Nickel (bio)availability in ultramafic systems from Goïas, Brazil: an overlook of the compartments

I. Zelano, Y. Sivry, D. Jouvin , M. Tharaud , C Quantin, A.Gelabert, E. Montarges-Pelletier , J. Garnier, O. Abollino and M.F. Benedetti.

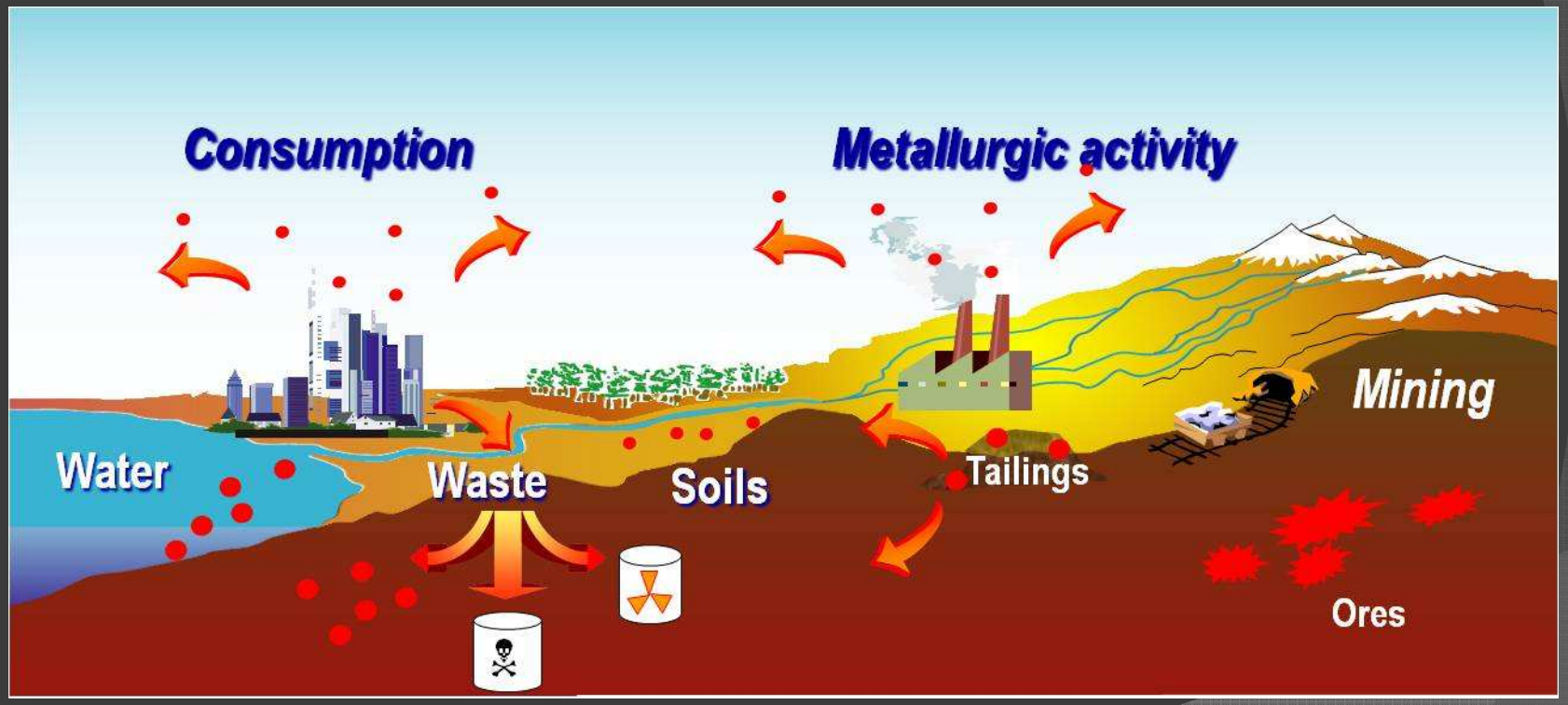
Summer school on Contaminated Soils: from characterization to remediation

18-22 June 2012 - France, Paris-Est

AIM of the PROJECT

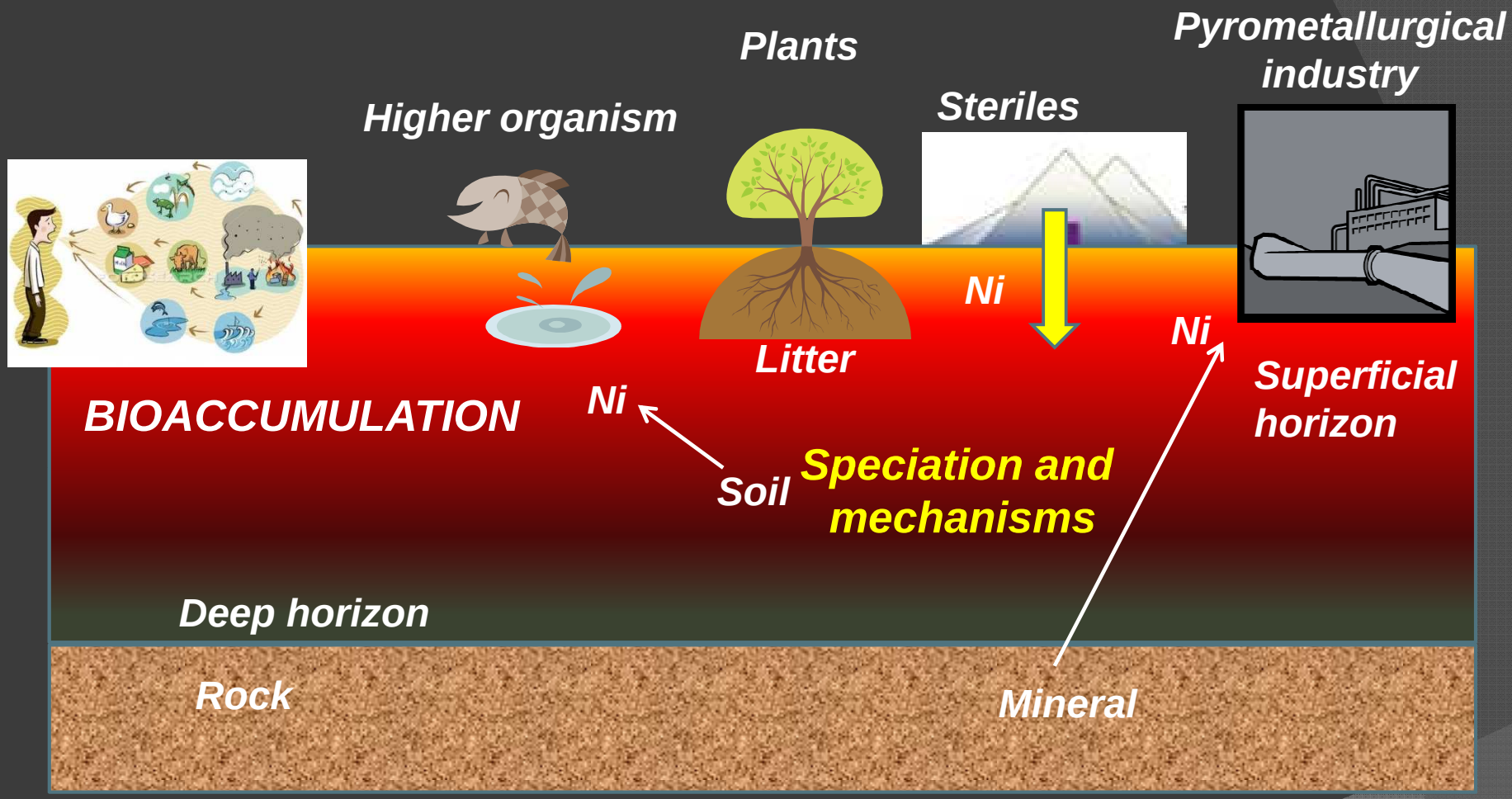
Quantify *Ni AVAILABILITY* and *MOBILITY*
in ultramafic ecosystems

