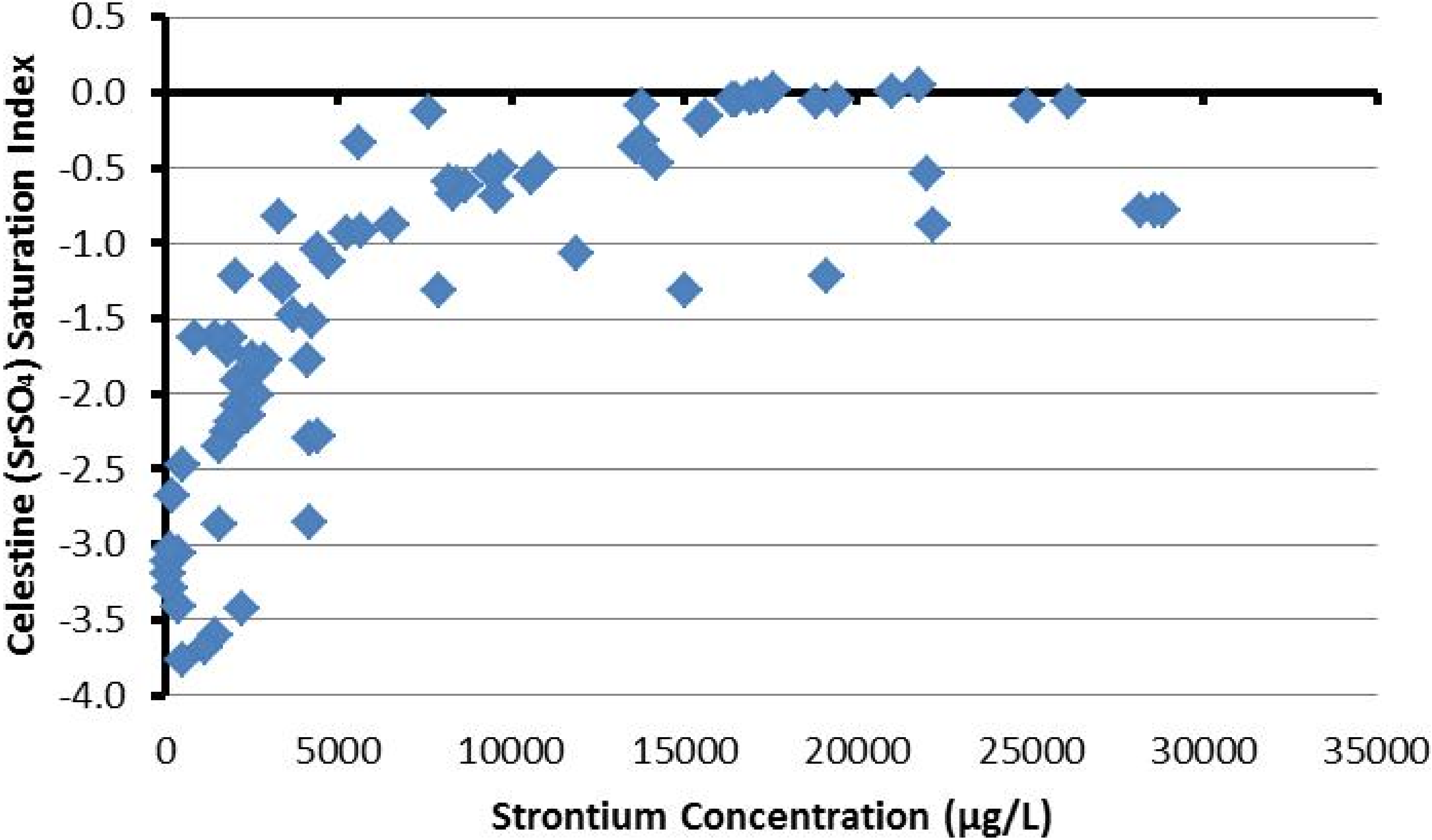
Heterogeneously distributed fractures, vugs, and intergranular cements contain a large variety of Mississippi Valley-Type minerals, ***including Sr-bearing minerals*.**

