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http://doi.org/10.54499/ERA-MIN/0003/2019
http://doi.org/10.54499/ERA-MIN/0005/2019
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ERA-MIN Joint Call 2019 (EU Horizon 2020 ERA-NET Co-fund Project ERA-MIN2, Grant agreement Nº 730238)

Trace element analysis of cassiterite and its effectiveness in the recognition of different provenances

Miguel Gaspar; P. Moita; A. Cravinho; M. Costa; P. Barrulas; M. Beltrane; J. Mirão; P. Reis; I. Martins; A. Mateus; N. Gracio; R. Salgueiro; A. Guedes

Trace element analysis of cassiterite and its effectiveness in the recognition of different provenances

Introduction

- Cassiterite (SnO_2) chemistry (common minor & trace elements)
- Substitution mecanisms
- Factors controlling incorporation of trace elements in Cassiterite

Cassiterite data from Góis-Panasqueira-Segura Sn-W belt

- Cathodoluminescence
- Cassiterite EMPA data (minor/trace elements fingerprints)

Aplication to alluvial cassiterite (Segura)

- Cassiterite EMPA data (minor/trace elements fingerprints)
- Cassiterite LA-ICPMS data (preliminary results on minor/trace elements fingerprints)

Wrap-up

Photo:Tony Peterson

Cassiterite (SnO_2) structure – Substitution mecanisms

Common minor/trace elements

M^{6+} - W

M^{5+} - Nb, Ta, As

M^{4+} - Ti, Hf, Zr, W, Nb, Ta, V, Mn

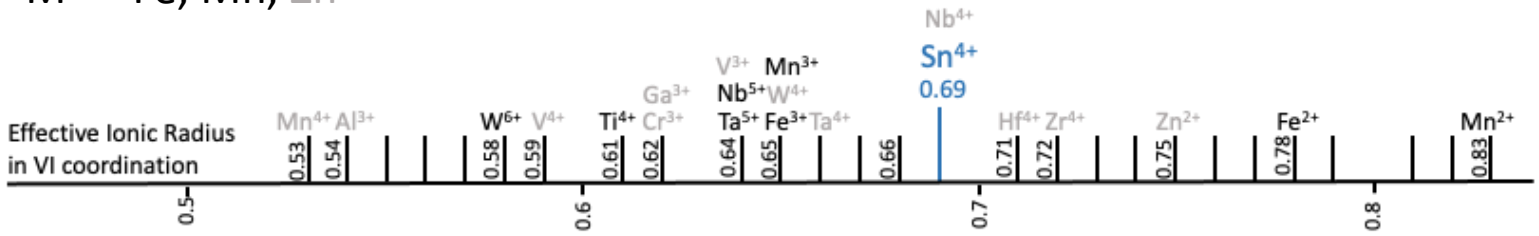
M^{3+} - Fe, Mn, V, Cr, Sc, Ga, Al

M^{2+} - Fe, Mn, Zn

What controls minor/trace elements content?

Crystal chemistry

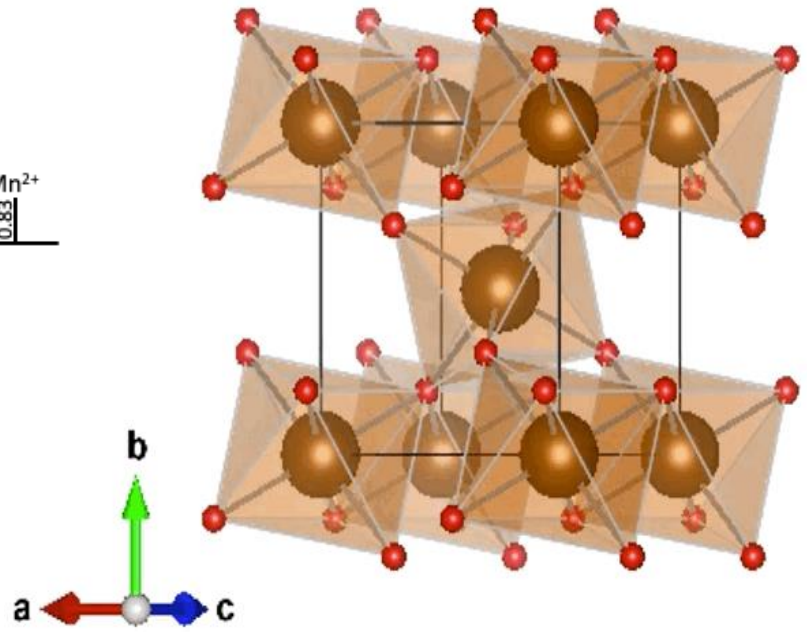
Effective ionic radius



Thermodynamics

Nearest neighbour interactions
Polyhedral distortion
Enthalpy of mixing

MO_2 – rutile (TiO_2) structure

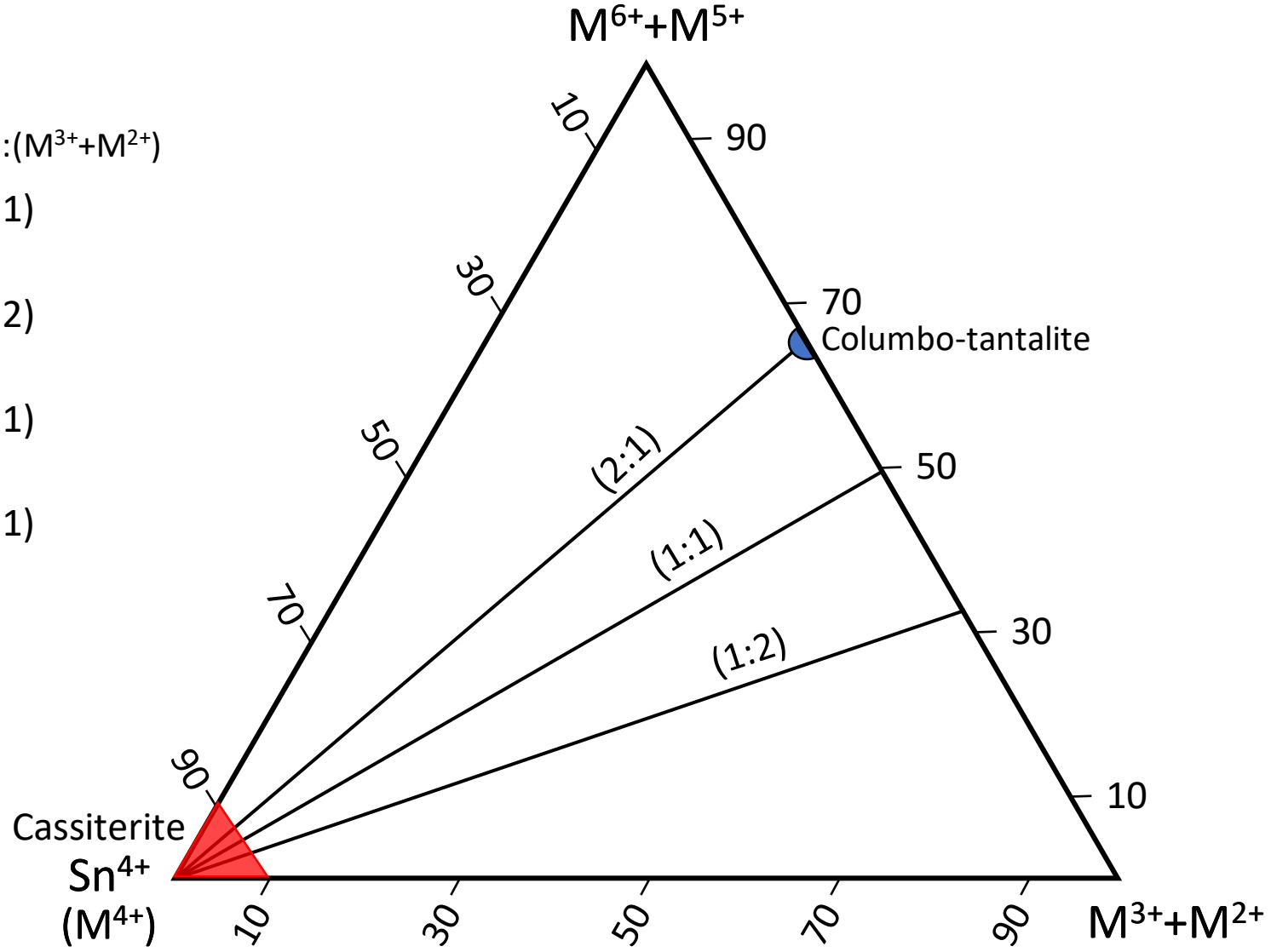


Cassiterite - Substitution mecanisms

Substitution mechanisms

	$(M^{6+}+M^{5+}):(M^{3+}+M^{2+})$
$M^{6+} + M^{2+} \leftrightarrow 2Sn^{4+}$	(1:1)
$M^{6+} + 2M^{3+} \leftrightarrow 3Sn^{4+}$	(1:2)
$M^{5+} + M^{3+} \leftrightarrow 2Sn^{4+}$	(1:1)
$2M^{5+} + M^{2+} \leftrightarrow 3Sn^{4+}$	(2:1)
$M^{4+} \leftrightarrow Sn^{4+}$	
$M^{3+} + OH^{-} \leftrightarrow Sn^{4+} + O^{2-}$	

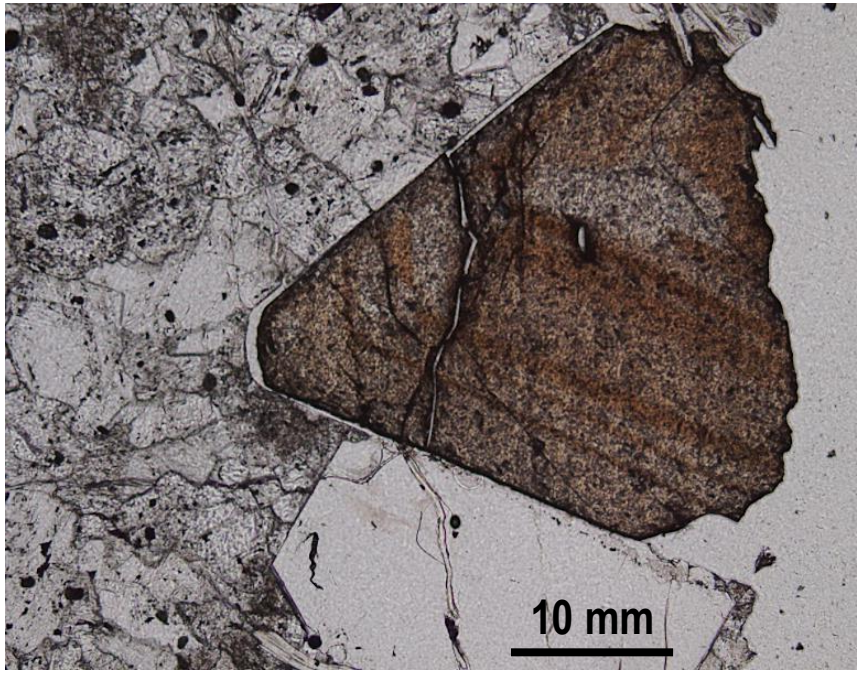
If we assume no vacancies!



Factors Controlling Incorporation of Trace Elements in Cassiterite

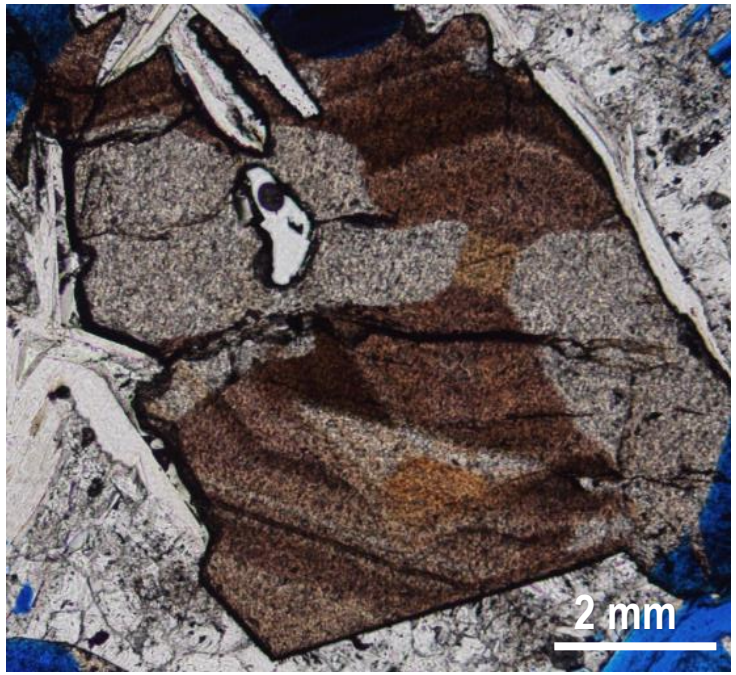
Crystal growth/kinetics

Oscillatory zoning



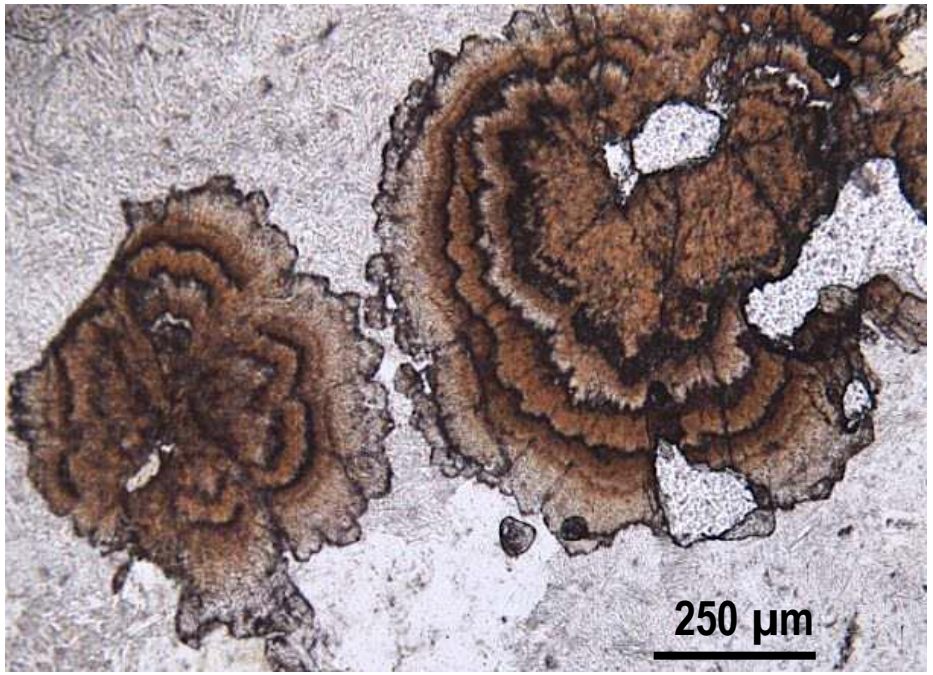
Qz vein (Panasqueira) Photo: Ivo Martins

