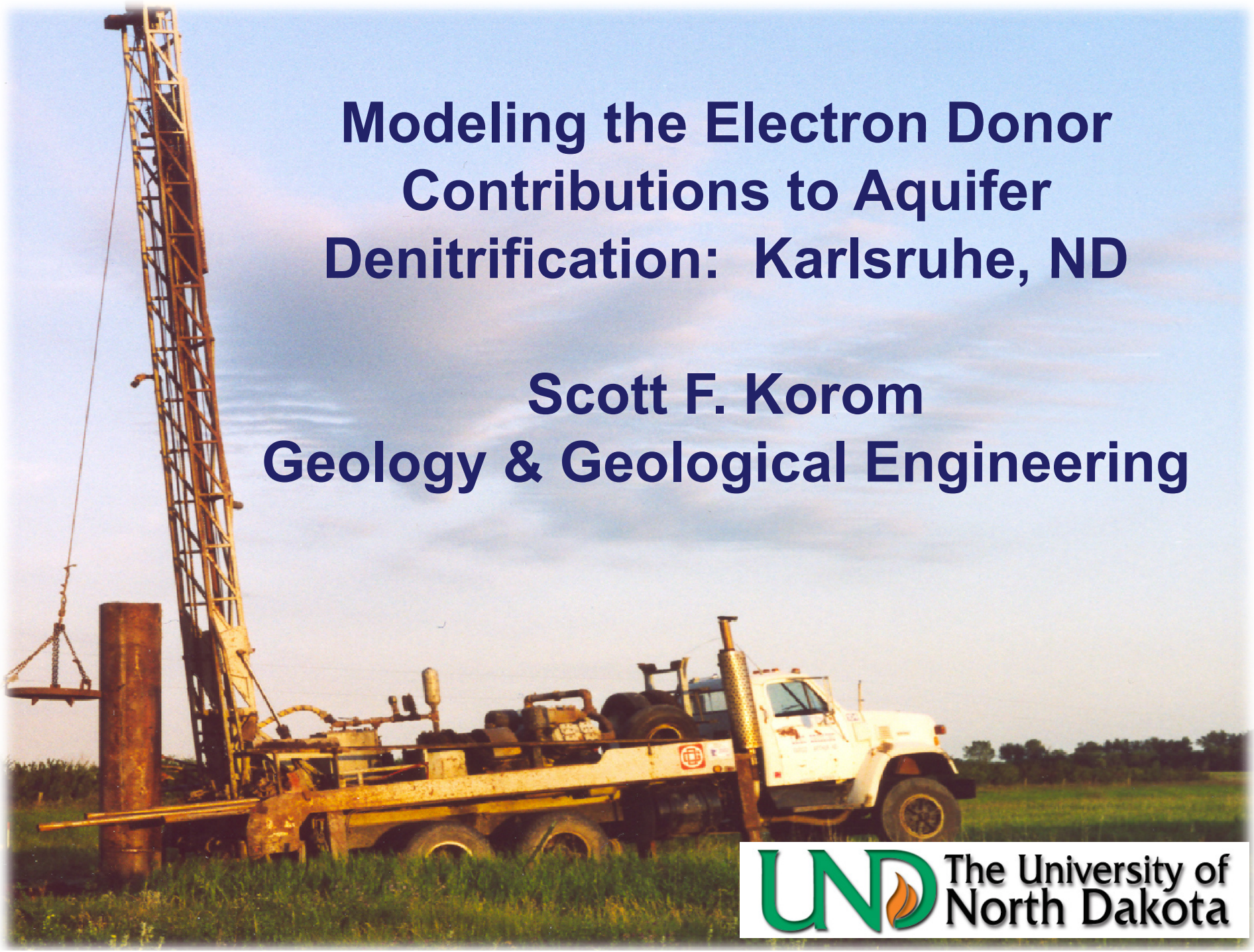
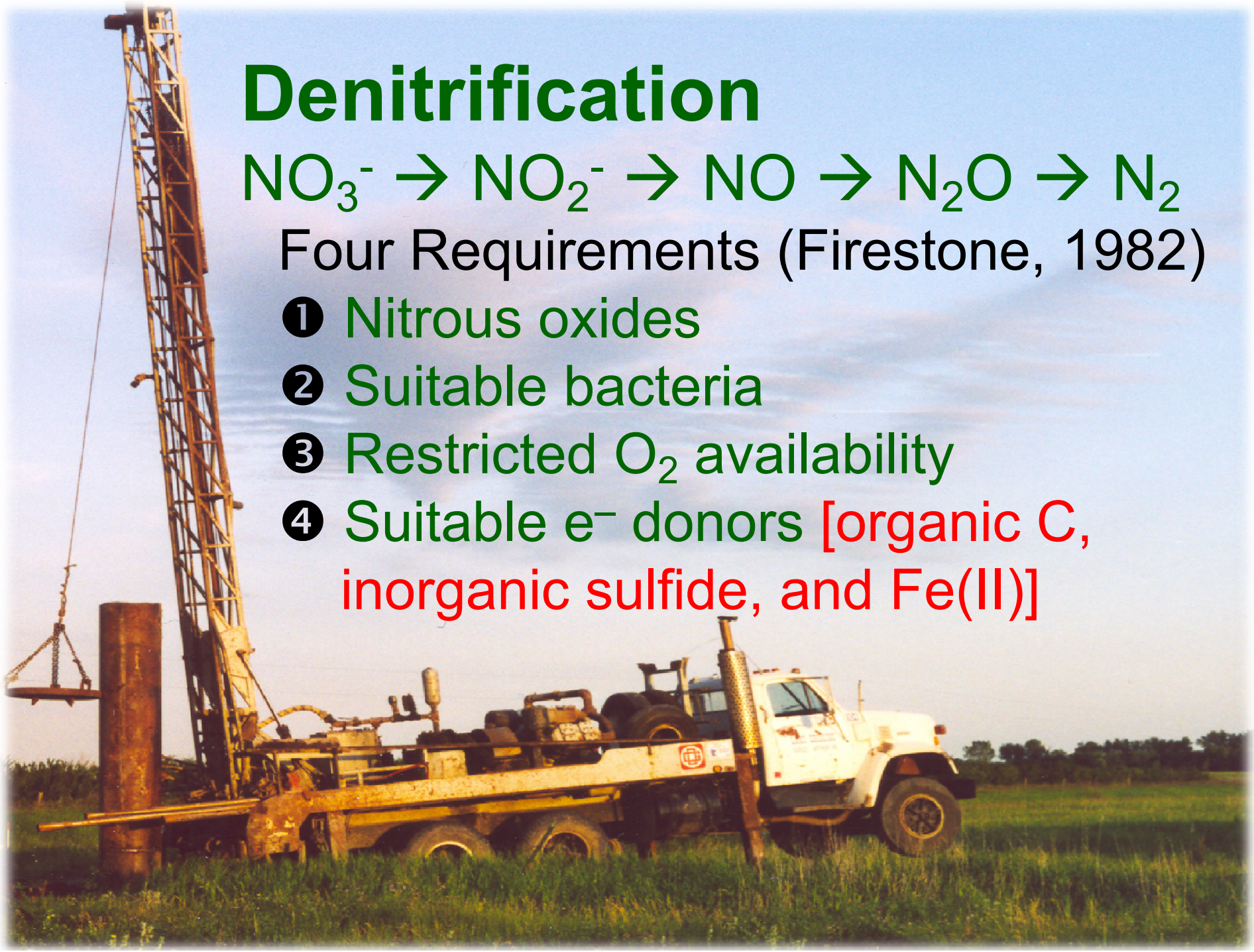


Modeling the Electron Donor Contributions to Aquifer Denitrification: Karlsruhe, ND

