Rocks for crops: The use of locally available minerals and rocks to enhance soil productivity

By

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Outline

- Introduction: What is agrogeology
- Known rock resources for agricultural use
- Focus on Phosphate Rock
  - Direct application of PR
  - Modified PRs
- Focus on Potassium Silicates
  - Direct application
  - Modified potassium silicates
- Focus on Total Silicate Rock
  - Direct application
  - Modified total rock
  - Outlook

What is agrogeology?

There are two aspects of agrogeology:

1. Influence of parent material on soil development and soil fertility
2. Beneficial application of rocks and minerals to enhance productivity of soils: ROCKS FOR CROPS

Agrogeology: an interdisciplinary approach

Inter-disciplinary
research and
development including
soil scientists, biologists,
geologists, process engineers,
farmers -
Agrogeology is a 'bridging science'

Agrogeology

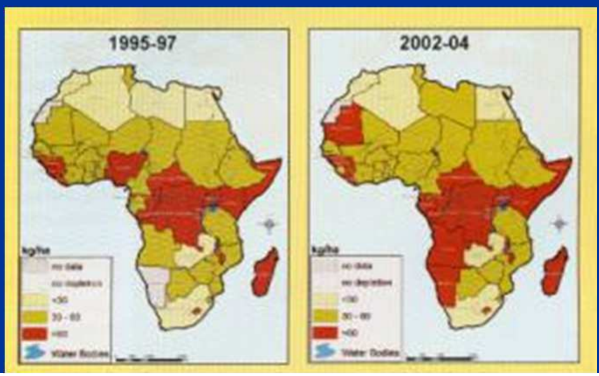
- Science-based search for and use of alternative -mineral- nutrient resources
- Search for and use of unconventional and small agromineral deposits, quarry wastes, industrial mineral extraction wastes
- Part of local plant nutrient replenishment strategies
- Supplements other plant nutrient replenishment strategies
- Inclusive, pragmatic

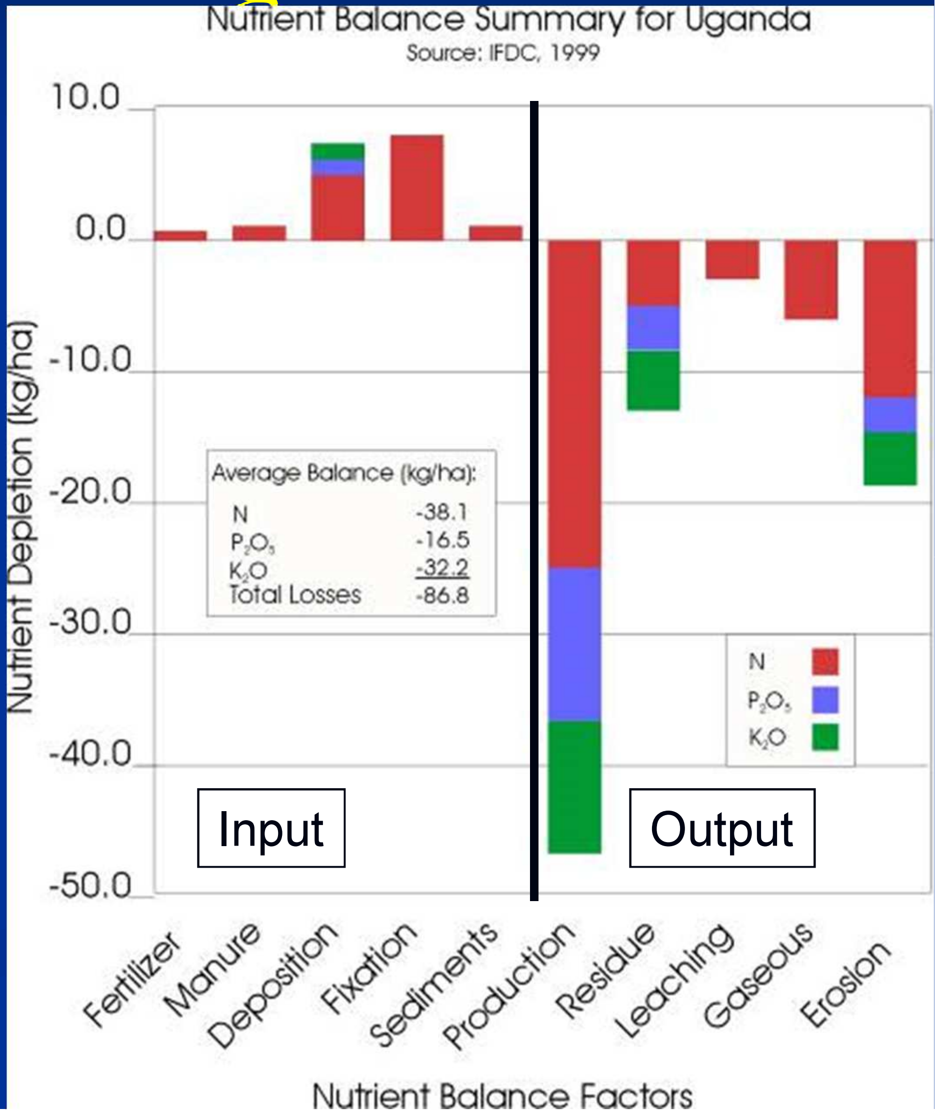
A major 'silent' crisis
Human-induced soil fertility depletion
'Nutrient mining'

- More nutrients are exported through harvesting, erosion etc. than replenished.

Total nutrient imbalance:

Uganda: Nutrient Deficit: - 86.8 kg/ha





HIGH fertilizer prices and LOW fertilizer use efficiencies

High Fertilizer prices, too high for most smallholder farmers

- **Urea** Arab Gulf fob: US$ 350/t

  Uganda up-country : US$ 1,061/t
- **DAP** Saudi Arabia: US$: 500-510/t

  Uganda up-country : US$ 1,224/t
- **K_2SO_4** (no KCl available in Kampala in Feb 2014):

  Kampala: US$ 1,100/t

Low Fertilizer Use Efficiencies

- Fertilizer use efficiencies in 1^{st} year of application: N use efficiency ~ 50%, P use efficiency = 10-15%, K use efficiency = 40% (source: Balligar and Bennett 1986)
- Trends in fertilizer industry is opposite to the trend in 'rocks for crops' application
-

Chemical fertilizer	**Nutrient release rates are too fast; low nutrient use efficiency (NUE)**	**Trend: slow release fertilizer** →
Agromineral application	Nutrient release rates from minerals are too slow	Trend: increase nutrient release ←

Known agromineral resources for agricultural use

- **Sedimentary rocks and minerals**:
  - **Phosphate rocks for direct application and for P fertilizer production**
  - K-salts
  - Limestone/dolostone for liming
  - Gypsum/anhydrite as S sources
- **Metamorphic rocks**:
  - Glauconite and mica schists as potential slow release K sources
  - Marble/amphibolites as Ca/Mg sources
- **Igneous rocks and minerals**:
  - Carbonatites with **phosphates**, kimberlitic associations (Mg-sources),
  - vermiculites, zeolites
  - **K-Mg-Ca rich alkaline volcanics, ultra-potassic rocks (e.g. in agromineral provinces of Italy, Brazil, Germany, Turkey, Indonesia)**

What locally available mineral and organic resources do we have that can increase soil productivity?

- N in biomass, in green and animal manures, through N-fixing crops




- P - Local or regionally available big and small Phosphate Rock (PR) resources
- K-salts, K-silicates from quarries, organic-K resources
- Ca, Mg, S – locally available limestone, dolostone, gypsum
- Trace elements: e.g. from mafic rocks, from 'wastes' – Cu, Zn,

Focus on phosphate rock (PR)

What can we agrogeologists contribute to finding nutrient resources for agriculture?

- **P – phosphate rock (PR)**, from sedimentary, igneous and biological resources

Mining operations:
Big
and
small

Where there are mines
there are (low grade) mine 'wastes'

Know your rocks!

Not all phosphate rocks are equal

- **Fluor-apatite** ($Ca_{10}(PO_4)_6F_2$ in igneous phosphate rocks
- **Hydroxy-apatite** ($Ca_{10}(PO_4)_6(OH)_2$ in bones
- **Francolite**

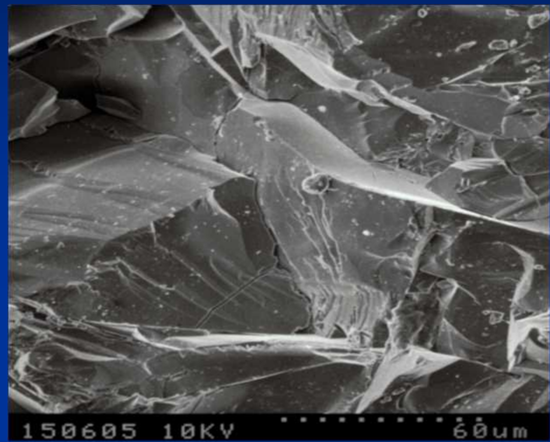
  ($Ca_{10-x-y}Na_xMg_y(PO_4)_{6-z}(CO_3)_zF_{0.4z}F_2$
  (whereby x 0-0.35, y 0-0.14, z 0-1.26)

  mainly found in marine environments, in 'phosphorites'.

