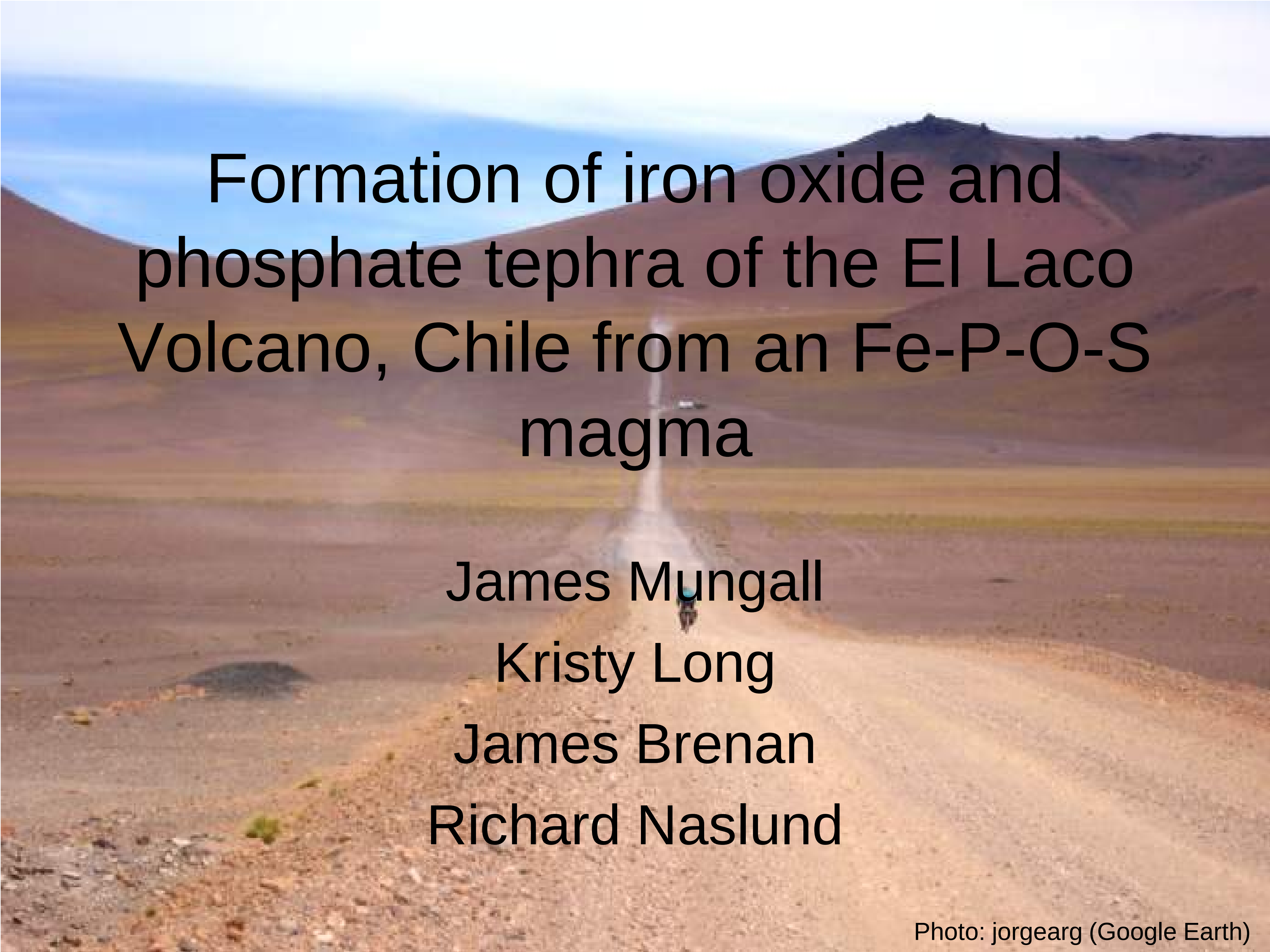


# Formation of iron oxide and phosphate tephra of the El Laco Volcano, Chile from an Fe-P-O-S magma

James Mungall

Kristy Long

James Brenan

Richard Naslund

Photo: jorgearg (Google Earth)

# Outline

- Define and describe El Laco/Kiruna type Fe oxide deposits; demonstrate that they are magmatic in origin
  - Large scale structures
  - Field occurrences
  - Petrography, mineral compositions, fluid inclusions
  - Occurrence of coexisting silicate and oxide melt in same samples
- Discuss petrogenetic processes – how can oxide magmas form?
- New experimental observations bearing on liquid immiscibility
- Discussion of phase relations
- Problems and solutions to petrogenetic riddles

# El Laco-type Fe ore deposits

- Worldwide distribution but rare
- Proterozoic to Tertiary ages
- Massive magnetite and hematite
  - Low $TiO_2$, low $SiO_2$
  - Up to a few % apatite
  - Trace amounts of clinopyroxene, quartz
  - REE rich
  - Spatial association with hydrothermal IOCG deposits
  - Associated with potassic arc magma suites
- NOT nelsonites (i.e., Ti-rich magnetite-apatite bodies)
- NOT ilmenite deposits like Tellnes or Tio deposits
- Igneous textures and structures
  - Massive dikes
  - Vesicular and brecciated flows
  - Intrusive breccias
  - Unconsolidated ash and crystal tuffs
- Common association with intense hydrothermal alteration
- Supposed by some workers to be hydrothermal themselves

# Composition of the Ore (without minor veins)

$\sum$ FeO ~ 98 %

MgO = 0.5 - 1.3 %

$SiO_2$ = 0.0 - 1.0%

$P_2O_5$ = 0.0 - 1.0 %

$TiO_2$ = 0.15 - 0.85 %

Al Ca Na K <<< 1%

REE = 5000-10000

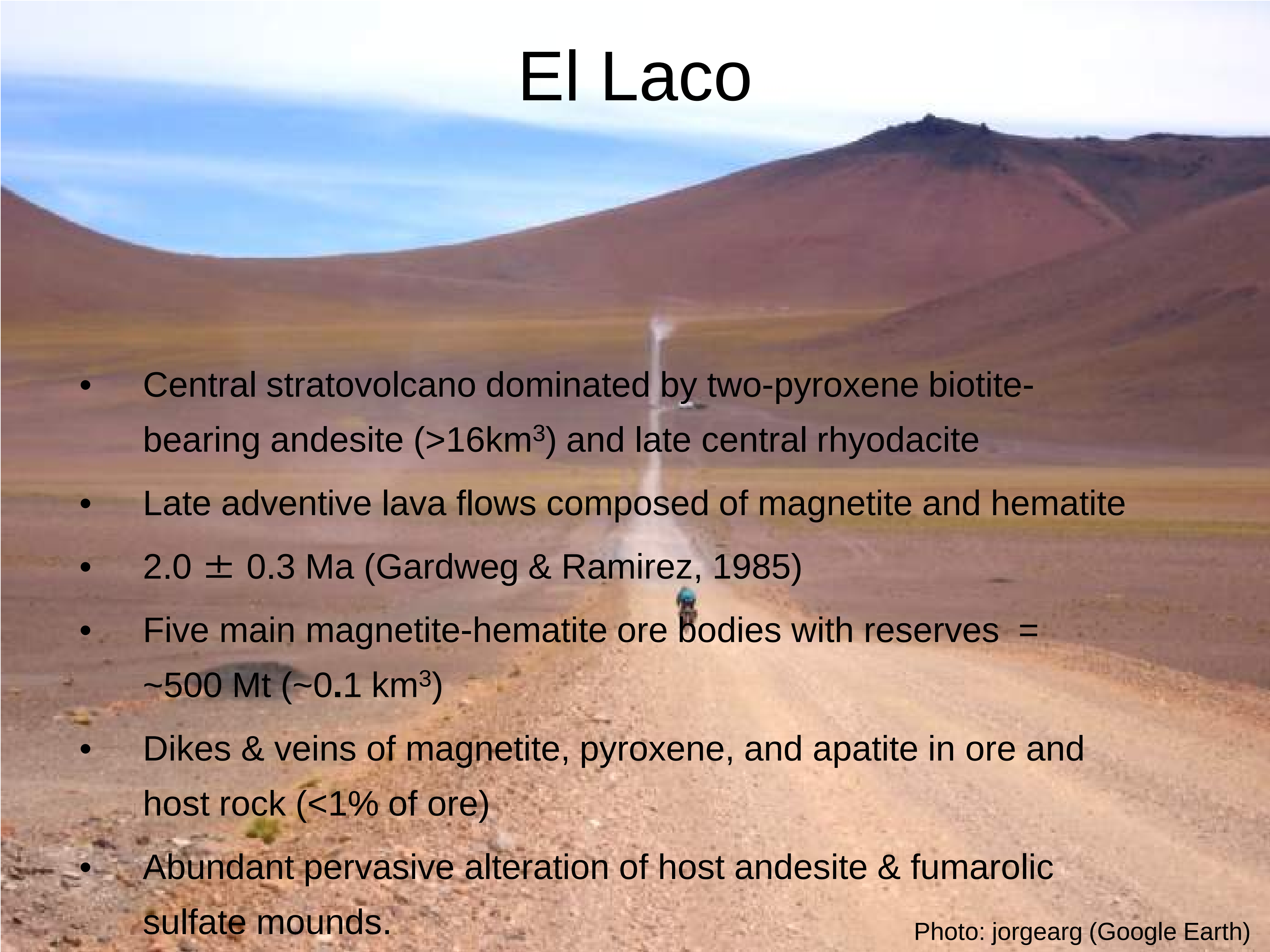
V = 900 - 2500 ppm

Ni = 90 - 360 ppm

Mn = 300 - 700 ppm

Zr = 10 - 100 ppm

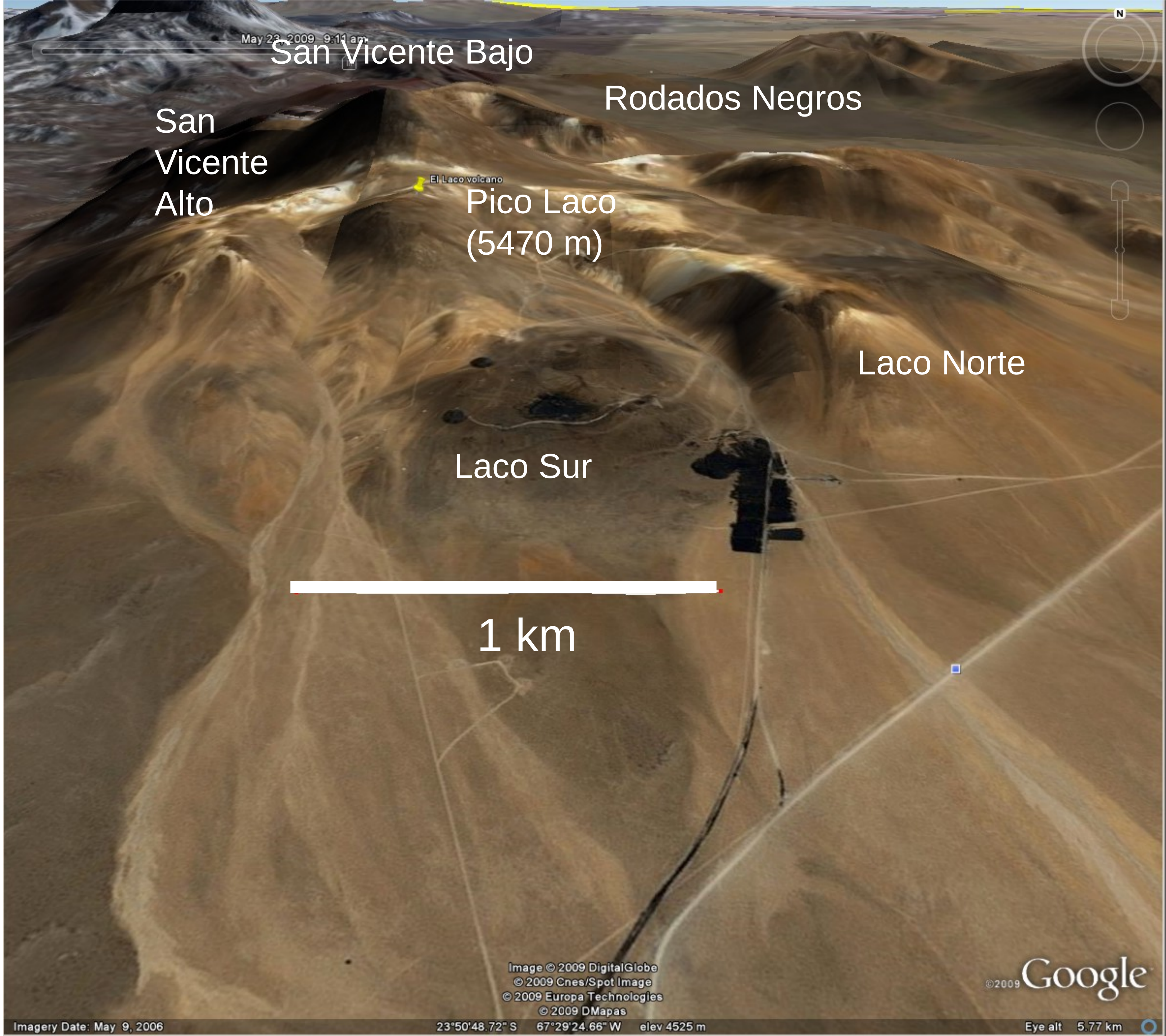
# El Laco



- Central stratovolcano dominated by two-pyroxene biotite-bearing andesite (>16km$^3$) and late central rhyodacite
- Late adventive lava flows composed of magnetite and hematite
- 2.0 $\pm$ 0.3 Ma (Gardweg & Ramirez, 1985)
- Five main magnetite-hematite ore bodies with reserves = ~500 Mt (~0.1 km$^3$)
- Dikes & veins of magnetite, pyroxene, and apatite in ore and host rock (<1% of ore)
- Abundant pervasive alteration of host andesite & fumarolic sulfate mounds.

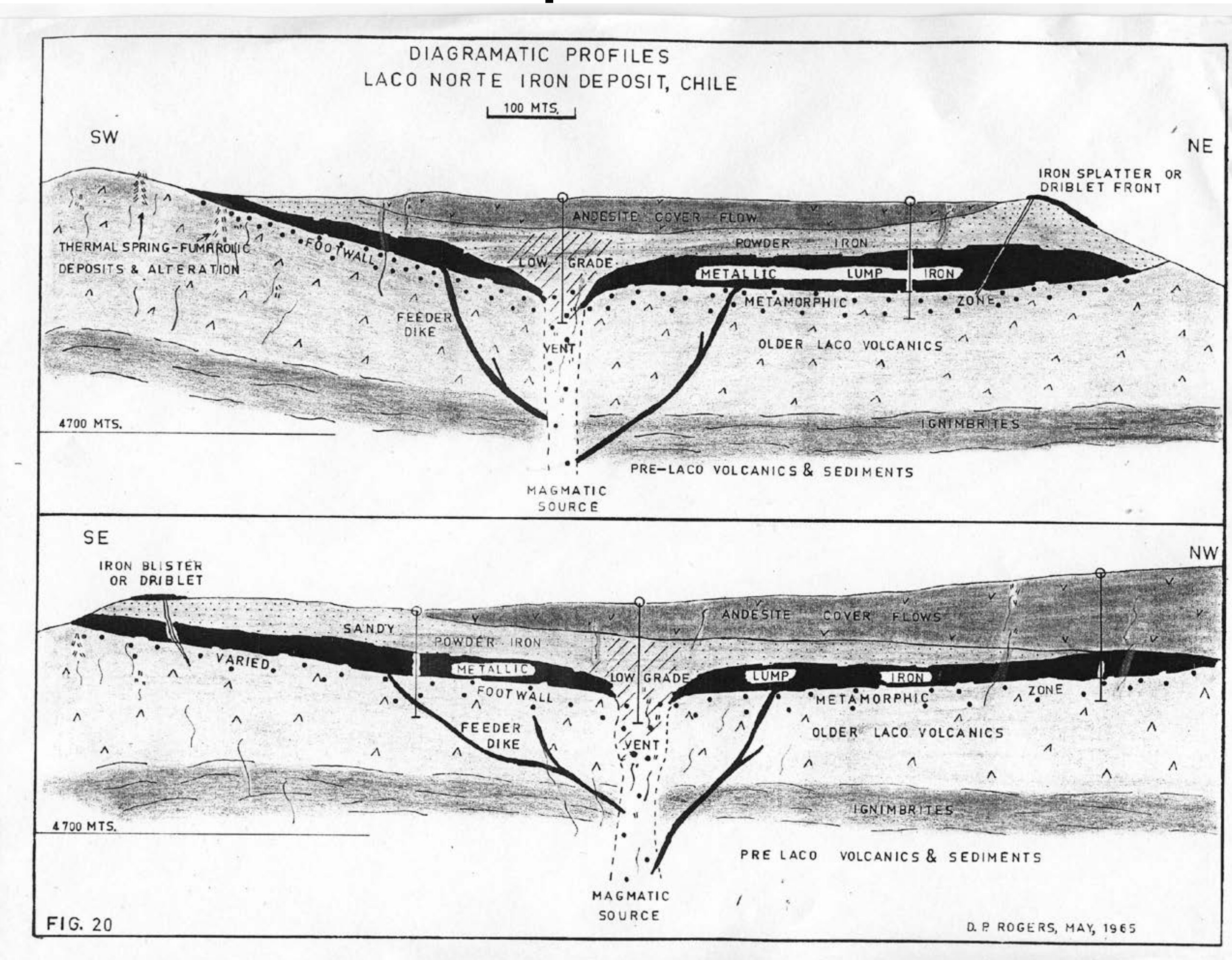
Photo: jorgearg (Google Earth)


San Vicente Bajo
Rodados Negros
San Vicente Alto
El Laco volcano
Pico Laco (5470 m)
Laco Norte
Laco Sur
Image © 2009 DigitalGlobe
© 2009 Cnes/Spot Image
© 2009 Inav/Geosistemas SRL
© 2009 Google
©2009 Google
Imagery Date: May 9, 2006
23°49'57.14" S 67°29'13.54" W elev 4776 m
Eye alt 12.32 km

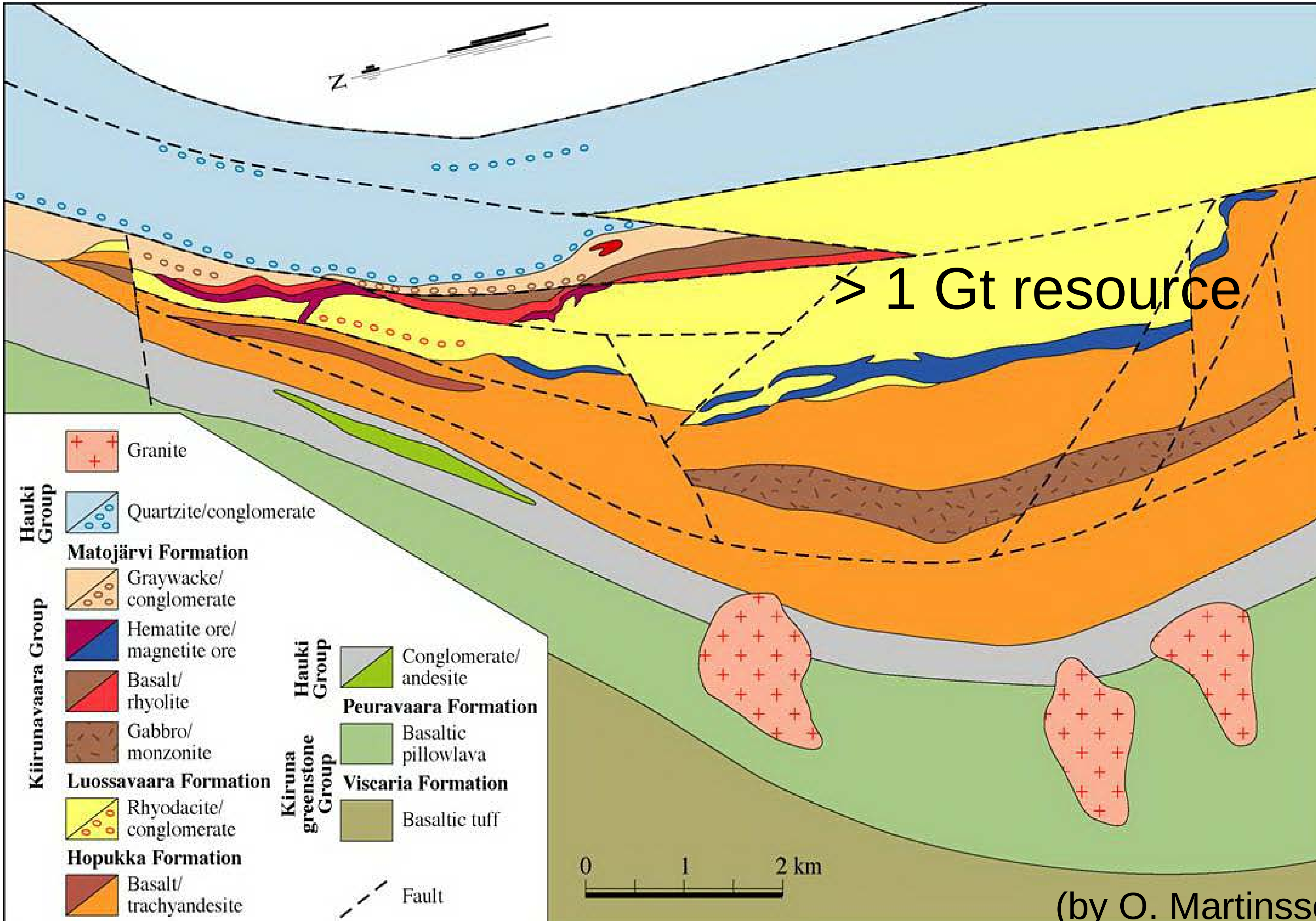

May 23, 2009 9:11 am
San Vicente Bajo
Rodados Negros
San
Vicente
Alto
El Laco volcano
Pico Laco
(5470 m)
Laco Norte
Laco Sur
1 km
Image © 2009 DigitalGlobe
© 2009 Cnes/Spot Image
© 2009 Europa Technologies
© 2009 DMapas
©2009 Google
Imagery Date: May 9, 2006
23°50'48.72" S 67°29'24.66" W elev 4525 m
Eye alt 5.77 km


Magnetite Lava Flow El Laco
~100m
Photo: HR Naslund

# Map scale


DIAGRAMATIC PROFILES
LACO NORTE IRON DEPOSIT, CHILE
100 MTS.
SW
NE
IRON SPLATTER OR DRIBLET FRONT
ANDESITE COVER FLOW
POWDER IRON
THERMAL SPRING-FUMAROLIC DEPOSITS & ALTERATION
FOOTWALL
LOW GRADE
METALLIC LUMP IRON
METAMORPHIC ZONE
FEEDER DIKE
VENT
OLDER LACO VOLCANICS
4700 MTS.
IGNIMBRITES
PRE-LACO VOLCANICS & SEDIMENTS
MAGMATIC SOURCE
SE
NW
IRON BLISTER OR DRIBLET
ANDESITE COVER FLOWS
SANDY POWDER IRON
VARIED
METALLIC
FOOTWALL
LOW GRADE
LUMP
IRON
METAMORPHIC
ZONE
FEEDER DIKE
VENT
OLDER LACO VOLCANICS
IGNIMBRITES
4700 MTS.
PRE LACO VOLCANICS & SEDIMENTS
MAGMATIC SOURCE
FIG. 20
D. P. ROGERS, MAY, 1965

