Mobilization of nickel in a German aquifer induced by industrial agriculture?

Tim Mansfeldt[1], Heike Mandt[1], Katrin Matern[1], Herbert Röhm[2], Jörg Elbracht[2], Irene Bitz[2], Maria Sitnikova[3] and Reiner Dohrmann[2,3]

[1] Soil Geography/Soil Science, Department of Geosciences, University of Cologne

[2] State Office for Mining, Energy und Geology (Lower Saxony), Hannover

[3] Federal Institute for Geosciences and Natural Resources, Hannover

Research area in county Grafschaft Bentheim

Farms and livestock

... and biogas plants

Farms and livestock

County Grafschaft Bentheim

	2001	2010	
number of farms	1,975	1,327	-32.8%
agricultural area [ha]	59,841	57,410	-4.1%
number of cattle	28,047	98,907	+253%
number of swine	401,704	408,652	+1.7%
number of chicken	4,267,493	5,296,578	+24.1%

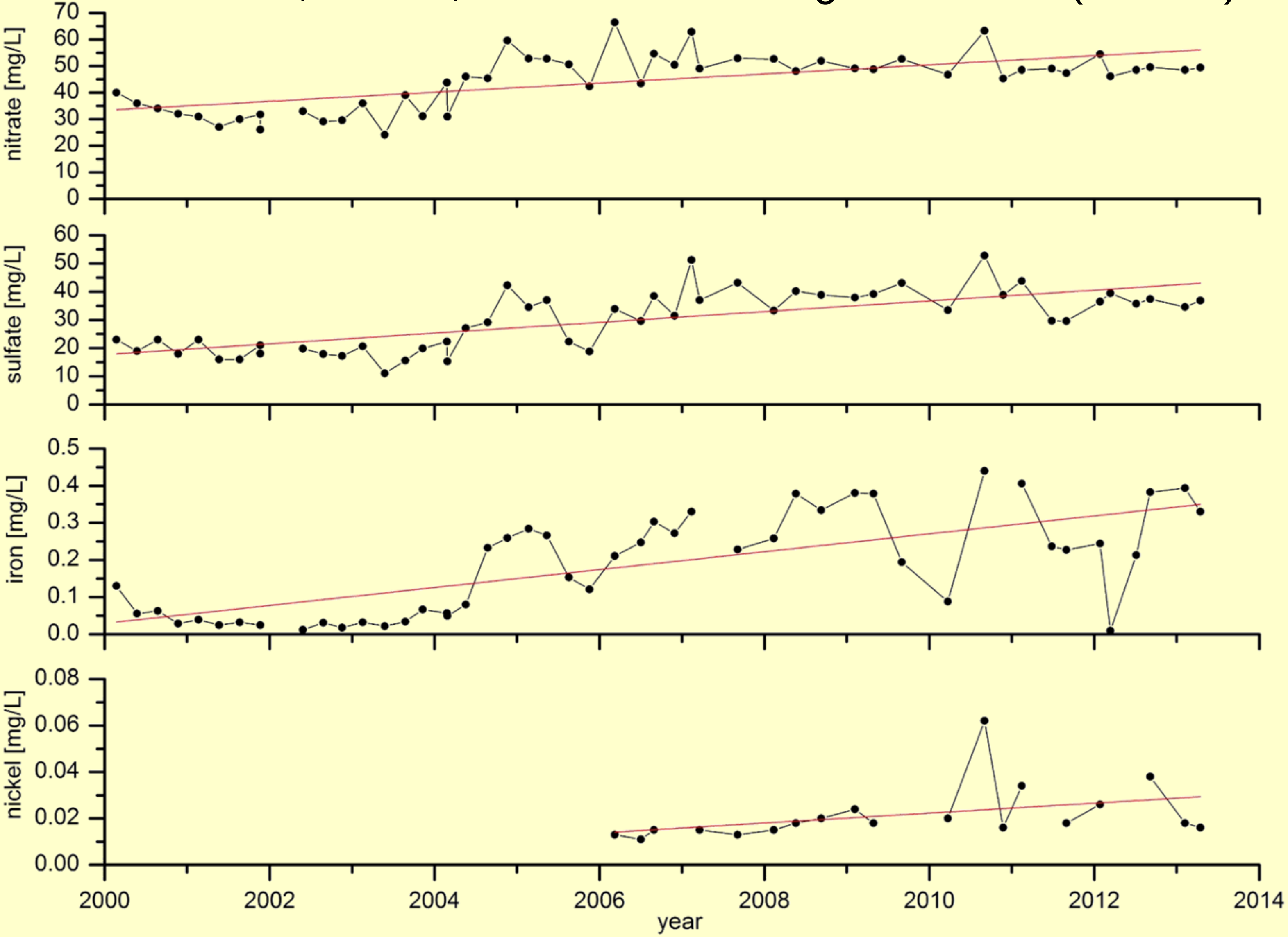
Agrarstrukturerhebungen 2003 und 2012 des NLS (Niedersächsisches Landesamt für Statistik) und Landesbetrieb für Statistik und Kommunikationstechnologie Niedersachsen (LSKN)

→ strong increase in the use of organic fertilizers (liquid manure, residues of biogas plants)

→ high inputs of nitrogen (NH_4^+, NO_3^-, organic N)

Background and motivation

nitrate, sulfate, iron and nickel in groundwater (well B6)



Why do nickel concentrations increase?

Threshold values

Drinking Water Ordinance 2001 (amendment to the act in 2011)

nickel

→ 20 µg/l (until 2011: 50 µg/l)

nitrate

→ 50 mg/l

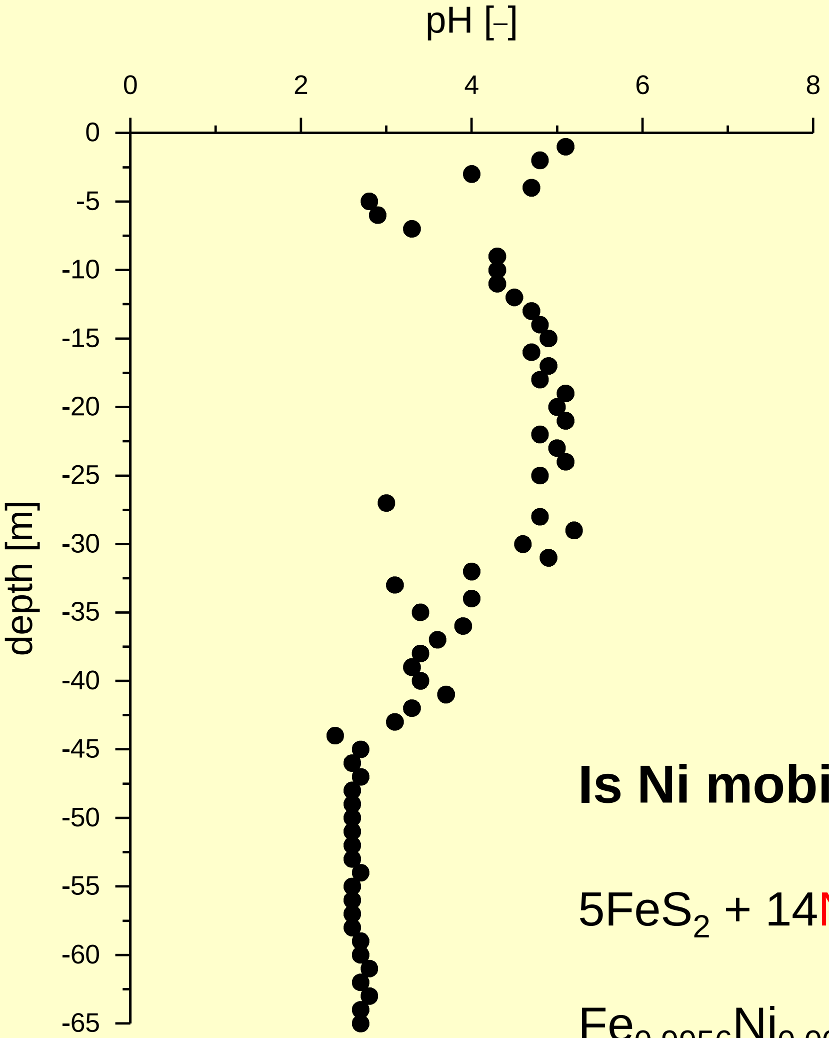
sulphate

→ 250 mg/l

→ wells in this region are polluted with Ni

Hypotheses

pH ($CaCl_2$) after aerobe storage since 2009 (B14)



→ extremely low pH (5 to 7 m; 42…65 m)

→ acid sulfate soils, coal-mining affected soils

→ hypothesis: oxidation of reduced sulfur compounds

$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$

aerobe pyrite oxidation

Is Ni mobilized by the anaerobe oxidation of pyrite?