Sector zoning/crystal forms



Qz vein (Panasqueira) Photo: Ivo Martins

Fast growing/oscillatory zoning



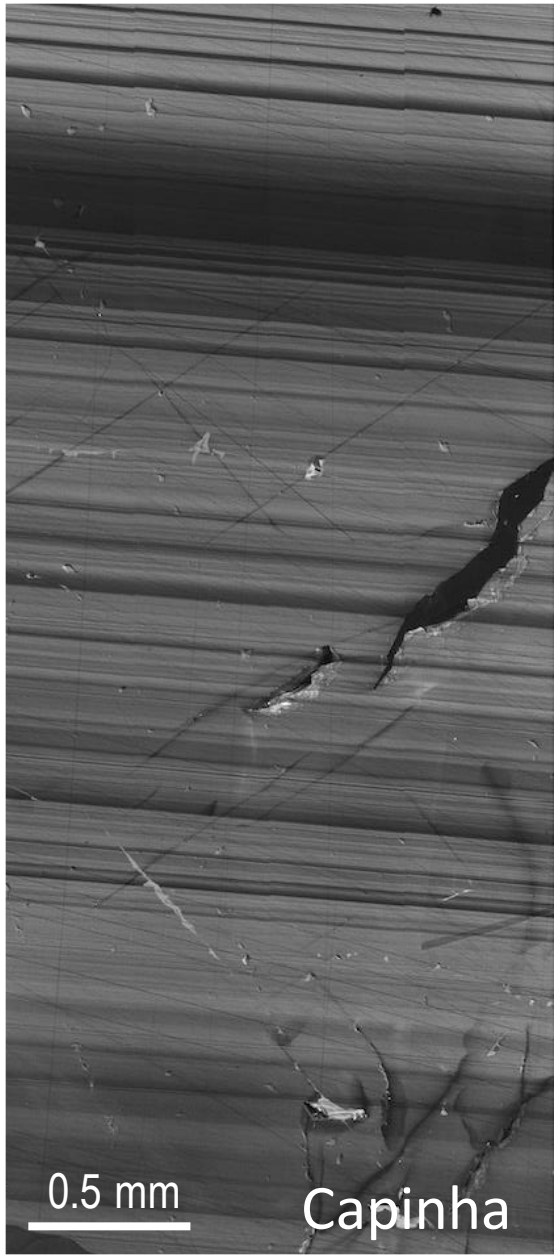
Aplite (Góis) Photo: Frederico Martins

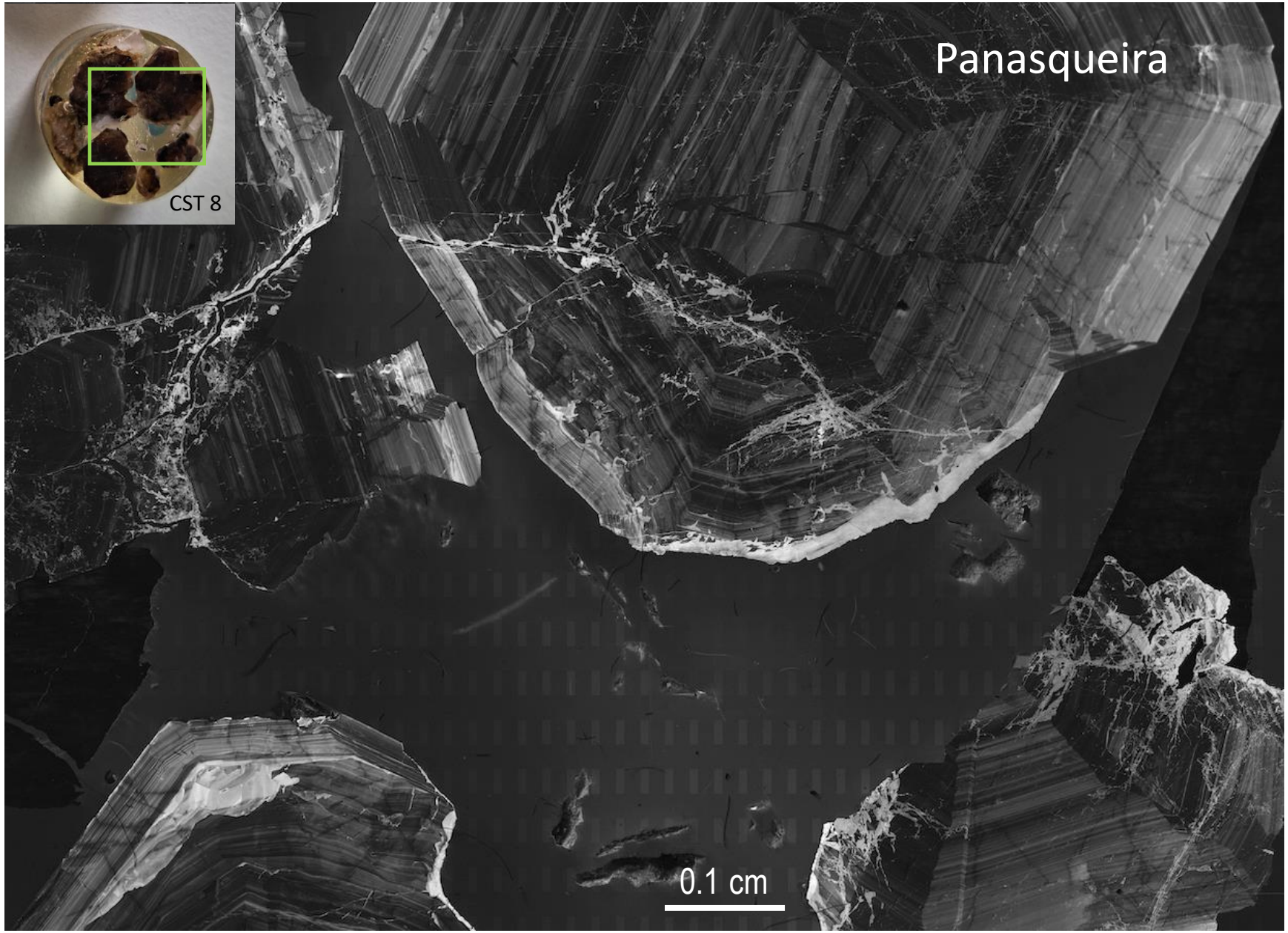
External factors

P, T, μ (chemical potentials-element availability; dependent on competing mineral species), diffusion rates.

Compositions can also change due to alteration!

Cathodoluminescence (CL) Imaging





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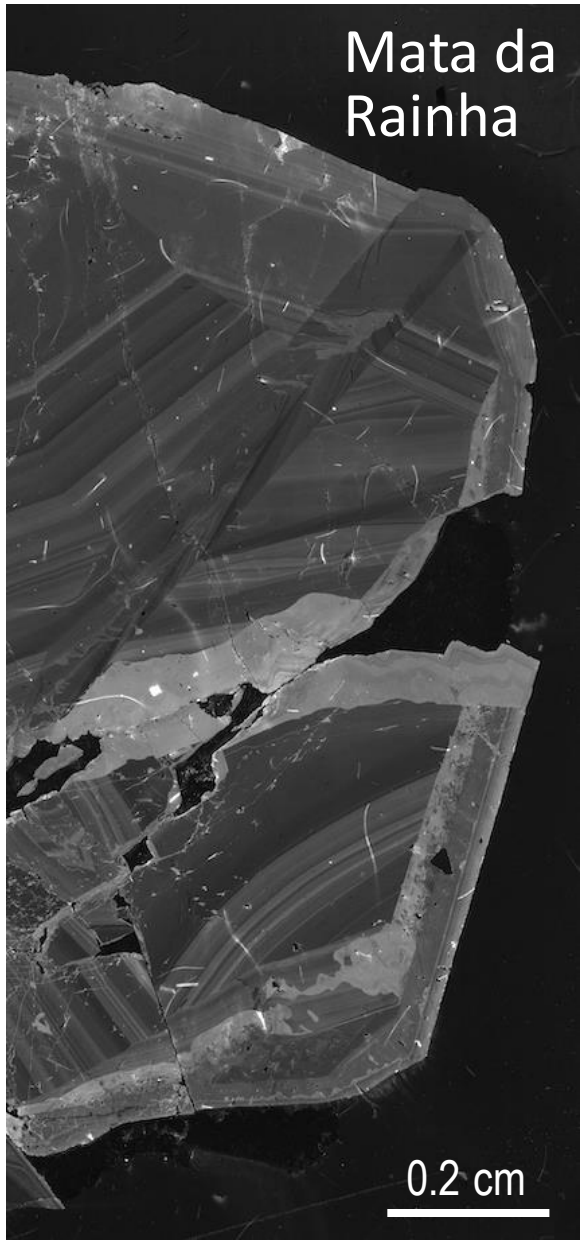
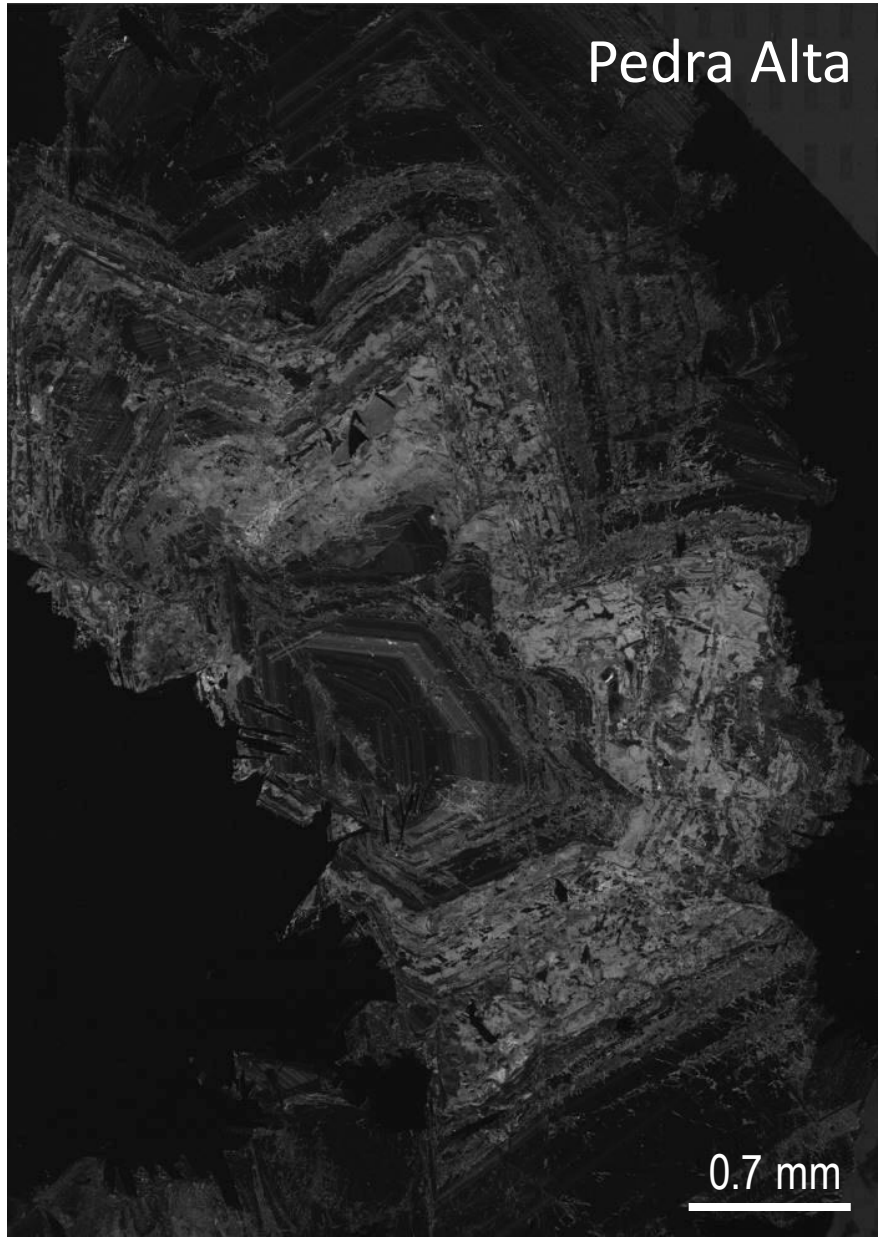
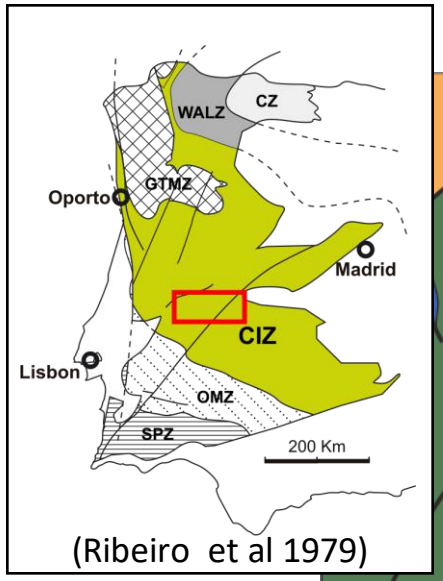
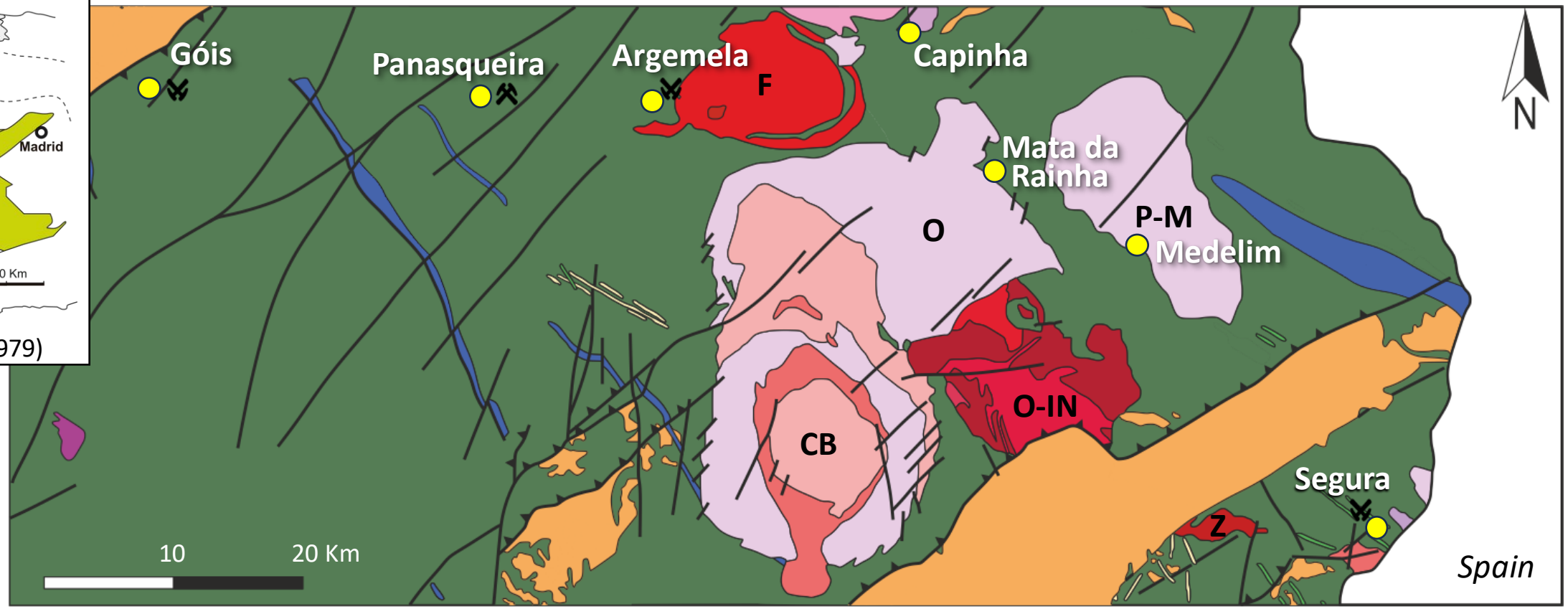