Scott F. Korom
Geology & Geological Engineering

The University of North Dakota



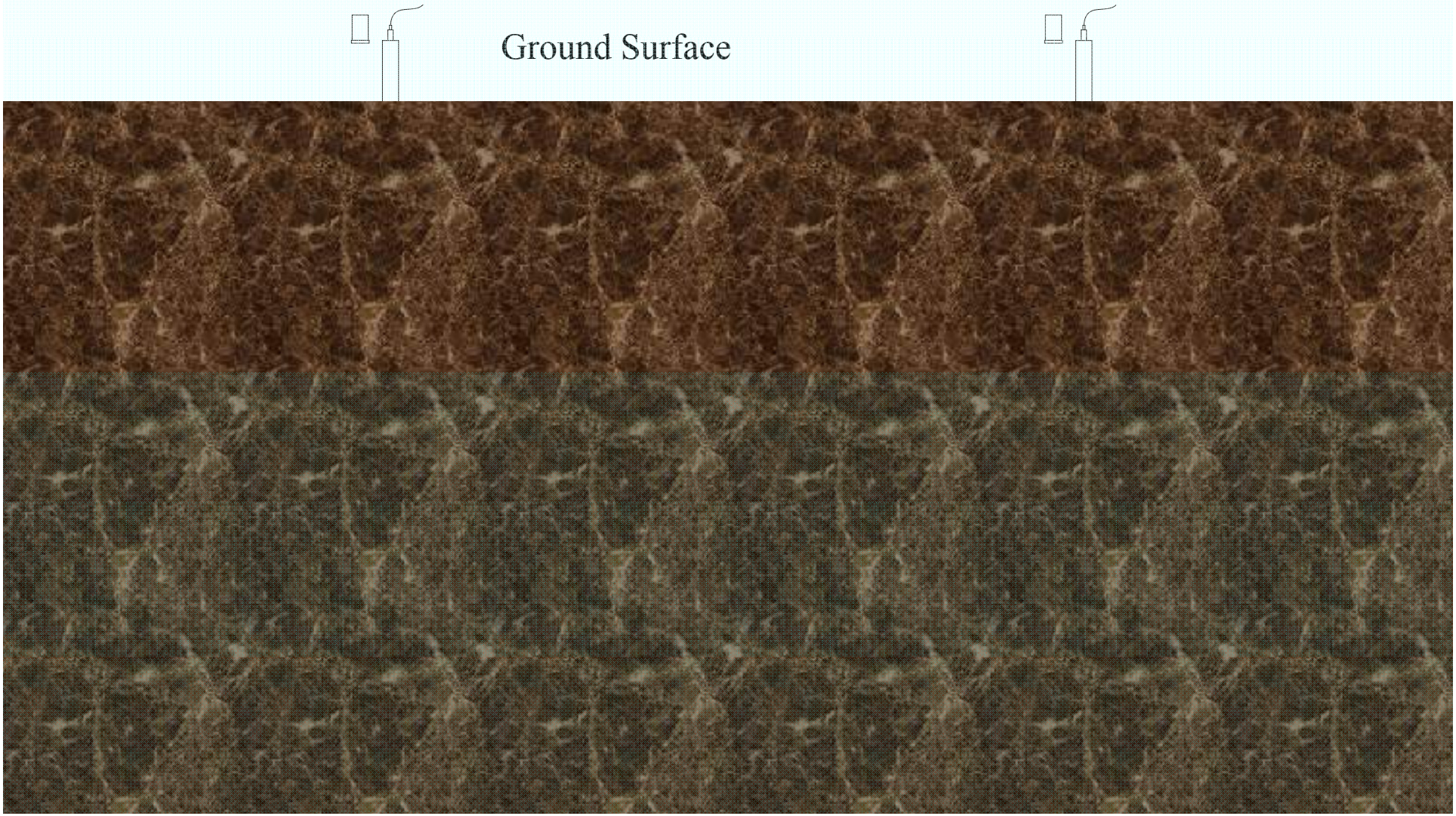
Denitrification

$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$

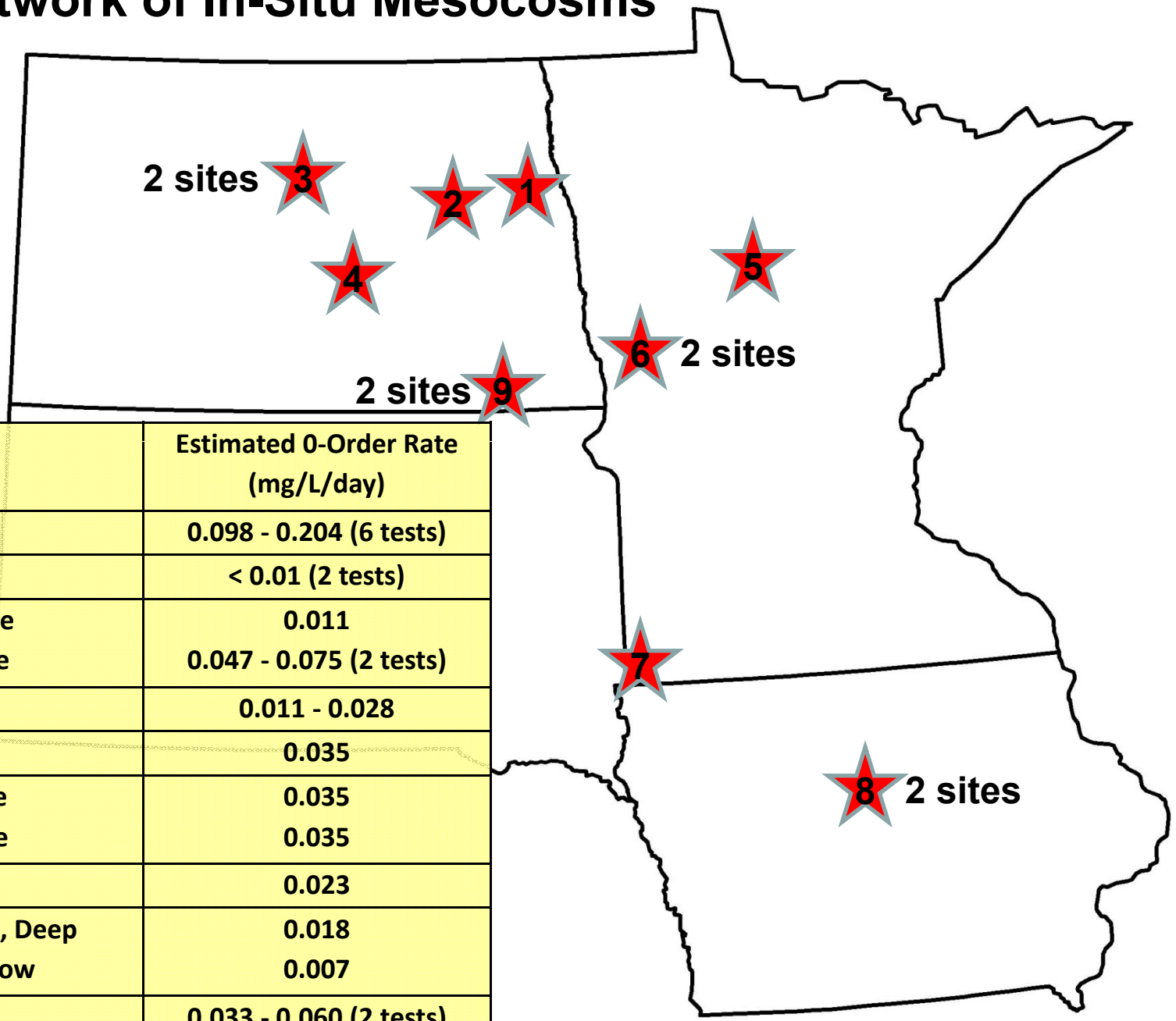
Four Requirements (Firestone, 1982)

