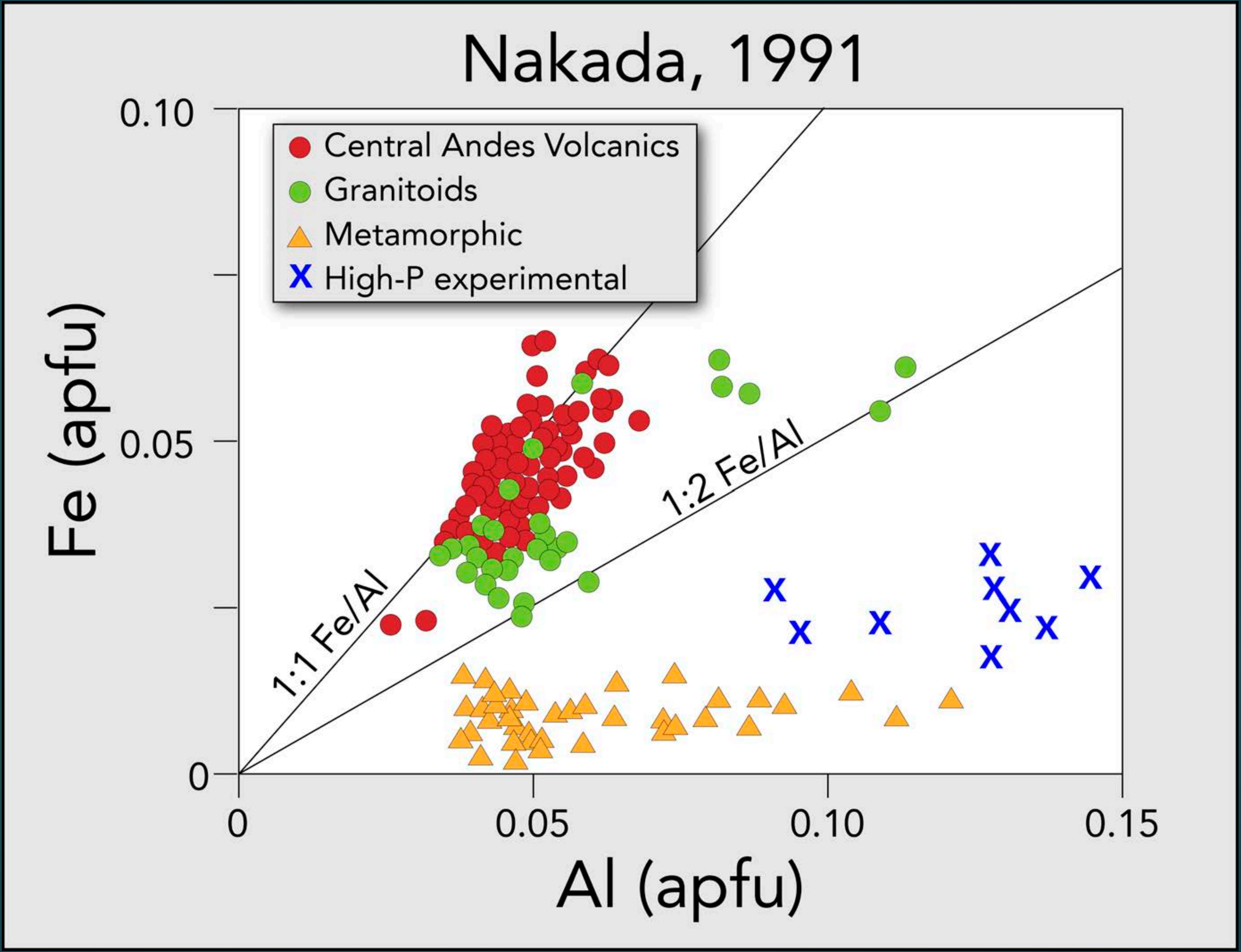
GSA Annual Meeting – 2018 Indianapolis

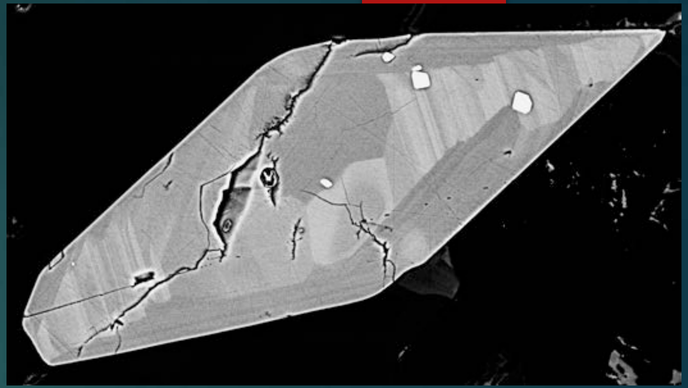
Compositional Variation of Fe, Al, & F in Titanite

Bart J. Kowallis, Eric H Christiansen, Michael J. Dorais, Tony Winkel, Porter Henze, Lauren Franzen, and Haley Mosher – Brigham Young U.



Nakada, 1991
Central Andes Volcanics
Granitoids
Metamorphic
High-P experimental
1:1 Fe/Al
1:2 Fe/Al
Fe (apfu)
Al (apfu)
0.10
0.05
0
0
0.05
0.10
0.15

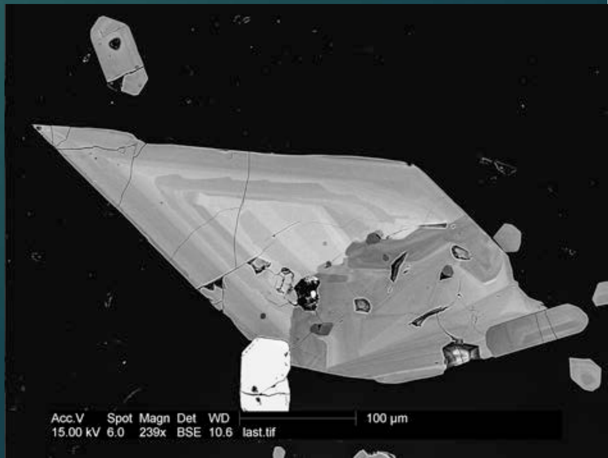
Conclusions – Fe/Al ratios



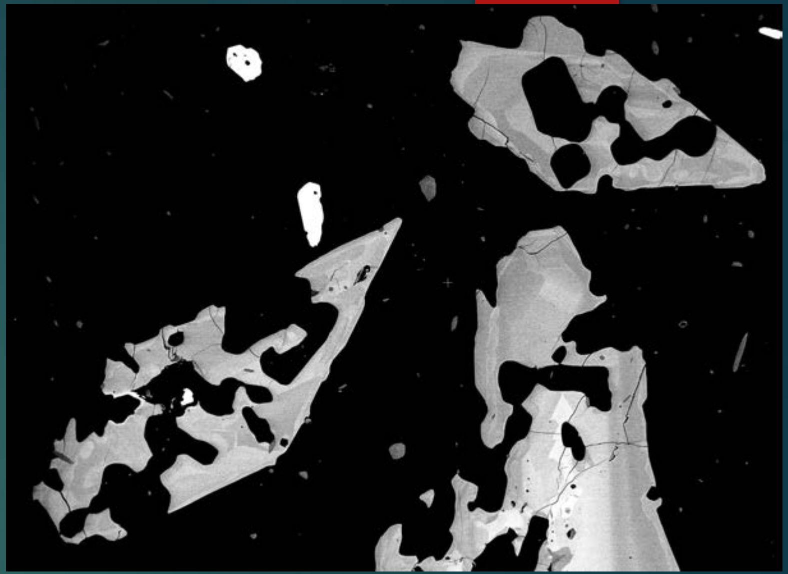
- The atomic ratio of Fe/Al in titanite from both volcanic and plutonic rocks is typically close to 1:1 and almost always >1:2.
- Volcanic titanite compositions typically cluster more tightly in terms Fe, Al, and F than do titanite compositions from any other environment.
- Fe/Al ratios in titanite from peralkaline silica-undersaturated volcanic and plutonic rocks are typically >1:1.
- Titanite from metamorphic, hydrothermal, and pegmatitic environments scatter widely in Fe/Al.
- Titanite from eclogite tends to have the lowest Fe/Al ratios, typically <1:8.

Conclusions – Charge Balancing

- Charge balance in metamorphic, hydrothermal, and pegmatitic titanite due to Fe^{+3} and Al^{+3} substitution into the Ti^{+4} site is largely accomplished by the coupled substitution of F^{-} for O^{-2}.
- However, in volcanic and plutonic titanite the charge imbalance due to Fe^{+3} and Al^{+3} substitution appears to be mainly coupled with REE^{+3} and Y^{+3} substitution into the Ca^{+2} site with a more minor contribution from F^{-} substitution.
- In Si-undersaturated rocks, substitution into the Ti^{+4} site by Nb^{+5} coupled with Fe^{+3} is a major factor in charge balancing.



Data Base



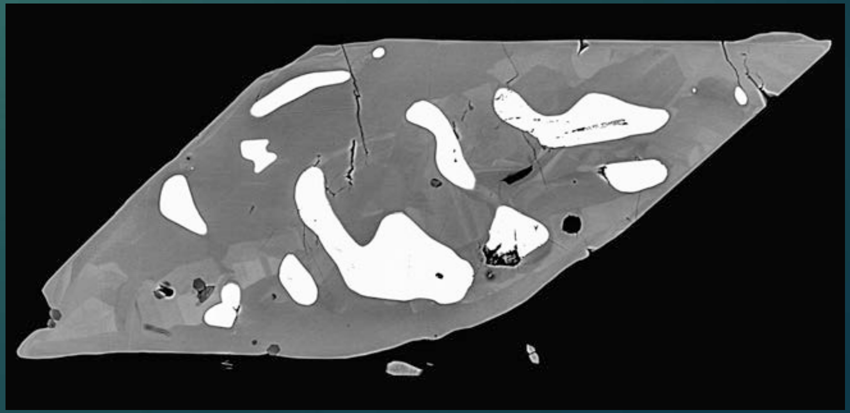
- 8,100+ titanite analyses
  - Most include Fe and Al
  - A large number also include F

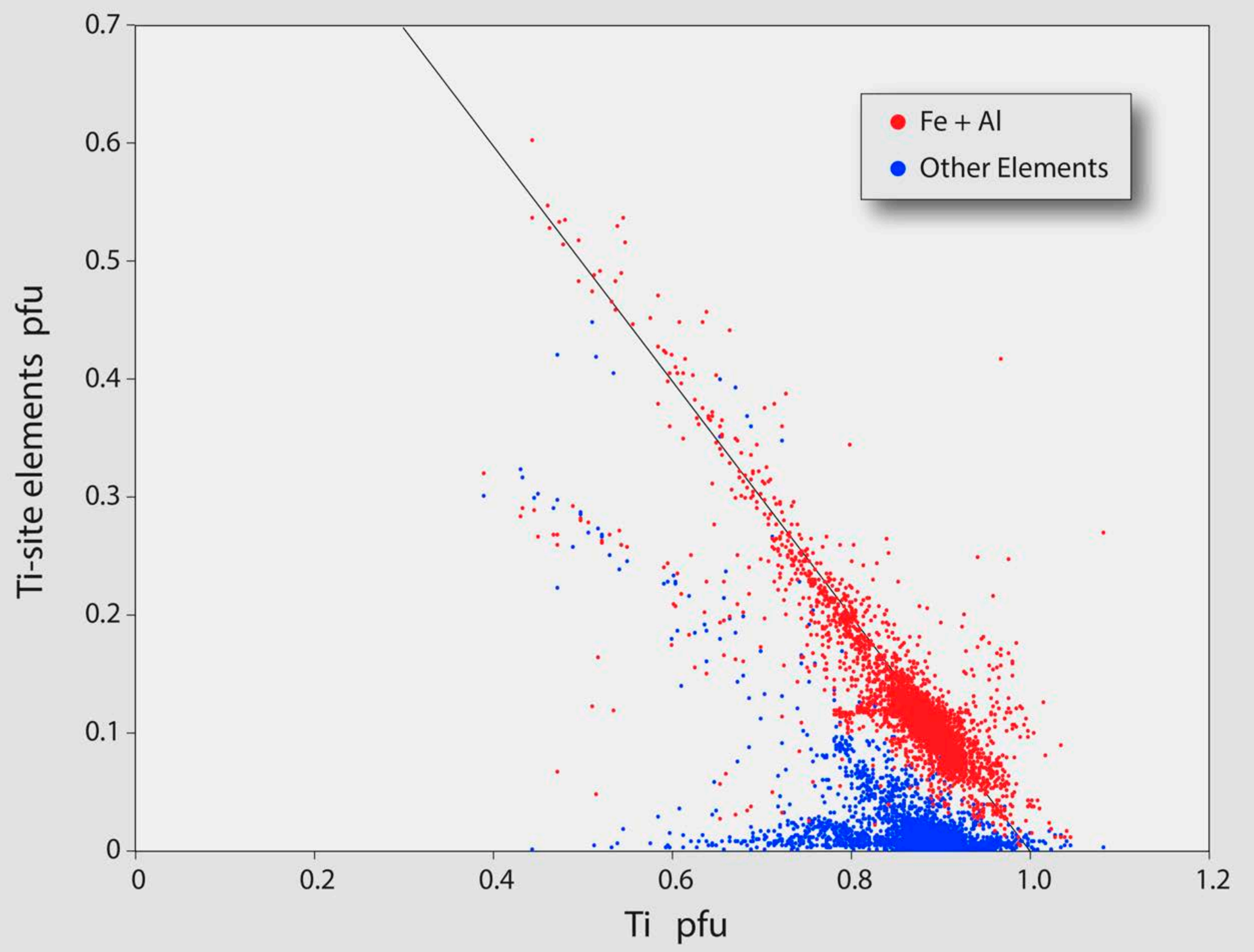
- ~4,800 analyses are from Brigham Young Univ. and Univ. of Utah microprobe labs

