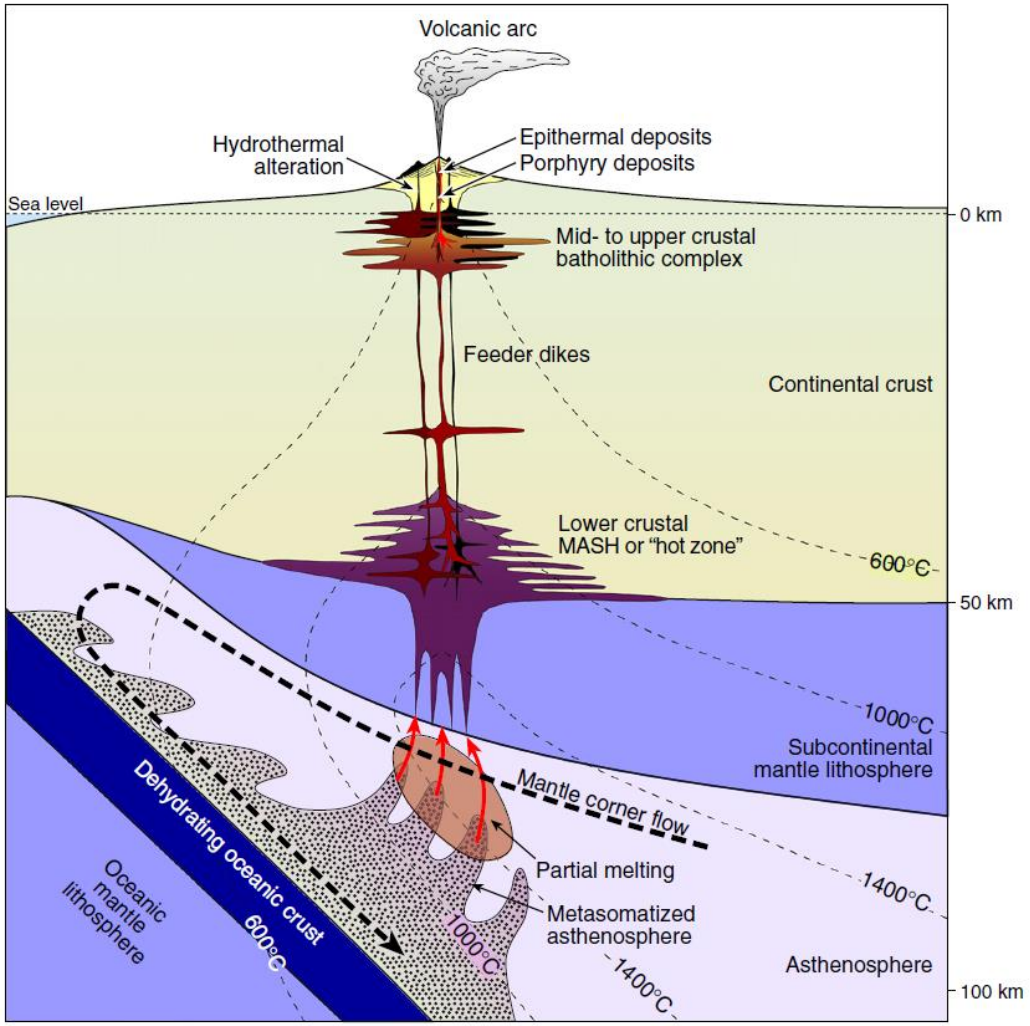
Apatite inclusions in zircon *vs.* matrix apatite:

exploring the magmatic-hydrothermal volatile evolution of high-grade, hypogene **porphyry Cu deposits**

Giulia Consuma (Research Fellow)

Tony Kemp, Steffen Hagemann, Brian Tattitch, Marco Fiorentini, Laure Martin

High grade hypogene porphyry Cu deposits (PCDs): the importance of volatiles



Richards, 2011

"The concentration of **S** and **Cl** rather than the concentration of ore metals regulates magmatic-hydrothermal ore fertility"

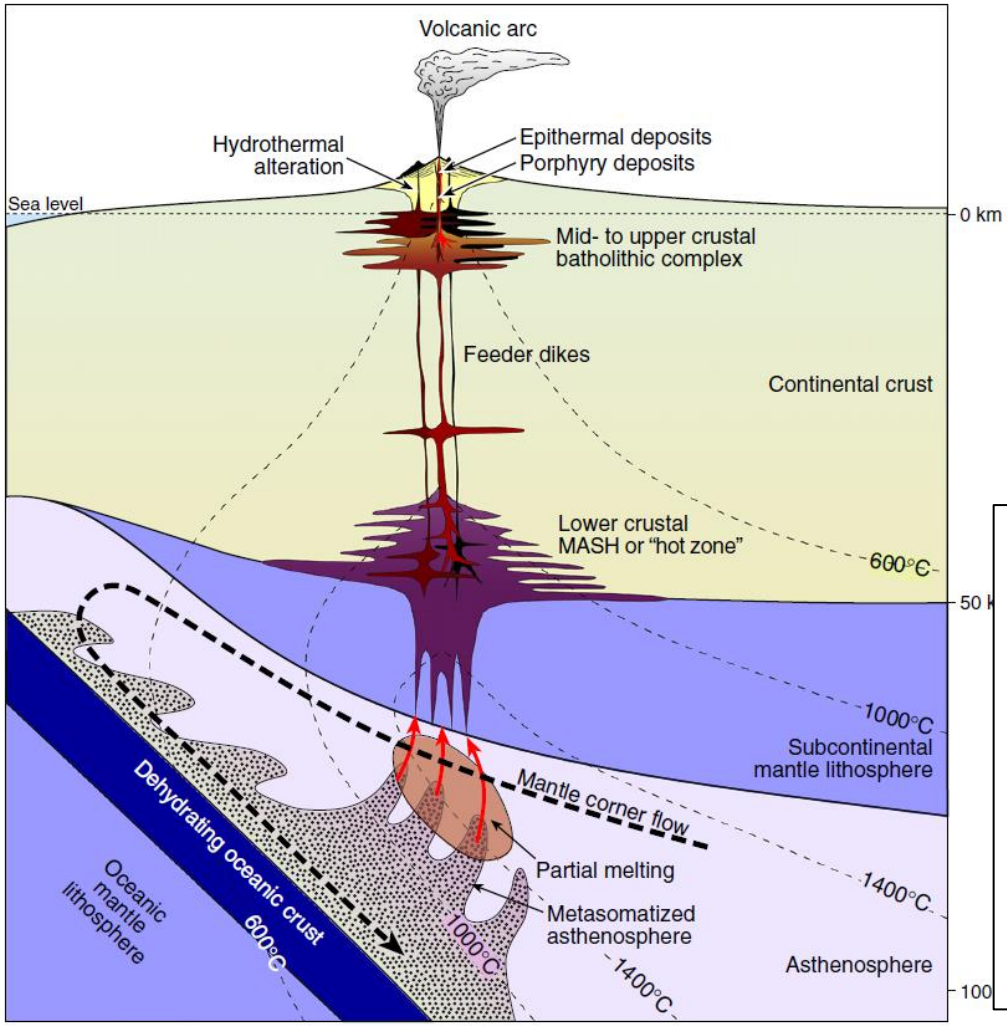
Grondhal & Zajacz , Nature Communications 2022

Open Questions:

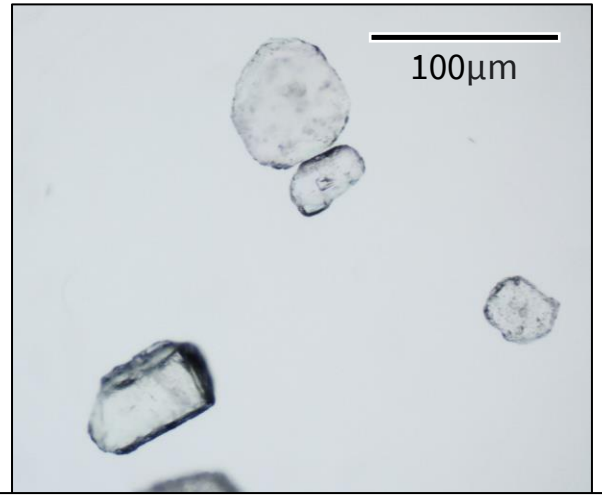
- **What is the magmatic volatile budget?**
- **How do the volatile concentrations change during the magmatic-hydrothermal evolution?**

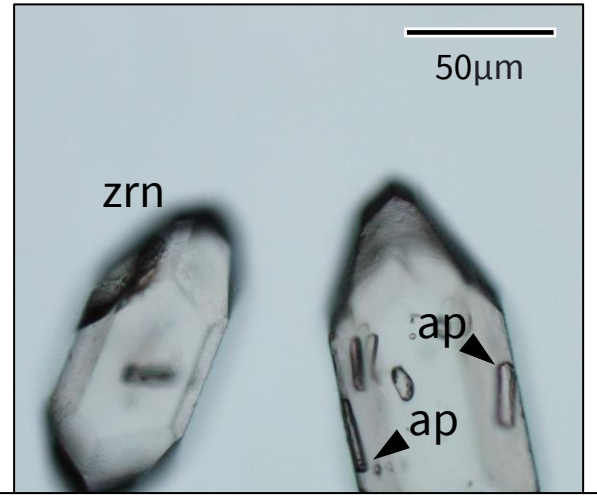
Apatite: key mineral for porphyries exploration

$Ca_5(PO_4)_3$ (OH, F, Cl) [S, C]



Richards, 2011

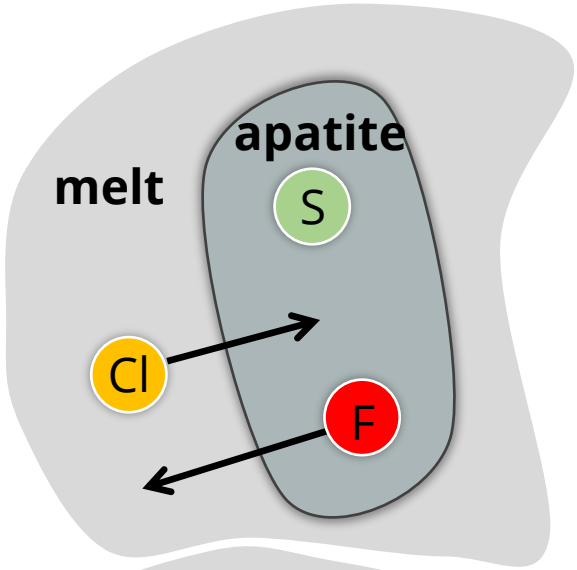




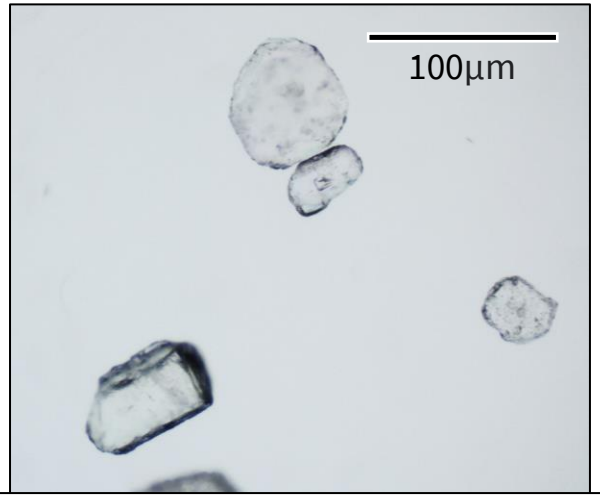
- Saturates **early** in magmas
- Crystallises **throughout the magmatic-hydrothermal history**
- Captures processes occurring at **different stages of the development of the system**

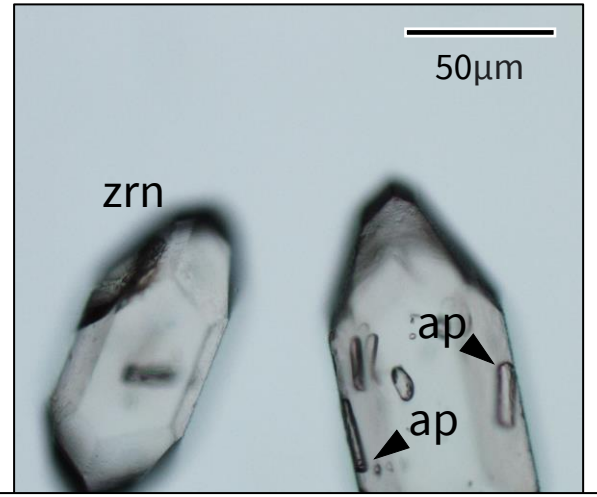
Apatite: key mineral for porphyries exploration

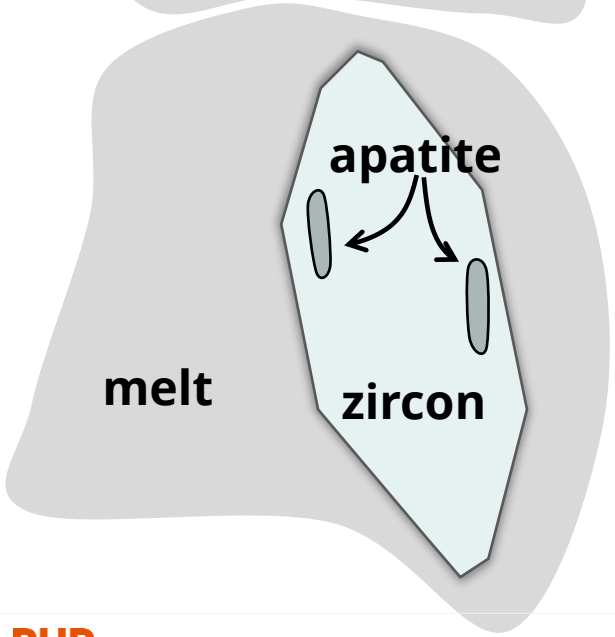
$Ca_5(PO_4)_3$ (OH, F, Cl) [S, C]