1. Nitrous oxides
2. Suitable bacteria
3. Restricted O_2 availability
4. Suitable e^- donors [organic C, inorganic sulfide, and Fe(II)]

ISMs: Finished Product

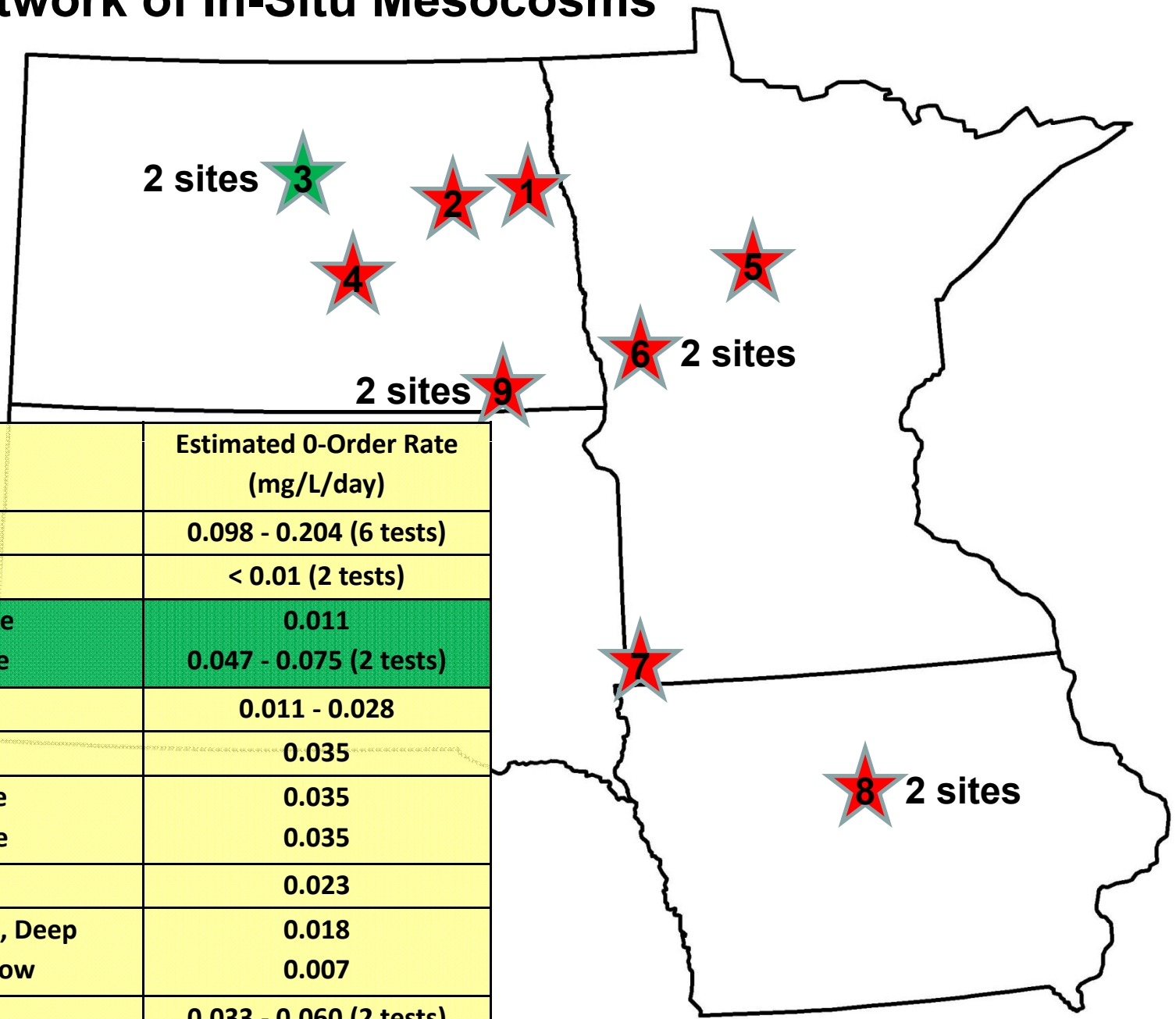


Network of In-Situ Mesocosms



Site	Estimated 0-Order Rate (mg/L/day)
1. Larimore, ND	0.098 - 0.204 (6 tests)
2. Hamar, ND	< 0.01 (2 tests)
3. Karlsruhe, ND, G Site 3. Karlsruhe, ND, S Site	0.011 0.047 - 0.075 (2 tests)
4. Robinson, ND	0.011 - 0.028
5. Akeley, MN	0.035
6. Perham, MN, M Site 6. Perham, MN, W Site	0.035 0.035
7. Luverne, MN	0.023
8. New Providence, IA, Deep 8. New Prov., IA, Shallow	0.018 0.007
9. Oakes C1 9. Oakes G1	0.033 - 0.060 (2 tests) 0.28 - 0.59 (2 tests)