- ~3,300 analyses from literature

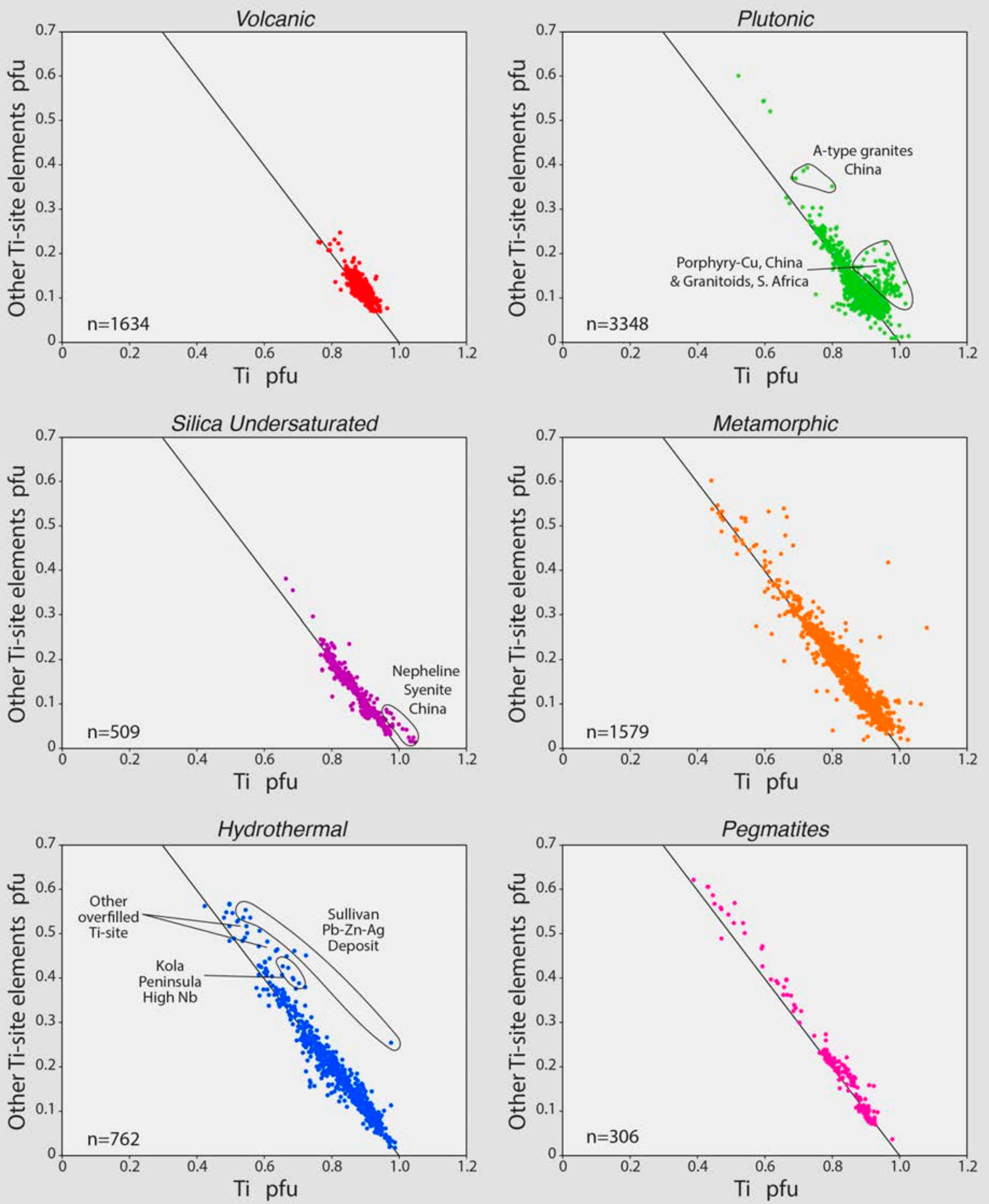
Element Substitutions

- Basic Formula = $CaTi(SiO_4)(O,F,OH)$
- Ti^{4+}-site elements = Al^{3+}, Fe^{3+}, Nb^{5+}, Ta^{5+}, V^{5+}, Zr^{4+}, etc.
- Ca^{2+}-site elements = REE^{3+}, Y^{3+}, Mn^{2+}, etc.

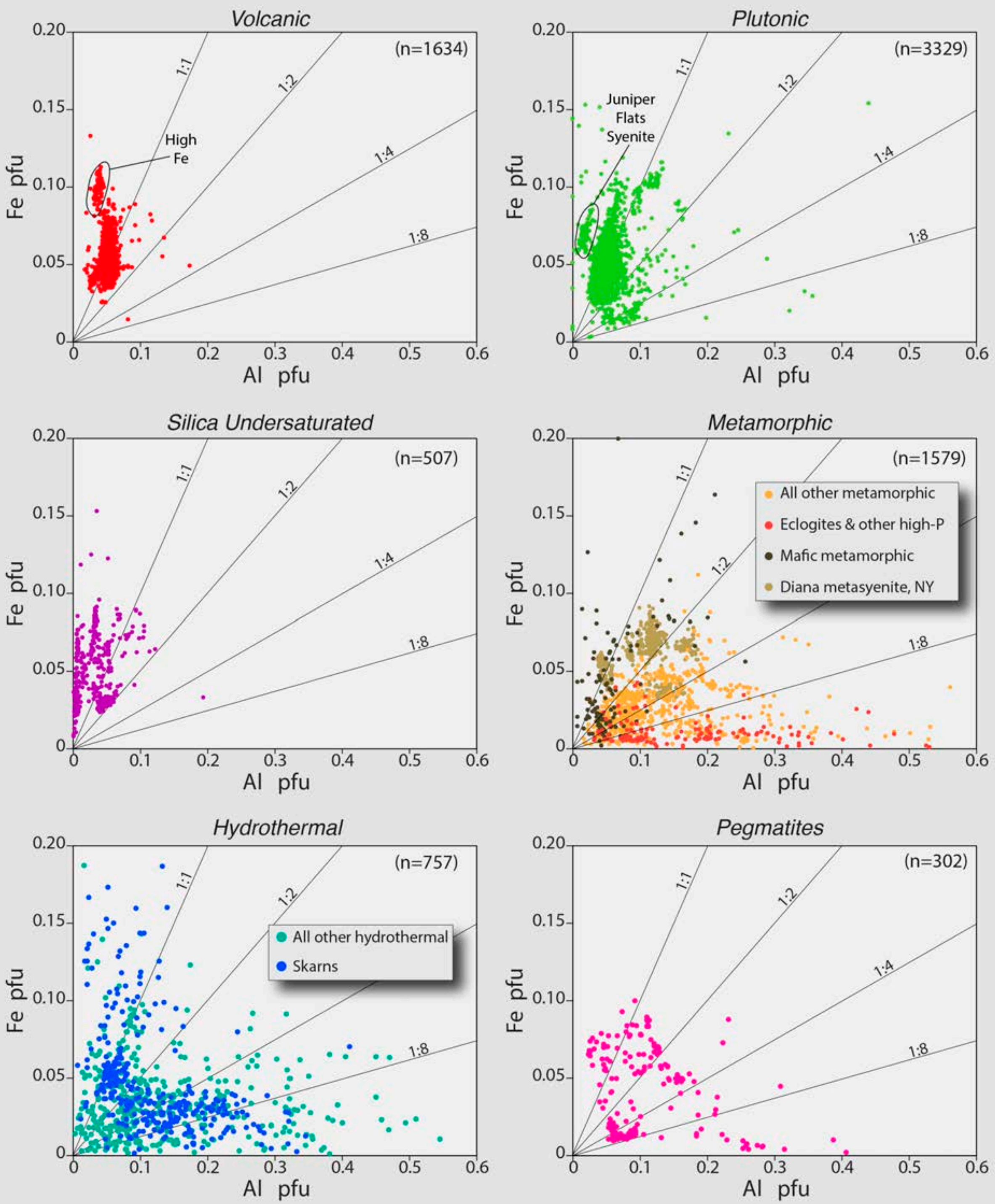




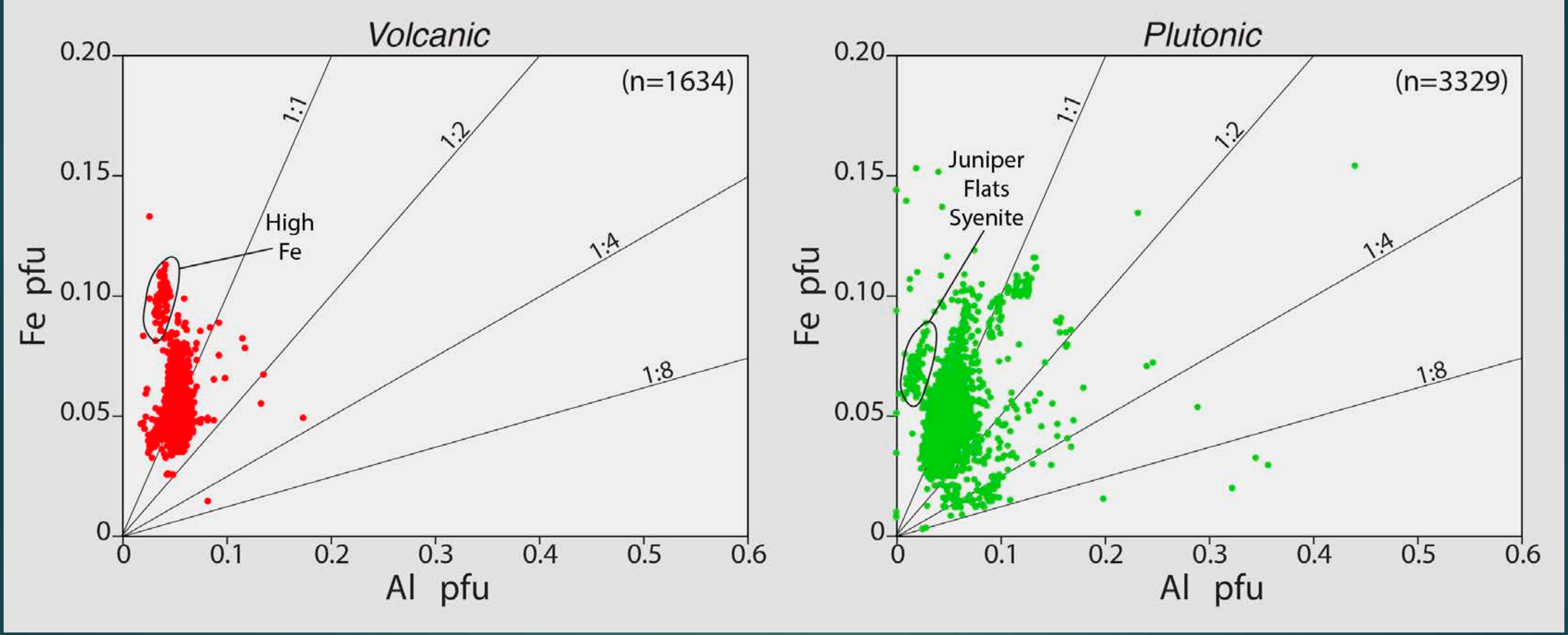
Fe + Al
Other Elements
Ti-site elements pfu
Ti pfu
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1.0
1.2



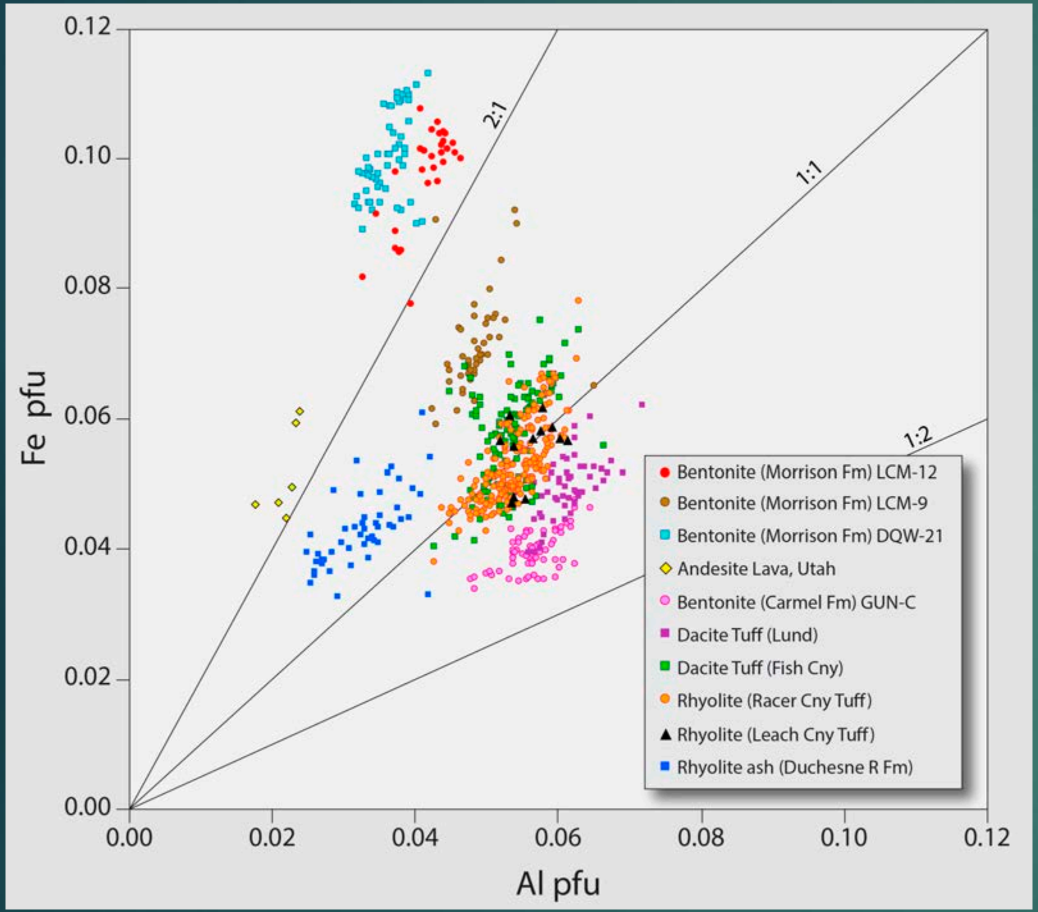
Volcanic
n=1634
Plutonic
A-type granites
China
Porphyry-Cu, China
& Granitoids, S. Africa
n=3348
Silica Undersaturated
Nepheline
Syenite
China
n=509
Metamorphic
n=1579
Hydrothermal
Other
overfilled
Ti-site
Sullivan
Pb-Zn-Ag
Deposit
Kola
Peninsula
High Nb
n=762
Pegmatites
n=306
Other Ti-site elements pfu
Ti pfu