$5FeS_2 + 14NO_3^- + 4H^+ \rightarrow 5Fe^{2+} + 7N_2 + 10SO_4^{2-} + 2H_2O$

$Fe_{0.9956}Ni_{0.0020}Co_{0.0024}As_{0.0038}$ (Cremer et al. 2002)

Drilling site

Core drilling

→ May, 5 to 9, 2014

→ 0 to 65 m depth

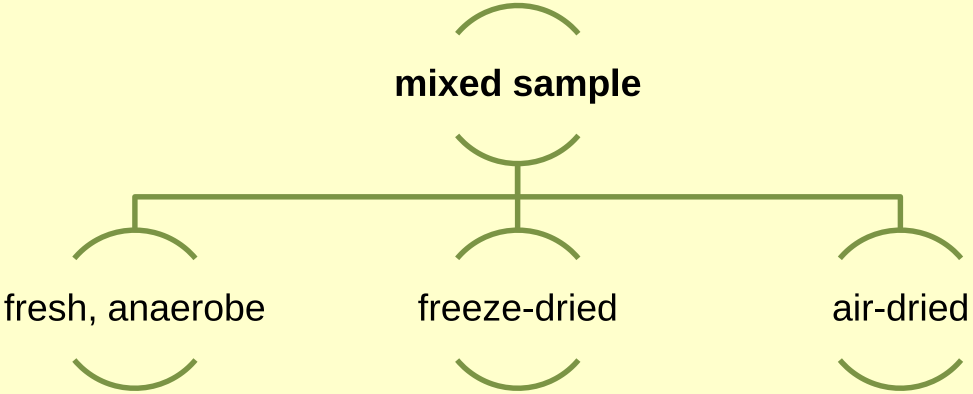
→ 0 to 2 m mixed sample

→ 63 core samples (1 m length,
0.1 m diameter)

Sample storage and preparation

→ n = 82 (+ 53 extra samples)

Sample preparation and analyses


mixed sample

fresh, anaerobe

freeze-dried

air-dried

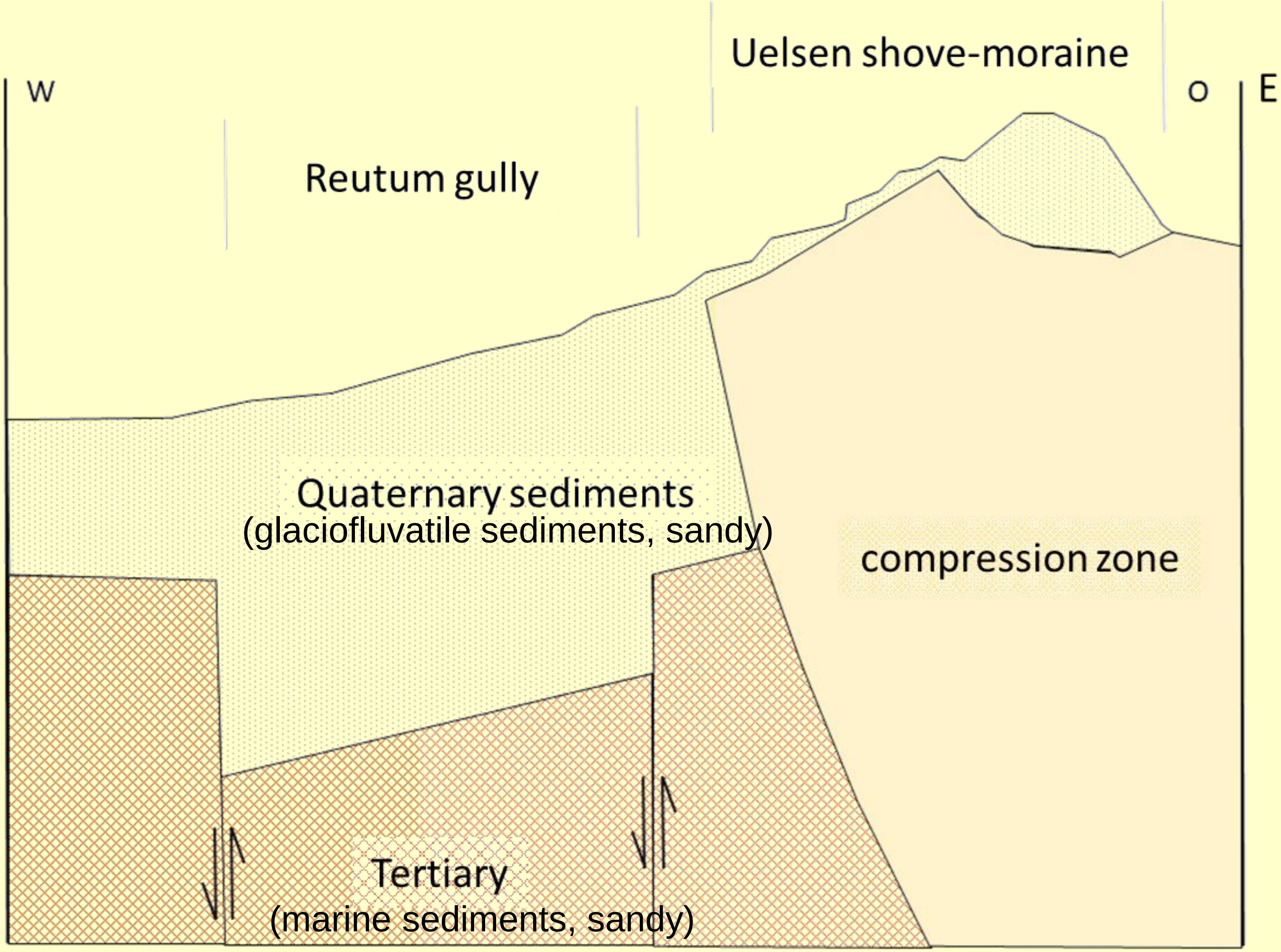
- pH in 0.01 *M* $CaCl_2$
- water-soluble anions (chloride, nitrate, sulfate)

- C, N, S
- oxalate-soluble Fe and Ni (Fe_o)
- dithionite-soluble Fe and Ni (Fe_d)
- NH_4NO_3-soluble Fe and Ni
- sulfide

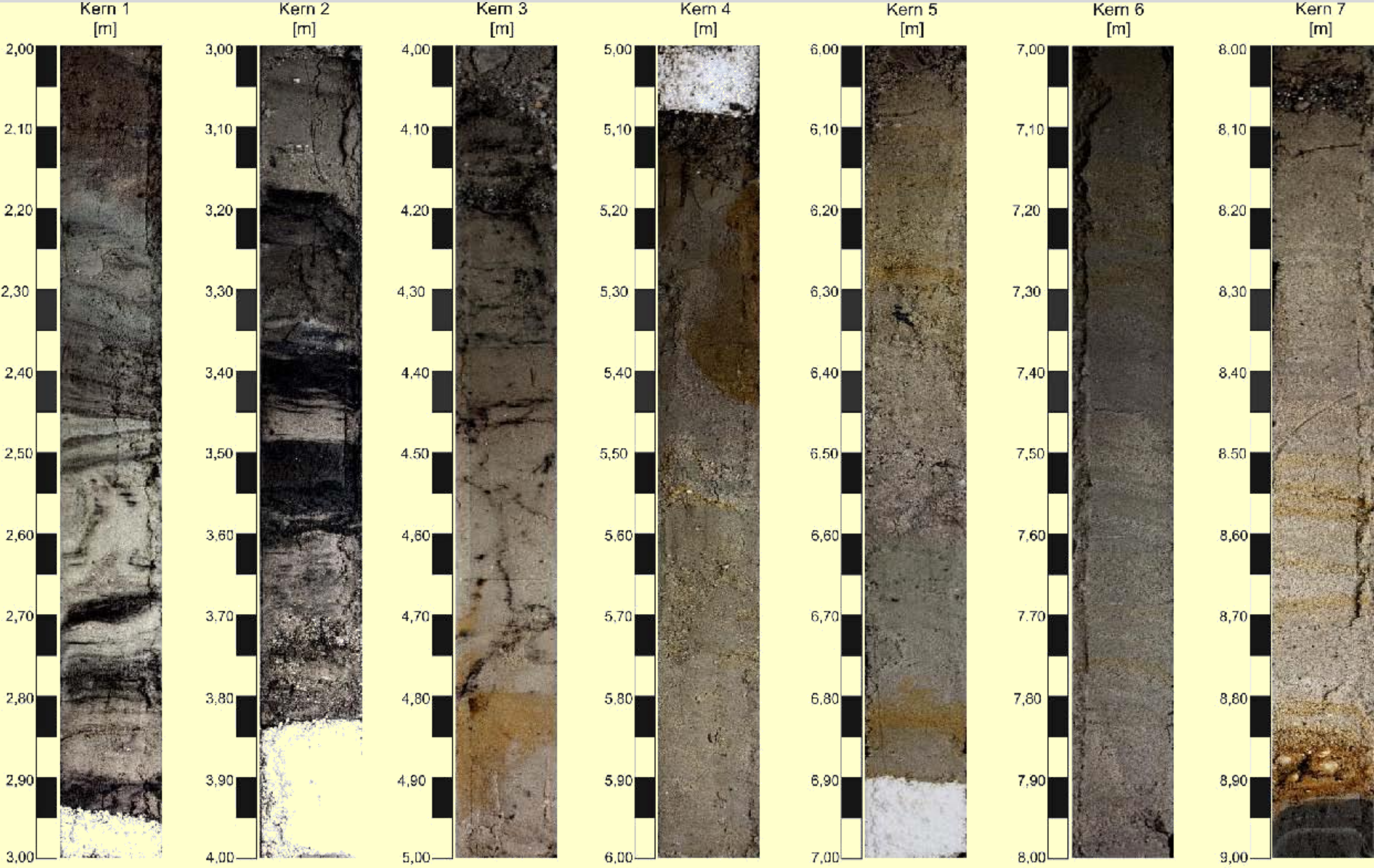
- particle-size distribution
- major and minor elements (XRF)
- Ni, Co, As (microwave induced total digestion with HNO_3/HCl/HF)
- biostratigraphy
- mineralogy (heavy minerals)