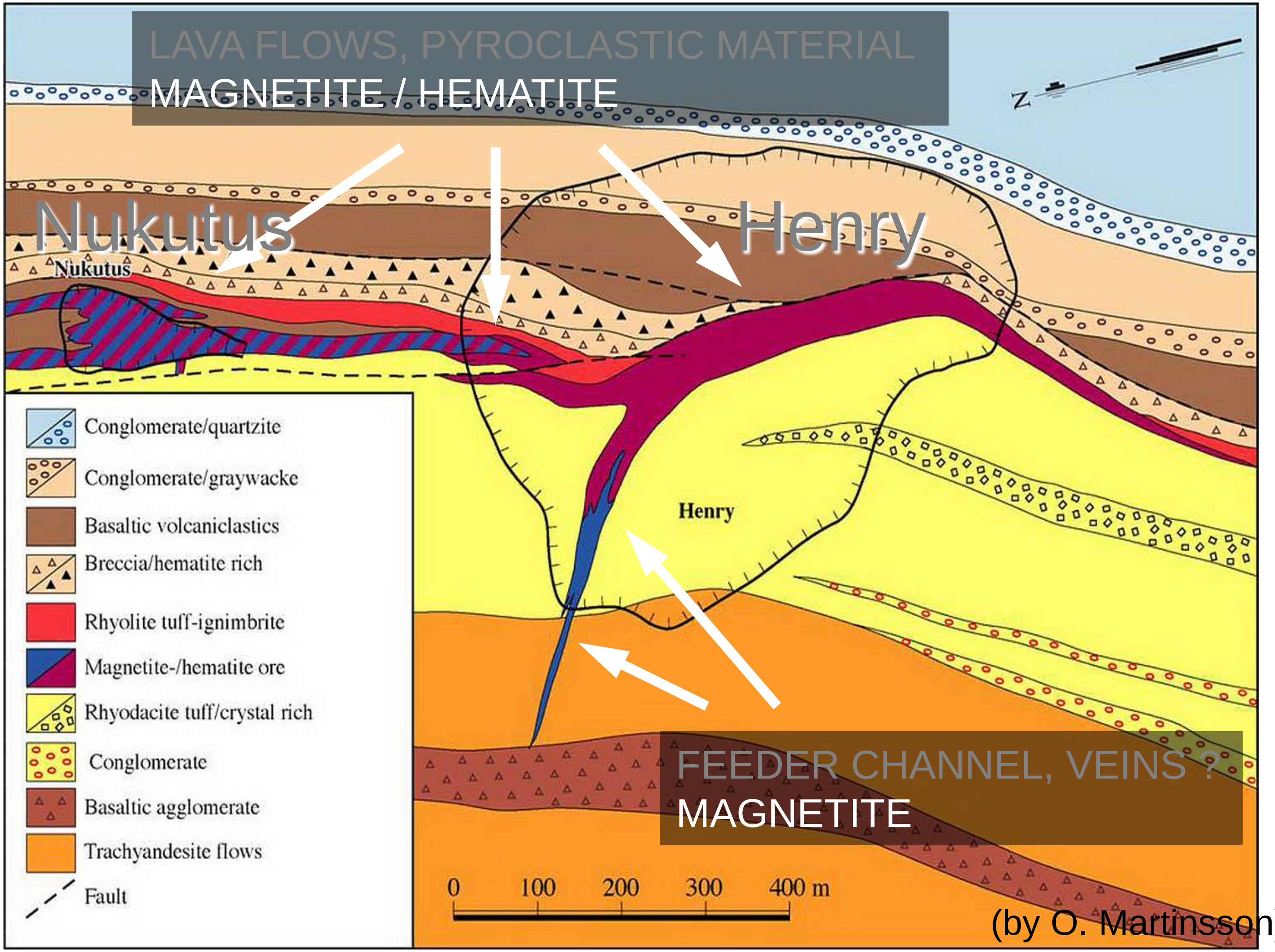
# Geology in the Kiruna area




(by O. Martinsson)

# STRATIGRAPHY OF HENRY AND NUKUTUS, Kiruna district,Sweden

TOP

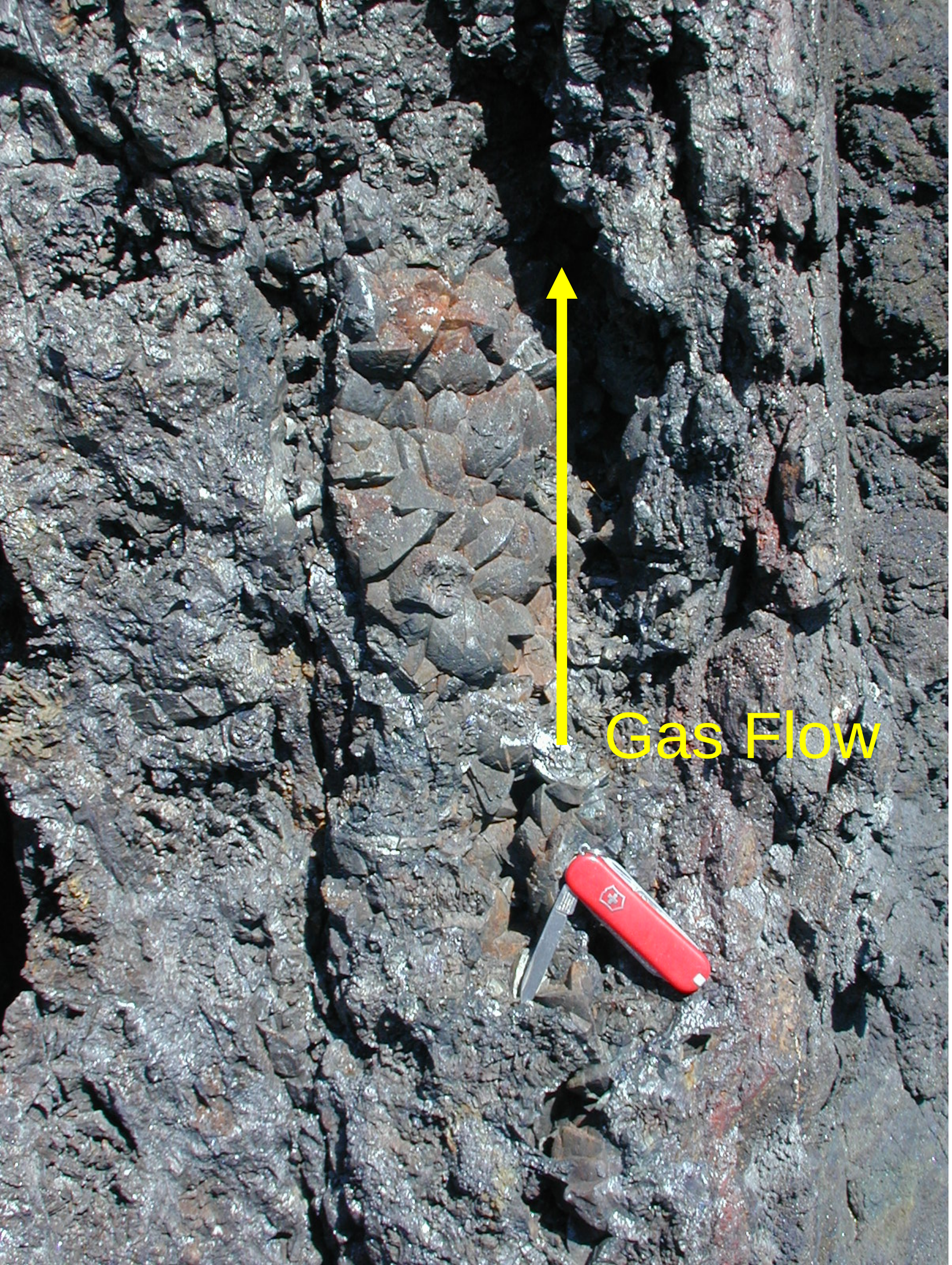



(by O. Martinsson)

# Map scale observations

- Massive magnetite dikes, sills
- Gradation into magnetite(hematite) flows
- Hematite(magnetite) pyroclastic deposits


Outcrop scale observations
<-- 6 cm -->
Vesicular ore at Laco Sur
Typical Ore Densities 1.9 - 3.1
Photo: HR Naslund




**Gas Escape Tube**
**Laco Sur**

**Lined with Magnetite**

Photo: HR Naslund

# Kirunavaara

## Vesicular iron ore


Nystrom & Henriquez, 1994, Econ Geol

# Ore contact at Laco Sur

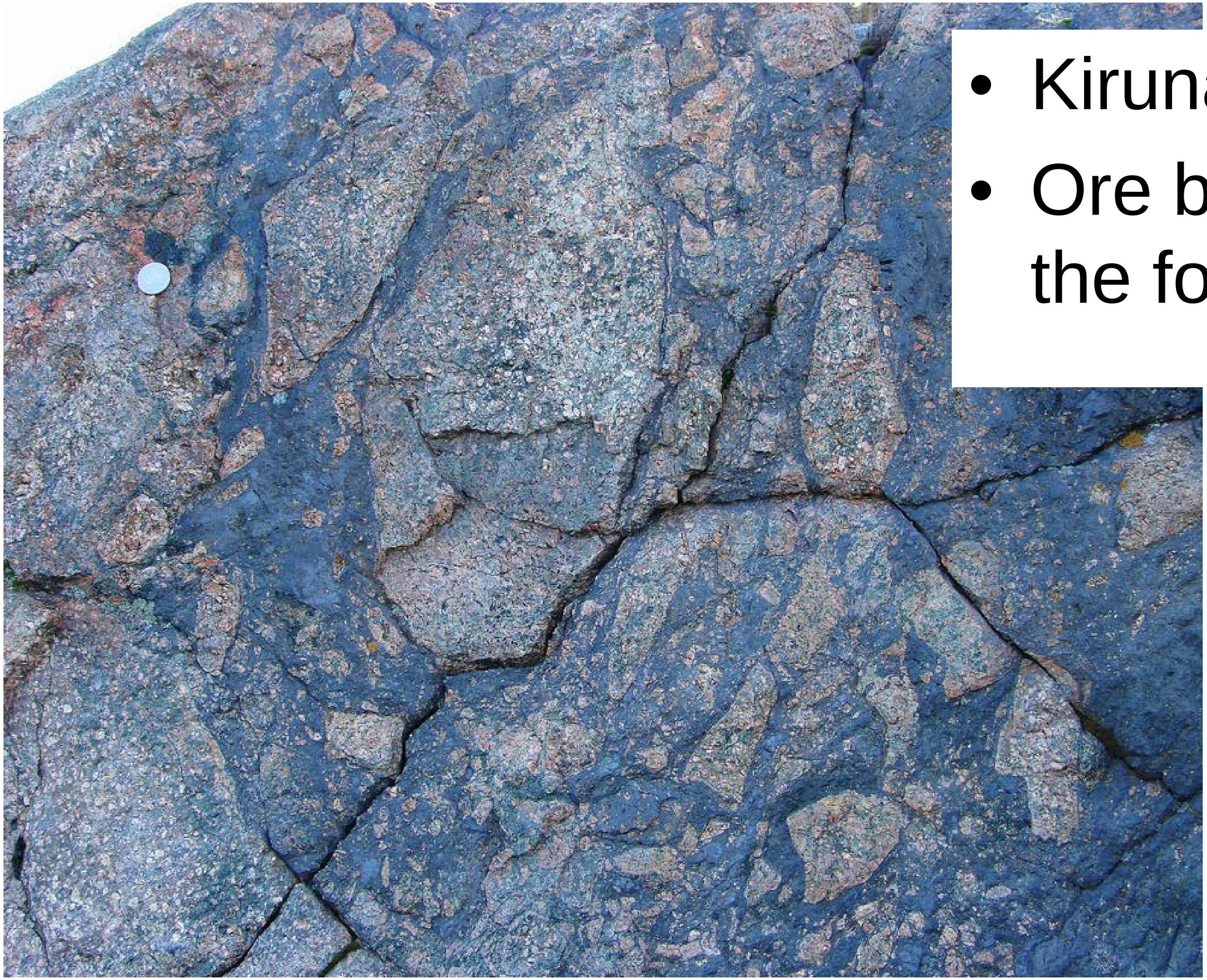
Razor sharp contact between iron ore and altered, iron-poor andesite.

Photo: HR Naslund


Altered Andesite
Fine-grained
Contact zone--
Chilled Margin
Coarse
porous
iron ore
Photo: HR Naslund


Magnetite dike
w/ sharp contacts
cutting host rock
below Laco Sur
Chilled
Margin
Photo: HR Naslund