Fracture fill in drill core from Sinnipee Group Dolostone; Menomiee, Michigan


A mineralized fracture from dolostone in Menominee, Michigan
$(Ba\text{-}Sr)SO_4$
Dolomite
Marcasite (FeS_2)
Calcite (Latest Mineral)
Sphalerite (ZnS)
Fluorite
SEM MAG: 233 x
HV: 30.0 kV
VAC: HiVac
DET: BSE Detector
DATE: 01/03/14
Device: 5136SB
1 mm
Vega ©Tescan
UW Green Bay

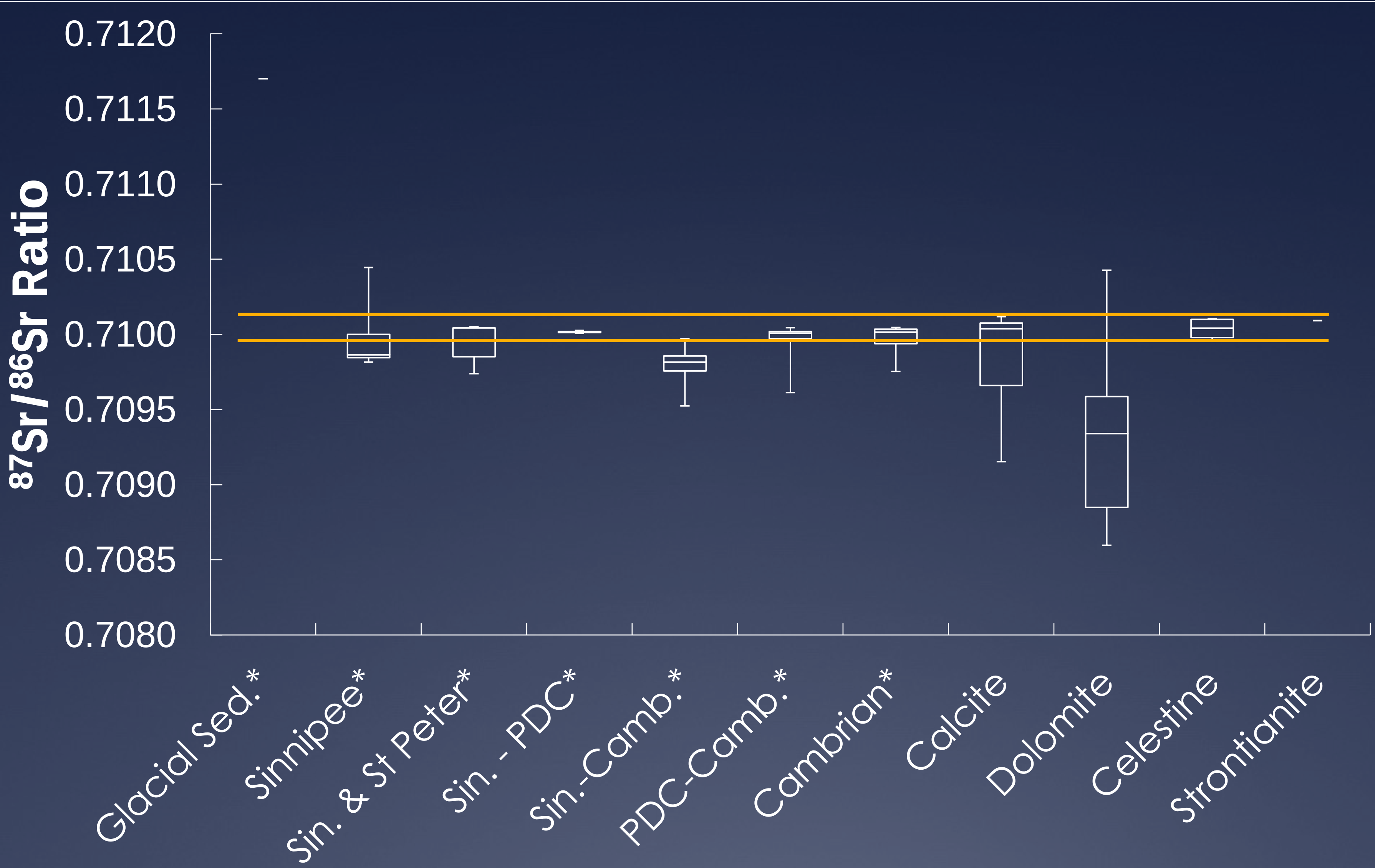
Celestine ($SrSO_4$) in dolostone from Brown County