focus of the talk

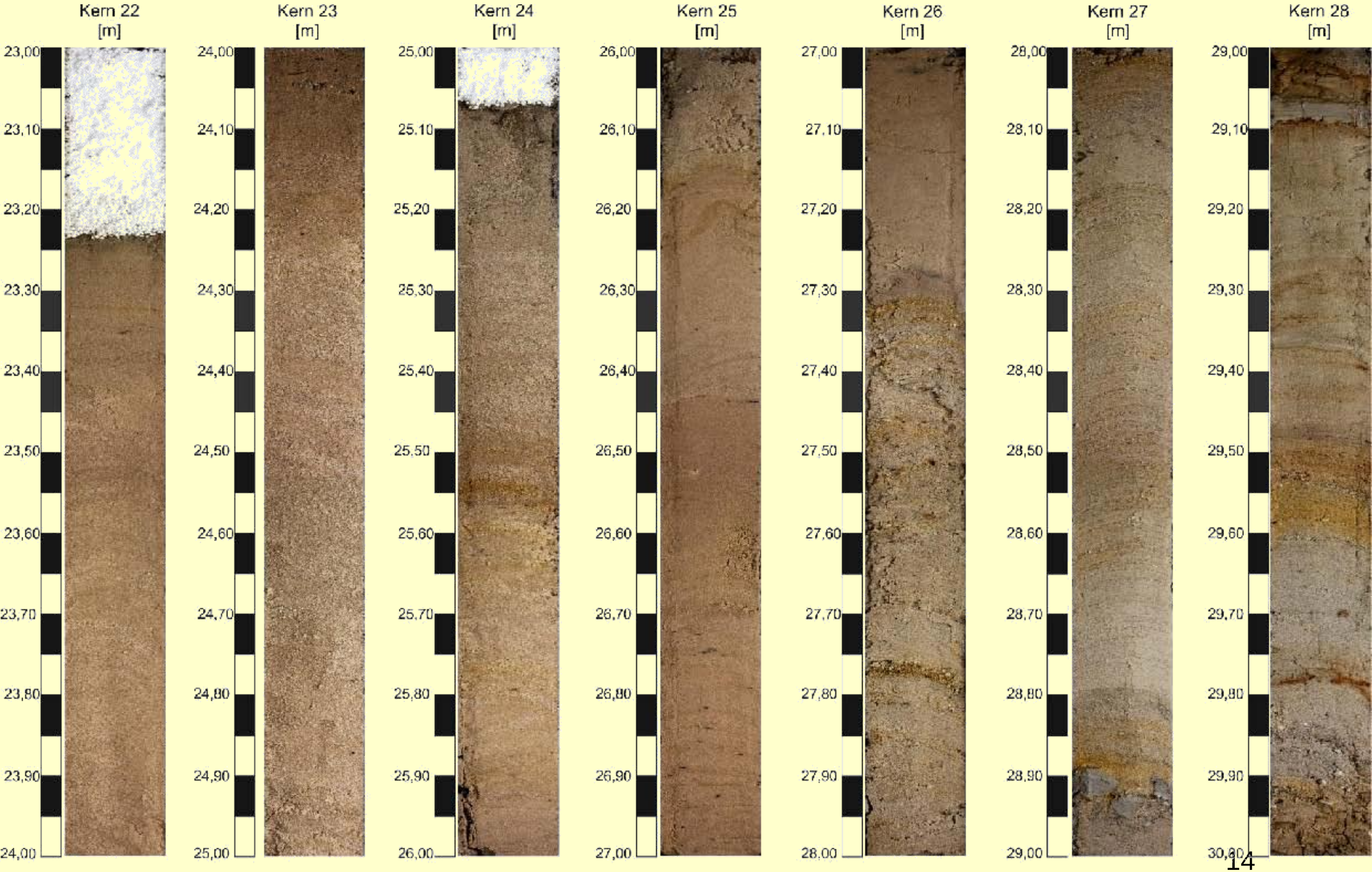
Geological situation



Cores 1 to 7 (+2 to 9 m)

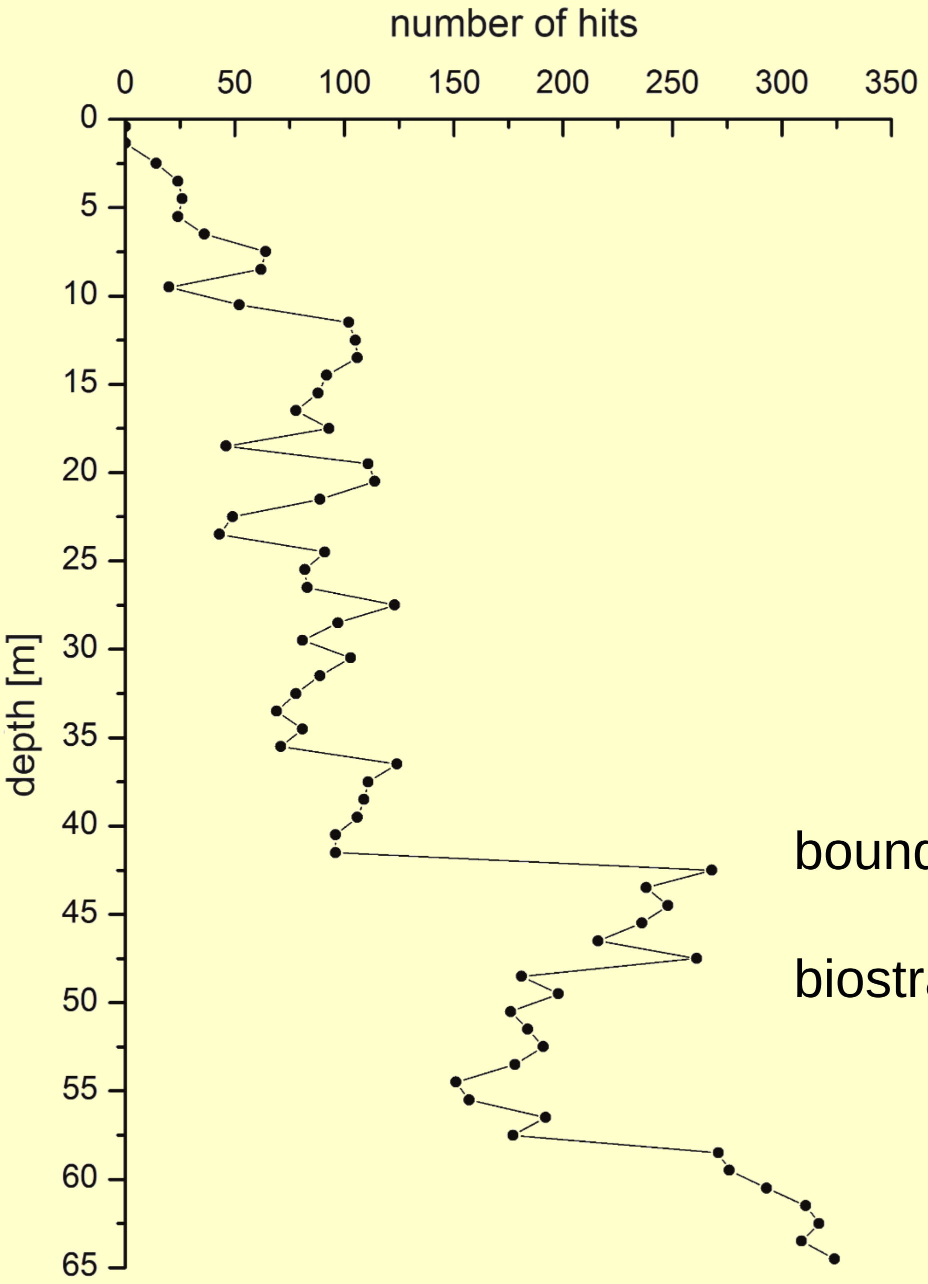


Cores 22 to 28 (+21 to 30 m)