WHY?



Modification of ***concentration/distribution of metals*** already existing as traces

MINING ACTIVITY AND Ni AVAILABILITY

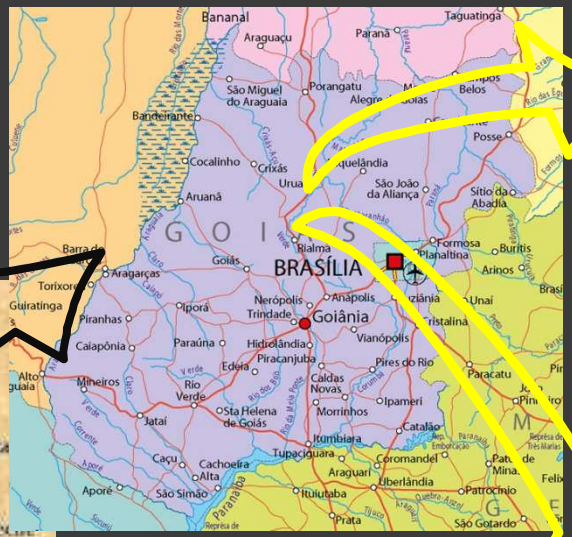


Intense explotation:

- **Alteration of the area**
- **Problem of wastes and steriles storage**
- **Metals leaching into the closed environment**