Volcanic
(n=1634)
High Fe
Plutonic
(n=3329)
Juniper Flats Syenite
Silica Undersaturated
(n=507)
Metamorphic
(n=1579)
All other metamorphic
Eclogites & other high-P
Mafic metamorphic
Diana metasyenite, NY
Hydrothermal
(n=757)
All other hydrothermal
Skarns
Pegmatites
(n=302)
1:1
1:2
1:4
1:8
Fe pfu
Al pfu

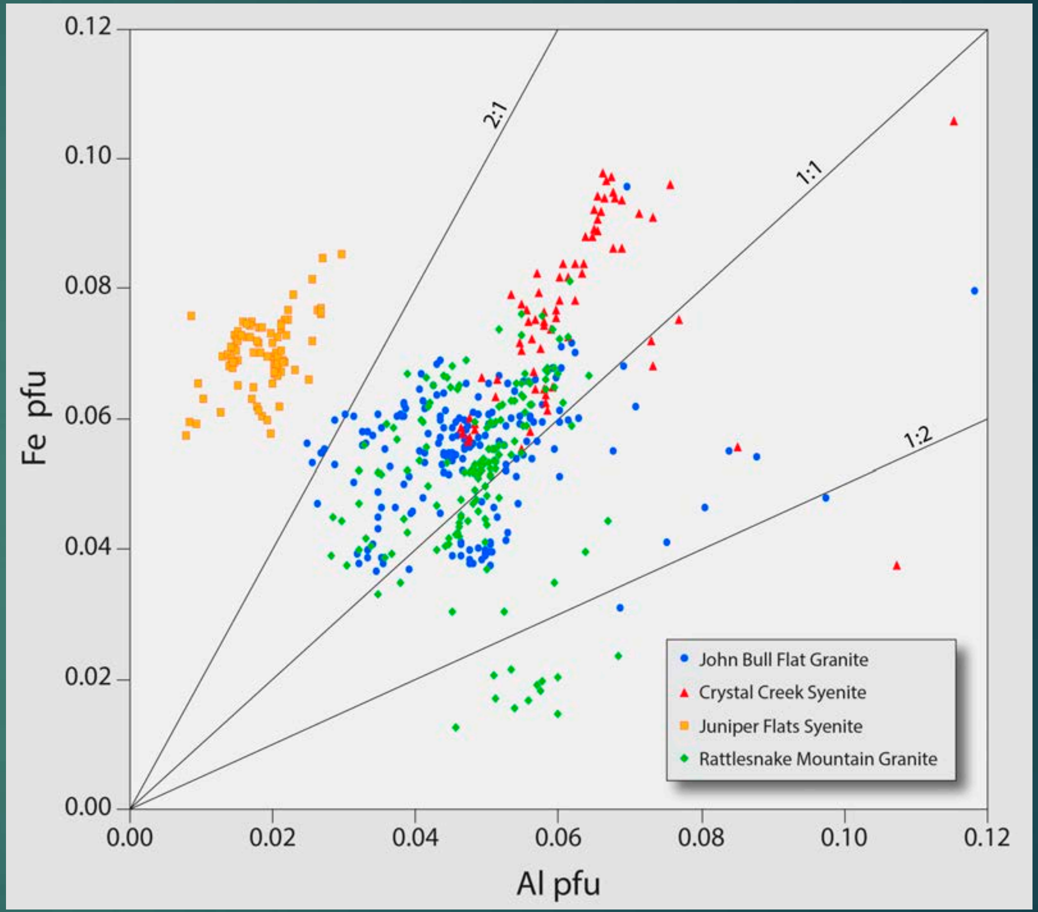
Fe versus Al in Titanite



Volcanic Samples

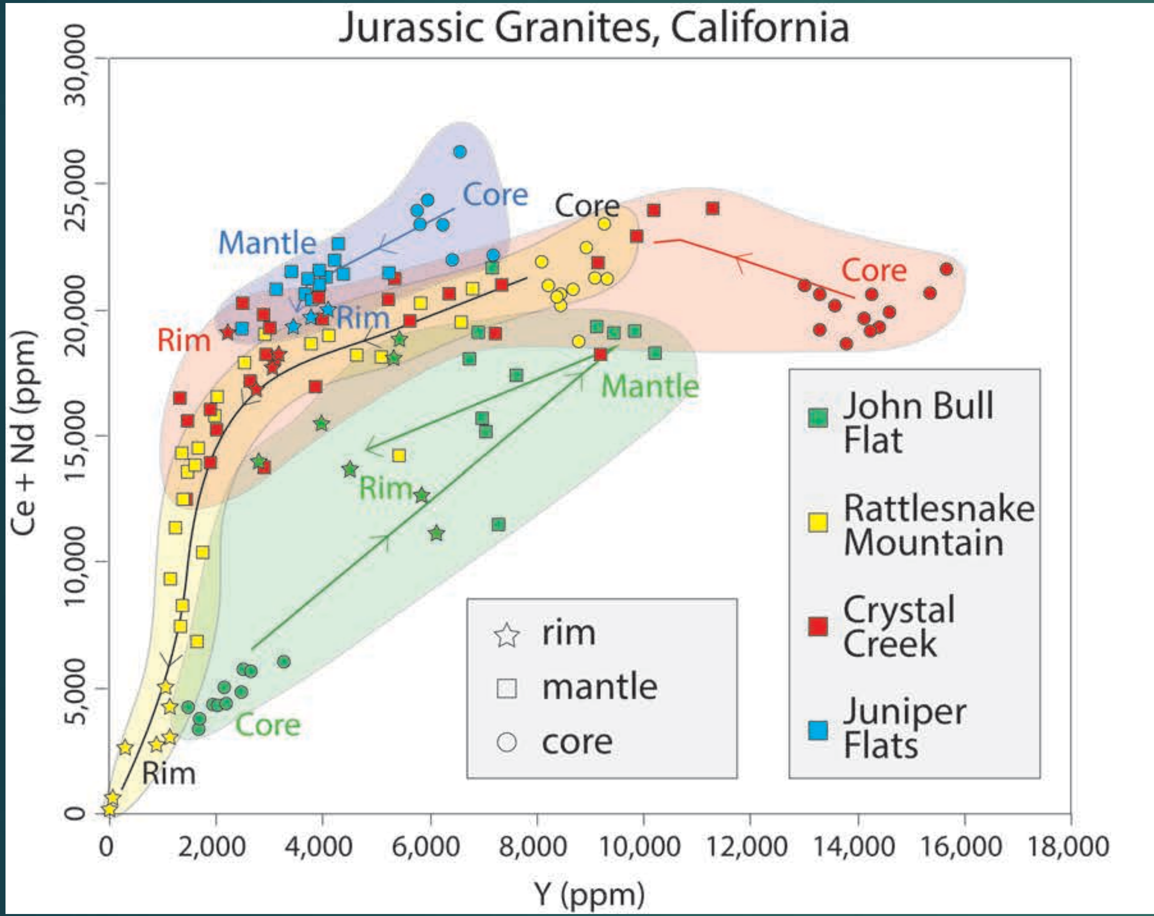


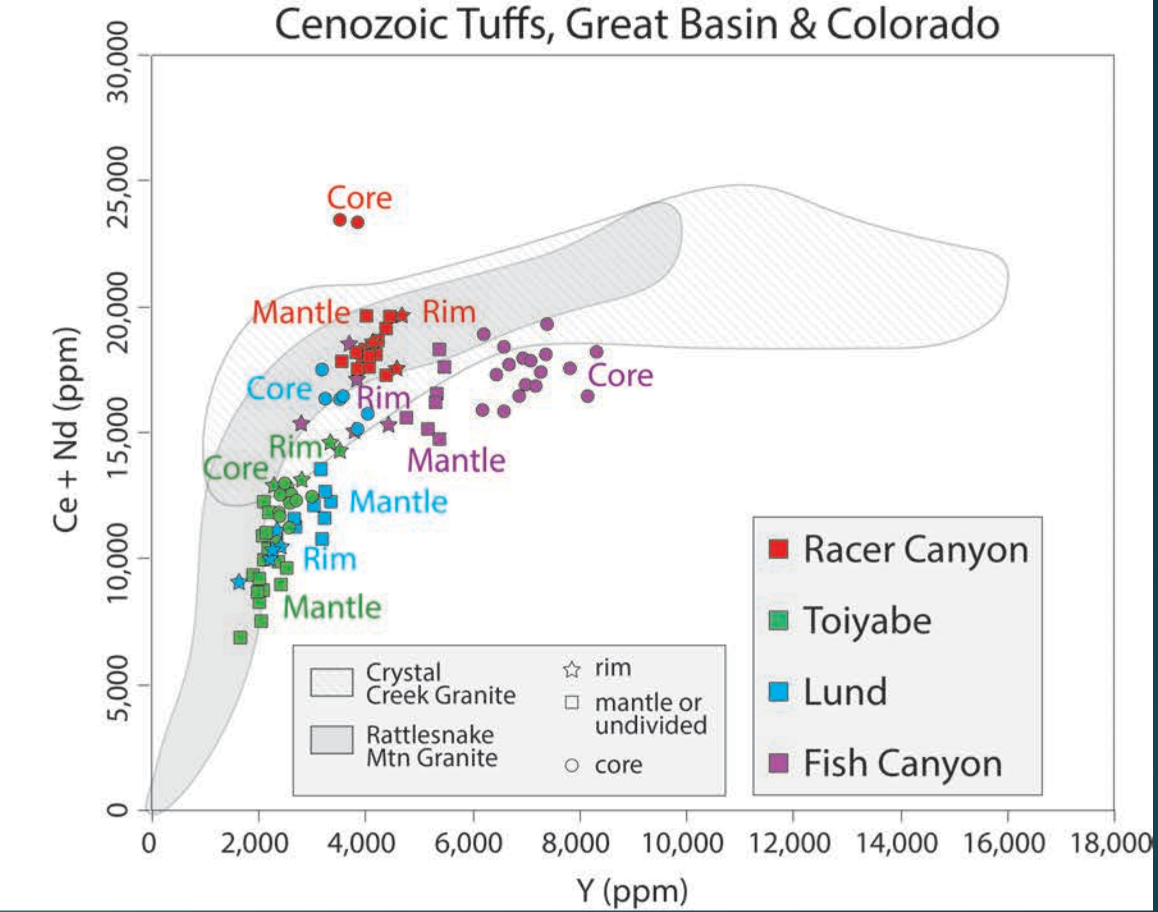
Plutonic Samples