Network of In-Situ Mesocosms



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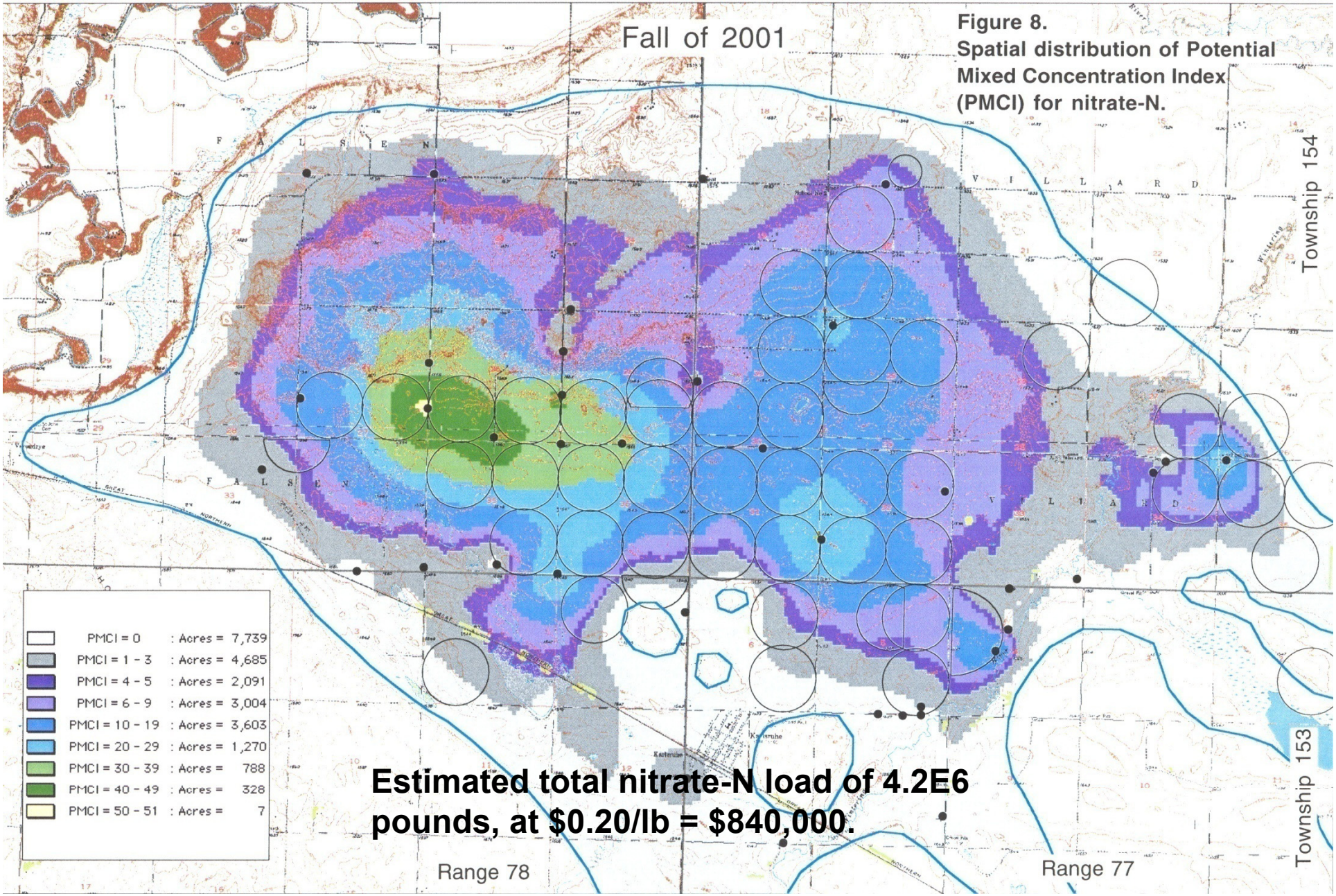
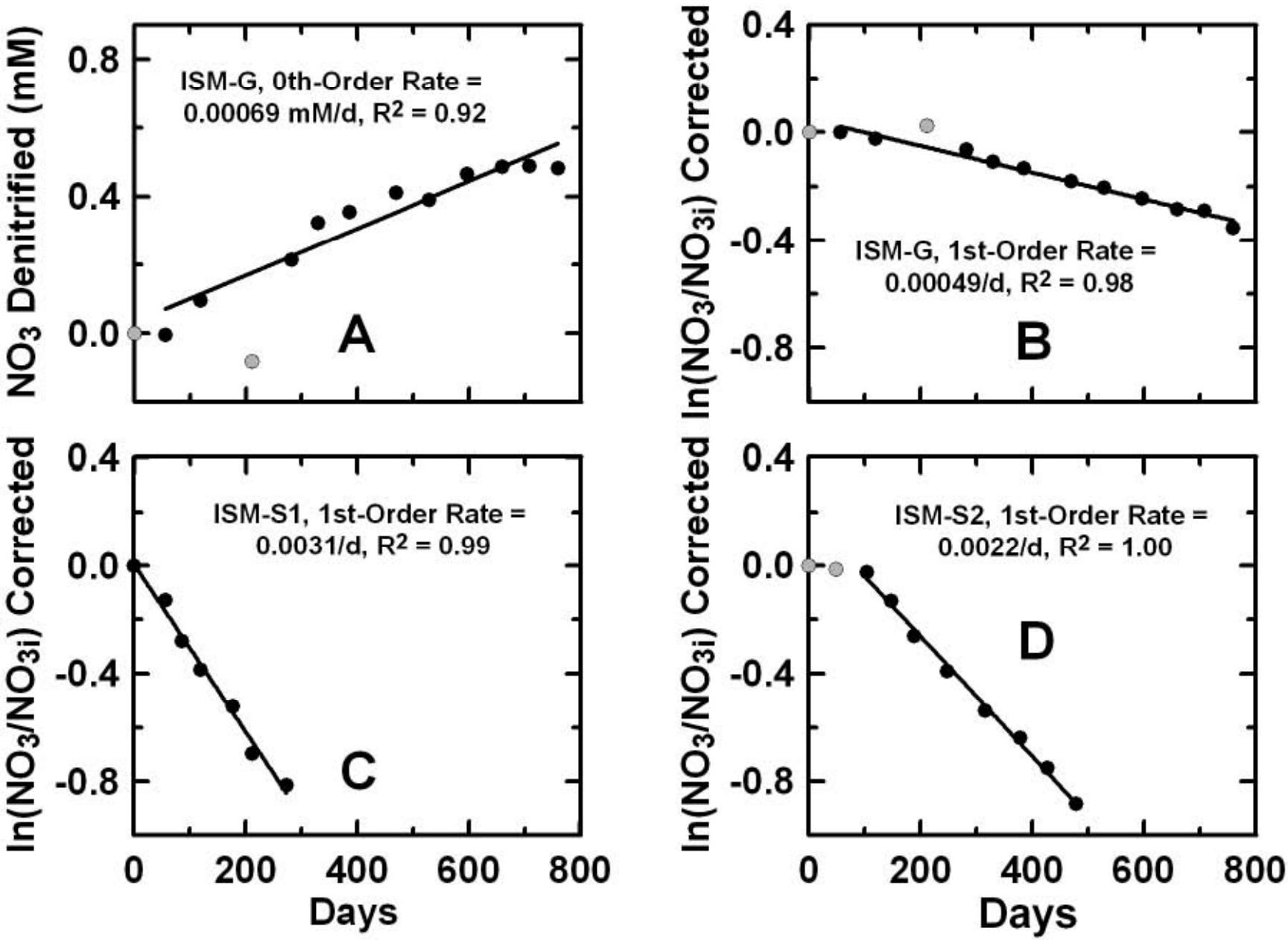
Adapted from Schuh et al. (2003)





Korom et al. (2012)

Table 1. Concentrations of dissolved ions measured in water samples collected from tracer tests in the Karlsruhe in situ mesocosms. All analyte values are mM, except for pH, which is in standard units, and $\delta^{15}N$, which is in permil.

Karlsruhe S ISM Tracer Test 1

Date	Days	Na	K	Ca	Mg	Mn	Fe	NH_3-N	Al	Ba
25 Aug 2003	0	8.48	0.14	2.62	1.70	0.015	0.00018	0.00842	< 0.0019	0.0029
20 Oct 2003	56	7.66	0.15	2.40	1.56	0.016	< 0.00018	Not done	< 0.0019	0.0026
19 Nov 2003	86	6.83	0.15	2.20	1.44	0.014	0.00036	0.00807	< 0.0019	0.0025
22 Dec 2003	119	5.96	0.14	2.05	1.33	0.013	< 0.00018	< 0.00071	< 0.0019	0.0020
18 Feb 2004	177	5.83	0.15	2.17	1.42	0.014	0.00023	< 0.00071	< 0.0019	0.0026
23 Mar 2004	211	5.48	0.15	2.12	1.39	0.014	< 0.00018	0.00129	< 0.0019	0.0022
24 May 2004	273	4.87	0.14	2.10	1.38	0.013	0.00030	< 0.00071	< 0.0019	0.0022

Karlsruhe S ISM Tracer Test 1 (continued)

Date	SiO_2	pH	F	Cl	SO_4	NO_3-N	Br	Inorg C	$\delta^{15}N$
25 Aug 2003	0.363	7.56	0.0050	0.15	1.16	6.30	0.637	7.68	0.63
20 Oct 2003	0.296	7.58	0.0057	0.13	1.18	5.25	0.602	7.68	
19 Nov 2003	0.261	7.50	0.0063	0.14	1.27	3.63	0.482	7.63	5.09
22 Dec 2003	0.240	7.70	0.0062	0.14	1.23	3.08	0.457	7.74	
18 Feb 2004	0.250	7.74	0.0057	0.13	1.32	2.31	0.397	7.76	10.05
23 Mar 2004	0.243	7.71	0.0061	0.14	1.34	1.50	0.304	8.18	
24 May 2004	0.233	7.62	0.0048	0.12	1.35	1.24	0.282	7.55	

Nitrate to 20% of initial value;
Bromide to 44% of initial value.

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Karlsruhe S ISM Tracer Test 1 (continued)

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Table 2. Saturation indices for the dissolved ion data measured for water samples collected in the in-situ mesocosms given in Table 1.