Possible volatiles diffusion-alteration



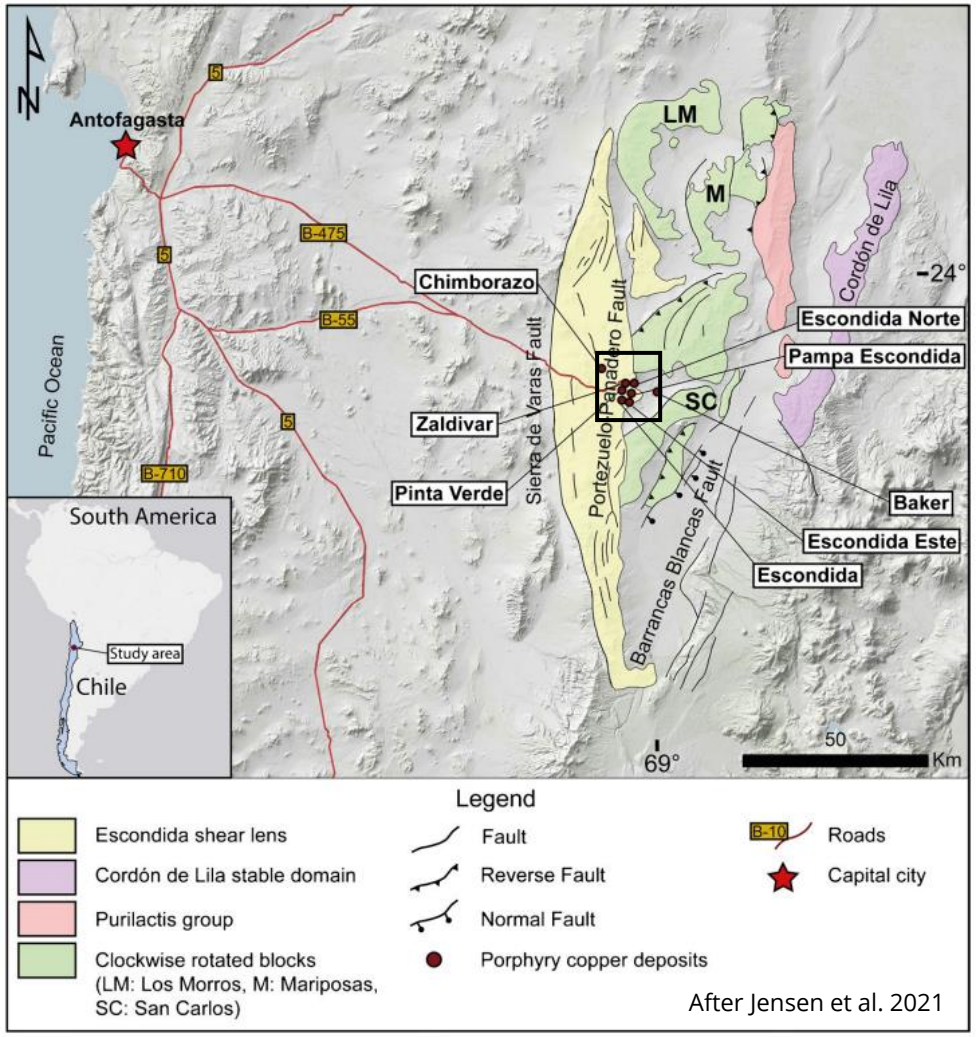




No volatiles diffusion-alteration

- Saturates **early** in magmas
- Crystallises **throughout the magmatic-hydrothermal history**
- Captures processes occurring at **different stages of the development of the system**

Escondida porphyry Cu-Mo-Au district



After Jensen et al. 2021

BHP (57.5%), Rio Tinto (30%) and JECO (12.5%)