Calcite
Celestine
Dolomite
Pyrite
SEM MAG: 115 x
HV: 30.0 kV
VAC: HiVac
DET: BSE Detector
DATE: 12/06/12
Device: 5136SB
1 mm
Vega ©Tescan
UW Green Bay



From Luczaj et al. (2013)

Strontium Isotopes Helped to Fingerprint the Source



*** Indicates groundwater sample collected from well open to specified units**

From Luczaj et al. (2013)

Sr Removal By Private Treatment Equipment			
WUWN	Percent Remaining After Softner	Percent Remaining After R/O	Percent Remaining After Iron Filter
KQ402	3.1	0.13	-
OD234	1.1	0.02	-
FP788	0.2	0.02	99.1

Sr Removal By Private Treatement Equipment			
WUWN	Raw	After Softner	After R/O
KQ402	16900	531	21.8
OD234	17100	187	2.7
FP788	22200	45.1	4.8

Sr Removal By Municipal Treatment Equipment		
WUWN	Percent Remaining After Iron Filter	Percent Remaining After Softner
TU539	97.1	26.3
TU107	-	43.4

Sr Removal By Municipal Treatment Equipment		
WUWN	Raw	After Softner
TU539	4410	1160
TU107	28800	12500

Conclusions

1. Elevated dissolved strontium is most prevalent within the Cambrian-Ordovician aquifers, with minor amounts in Silurian across a broad band in eastern Wisconsin.

2. Several hundred, if not thousands of wells exceed the EPA Lifetime Health Advisory level of 4 mg/L and possibly hundreds of wells exceed the One- and Ten-day advisory level of 25 mg/L.

3. The dissolved Sr was released by the dissolution of celestine ($SrSO_4$) – NOT mainly by dissolution of host rock dolomite, but possibly with minor amounts from calcite.

4. Compartmentalization of these aquifers due to regional fault zones is reflected in the major ion geochemistry of the groundwater.

Conclusions

5. The strontium shows a radiogenic signature consistent with a source derived from Michigan basin hydrothermal fluids and is related to the same hydrothermal system responsible for precipitating arsenic-bearing sulfide mineralization.

6. Distance from the edge of the Maquoketa subcrop and aquifer water levels do not appear to influence Sr distributions.

7. Additional elements of concern include boron (B) and lithium (Li), and in two cases boron exceeded the EPA MCL.

8. Household water softeners and RO systems should provide an adequate method of removing strontium, but municipal ion exchange systems are less effective.

Recommendations

1. We recommend that an advisory area or area of concern be established in eastern Wisconsin for strontium (Sr). Lithium (Li) and boron (B) should be analyzed in wells drawing from units confined by the Maquoketa Shale.

2. Future work should focus on areas further north and south to better define the region of high dissolved Sr.

3. Now is the best time for a detailed study assessing the health effects of high Sr on children in eastern Wisconsin to follow up on the very generalized dental health study in the 1970s.

QUESTIONS?