INVESTIGATED SITES: ULTRAMAFICS SYSTEMS

- Low contents of N, P, K
- Content of Fe and Mg OXIDES > 18%



NIQUELANDIA

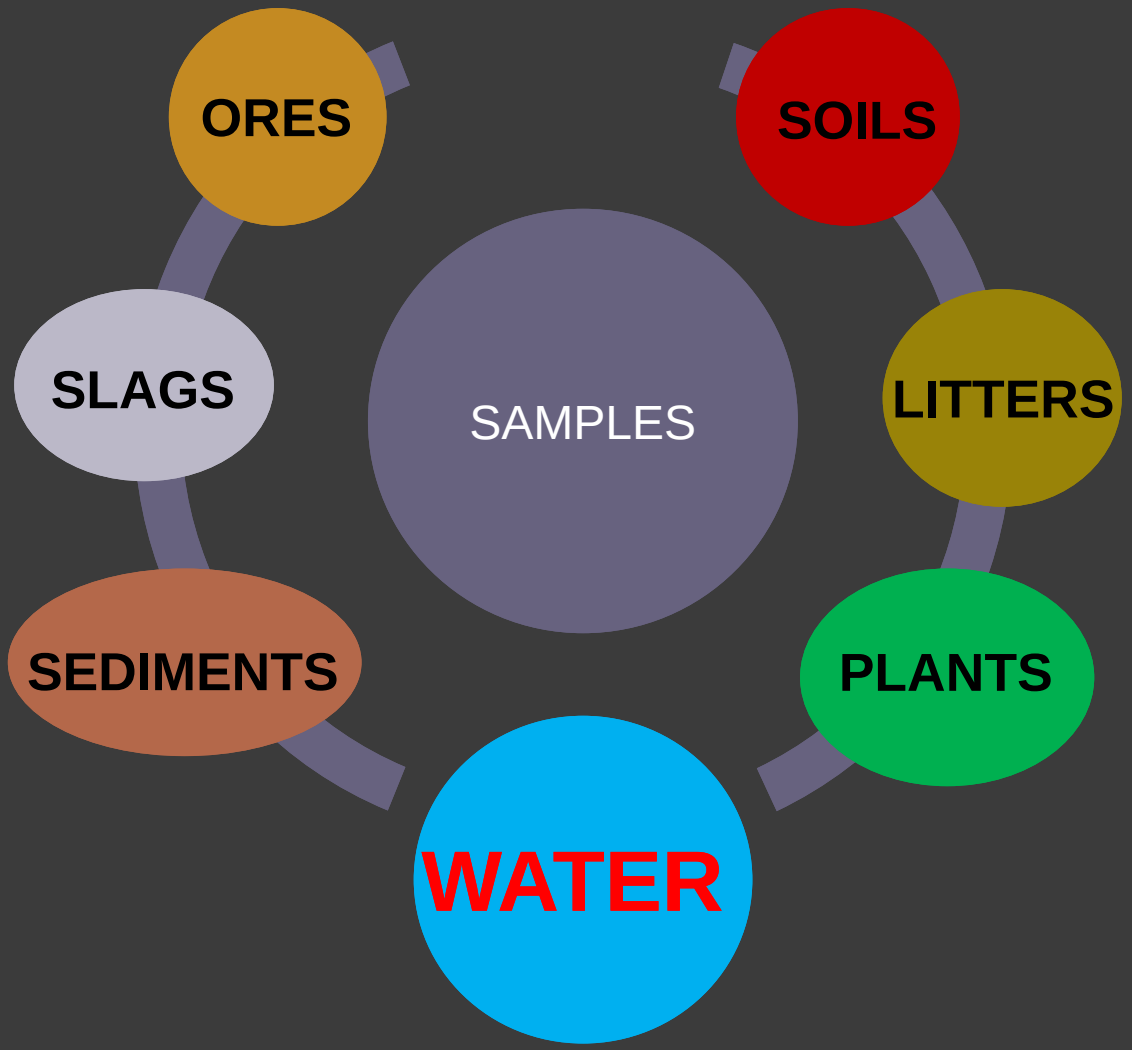
BARRO ALTO

- High contents of Ni, Cr, Co, Mn

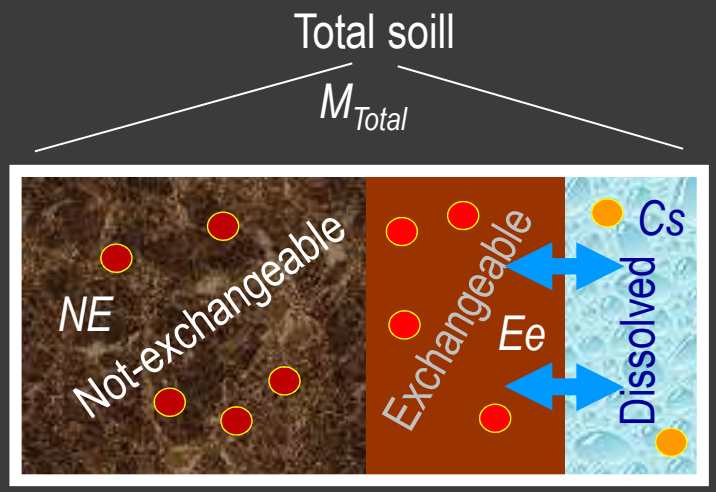
100 million tons of extractable Ni ores representing around 2 million tons of metallic

S. Raous et al. 2010

SAMPLING CAMPAIN November 2011



METAL AVAILABILITY AND MOBILITY



M Total = NE + Ea

Ea = Ee + Cs

Classical Techniques for **« Exchangeable pool »** quantification

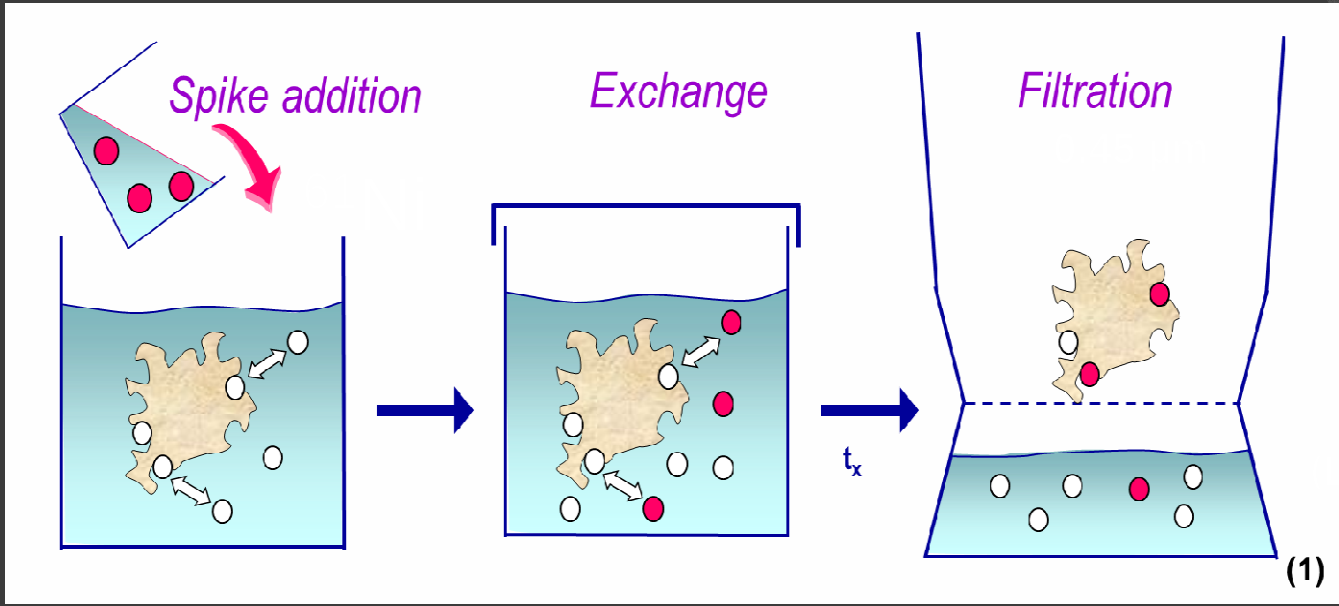
- *Diffusive Gradient in Thin film (DGT)* — *Fardeau et Guiraud, 1974*
- *Donnan Membrane Technique (DMT)* — *Zhang et al., 1998*
- *Chemical sequential extraction* — *Tessier & al., 1979*
- ***Stable isotopic dilution*** — *Ahnstrom et Parker, 2001*

Hamon et al., 2002

ISOTOPIC EXCHANGE KINETICS (IEK)

Natural Abundances:

^{61}Ni: 1.14%
^{58}Ni: 68.08%



$\text{-Ni)}^{n-} + \text{Ni}^{2+}$ (1)

$$E = Q \times \frac{M_{STD}}{M_S} \times \frac{A_S}{A_{STD}} \times \left[\frac{(I.R)_{Spike} - (I.R)_{Sample}}{(I.R)_{Sample} - (I.R)_{Natural}} \right]$$

Sivry et al. 2011

E calculated with classical Isotopic Dilution formula

The amount of exchangeable metal is determined by measuring the isotopic ratio in the filtered solution, the natural sample and the spike solution