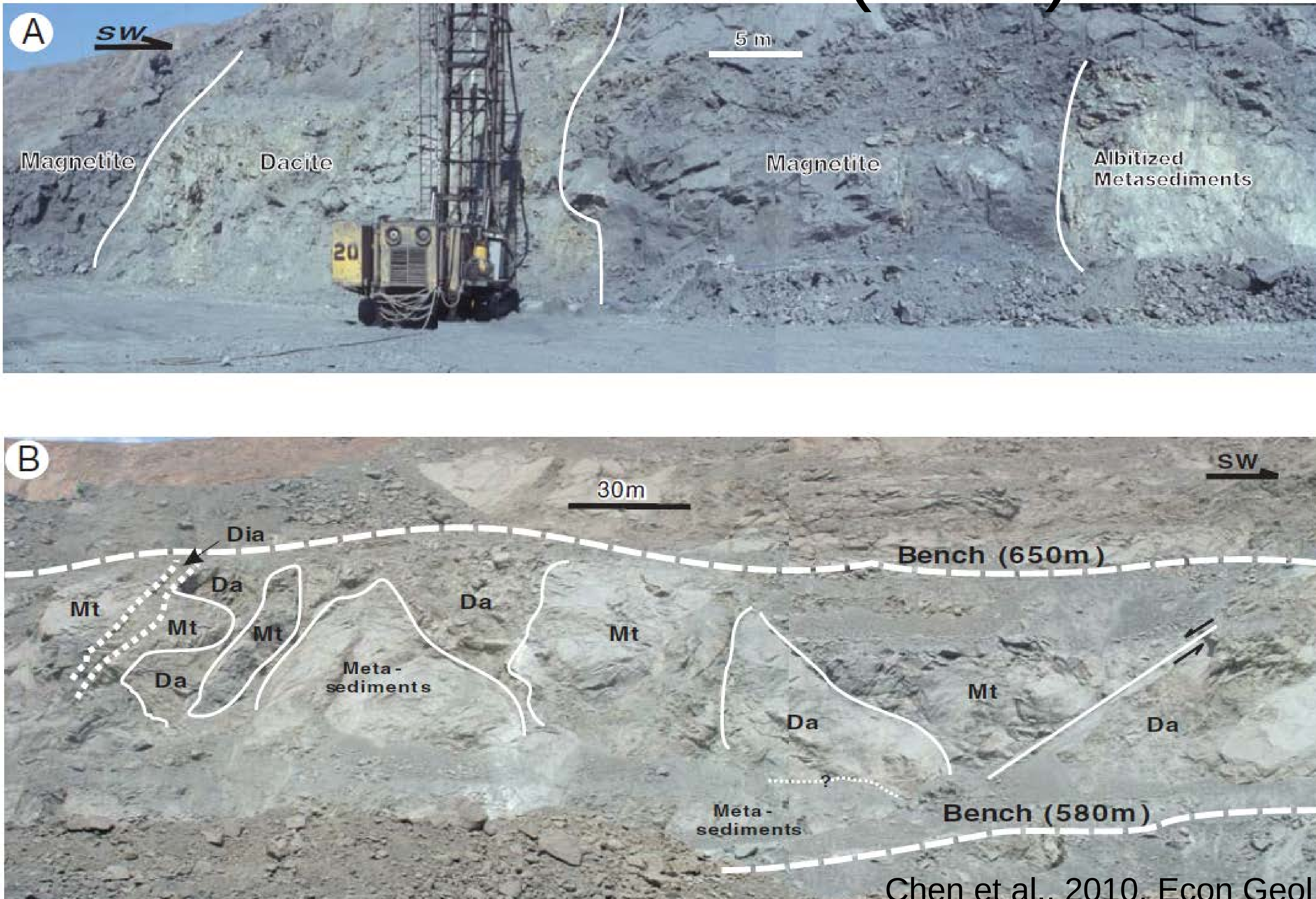
# Outcrop scale



- Kirunavaara
- Ore breccia in the footwall

Photo: Kari Niraanen

# Marcona 1.9 Gt (Peru)




Chen et al., 2010, Econ Geol

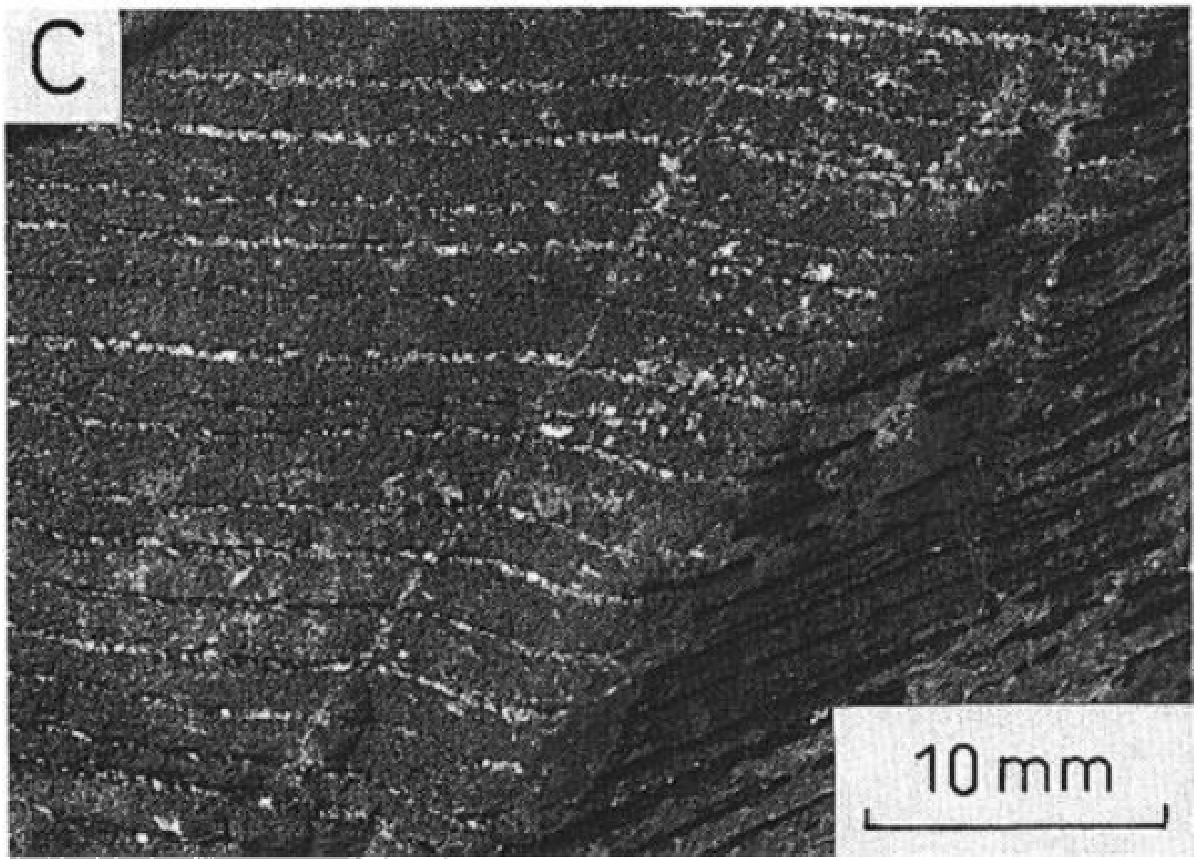

Magnetite Scoria
Laco Norte
Photo:  HR Naslund


Magnetite volcanic
bomb(?)
in hematite ash
Photo: HR Naslund


Diadochite = $Fe_2(PO_4)(SO_4)(OH) \cdot 5H_2O$
Photo: HR Naslund


Platey magnetite, Laco Sur tephra; Nystrom and Henriquez, Econ Geol, 1994

# Kirunavaara




- Crystal tuff
- Magnetite, apatite

Nystrom & Henriquez, 1994, Econ Geol

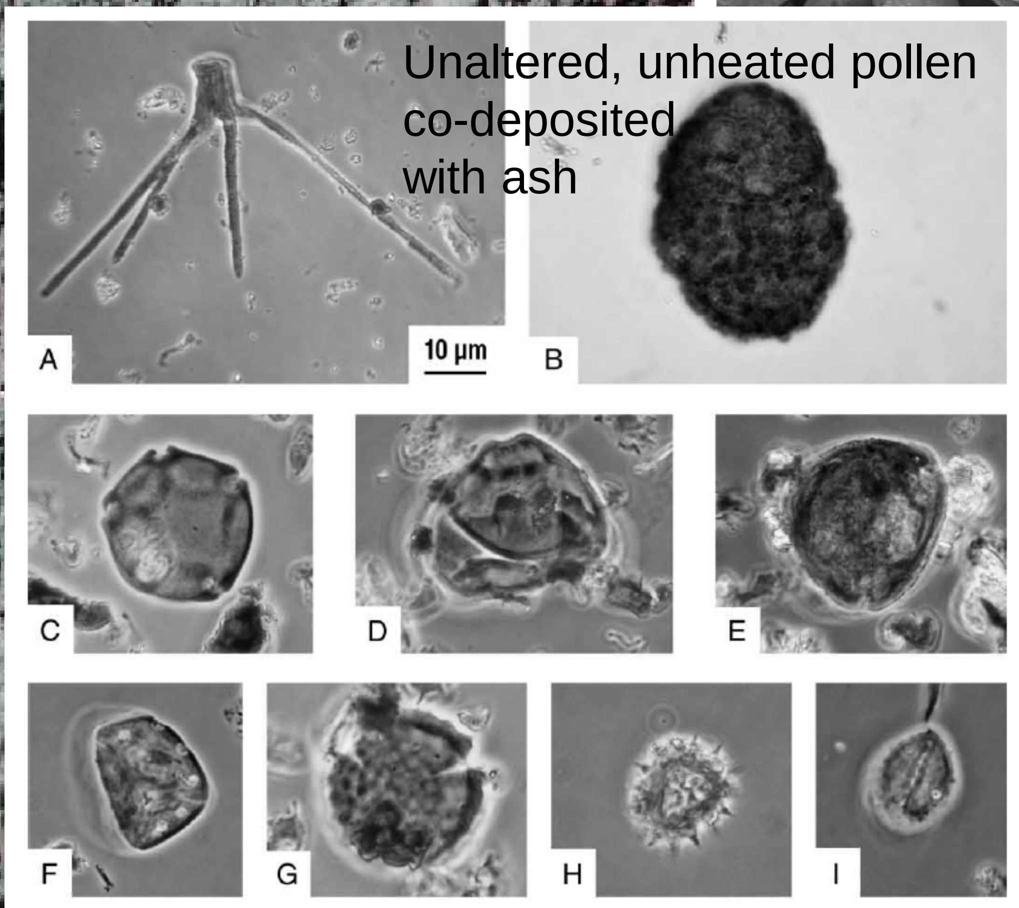
# Durango, Mexico

Iron oxide ignimbrite

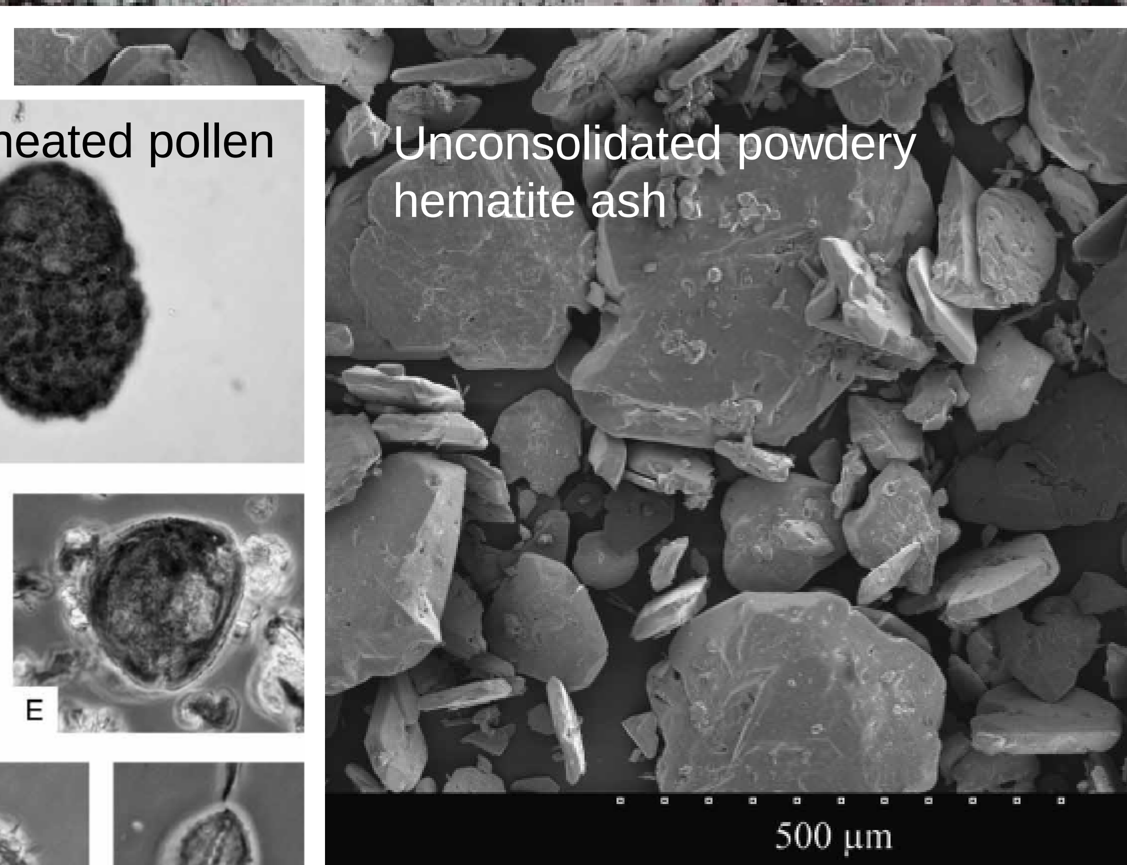

Vesicular iron ore

Photos: HR Naslund

# La Perla, Mexico




Unaltered, unheated pollen co-deposited with ash




Unconsolidated powdery hematite ash

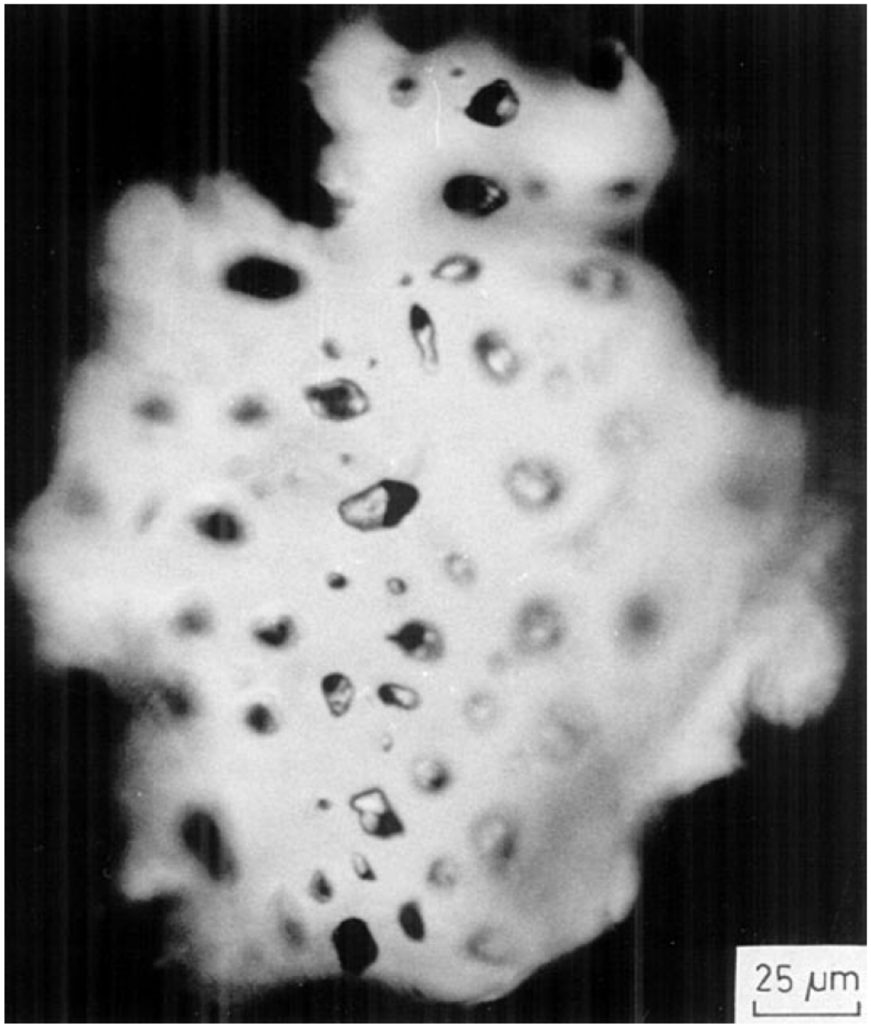
Corona-Esquival et al., 2010, GFF

# Outcrop scale observations

- Perfect preservation of complex primary magmatic structures
  - Vesicles
  - Unconsolidated air-fall crystal tuffs
  - Preservation of unaltered (cold) pollen grains
  - Chilled margins on dikes, sills
- Magnetite breccias, dikes, sills, flows
- Hematite in pyroclastic materials
- Intrusive breccias
- Plutonic zones of mingling of oxide and silicate magma

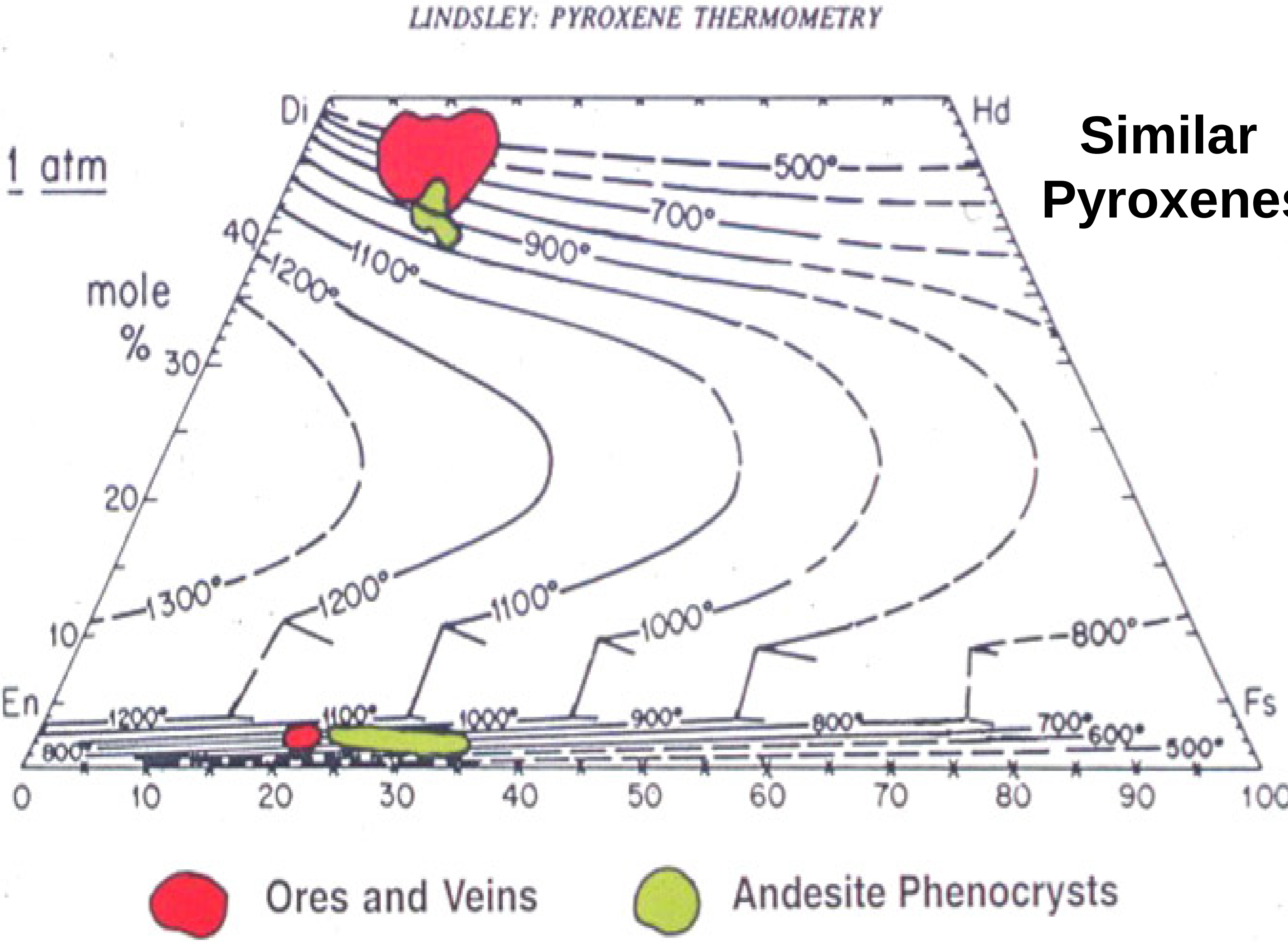
- Locally intense but not universal hydrothermal alteration

# Micro-scale observations at El Laco



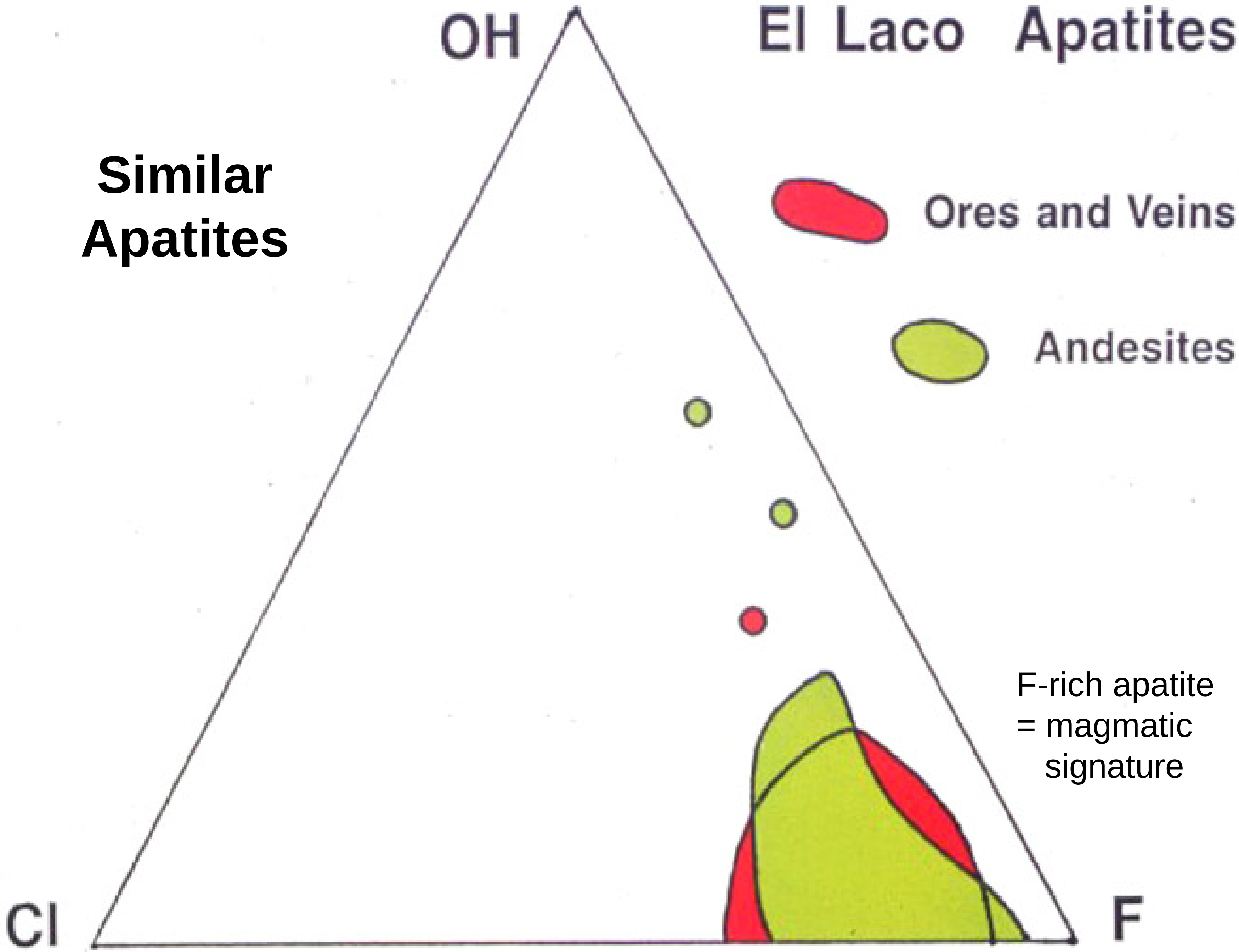

- Hydrous saline melt inclusions in pyroxene and apatite
- Homogenization temperatures > 800ºC

Broman et al., 1999, GFF




**Similar Pyroxenes**

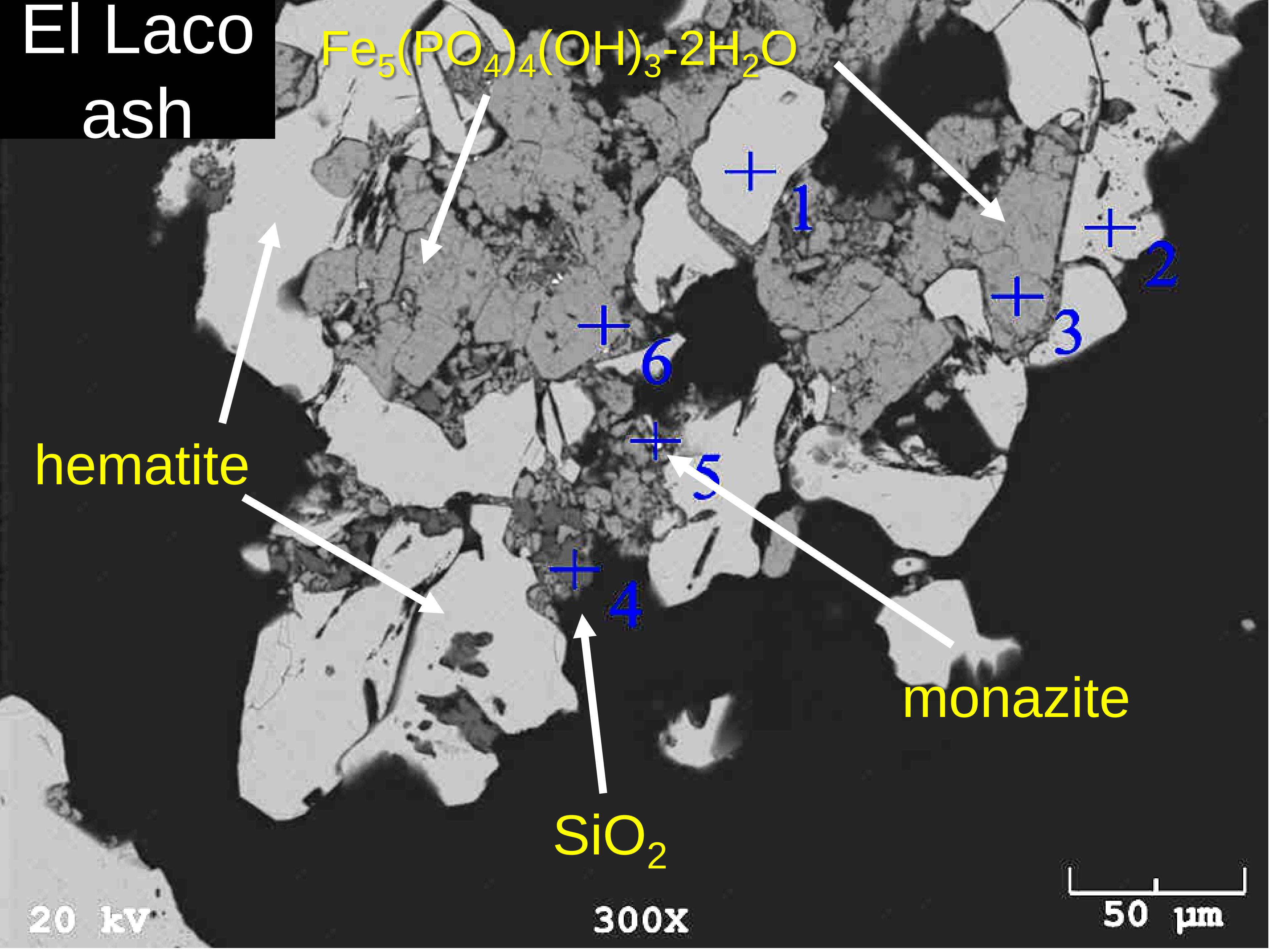
**Similar Apatites**



# New petrographic observations from El Laco

- Tephra cooled rapidly, hence may preserve traces of quenched igneous phases
- Petrography of oxide-phosphate tephra
- Preliminary melting experiments

- Bulk composition of ash:
  – 86 mol% $Fe_2O_3$
  – 12 mol% $FePO_4$
  – 2 mol% $SiO_2$


El Laco ash
$Fe_5(PO_4)_4(OH)_3$-$2H_2O$
1
2
3
6
5
4
hematite
monazite
$SiO_2$
20 kV
300x
50 µm

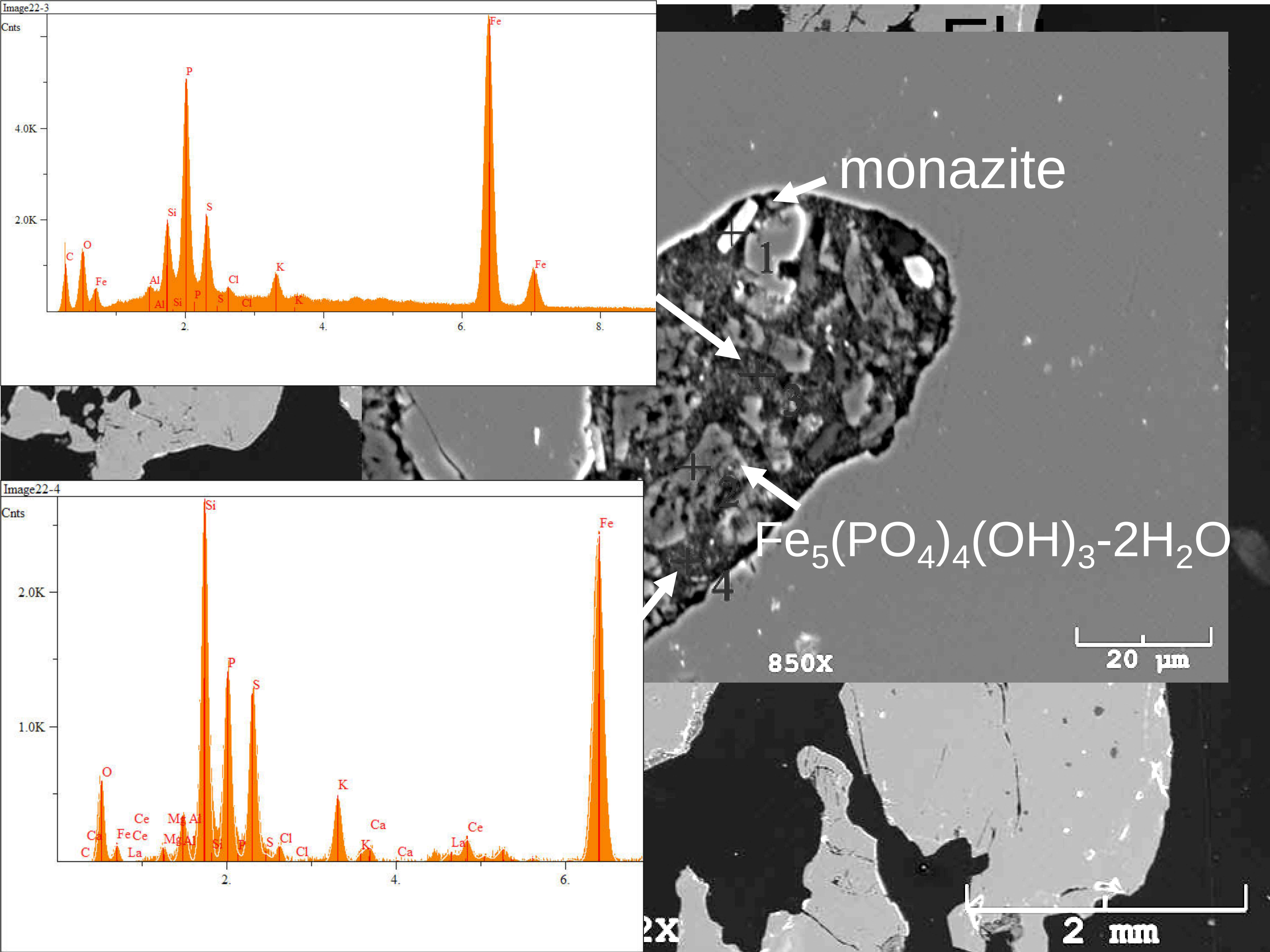


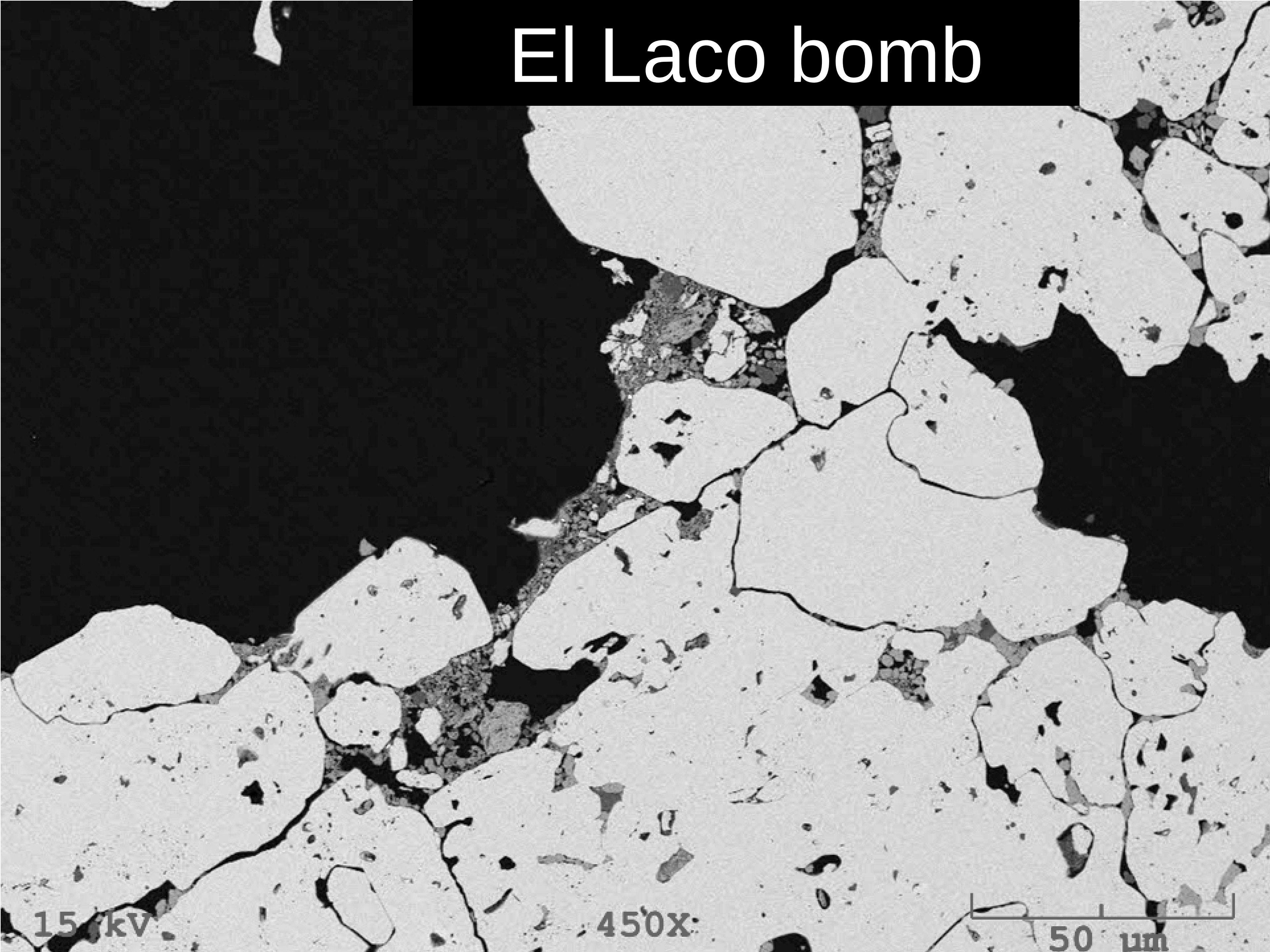
Image22-3
Cnts
4.0K
2.0K
C
O
Fe
Al
Si
P
S
Cl
K
Fe
2.
4.
6.
8.
Image22-4
Cnts
2.0K
1.0K
O
Si
P
S
K
Ca
Ce
La
Mg
Al
Cl
Fe
2.
4.
6.
monazite
1
2
3
4
Fe5(PO4)4(OH)3-2H2O
850x
20 µm
2 mm