Aquifer composition trends toward Michigan Basin brines

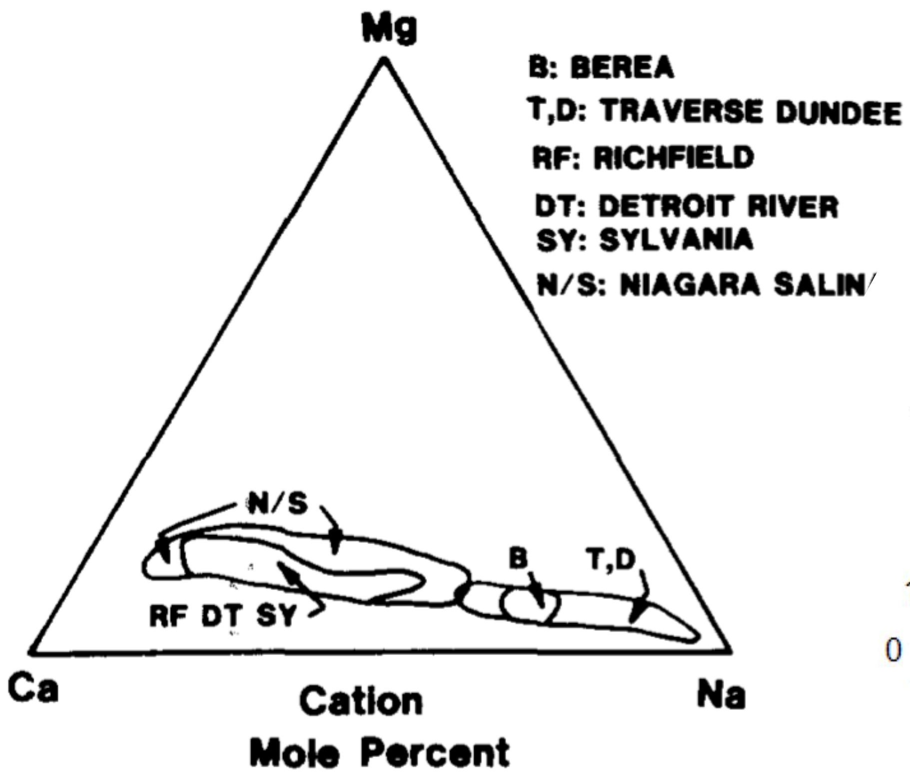
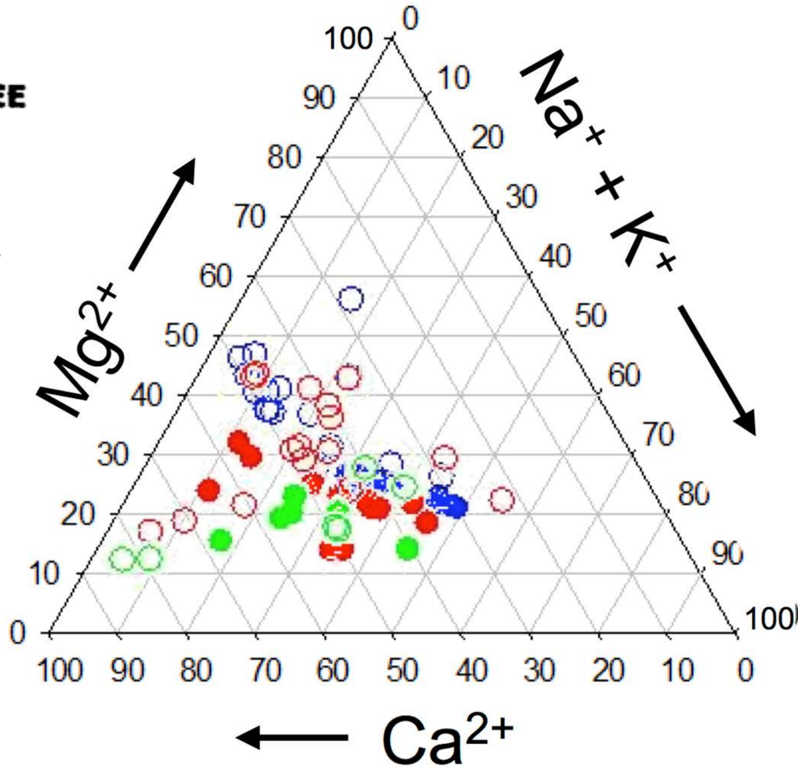


FIG. 5. Ternary diagram showing mole percentage of Ca, Mg and Na in the Michigan Basin brines.



From Wilson & Long (1993)