SAMPLING SITES

BARRO ALTO SITE 3
Pool on the road →

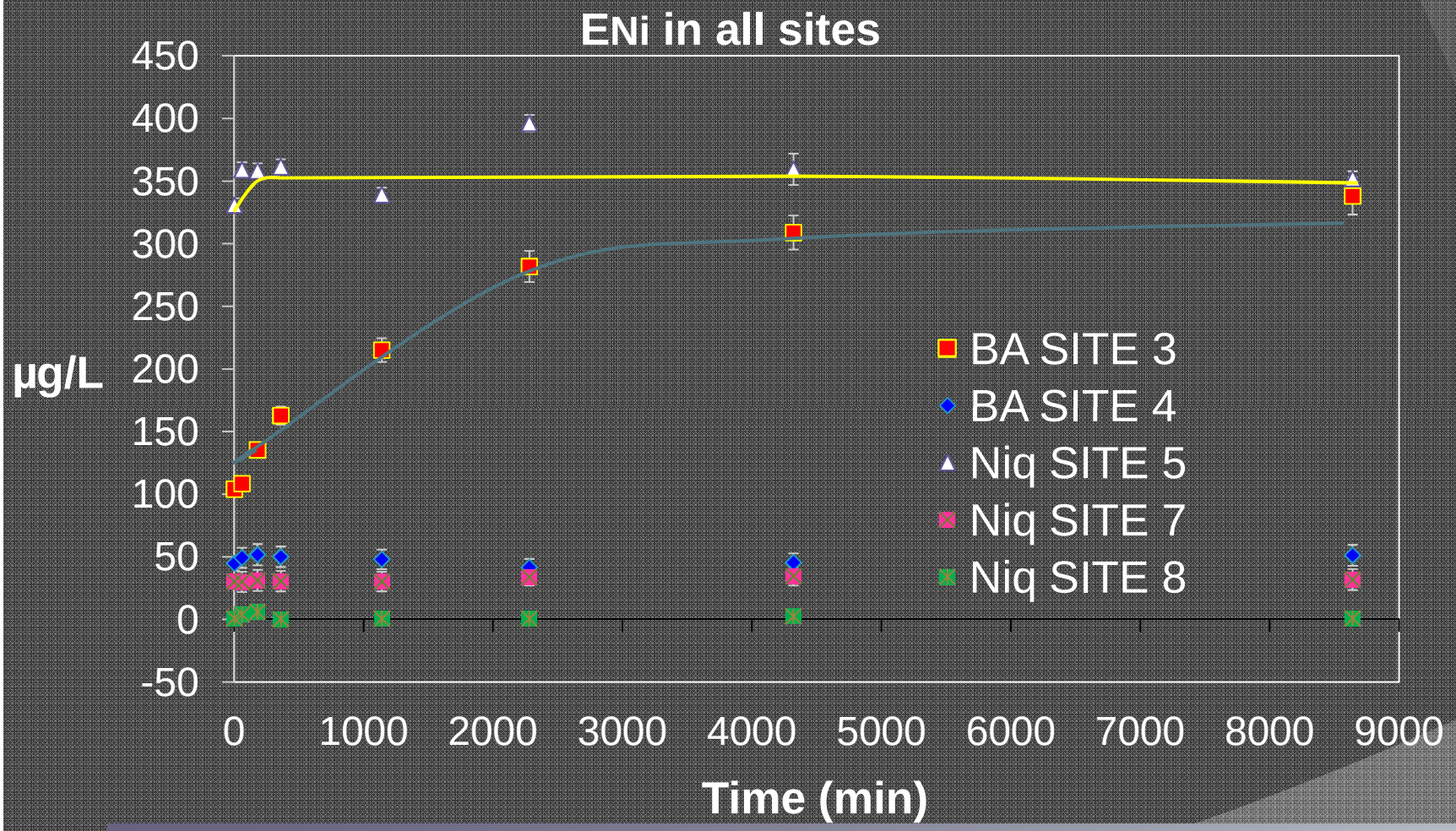
Niquelandia S5
Artificial lake →

BARRO ALTO
SITE4 → river
deviation for wetting
roads

Niquelandia SITE 7
Artificial lake used
for cooling system

Niquelandia SITE 8
Artificial lake, not mine property

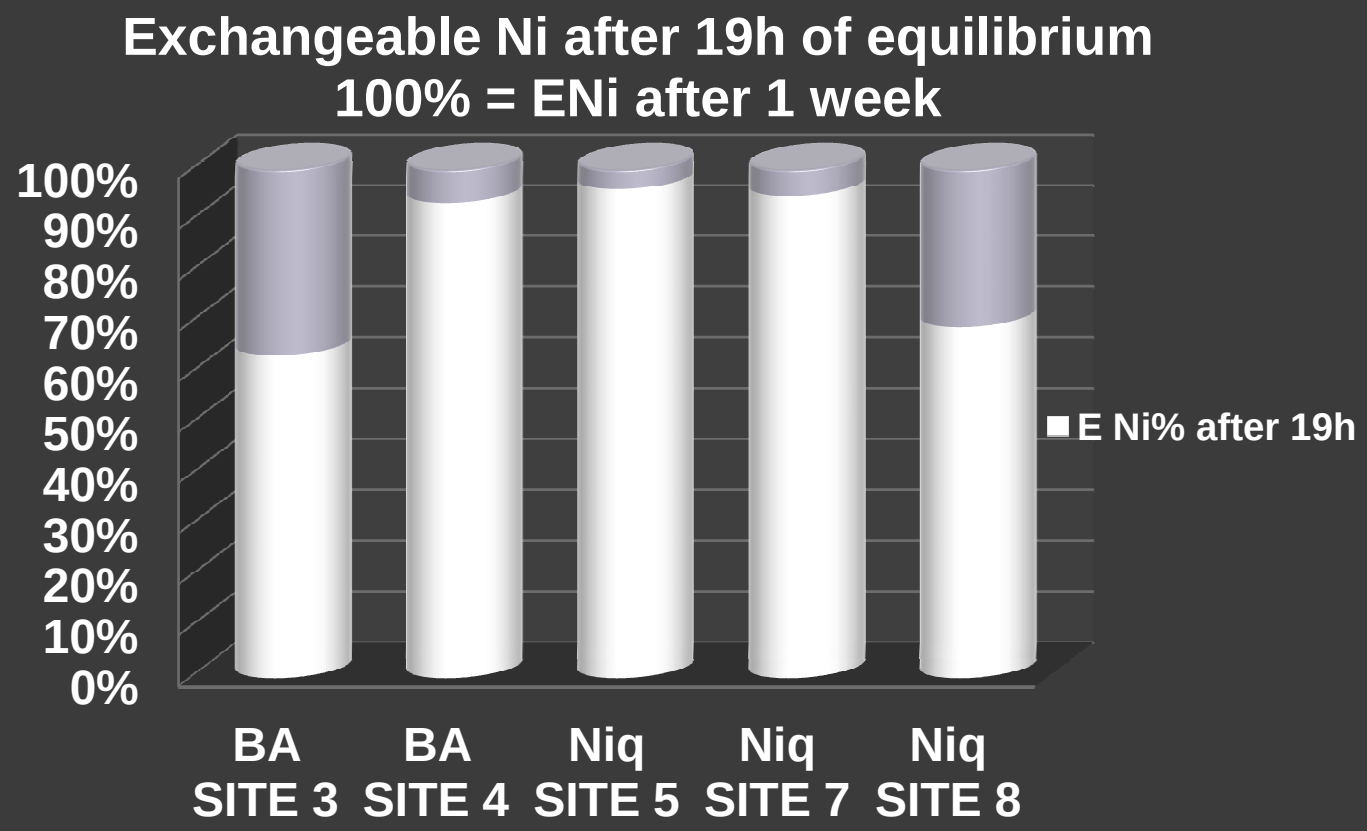
IEK RESULTS: KINETIC of EXCHANGES



Maximum E_{Ni} reached by NIQ SITE 5 and BA SITE 3

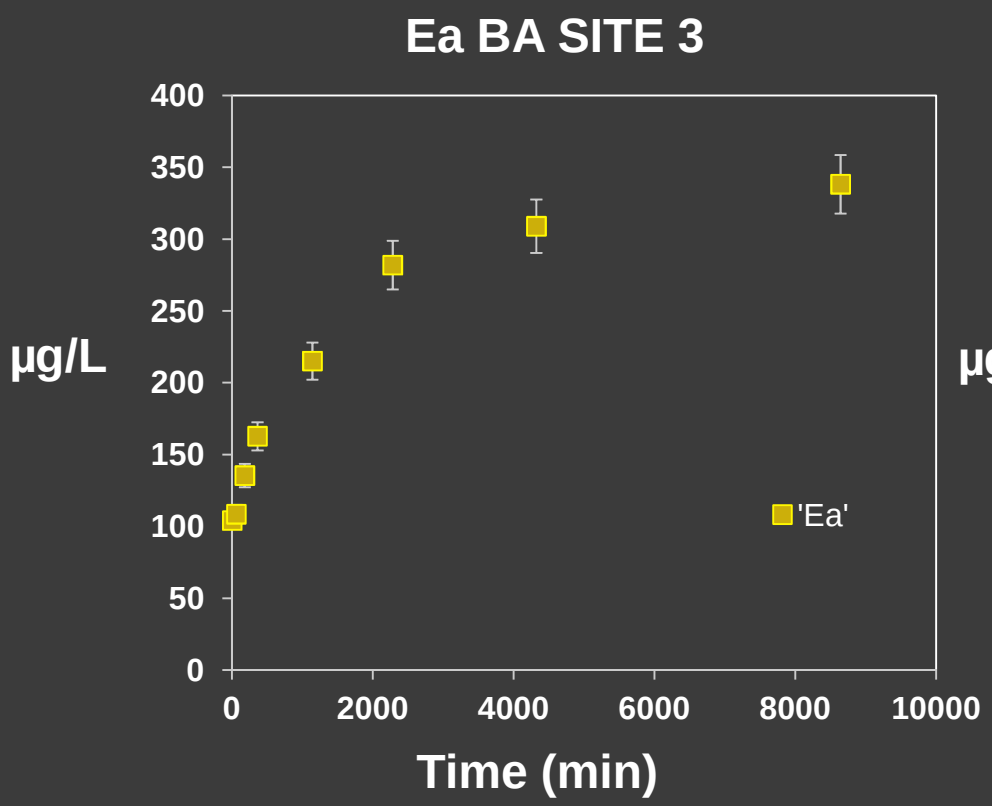
up to 100 times higher than other sites

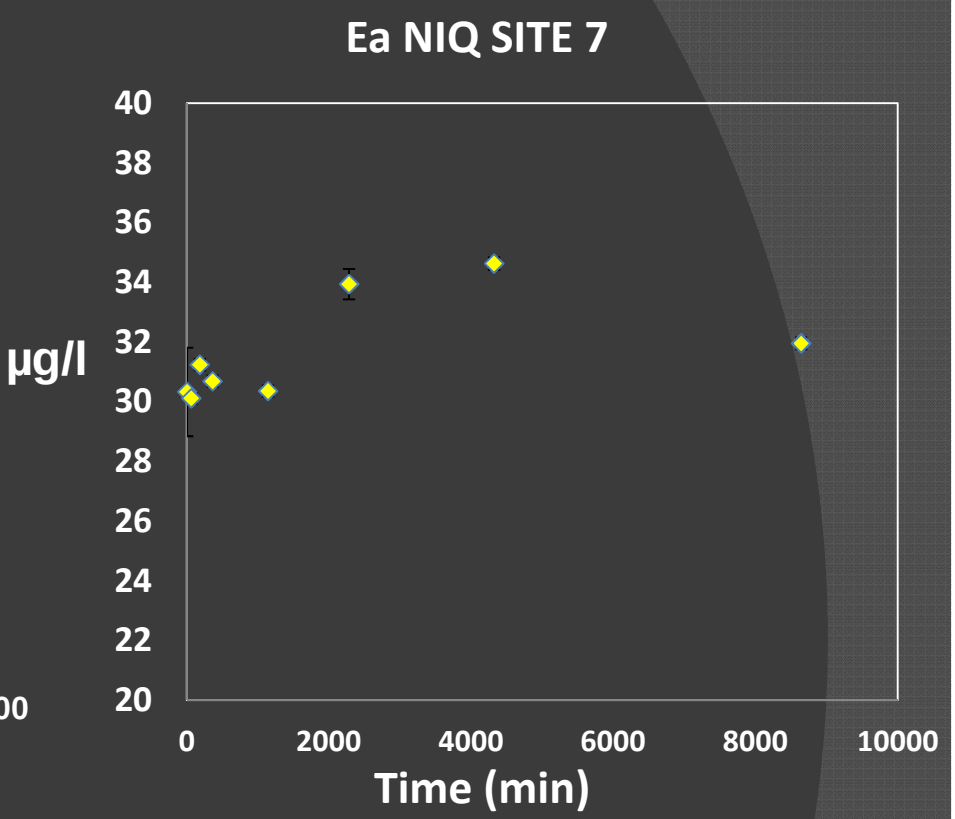
IEK RESULTS: KINETIC of EXCHANGES



Only 3 out of the 5 samples reach more than 90% excheangeable Ni after 19 h

IEK RESULTS: the role of bearing phases





pH: 6.85