# El Laco ash observations

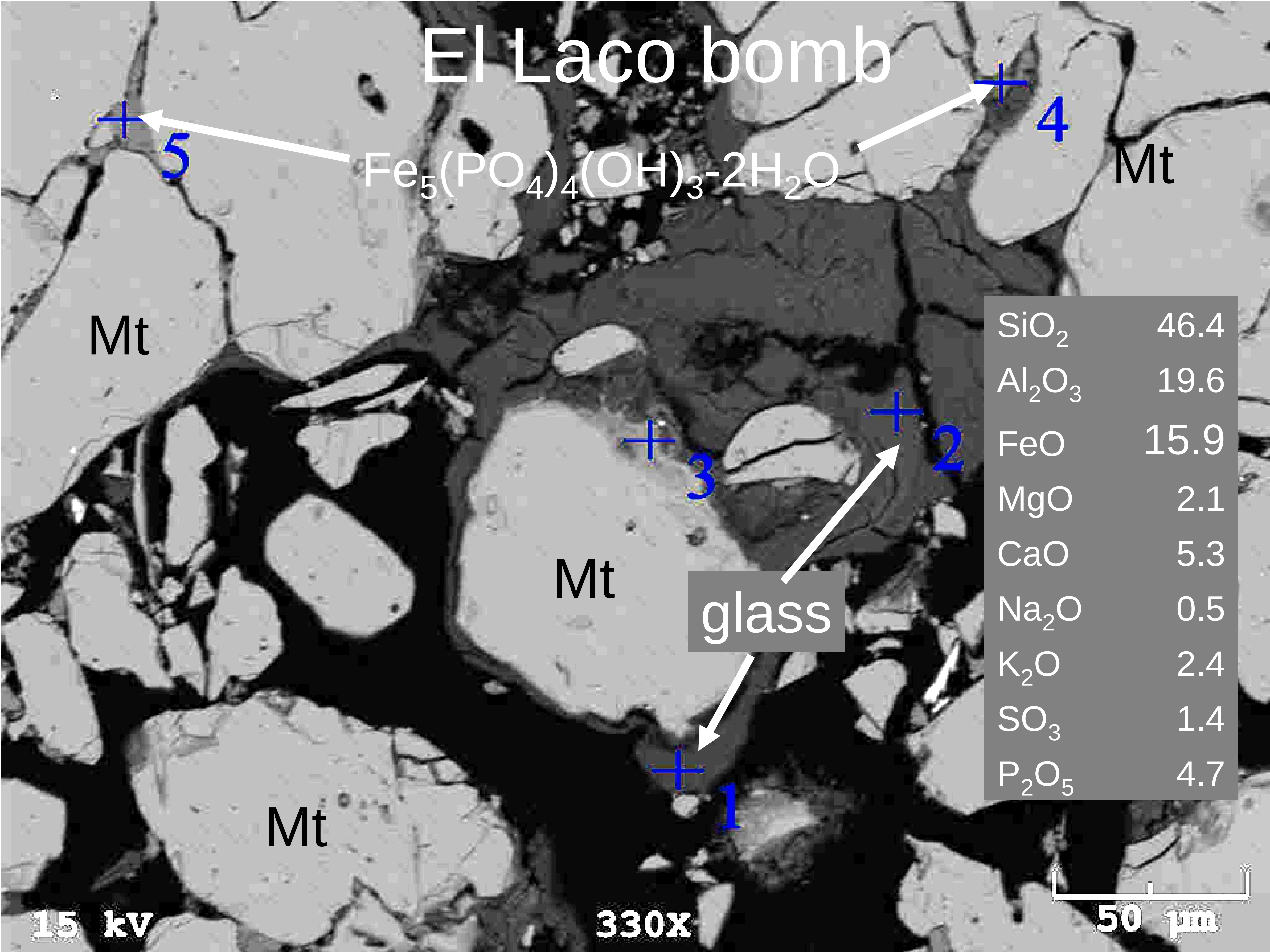
- Predominantly hematite, which armors patches of other phases
- Fe-P phases important – identified elsewhere at El Laco by Haggerty (1968) as $Fe_3^{2+}Fe^{3+}(PO_4)_3$ (anhydrous)
- Accessory Ca-rich monazite and $SiO_2$
- Subsidiary S, Cl (wt%)
- S presumably as $SO_3$ in presence of Mt, Hm

# El Laco bomb (El Bob)

# El Laco bomb

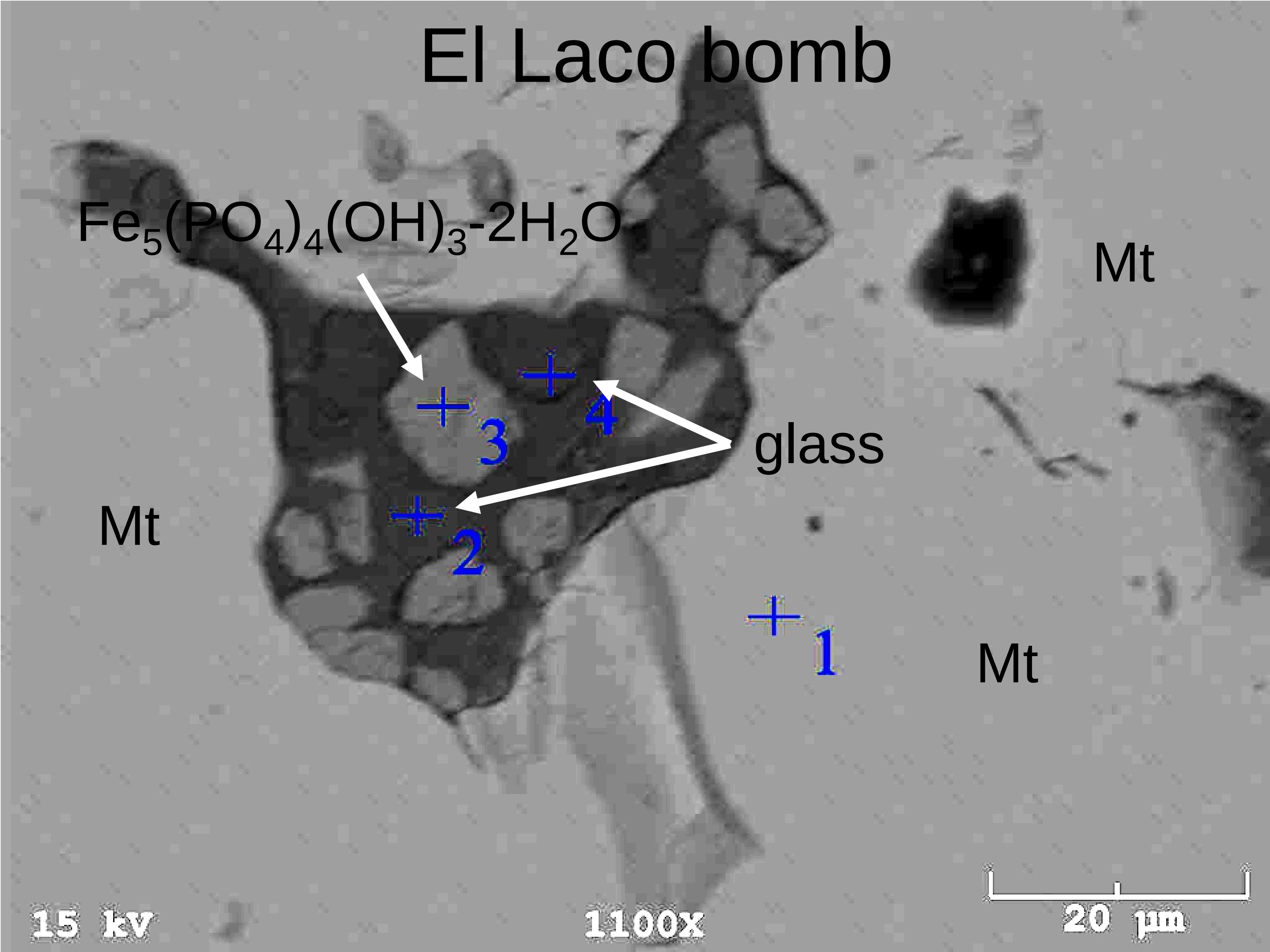


# El Laco bomb

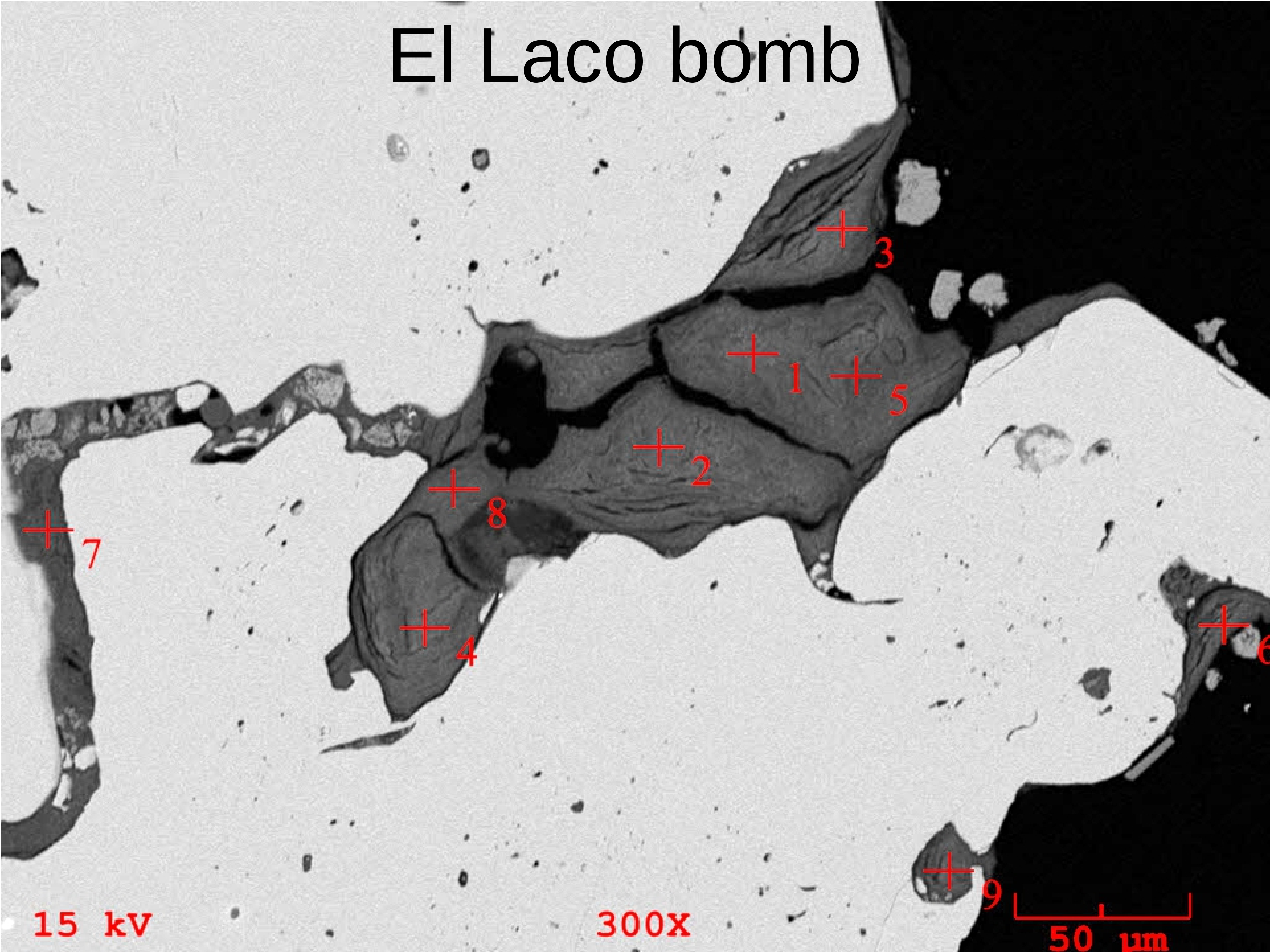



| | |
|---|---|
| $SiO_2$ | 46.4 |
| $Al_2O_3$ | 19.6 |
| FeO | 15.9 |
| MgO | 2.1 |
| CaO | 5.3 |
| $Na_2O$ | 0.5 |
| $K_2O$ | 2.4 |
| $SO_3$ | 1.4 |
| $P_2O_5$ | 4.7 |

# El Laco bomb



# El Laco bomb



# El Laco bomb observations

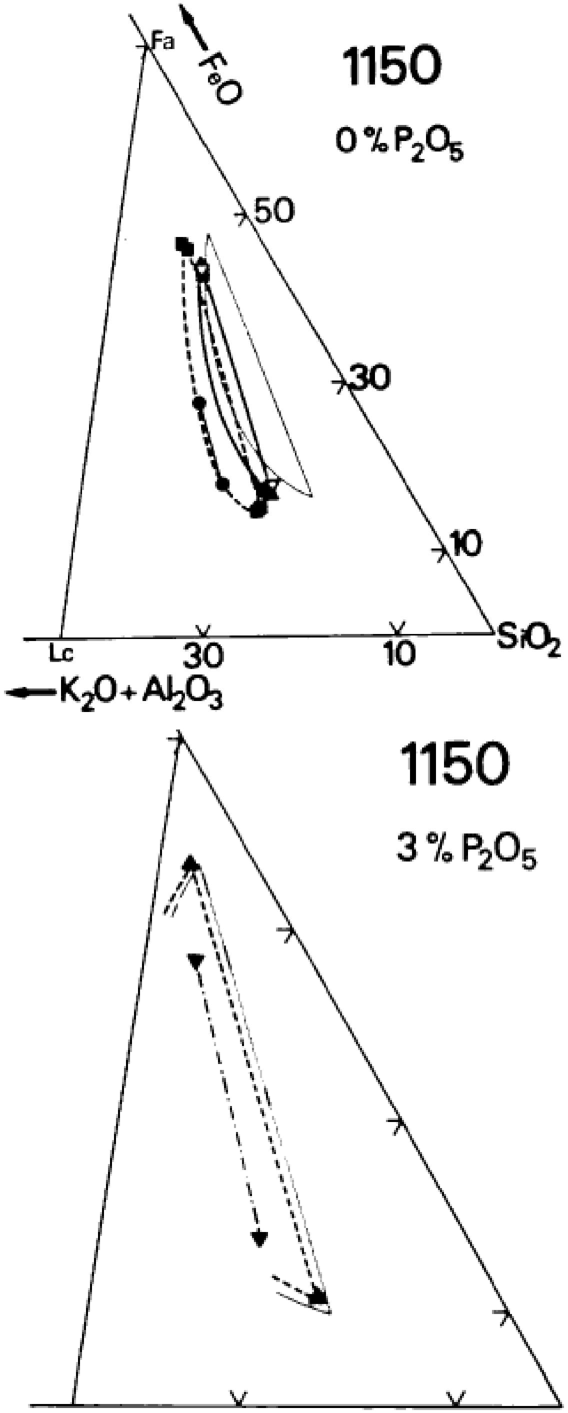
- Similar mineral assemblage as ash but more magnetite than hematite
- Similar intratelluric phosphate assemblage
- Also includes films of potassic basaltic glass intermittently coating interior surfaces
- Glass appears to be in contact (textural equilibrium?) with all solid phases including Fe phosphates
- Both glass and Fe phosphate accessory phases appear to form a meniscus between hematite crystals

# Genesis of Fe oxide magmas

- Partial melting
  - What on Earth could melt to form this composition?  Nothing.
- Fractional crystallization
  - No known silicate magma fractionates to $Fe_2O_3$ enrichment and $SiO_2$ exhaustion
- Liquid immiscibility
  - Iron rich silicate melts commonly show immiscible phase separation in the laboratory
  - Numerous field occurrences on microscopic scale of immiscible Fe-rich and Si-rich liquids
  - Problem:  these examples are all too $SiO_2$-rich to correspond to magnetite magmas

# Experimental occurrence of liquid immiscibility

- $K_2O$-$Al_2O_3$-FeO-$SiO_2$ system
  - Naslund, 1983, Am Mineral
  - Visser and Koster van Groos, 1979a,b, Am J Sci
  - Watson, 1976, CMP
- $K_2O$-$Al_2O_3$-FeO-$SiO_2$ system
  - Roedder 1978, GCA
- Magnetite-apatite-”diorite”
  - Philpots 1967, Econ Geol




# Leucite-fayalite-silica

- Immiscible liquids
- Works just as well in sodic magmas
- Too much silica for Fe-oxide magma

Photo: HR Naslund

Visser & Koster van Groos, 1979a,b, Am J Sci

# Liquid immiscibility: predictions for the field

- Cosaturation of both liquids with the same phases
- Continued exsolution of liquids during cooling
- Textural evidence for coexistence of two melts

- "The best type of evidence for the existence of one liquid as an immiscible separation from another, and one that would involve the element of interpretation in minimum degree, would be the occurrence of glassy globules in a glassy rock of different composition"

N. L. Bowen, 1928
The evolution of the Igneous Rocks

# Mesoscopic liquid immiscibility

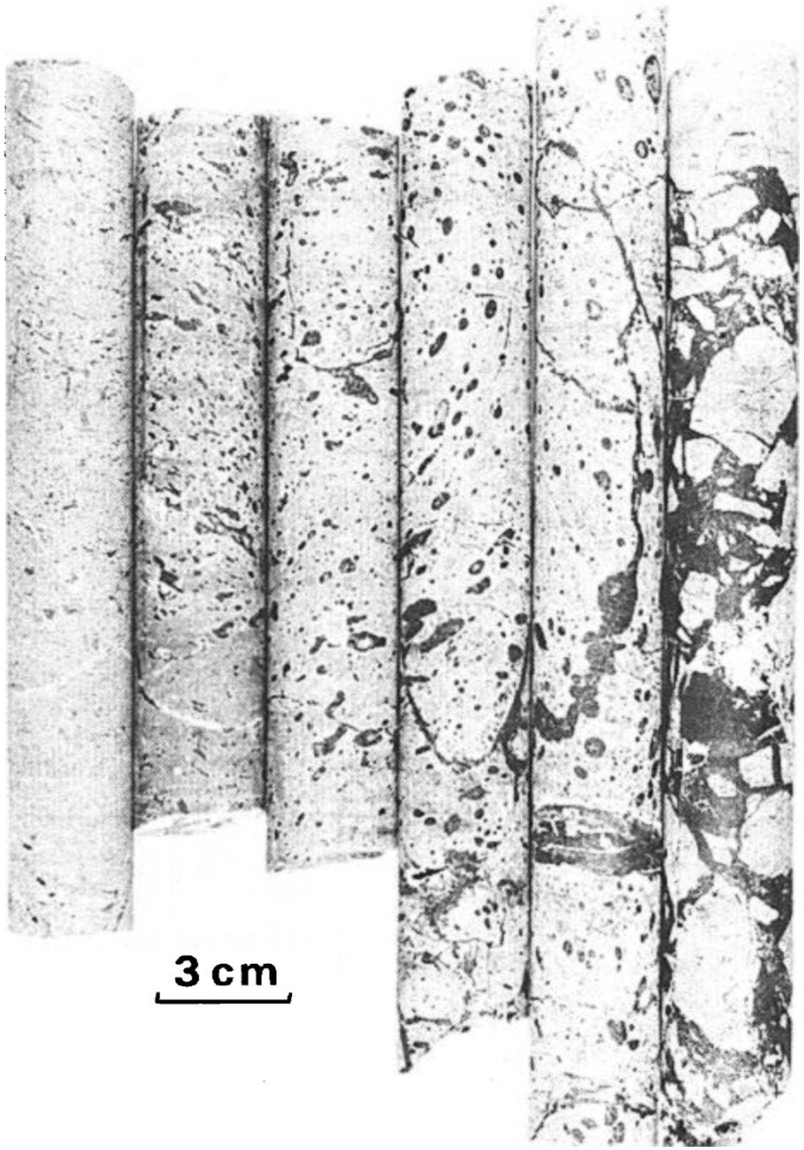



FIG. 16. Core samples from the Mertainen area (DH 63303). From left to right in the photograph are illustrated the textural forms of magnetite within the host trachyte. The textures primarily show the variation in size and shape of the magnetite-rich globular shapes, some of which are connected by a series of magnetite-infilled fractures or veins. Note the lighter colored depletion zones around the globules and fractures within the trachyte host rock.