Karlsruhe S ISM Tracer Test 1

Date	Barite	Gypsum	Epsomite	Jarosite-K	Calcite	Magnesite	Quartz
25 Aug 2003	1.13	-1.53	-4.05	-7.16	0.41	-0.39	0.76
20 Oct 2003	1.11	-1.54	-4.07	-7.13	0.41	-0.40	0.68
19 Nov 2003	1.15	-1.53	-4.05	-6.30	0.29	-0.51	0.62
22 Dec 2003	1.05	-1.56	-4.09	-6.73	0.48	-0.32	0.58
18 Feb 2004	1.19	-1.51	-4.03	-6.09	0.55	-0.26	0.60
23 Mar 2004	1.13	-1.51	-4.03	-6.62	0.53	-0.27	0.59
24 May 2004	1.14	-1.50	-4.02	-5.99	0.40	-0.40	0.57

Barite ($BaSO_4$)

Gypsum ($CaSO_4 \cdot 2H_2O$)

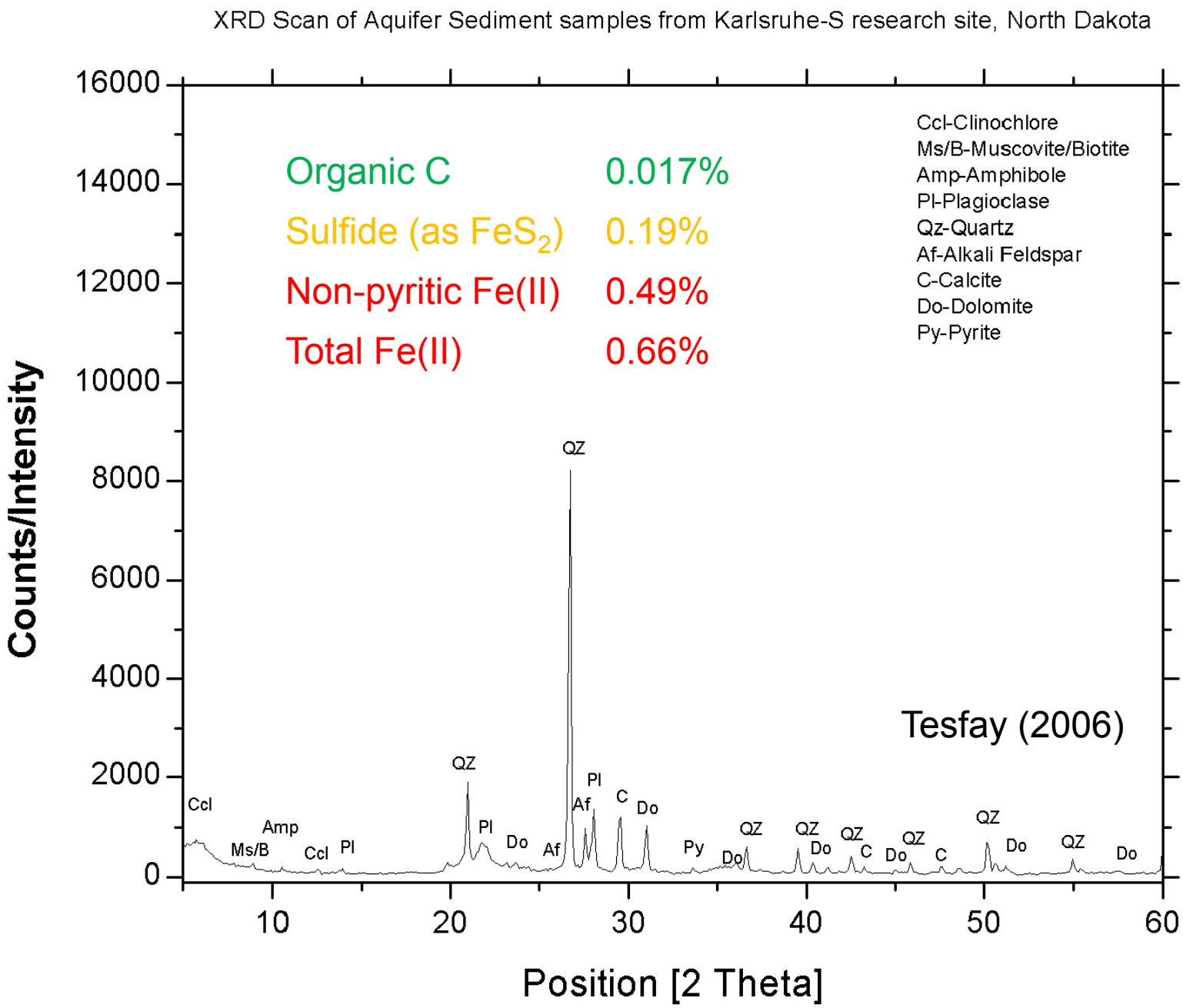
Epsomite ($MgSO_4 \cdot 7H_2O$)

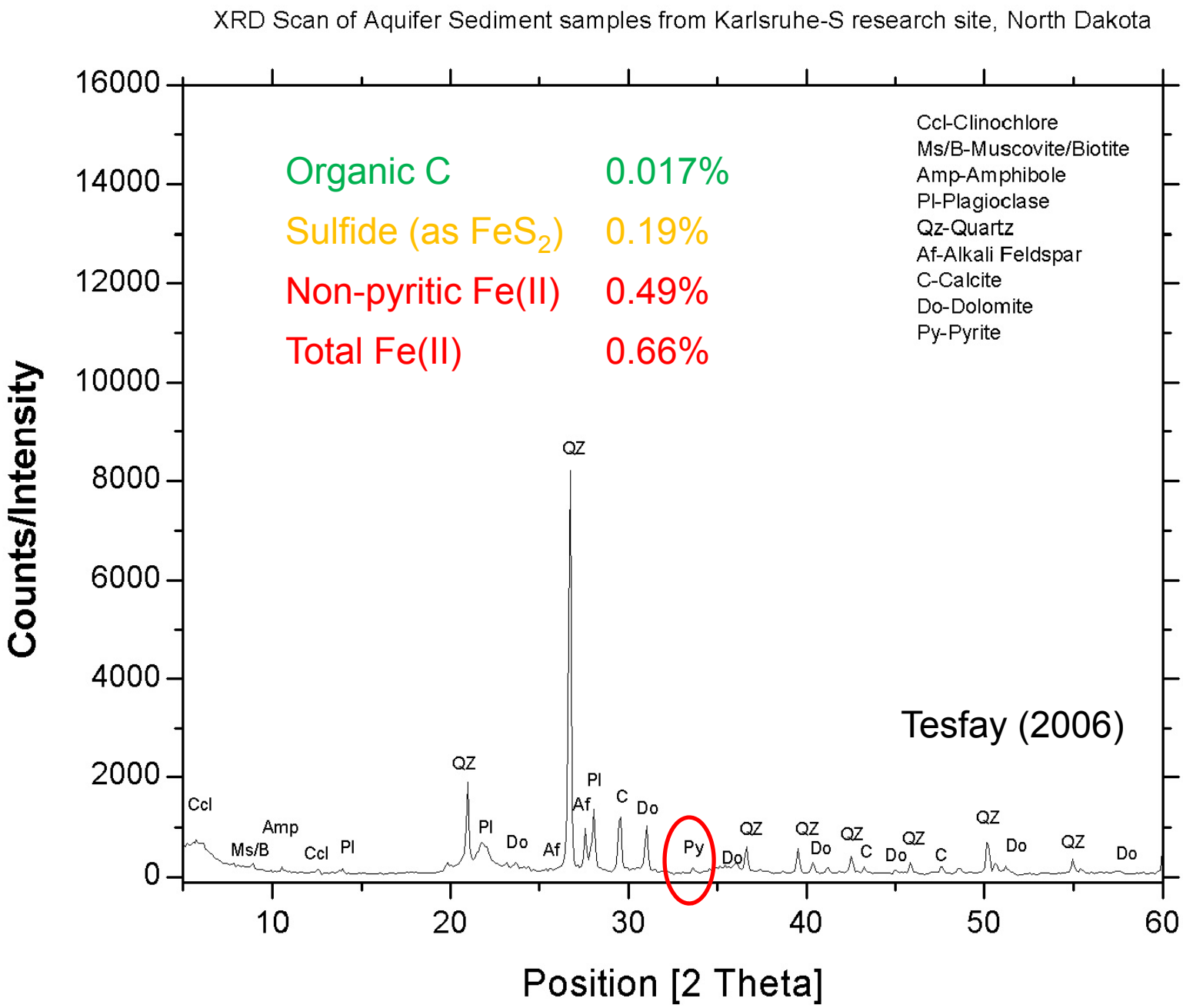
Jarosite-K [$KFe_3(SO_4)_2(OH)_6$]