This Study

Table 7

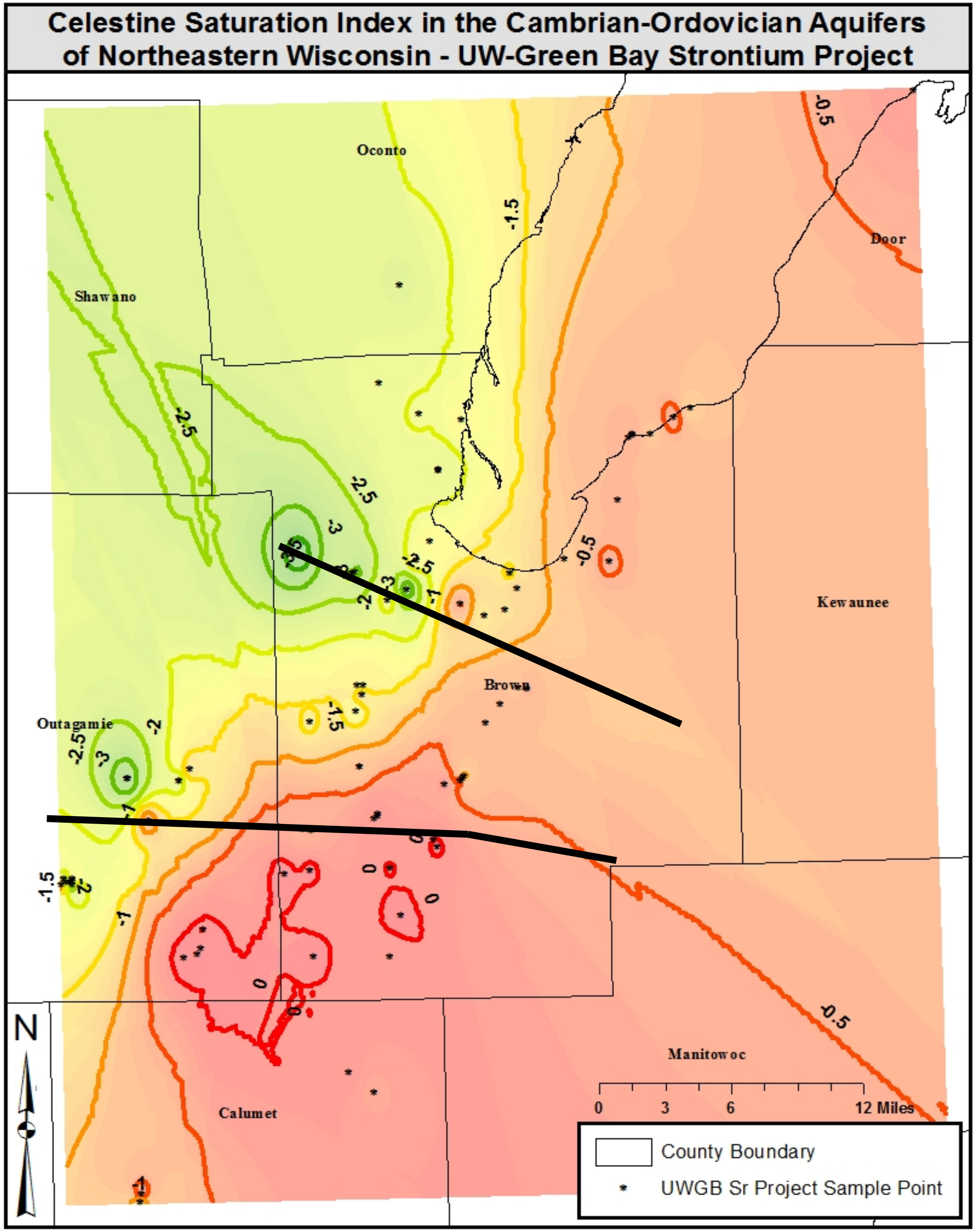
Town of Lawrence, WI Dissolved Strontium Stratigraphic Analysis			
WUWN	*Open Units*	*Feet of Open Borehole*	*Strontium (µg/L)*
SR443*	Sinnipee & PDC	255	41200
NX167*	Sinnipee & PDC	252	37420
FP788	Sinnipee	13	25200**
UA338	Sinnipee – PDC; thin sandstones	312	14200
WN502	Sinnipee – PDC; thin sandstones	318	9380
KL362	Cambrian (Elk Mound)	261.5	2850

* Samples are from those collected from Dennis Rohr of Seymour High School. All other samples used for this analysis are from the UWGB Sr Project.
** Well was sampled twice for the UWGB Sr Project and was average for this analysis. The two samples collected and analyzed had values of 28200 & 22200 µg/L.