- Mertainen, Sweden
- Trachyte host rocks
- Magnetite-rich globules
- Ore veins and breccias

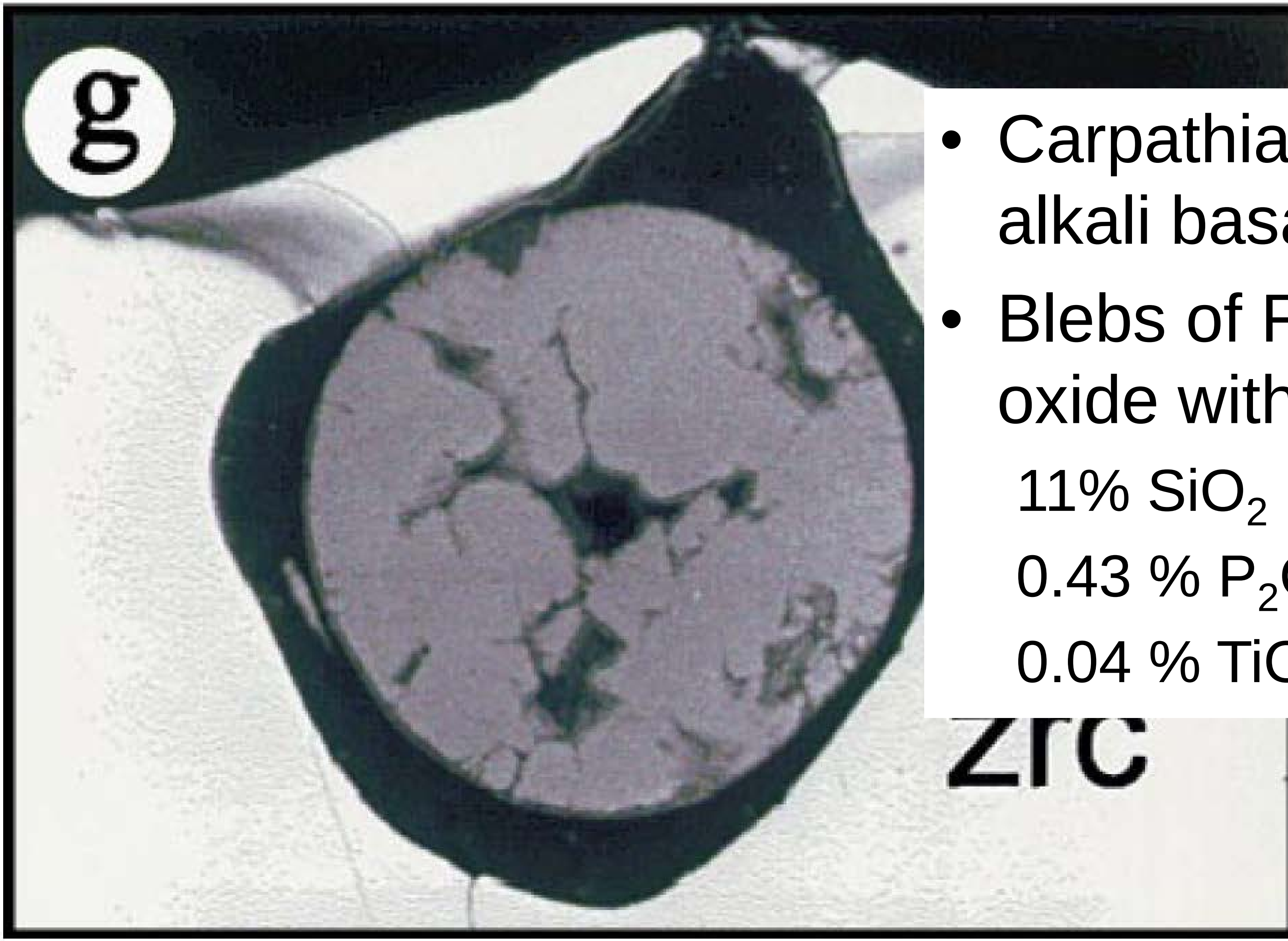
Lundberg and Smellie, 1979, Econ Geol

# Lunar basalts

- Metastable liquid immiscibility
- Below liquidus of supercooled magma

Roedder, 1978, GCA

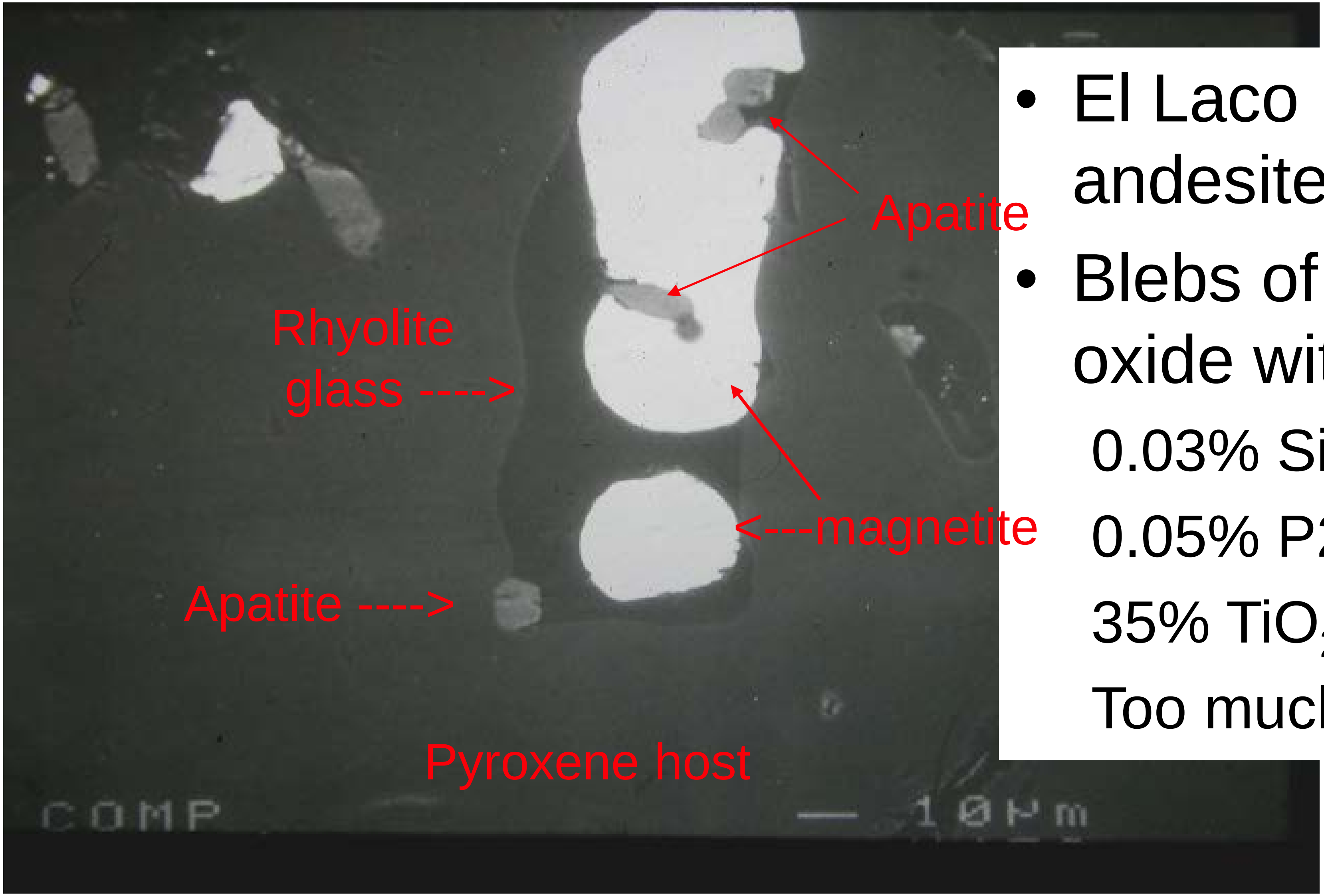
# Melt inclusions:




- Carpathian alkali basalt
- Blebs of Fe oxide with
  $11\%\ SiO_2$
  $0.43\ \%\ P_2O_5$
  $0.04\ \%\ TiO_2$

Hurai et al., 1998, CMP

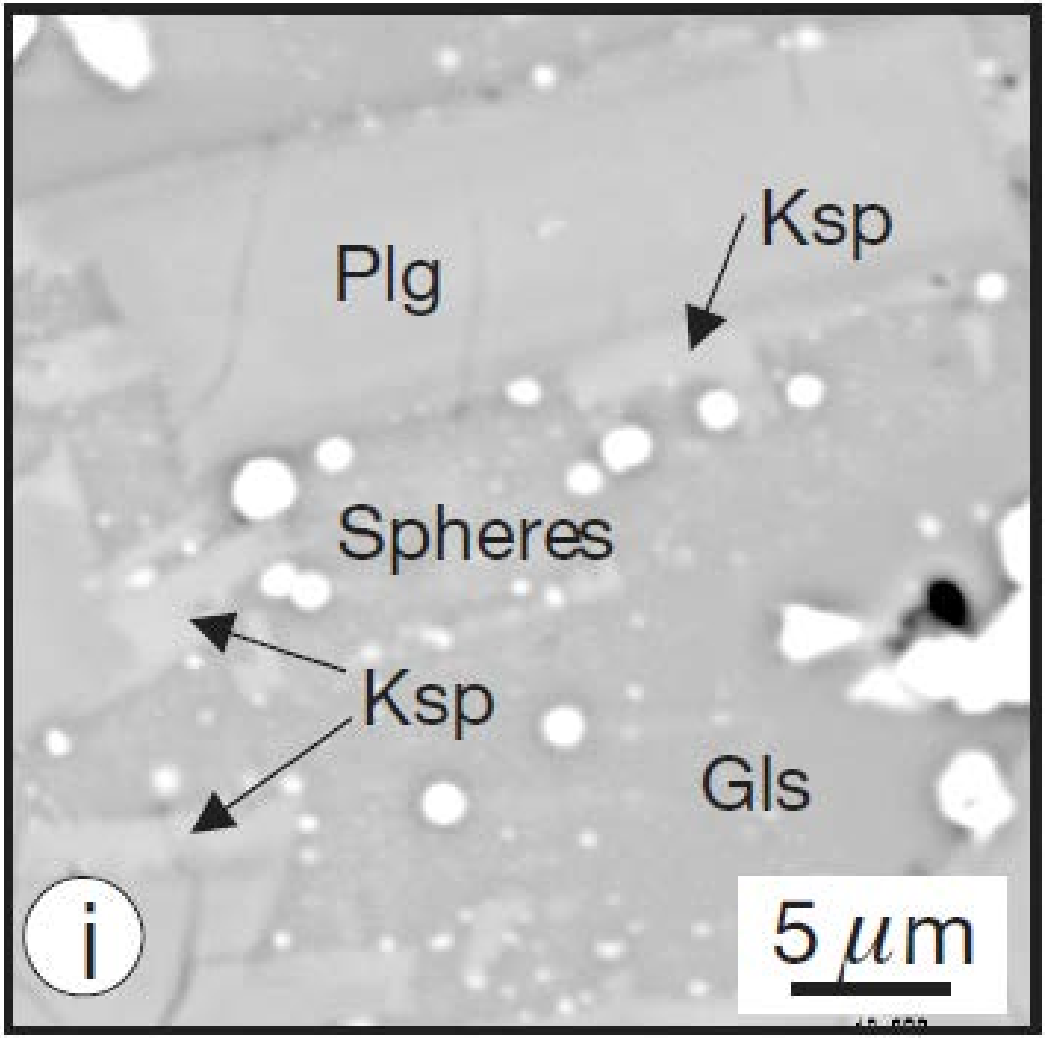
# Melt inclusions




- El Laco andesite
- Blebs of Fe oxide with
  - 0.03% $SiO_2$
  - 0.05% $P2O_5$
  - 35% $TiO_2$
  - Too much Ti

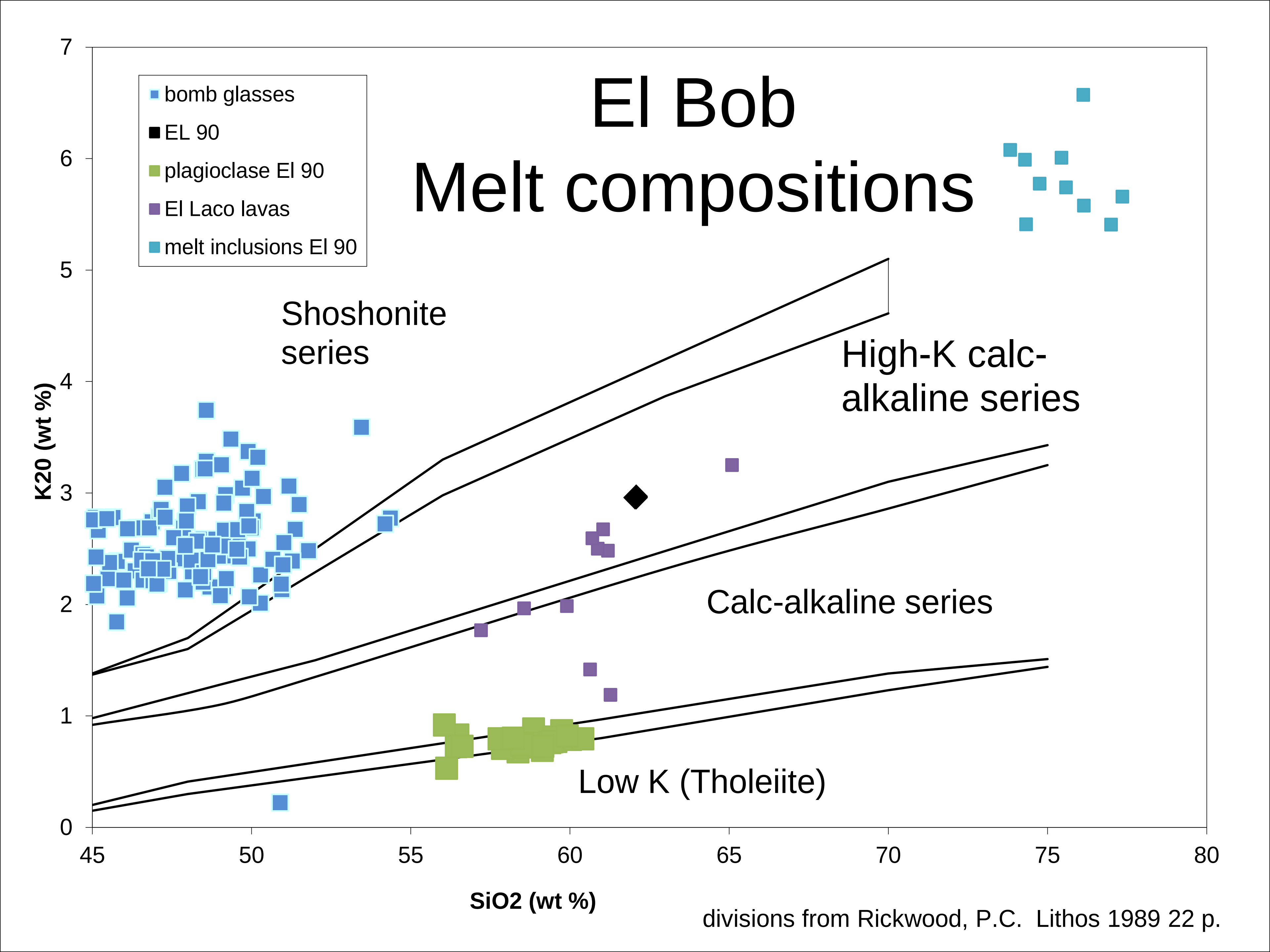
Photo: HR Naslund

# Antauta volcanic centre, Peru

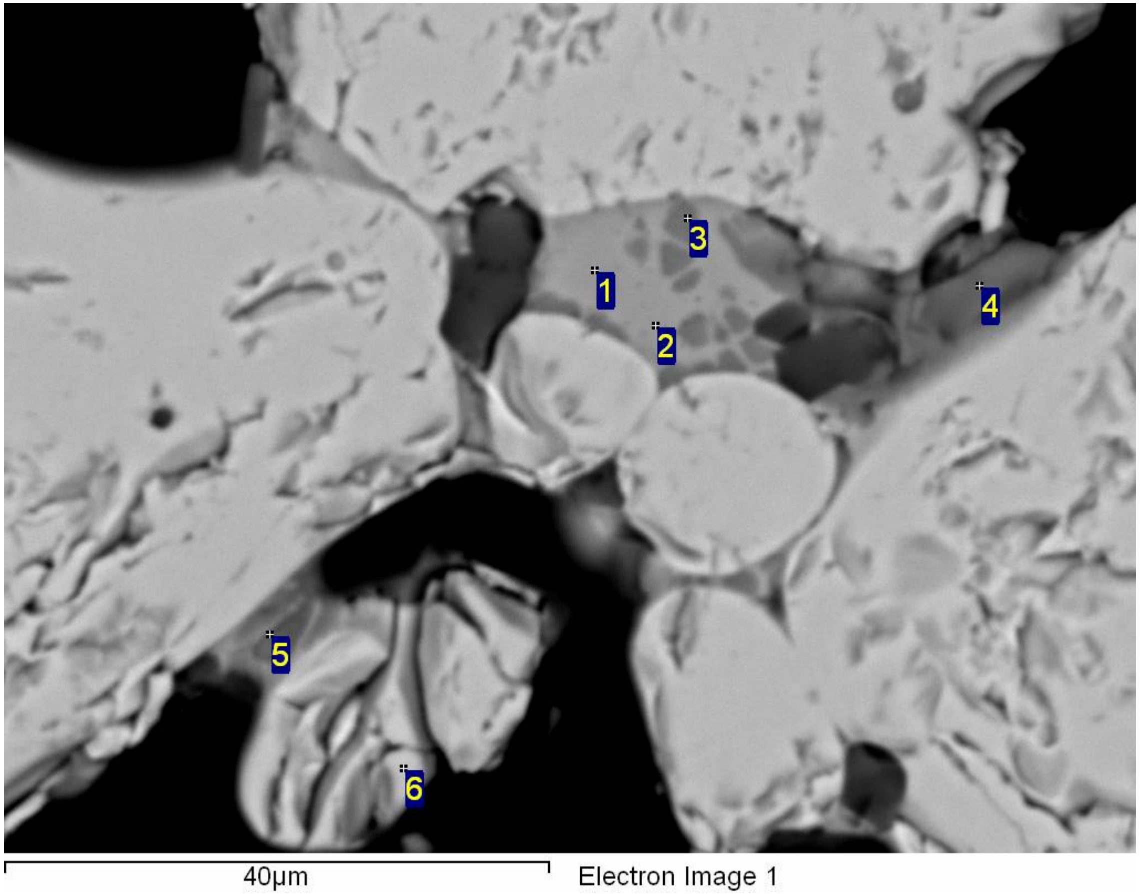



- Immiscible Fe-Ti rich liquids
- Absarokite – rhyodacite magma mixing
- Fe oxide with
  - ≥ 8.4 % SiO2
  - ≥ 23 % P2O5
  - ≥ 30 % TiO2
- Too much Ti

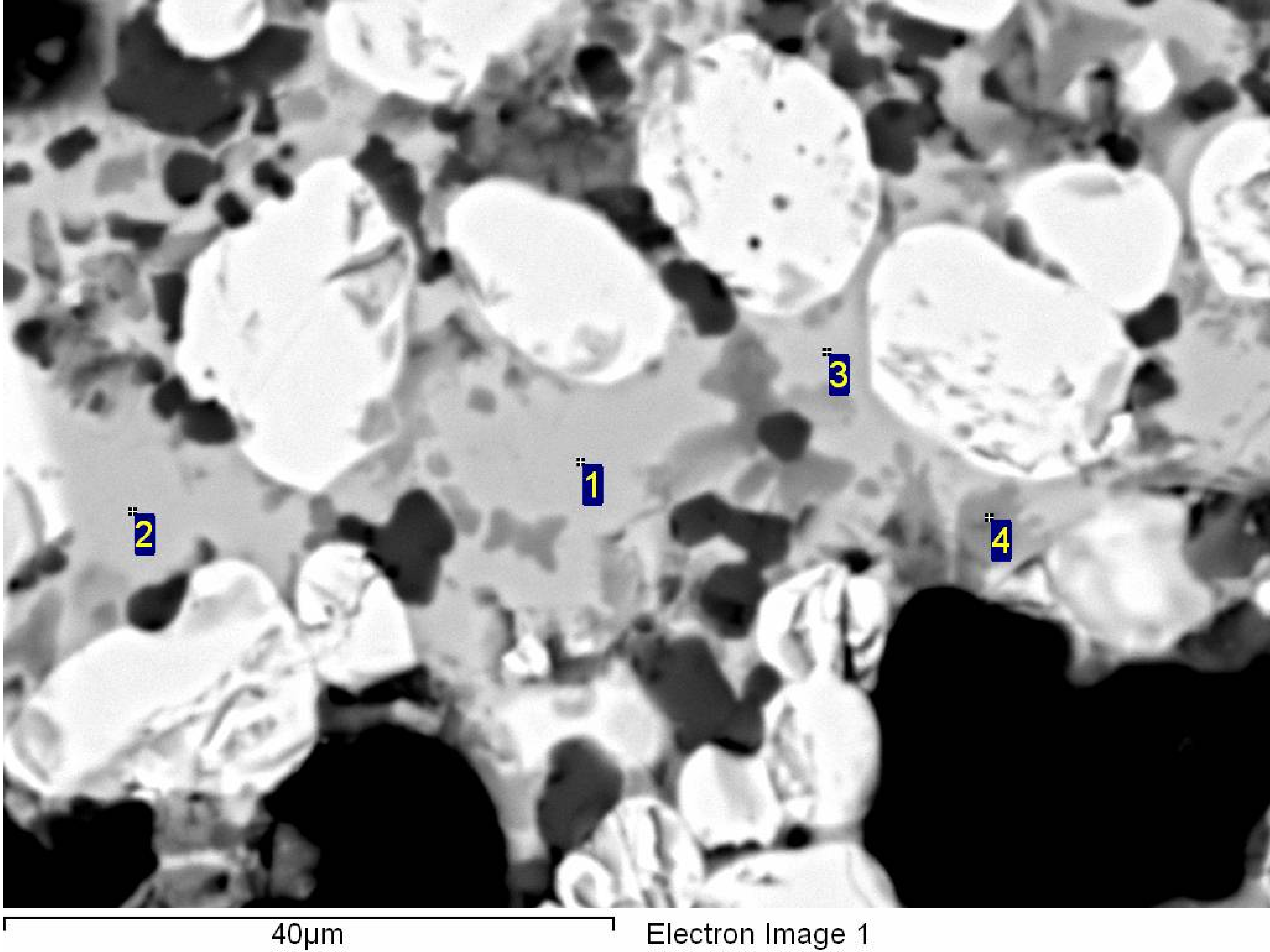
Clark & Kontak, 2004, Econ Geol


El Bob
Melt compositions
bomb glasses
EL 90
plagioclase El 90
El Laco lavas
melt inclusions El 90
Shoshonite series
High-K calc-alkaline series
Calc-alkaline series
Low K (Tholeiite)
K20 (wt %)
SiO2 (wt %)
0
1
2
3
4
5
6
7
45
50
55
60
65
70
75
80
divisions from Rickwood, P.C. Lithos 1989 22 p.