Cores 36 to 42 (+37 to 44 m)

Number of hits during drilling

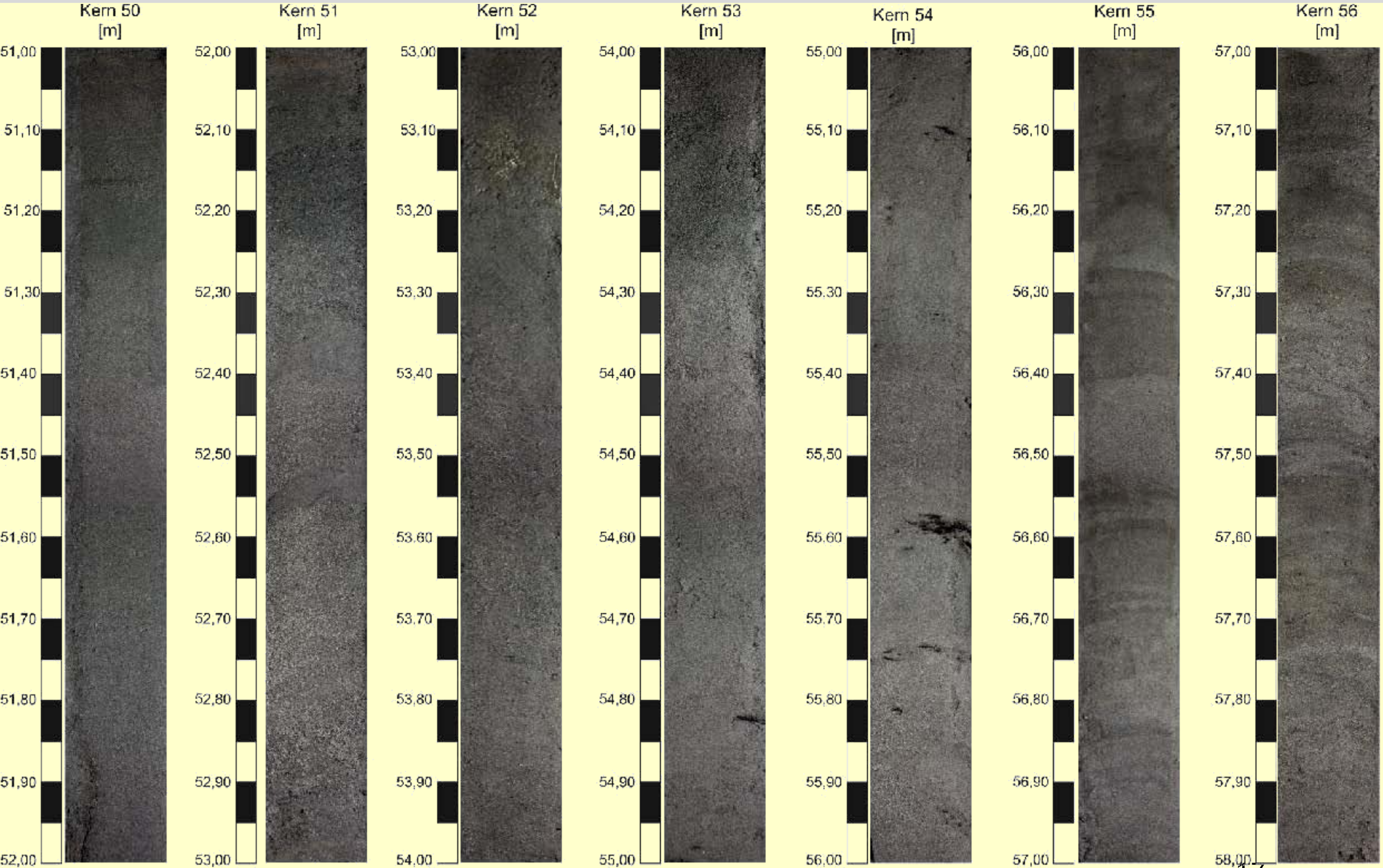


boundary Quaternary – Tertiary (Neogene)

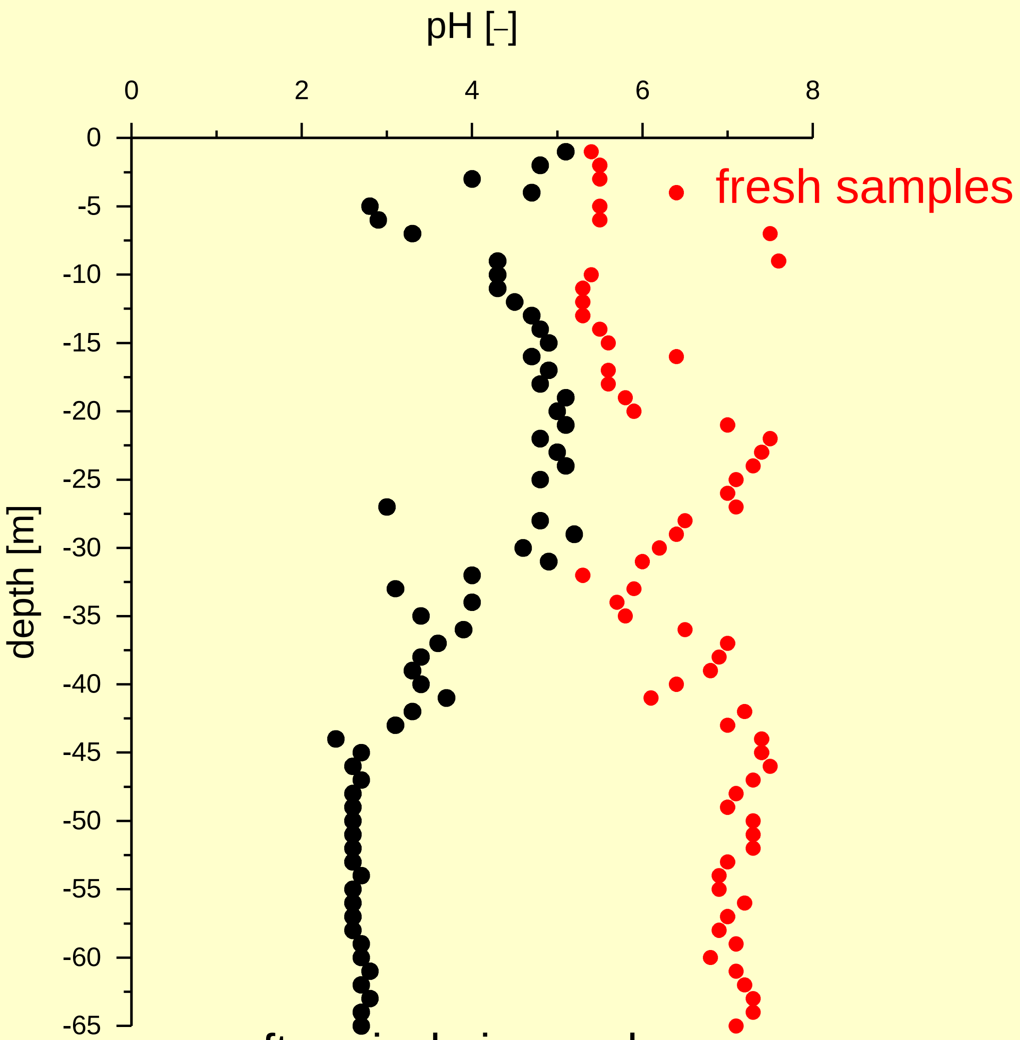
biostratigraphy:

Pliocene [5.333 – 2.58 age Ma]
Miocene [23.03 – 5.332 age Ma]

Cores 50 to 56 (+51 to 58 m)



pH ($CaCl_2$) values



after air-drying and
storage since 2009

<u>aerobe</u>
pH 2.5…5.2

<u>anaerobe</u>
pH 5.3…7.6

ΔpH
0.3…5.0

Inorganic reduced sulfur

sample	depth [m]	sulfide-sulfur [mg/kg]
#2781	3.00 – 3.70	3,000
#2789	9.00 – 9.72	480
#2801	17.51 – 18.00	<LOQ*
#2815	29.00 – 29.50	<LOQ*
#2821	31.72 – 32.00	150
#2823	33.00 – 34.00	530
#2825	35.00 – 36.00	500
#2835	41.38 – 42.00	500
#2835	42.00 – 43.00	520
#2841	48.00 – 49.00	770
#2747	54.00 – 55.00	1,100
#2854	61.07 – 62.00	880