5 %

of global copper production

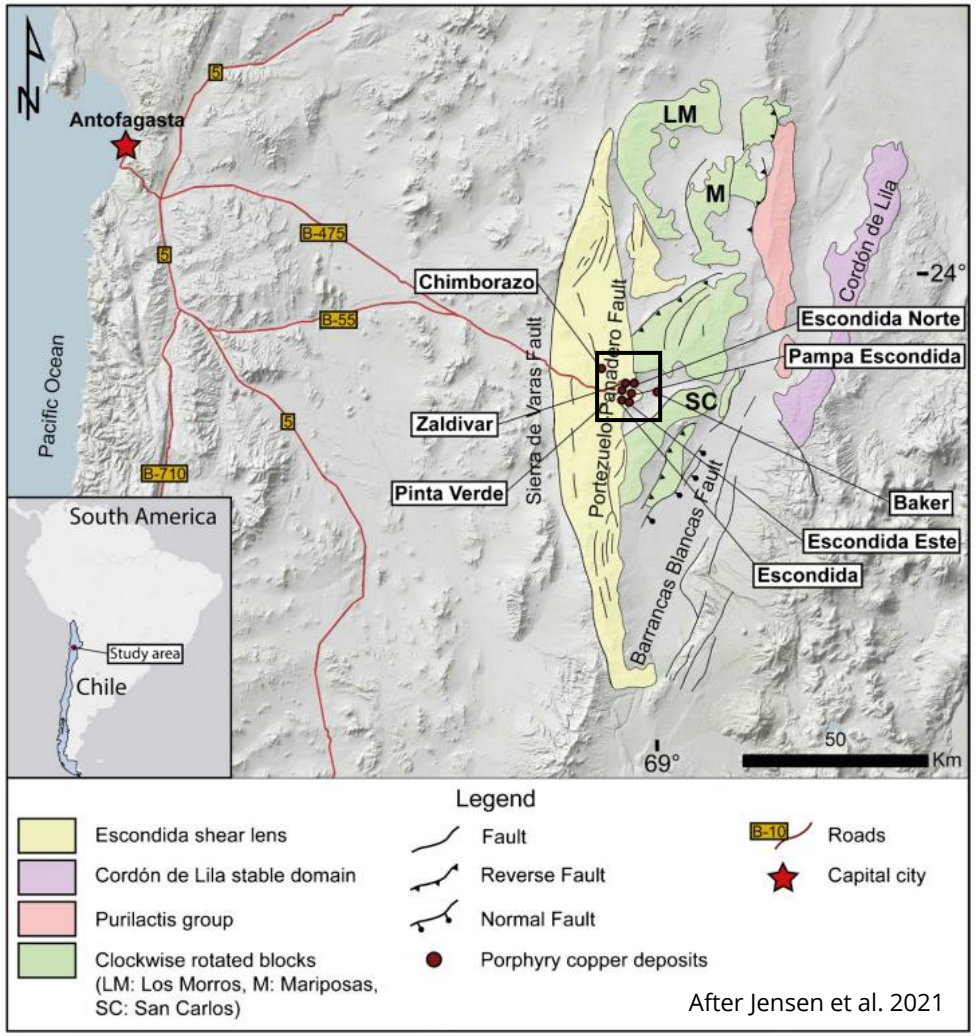
1.06 Mt

copper production in 2022

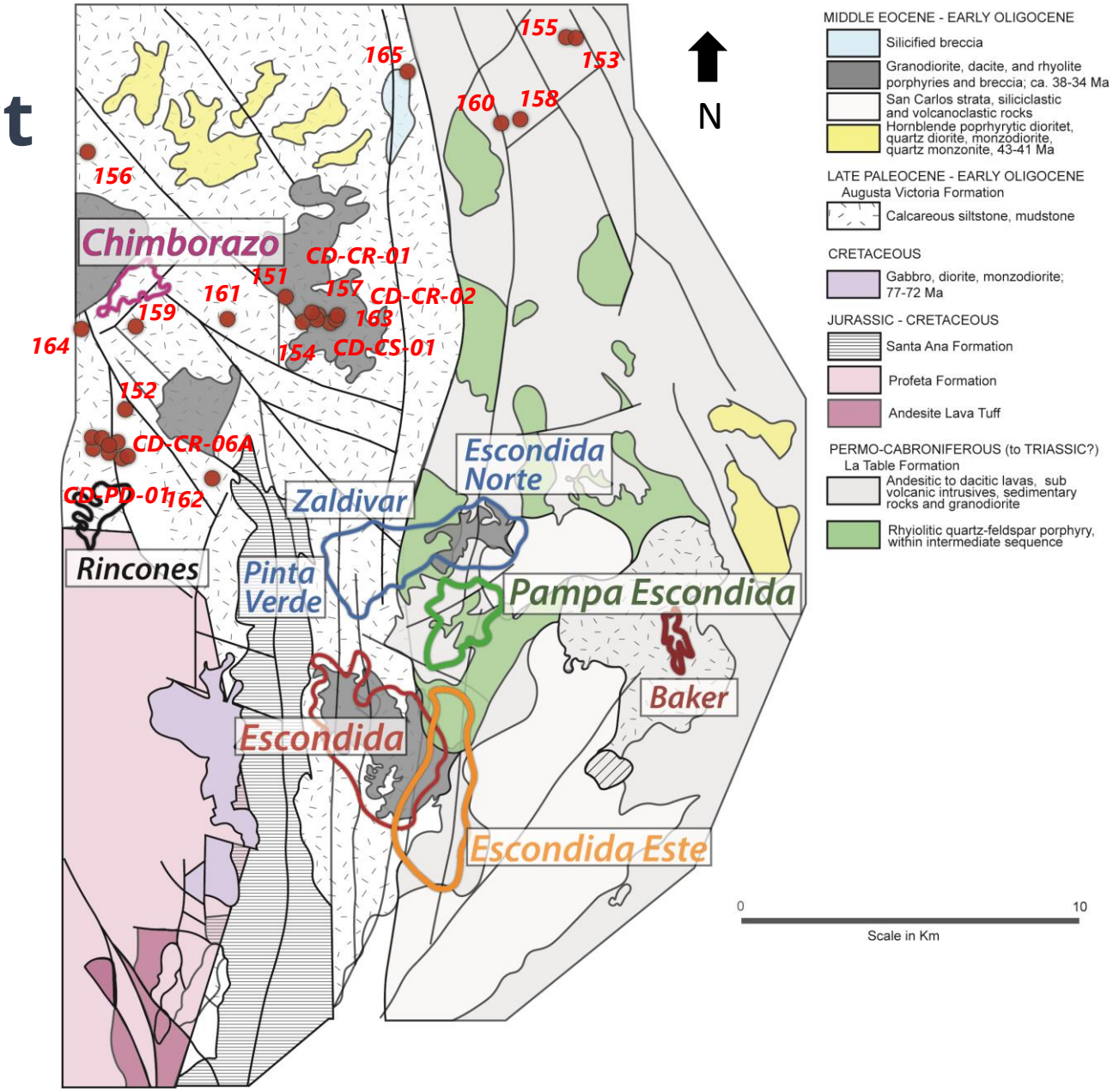
0.2 – 1%

copper grade

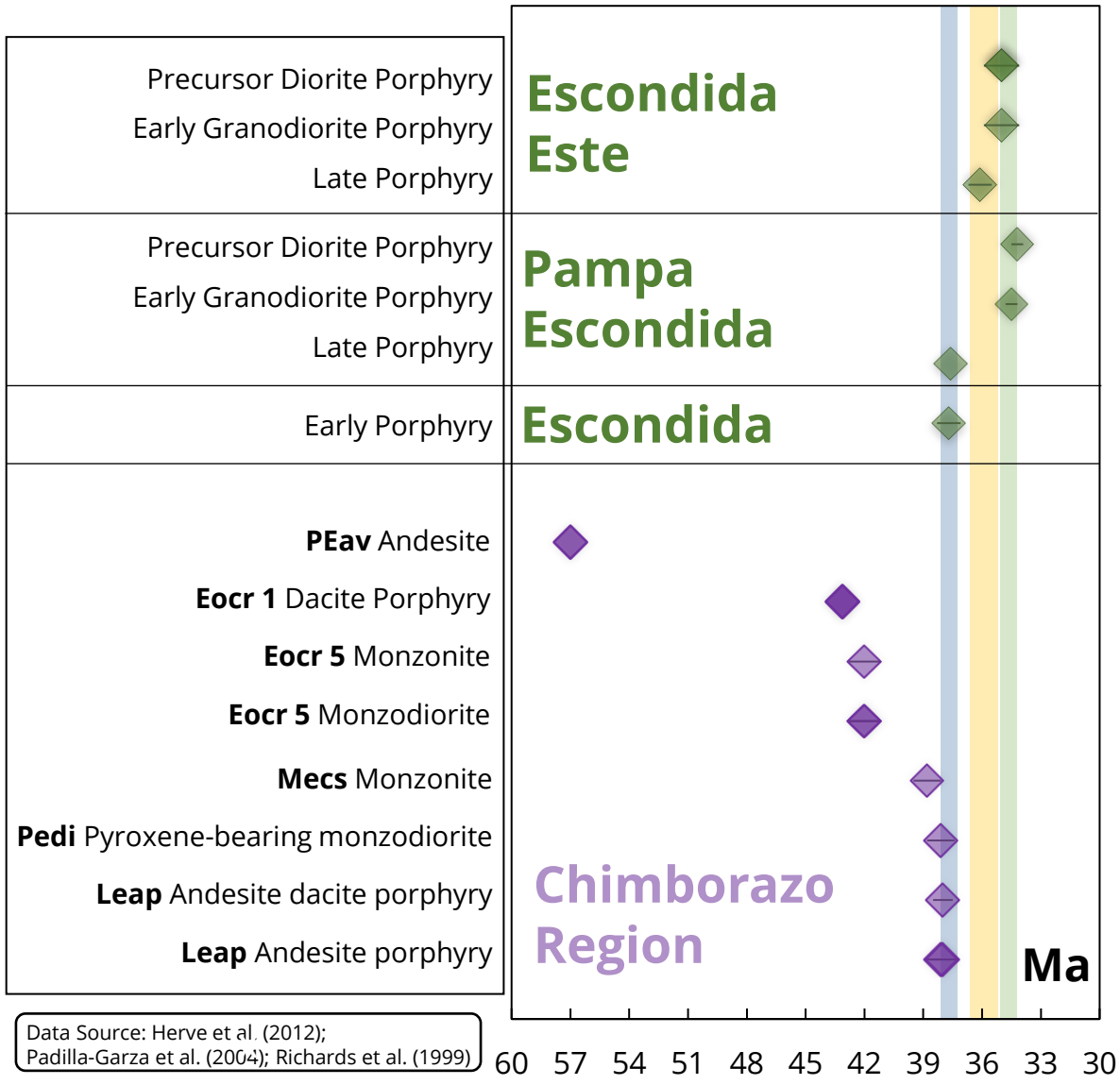
Escondida
porphyry Cu-Mo-Au district



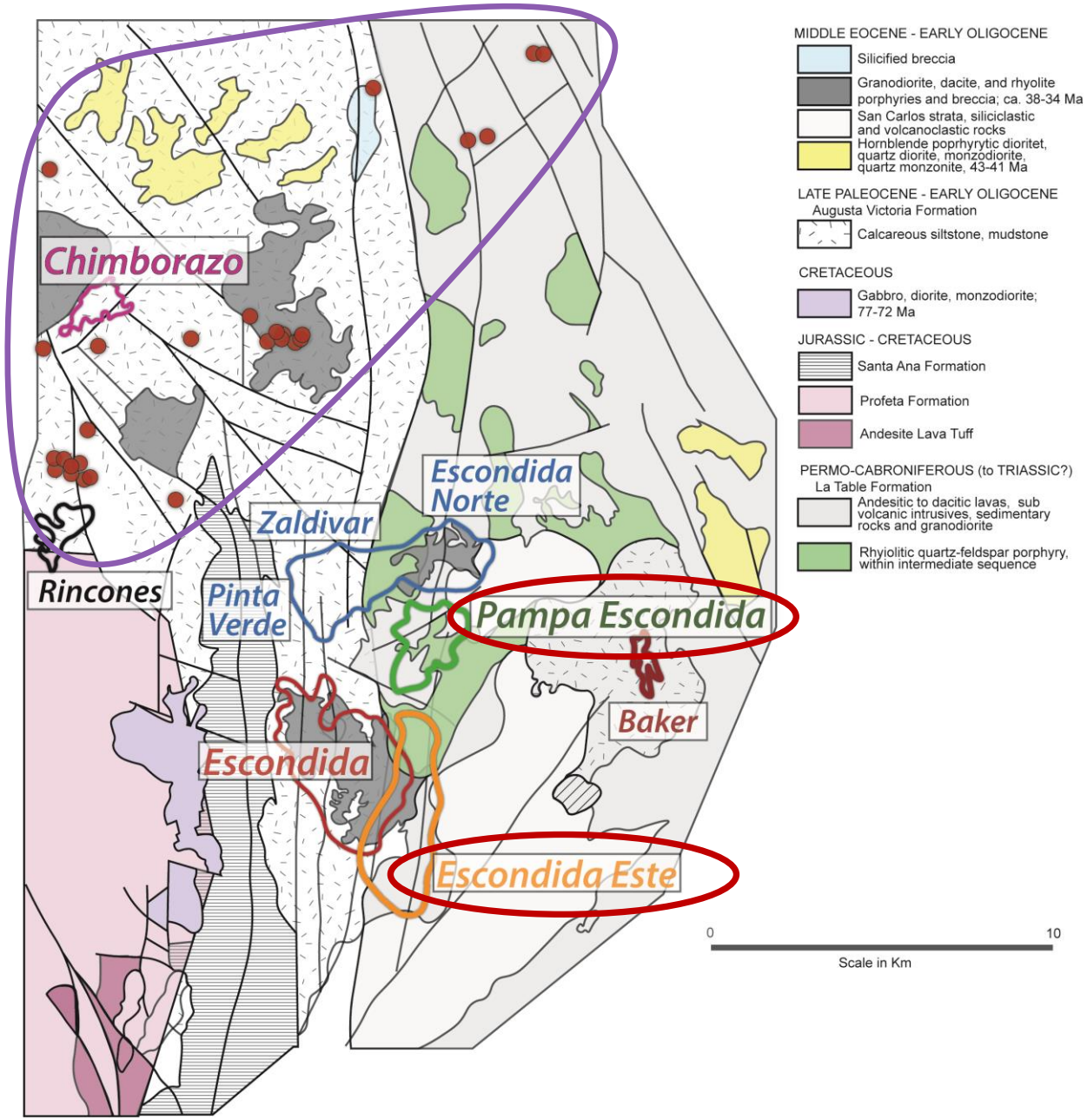
After Jensen et al. 2021



Escondida
porphyry Cu-Mo-Au district



Data Source: Herve et al. (2012); Padilla-Garza et al. (2004); Richards et al. (1999)

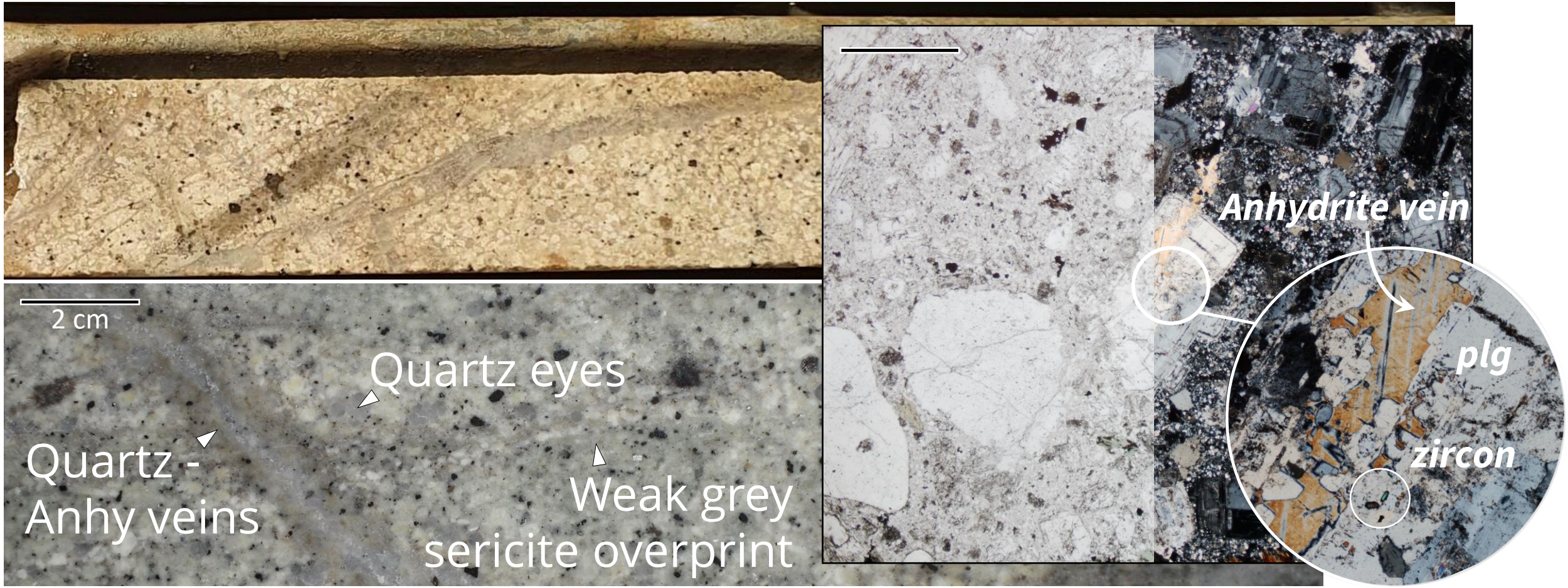


Sampling strategy

EE-23 Main Porphyry

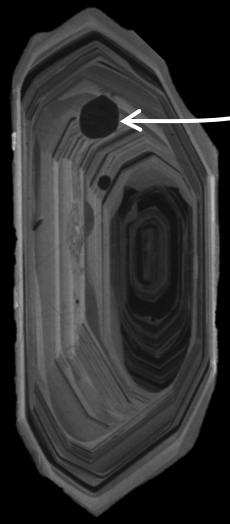
Depth: 1456 – 1458 m

Main Phases	Veins	Mineralisation	Apatite	Zircon
Qtz, Plg, Kfs, Bt, ± Chl, Ap, Anhy	Qtz-anhy Qtz-anhy-sulf	1-2% Cp > Bo, Mo	Low yield	Good yield