# 1 Atm melting of ash

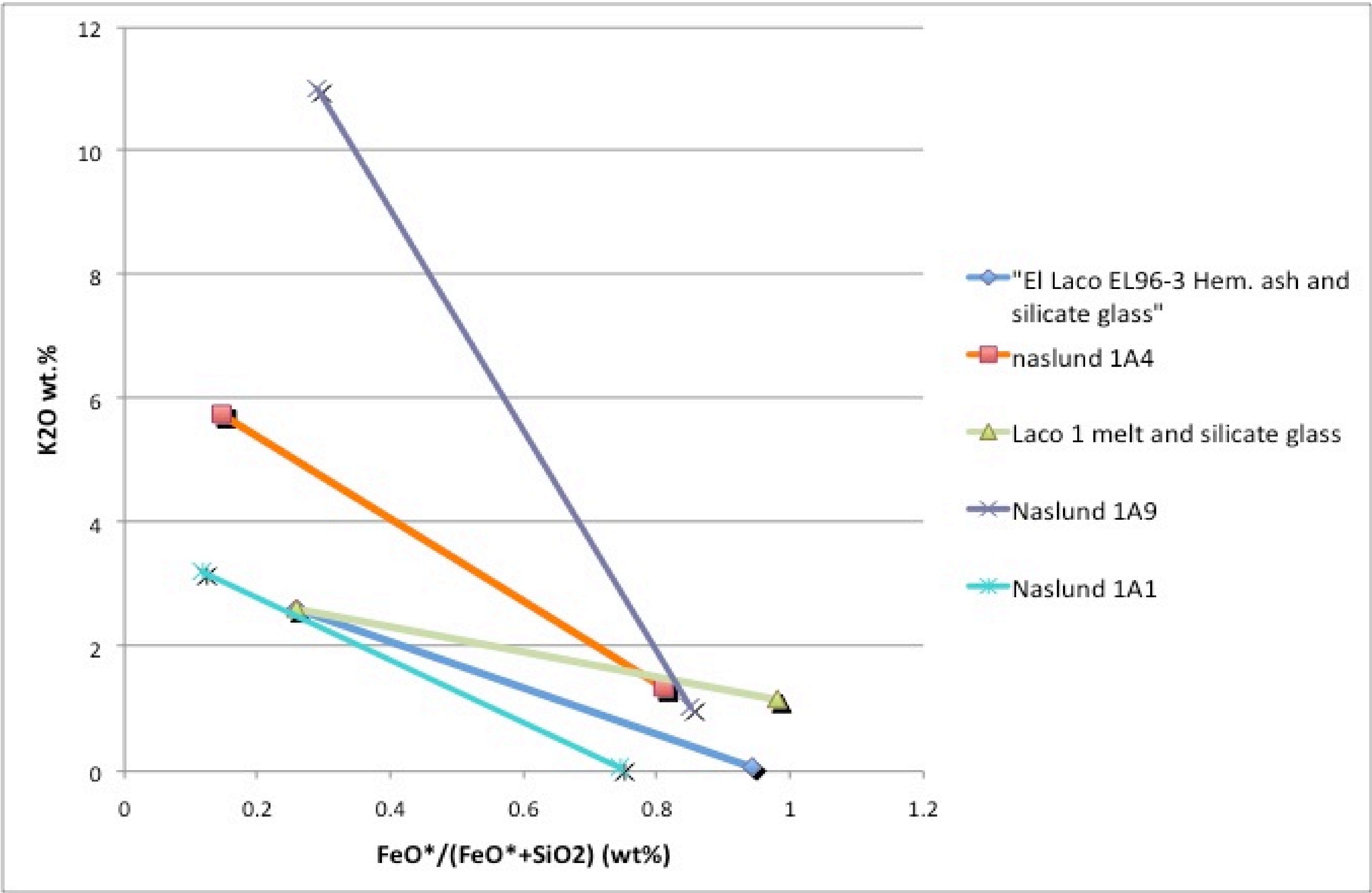



- Evacuated silica tube
- Ash dehydrated at 800 ºC
- Hematite-magnetite $fO_2$ buffer
- Melted at 1081 ºC for 6 hours
- Fe-P-O glass between hematite crystals
- Eutectic composition in $FePO_4$-$Fe_2O_3$ system

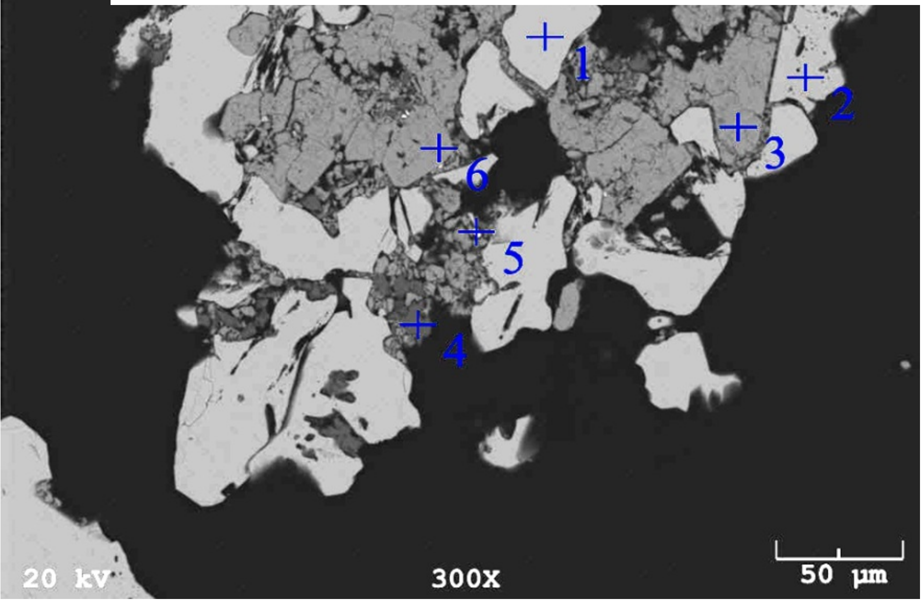


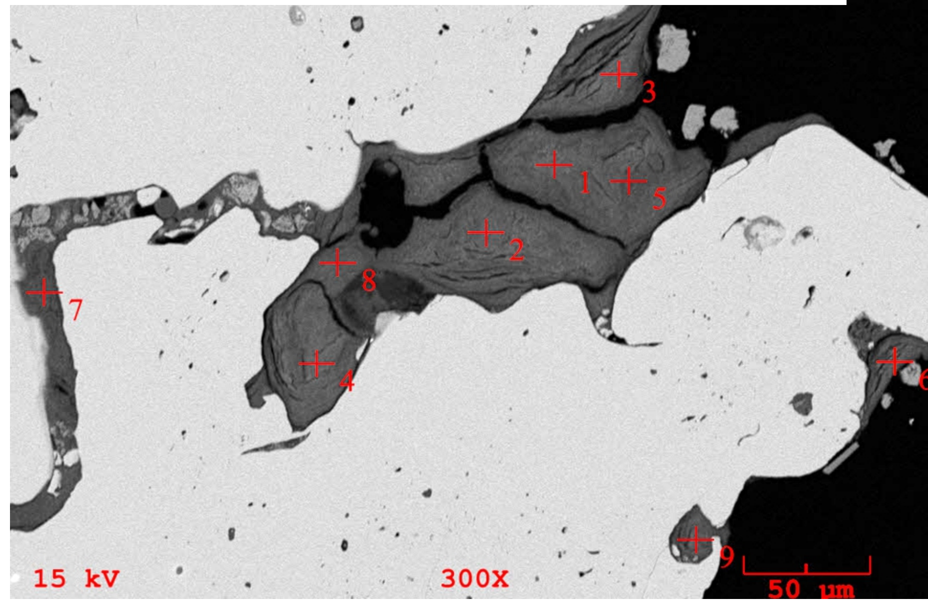
1
2
3
4
40µm
Electron Image 1

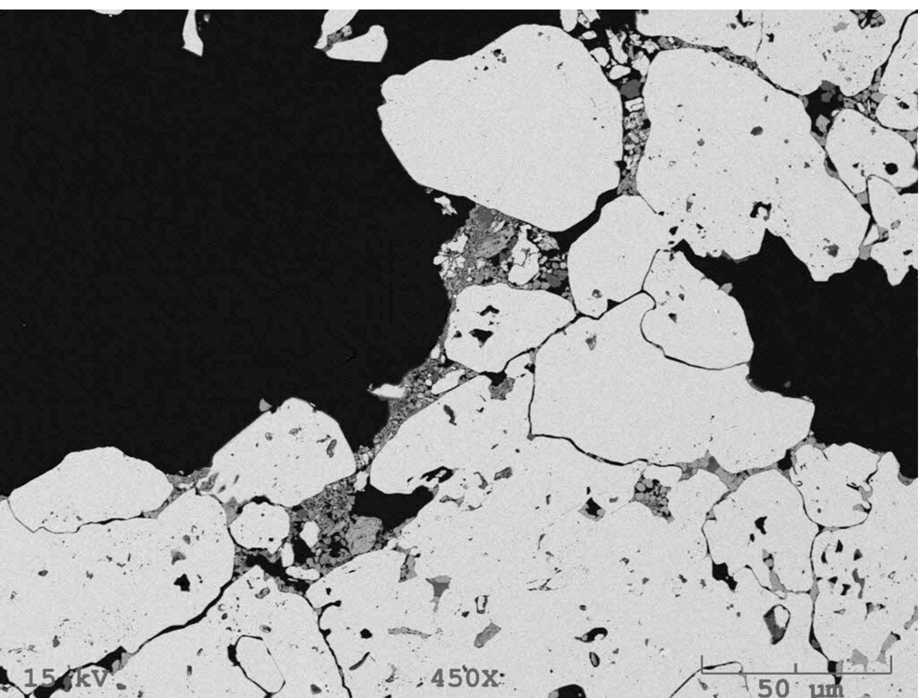
# Shoshonite-ash immiscibility?

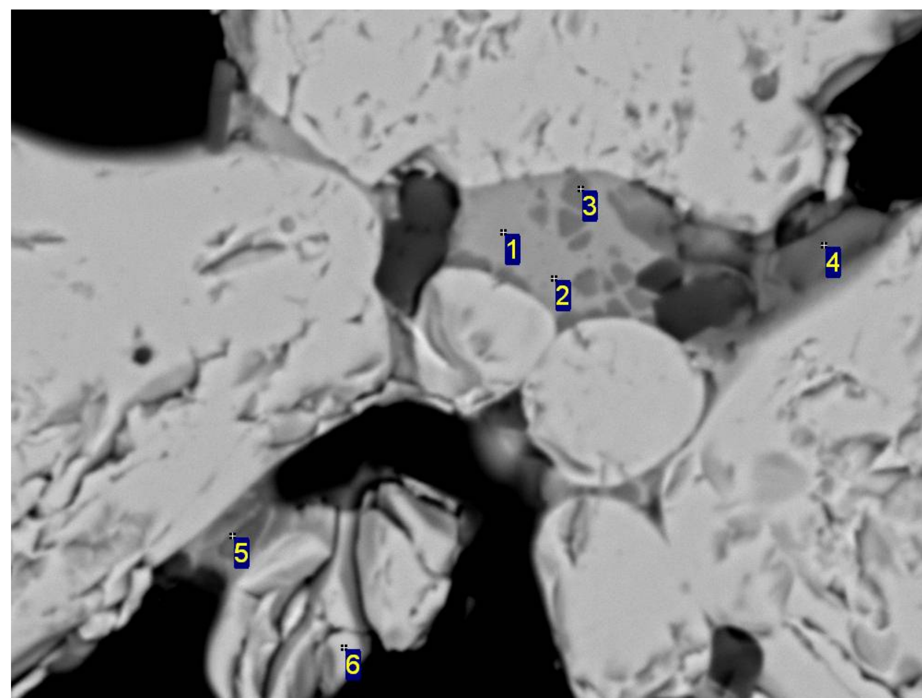


# Textural evidence for two coexisting liquids at El Laco

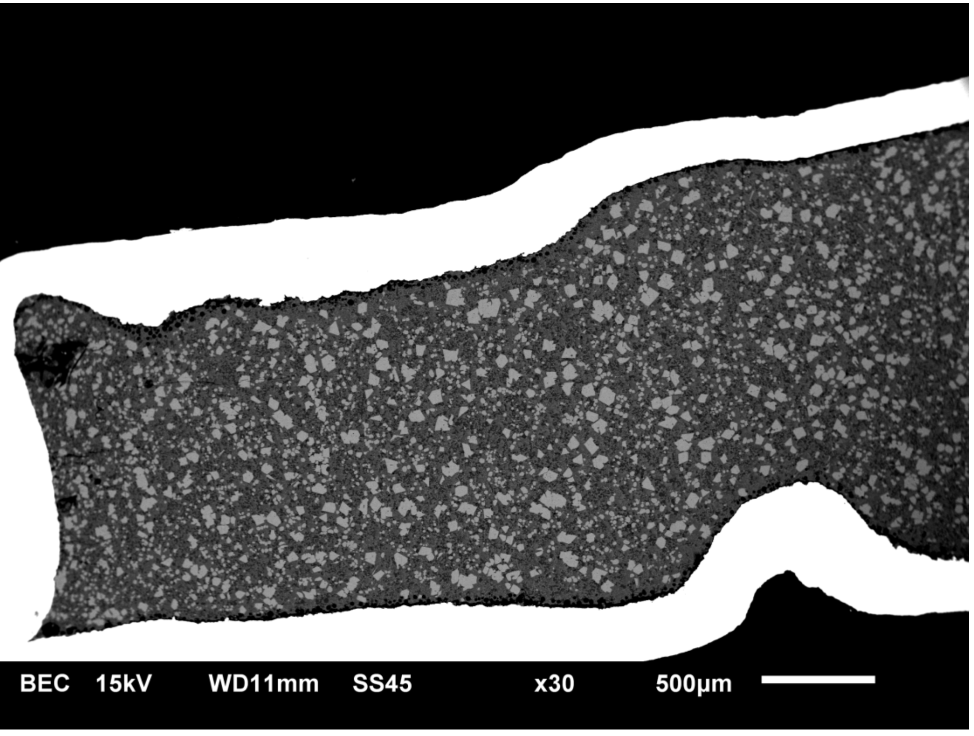


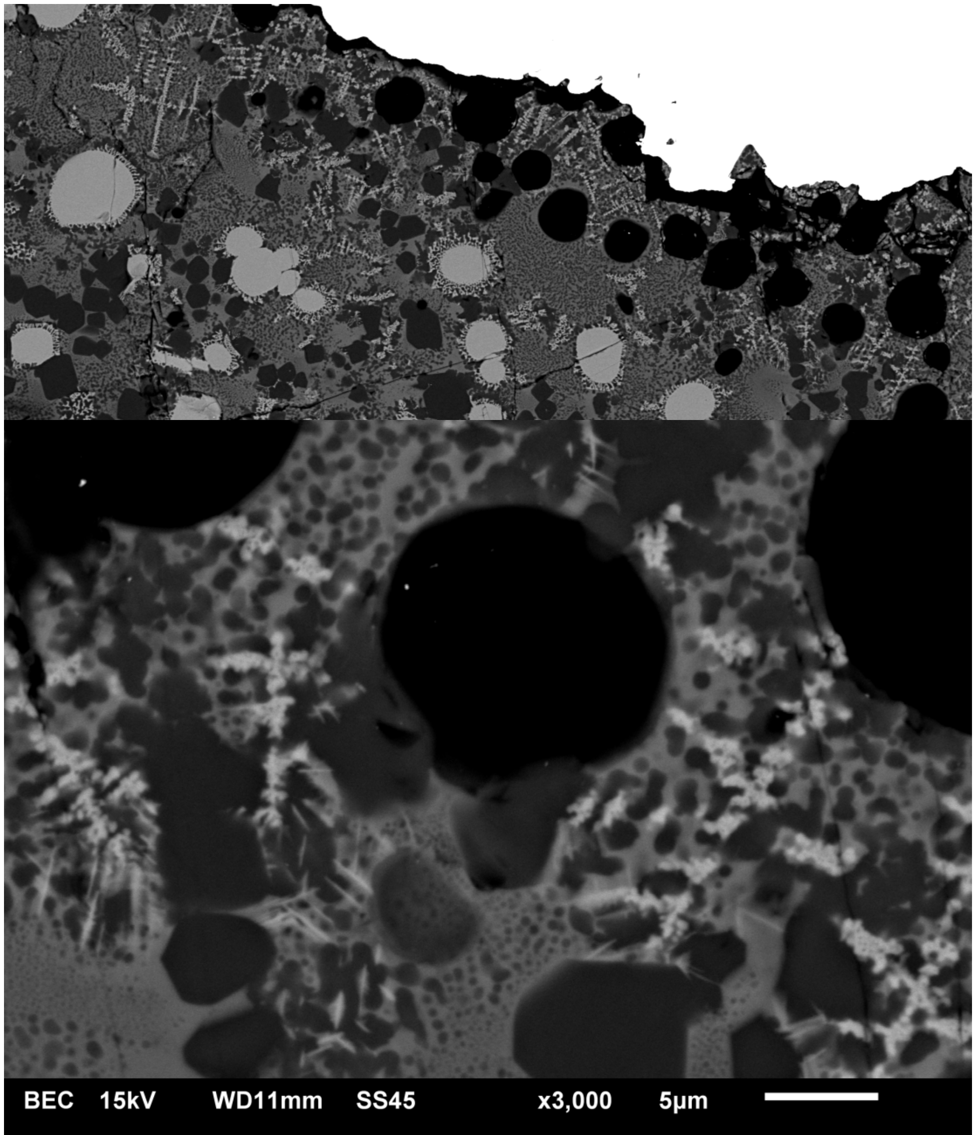



# High pressure melting experiment (U of Toronto)



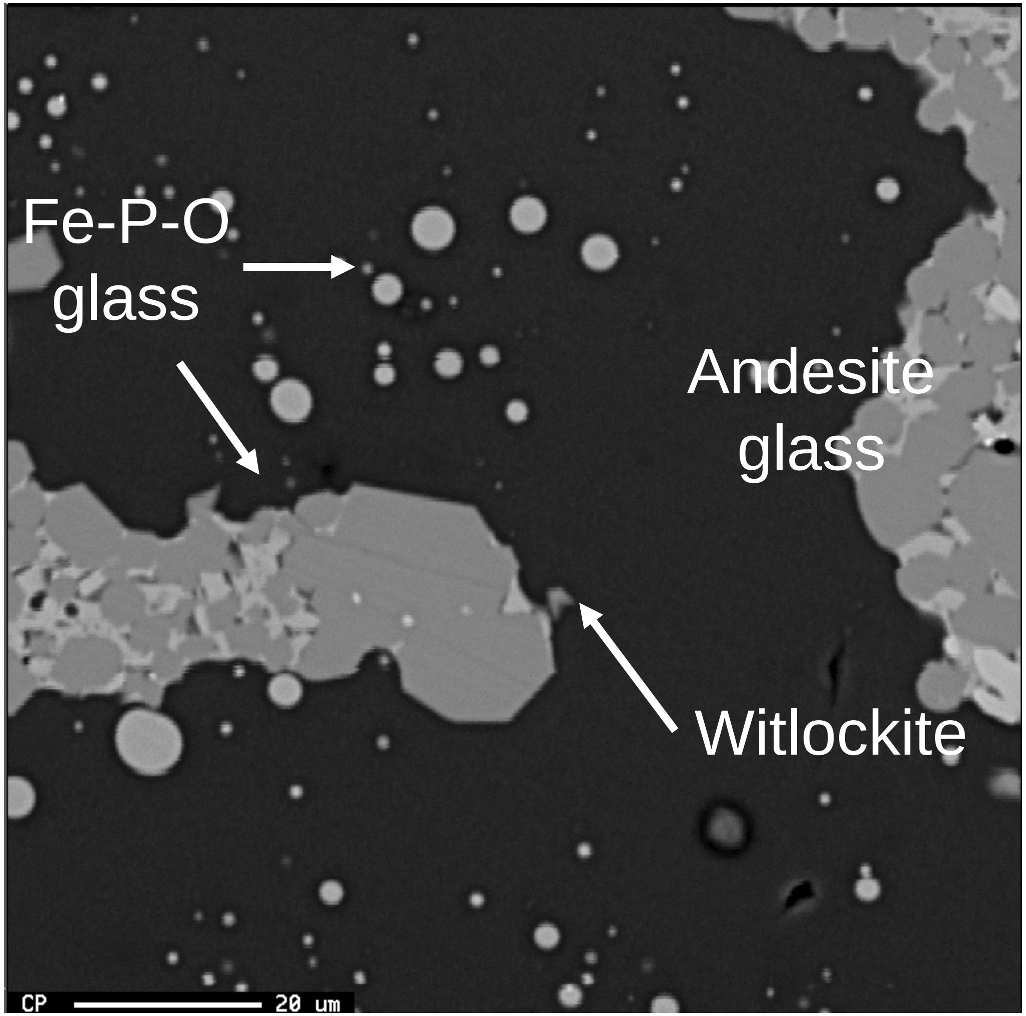

- Synthetic shoshonite glass
- Anhydrous magnetite
- Anhydrous $FePO_4$
- Pt capsule
- 1.0 GPa, 1200 ºC

# Phase assemblage



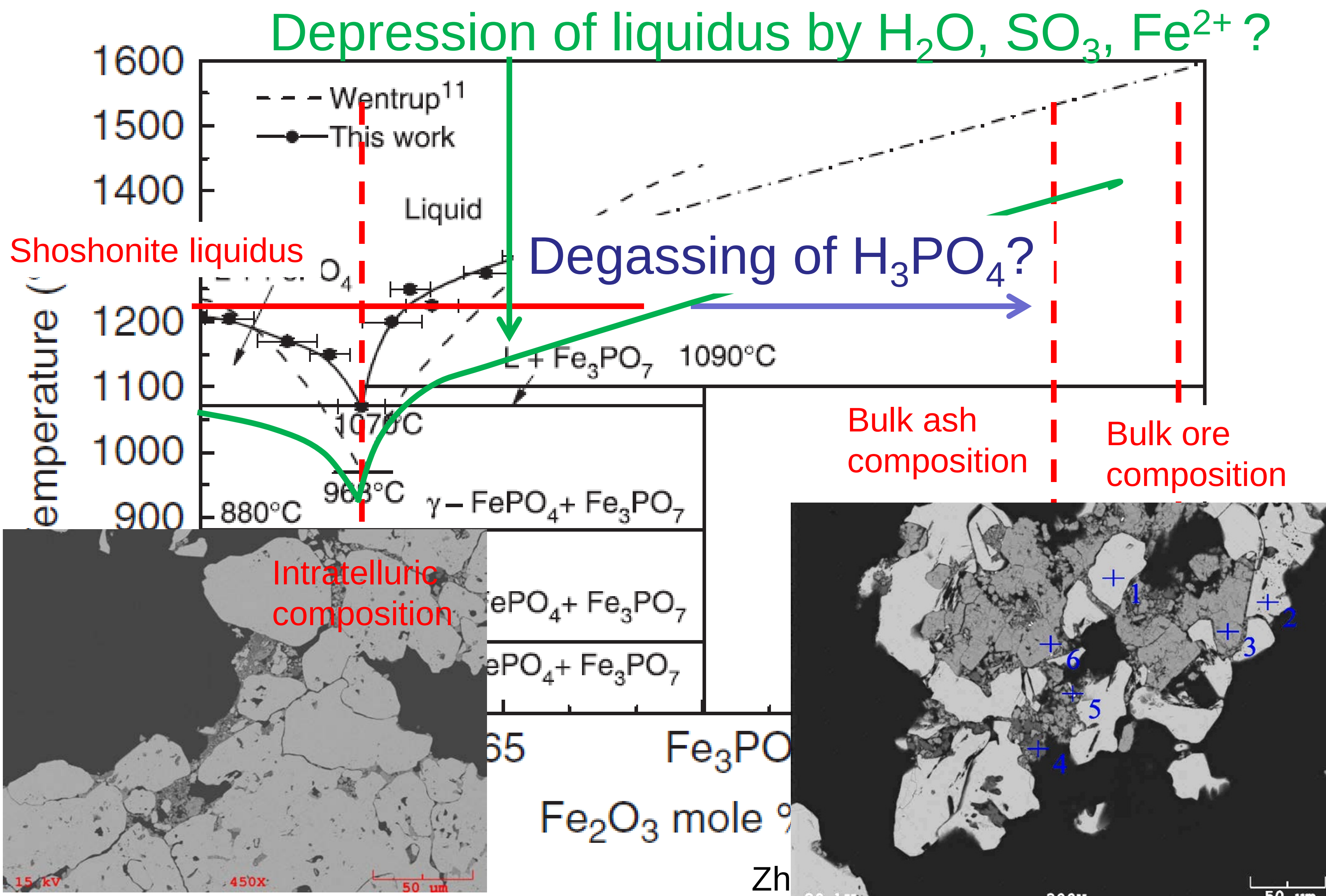

- Magnetite
- Hematite
- Silica mineral
- Phosphate-silicate melt (P>Si)
- Vapour bubbles (possible quench phase)
- No immiscible liquids
- No, the hematite is not an immiscible liquid

# High pressure melting experiment (SUNY)




- AGV1 andesite standard
- $H_2O$-saturated
- $H_3PO_4$ added
- 0.4 GPa, 900 ºC
- Immiscible liquids