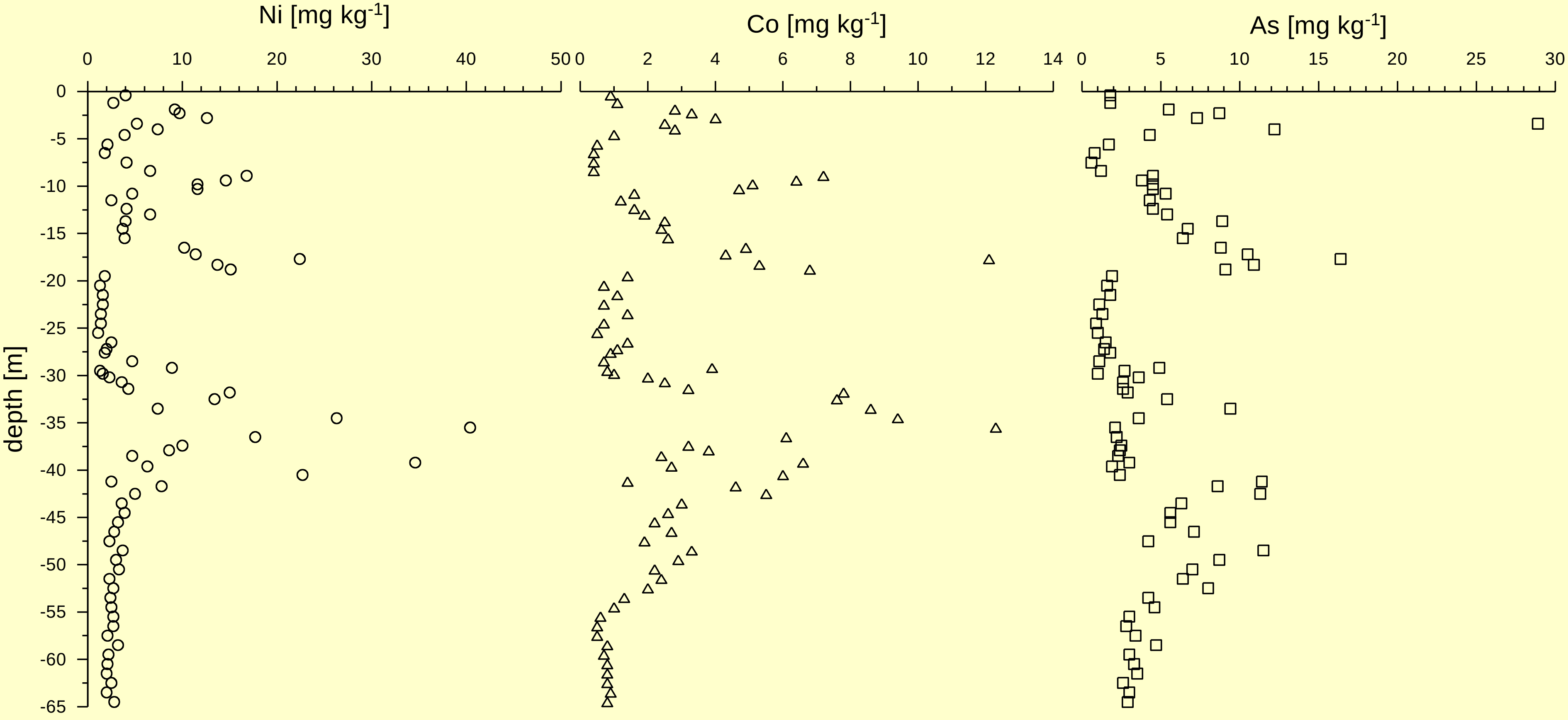
Holocene sulfides

Tertiary sulfides

* below limit of quality [50 mg/kg]

$$5FeS_2 + 14NO_3^- + 4H^+ \rightarrow 5Fe^{2+} + 7N_2 + 10SO_4^{2-} + 2H_2O$$

Total nickel, cobalt and arsenic



Mean:	6.7+/-7.3	Mean:	2.9+/-2.6	Mean:	4.9+/-4.2
Median:	3.8	Median:	2.2	Median:	3.7
Min.:	1.1	Min.:	0.4	Min.:	0.6
Max.:	40.4	Max.:	12.3	Max.:	28.9

pyrite, 0.12% (Cremer et al. 2002) $Fe_{0.9956}Ni_{0.0020}Co_{0.0024}As_{0.0038}$

Mineralogy of heavy minerals

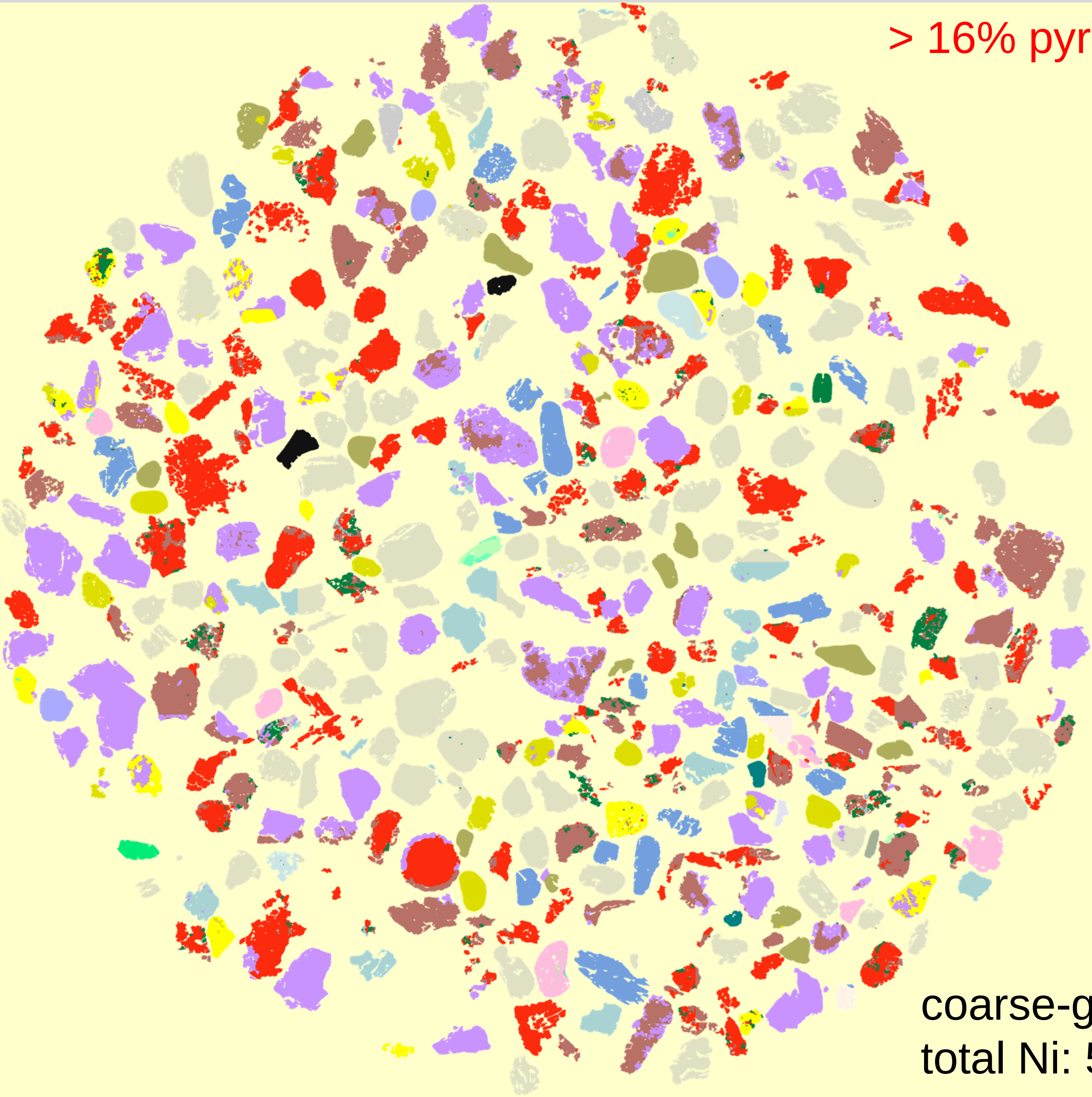
pre-concentration

thin polished section

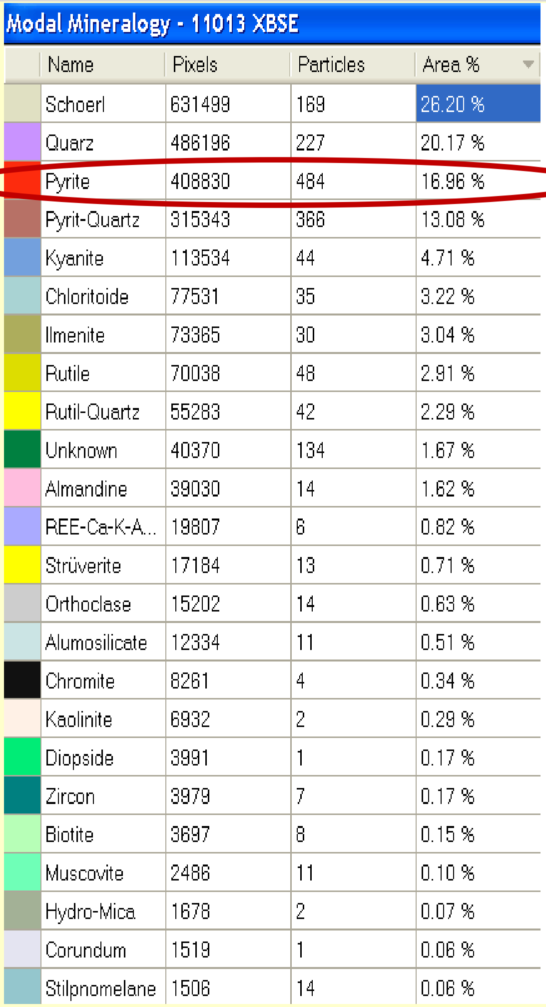
Mineralogy of heavy minerals

Scanning Electron Microscope (SEM) / Mineral Liberation Analysis (MLA); energy dispersive X-ray spectroscopy (EDX), wave-length dispersive X-ray spectroscopy (WDX)