Direct application of phosphate rock has limitations

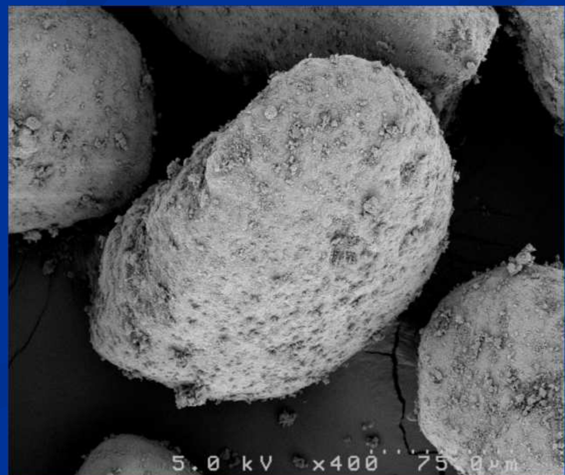
- The reactivity/solubility of PRs varies widely amongst apatite minerals due to mineralogy/chemistry, e.g. – igneous fluor-apatite versus sedimentary apatite (francolite)

- To become agronomically effective, PR may require dissolution by inorganic or organic acids, or other release mechanisms of P from apatite



Fluor-apatite

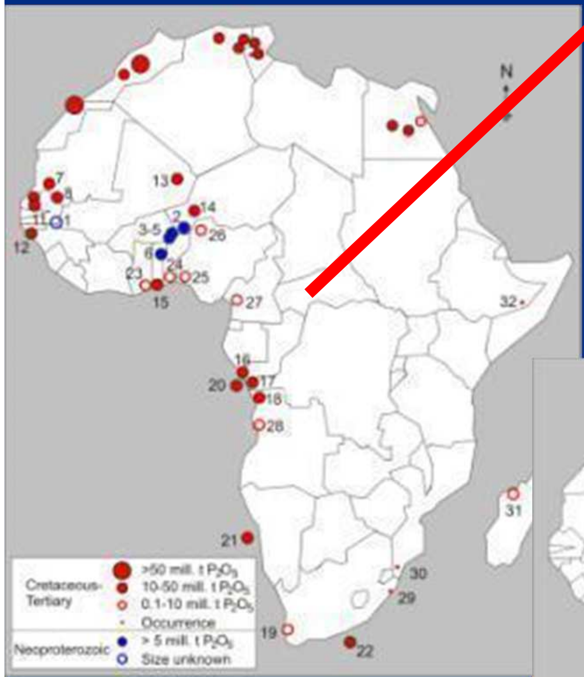
Low surface area, low reactivity



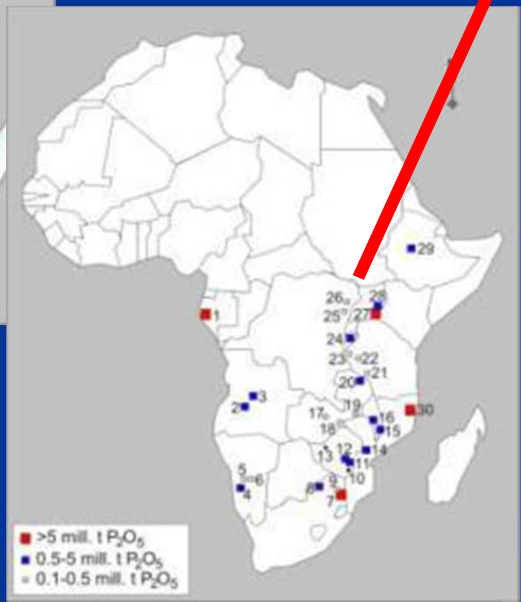
Francolite

High surface area, higher reactivity

Phosphate rock (PR) resources in Africa: <u>most are unreactive</u>



Sedimentary resources:
low – medium reactive PR,
West Africa

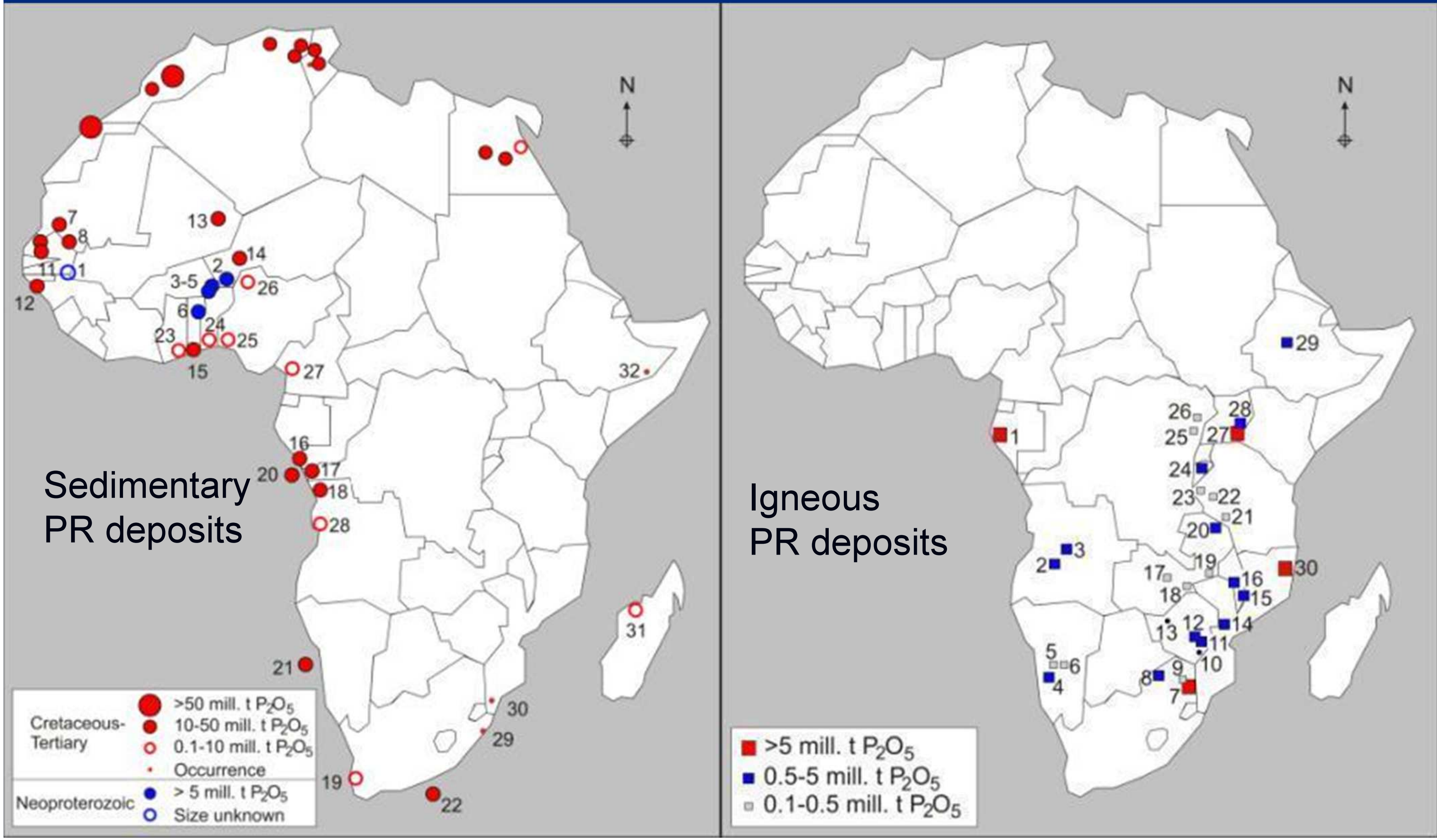


P resources: igneous resources; mainly low grade low reactive PRs, Eastern and Southern Africa

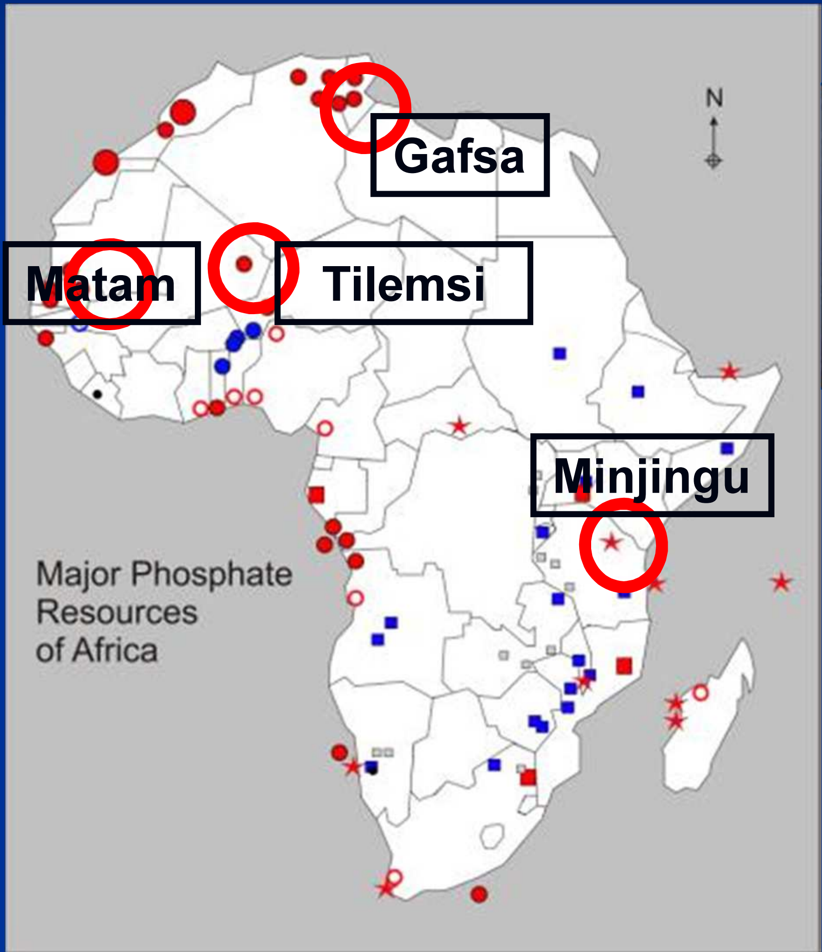
Very few biogenic/sedimentary PR resources
(fossil bone deposits, Mali, Senegal, Tanzania)
Good reactivity