Calcite ($CaCO_3$)

Magnesite ($MgCO_3$)

Quartz (SiO_2)


XRD Scan of Aquifer Sediment samples from Karlsruhe-S research site, North Dakota
Organic C 0.017%
Sulfide (as FeS2) 0.19%
Non-pyritic Fe(II) 0.49%
Total Fe(II) 0.66%
Ccl-Clinochlore
Ms/B-Muscovite/Biotite
Amp-Amphibole
Pl-Plagioclase
Qz-Quartz
Af-Alkali Feldspar
C-Calcite
Do-Dolomite
Py-Pyrite
Tesfay (2006)
Counts/Intensity
Position [2 Theta]
16000
14000
12000
10000
8000
6000
4000
2000
0
10
20
30
40
50
60
Ccl
Amp
Ms/B
Ccl
Pl
QZ
Pl
Do
Af
QZ
Af
Pl
C
Do
Py
Do
QZ
QZ
Do
QZ
C
Do
QZ
C
QZ
Do
QZ
Do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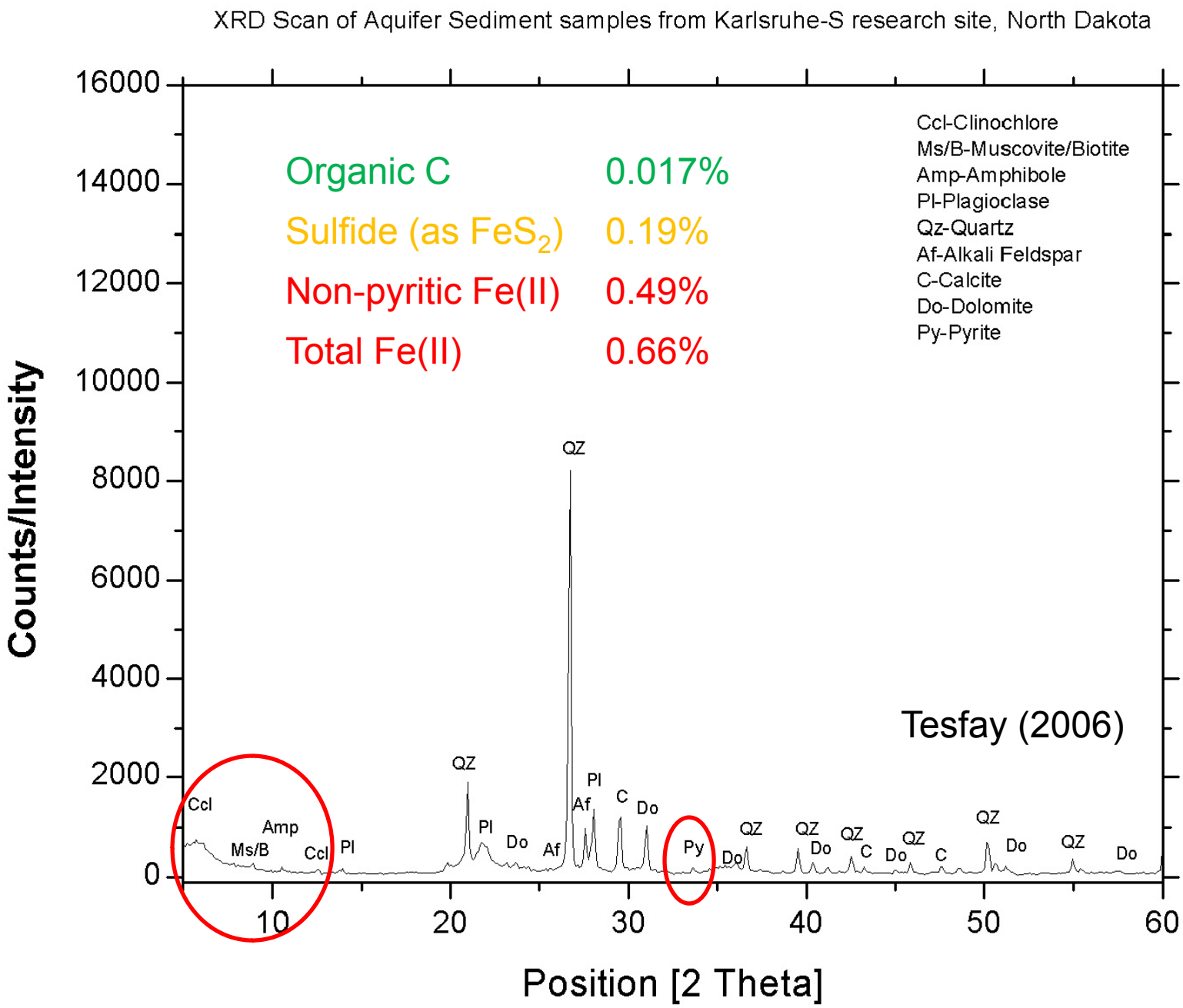
Py-Pyrite
Tesfay (2006)
Counts/Intensity
Position [2 Theta]
16000
14000
12000
10000
8000
6000
4000
2000
0
10
20
30
40
50
60
Ccl
Amp
Ms/B
Ccl
Pl
QZ
Pl
Do
Af
QZ
Af
Pl
C
Do
Py
Do
QZ
QZ
Do
QZ
C
Do
QZ
C
QZ
Do
QZ
Do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Py-Pyrite
Tesfay (2006)
Counts/Intensity
Position [2 Theta]
16000
14000
12000
10000
8000
6000
4000
2000
0
10
20
30
40
50
60
Ccl
Amp
Ms/B
Ccl
Pl
QZ
Pl
Do
Af
QZ
Pl
Af
C
Do
Py
Do
QZ
QZ
Do
QZ
C
Do
QZ
C
QZ
Do
QZ
Do

Geochemical Modeling of Denitrification at Karlsruhe S Site

Denitrification half-reaction:

$2NO_3^- + 12H^+ + 10e^- \leftrightarrow N_2 + 6H_2O$

e^- Donor half-reactions:

Organic Carbon

$CH_2O + H_2O \leftrightarrow CO_2 + 4H^+ + 4e^-$

Pyrite

$FeS_2 + 8H_2O \leftrightarrow 2SO_4^{2-} + Fe^{3+} + 16H^+ + 15e^-$

Table 3. Concentrations of dissolved ions measured in water samples collected from tracer tests in the Karlsruhe in situ mesocosms. All analyte values are mM.

Karlsruhe S ISM Tracer Test 1

Date	Days	Na	K	Ca	Rel Ca	Mg	Rel Mg
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23 Mar 2004	211	5.48	0.15	2.12	0.809	1.39	0.818
24 May 2004	273	4.87	0.14	2.10	0.802	1.38	0.812

Mössbauer analysis showed Fe(II)/Total Fe = 50 – 65%.