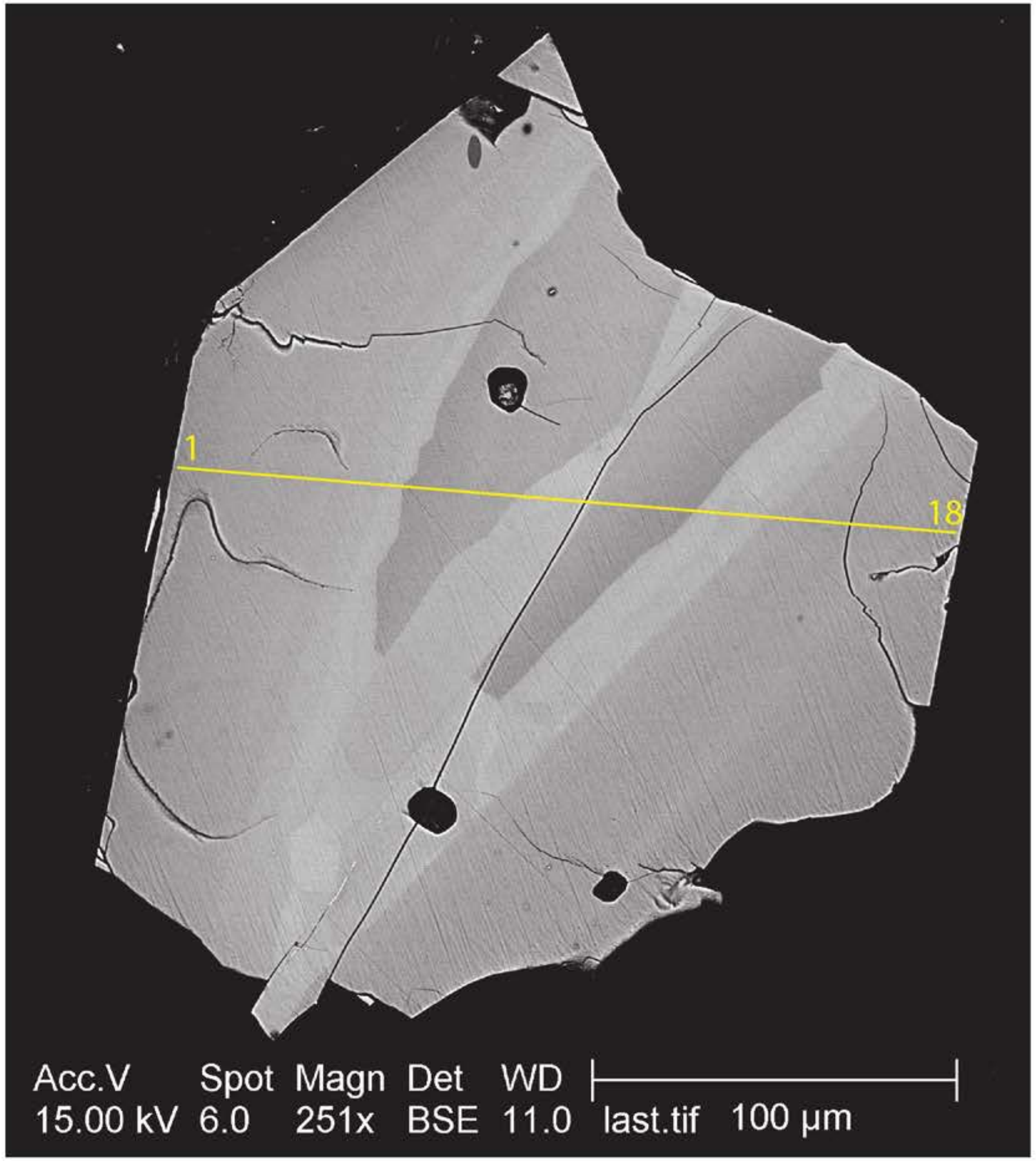


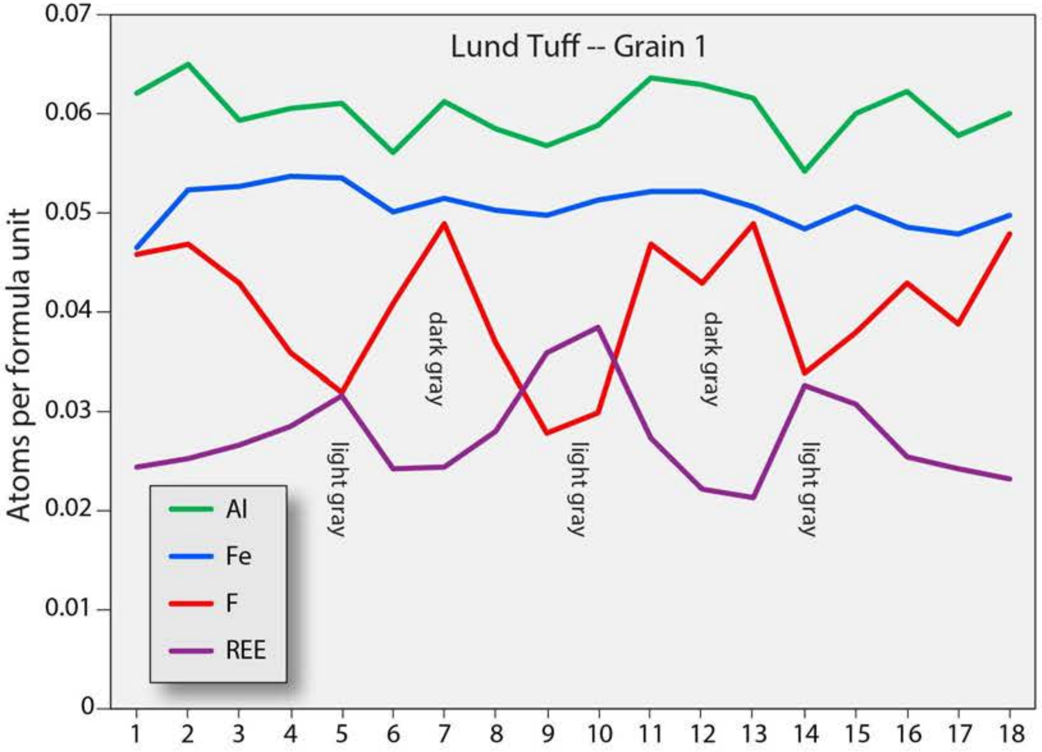
Plutonic Grains

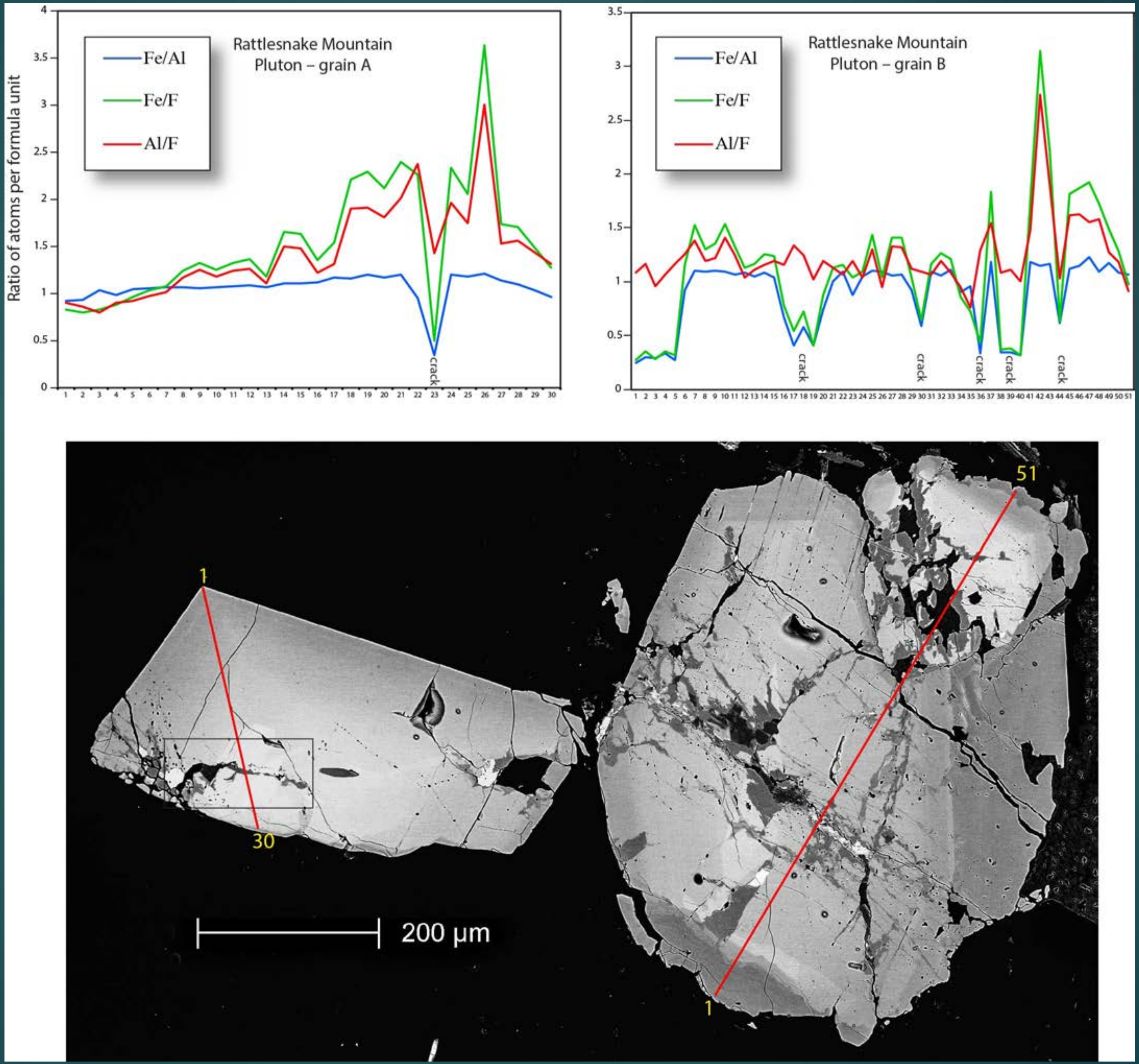
Volcanic Grains

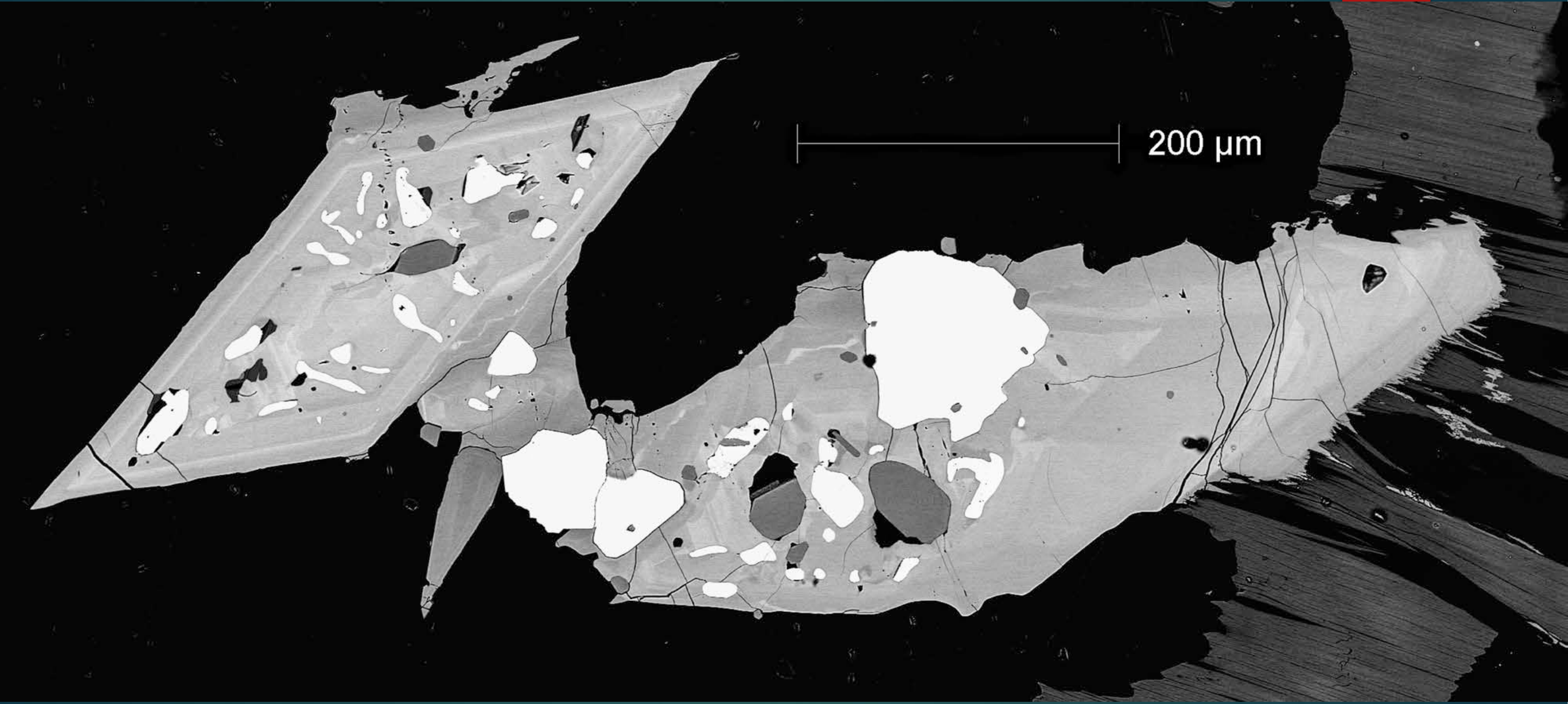





1
18
Acc.V Spot Magn Det WD
15.00 kV 6.0 251x BSE 11.0 last.tif 100 µm

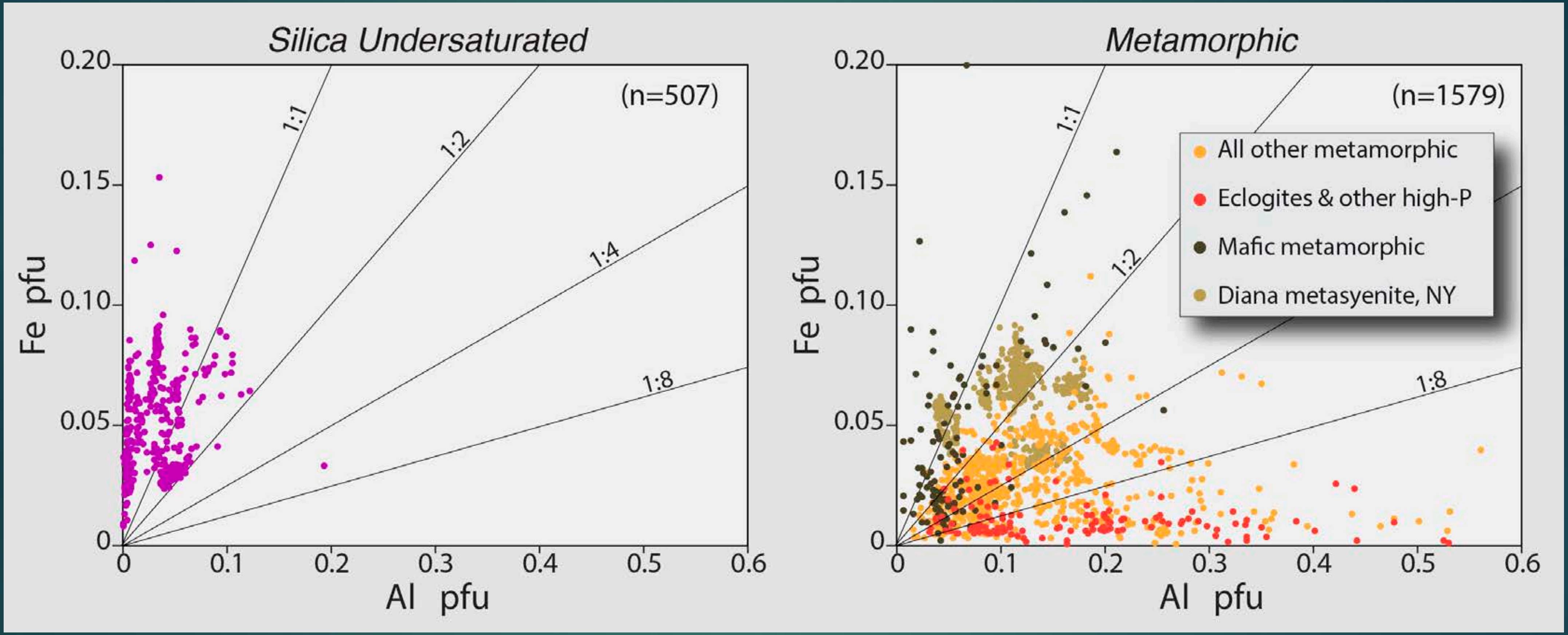

Lund Tuff -- Grain 1
Atoms per formula unit
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
dark gray
dark gray
light gray
light gray
light gray
Al
Fe
F
REE