Source: van Straaten 2011

More than 90% of PR resources in Africa are unreactive



Only very few reactive PR resources in Africa, useful for direct application



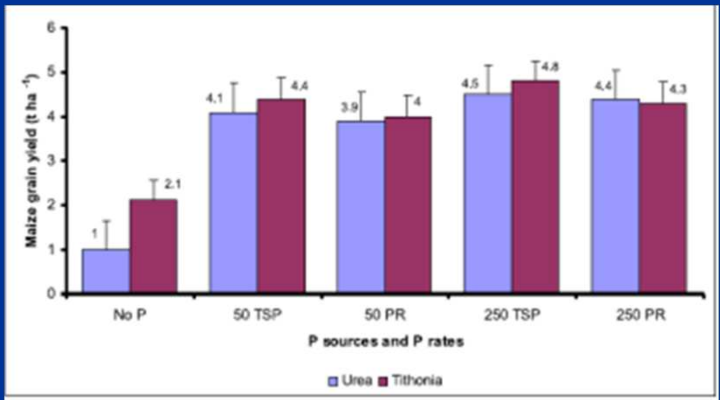
Minjingu, Tanzania (20 000 tpa)

Tilemsi, Mali

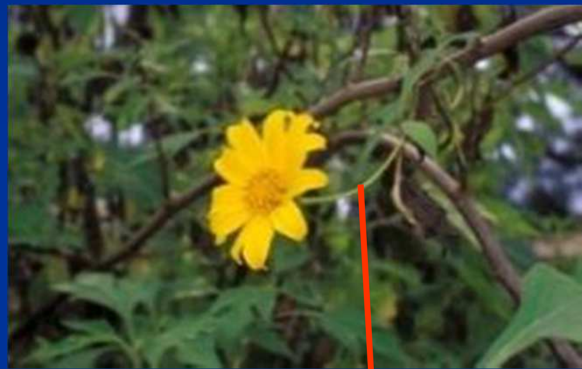
UTILIZATION OF REACTIVE PR for direct application

Success story from Tanzania: Minjingu PR (bone deposit)

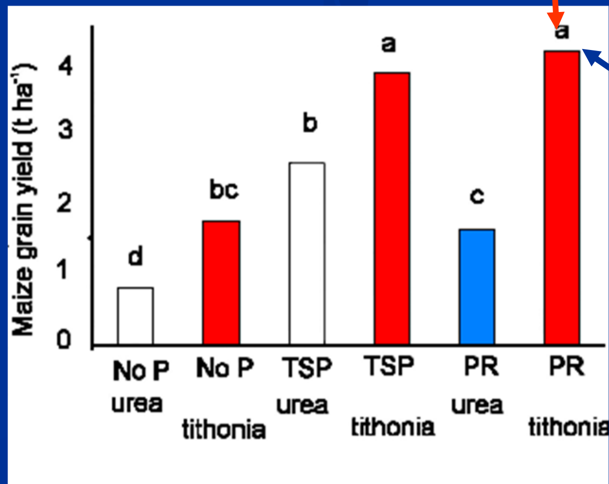
Production: > 20 000 t PR based P fertilizers per annum



Source: Jama and van Straaten 2006



Tithonia diversifolia, 4% N, 0.4% P_2O_5 4 % K

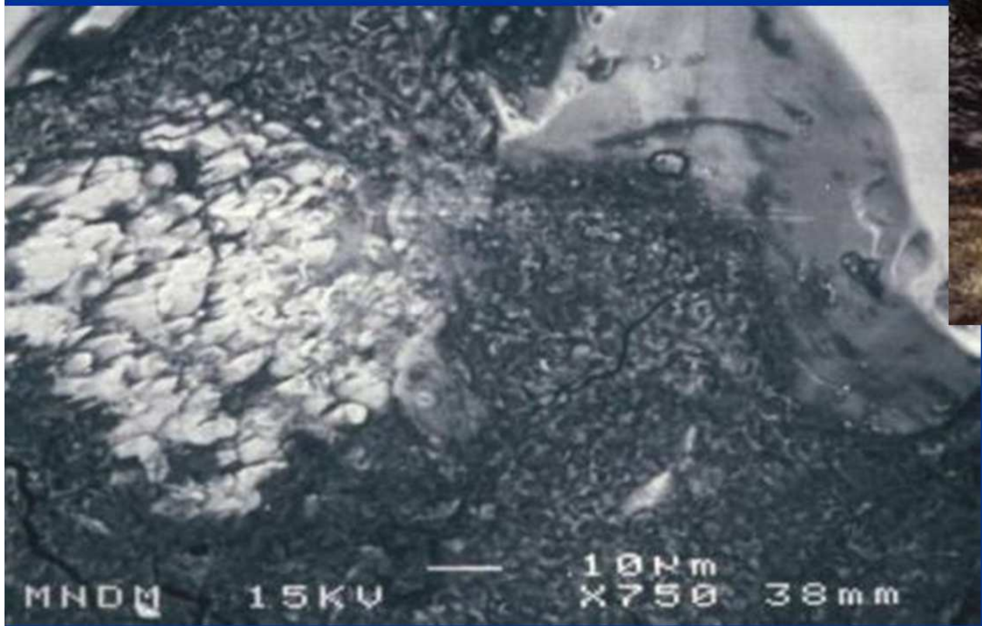


(Source: Buresh et al., 1997)

Most PR resources in Africa are unreactive and need modification to become effective. What modification options do we have?

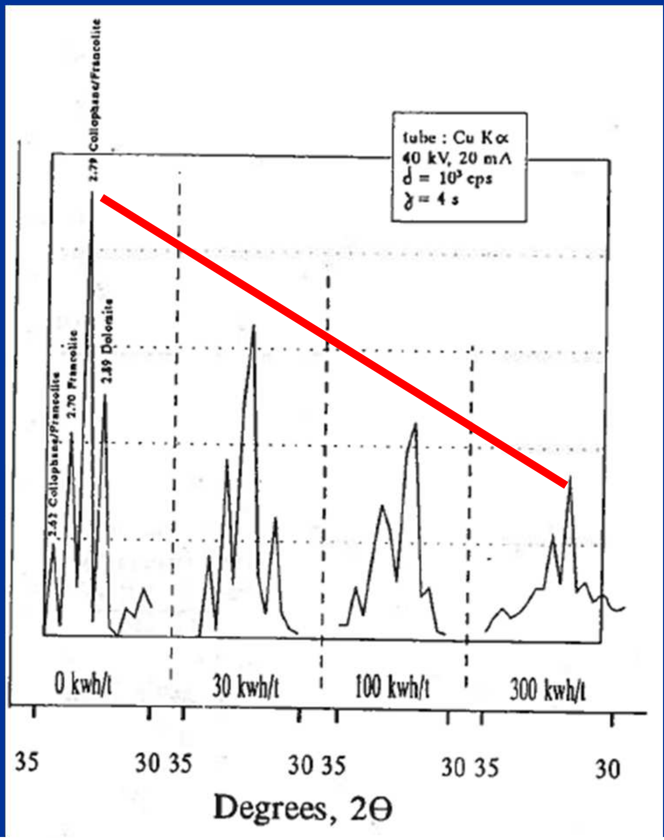
- Physical modification:
  - Mechanical activation
  - Thermal treatment
- Chemical modification:
  - Acidulation with mineral and organic acids
  - Partial acidulation (PAPR)
  - Blending, compacting, granulation , e.g TSP +PR
  - PR + S
- Biological modification:
  - Biosolubilization with PR solubilizing microorganisms (fungi/bacteria)
  - Phospho-composting
  - Use of Mycorrhizae

Successful *HYBRID* PR modification: blending PR with TSP 'Hydrolysis induced acidulation' with 'Waste' PR – TSP blend (70/30), with starter effect

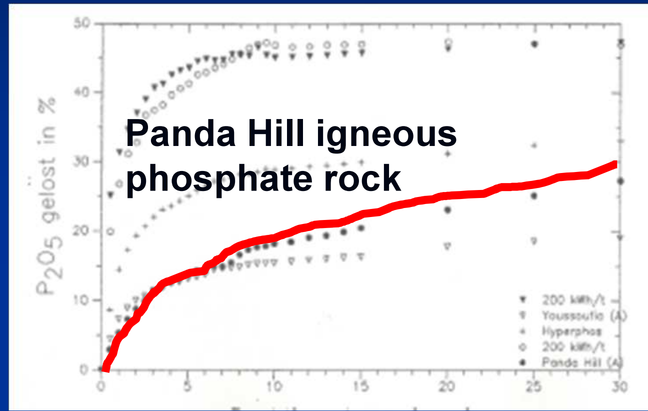


Phosphate mine 'wastes'
Wastes = misplaced resources!