XRD analysis showed Fe(II) minerals present were:

Clinochlore $[(Mg,Fe^{2+})5Al(Si_3Al)O_{10}(OH)_8]$

Biotite $[K(Mg,Fe^{2+})_3(Al,Fe^{3+})Si_3O_{10}(OH)_2]$

Amphibole $[(Ca_2Mg_2 1.5Fe^{2+}Fe^{3+})Si_8O_{22}(OH)_2]$ “Minimizing“ Fe(II)
$[(4Fe^{2+}2Fe^{3+})Si_8O_{22}(OH)_2]$ “Maximizing” Fe(II)

Geochemical Modeling of Denitrification at Karlsruhe S Site

Denitrification half-reaction:

$2NO_3^- + 12H^+ + 10e^- \leftrightarrow N_2 + 6H_2O$

e^- Donor half-reactions (continued):

Ferrous Iron

$Ca_2Mg_2Fe_{2.5}Si_8O_{22}(OH)_2 + 14H^+ + 8H_2O \leftrightarrow 2Ca^{2+} + 2Mg^{2+} + 1.5Fe^{2+} + Fe^{3+} + 8H_4SiO_4$

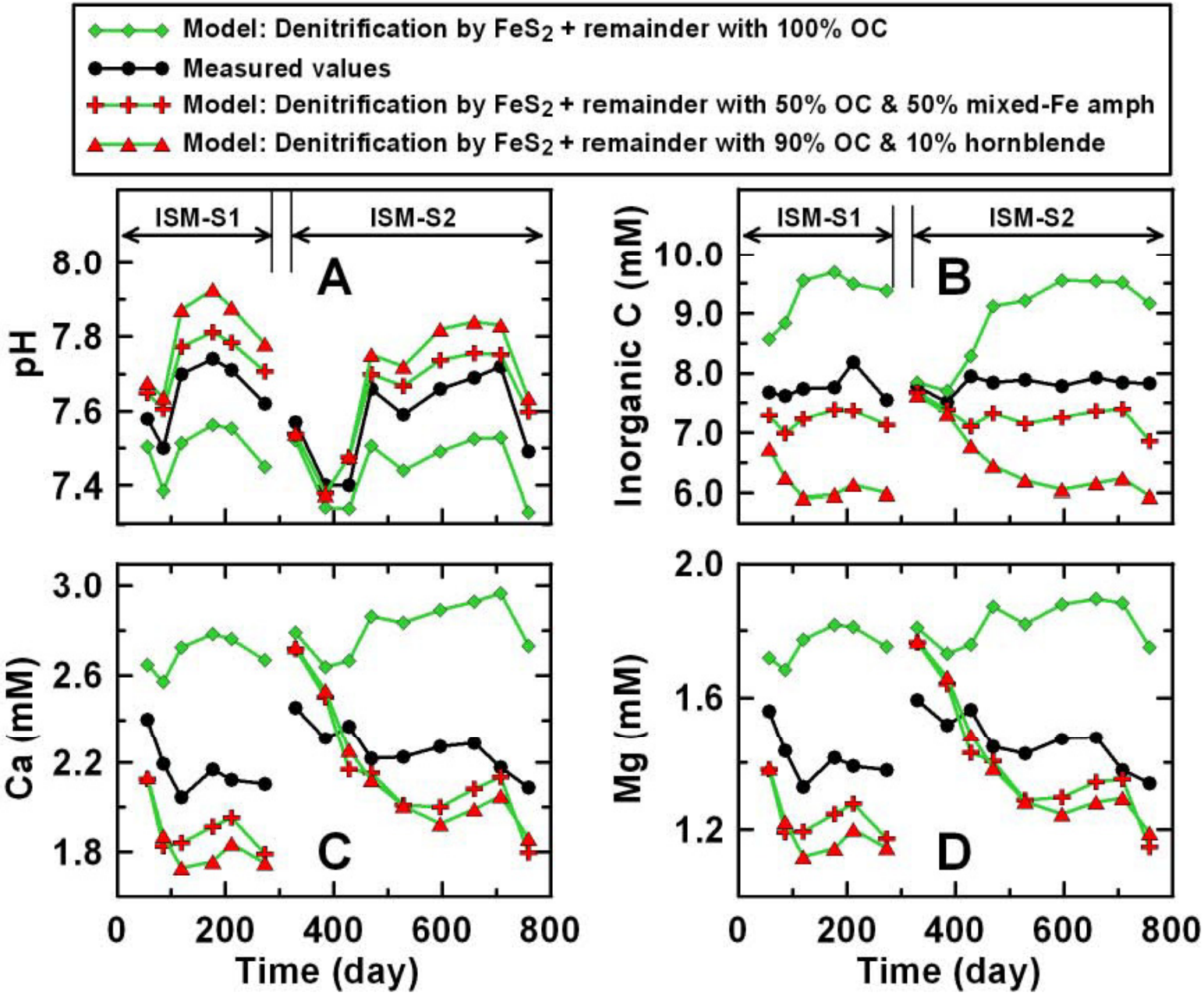
OR

$Fe_6Si_8O_{22}(OH)_2 + 14H^+ + 8H_2O \leftrightarrow 4Fe^{2+} + 2Fe^{3+} + 8H_4SiO_4$

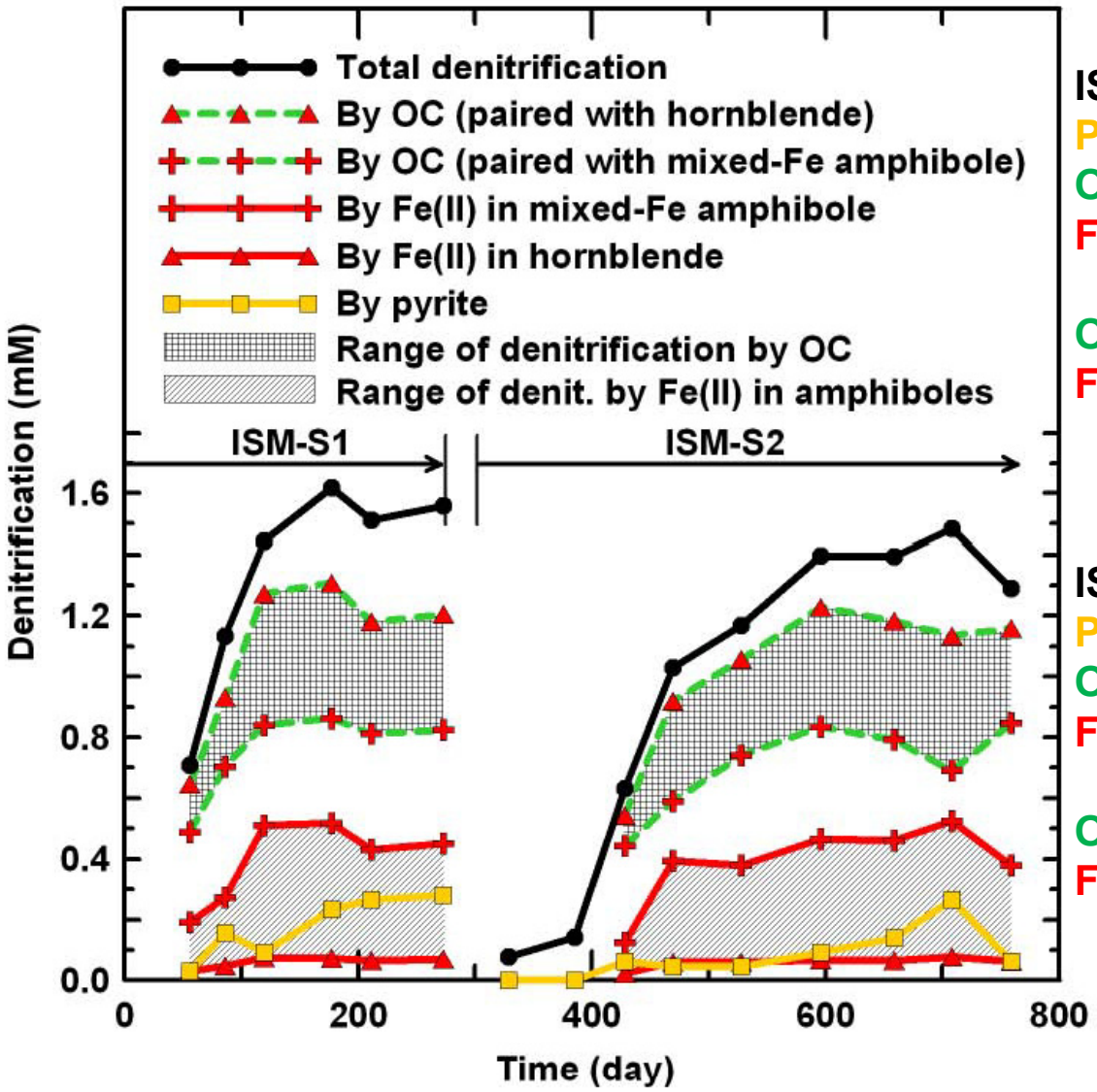
Geochemical Modeling of Denitrification at Karlsruhe S Site