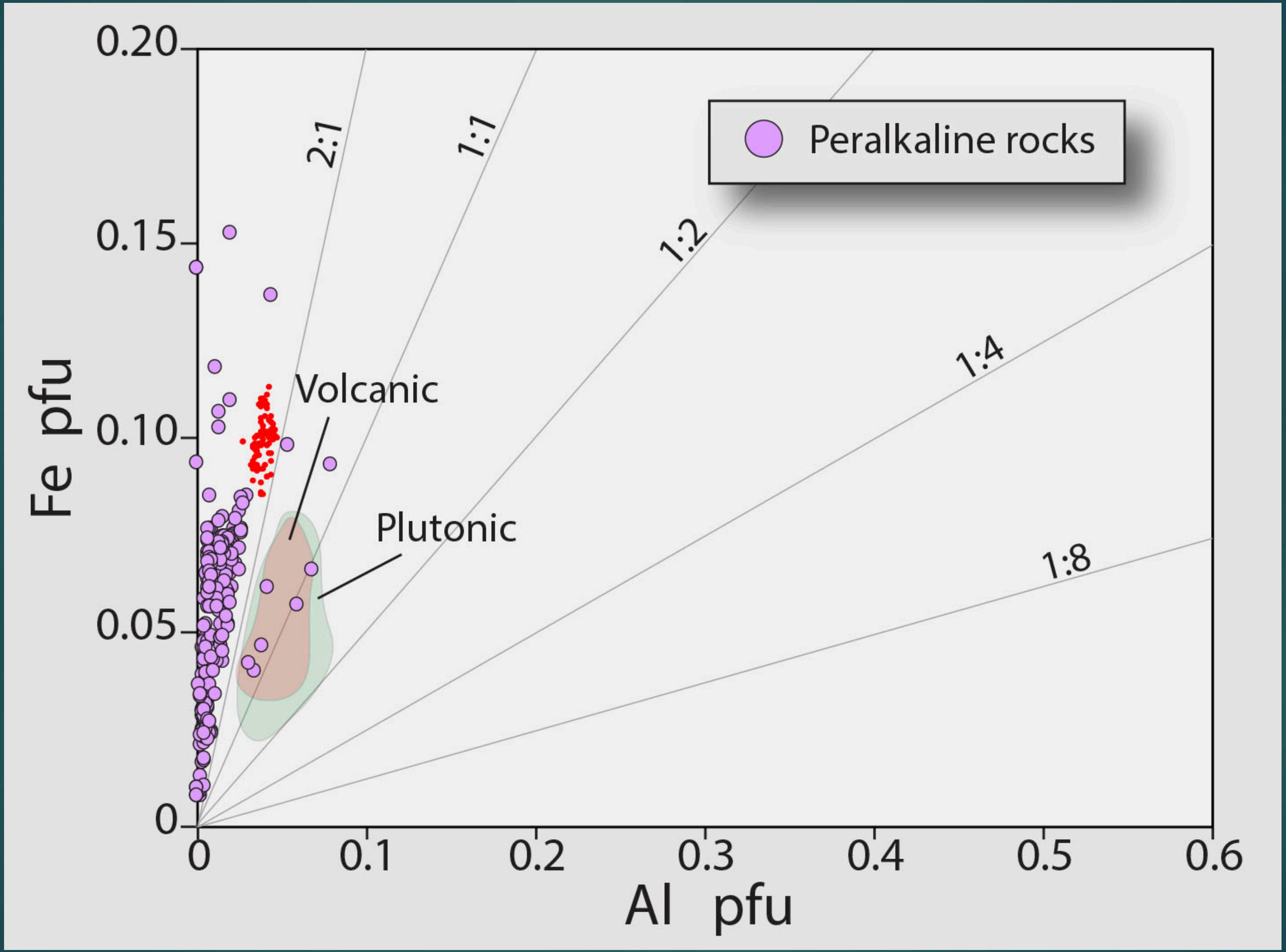

Rattlesnake Mountain Pluton – grain A
Fe/Al
Fe/F
Al/F
Ratio of atoms per formula unit
crack
Rattlesnake Mountain Pluton – grain B
Fe/Al
Fe/F
Al/F
crack
crack
crack
crack
crack
1
30
1
51
200 µm

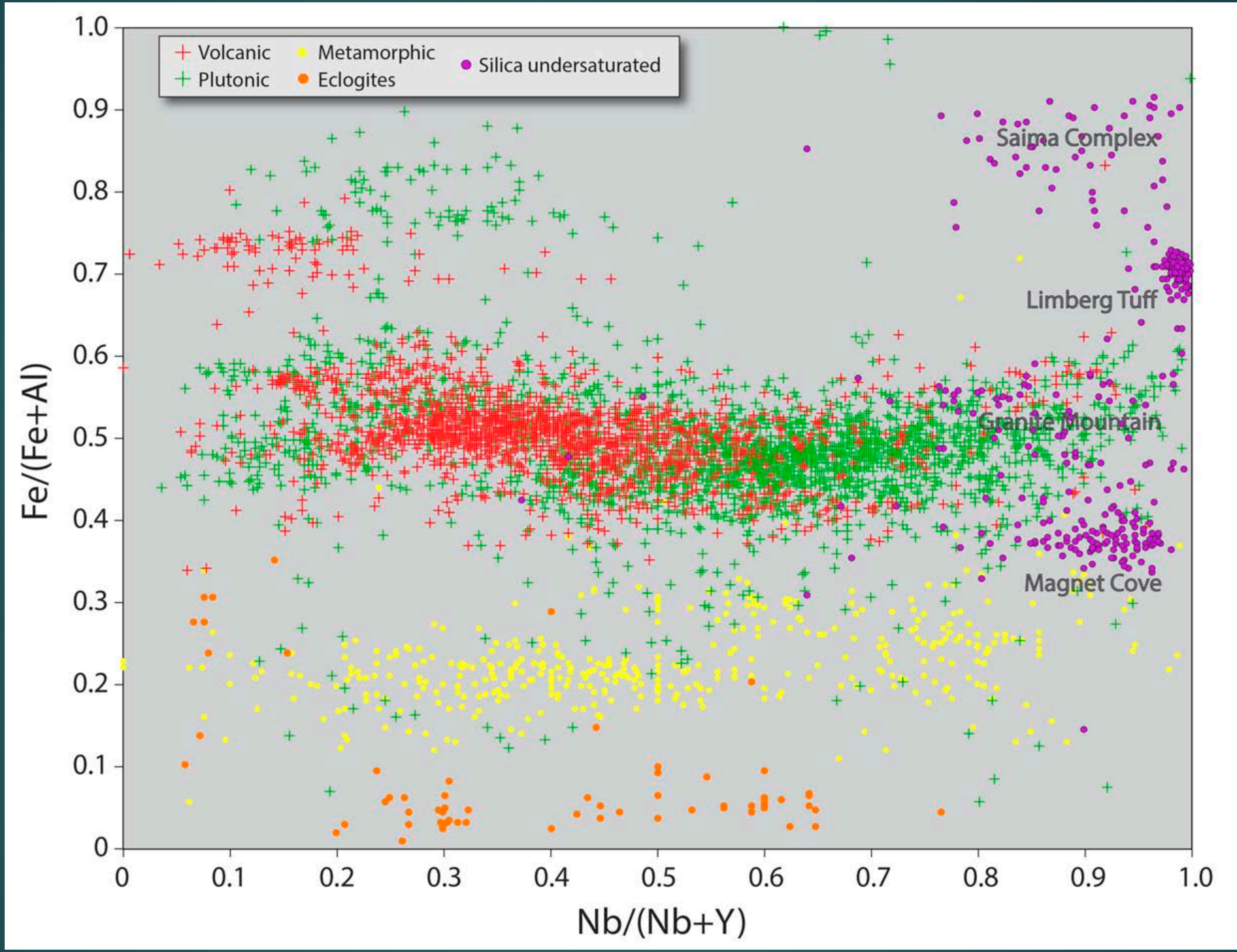

200 µm


Acc.V Spot Magn Det WD 100 µm
15.00 kV 6.0 239x BSE 10.6 last.tif

Fe versus Al in Titanite

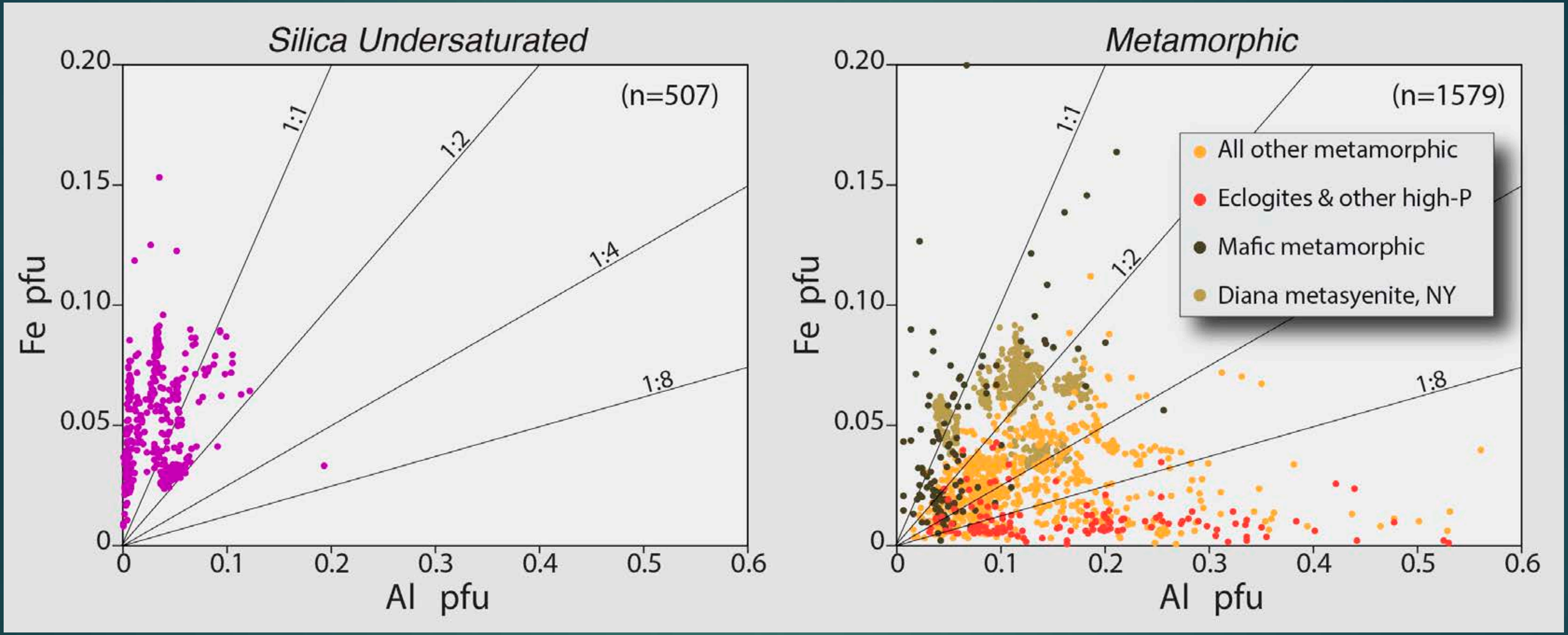


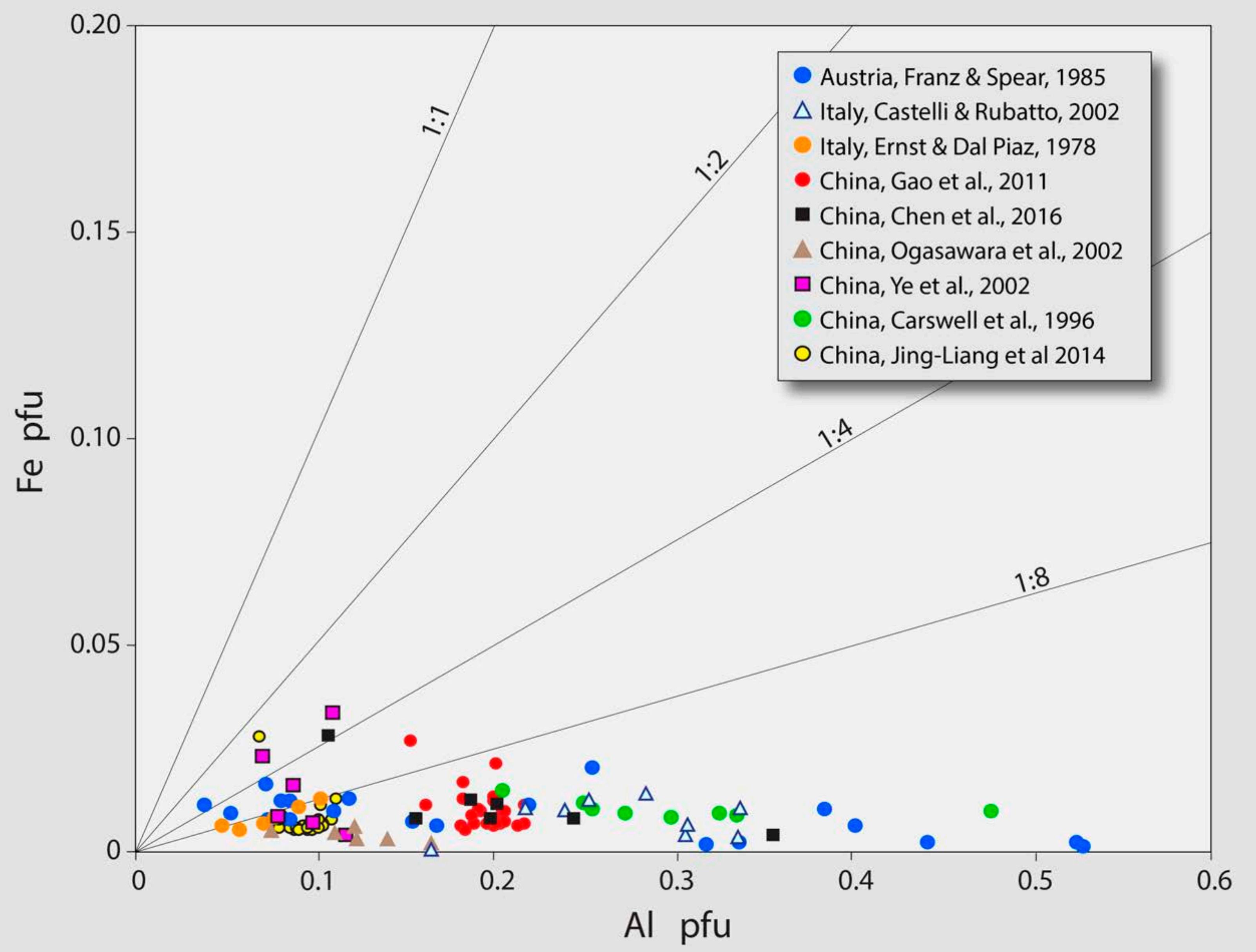

0.20
0.15
0.10
0.05
0
Fe pfu
0
0.1
0.2
0.3
0.4
0.5
0.6
Al pfu
2:1
1:1
1:2
1:4
1:8
Peralkaline rocks
Volcanic
Plutonic