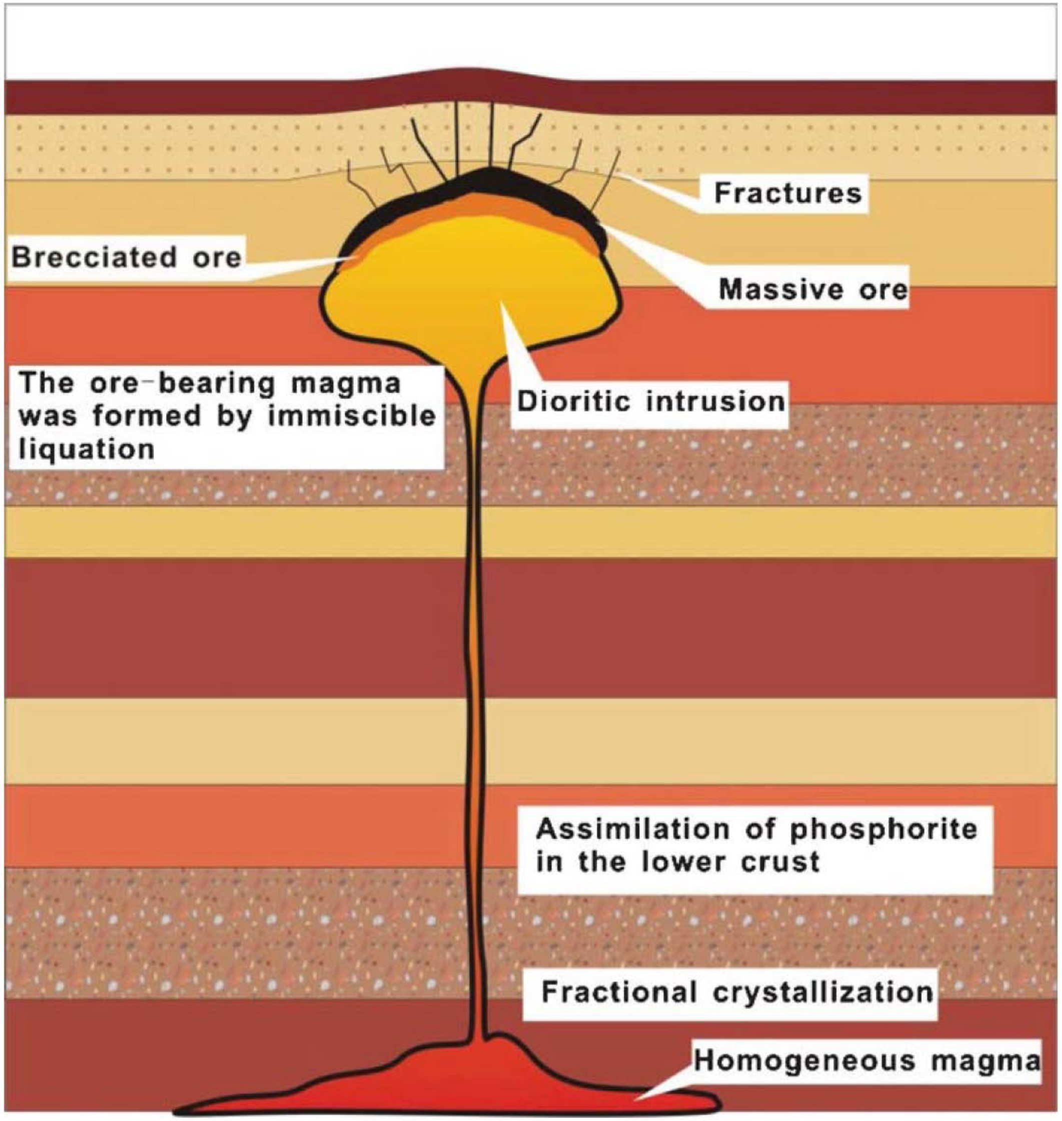
# Phase relations in $Fe_2O_3$-$FePO_4$



# Summary

- El Laco/Kiruna type Fe ores are magmatic
- Immiscible Fe-rich liquids form in many systems
- FeO-rich liquids are very diverse
- El Laco/Kiruna liquids are unusually low in $SiO_2$, $TiO_2$, apatite
- The El Laco/Kiruna-type liquid differs from most others in its abundance – Gt compared to milligrams
- The ore magma was close to magnetite composition but must have contained phosphate and other components
- Immiscibility between shoshonite and Fe-P-O liquid
- Additional components likely ($H_2O$, $SO_3$, Cl …)

# Where did the P come from?




- Gushan, China
- Assimilation of phosphorite?
- Liquation of Fe-P-O melt from calcalkaline silicate magma

Hou et al., 2009 Int Geol Rev.


Where did all the P go (how much was there in the first place)?
$H_3PO_4$?

# Future directions

- Further experiments – can we reduce the amount of P required?
- Addition of fluxing components $H_2O$, $SO_3$, Cl
- Effects of pressure
- Effect of water on liquidus temperature vs liquid-liquid solvus

# Phase relations

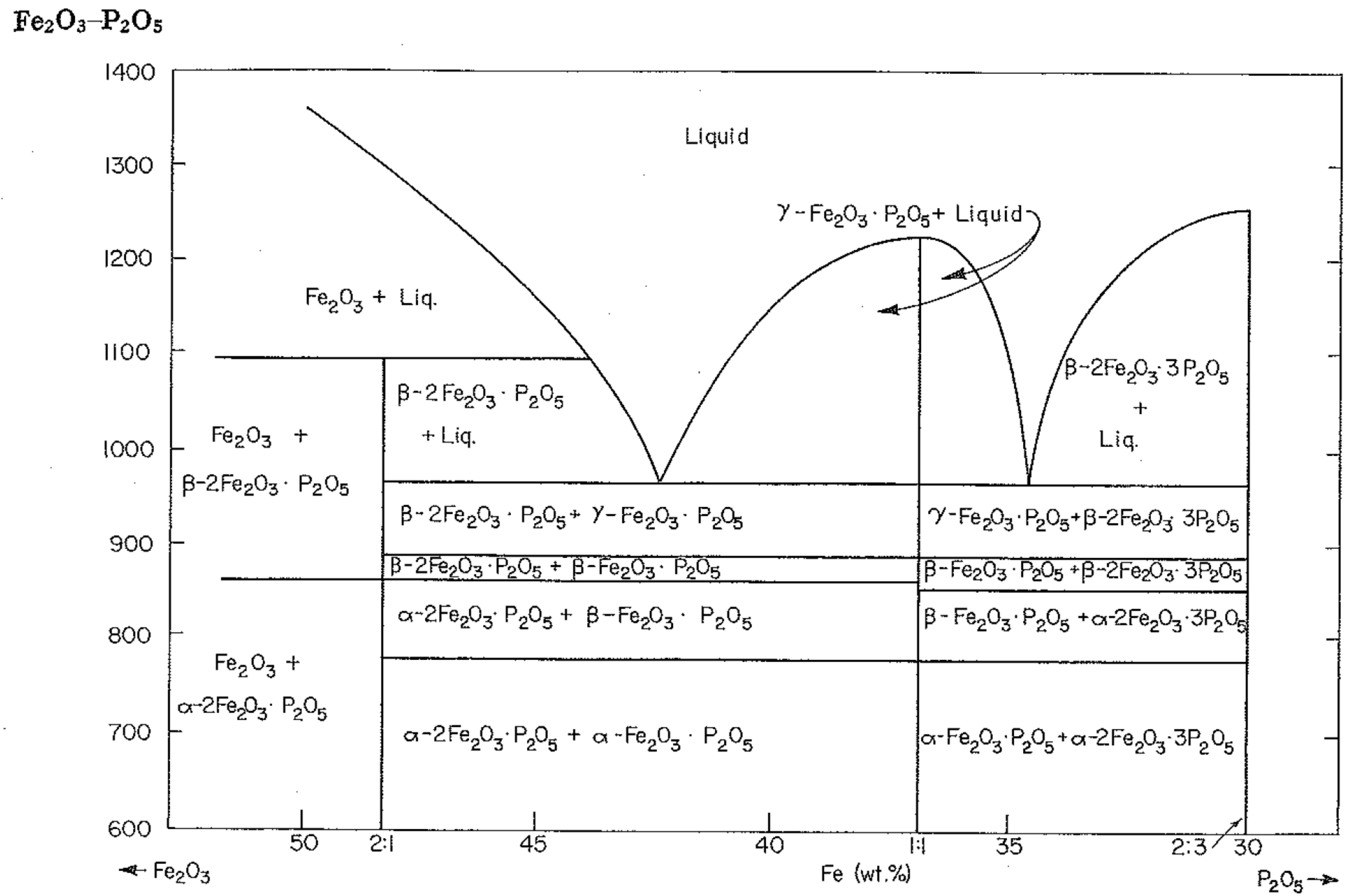



Fig. 338.—System $2Fe_2O_3 \cdot P_2O_5$–$2Fe_2O_3 \cdot 3P_2O_5$.

H. Wentrup, *Arch. Eisenhüettenw.*, 9, 57 (1935–36).

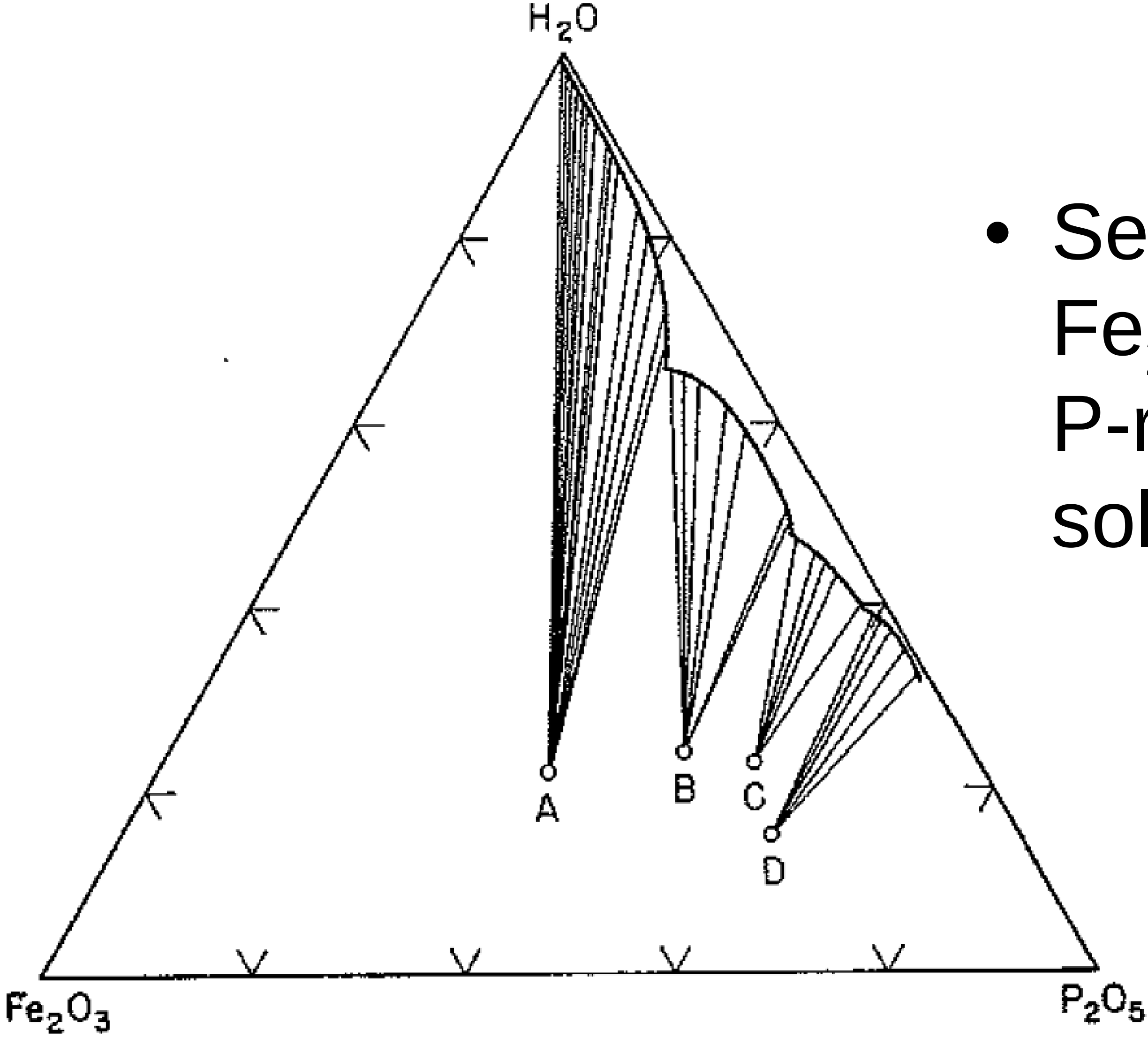
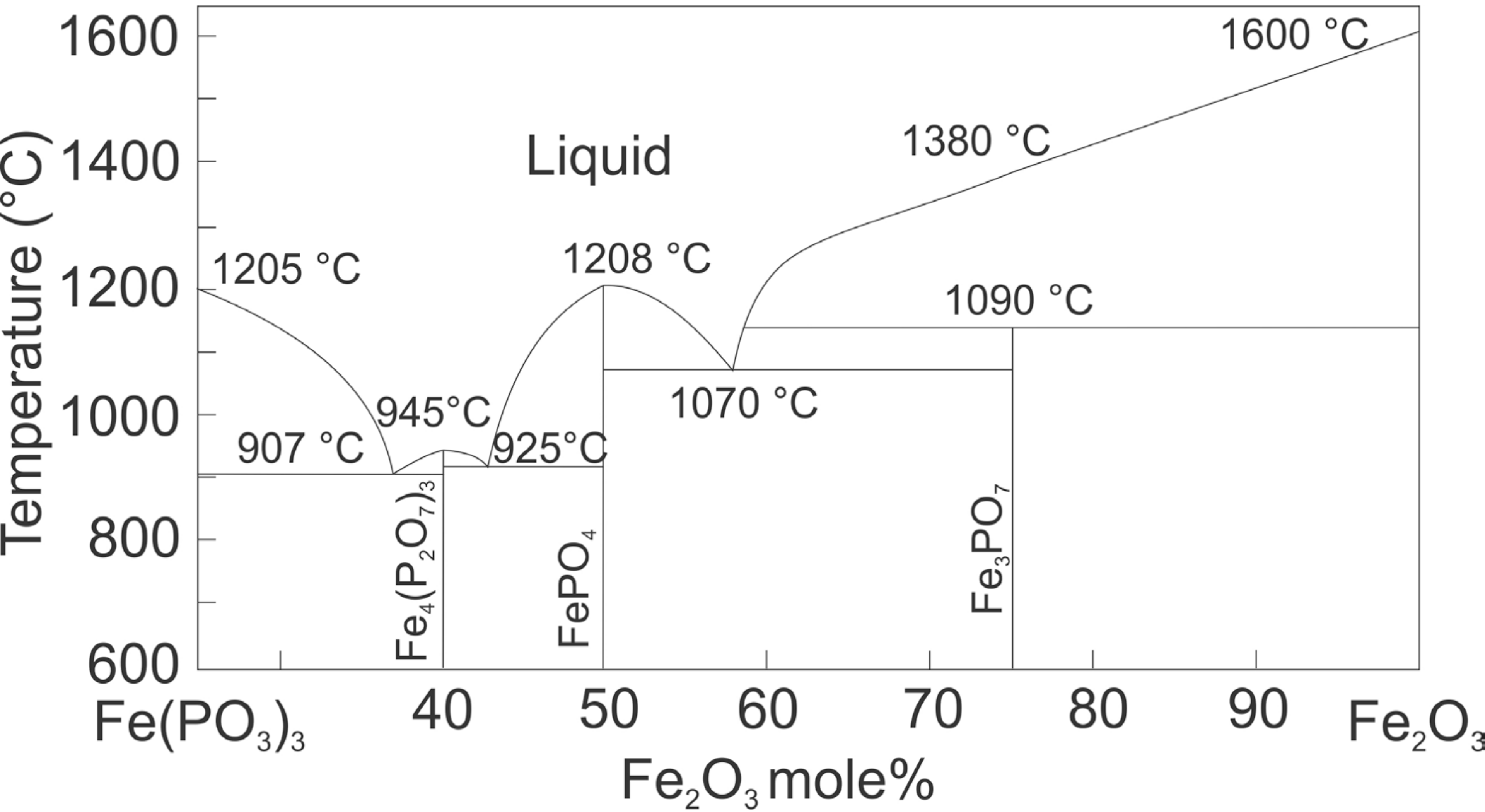



FIG. 2016.—System $Fe_2O_3$–$P_2O_5$–$H_2O$, at 25°C. A = $Fe_2O_3 \cdot P_2O_5 \cdot 5H_2O$; B = $Fe_2O_3 \cdot 2P_2O_5 \cdot 8H_2O$; C = $Fe_2O_3 \cdot 3P_2O_5 \cdot 10H_2O$; D = $Fe_2O_3 \cdot 3P_2O_5 \cdot 6H_2O$.

R. F. Jameson and J. E. Salmon, *J. Chem. Soc.*, 1954, p. 29.

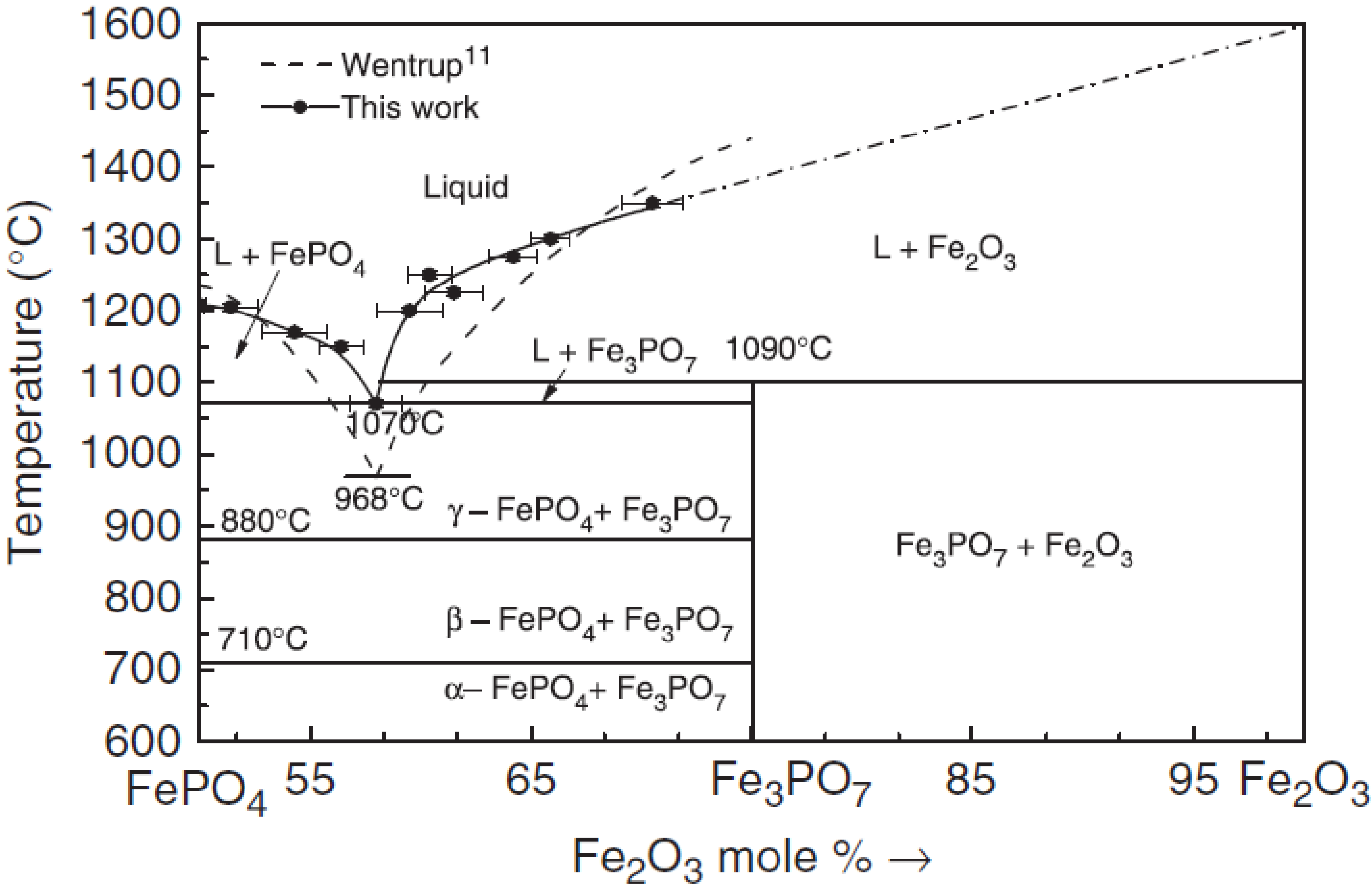
- Several wt% $Fe_2O_3$ dissolve in P-rich aqueous solution at 25°C