Góis-Panasqueira-Segura Sn-W belt (Central Portugal)



(Ribeiro et al 1979)



Variscan Granites

Ordovician Granites

Cadomian Granites

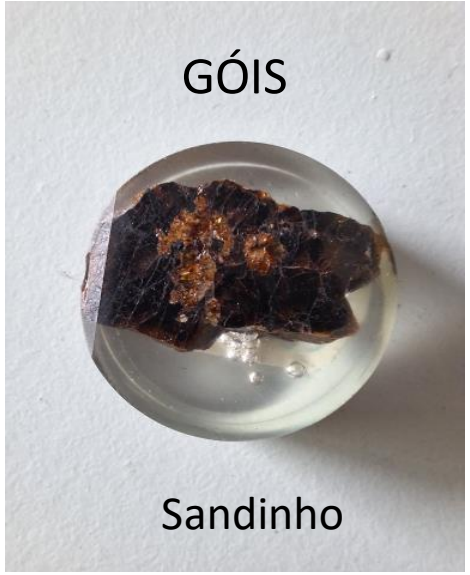
Ordovician Metasediments

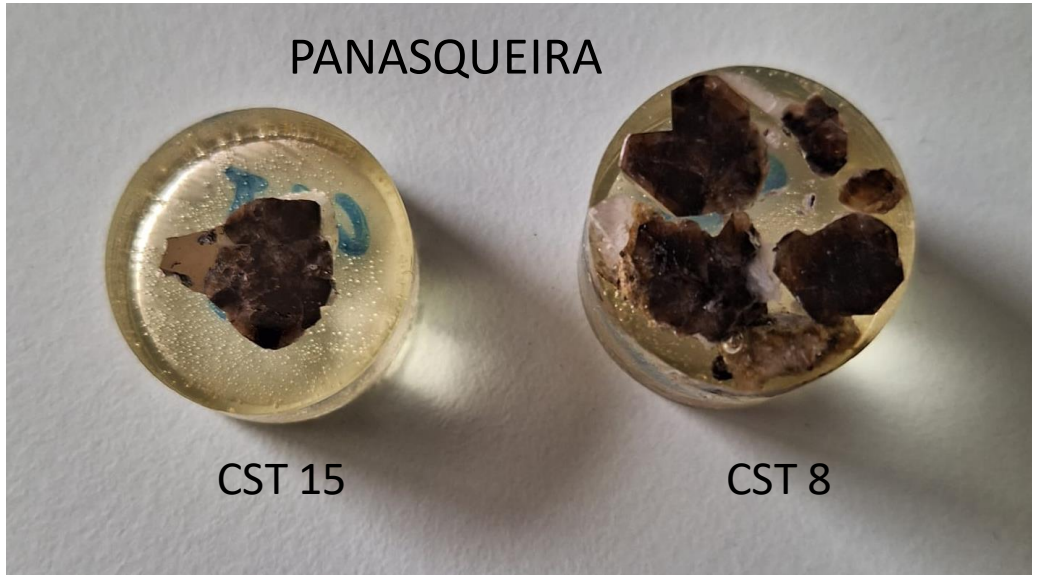
Ante-Ordovician Metasediments (Beiras Group)

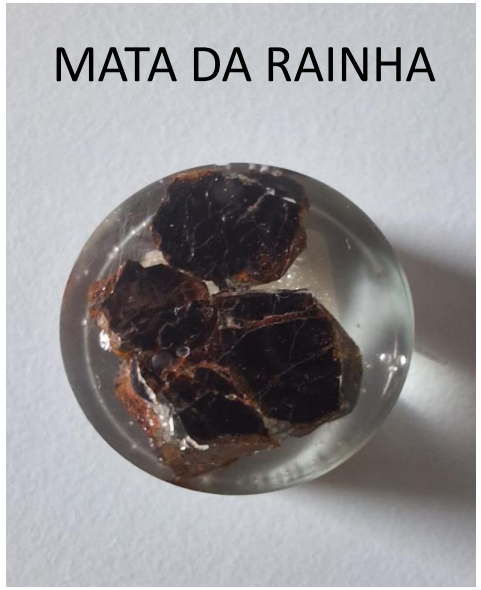
Tertiary deposits

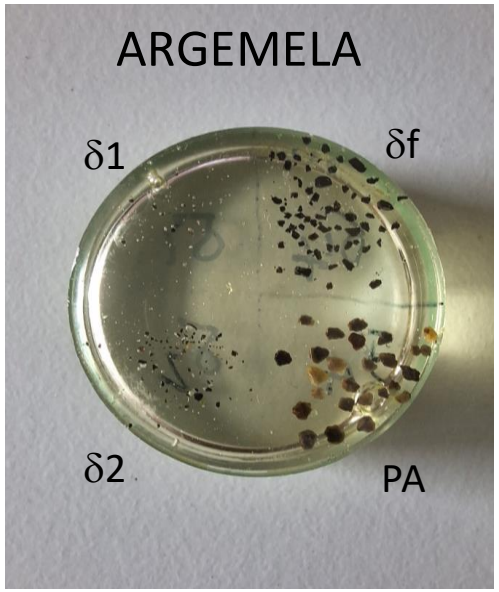
(Mostmeg 2020)

Cassiterite Mounts









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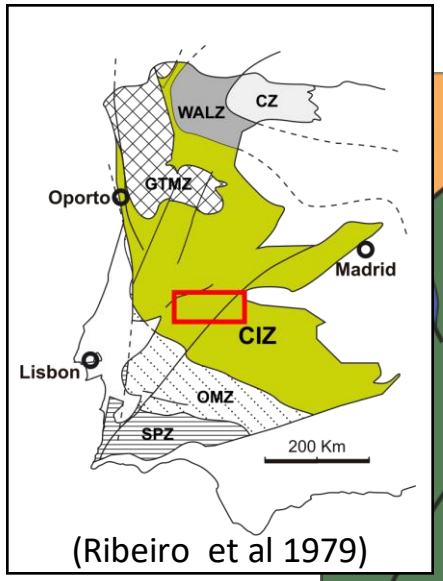

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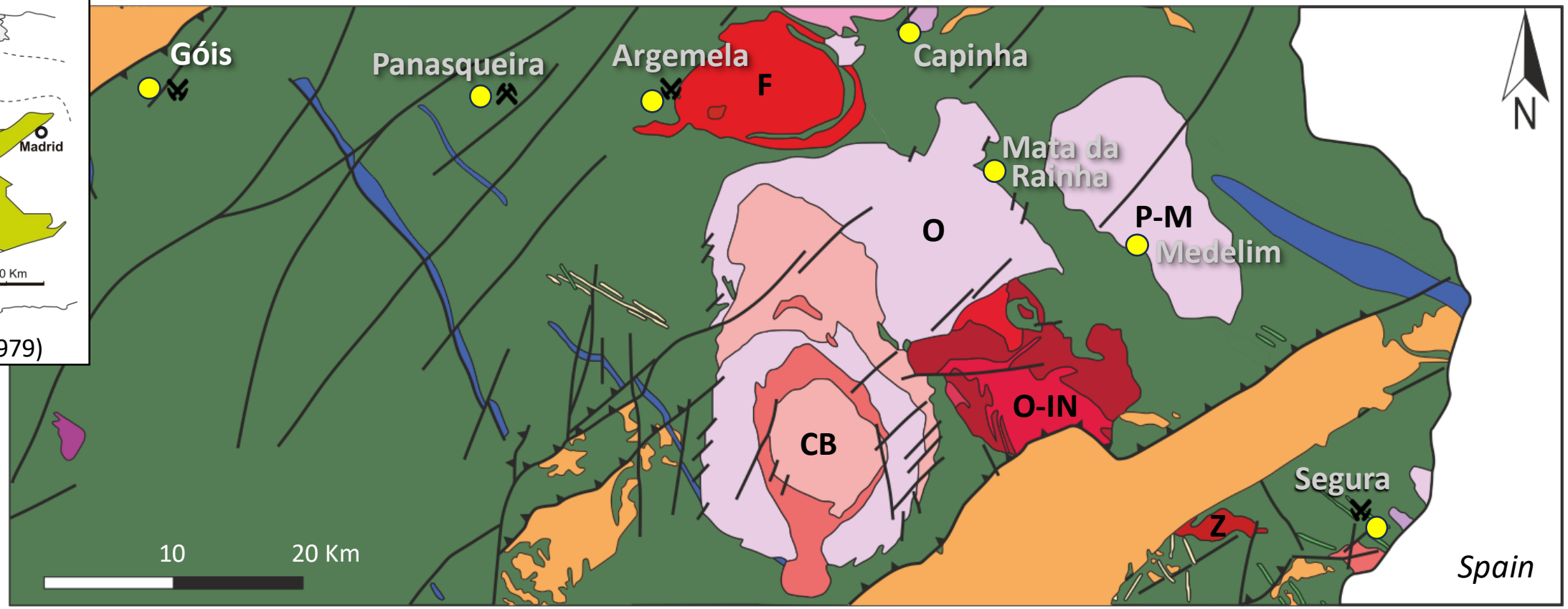