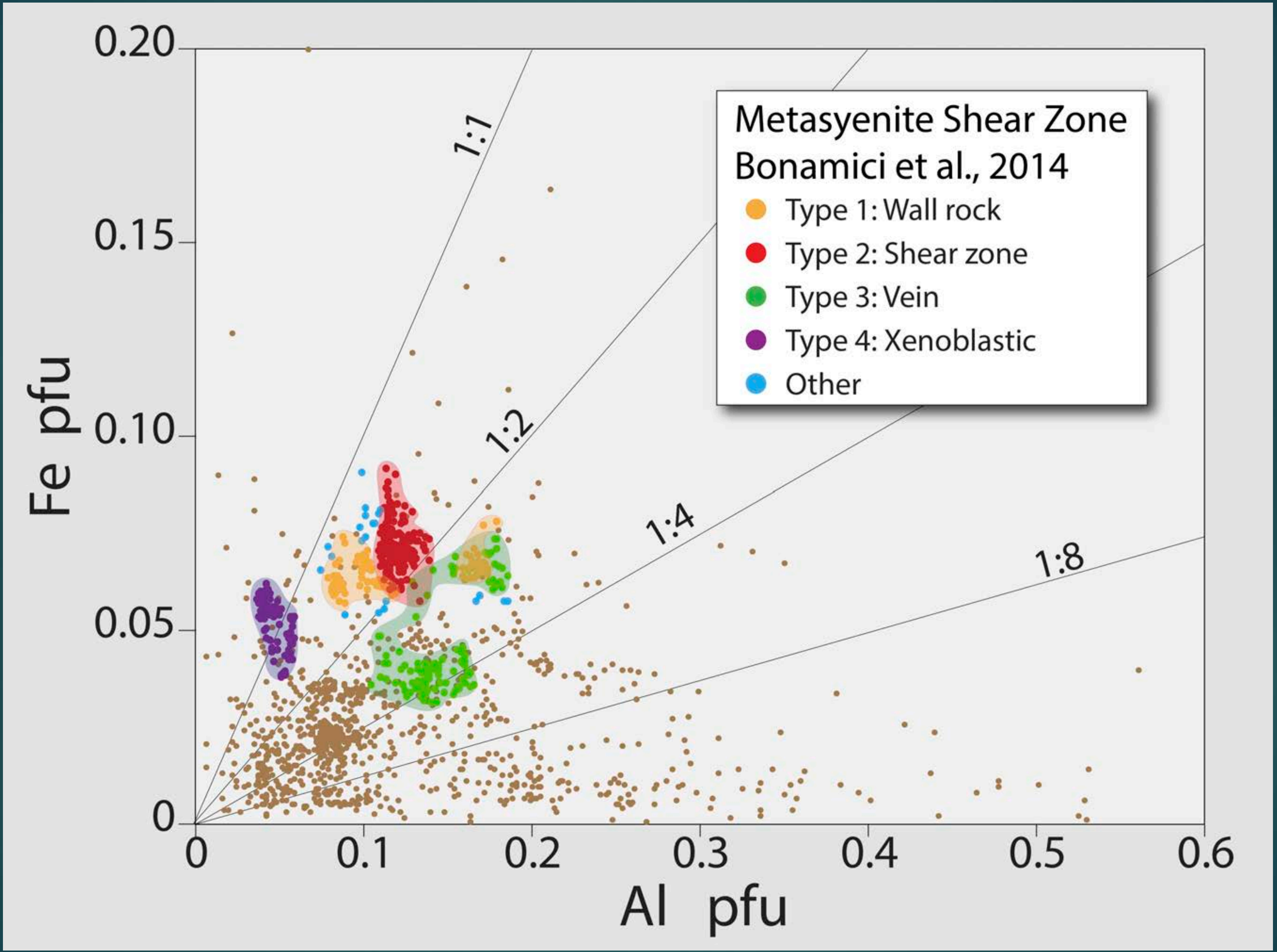


Saima alkaline complex, China (Wu et al., 2016), all other data from BYU.

Fe versus Al in Titanite

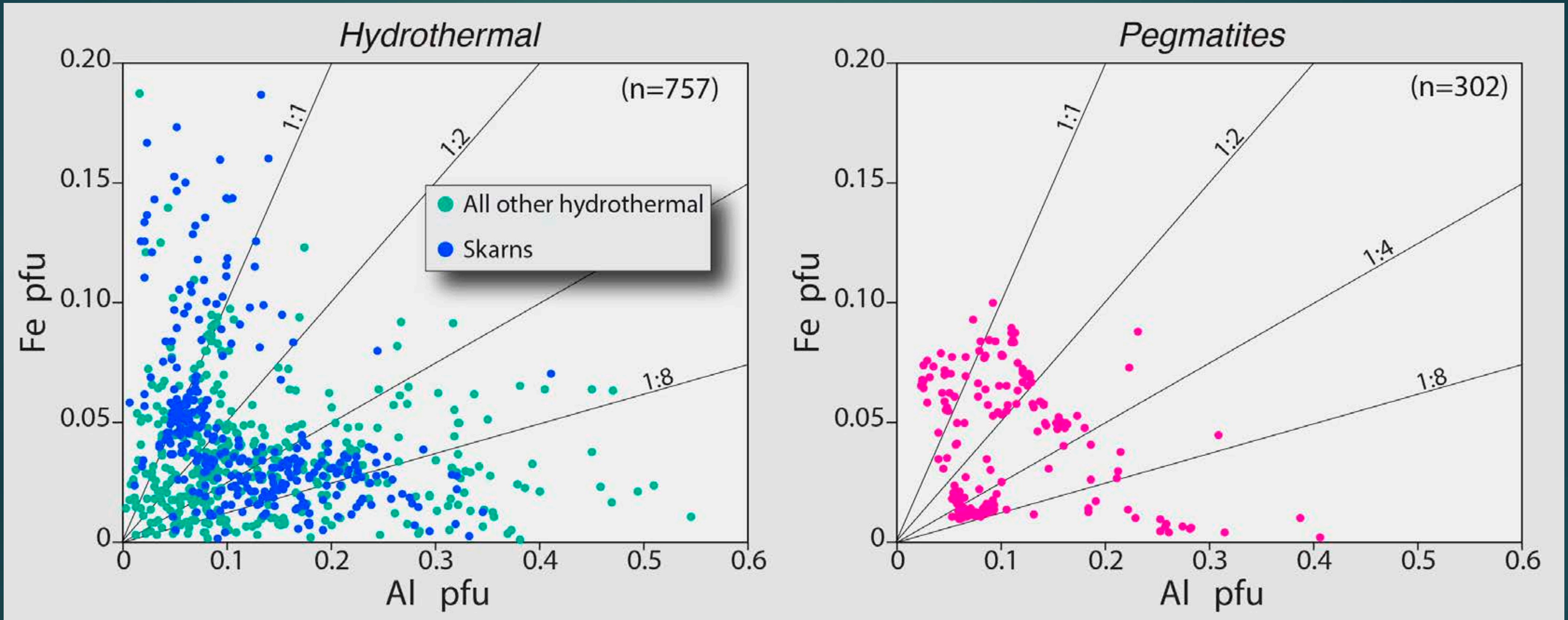


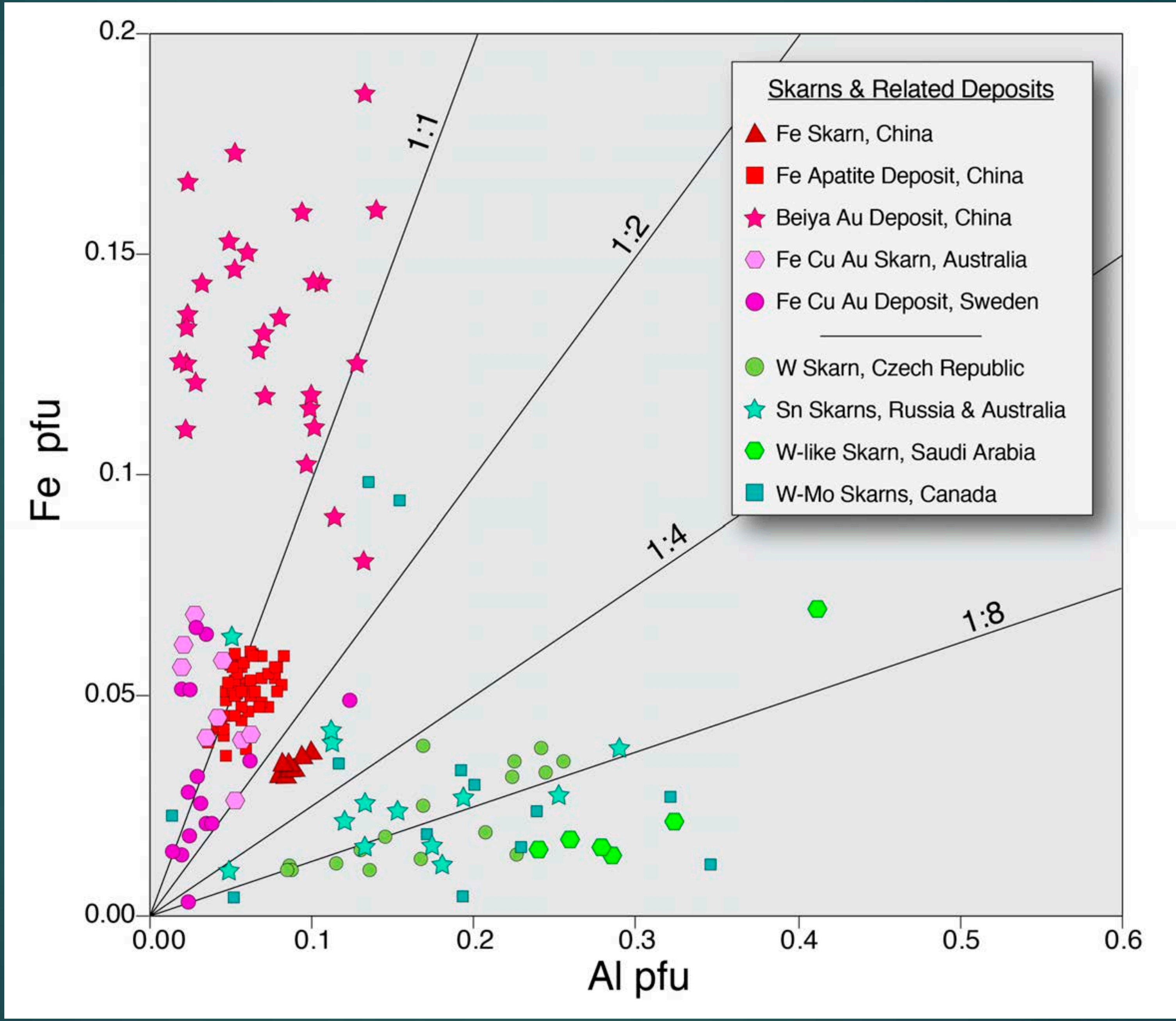

Austria, Franz & Spear, 1985
Italy, Castelli & Rubatto, 2002
Italy, Ernst & Dal Piaz, 1978
China, Gao et al., 2011
China, Chen et al., 2016
China, Ogasawara et al., 2002
China, Ye et al., 2002
China, Carswell et al., 1996
China, Jing-Liang et al 2014
1:1
1:2
1:4
1:8
Fe pfu
Al pfu
0.20
0.15
0.10
0.05
0
0.1
0.2
0.3
0.4
0.5
0.6