Apatite textures record magmatic-hydrothermal stages

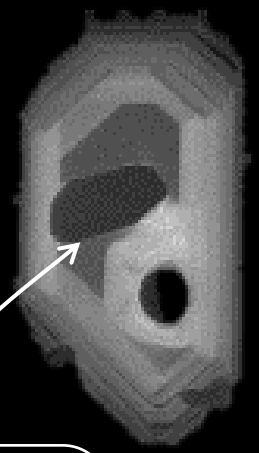
Zircon



Zircon from <u>mineralised</u> porphyry

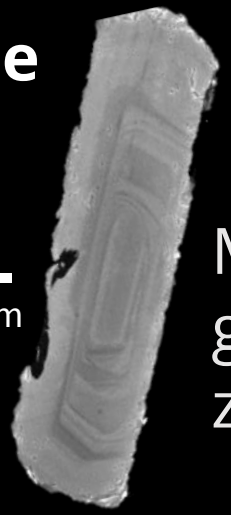
50µm

Zircon from <u>un-mineralised</u> porphyry intrusions



100µm

Apatite

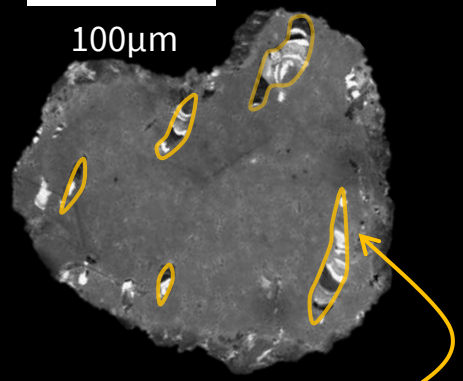


100µm

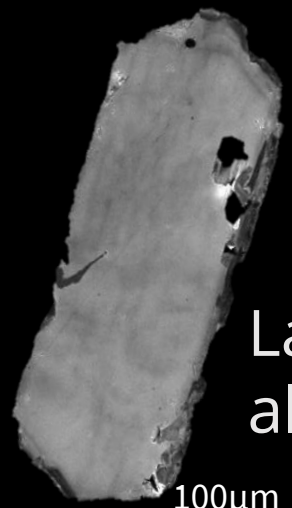
Magmatic growth zoning

Irregular CL patches

100µm



Hydrothermal fluid pulses



Late pervasive alteration

100µm

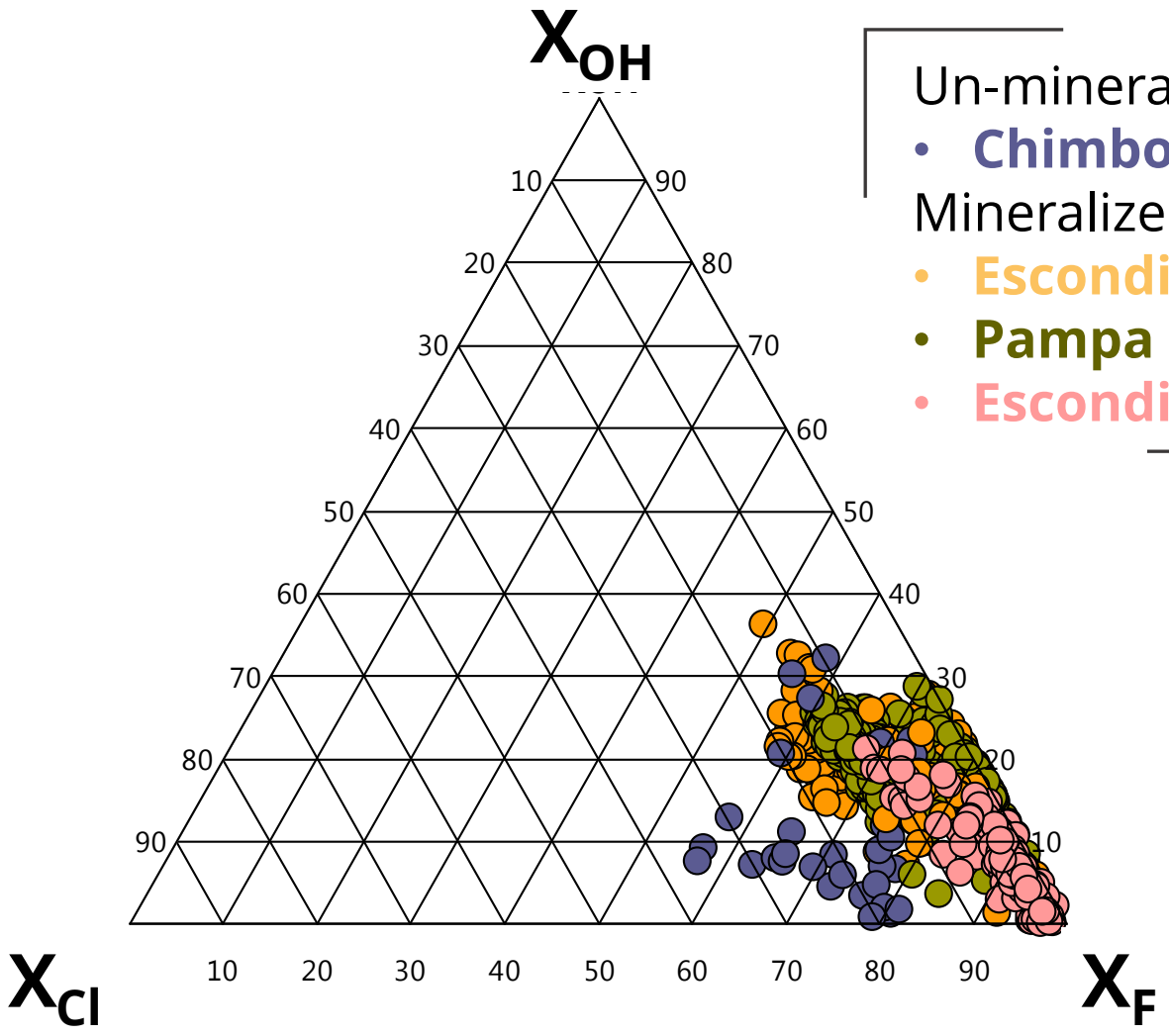
BHP

Center for EXPLORATION TARGETING

THE UNIVERSITY OF WESTERN AUSTRALIA

A look into apatite halogens composition

Groundmass apatite



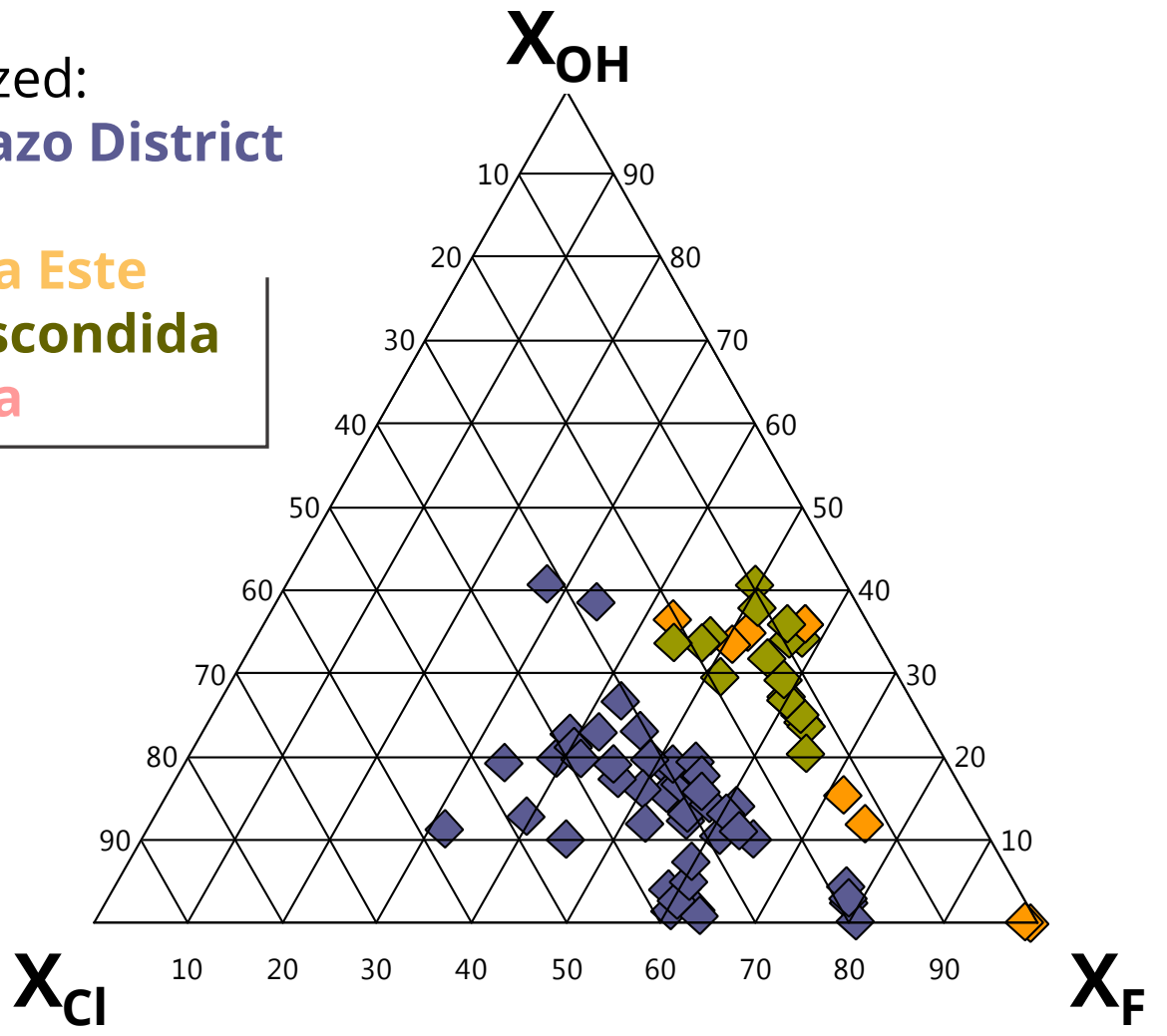
Un-mineralized:

- **Chimborazo District**

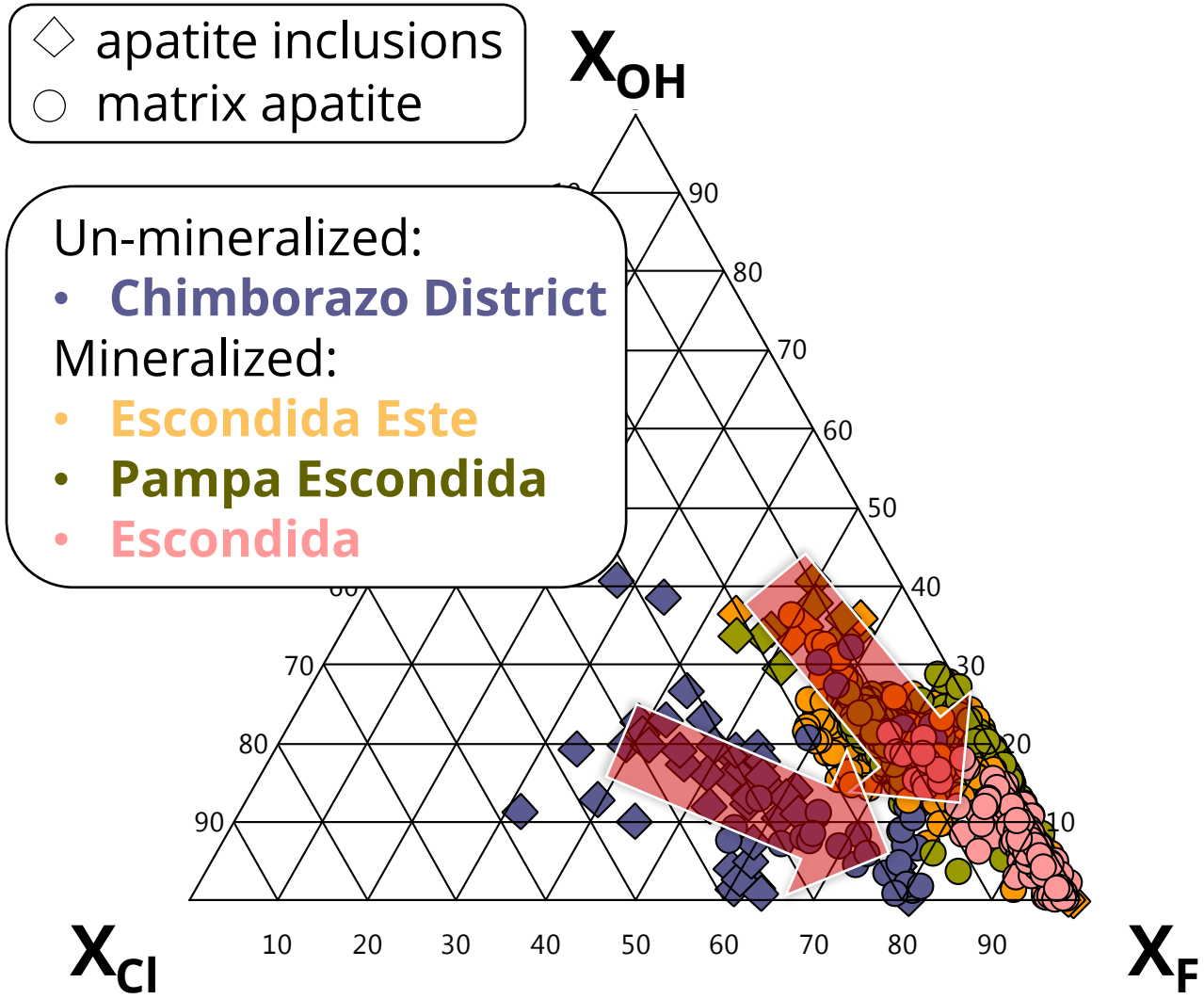
Mineralized:

- **Escondida Este**
- **Pampa Escondida**
- **Escondida**

Apatite Inclusions

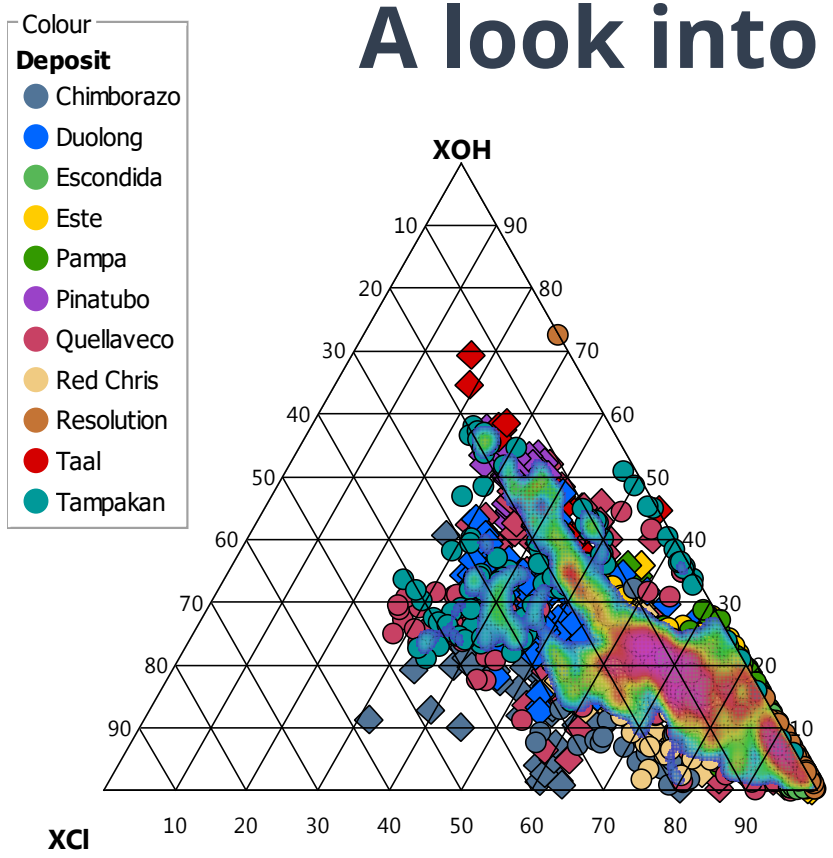


A look into apatite halogens composition



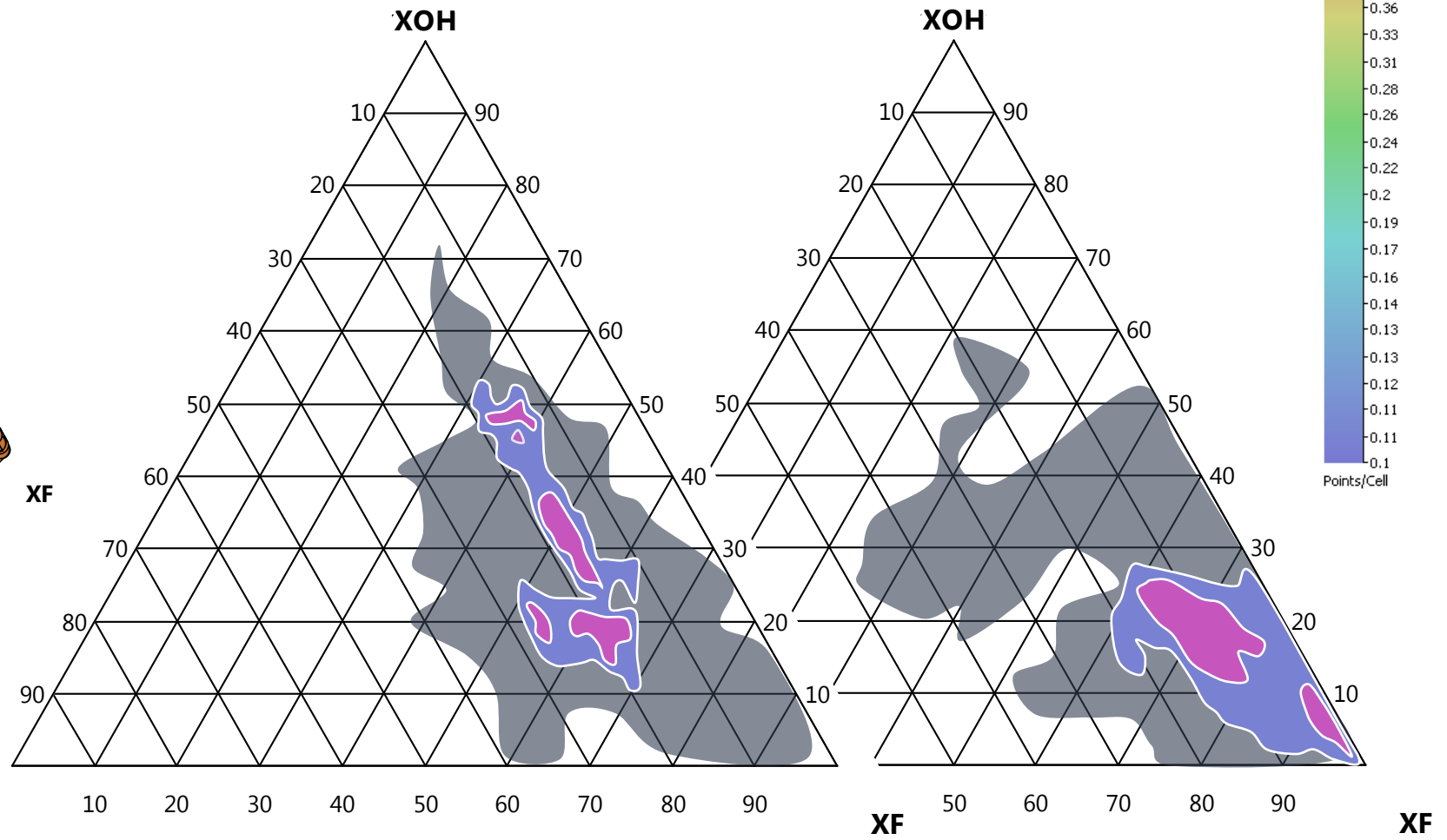
- **Apatite inclusions** crystallised from less evolved melt **before exsolving hydrothermal fluids**
- **Groundmass apatite** crystallised from or equilibrated with residual - more evolved - melt from which **hydrothermal fluids already exsolved** (Cl and H_2O loss)