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Tertiary deposits

(Mostmeg 2020)

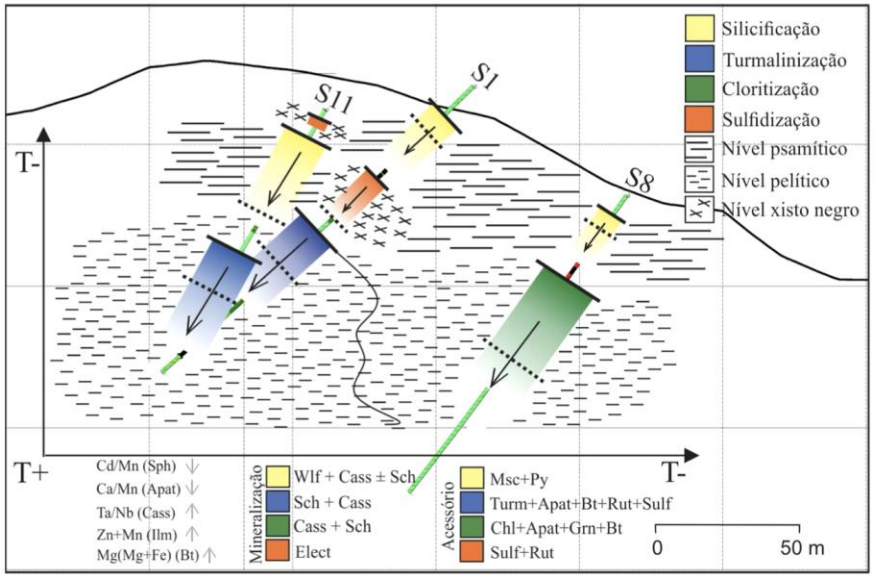
GÓIS

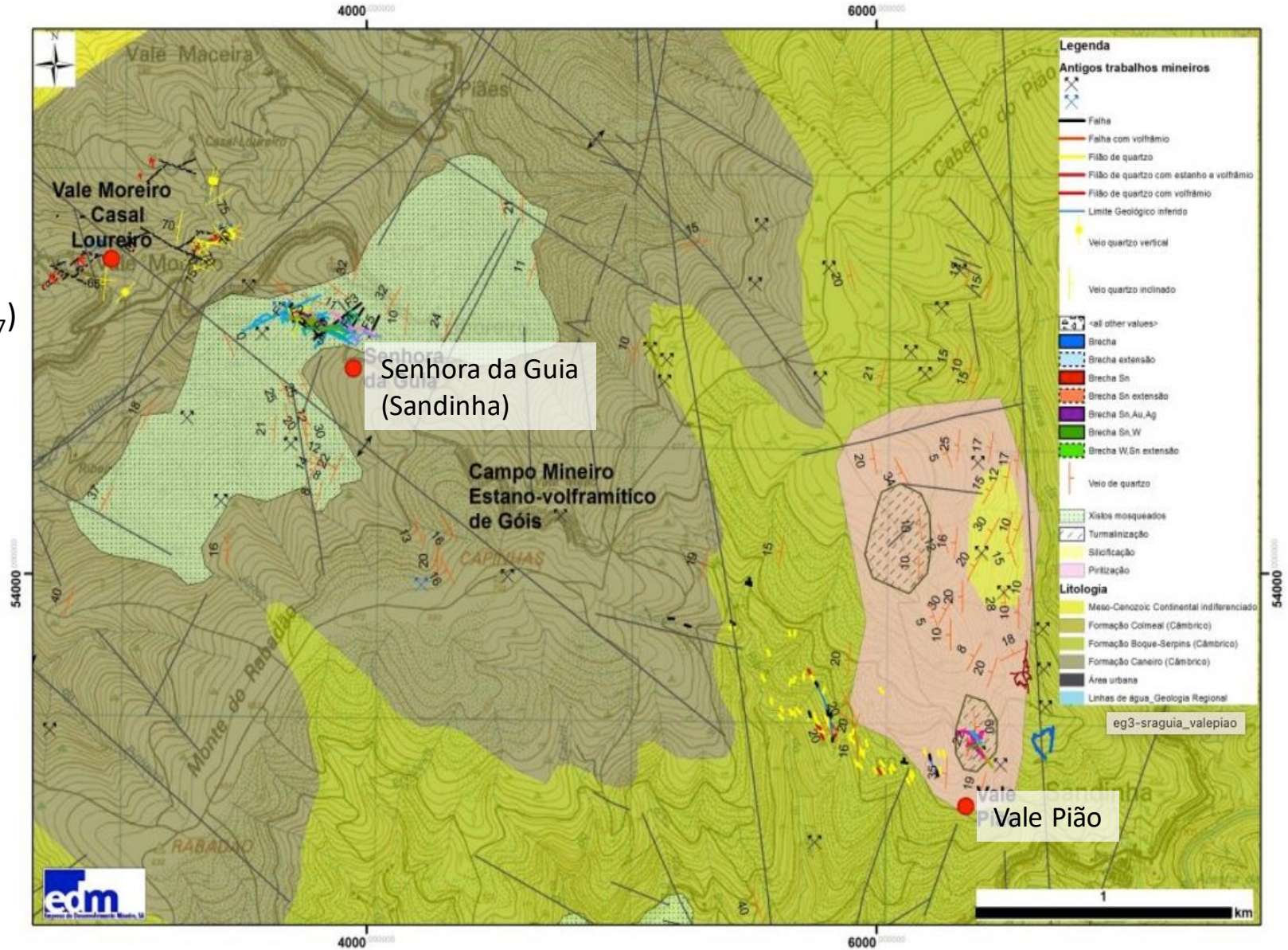
Senhora da Guia (Sandinha)

- Qz veins (Cst + W)

Vale Pião (F. Martins, 2017; I. Fernandes, 2020)

- Qz veins (Cst + W)
- Aplite (Cst + W + Li-mica + Au)
- Calcsilicate veins (Cst + garnet-$Gr_{33}Sps_{30}Alm_{27}$)
- Disseminated in metasomatized SCG (silicification/sulfides - W)





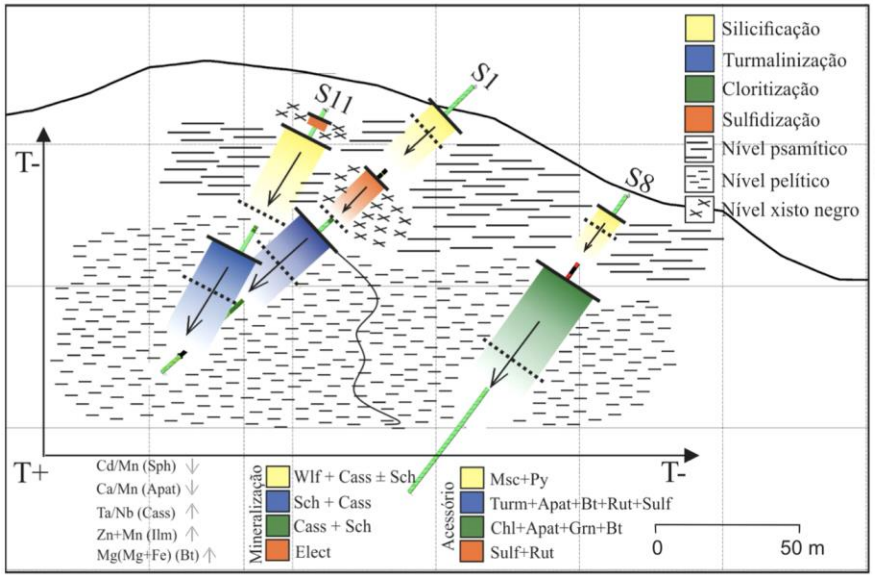
GÓIS

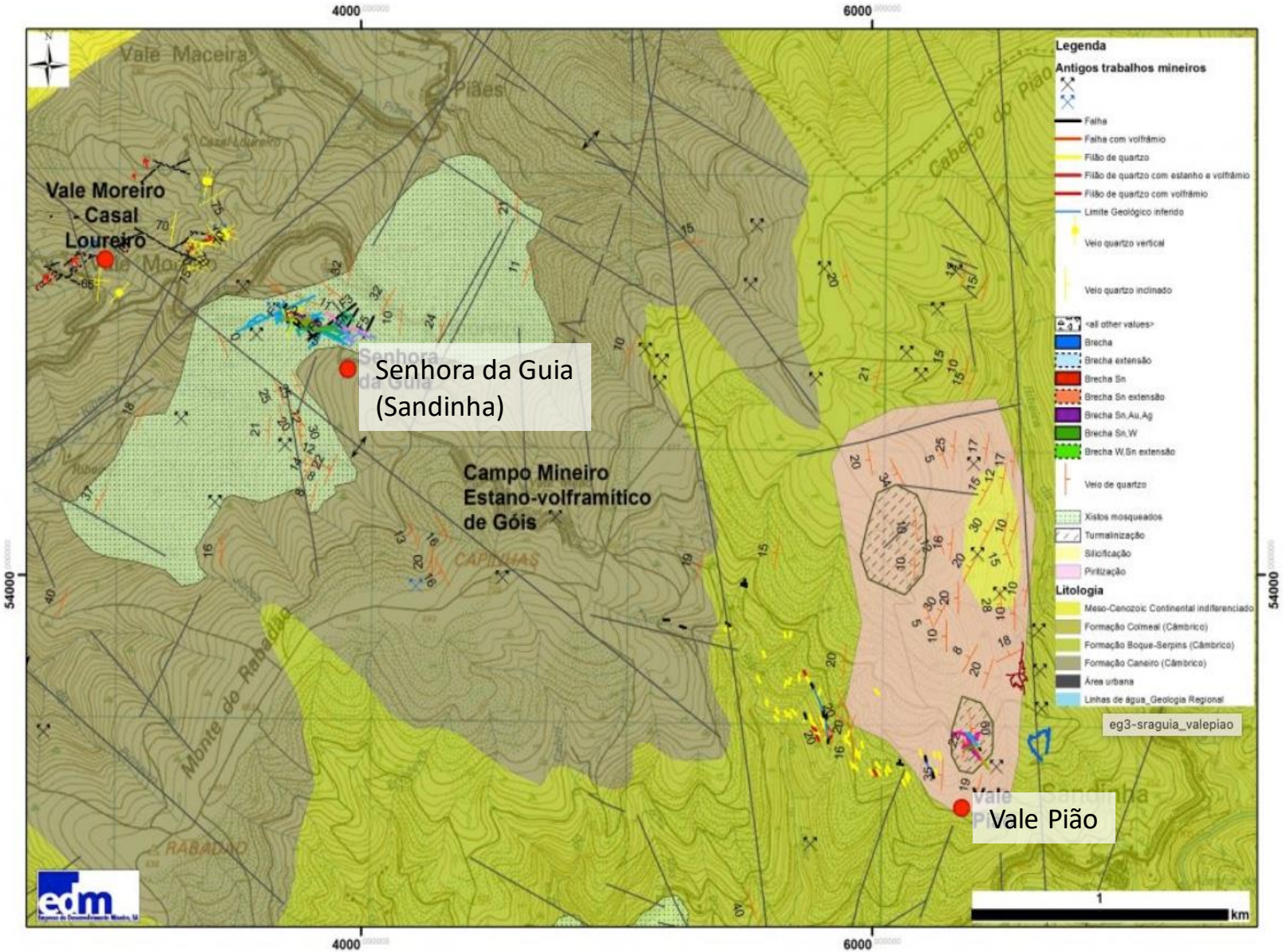
Senhora da Guia (Sandinha)

- Qz veins (Cst + W)