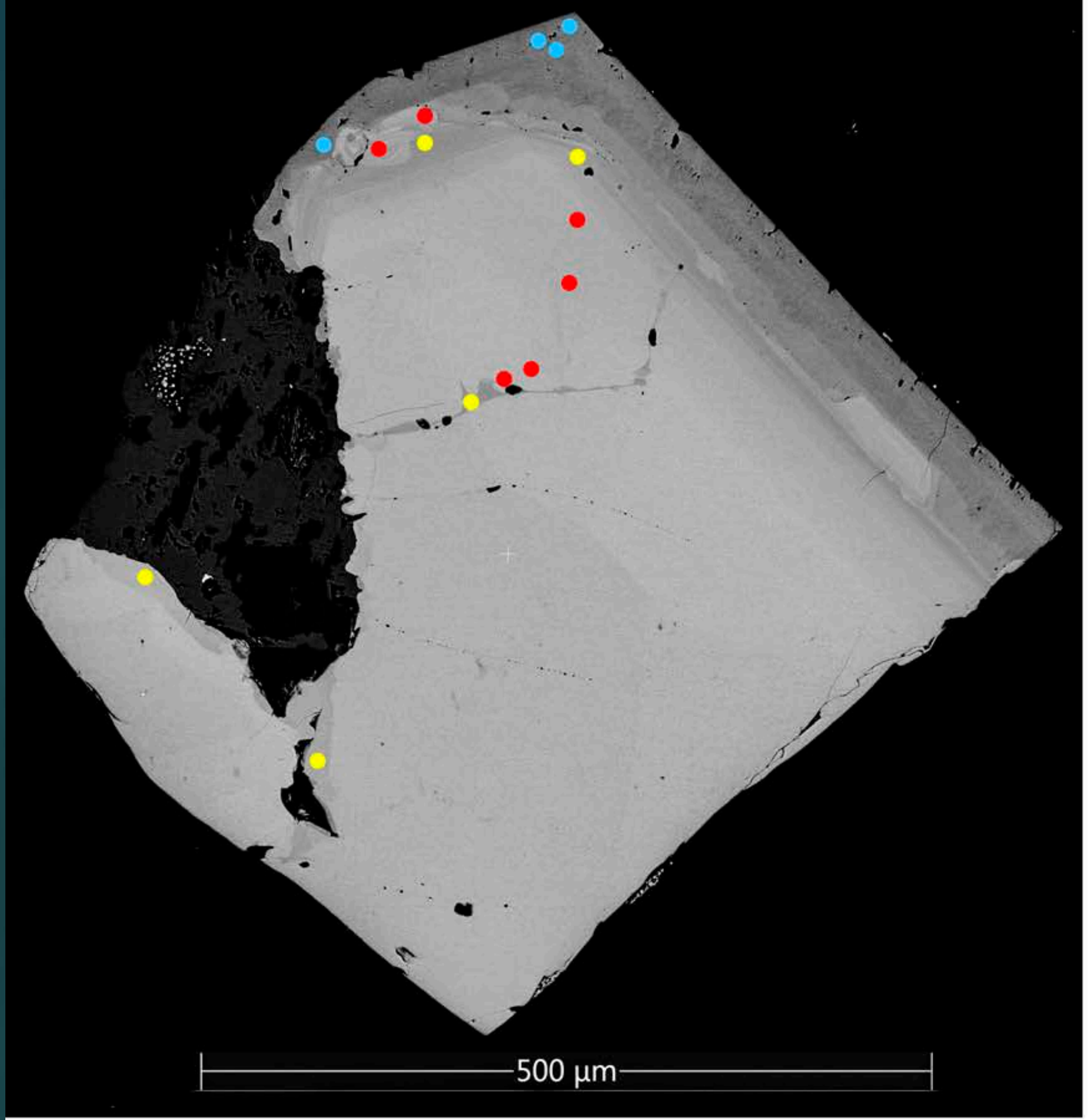
Metasyenite Shear Zone
Bonamici et al., 2014
Type 1: Wall rock
Type 2: Shear zone
Type 3: Vein
Type 4: Xenoblastic
Other
1:1
1:2
1:4
1:8
Fe pfu
Al pfu
0.20
0.15
0.10
0.05
0
0.1
0.2
0.3
0.4
0.5
0.6

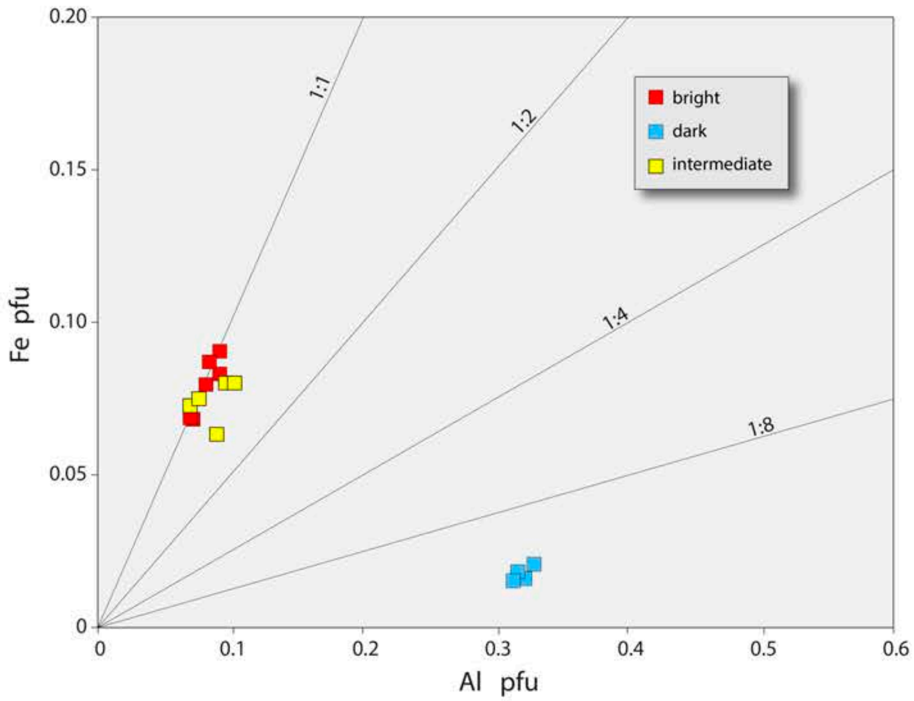
Fe versus Al in Titanite

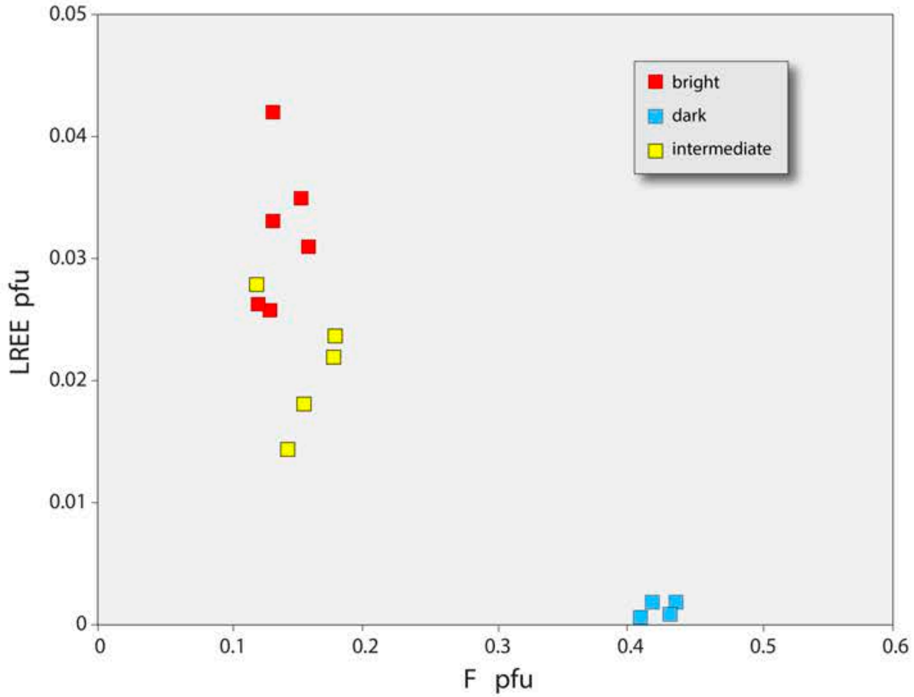


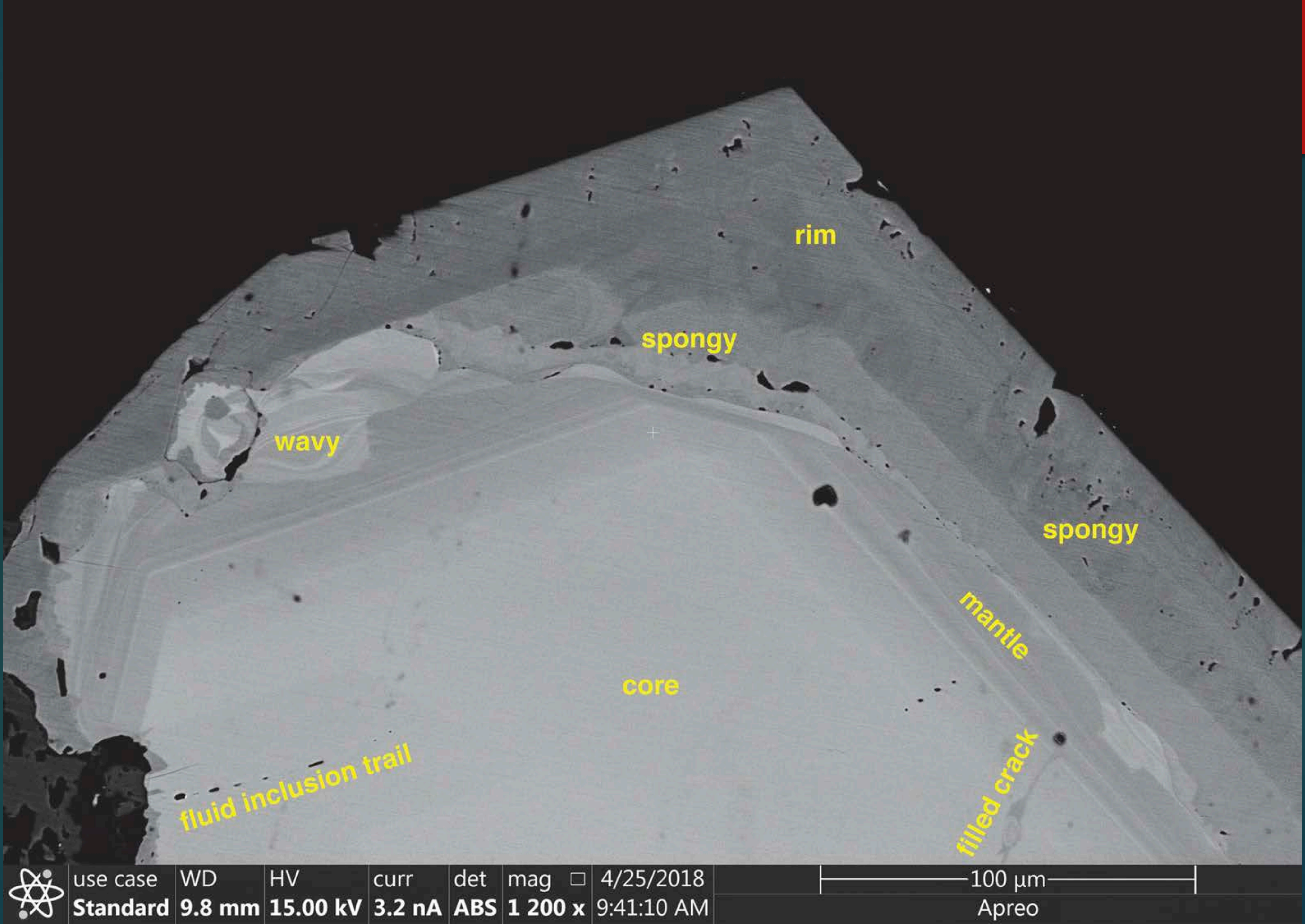


Skarns & Related Deposits
Fe Skarn, China
Fe Apatite Deposit, China
Beiya Au Deposit, China
Fe Cu Au Skarn, Australia
Fe Cu Au Deposit, Sweden
W Skarn, Czech Republic
Sn Skarns, Russia & Australia
W-like Skarn, Saudi Arabia
W-Mo Skarns, Canada
1:1
1:2
1:4
1:8
Fe pfu
Al pfu
0.2
0.15
0.1
0.05
0.00
0.00
0.1
0.2
0.3
0.4
0.5
0.6

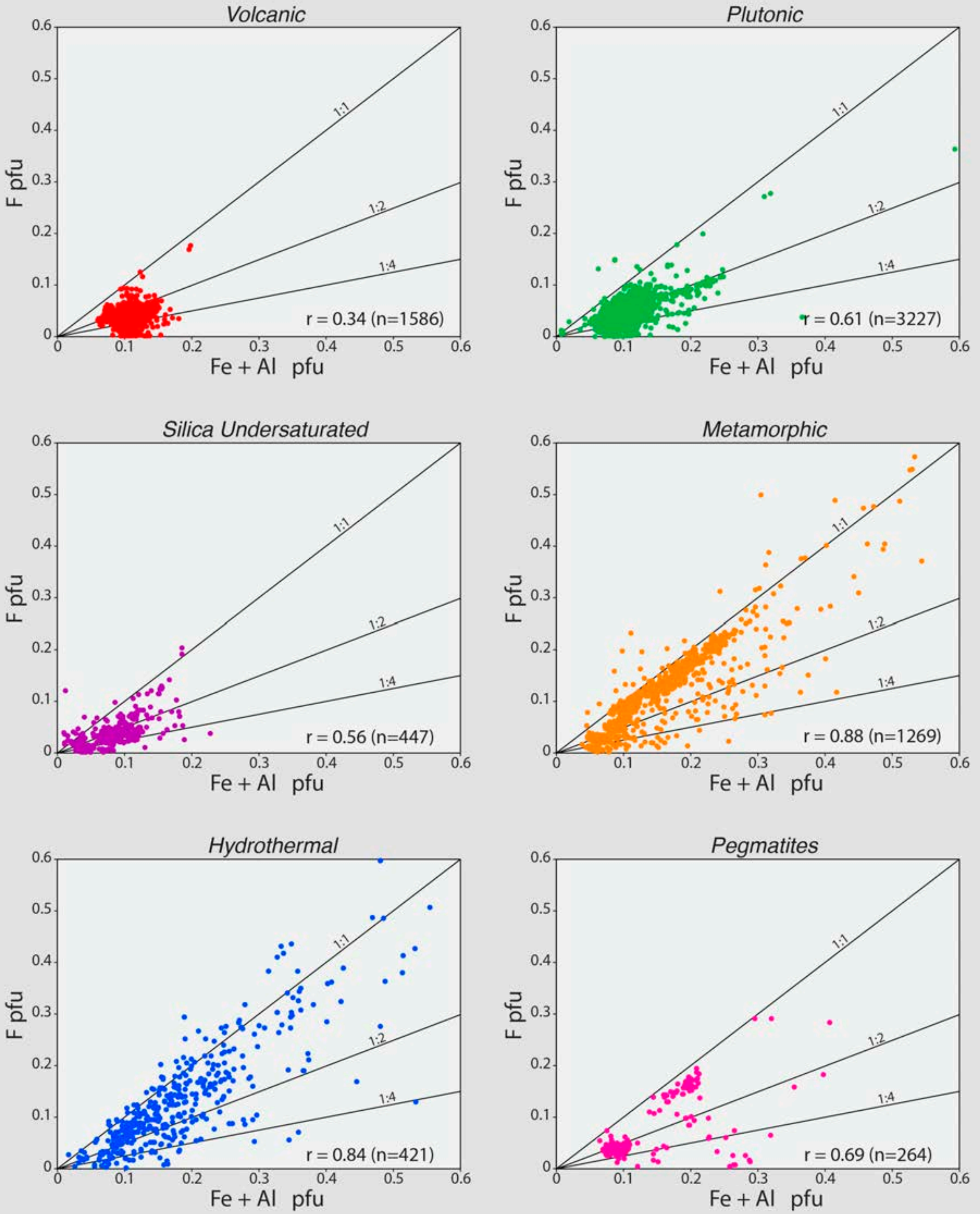

500 µm


0.20
0.15
0.10
0.05
0
Fe pfu
0
0.1
0.2
0.3
0.4
0.5
0.6
Al pfu
1:1
1:2
1:4
1:8
bright
dark
intermediate