A look into apatite halogens composition



Inclusions

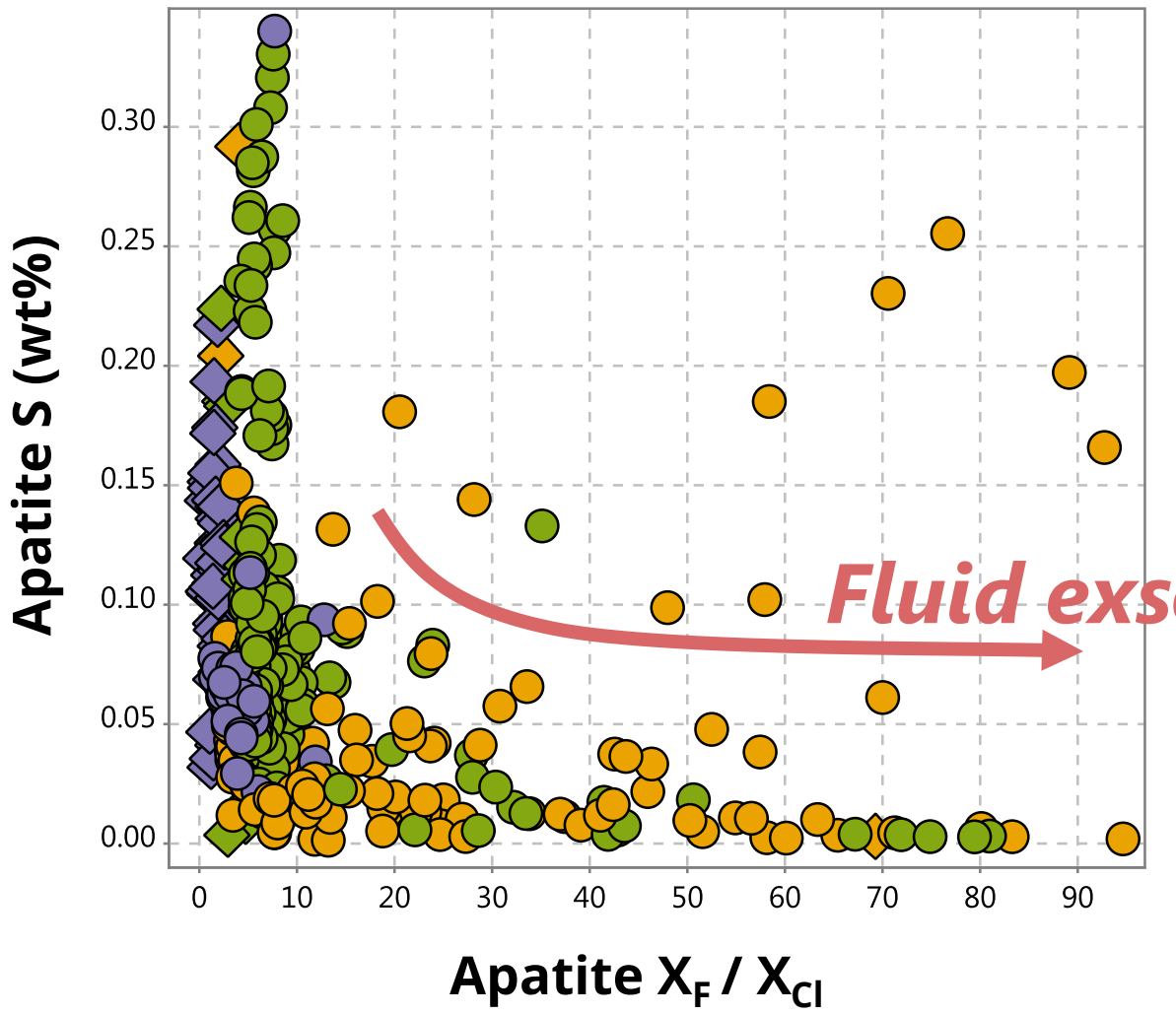
Groundmass apatite



Data from:

- This study
- Chelle-Michou & Chiaradia 2017
- Zhu et al. 2018
- Li et al. 2020
- Parra-Avila et al. 2022
- Nathwani et al. 2023
- Stonadge et al. 2023

Is Sulfur affected by fluid exsolution?



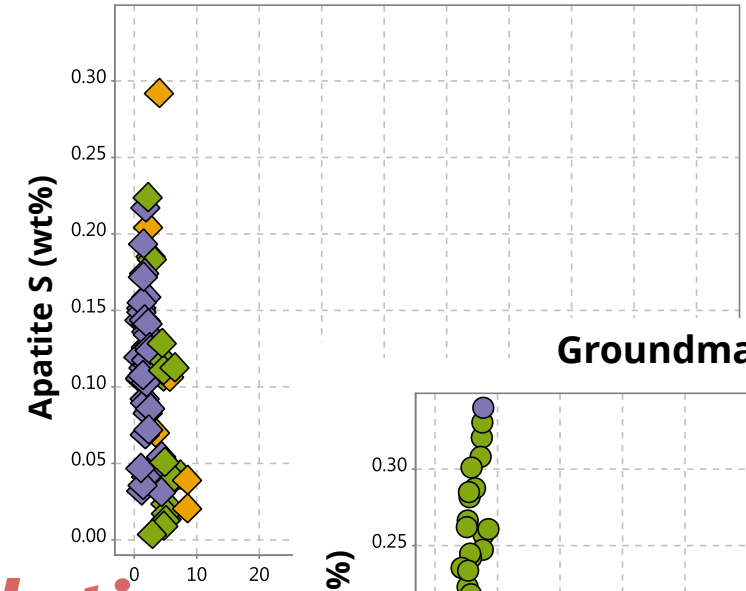
Fluid exsolution

Chimborazo

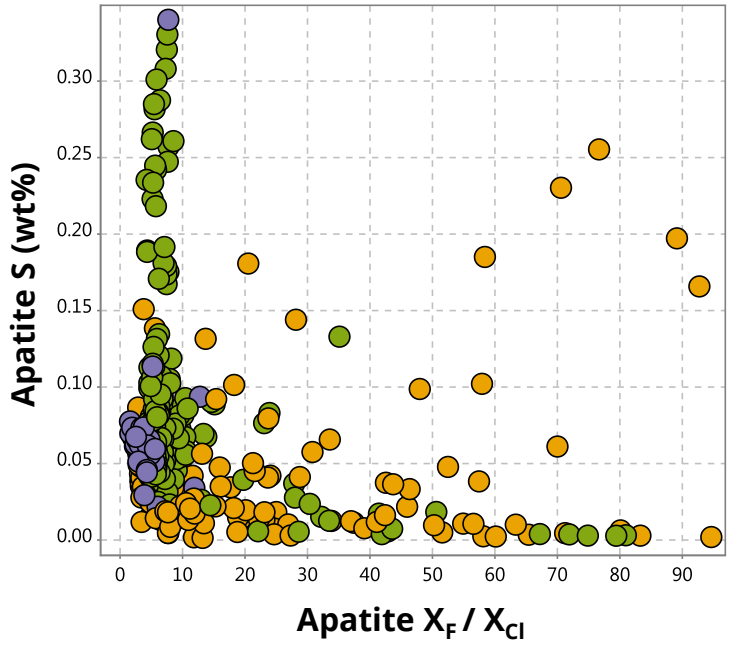
Pampa Escondida

Escondida Este

Apatite inclusions



Groundmass apatite



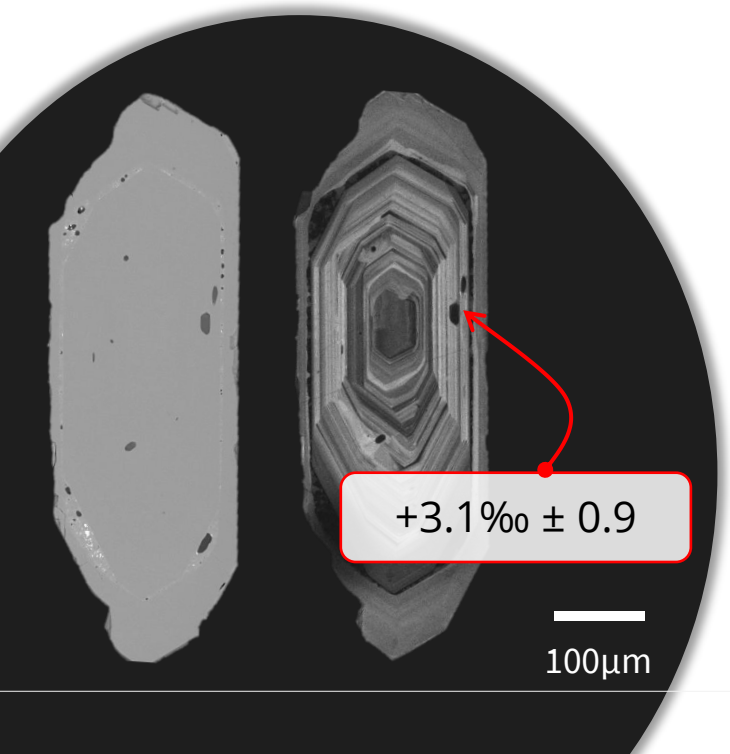
$\delta^{34}S_{apatite}$ records sulfur degassing

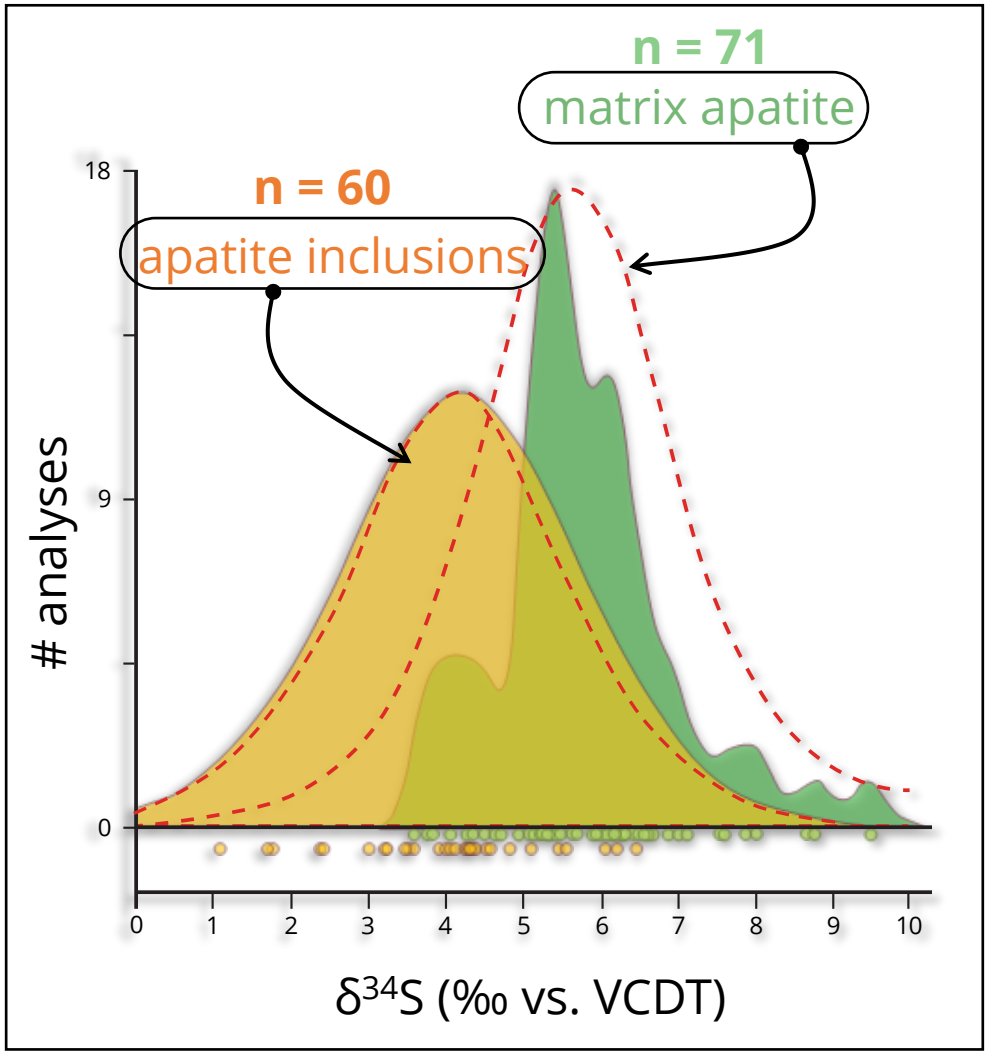
Probability Density Plot

----- KDE

2σ = 0.8 ‰ (5 µm)

0.2 ‰ (10 µm)





Apatite inclusions

- Within the $\delta^{34}S$ range of porphyry Cu deposits (-10 to +10 ‰)
- Up to 6‰ $\delta^{34}S$ variations within single hand samples
- No correlation between S content and $\delta^{34}S$