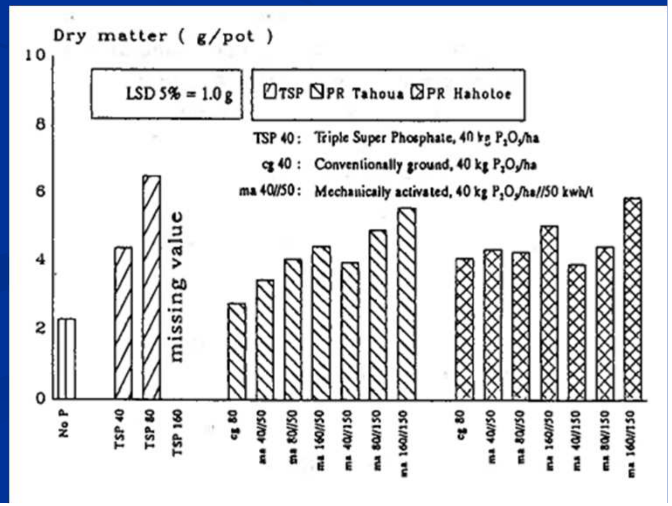
Successful physical modification: Mechanical activation



Decrease of XRD intensities of apatite (francolite) as a function of mechanical activation



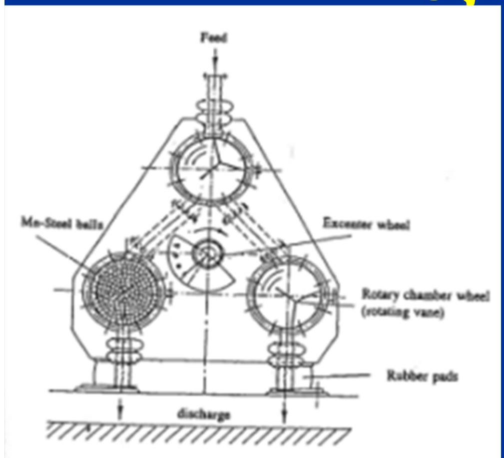
Reaction time: in minutes,
Increase in 2% citric acid solubility of igneous PR from 27.28% to 46.93%

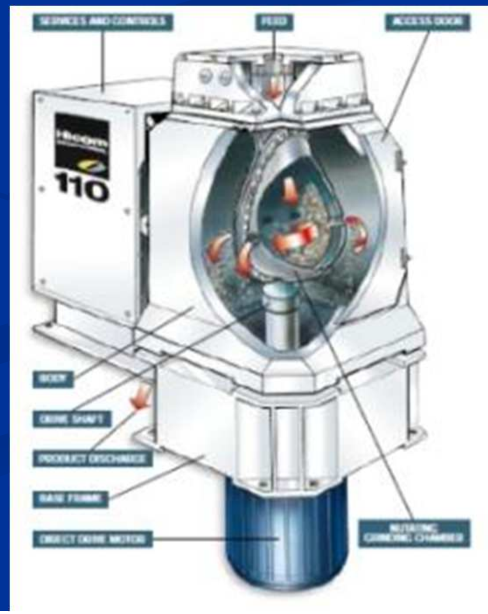


Source: Müller 1995

No chemicals involved:

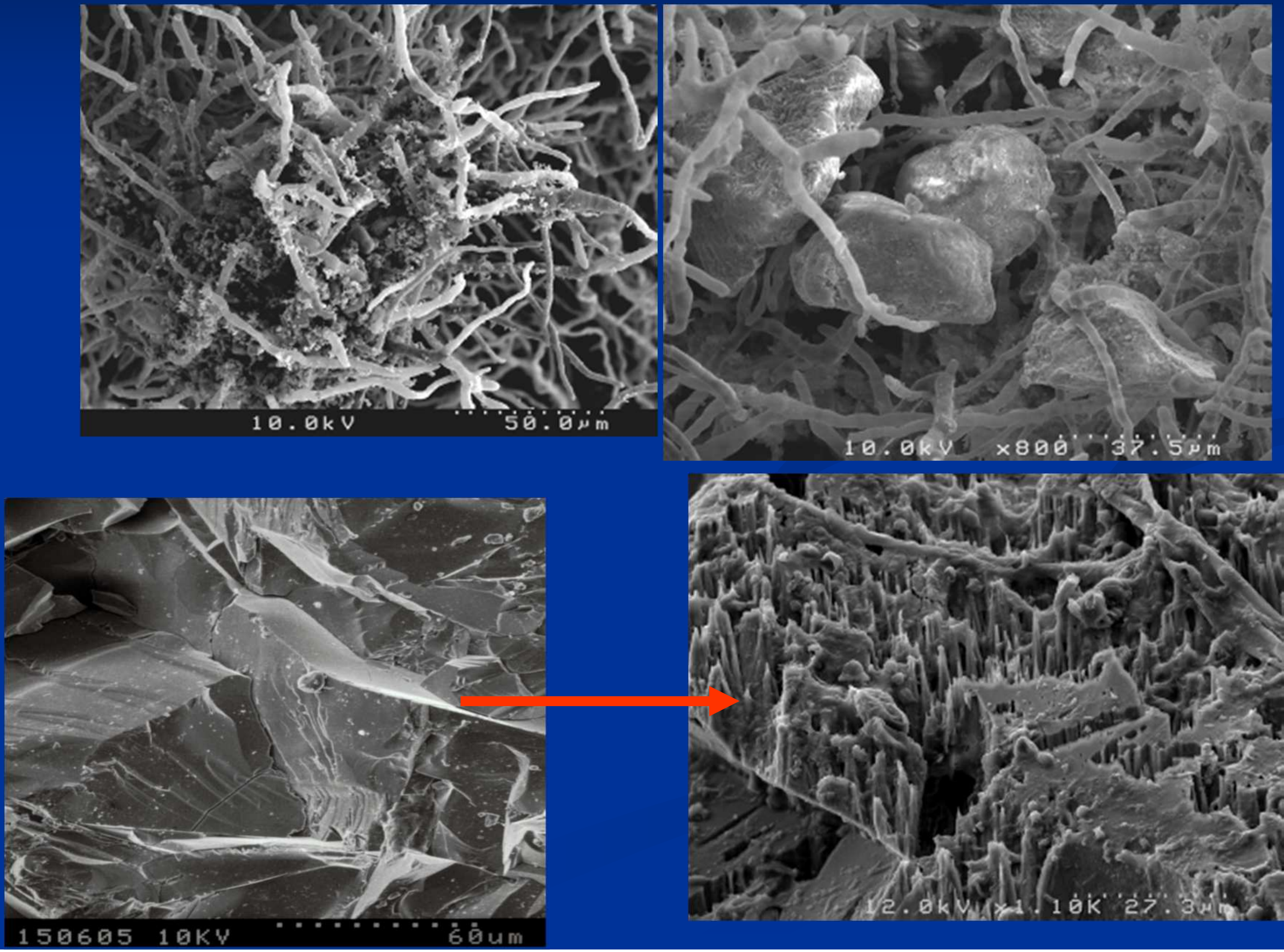
Inexpensive milling technologies developed with mechanical activation using eccentric vibrating mills, nutating mills, high-energy stirred ball mills



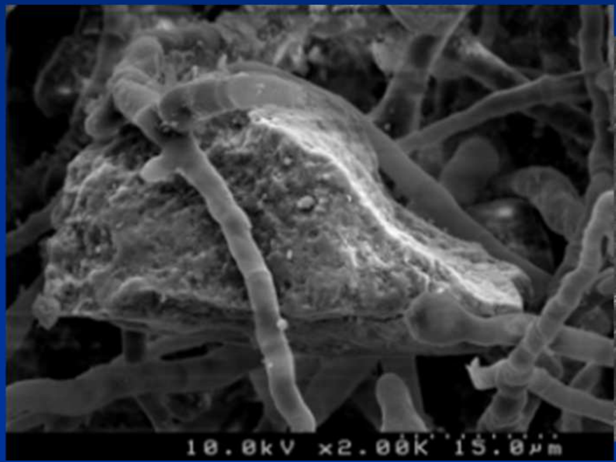


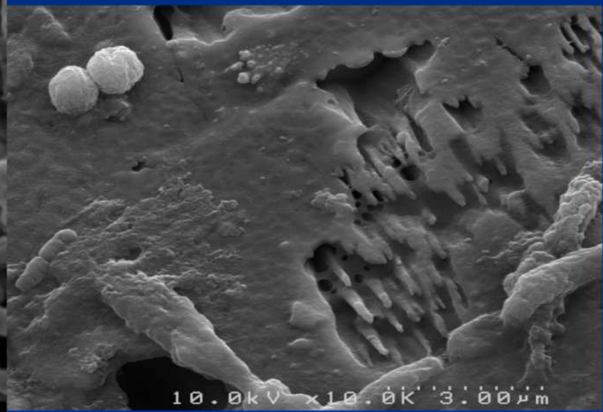
Milling costs: $20-30/t

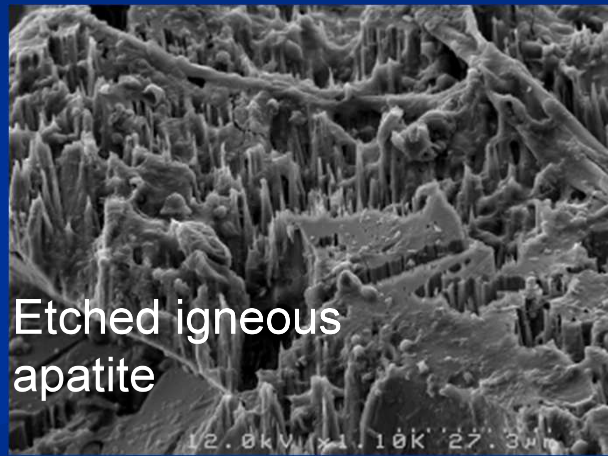
Biosolubilization of apatite with *Aspergillus niger*

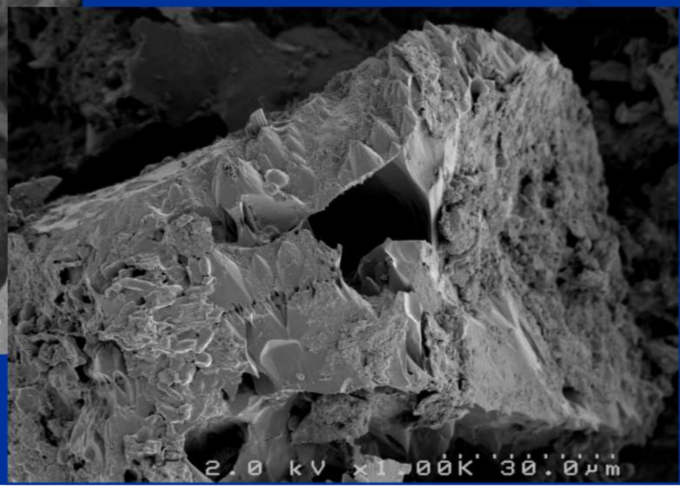


Enhanced biosolubilization of ‘unreactive’ igneous Ca-phosphate









<u>BEFORE AND AFTER STUDY</u>

Time of exposure of
IGNEOUS APATITE
to A. *niger* containing
cassava waste:
dissolution > 30% in 5 days