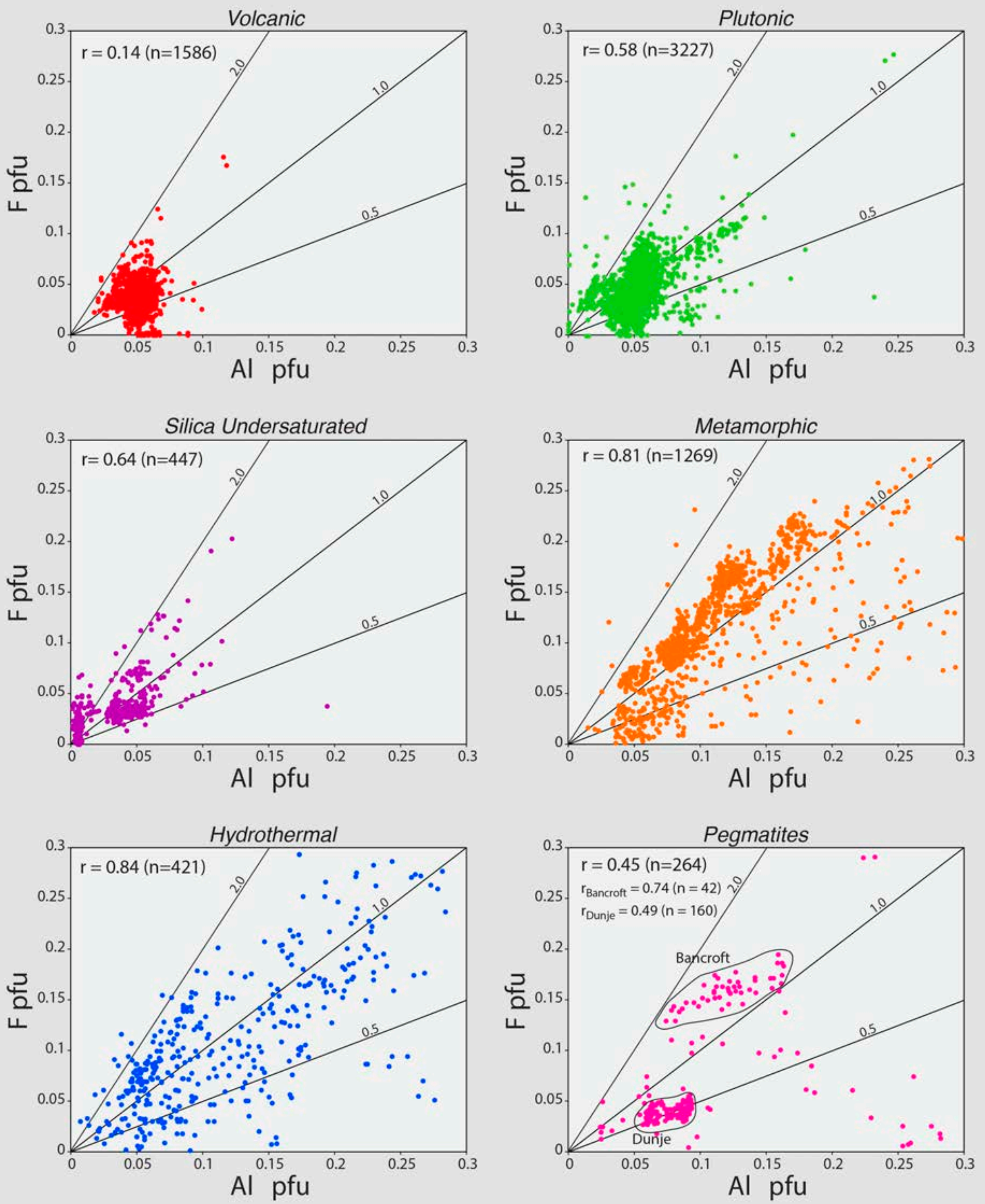

0.05
0.04
0.03
0.02
0.01
0
LREE pfu
0
0.1
0.2
0.3
0.4
0.5
0.6
F pfu
bright
dark
intermediate


rim
spongy
wavy
spongy
mantle
core
fluid inclusion trail
filled crack
use case
Standard
WD
9.8 mm
HV
15.00 kV
curr
3.2 nA
det
ABS
mag
1 200 x
4/25/2018
9:41:10 AM
100 µm
Apreo

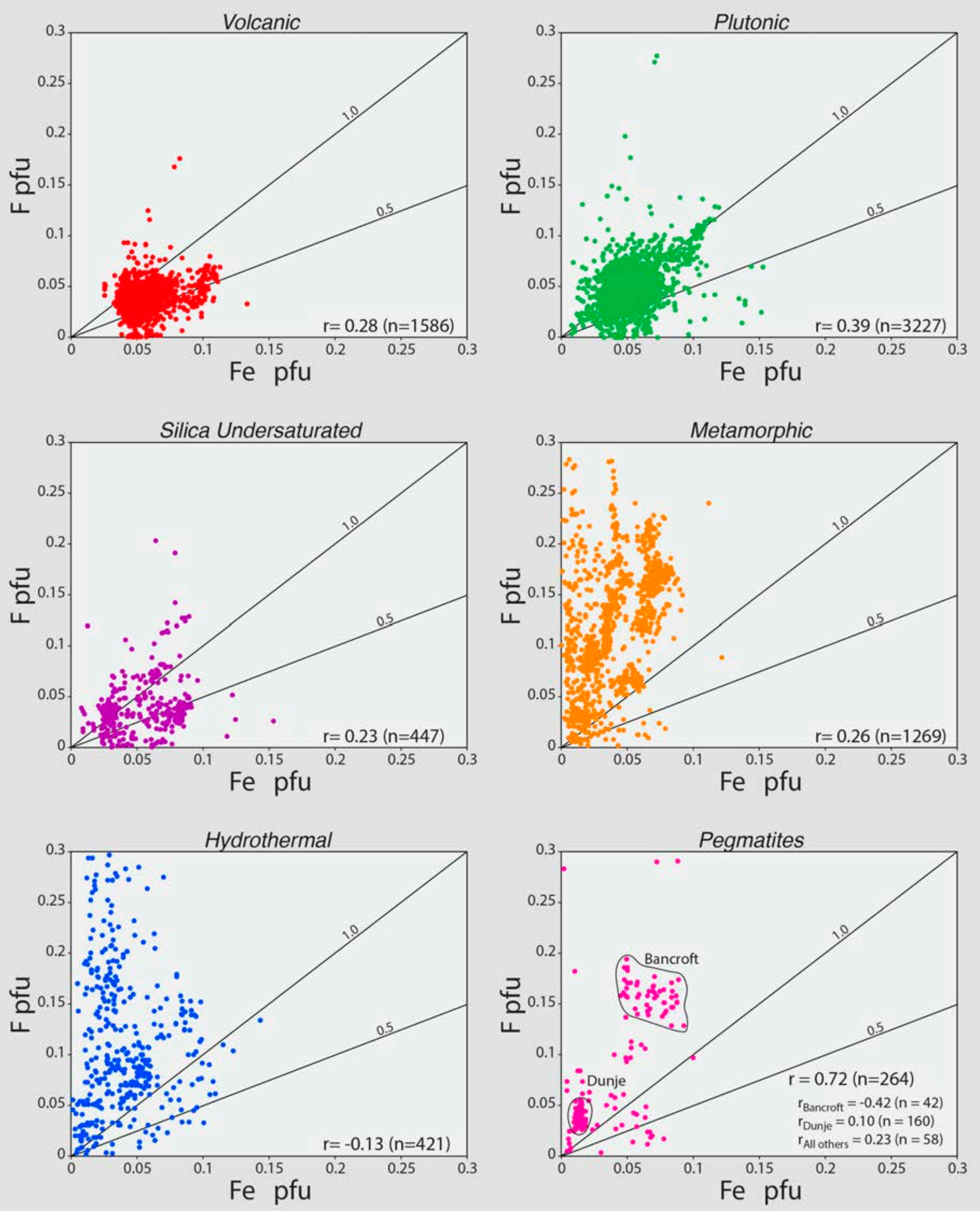
Fe + Al versus F in Titanite

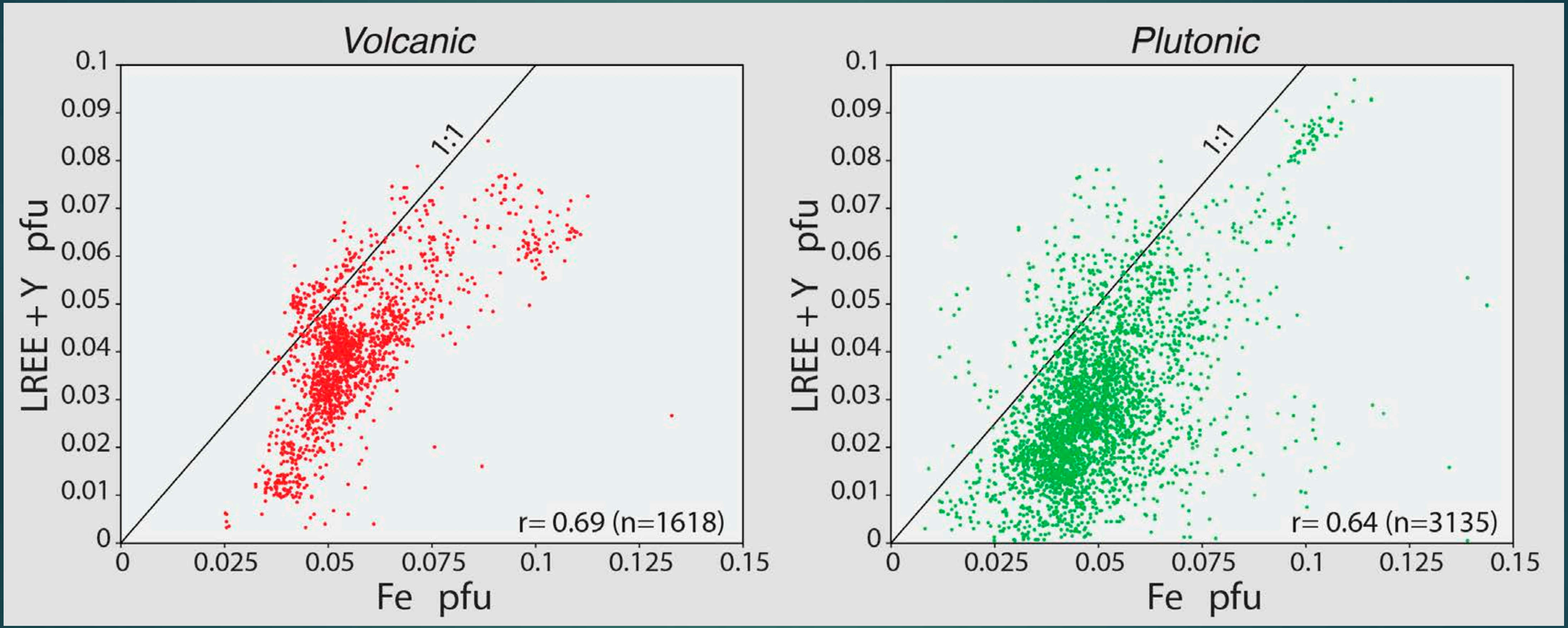


Al versus F in Titanite



Fe versus F in Titanite





Volcanic
Plutonic
LREE + Y pfu
Fe pfu
1:1
r= 0.69 (n=1618)
r= 0.64 (n=3135)
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.025
0.05
0.075
0.1
0.125
0.15

Conclusions – Fe/Al ratios

- The atomic ratio of Fe/Al in titanite from both volcanic and plutonic rocks is typically close to 1:1 and almost always >1:2.
- Volcanic titanite compositions typically cluster more tightly in terms Fe, Al, and F than do titanite compositions from any other environment.
- Fe/Al ratios in titanite from silica-undersaturated volcanic and plutonic rocks are typically >1:2.
- Titanite from metamorphic, hydrothermal, and pegmatitic environments scatter widely in Fe/Al.
- Titanite from eclogite tends to have the lowest Fe/Al ratios, typically <1:8.

Conclusions – Charge Balancing

- Charge balance in metamorphic, hydrothermal, and pegmatitic titanite due to Fe^{+3} and Al^{+3} substitution into the Ti^{+4} site is largely accomplished by the coupled substitution of F^{-} for O^{-2}.
- However, in volcanic and plutonic titanite the charge imbalance due to Fe^{+3} and Al^{+3} substitution appears to be mainly coupled with REE^{+3} and Y^{+3} substitution into the Ca^{+2} site with a more minor contribution from F^{-} substitution.
- In Si-undersaturated rocks, substitution into the Ti^{+4} site by Nb^{+5} coupled with Fe^{+3} is a major factor in charge balancing.