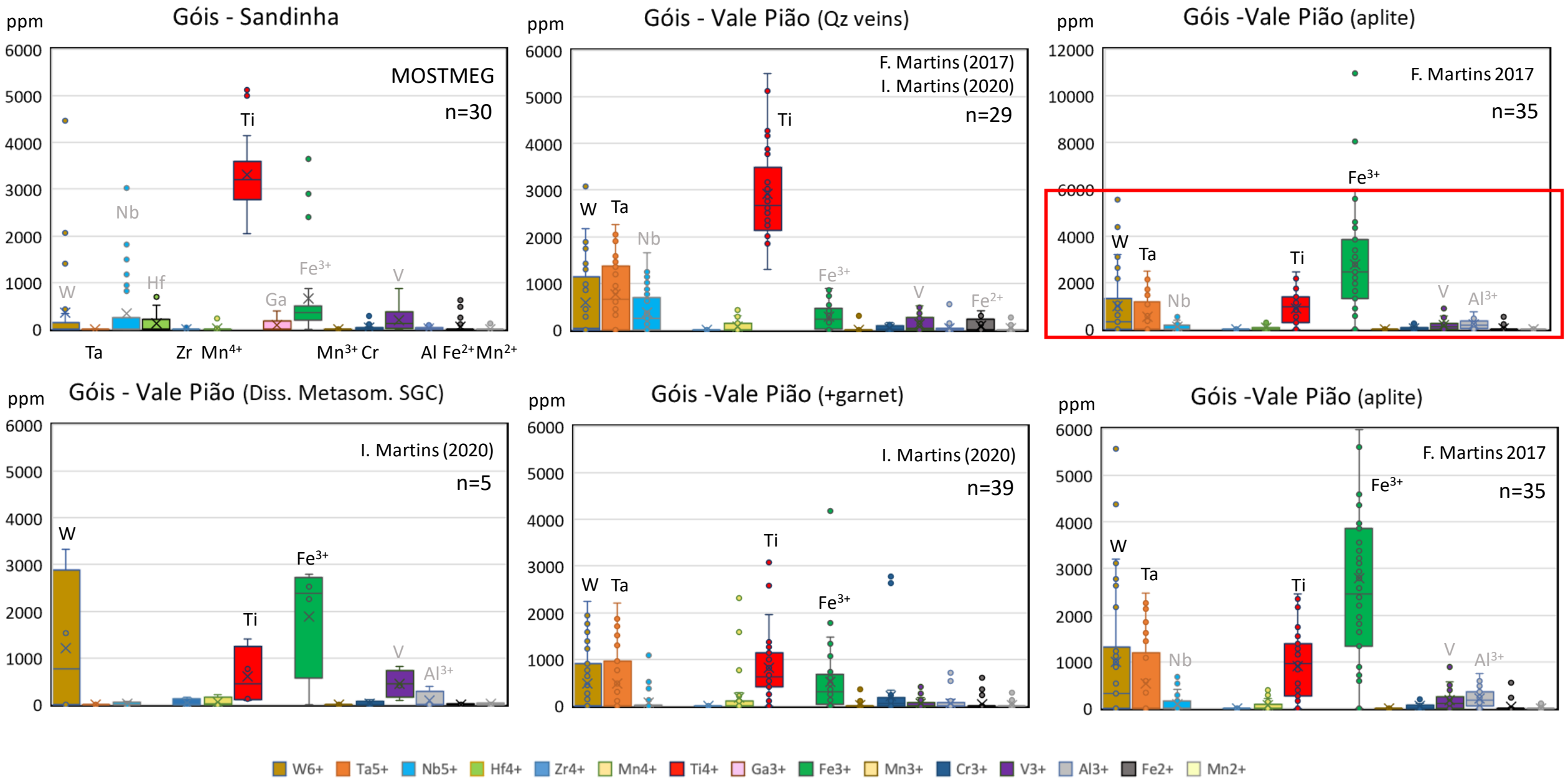
Vale Pião (F. Martins, 2017; I. Fernandes, 2020)

- Qz veins (Cst + W)
- Aplite (Cst + W + Li-mica + Au)
- Some people will call this “Skarns”
- Disseminated in metasomatized SCG (silicification/sulfides - W)





Cassiterite – Electron Microprobe Analyses (EMPA)



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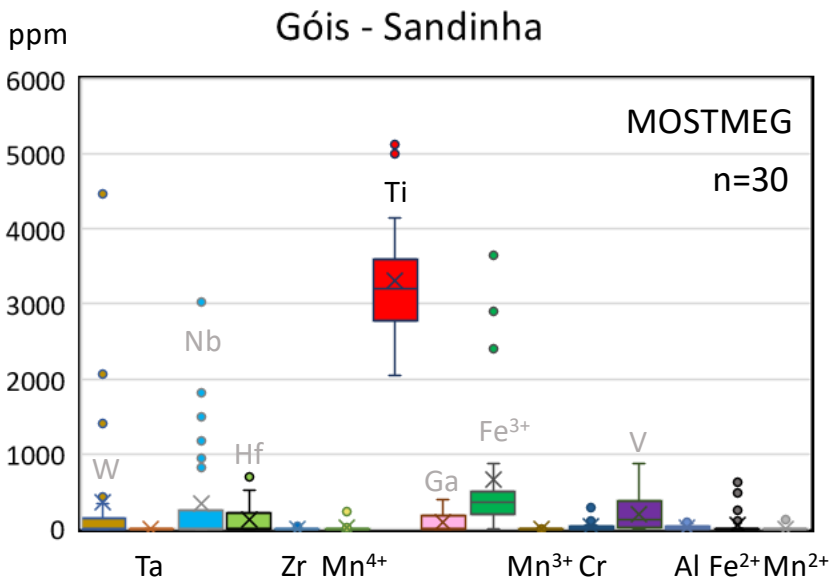