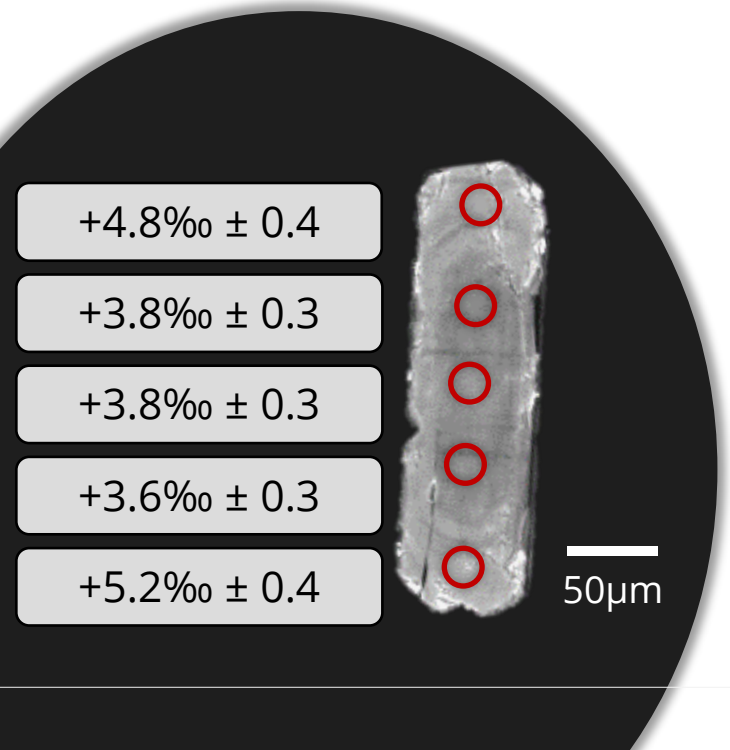
$\delta^{34}S_{apatite}$ records sulfur degassing

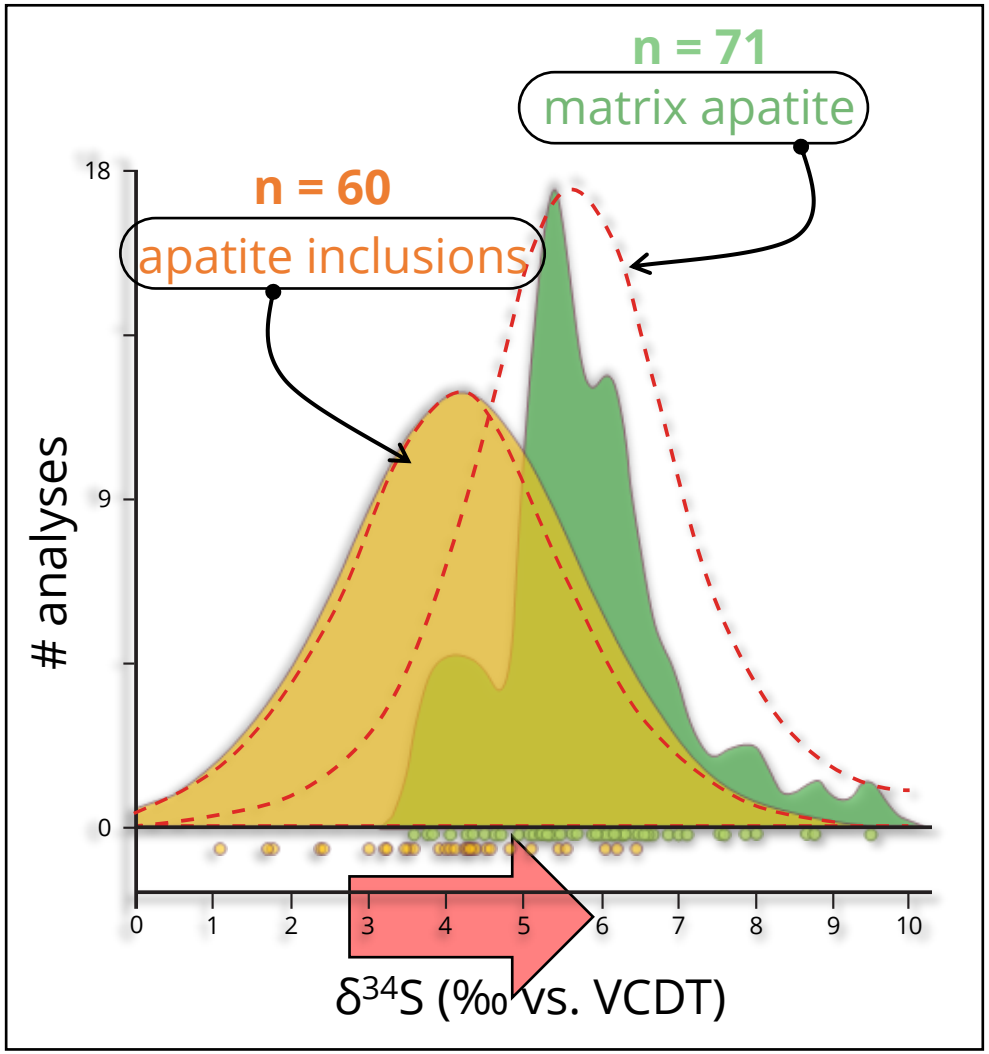
Probability Density Plot

----- KDE

2σ = 0.8 ‰ (5 µm)

0.2 ‰ (10 µm)





Matrix apatite

- $\delta^{34}S_{mean}$ = + 5.79‰; Intra-grain variation up to ~ 3‰
- Values of $\delta^{34}S$ < 5‰ only found in the core
- No correlation between S content and $\delta^{34}S$

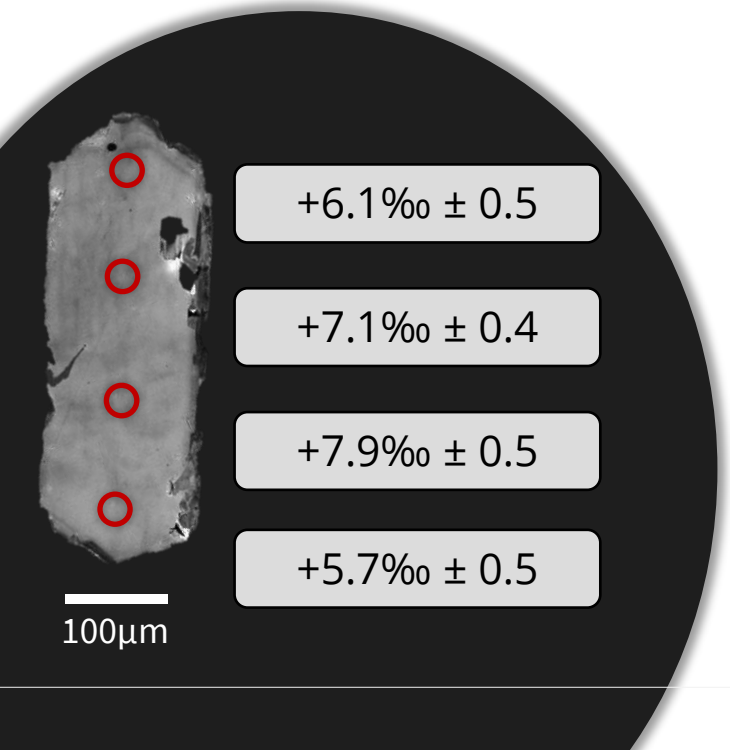
$\delta^{34}S_{apatite}$ records sulfur degassing

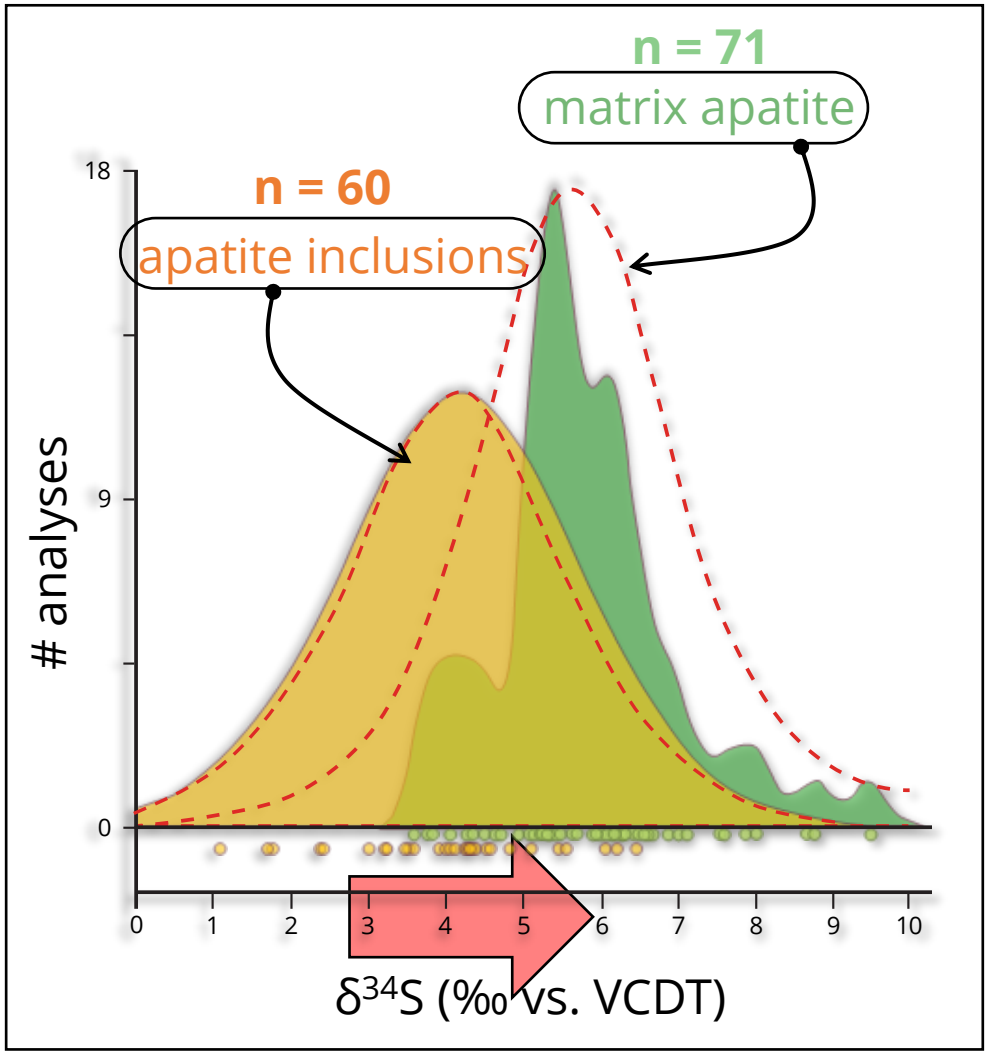
Probability Density Plot

----- KDE

2σ = 0.8 ‰ (5 µm)

0.2 ‰ (10 µm)