Mineralogy of heavy minerals (42 to 43 m)



> 16% pyrite



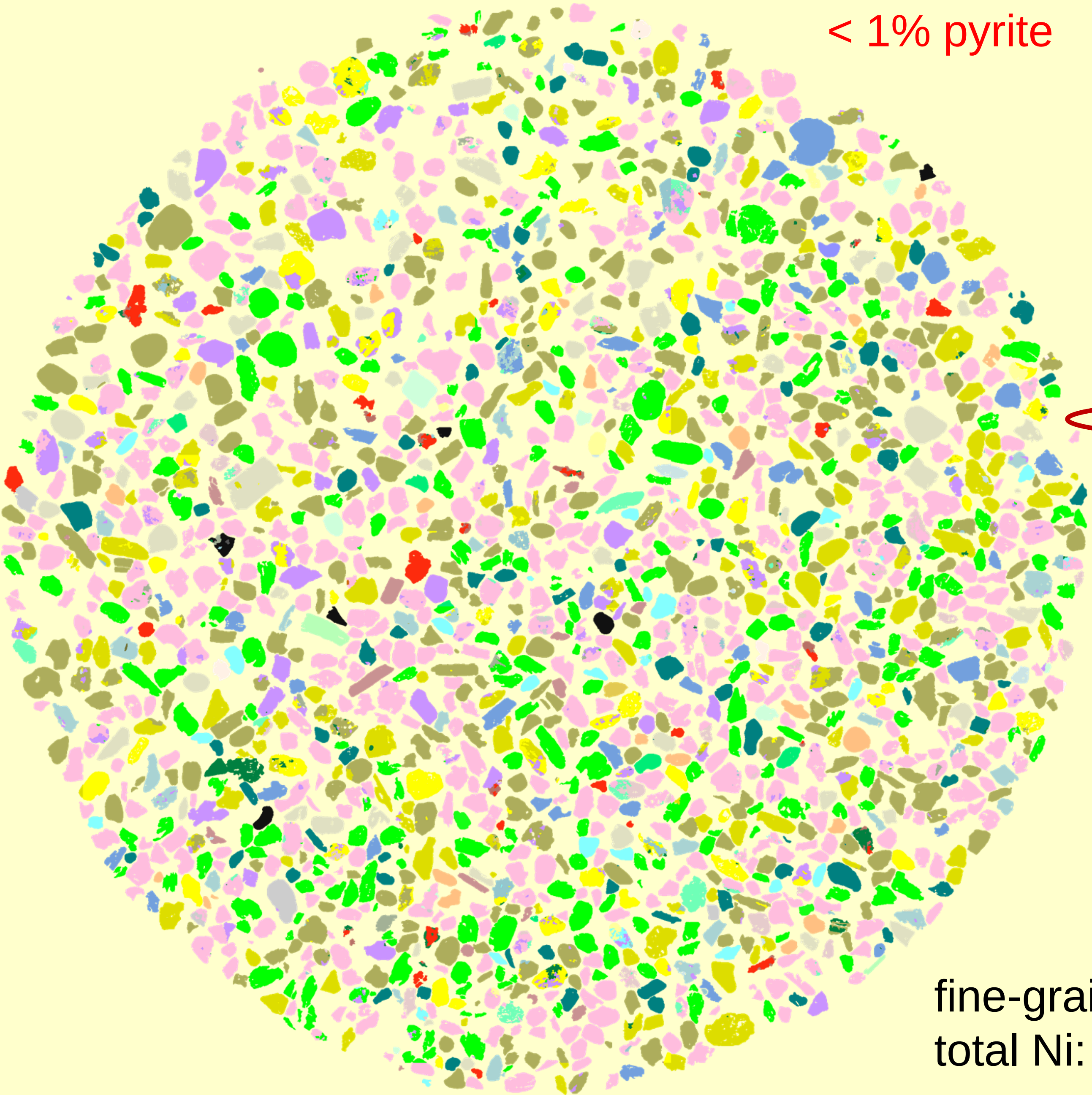
Modal Mineralogy - 11013 XBSE

Name	Pixels	Particles	Area %
Schoerl	631499	169	26.20 %
Quarz	486196	227	20.17 %
Pyrite	408830	484	16.96 %
Pyrit-Quartz	315343	366	13.08 %
Kyanite	113534	44	4.71 %
Chloritoide	77531	35	3.22 %
Ilmenite	73365	30	3.04 %
Rutile	70038	48	2.91 %
Rutil-Quartz	55283	42	2.29 %
Unknown	40370	134	1.67 %
Almandine	39030	14	1.62 %
REE-Ca-K-A...	19807	6	0.82 %
Strüverite	17184	13	0.71 %
Orthoclase	15202	14	0.63 %
Alumosilicate	12334	11	0.51 %
Chromite	8261	4	0.34 %
Kaolinite	6932	2	0.29 %
Diopside	3991	1	0.17 %
Zircon	3979	7	0.17 %
Biotite	3697	8	0.15 %
Muscovite	2486	11	0.10 %
Hydro-Mica	1678	2	0.07 %
Corundum	1519	1	0.06 %
Stilpnomelane	1506	14	0.06 %

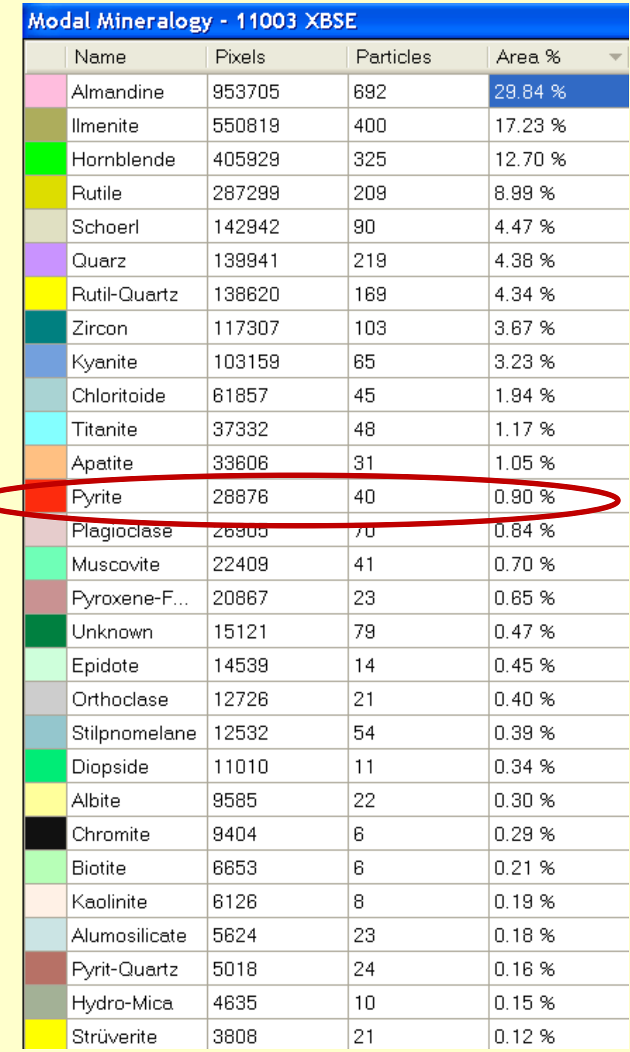
coarse-grained concentrate

total Ni: 5.0 mg kg^{-1}

Mineralogy of heavy minerals (35 to 36 m)