PROCESSING OF PHOSPHATE ROCK
TO PRODUCE BIO-SP
Courtesy: Laksmita Prima Santi & Didiek Hadjar Goenadi

Commercial bio-phosphate fertilizer, Indonesia

Production: 5 000 tpa

Another successful PR modification technique: Thermal treatment

Glass

P_2O_5 total=18%,
P_2O_5 in 2% citric acid soluble = 16.5%
CaO = 20%
MgO = 9%
Si in 2%citric acid soluble = 9.16%
(SiO_2 – soluble = 19.6%)

Promising directions in PR modification

- High energy mechanical activation of phosphate rock using more effective and less expensive milling techniques
- Development of bio-phosphates (microbial solubilization)
- Blending and compacting with acidifying fertilizers, e.g. TSP
- Thermo-phosphates **+ K** and trace elements
- Developing slow-release organo-mineral pelletized fertilizers, in combination with other mineral nutrients and/or organics

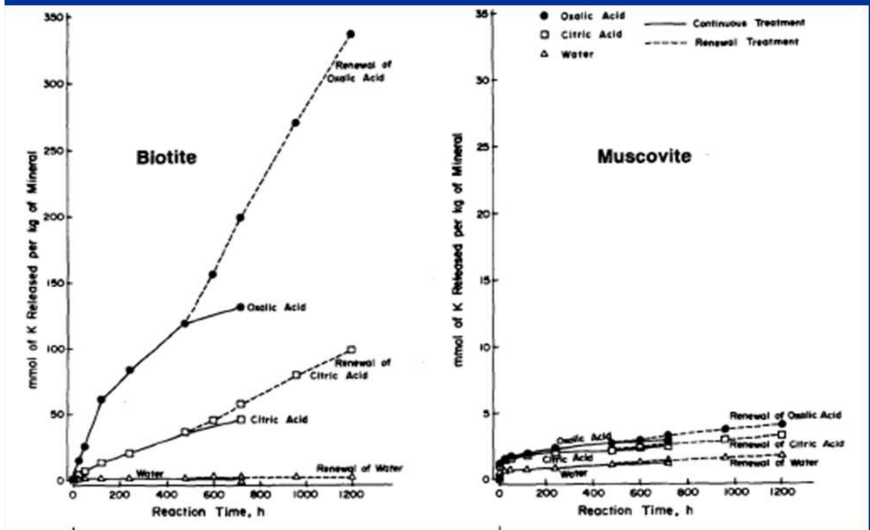
Focus on Potassium silicates

K-Silicate minerals as potential alternative K sources

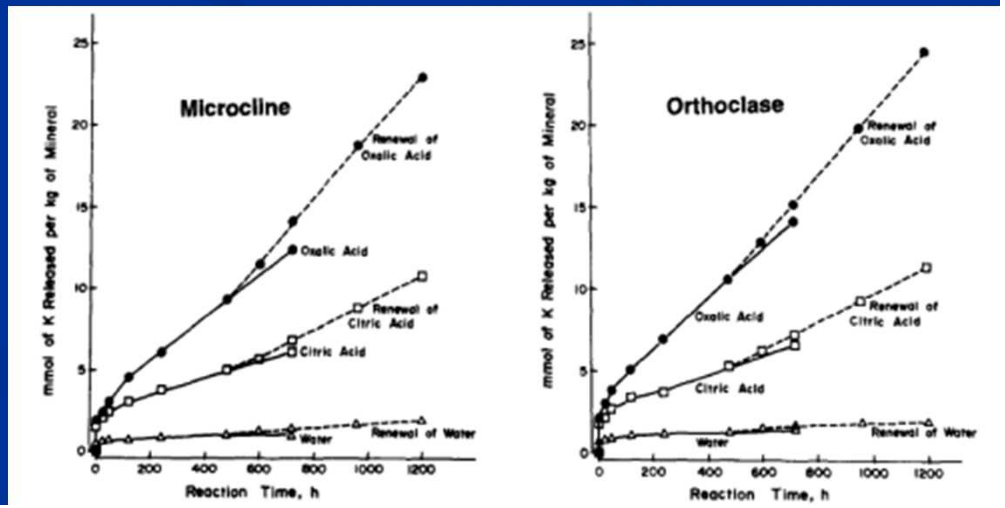
- K-feldspar 8-15% K_2O (*very* low solubility)
- Biotite 7-12% K_2O (low solubility)
- Phlogopite 7-11% K_2O (low solubility)
- Muscovite 7-10% K_2O (*very* low solubility)
- Illite 4 - 8% K_2O (low solubility)
- Glauconite 5 - 8% K_2O (medium solubility)
- Nepheline $KNa_3(AlSiO_4)_4$ 8 % K_2O (medium solubility, high NaO)
- Leucite $K(AlSi_2O_6)$ up to 21% K_2O! (medium solubility)
- Kalsilite (very rare) up to 30% K_2O! (medium solubility)

Know your rocks!

Not all K-silicates are equal: Example micas and K feldspar solubility in citric and oxalic acids



Source: Song and Huang 1988



Dissolution rates of selected K silicate minerals

Mineral	Mineral family	Formula	Weight % K	Weight % K_2O	Dissolution rate (acid mechanism), log mol m^{-2} s^{-1}
Potassium feldspar	Feldspar	$KAlSi_3O_8$	14.0	16.9	-10.06
Leucite	Feldspathoid	$KAlSi_2O_6$	17.9	21.6	**-6.00**
Nepheline	Feldspathoid	(**Na**,K)$AlSiO_4$	8.3	10.0	**-2.73**
Muscovite	Mica	$KAl_3Si_3O_{10}(OH)_2$	9.0	10.9	-11.85
Biotite	Mica	$K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$	9.02	10.86	-9.84
Phlogopite	Mica	$KMg_3(SiAl)O_{10}(F,OH)_2$	9.33	11.23	-10.00
Glauconite	Mica	$(K,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$	5.49	6.62	**-4.80**

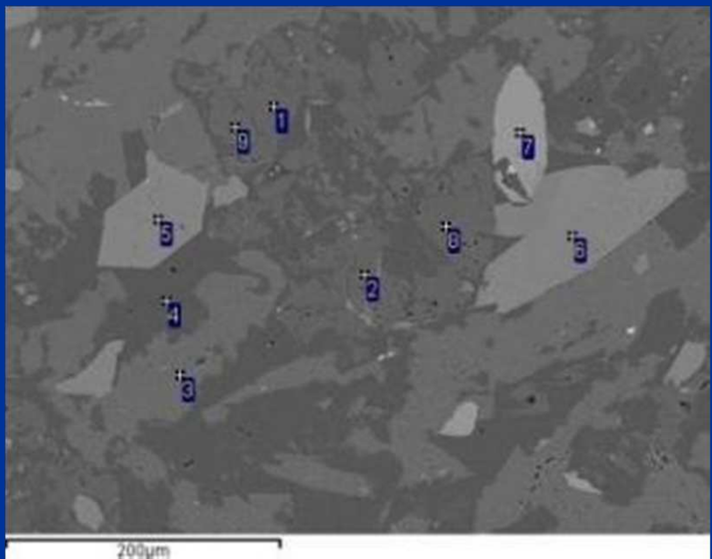
Source: Palandri and Kharaka, 2004, USGS

Commercial K-silicate fertilizers from Poços de Caldas, Brazil: Nepheline bearing phonolite

Know your rocks!

Comprehensive mineralogical and chemical characterization of rocks and minerals before use is crucial

- Example: PHONOLITE from Poços de Caldas, Brazil



1 = nepheline
2 = nepheline
3 = Kfsp
4 = albite
5 = amphibole
6 = amphibole
7 = titanite
8 = nepheline
9 = nepheline

Chemical analysis in %:

SiO_2	MgO	CaO	K_2O
54	0.3	1.5	8.6

XRD:

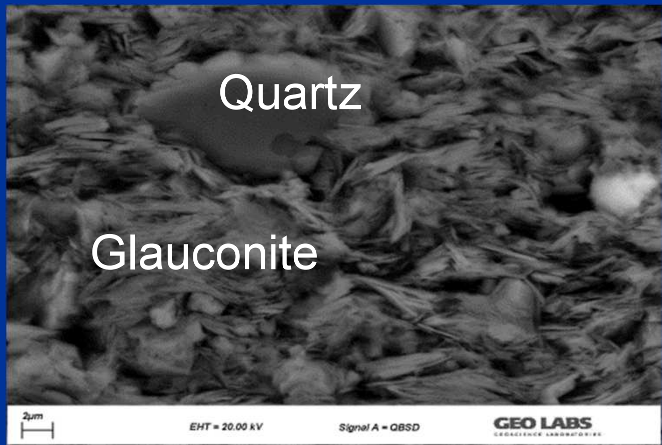
Direct application of phonolite products in Brazil

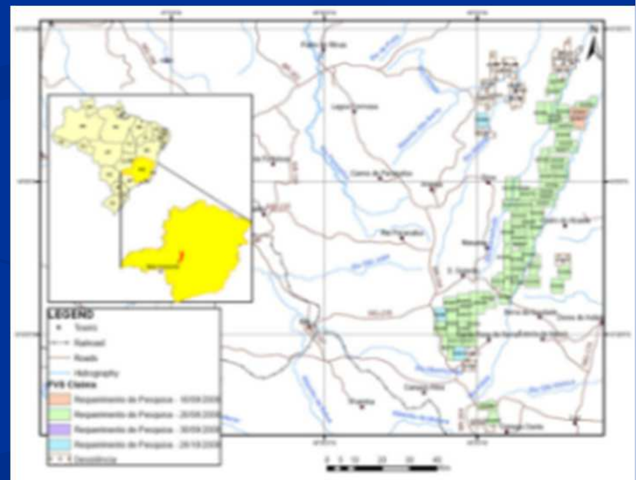
- Production: > 15 000 tpa
- Main crops: sugar cane, soybean, coffee, maize