# Iron oxide – phosphate system




Zhang et al., 2011, J. Am Ceram Soc

# $FePO_4$-$Fe_2O_3$ (detail)

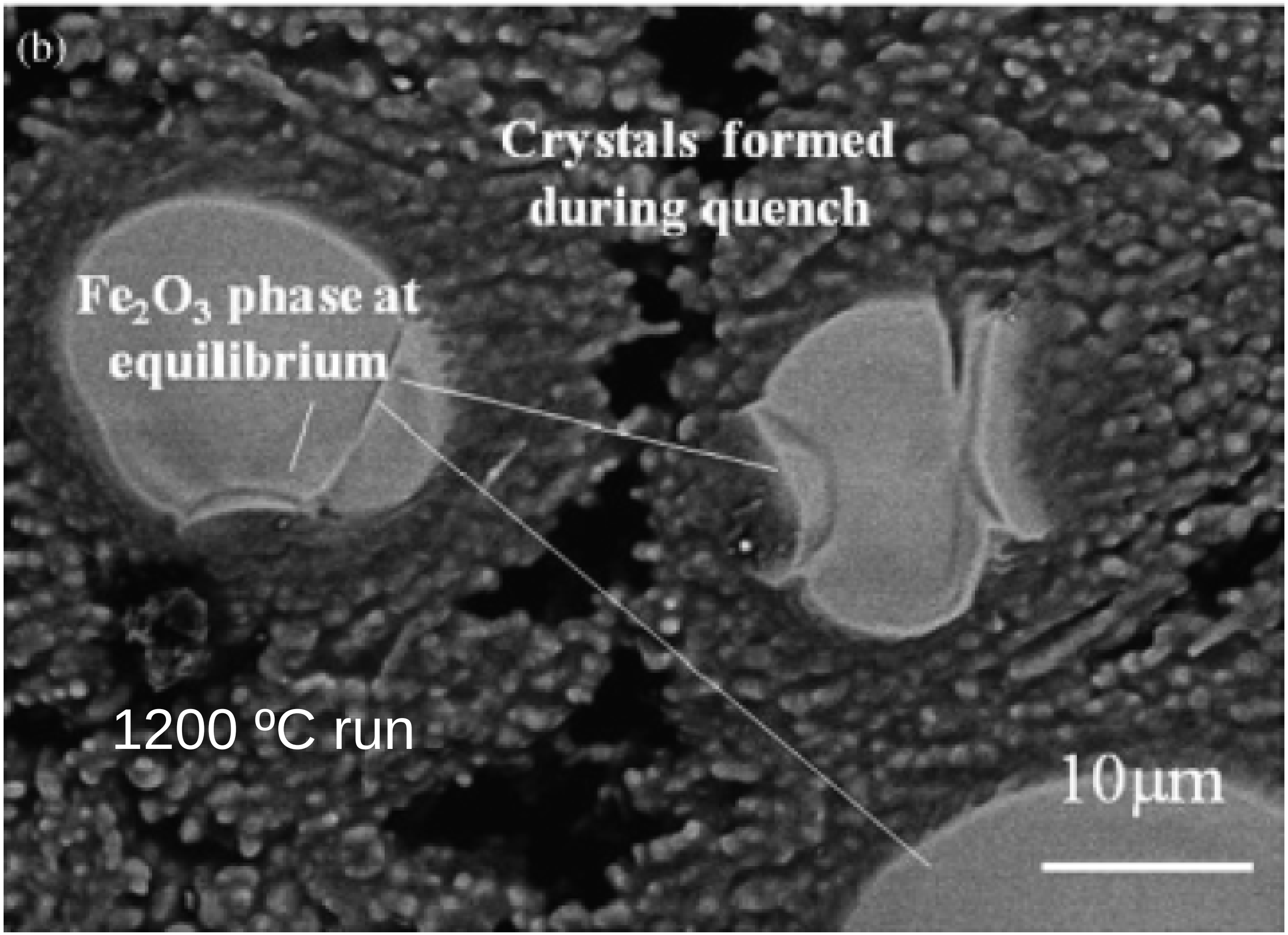



Zhang et al., 2011, J. Am Ceram Soc

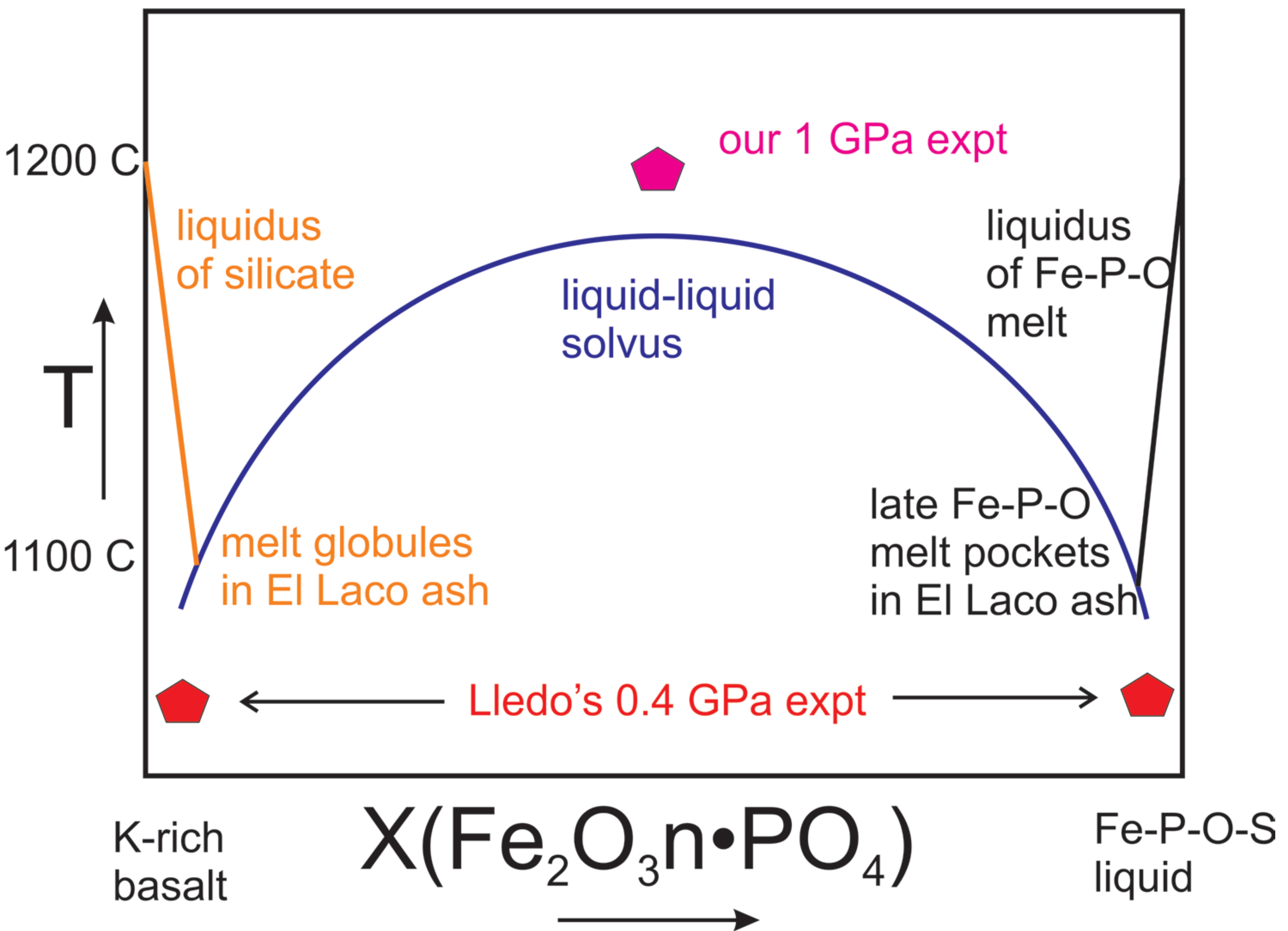
# $FeO$-$Fe_2O_3$-$P_2O_5$-$H_2O$

- Liquids present below 1000$^oC$
- Low viscosity (< 1 PaS)
- Popular choice for nuclear waste storage
- Dissolve abundant oxides, > 1% $SO_3$
- $Fe^{2+}/Fe^{tot} > 0.25$ under air, anhydrous
- What happens to eutectic with added degree of freedom in $FePO_4$-Hm-Mt?
- At moderate $fO_2$, $Fe_3O_4$ will likely predominate
- $H_2O$ is probably a very effective flux
- $P_2O_5$ evaporates rapidly from melts

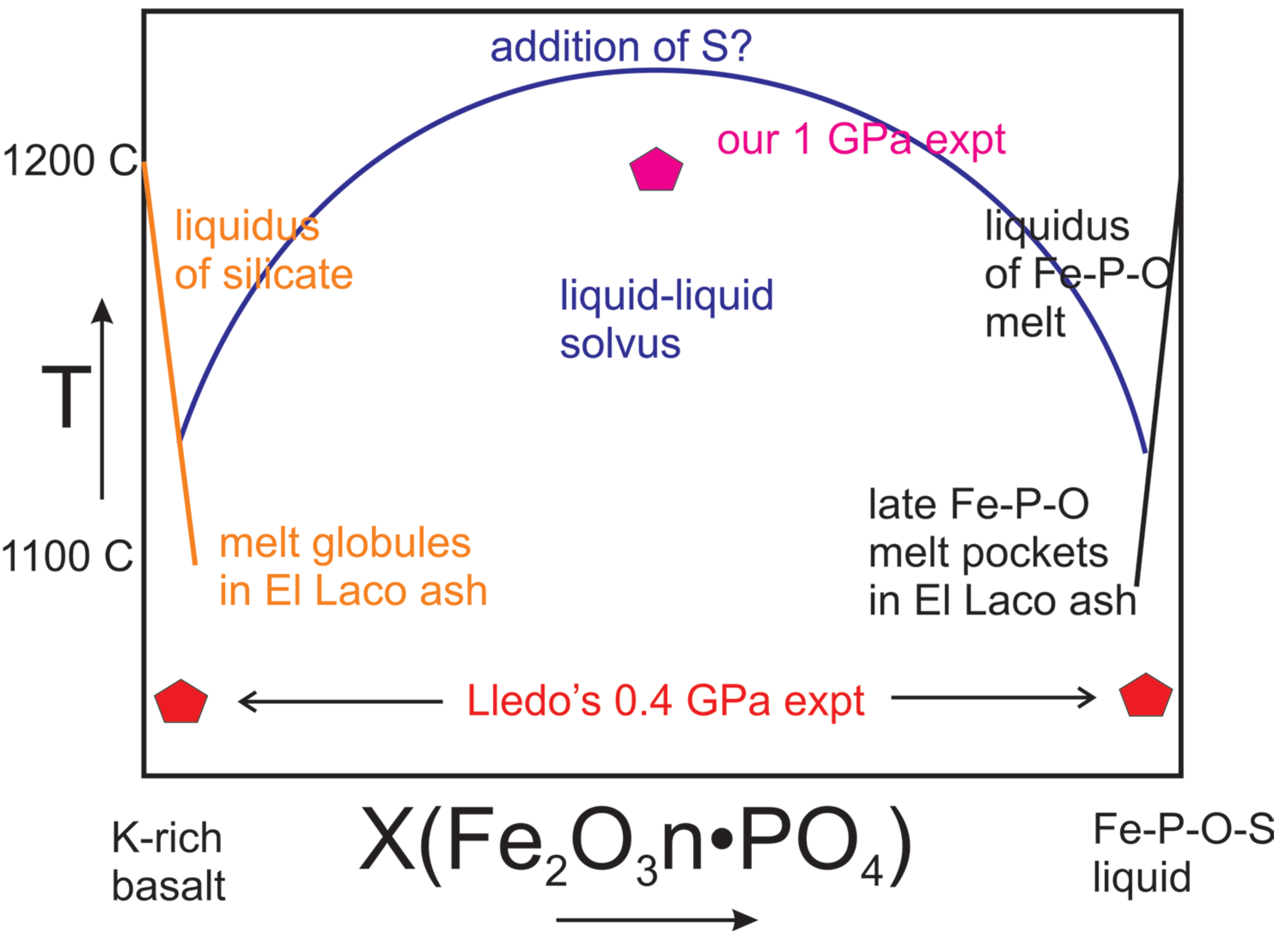
# $Fe_3PO_7$ peritectic at 1090±8ºC

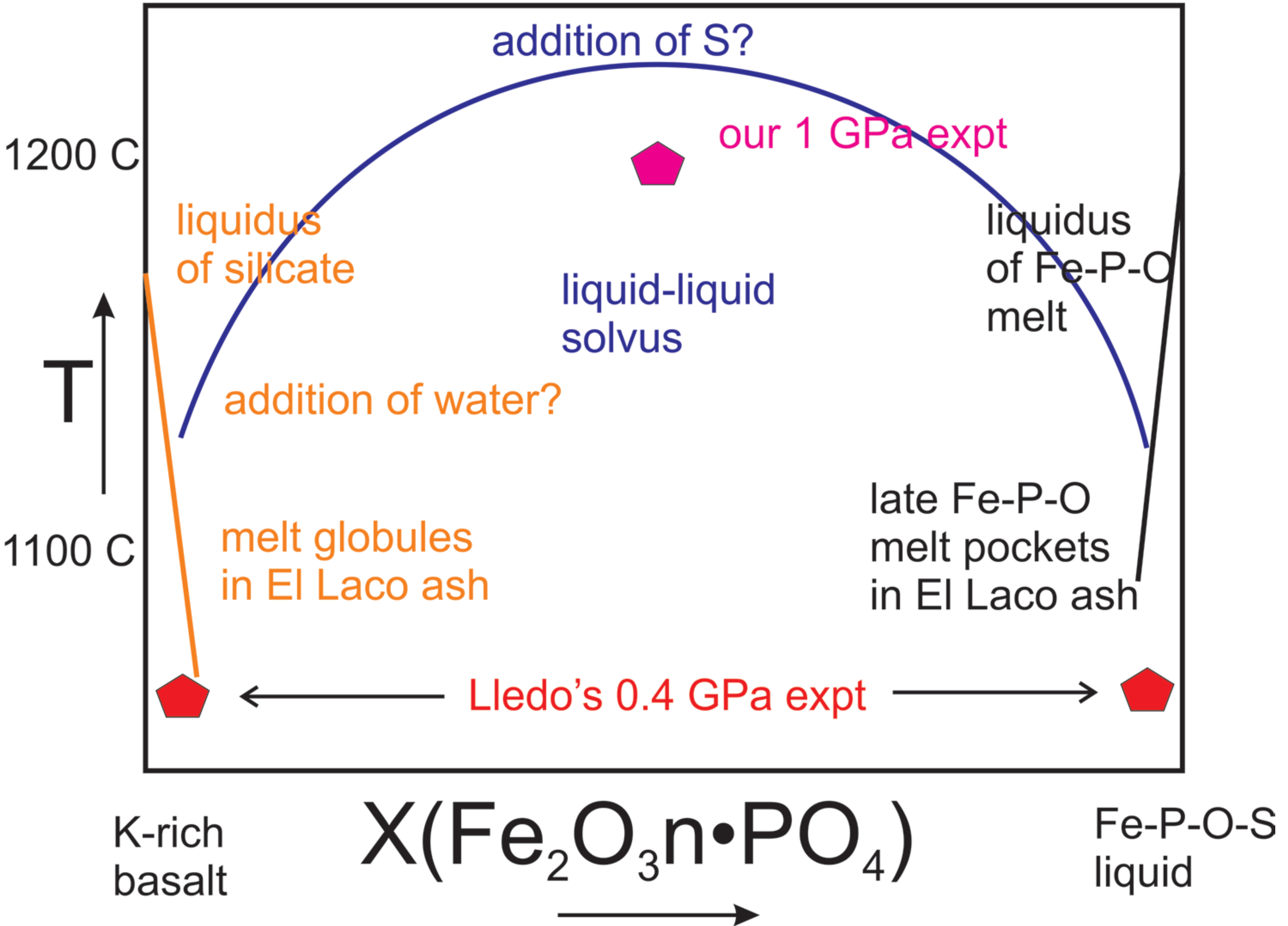


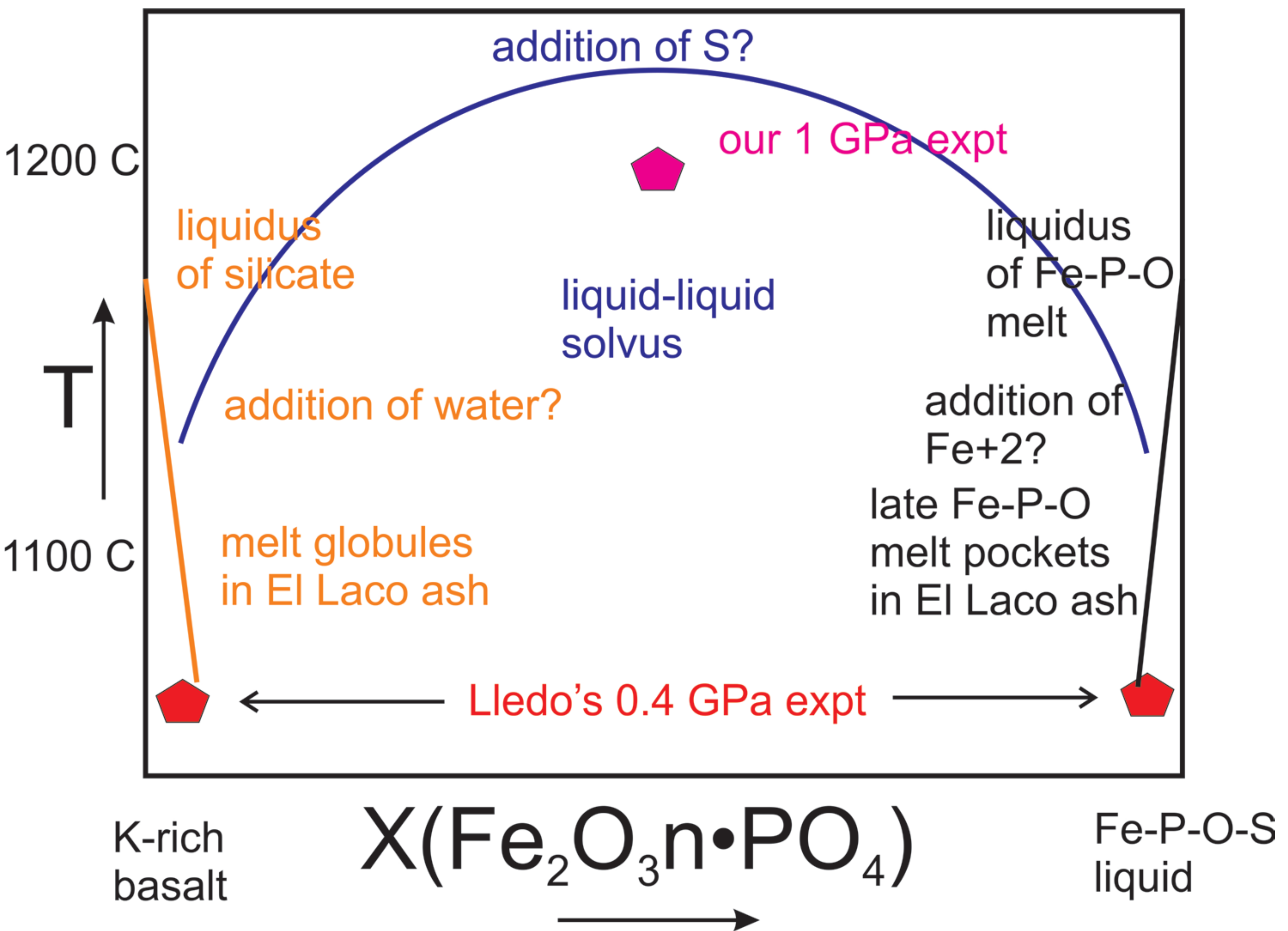

Zhang et al., 2011, J. Am Ceram Soc

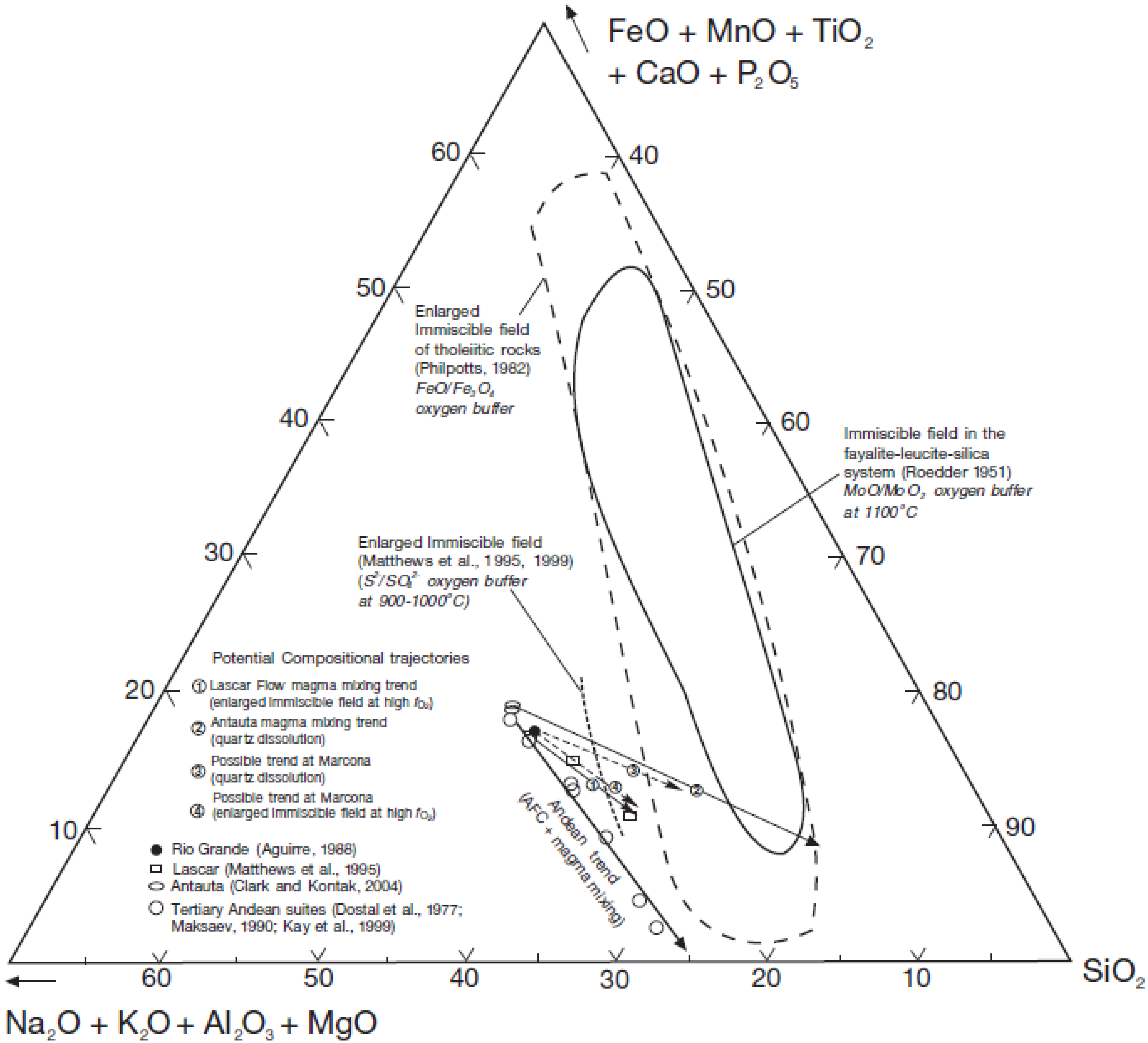


1200 C
1100 C
T
liquidus
of silicate
our 1 GPa expt
liquid-liquid
solvus
liquidus
of Fe-P-O
melt
melt globules
in El Laco ash
late Fe-P-O
melt pockets
in El Laco ash
Lledo's 0.4 GPa expt
K-rich
basalt
X(Fe2O3n•PO4)
Fe-P-O-S
liquid


addition of S?
our 1 GPa expt
1200 C
liquidus
of silicate
liquid-liquid
solvus
liquidus
of Fe-P-O
melt
T
late Fe-P-O
melt pockets
in El Laco ash
1100 C
melt globules
in El Laco ash
Lledo's 0.4 GPa expt
K-rich
basalt
X(Fe2O3n•PO4)
Fe-P-O-S
liquid


addition of S?
our 1 GPa expt
1200 C
liquidus of silicate
liquid-liquid solvus
liquidus of Fe-P-O melt
T
addition of water?
late Fe-P-O melt pockets in El Laco ash
1100 C
melt globules in El Laco ash
Lledo's 0.4 GPa expt
K-rich basalt
X(Fe2O3n•PO4)
Fe-P-O-S liquid


addition of S?
our 1 GPa expt
1200 C
liquidus of silicate
liquid-liquid solvus
liquidus of Fe-P-O melt
T
addition of water?
addition of Fe+2?
late Fe-P-O melt pockets in El Laco ash
1100 C
melt globules in El Laco ash
Lledo's 0.4 GPa expt
K-rich basalt
X(Fe2O3n•PO4)
Fe-P-O-S liquid


FeO + MnO + TiO2
+ CaO + P2O5
60
50
40
30
20
10
40
50
60
70
80
90
60
50
40
30
20
10
SiO2
Na2O + K2O + Al2O3 + MgO
Enlarged
Immiscible field
of tholeiitic rocks
(Philpotts, 1982)
FeO/Fe3O4
oxygen buffer
Immiscible field in the
fayalite-leucite-silica
system (Roedder 1951)
MoO/MoO2 oxygen buffer
at 1100°C
Enlarged Immiscible field
(Matthews et al., 1995, 1999)
(S2-/SO42- oxygen buffer
at 900-1000°C)
Potential Compositional trajectories
① Lascar Flow magma mixing trend
(enlarged immiscible field at high fO2)
② Antauta magma mixing trend
(quartz dissolution)
③ Possible trend at Marcona
(quartz dissolution)
④ Possible trend at Marcona
(enlarged immiscible field at high fO2)
Rio Grande (Aguirre, 1988)
Lascar (Matthews et al., 1995)
Antauta (Clark and Kontak, 2004)
Tertiary Andean suites (Dostal et al., 1977;
Maksaev, 1990; Kay et al., 1999)
Andean trend
(AFC + magma mixing)