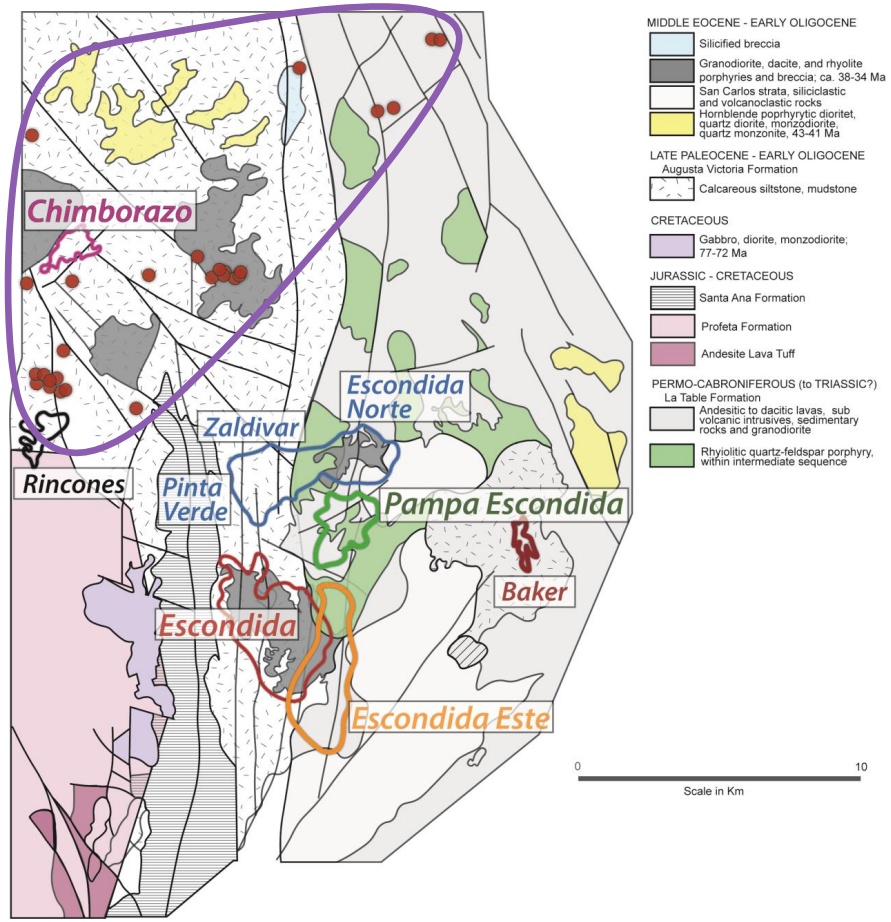


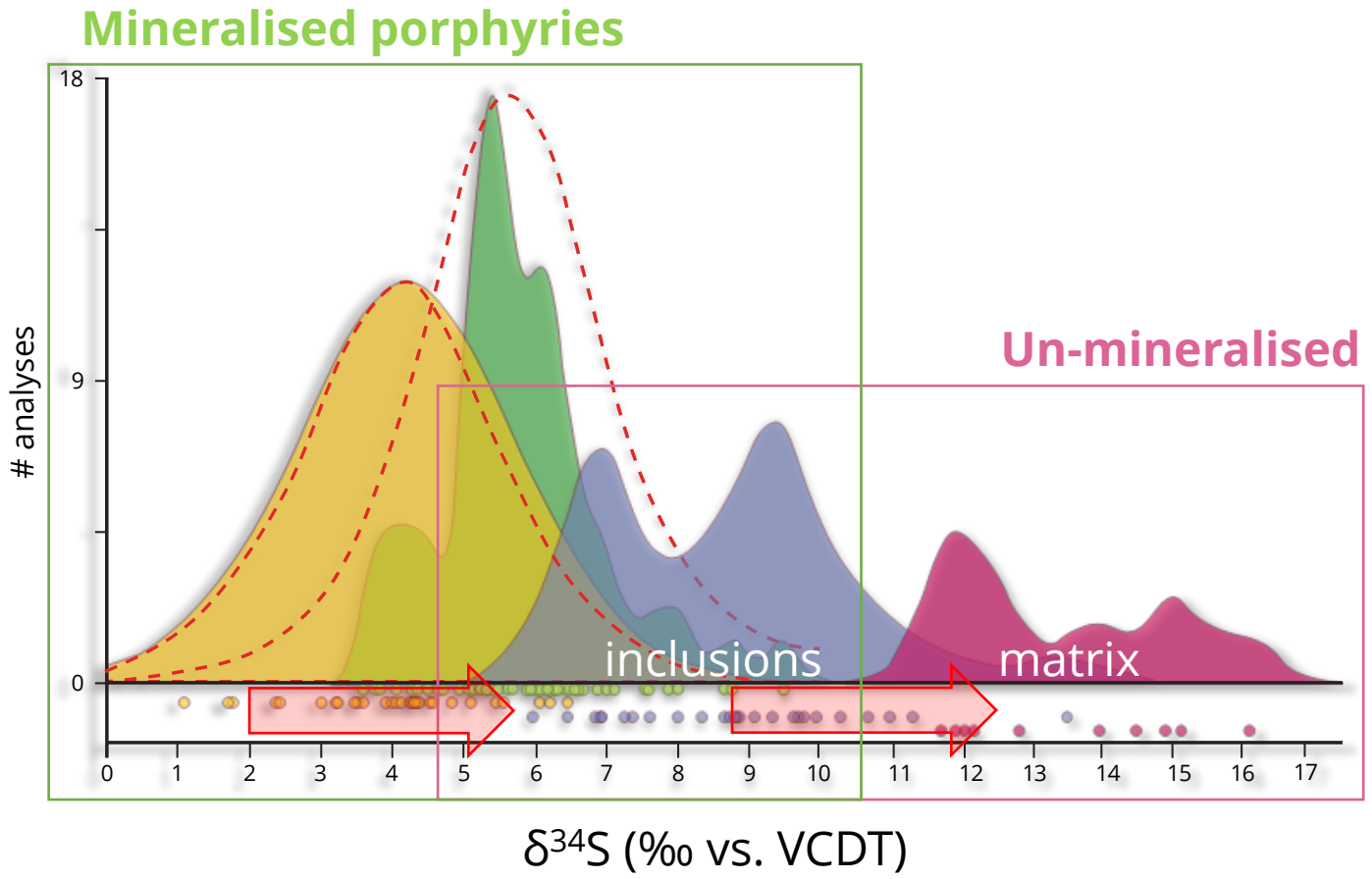
Hypotheses

1) **$\delta^{34}S_{melt}$ increases upon degassing** at oxidizing conditions

2) Hydrothermal **overprinting**

$\delta^{34}S_{apatite}$ records sulfur degassing





- Same **trend toward heavier $\delta^{34}S$** from inclusions to groundmass apatite
- **Distinct $\delta^{34}S_{apatite}$ between mineralised porphyries and un-mineralised intrusions**

Main learnings from apatite

- **Apatite inclusions record the magmatic enrichment in volatiles**
- **Volatiles are lost** prior or during groundmass apatite crystallisation
- **Sulfur content** in the inclusions is minimally affected by fluid exsolution
- **Residual melt is oxidised** along with degassing/fluid exsolution

Ongoing study:

- Understanding apatite entrapment and melt volatile concentrations by studying the host zircon

Redefining porphyry Cu mineral indicators

Zircon

Geochronometer

Oxybarometer

Degree of magma fractionation

Apatite

Halogens and Sulfur quantification

Melt hydration

Timing of fluid exsolution

Sulfur degassing, sulfur speciation, redox conditions


Thanks to BHP
and the HGHP Team
Bristol University
Imperial College of London
Natural History Museum
Vamonos!

Additional slides

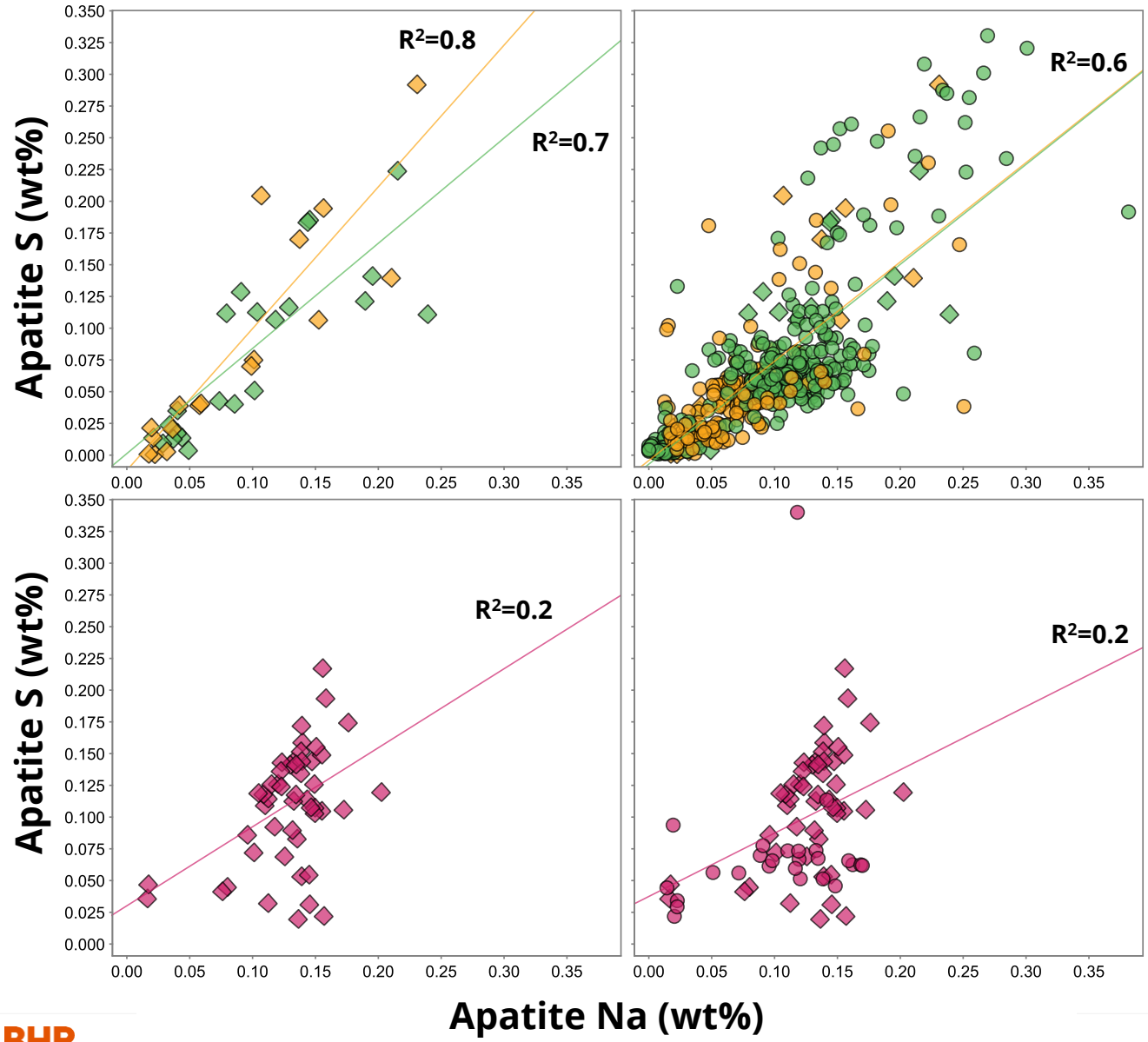
Apatite mineral chemistry (EPMA): sulfur

Un-mineralized:
- Chimborazo District

Mineralized:
- Escondida Este
- Pampa Escondida

◇ apatite inclusions

○ matrix apatite



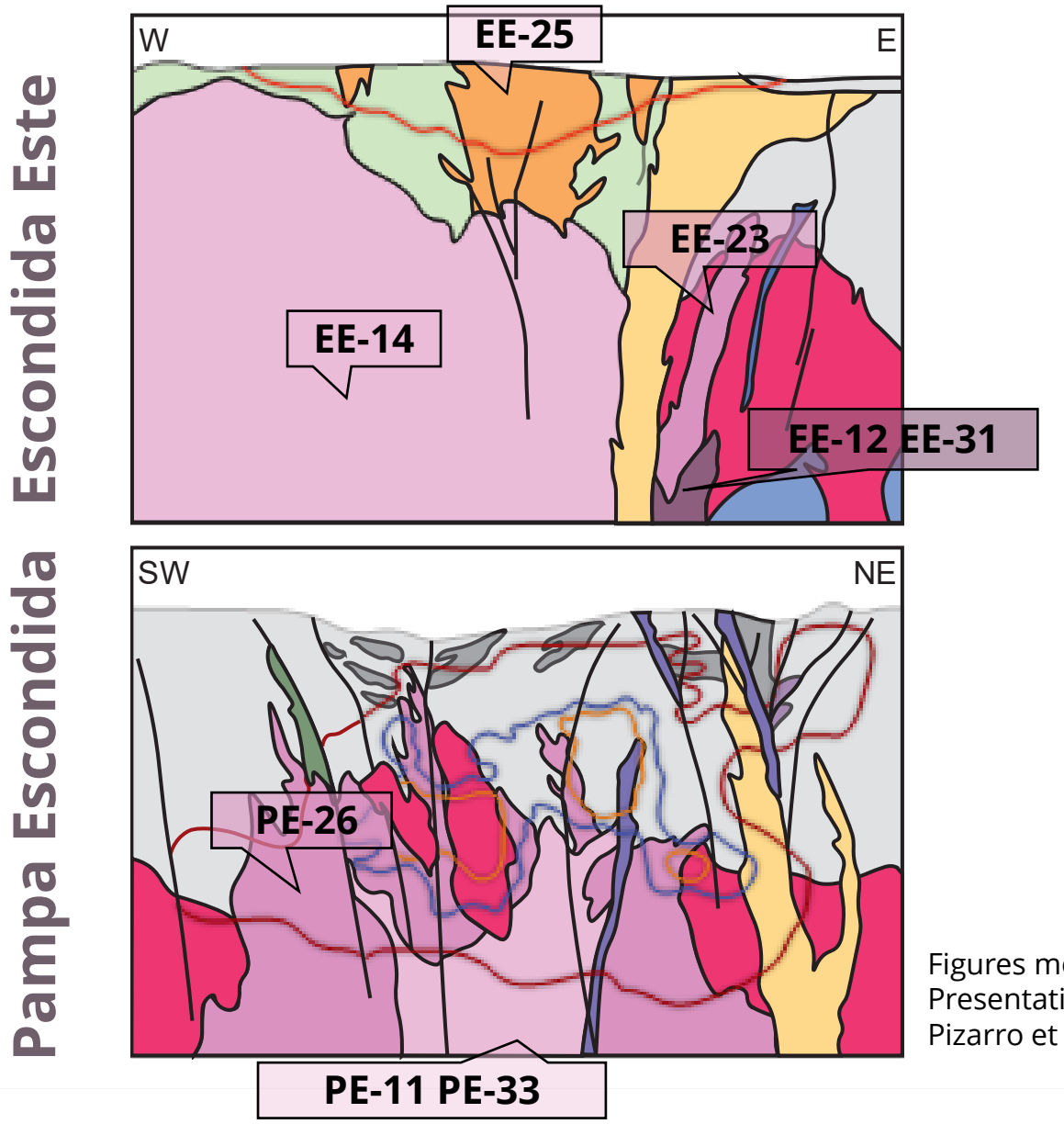
- **Positive S-Na correlation** from mineralised porphyries

- **S-Na coupling substitution** of apatite

$$S^{6+} + Na^{+} \Leftrightarrow P^{5+} + Ca^{2+}$$

(cf. Liu and Comodi 1993)

Sampling strategy



- > 0.3%
- 0.75%
- 1.0% Cu contours

Legend

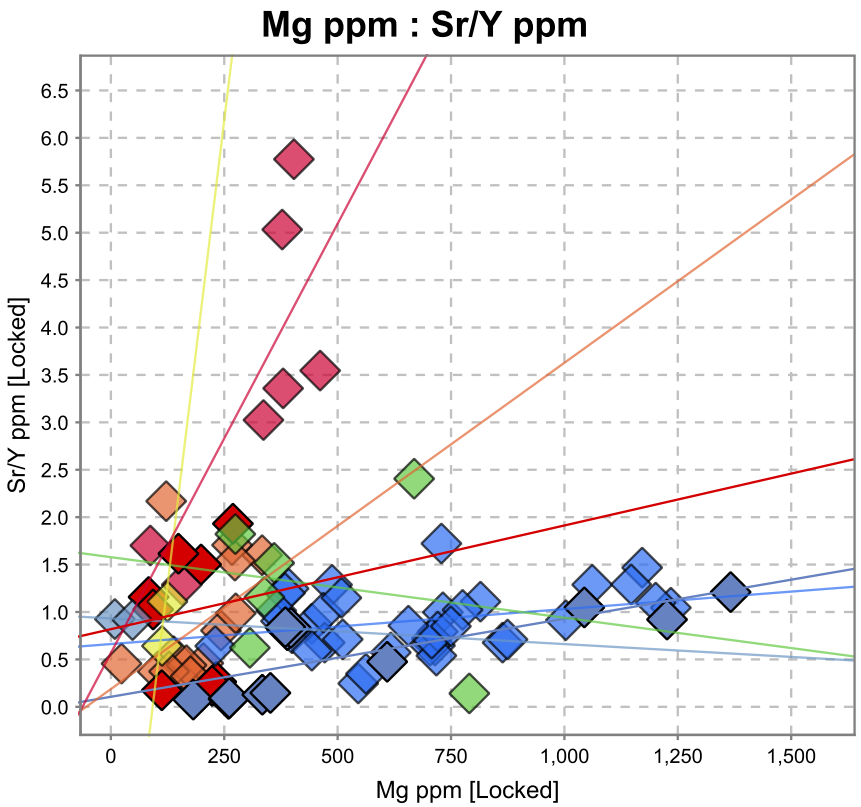
- Superficial gravel
- Breccias
- La Tabla Formation
- Pre-mineral diorite
- Late mineral hbl dacite/rhyolite porphyry
- Late intermineral granodiorite porphyry
- Early mineral granodiorite porphyry
- Permian monzodiorite porphyry