Example: Coffee, Minas Gerais, Brazil:
KCl: 540kg/ha → 2,520 kg coffee/ha
Phonolite: 2,200kg/ha → 2,760kg/ha

Alternative K-source in Brazil: Glauconite bearing (meta-)sediments 'Verdete'

- Composed of mainly quartz and glauconite (K, Al,–silicate + Mg, Fe)
- 'Verde Potash' intends to produce thermo-potassic fertilizers





Chemical analysis, in %

	SiO_2	MgO	CaO	K_2O
Glauconite	52	3.7	4.8	9.9

Deposit size:
100 x 6km x 20-80m thick
253 million tonnes of in-situ K_2O

A new process

- 'HYDROSYENITE': hydrothermally transformed syenite

- Developed by Massachusetts Institute of Technology (MIT) and Terravita

See POSTER outside Conference Hall

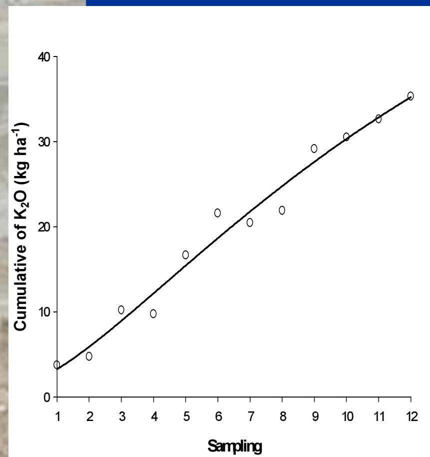
Focus on quarry 'wastes'

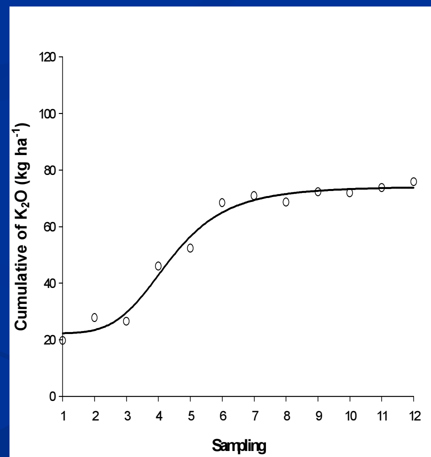
- Separation of mafic and felsic components from granite quarry 'waste' (+ mechanical activation)

Biotite concentrate 'waste'

SiO_2	MgO	CaO	K_2O
53	3.3	2.0	6.4

Focus on quarry wastes: use of separated quarry fines of monzogranite as potential K source



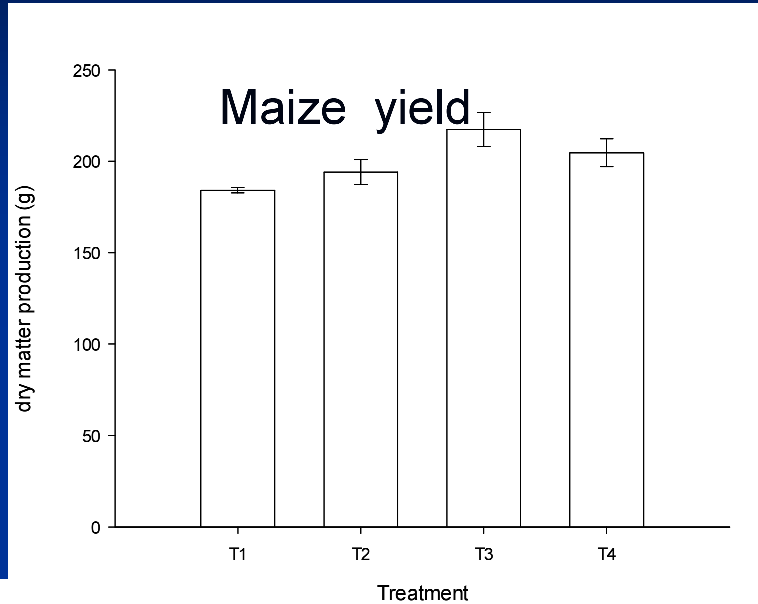


Source: Posser *et al* 2013

Monzogranite aggregate quarry Pedreira Silveira, Pelotas RS, Brazil

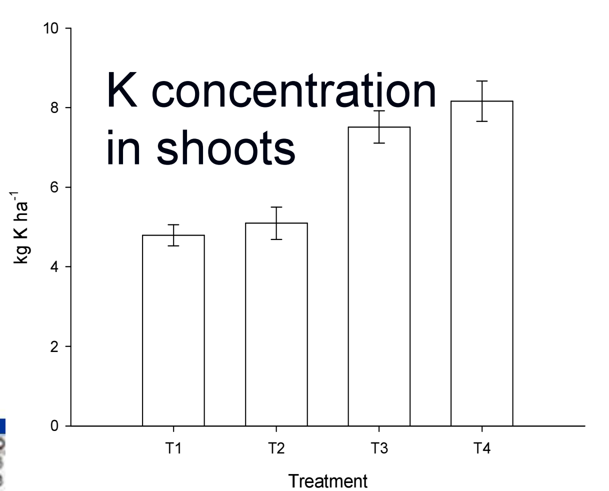
Separation and use of felsic + mafic fractions of monzogranite 'wastes'

Novel optical separation of felsic and mafic rock fractions



Sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	
FrE*	68,34	15,56	3,30	1,01	3,11	3,51	3,54	0,44	0,14	0,06	
FrMafic	60,84	16,55	7,11	2,32	4,31	3,58	2,85	1,02	0,31	0,13	
FrFelsic	73,82	14,56	0,60	0,07	1,25	2,97	5,89	0,04	0,04	0,01	0,052

*FrE- Original fraction (inlet)



T1 = Control,:0 K, + 375 kg Arad PR (105kg P_2O_5/ha)+ 140 kg N/ha (as urea)

T2 = 4t of felsic faction (**K-feldspar rich**) + 375kg Arad PR + 140 kg N /ha (urea)

T3 = 4t of mafic fraction (**Biotite + hornblende rich**) + 375 kg Arad PR +140kgN/ha

T4 = 183 kg KCl (+ 375kg Arad PR +140 kgN/ha (urea)

Source: Grecco *et al*. 2014

Promising directions

- Enhanced liberation of K from various primary K-silicate rocks, mainly foidites
- Separation and use of K + Ca-Mg silicate minerals from 'quarry wastes'
- Development of bio-potassic fertilizers (Bio-K)
- Development of thermo-potassic fertilizers
- Development of thermo-potassic phosphate fertilizers

Focus on Total Silicate Rock amendment

(rock powder)

Challenge: silicate rock amendment

Nutrient Cycling in Agroecosystems **56:** 11–36, 2000.

Factors influencing the release of plant nutrient elements from silicate rock powders: a geochemical overview

A.D. Harley* & R.J. Gilkes
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Silicate rock amendments (rock powder): Weathering rates of silicate minerals in aqueous solutions at 25°, pH = 5

Mineral	R ($mol\ m^{-2}\ s^{-1}$)
Quartz	4.1×10^{-14}
Muscovite	2.56×10^{-13}
K-feldspar	1.67×10^{-12}
Albite (Na-rich)	1.19×10^{-11}
Diopsite	1.4×10^{-10}
Nepheline	2.8×10^{-9}
Anorthite (Ca-rich)	5.6×10^{-9}

Most stable

Least stable

Source: Lasaga 1984

The mean lifetime in years of 1mm crystals of various minerals, calculated from laboratory dissolution studies at 25 deg C and pH5 (Lasaga, 1984)

	years
Quartz	34 000 000
Muscovite	2 700 000
K-feldspar	520 000
Albite	80 000
Enstatite	8 800
Diopsite	6 800
Nepheline	211
Anorthite	112

Source: Lasaga 1984

Challenge to increase nutrient release rates

- Published data from laboratory settings with H_2O @ pH 5 and @ 25° C
- Tropical conditions – **higher T**
- Complex interaction in soils with organic acids
- Root exudates of plants differ strongly and contribute to mineral weathering (bioweathering)

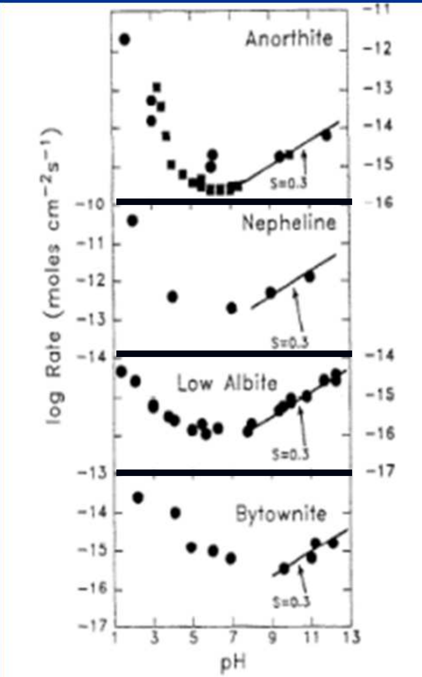


FIG. 4. 25°C dissolution rates of anorthite (Squares—AMRHEIN and SUAREZ, 1988, Hexagons—HOLDREN and SPEYER, 1987, Circles—BRADY and WALTHER, in prep), nepheline (TOLE et al., 1986), low albite (CHOU and WOLLAST, 1985), bytownite (BRADY and WALTHER, in prep.). *S* denotes slope.