Table 8

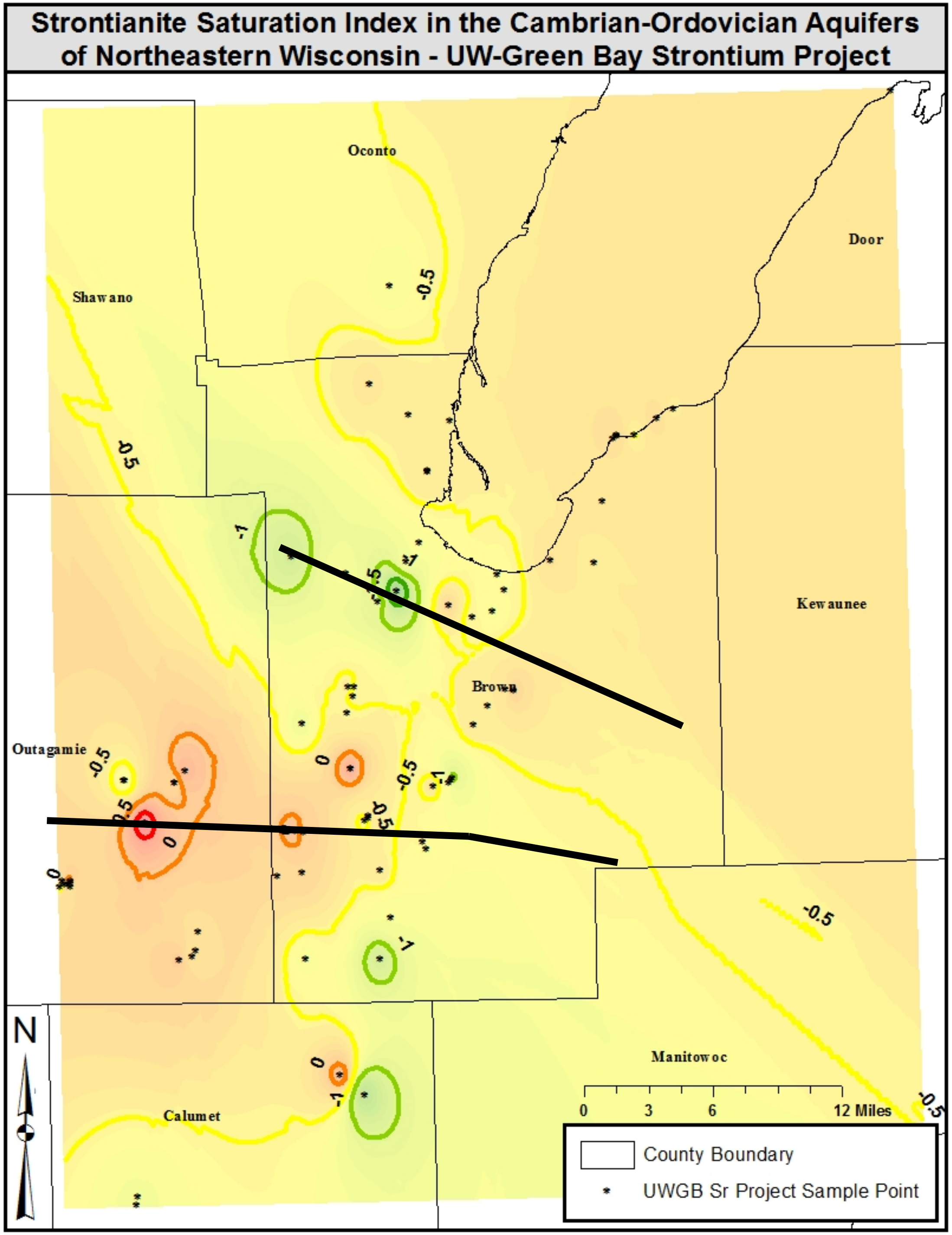
Town of Freedom, WI Dissolved Strontium Stratigraphic Analysis			
WUWN	*Open Units*	*Feet of Open Borehole*	*Strontium (µg/L)*
HN208	Sinnipee	97	1580
QK574	Sinnipee & St. Peter	59	7890
GK225	St. Peter	100	1140
TU107	Cambrian (Tunnel City)	98	28700*
TU539	Cambrian (Elk Mound)	270	4285*

* These wells were sampled twice. Numbers show in table indicate the average of both samples.