Conductivity: 20.8 µs/cm

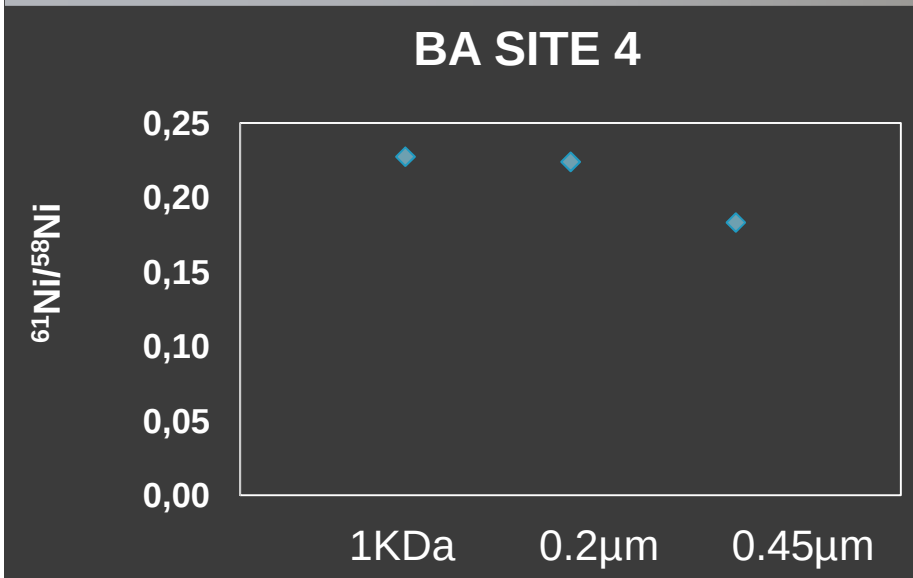
pH:8.48
Conductivity: 416 µs/cm

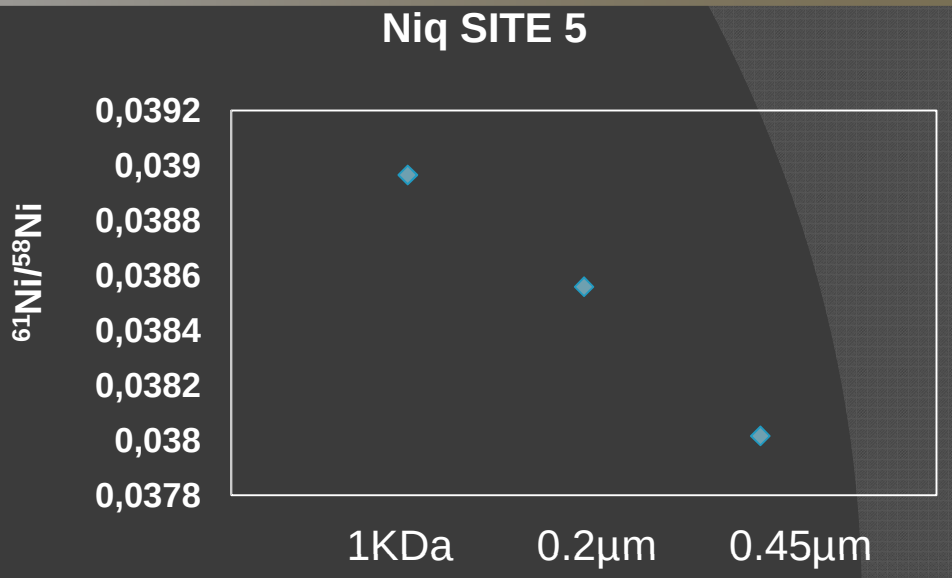
Different behaviour

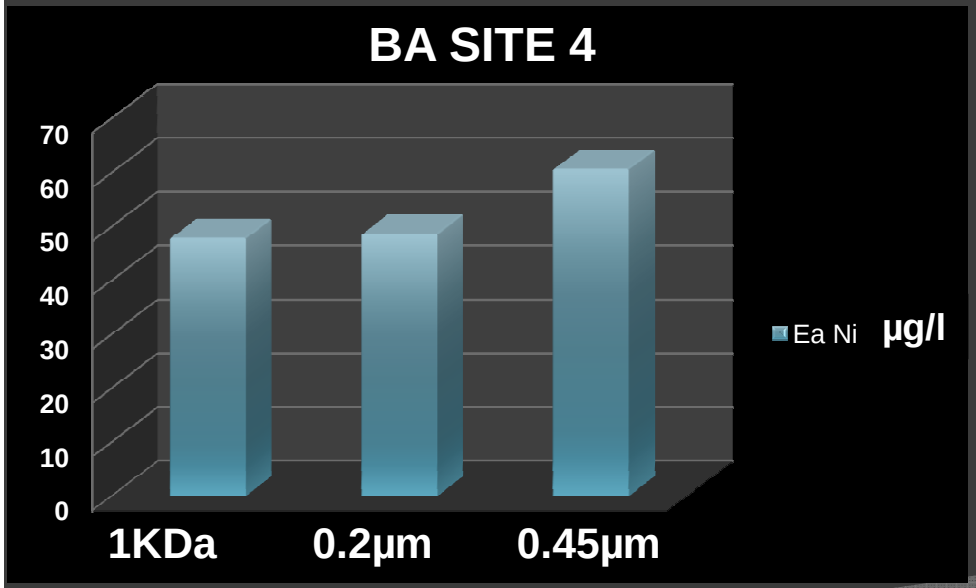
different SPM/Ni bearing phases

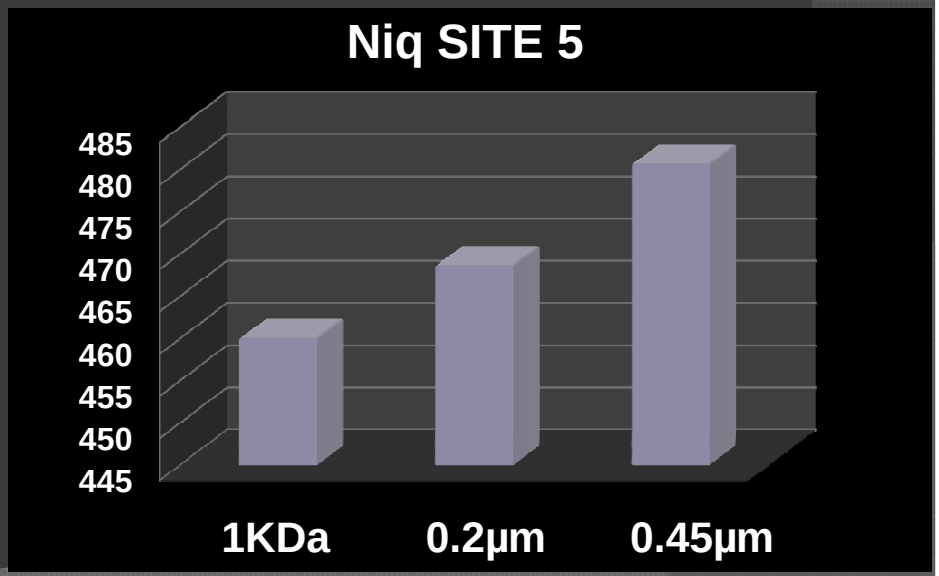
EXCHANGEABLE Ni vs size of SPM

1KDa, 0.2µm, 0.45µm



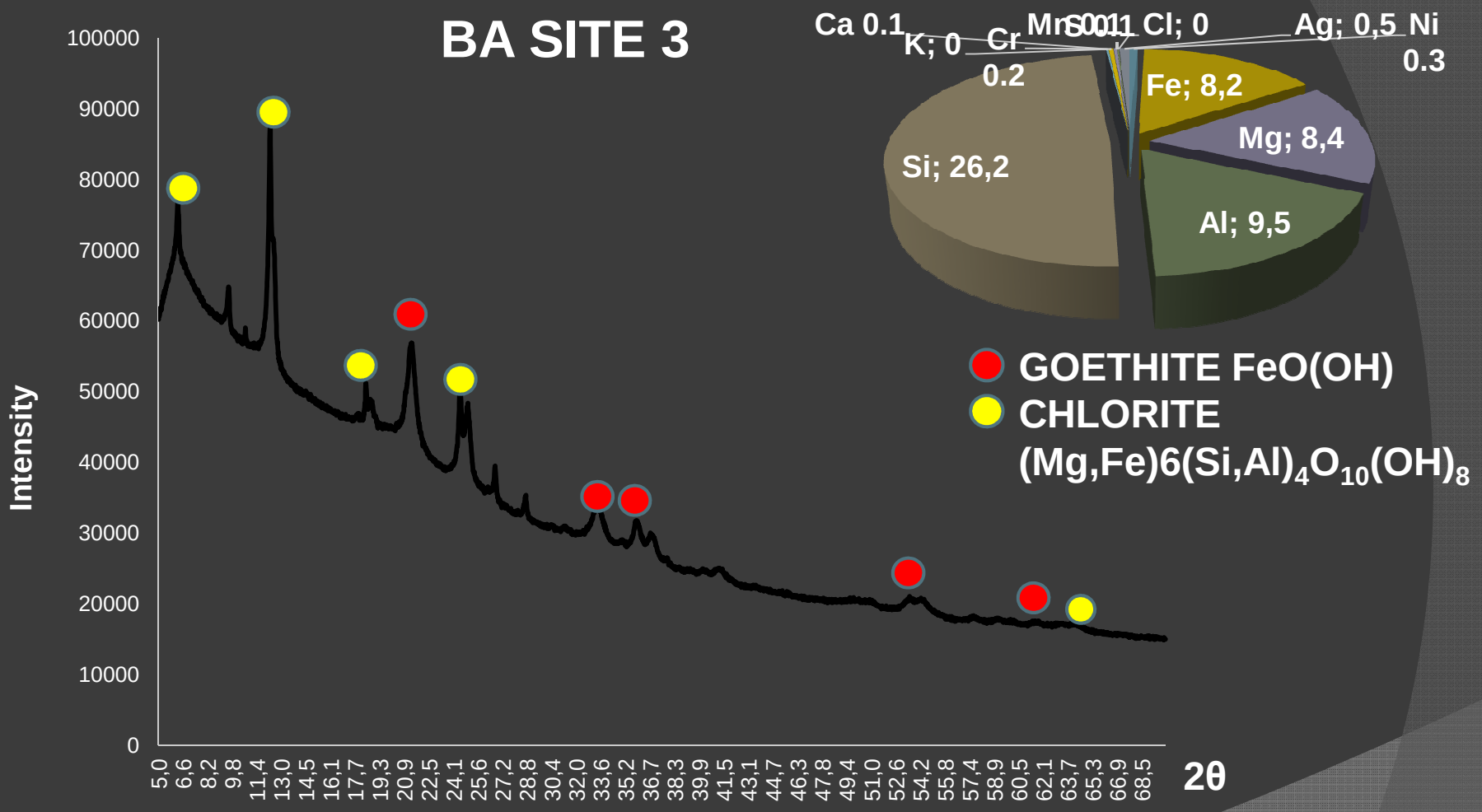






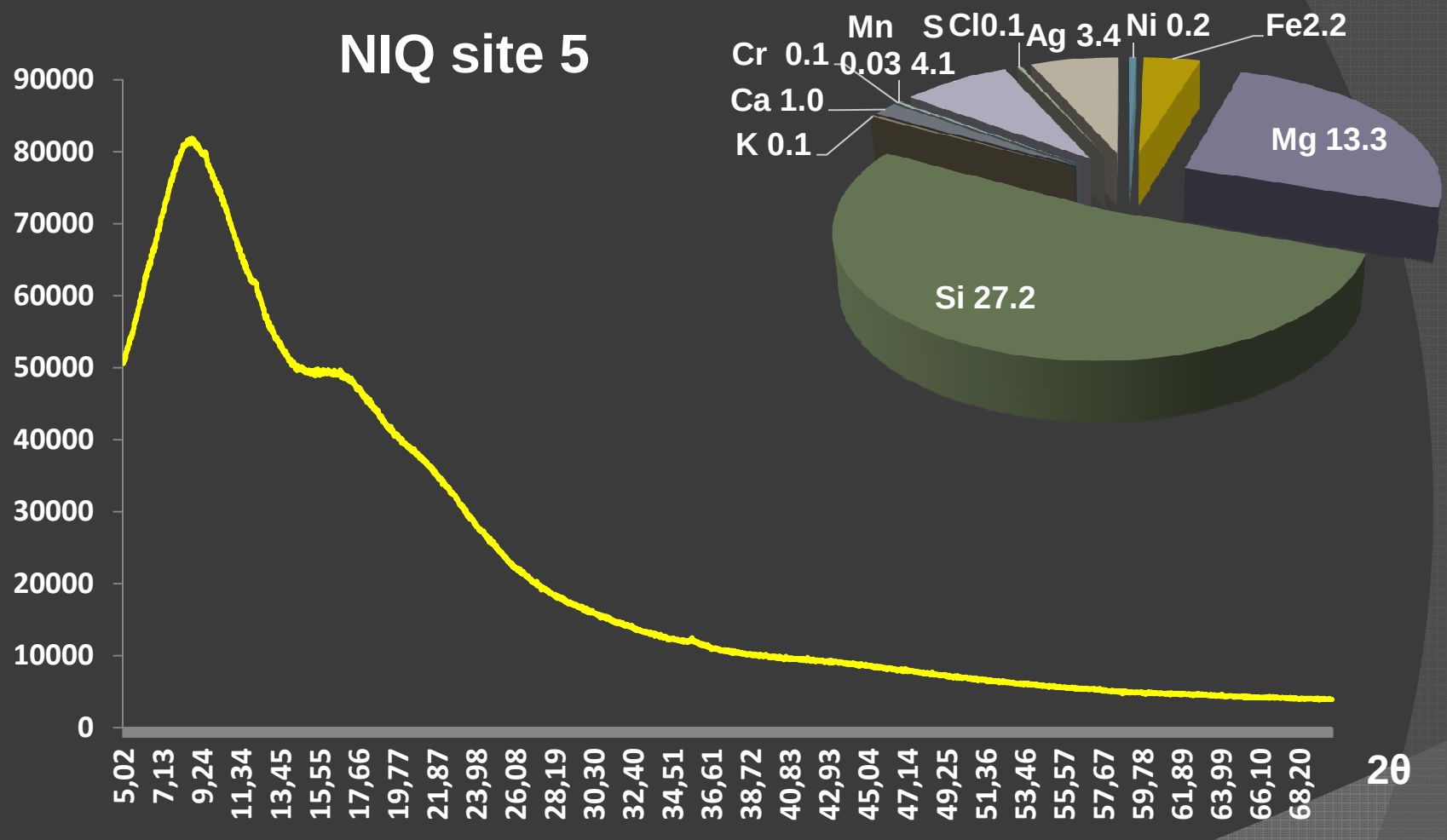
1 DALTON= 1 g/mol

XRD, XRF RESULTS



Identification of two major phases

XRD, XRF RESULTS



Strong filter signal, no identified phases
Probably only amorphous matter

CONCLUSIONS

- Ni availability in water samples from Barro Alto and Niquelandia shows different trend both in kinetic equilibrium and in concentration that correspond to the 5% up to 16 % of the total Ni in the system.