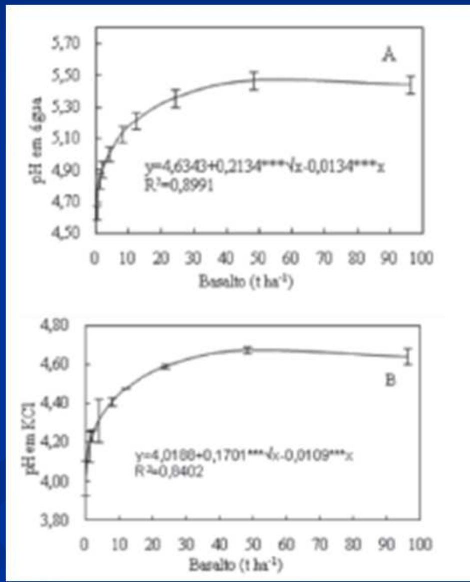
General results from using BASALT as soil amendment

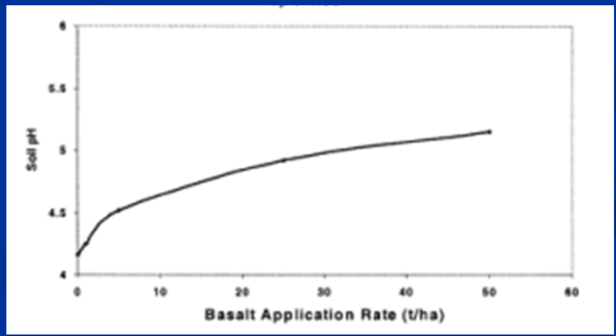
- Raising the pH of soils

with large tonnage applications

Rock/mineral type	Abrasion pH
Ultramafic rock	9.4
Basalt	8.5
Phonolite	9.24
Phlogopite schist	8.8
Olivine	10-11
K feldspar	8-9
Plagioclase	8-10
Biotite	8-9

Melo *et al*. 2012

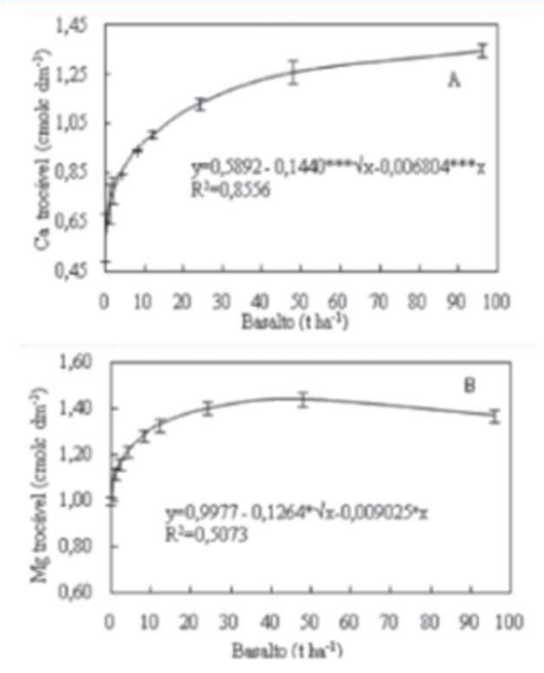




Gillman *et al*. 2002

General results from using BASALT as soil amendment

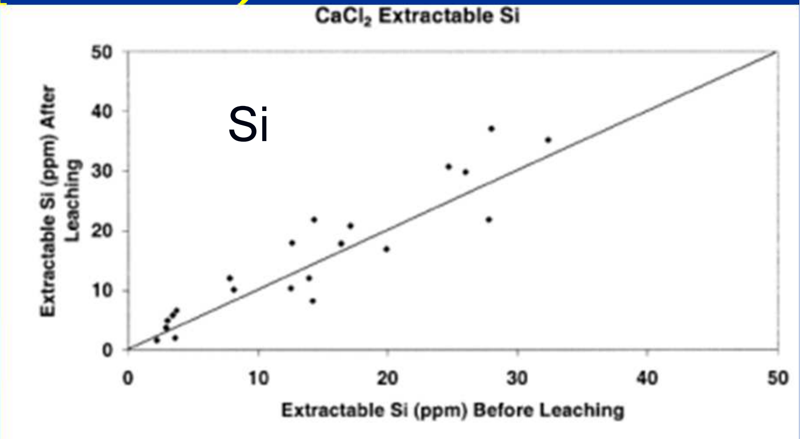
- Increase exchangeable Ca and Mg, little K, **plus Si + little P (from glass component)**

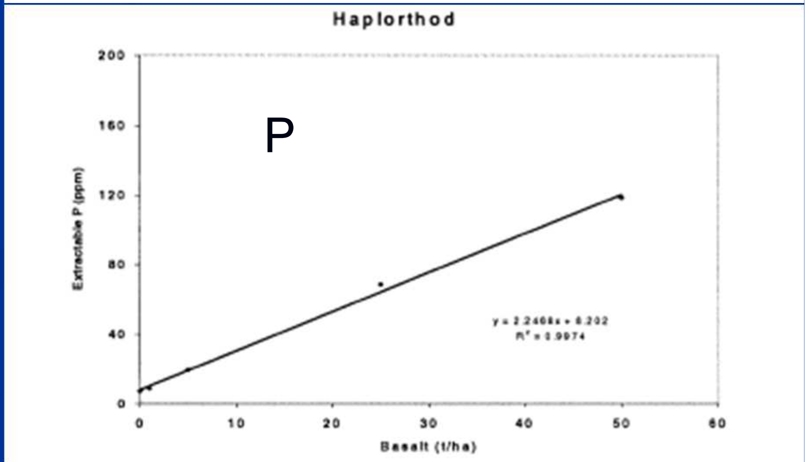


Melo *et al.* 2012

Gillman *et al.* 2002

Note: High application rates

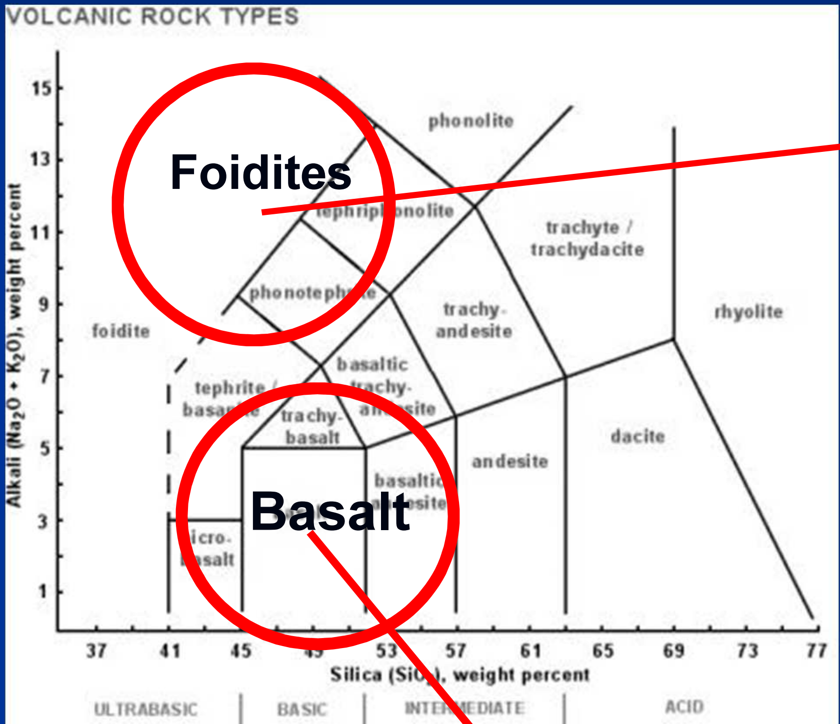




Also provides trace elements Cu, Zn, little Ni

Know your rocks!

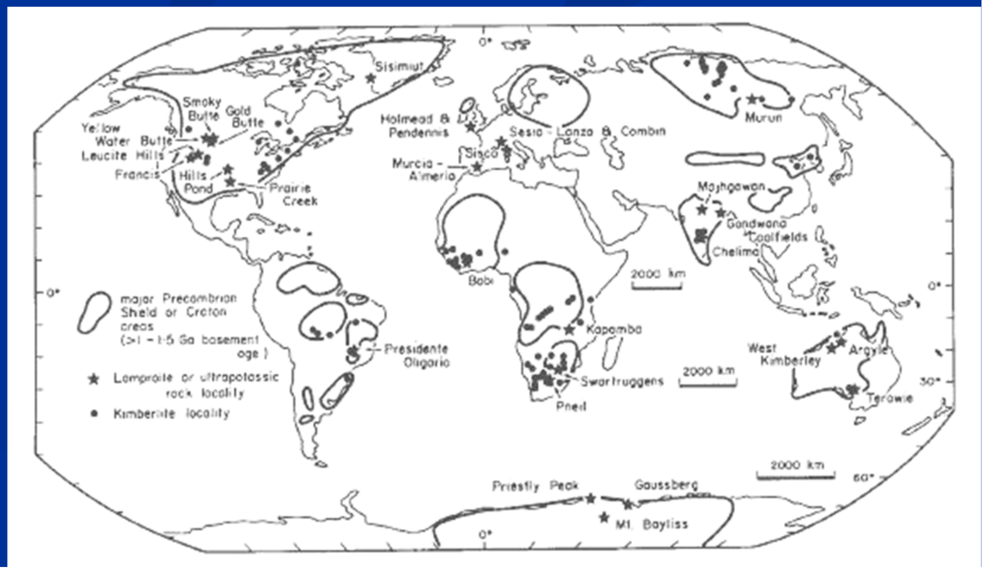
Which igneous rocks are suitable?