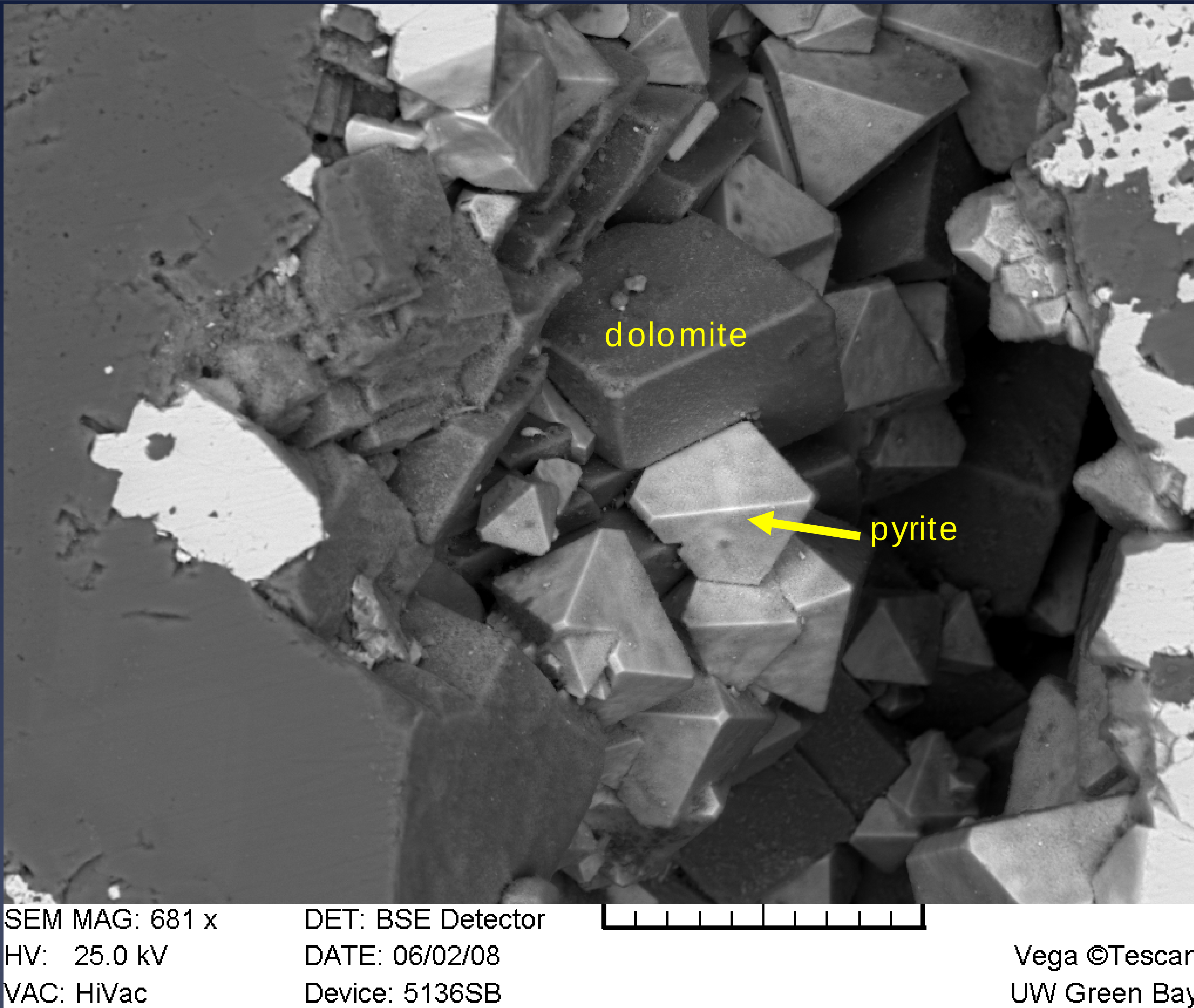
Celestine Saturation Index also shows some relationship to regional fault zones.