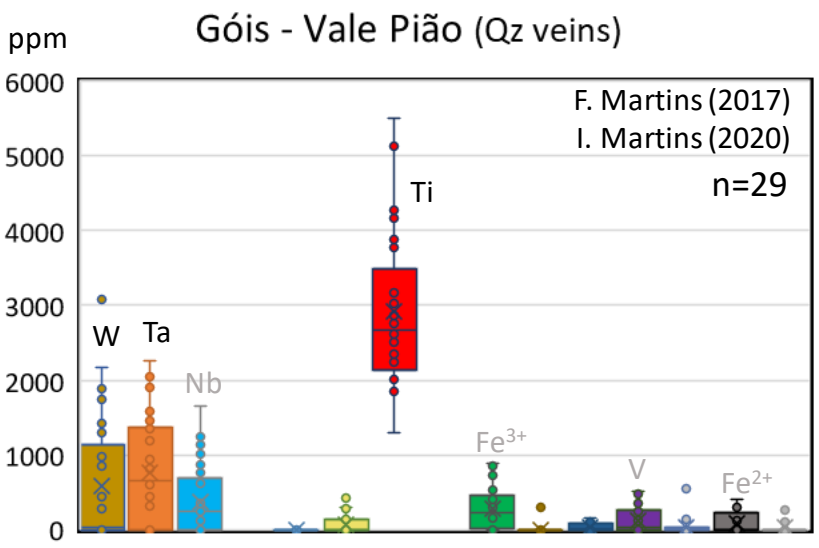

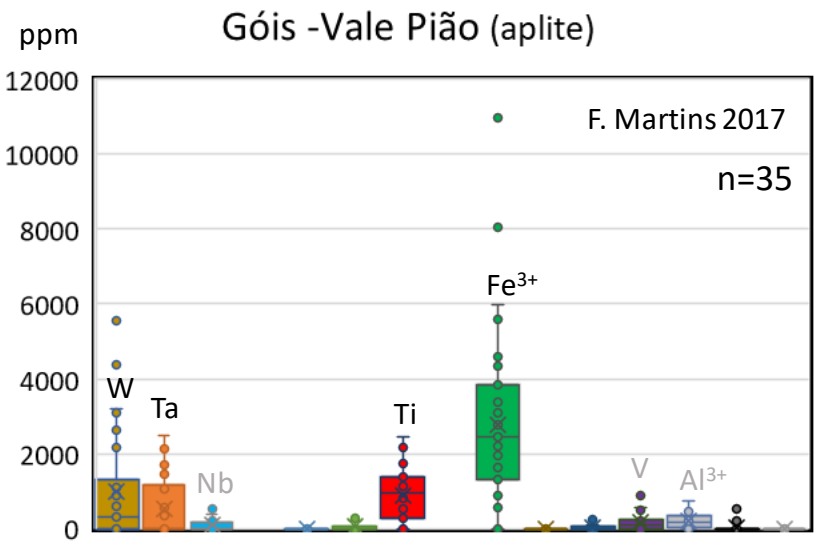

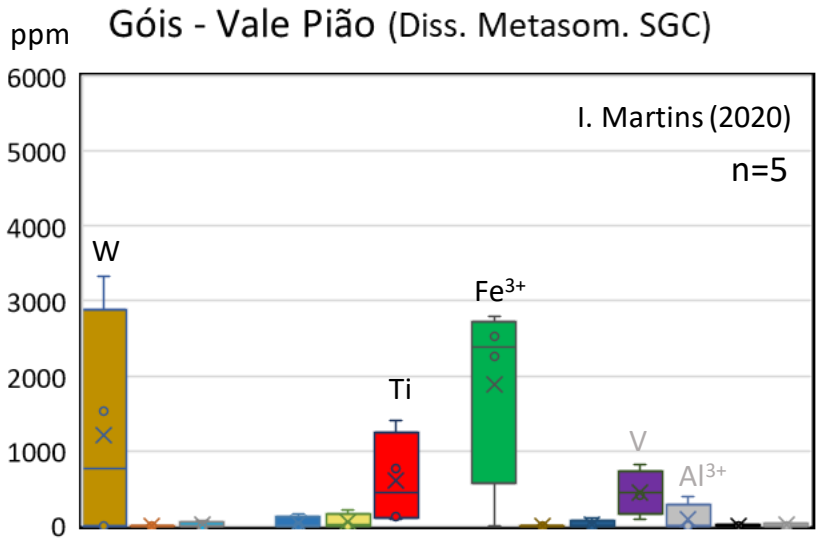

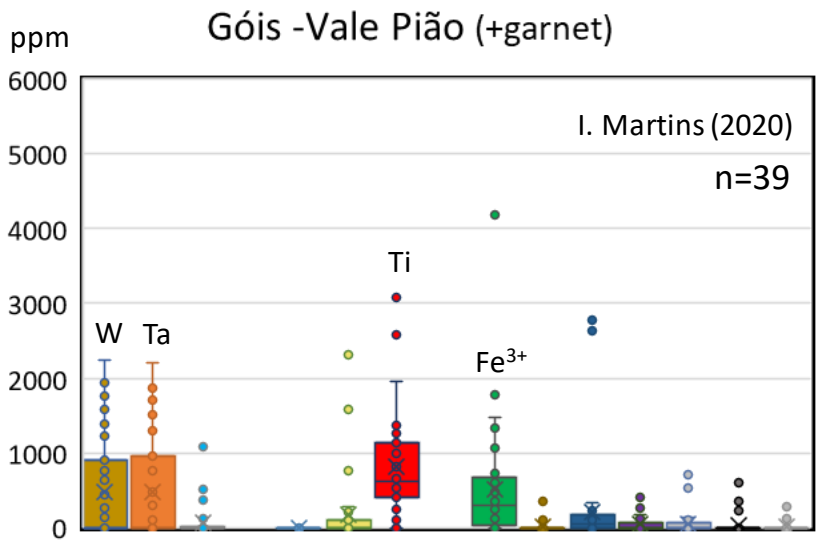

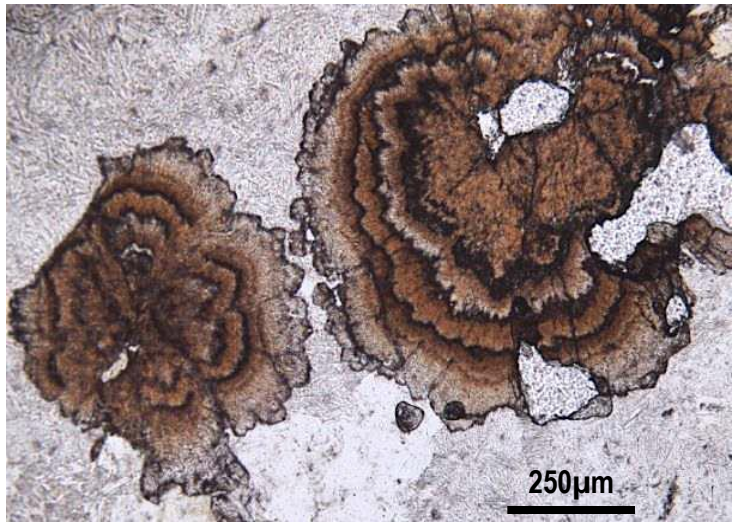

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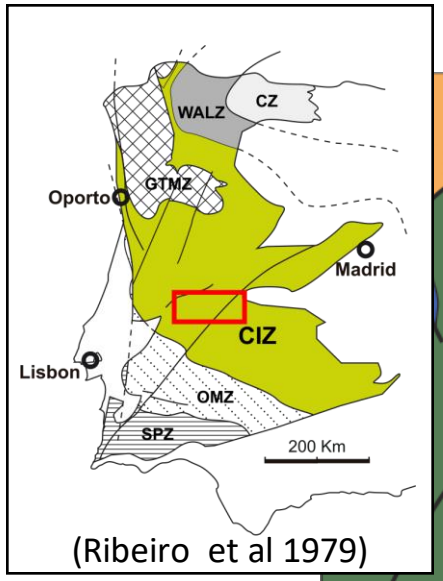
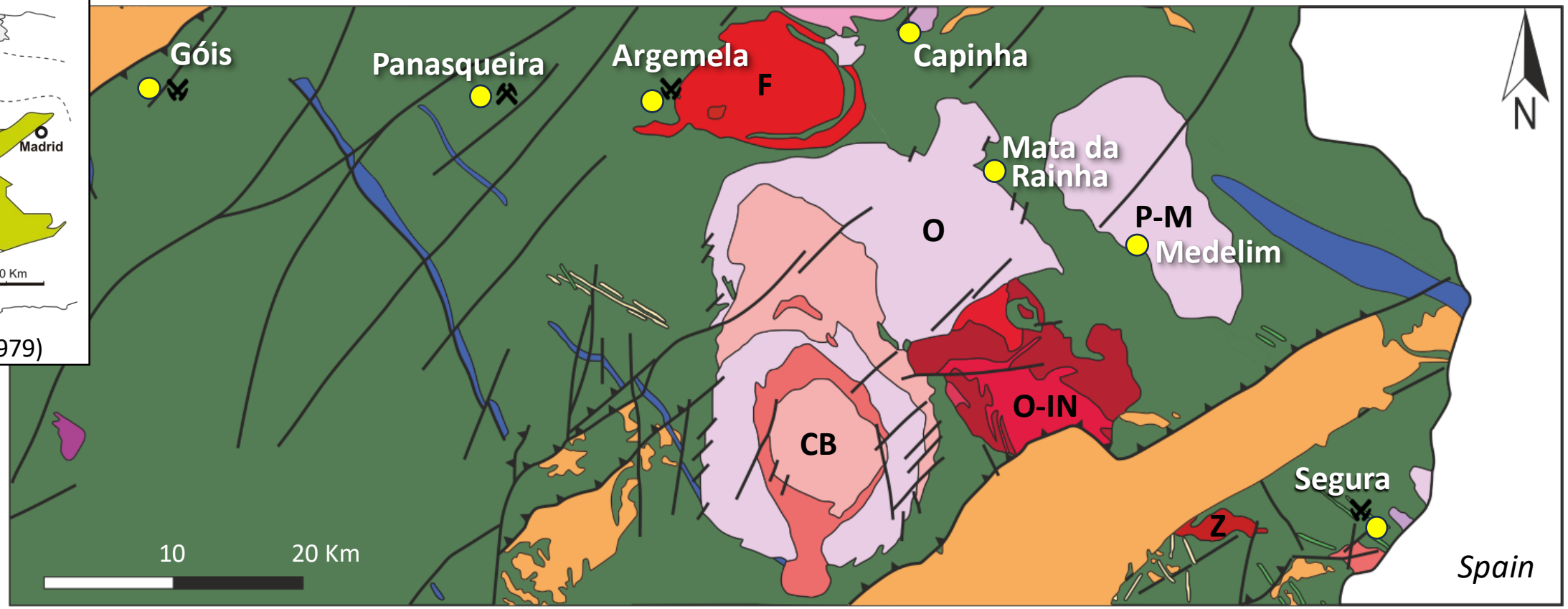


(Ribeiro et al 1979)



Variscan Granites

Ordovician Granites

Cadomian Granites

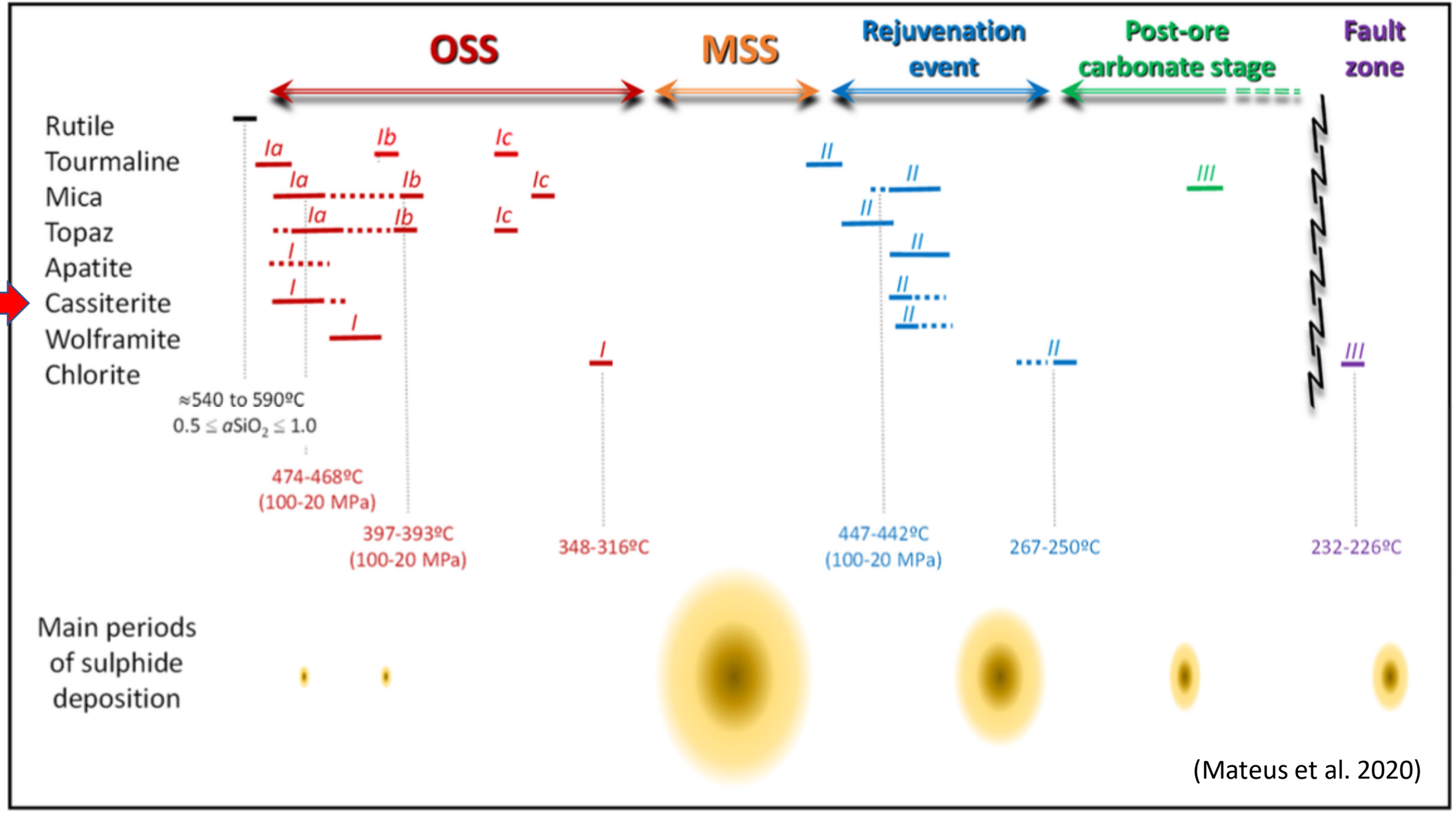
Ordovician Metasediments

Ante-Ordovician Metasediments (Beiras Group)

Tertiary deposits

(Mostmeg 2020)

Simplified paragenitic sequence of Panasqueira deposit



(Mateus et al. 2020)

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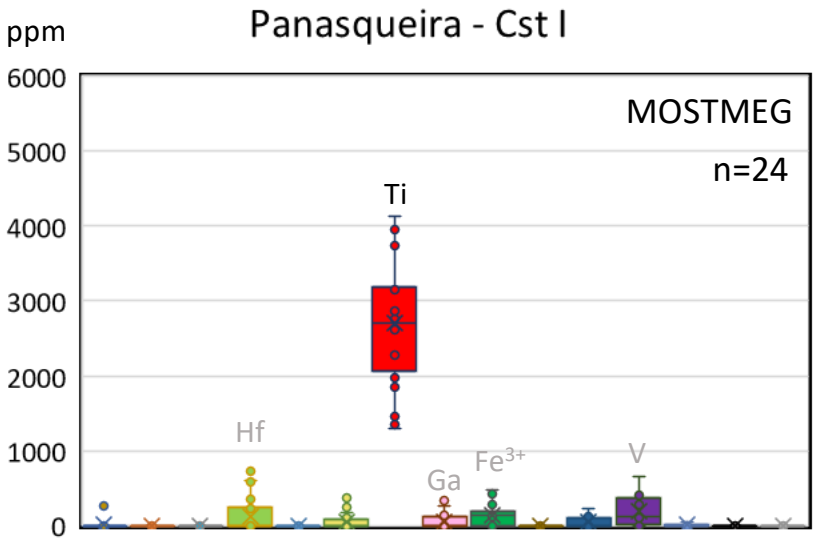