Source: Le Bas *et al.* 1986

Leucite and nepheline bearing alkaline rocks: **K, Si**, Ca, Mg, trace elements

Ultramafic-ultra-potassic rocks (molar K_2O/Na_2O ratios of >3)



Basalt: Ca, Mg, Si, trace elements; good source= **Hydrothermally altered basalt (+ K)**

Reality check of using rock powder amendments:

- **Mixed results** of agronomic efficacy of 'silicate rock' application **due to complexity of system**

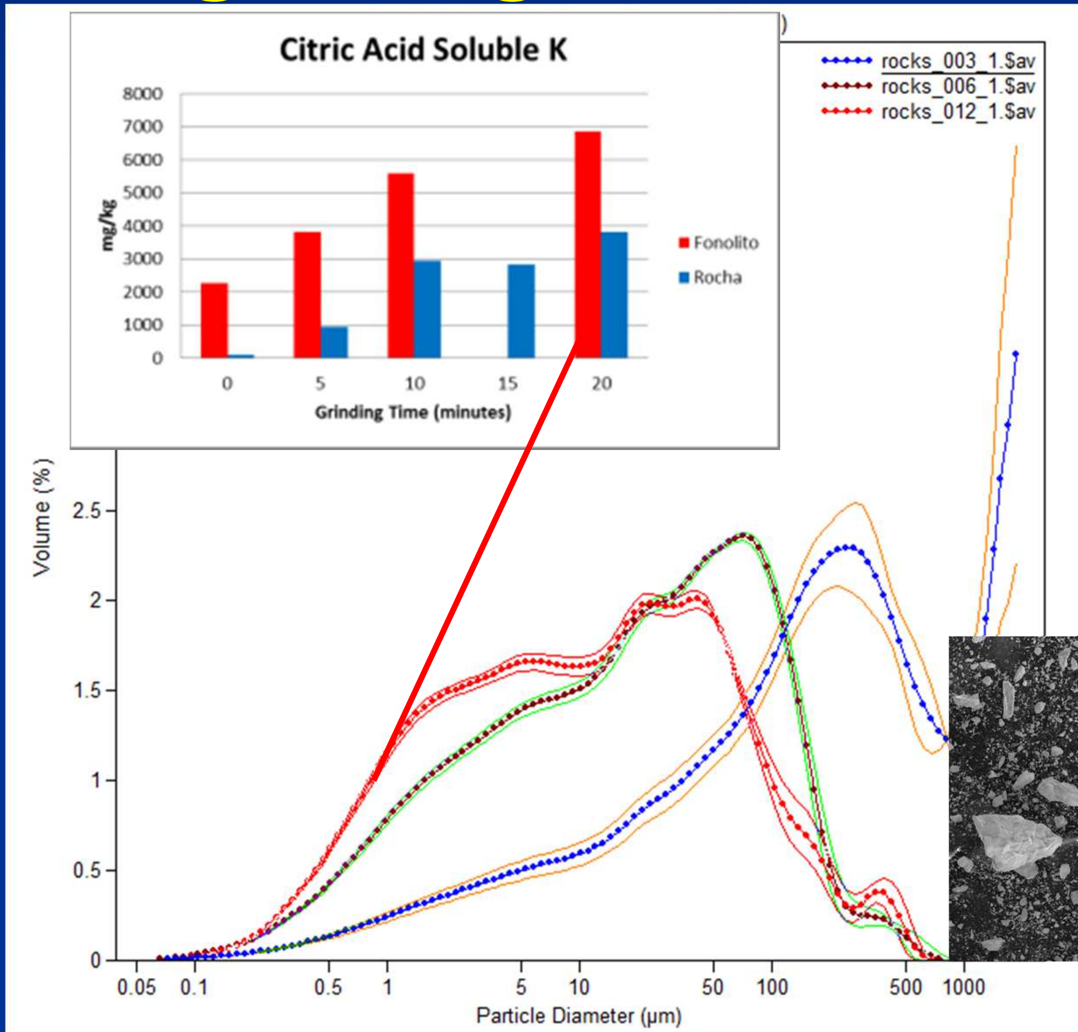
- Inconsistent results: best performance (pH and Ca, Mg increase) on highly depleted tropical soils using mafic to ultra-mafic, ultra-potassic rocks or mafic fractions from 'wastes'

- Few commercial operations, usually using inexpensive 'waste rock' from quarry operations

Where does it make sense to use direct application high volume total silicate K rock amendments?

- In humid climates with high dissolution rates
- On nutrient deficient sandy acid soils and high precipitation rates, where soluble fertilizers are easily leached
- On tree crops and perennial crops, like fruit trees, coffee, grape; on sugar cane (K-Si), and - in modified form – on rice (K-Si)
- In organic farming systems

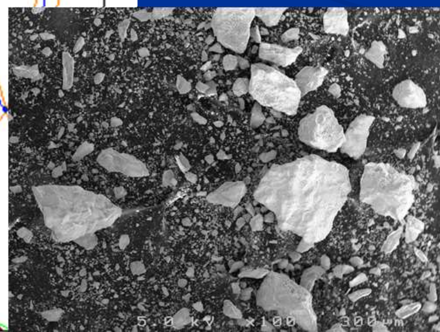
New developments:
Modification of silicate rock:
Fine grinding increases solubility of phonolite



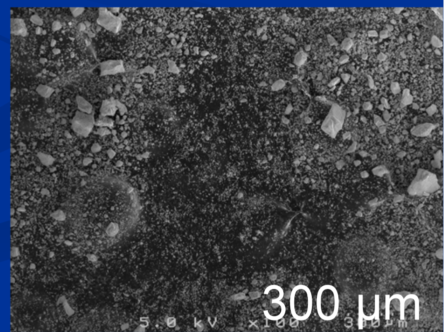
Median: 5 min: 182.41 µm
Mean: 5 min: 42.80 µm

Median: 10 min: 45.44 µm
Mean: 10 min: 20.50 µm

20 min grinding: 50% < 11.48 µm
25% < 2.72 µm, 10% < 0.99 µm



after 5 minutes



after 20 minutes

A technical breakthrough: Mechanical breakdown of K feldspar through high energy milling

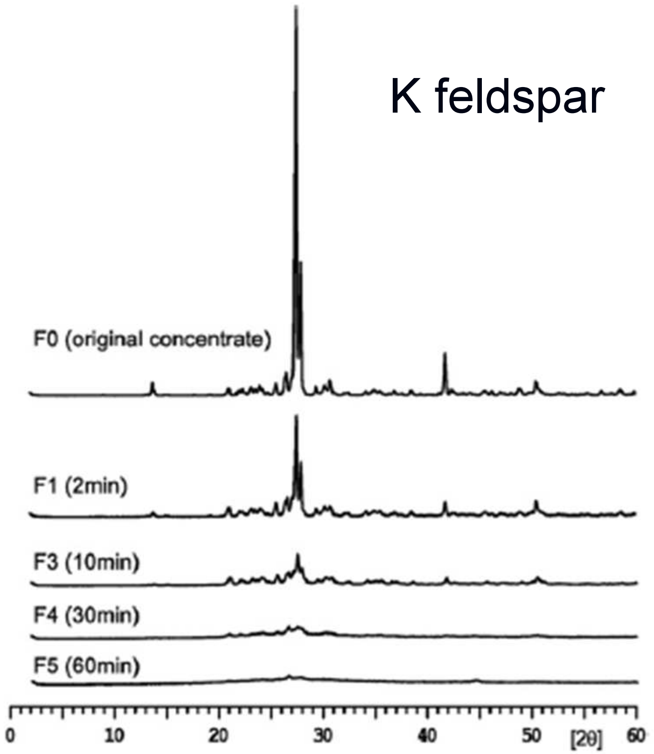
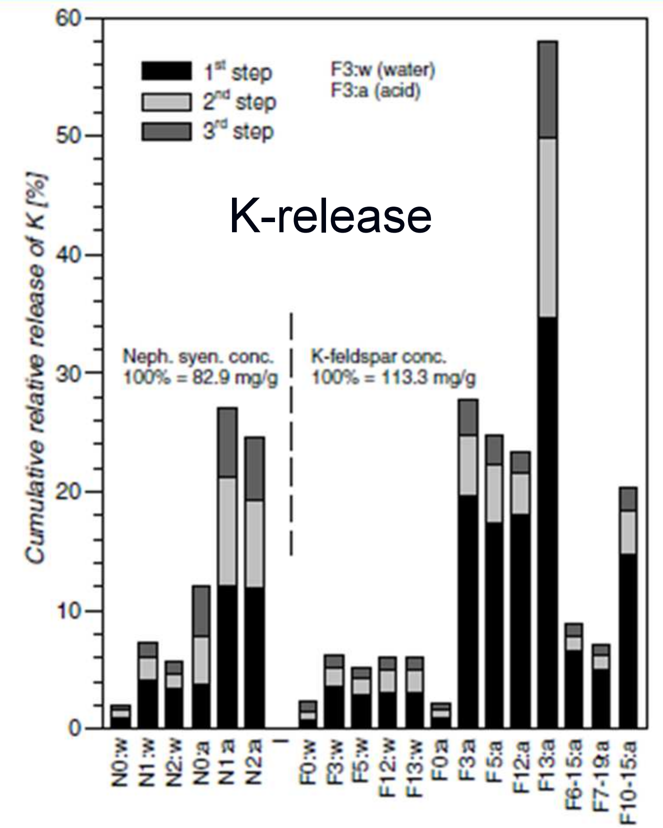


Fig. 3. XRD signature of PM-activated K-feldspar concentrate as a function of milling time.



Source: Kleiv and Thornhill 2007

Silicate minerals and rocks need modification to be more effective

Modification:

- **Biological/chemical** modification of rocks and minerals using LMW organic acids
- **Physical** modification (mineral separation from 'wastes' and/or high energy milling),
- Combination of physical and chemical/biological modification

In general: Promising new directions

- Enhancing efficacy of nutrient release from phosphate rock, and K bearing silicate rocks through thermal treatment, mechanical activation by high energy-milling, and/or combined with microbiological and LMW organic acid solubilization techniques

Outlook

- There are many untapped agromineral resources for agricultural use, many of them **'wastes'**
- **'Wastes'** from many quarry operations and industrial mineral mines need to be evaluated on their role as potential forms of soil amendments
- Success rate is higher when you KNOW YOUR ROCKS
- So far, nutrient release of many local rock and mineral amendments is slow, and large volumes are required to form effective amendments. Novel physical, chemical and biological modification techniques are being developed to enhance these rocks' nutrient release rates and agronomic effectiveness

Thank you

Obrigado

Asante sana