- Filtration of solutions at different pore filter size indicate the presece of Ni bearing phases of different nature.
- XRD results on filters show, in BA samples, the presence of goethite and chlorite, according to soil composition of ultramafic soils of this area; in Niq samples the Ni bearing phases are amorphous.

FUTURE WORK: solid samples

- Obtained results will be compared with solid phases present in the system.
- Soil-water solution will be studied with DDM for speciation investigation.
- A model for a better evaluation of Ni mobility and bioavailabilty in water and a surface complexation on solid phases will be developed with MINTEQ model.

Many Thanks to

INSU - EC2CO program

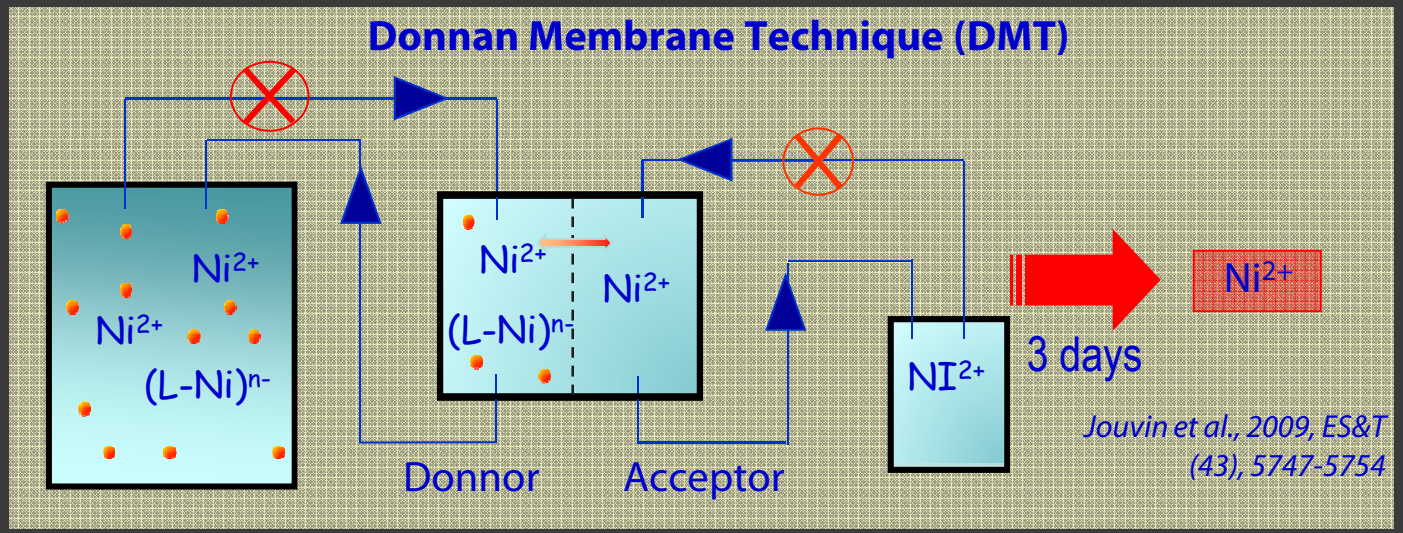
Yann Sivry
Marc Benedetti
Alexandre Gelabert

People from LGE-IPGP team

And you for your attention!

ANIONS-CATIONS-TOC

	BA SITE 3	BA SITE4	Niq SITE 5	Niq SITE7	Niq SIte8	
Fluorure	1.25	1.04	265.79	16.36	2.72	(µM)
Chlorure	3	4.93	205.71	153.72	21.58	(µM)
Nitrate	19.32	9.38	0	10.92	2.18	(µM)
Sulfate	16.31	1.38	1687.26	737.68	10.21	(µM)
Al	60.34	18.66	34.54	0.00	2.78	ppb
As	0.99	0	0	0	0	ppb
B	0	0	0	0	0	ppb
Ba	0.42	0	0	0	0	ppb
Ca	546.60	1903.68	28616.20	22243.84	9607.49	ppb
Cd	0	0	0	0	0	ppb
Co	0.94	0	10.66	0.79	0	ppb
Cu	0.28	1.97	13.42	2.98	5.26	ppb
Fe	291.10	32.78	1459.03	17.87	34.33	ppb
K	183.00	213.08	2599.14	2373.34	1793.90	ppb
Mg	2484.00	11246.34	88848.37	55271.98	4380.57	ppb
Mn	12.87	0	451.74	0.00	17.36	ppb
Mo	0	0	0	0	0	ppb
Na	65.09	413.32	2849.78	2653.37	1513.11	ppb
Ni	**36.57**	**41.67**	**540.35**	**48.06**	**0.50**	ppb
Pb	1.45	82.05	177.42	165.24	68.16	ppb
Sb	1.55	26.96	64.34	89.57	31.06	ppb
Si	2136	10150.34	30214.76	18831.80	5010.62	ppb
Zn	2.55	34.66	84.86	73.48	30.66	ppb
TOC	2132	719.8	65900	3240	1817	mg/l


Donnan Membrane Technique (DMT)
Ni2+
Ni2+
(L-Ni)n-
Ni2+
Ni2+
(L-Ni)n-
NI2+
3 days
Ni2+
Donnor
Acceptor
Jouvin et al., 2009, ES&T (43), 5747-5754

ULTRAMAFICS SYSTEMS

- Rocks are mainly composed by OLIVINE and PYROXENES
- Low content of SILICA (< 45%)
- Content of Fe and Mg OXIDES > 18%
- Low content of N, P, K

- High content of Ni, Cr,Co,Mn