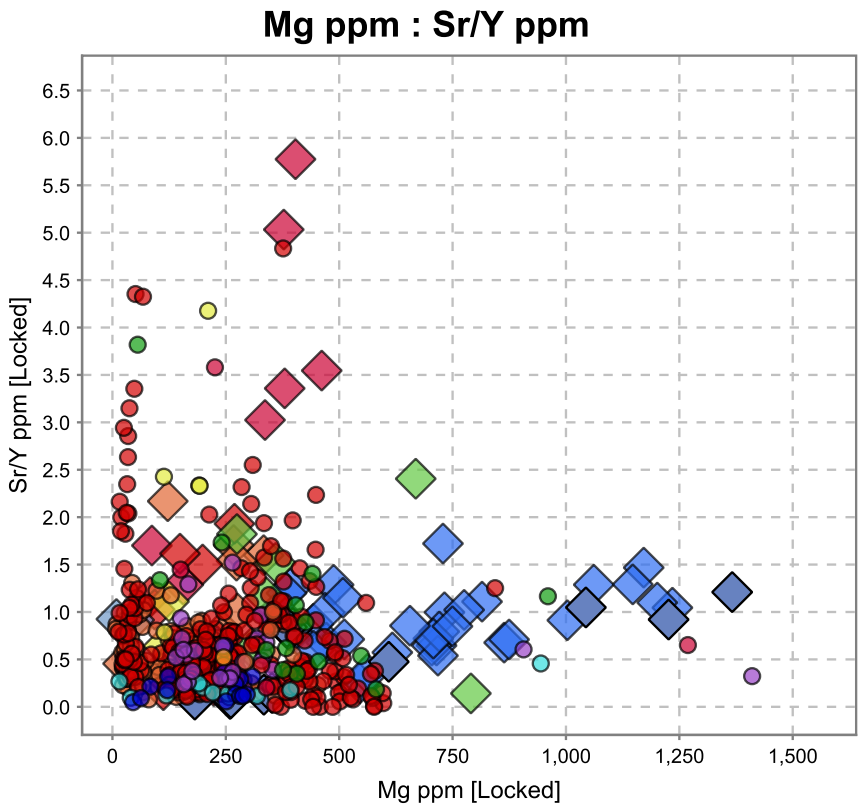
Escondida Este

- AVF
- Escondida early granodiorite Porphyry (38-37 Ma)
- EE Intermineral granodiorite porphyry
- EE early mineral granodiorite porphyry
- Tonalite (300 Ma)

Figures modified after BHP Billiton Presentation, August, 2014; Pizarro et al. 2015

Additional slide. Apatite **Mg vs. Sr/Y – sample scale**





Colour
Sample
- CHL186505
- CHL186511
- CHL186521
- CHL258151
- D-9088
- EE-11
- EE-12
- EE-14
- EE-23
- PE-11
- PE-12
- PE-33
- TS-151
- TS-152

Shape
Text Position
- Matrix

Size
Text Position
- Inclusion
- Matrix

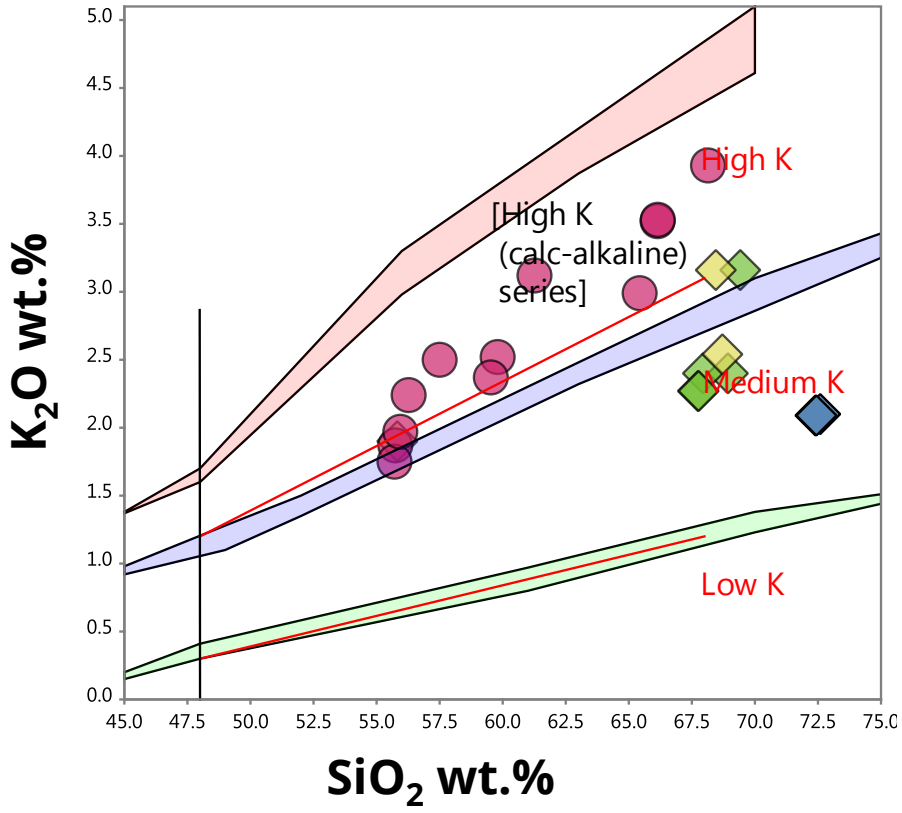
Label
Sample ID

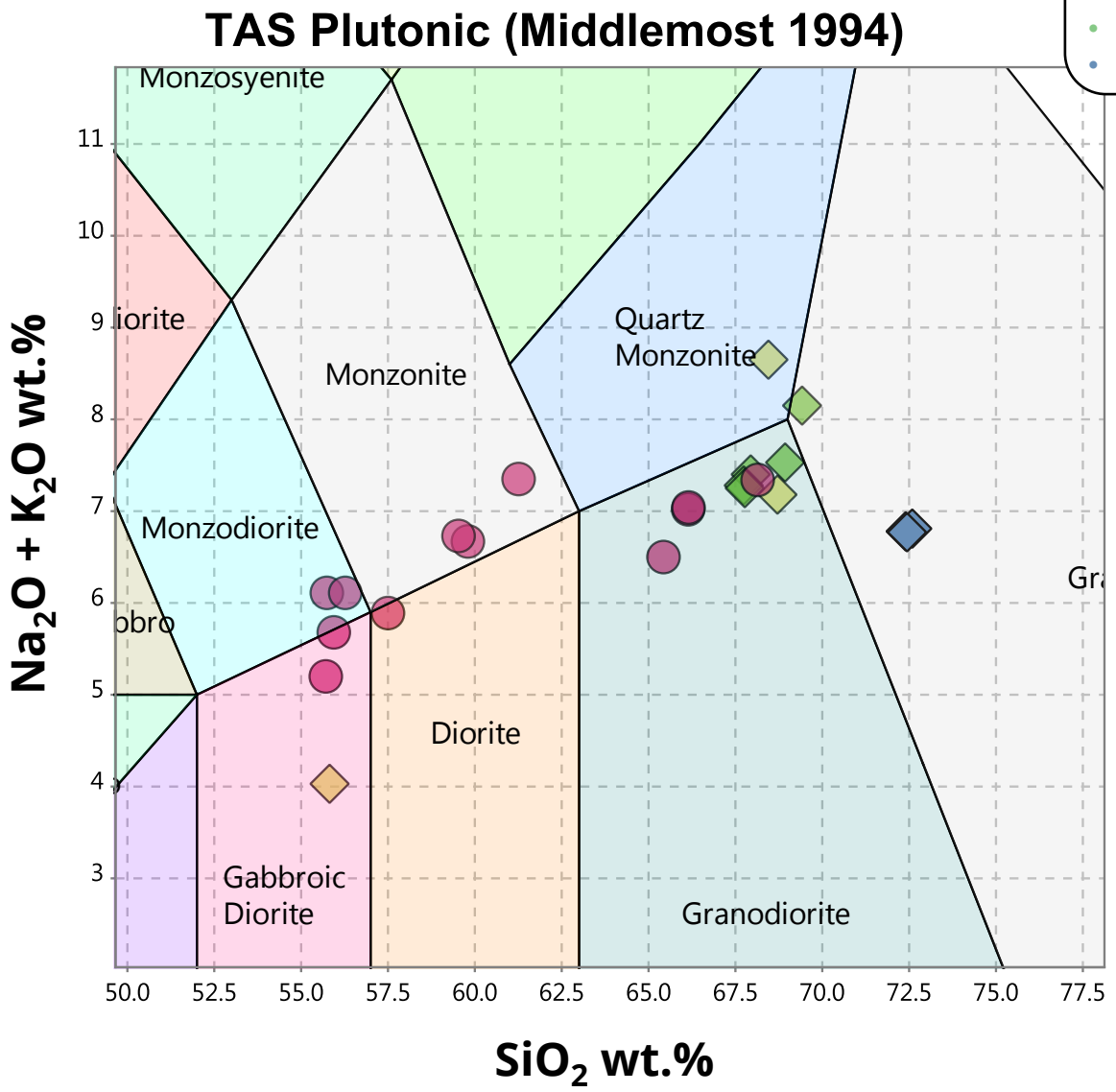
- No intra-sample trend of increasing $Sr/Y_{apatite}$ with differentiation observed

Additional slide. Results – **Whole Rock Geochemistry**

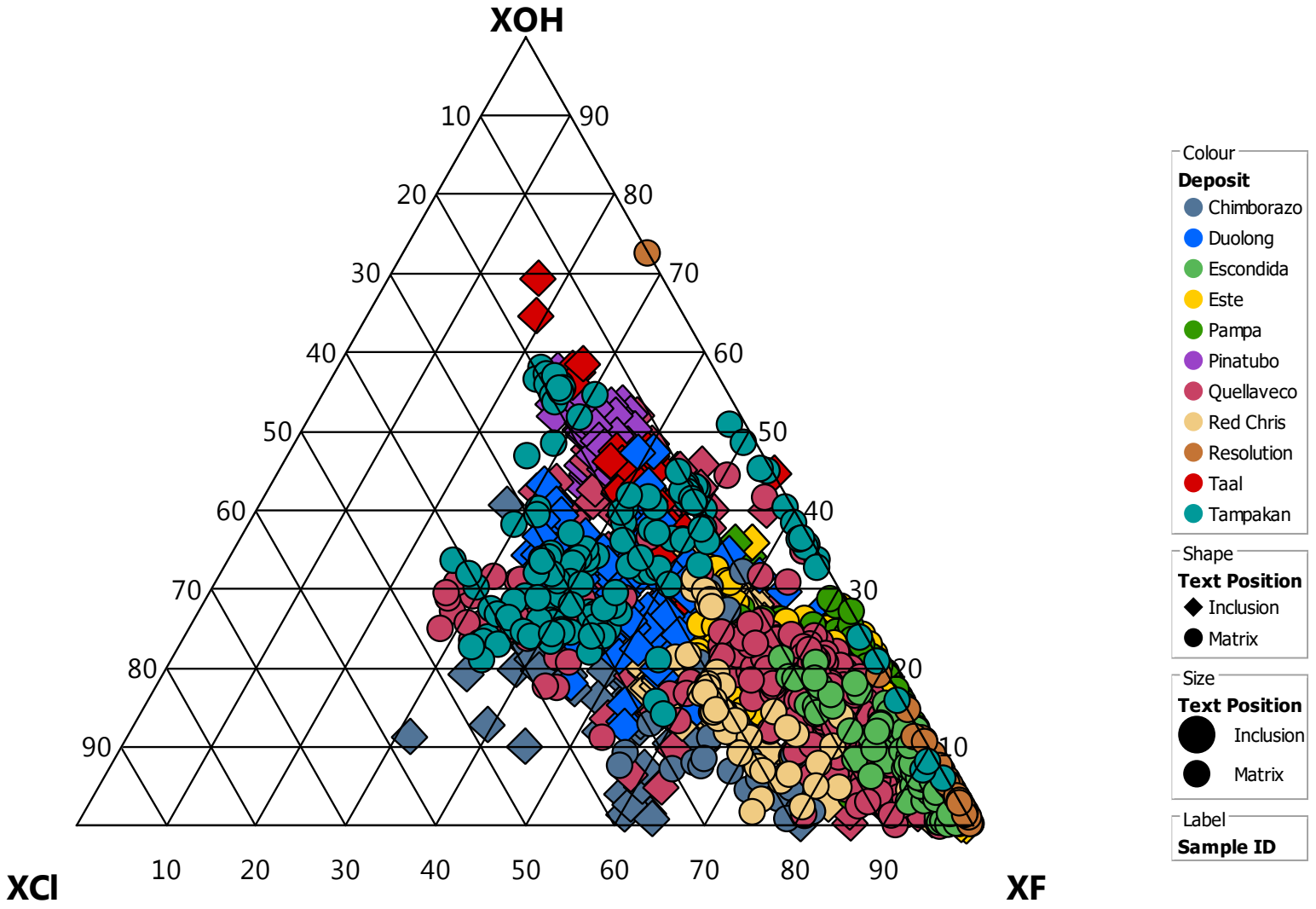
Un-mineralized:
- Chimborazo District

Mineralized:
- Escondida Este
- Pampa Escondida
- Escondida





A look into apatite halogens composition



Colour
Deposit
- Chimborazo
- Duolong
- Escondida
- Este
- Pampa
- Pinatubo
- Quellaveco
- Red Chris
- Resolution
- Taal
- Tampakan

Shape
Text Position
- Inclusion
- Matrix

Size
Text Position
- Inclusion
- Matrix

Label
Sample ID

Additional slide. Apatite mineral chemistry (EPMA)

Un-mineralized:
- Chimborazo District

Mineralized:
- Escondida Este
- Pampa Escondida

apatite inclusions

matrix apatite