< 1% pyrite

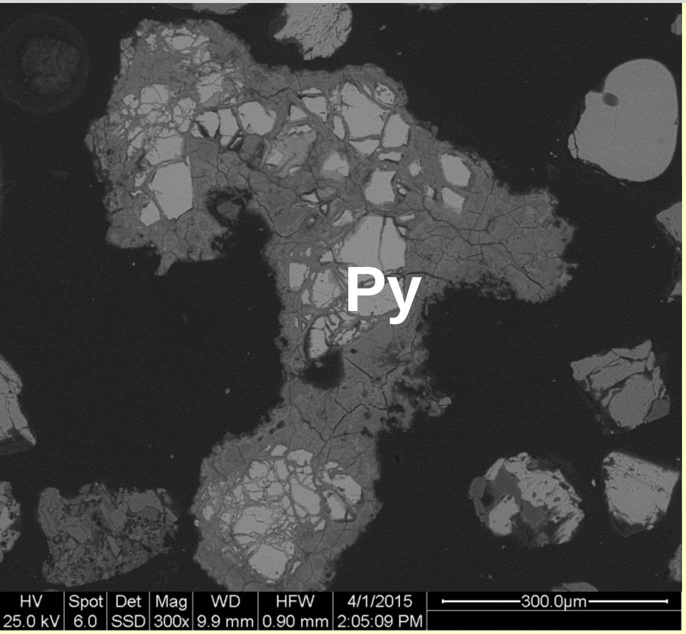


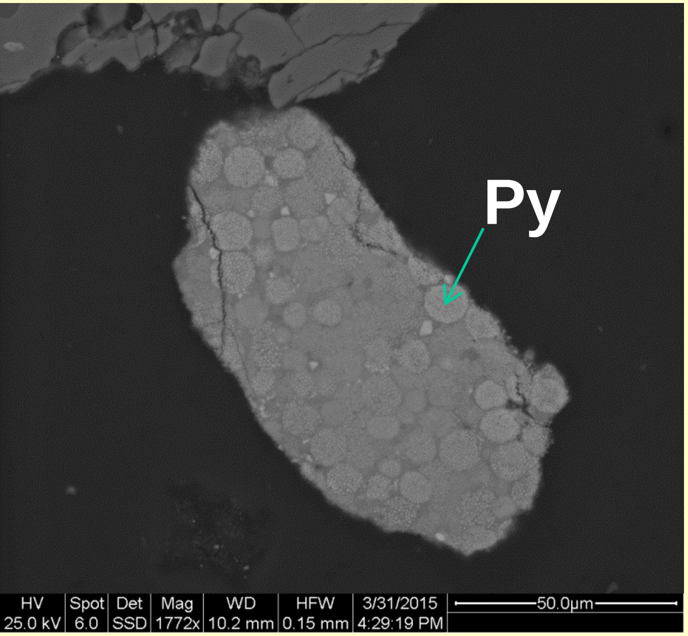
Modal Mineralogy - 11003 XBSE

Name	Pixels	Particles	Area %
Almandine	953705	692	29.84 %
Ilmenite	550819	400	17.23 %
Hornblende	405929	325	12.70 %
Rutile	287299	209	8.99 %
Schoerl	142942	90	4.47 %
Quarz	139941	219	4.38 %
Rutil-Quartz	138620	169	4.34 %
Zircon	117307	103	3.67 %
Kyanite	103159	65	3.23 %
Chloritoide	61857	45	1.94 %
Titanite	37332	48	1.17 %
Apatite	33606	31	1.05 %
Pyrite	28876	40	0.90 %
Plagioclase	26905	70	0.84 %
Muscovite	22409	41	0.70 %
Pyroxene-F...	20867	23	0.65 %
Unknown	15121	79	0.47 %
Epidote	14539	14	0.45 %
Orthoclase	12726	21	0.40 %
Stilpnomelane	12532	54	0.39 %
Diopside	11010	11	0.34 %
Albite	9585	22	0.30 %
Chromite	9404	6	0.29 %
Biotite	6653	6	0.21 %
Kaolinite	6126	8	0.19 %
Alumosilicate	5624	23	0.18 %
Pyrit-Quartz	5018	24	0.16 %
Hydro-Mica	4635	10	0.15 %
Strüverite	3808	21	0.12 %