1. Model: PHREEQC (Parkhurst and Appelo, 1999).
2. For each sampling date use Br dilution to estimate diluted NO_3 conc.
3. Import water quality data for each date and reduce Na with Br dilution factor.
4. Force denitrification by pyrite to match actual sulfate increase.
5. React remaining nitrate lost with the following e^- donors:
    a. By organic C only
    b. Equal amounts of mixed-Fe amphibole and organic C.
    c. 90% organic C and 10% hornblende.
6. Force water into equilibrium with calcite, magnesite, and quartz.
7. Repeat steps 2-6 for each successive sampling date.

This methodology forced exact matches between simulated and actual dissolved concentrations for sulfate, nitrate, and Br and resulted in an exact match for silica and approximate matches for Na, K, Mn, Fe, ammonium, Al, Ba, F, and Cl. The remaining four analytes, **pH, inorganic C, Ca, and Mg** were compared to see which mix of e^- donors best explained the evolution of these analytes with denitrification in the ISMs.



Korom et al. (2012)



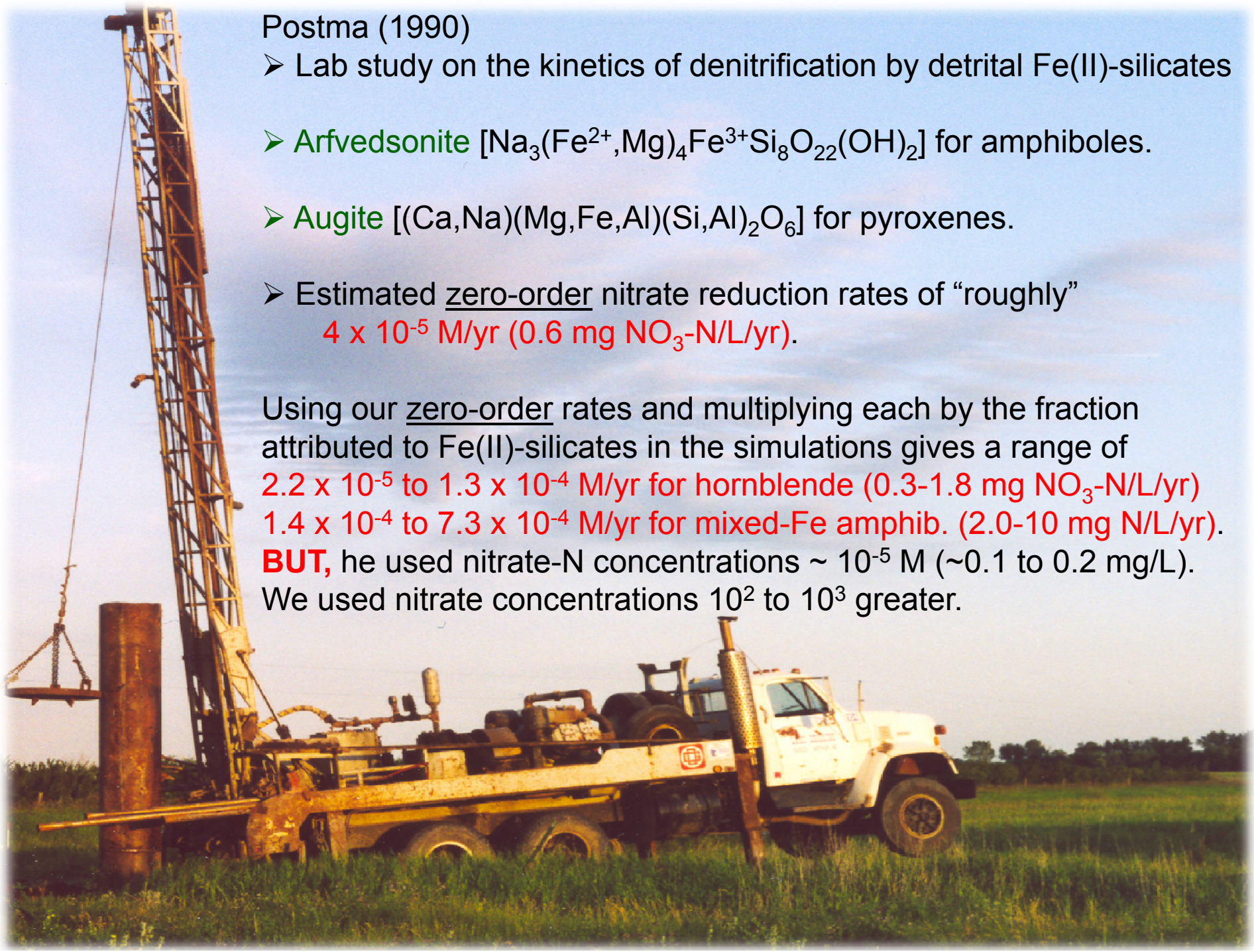
ISM-S1

Pyrite	4-18%
Organic C	77-91%
Fe(II) hornblende	3-6%
Organic C	49-73%
Fe(II) mixed-Fe amphib.	22-37%

ISM-S2

Pyrite	4-18%
Organic C	75-92%
Fe(II) hornblende	2-8%
Organic C	43-68%
Fe(II) mixed-Fe amphib.	13-43%

Korom et al. (2012)



Postma (1990)

- Lab study on the kinetics of denitrification by detrital Fe(II)-silicates
- Arfvedsonite [$Na_3(Fe^{2+},Mg)_4Fe^{3+}Si_8O_{22}(OH)_2$] for amphiboles.
- Augite [$(Ca,Na)(Mg,Fe,Al)(Si,Al)_2O_6$] for pyroxenes.
- Estimated zero-order nitrate reduction rates of "roughly"
  4×10^{-5} M/yr (0.6 mg NO_3-N/L/yr).

Using our zero-order rates and multiplying each by the fraction attributed to Fe(II)-silicates in the simulations gives a range of
2.2×10^{-5} to 1.3×10^{-4} M/yr for hornblende (0.3-1.8 mg NO_3-N/L/yr)
1.4×10^{-4} to 7.3×10^{-4} M/yr for mixed-Fe amphib. (2.0-10 mg N/L/yr).
BUT, he used nitrate-N concentrations ~ 10^{-5} M (~0.1 to 0.2 mg/L).
We used nitrate concentrations 10^2 to 10^3 greater.

Conclusions

- Using CH_2O for organic C and silicates for Fe(II), pyrite explained 4-18% of the denitrification, Fe(II) (silicates) explained 2-43%, and OC explained 43-92%, depending on the sample date.
- Rates by Fe(II) (silicates) were 10^0-10^1 greater than lab rates, but concentrations were 10^2 to 10^3 times greater.

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