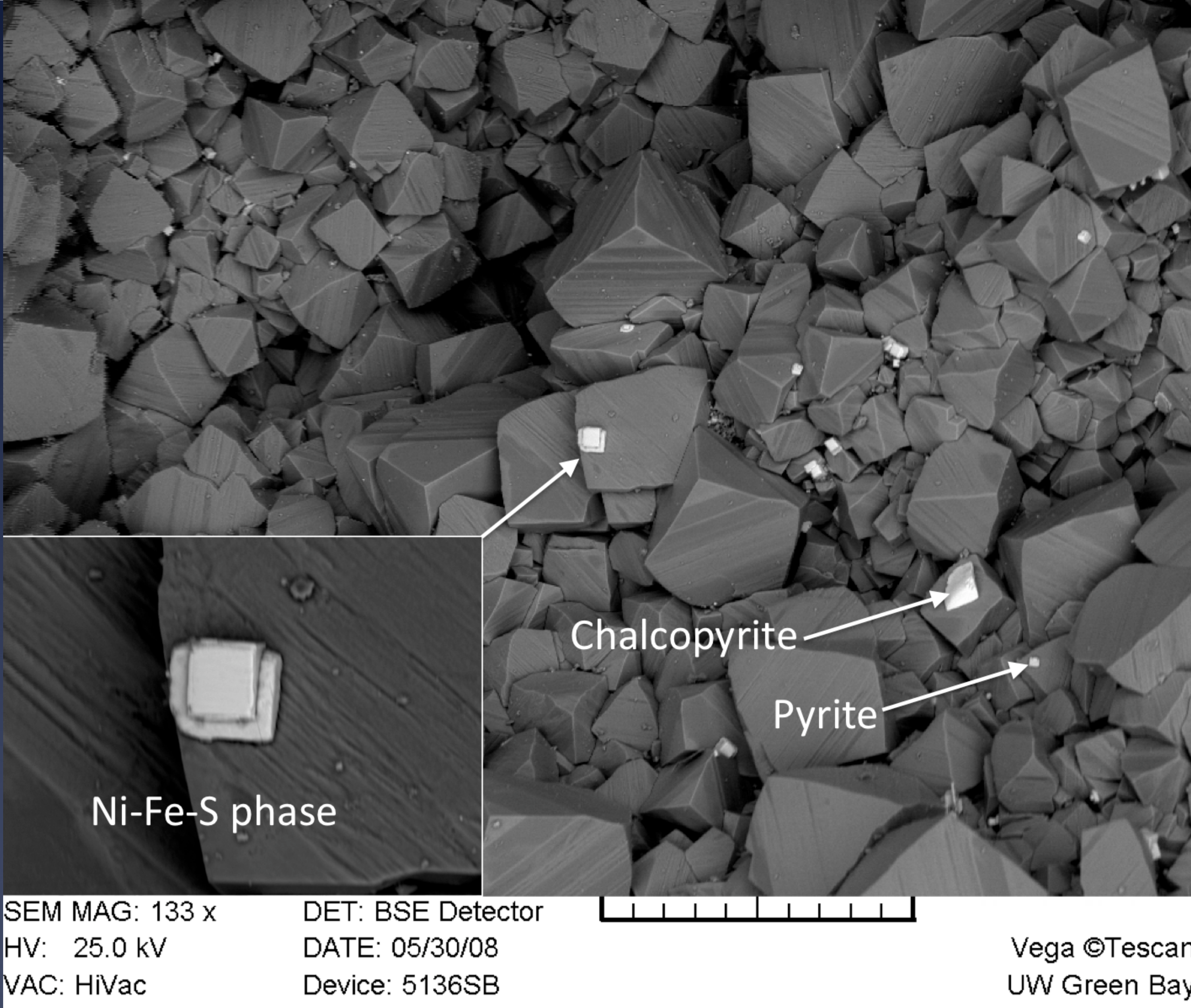
Data Through March 2013



Most areas are Undersaturated, except for Lawrence and Outagamie County.

Data Through March 2013


dolomite
pyrite
SEM MAG: 681 x
HV: 25.0 kV
VAC: HiVac
DET: BSE Detector
DATE: 06/02/08
Device: 5136SB
Vega ©Tescan
UW Green Bay


Ni-Fe-S phase
Chalcopyrite
Pyrite
SEM MAG: 133 x
HV: 25.0 kV
VAC: HiVac
DET: BSE Detector
DATE: 05/30/08
Device: 5136SB
Vega ©Tescan
UW Green Bay

Title: An Evaluation of the Distribution and Sources of Dissolved Strontium in the Groundwater of Eastern Wisconsin, with a Focus on Brown and Outagamie Counties.

Project I.D.: UWS Project Number WR12R0004

Investigators:

Principal Investigators:

Dr. John Luczaj, Associate Professor (Geoscience)
Dr. Michael Zorn, Associate Professor (Chemistry)
University of Wisconsin – Green Bay

Research Assistants:

Joseph Baeten, M.S. Candidate, Environmental Science & Policy Graduate Program, University of Wisconsin – Green Bay

Mick Kiehl, Undergraduate Assistant, Geoscience Major
University of Wisconsin – Green Bay

Period of Contract: 7/1/2012 – 6/30/2013

Strontium, Fluoride, & Salts

1. Strontium and fluoride can both cause tooth and bone deformities (strontium rickets, and enamel mottling)

2. Highest Strontium occurs in Eastern Wisconsin – especially in the Cambrian & Ordovician aquifers.

3. Salty water (> 500 mg/L total dissolved solids) is also a problem. Our recent study showed ~ 61% of the wells (71 of 115) have TDS > 500 mg/L, the EPA secondary MCL.