fine-grained concentrate
total Ni: 40.4 mg kg^{-1}

Mineralogy of heavy minerals



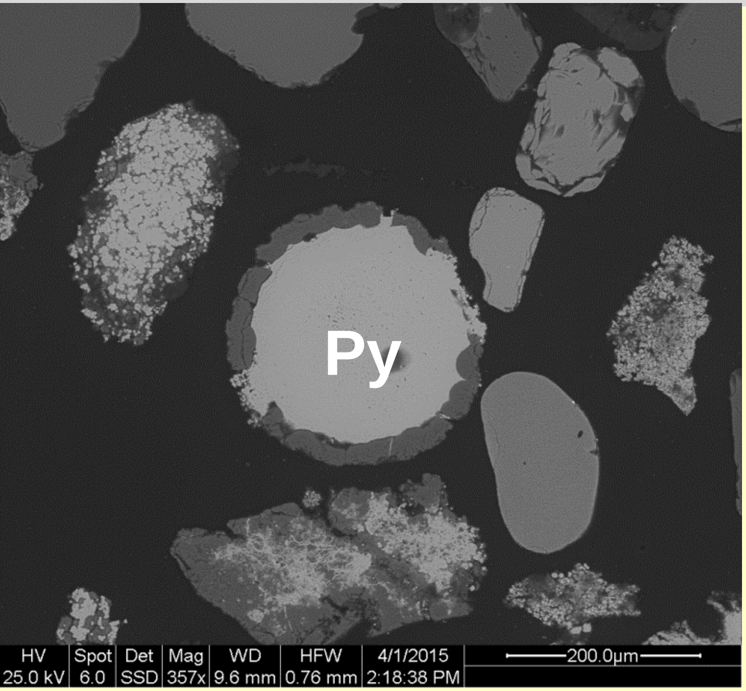


- crystalline pyrite

- relatively high in Ni

- detrital

Mineralogy of heavy minerals

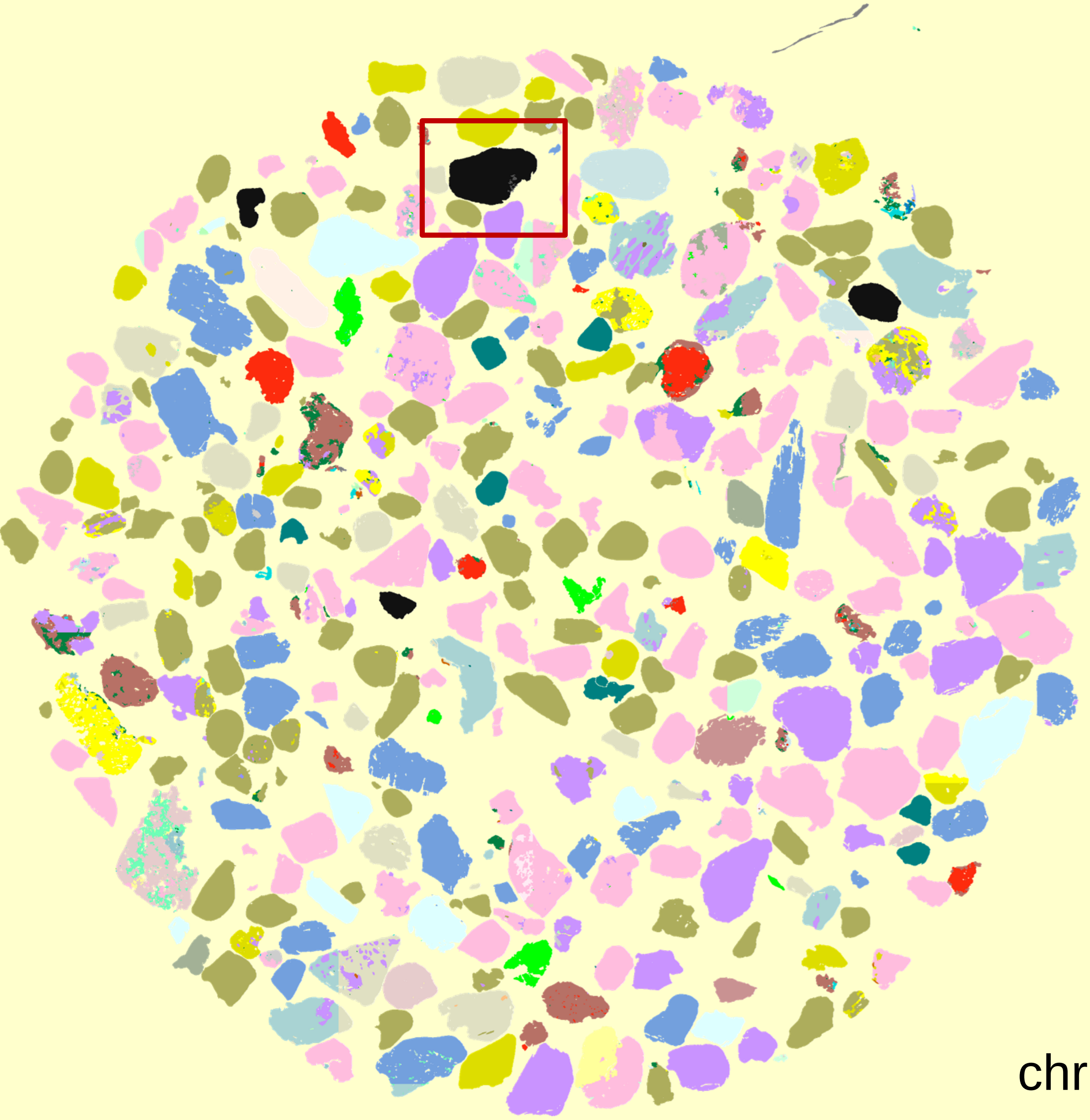


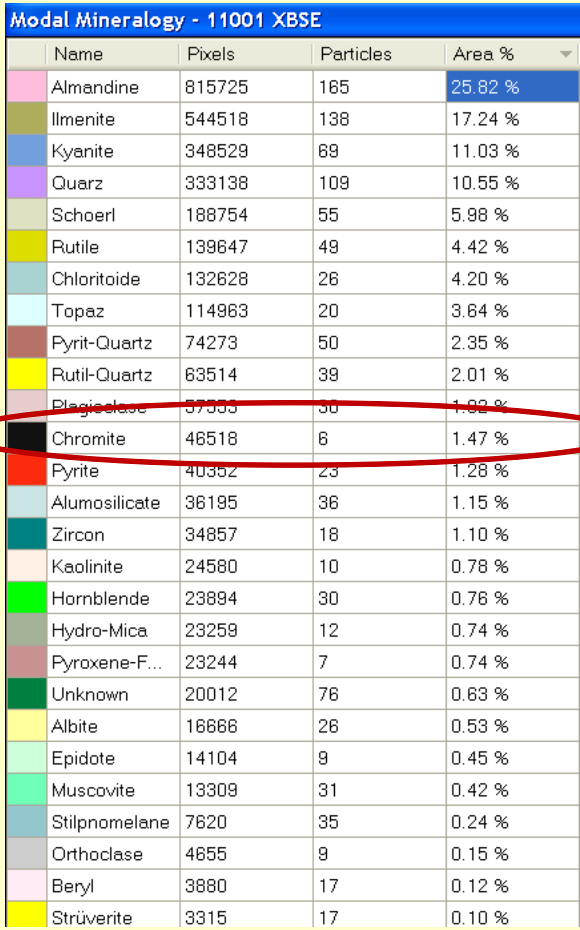
- framboidale pyrite (‘raspberry-like)

- relatively low in Ni

- in situ formation?

Mineralogy of heavy minerals (33 to 34 m)





Modal Mineralogy - 11001 XBSE

	Name	Pixels	Particles	Area %
	Almandine	815725	165	25.82 %
	Ilmenite	544518	138	17.24 %
	Kyanite	348529	69	11.03 %
	Quarz	333138	109	10.55 %
	Schoerl	188754	55	5.98 %
	Rutile	139647	49	4.42 %
	Chloritoide	132628	26	4.20 %
	Topaz	114963	20	3.64 %
	Pyrit-Quartz	74273	50	2.35 %
	Rutil-Quartz	63514	39	2.01 %
	Plagioclase	57553	30	1.82 %
	Chromite	46518	6	1.47 %
	Pyrite	40352	23	1.28 %
	Alumosilicate	36195	36	1.15 %
	Zircon	34857	18	1.10 %
	Kaolinite	24580	10	0.78 %
	Hornblende	23894	30	0.76 %
	Hydro-Mica	23259	12	0.74 %
	Pyroxene-F...	23244	7	0.74 %
	Unknown	20012	76	0.63 %
	Albite	16666	26	0.53 %
	Epidote	14104	9	0.45 %
	Muscovite	13309	31	0.42 %
	Stilpnomelane	7620	35	0.24 %
	Orthoclase	4655	9	0.15 %
	Beryl	3880	17	0.12 %
	Strüverite	3315	17	0.10 %

chromite: $(Fe,Mg)Cr_2O_4$

Hosting nickel minerals

Nickel is **sequestered** in

pyrite, altered crystals (high in Ni)

pyrite, framboidale (low in Ni)

chromite, extremely stable mineral

iron oxides, under investigation

$10Fe^{2+} + 2NO_3^- + 24H_2O \rightleftharpoons N_2 + 10Fe(OH)_3 + 18H^+$

→ iron oxides as adsorbents for Ni (pH)

Conclusions

1)This reaction is possible:

$$5FeS_2 + 14NO_3^- + 4H^+ \rightarrow 5Fe^{2+} + 7N_2 + 10SO_4^{2-} + 2H_2O$$

→ explaining elevated sulfate and ferrous iron concentrations

2) Nickel is mainly hosted in altered “crystalline” pyrite which can be oxidized by nitrate

→ explaining elevated nickel concentrations

3) Co-mobilization of arsenic and cobalt should be considered

4) Formation of iron oxides by industrial agriculture?

Mobilization of nickel in a German aquifer induced by industrial agriculture?

5) Nitrate originates from industrial agriculture

Acknowledgments

We are grateful to

Wasser- und Abwasser-Zweckverband (WAZ) Neuenhaus, Niedergrafschaft

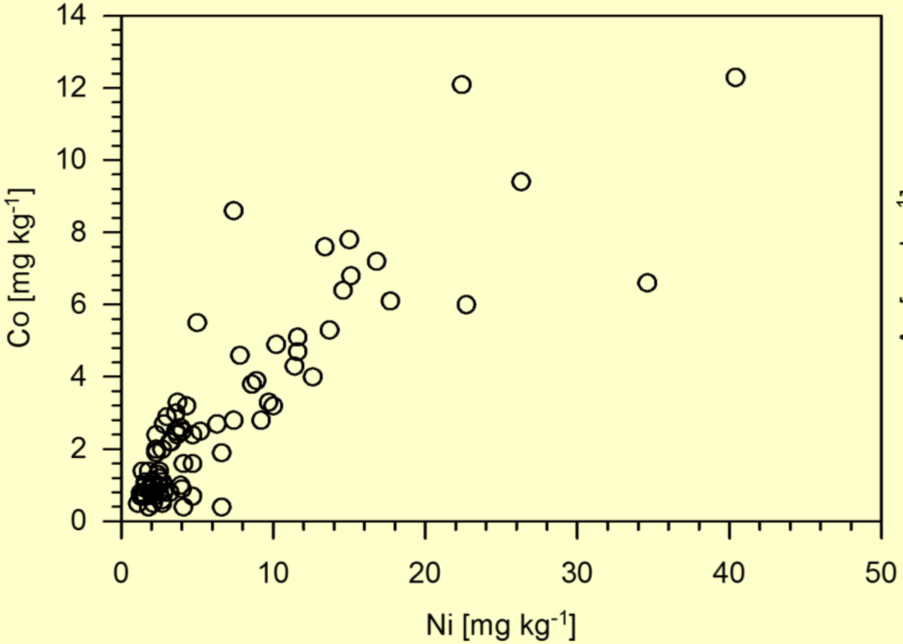
Mr. Hans

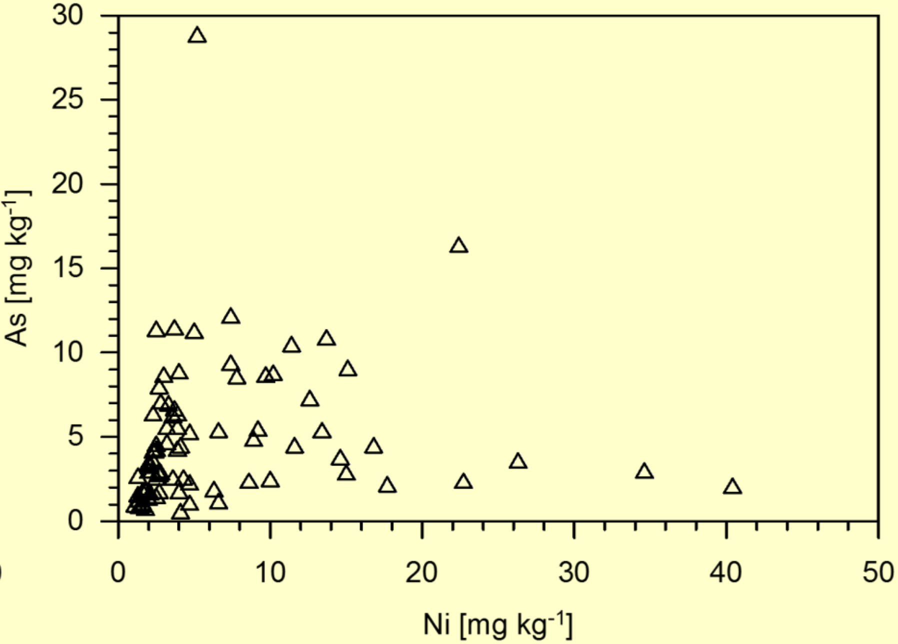
Mr. Schnieders

for financial and technical support.

Thank you very much for your attention!

Total nickel, cobalt, and arsenic





$y = 0.819+0.31x$
$r = 0.859$
$p < 0.00001$
$n = 82$

$r_s = 0.806$

$y = 4.52+0.063x$
$r = 0.108$
$p = 0.1669$
$n = 82$

$r_s = 0.409$