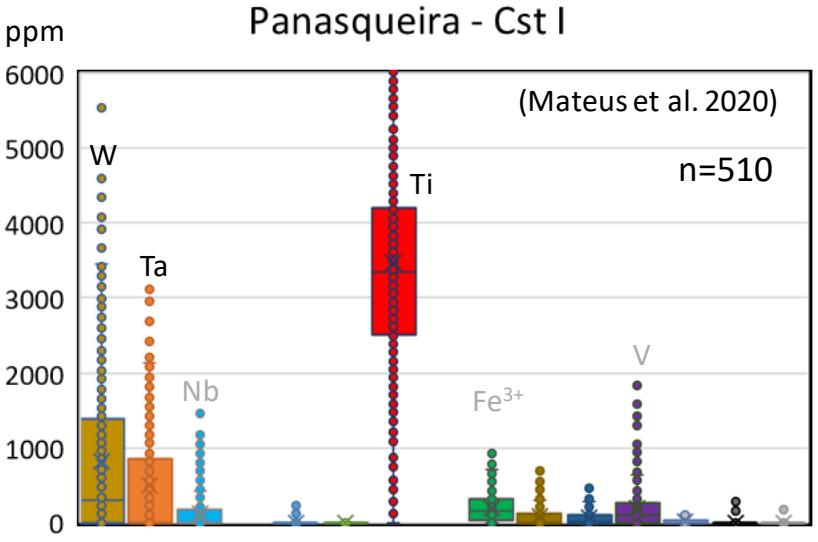

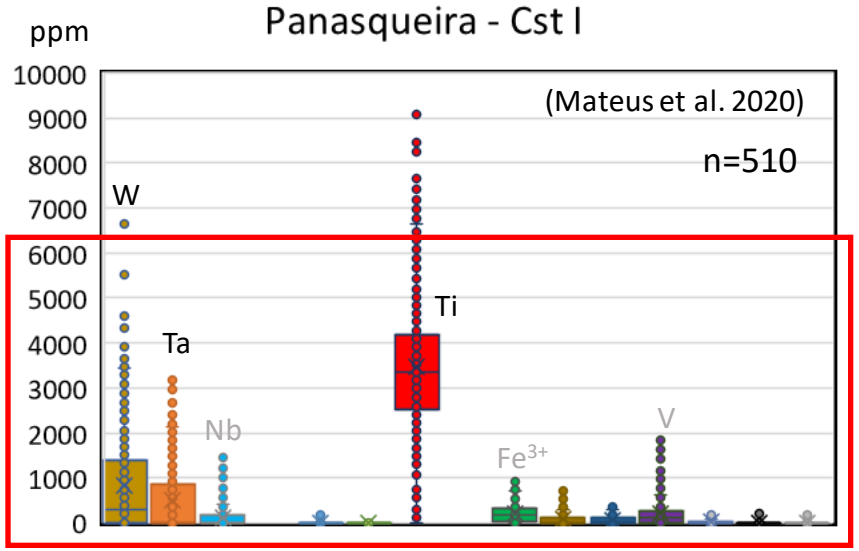

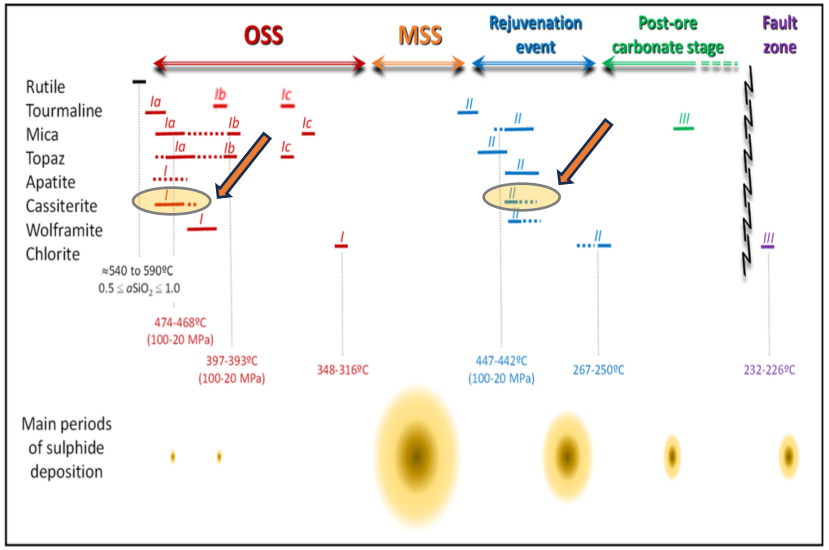

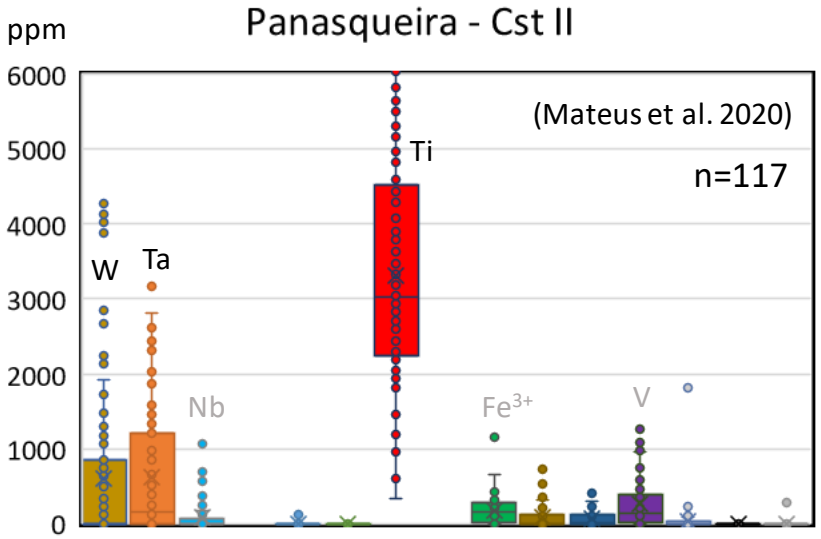

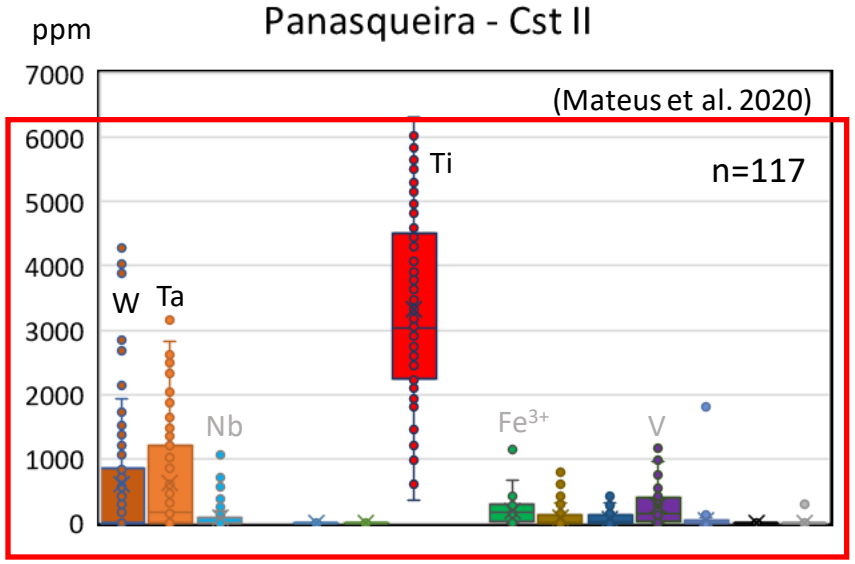

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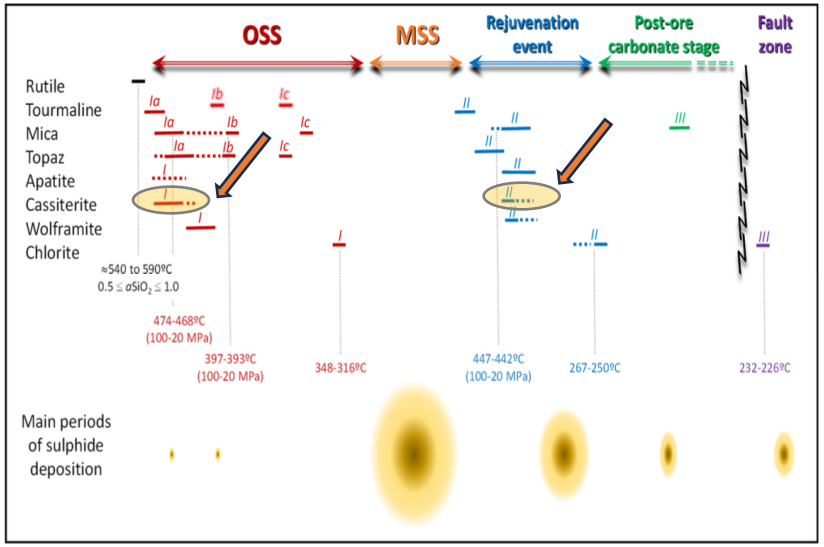

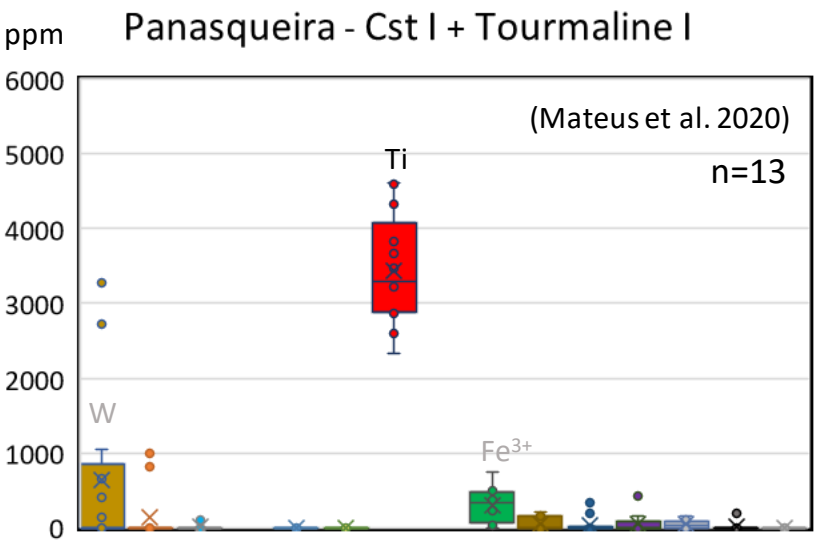

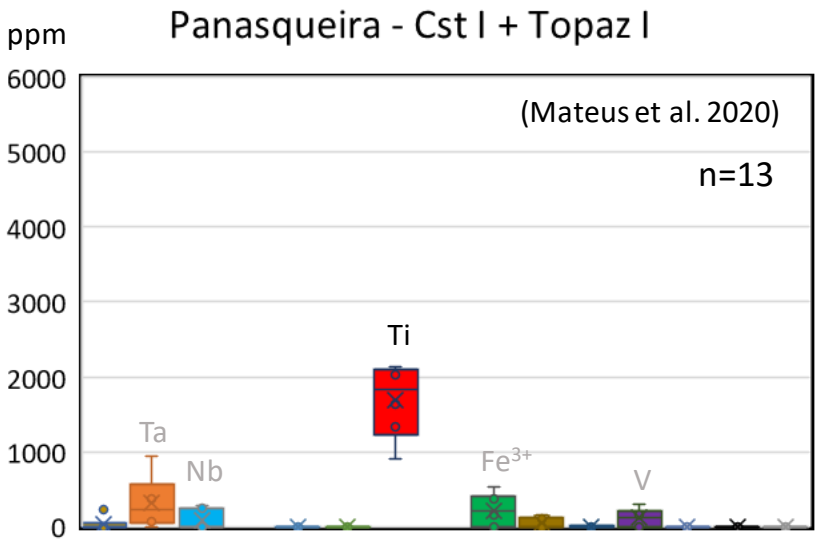

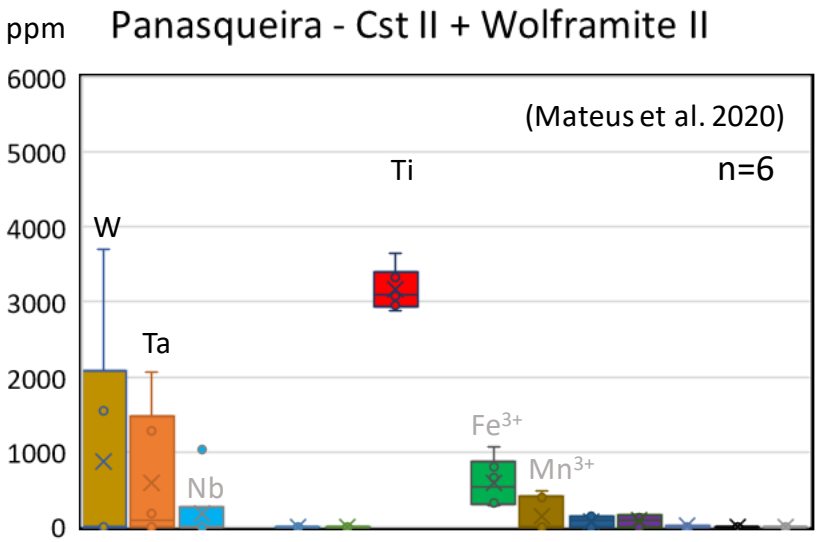

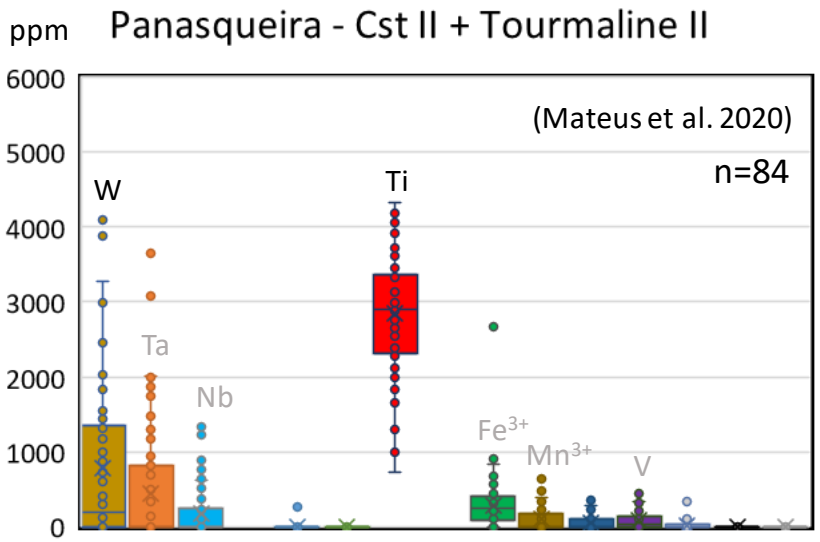

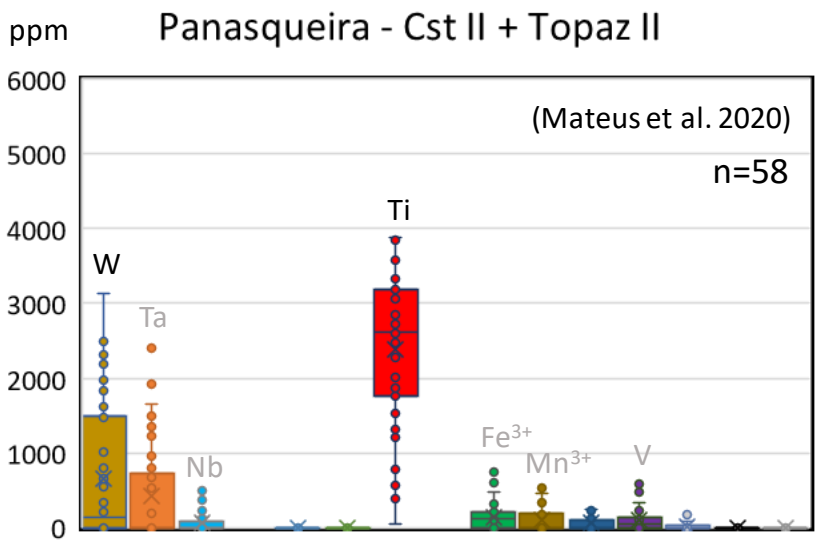

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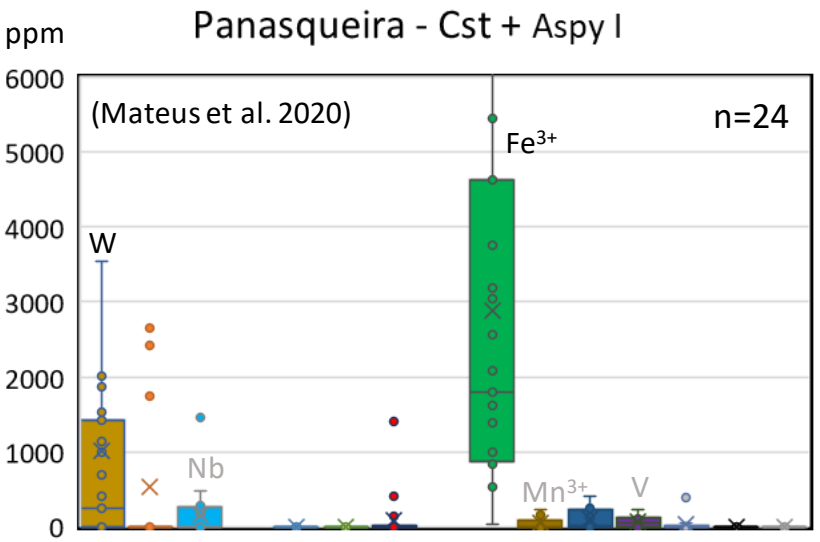
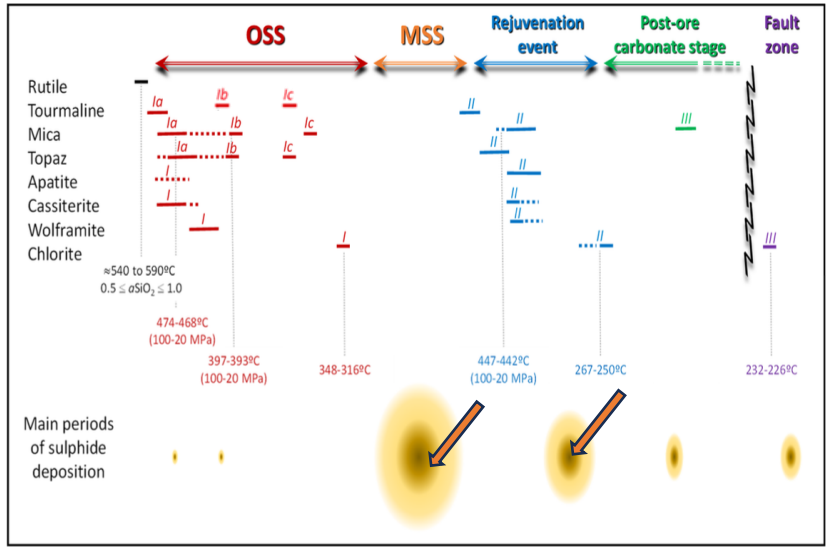
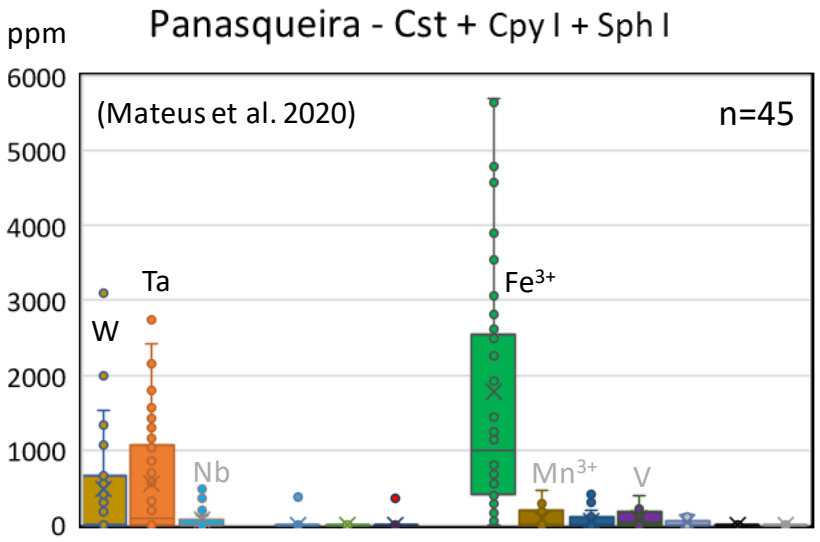
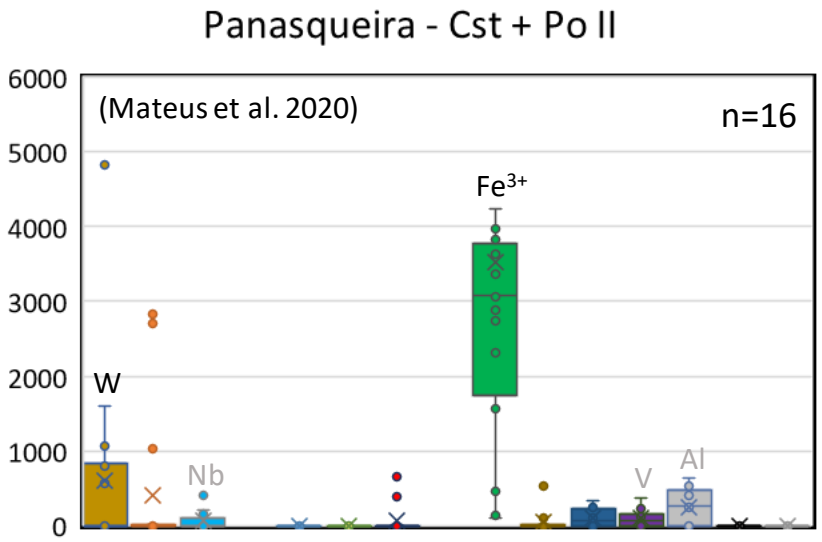
Cassiterite – Electron Microprobe Analyses (EMPA)







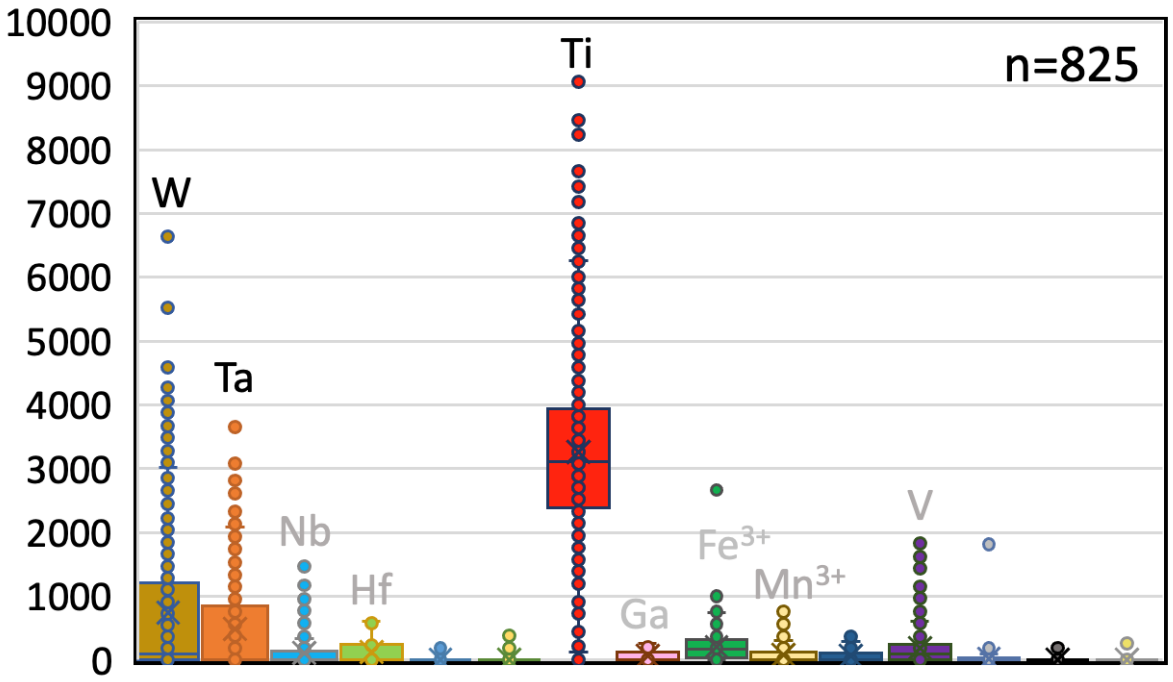


W6+ Ta5+ Nb5+ Hf4+ Zr4+ Mn4+ Ti4+ Ga3+ Fe3+ Mn3+ Cr3+ V3+ Al3+ Fe2+ Mn2+

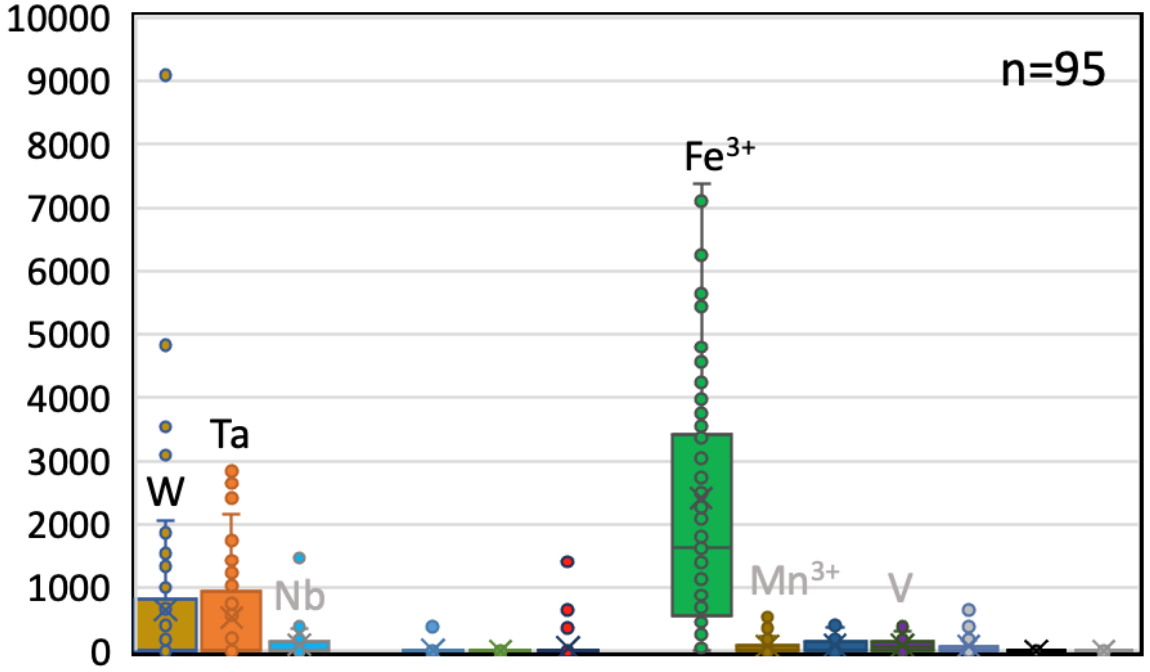
Cassiterite – Electron Microprobe Analyses (EMPA)

Panasqueira

Oxide stage Cassiterite

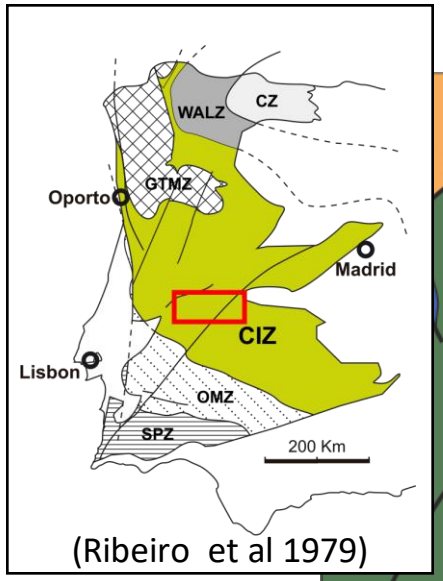


Cassiterite + Sulfides

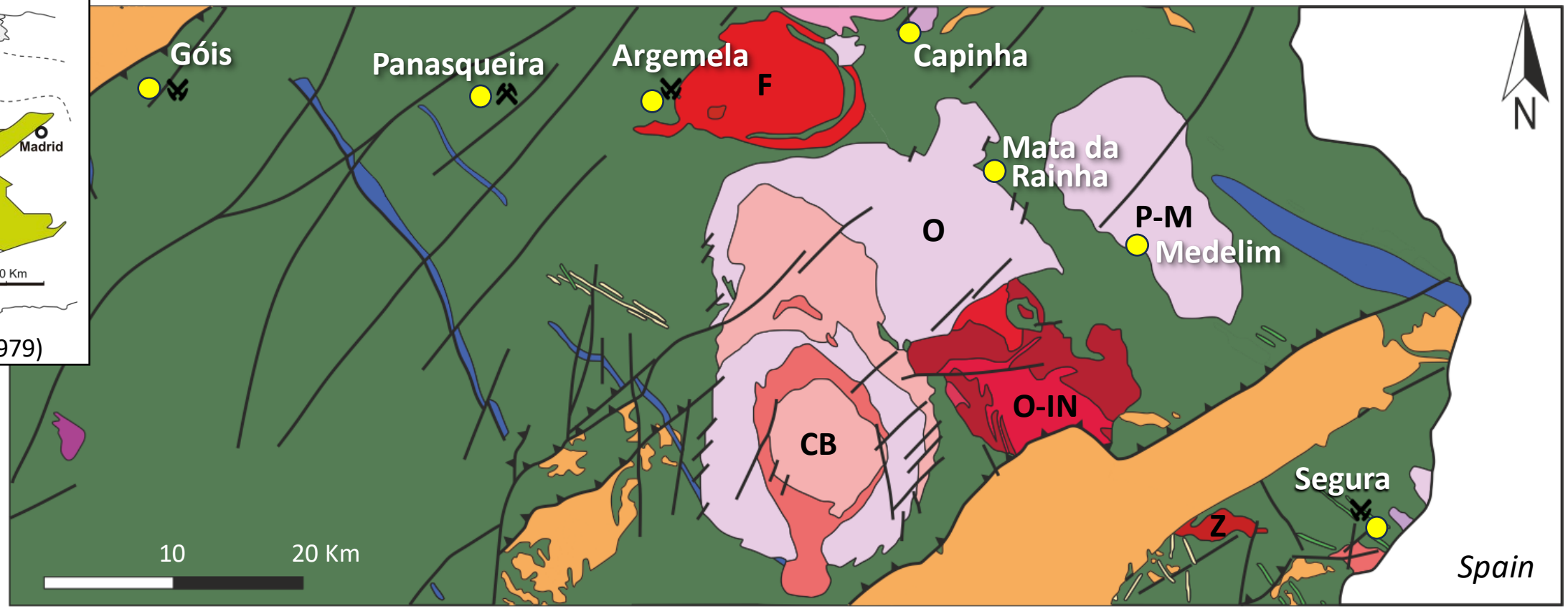


W6+ Ta5+ Nb5+ Hf4+ Zr4+ Mn4+ Ti4+ Ga3+ Fe3+ Mn3+ Cr3+ V3+ Al3+ Fe2+ Mn2+

Góis-Panasqueira-Segura Sn-W belt (Central Portugal)



(Ribeiro et al 1979)



Variscan Granites

Ordovician Granites

Cadomian Granites

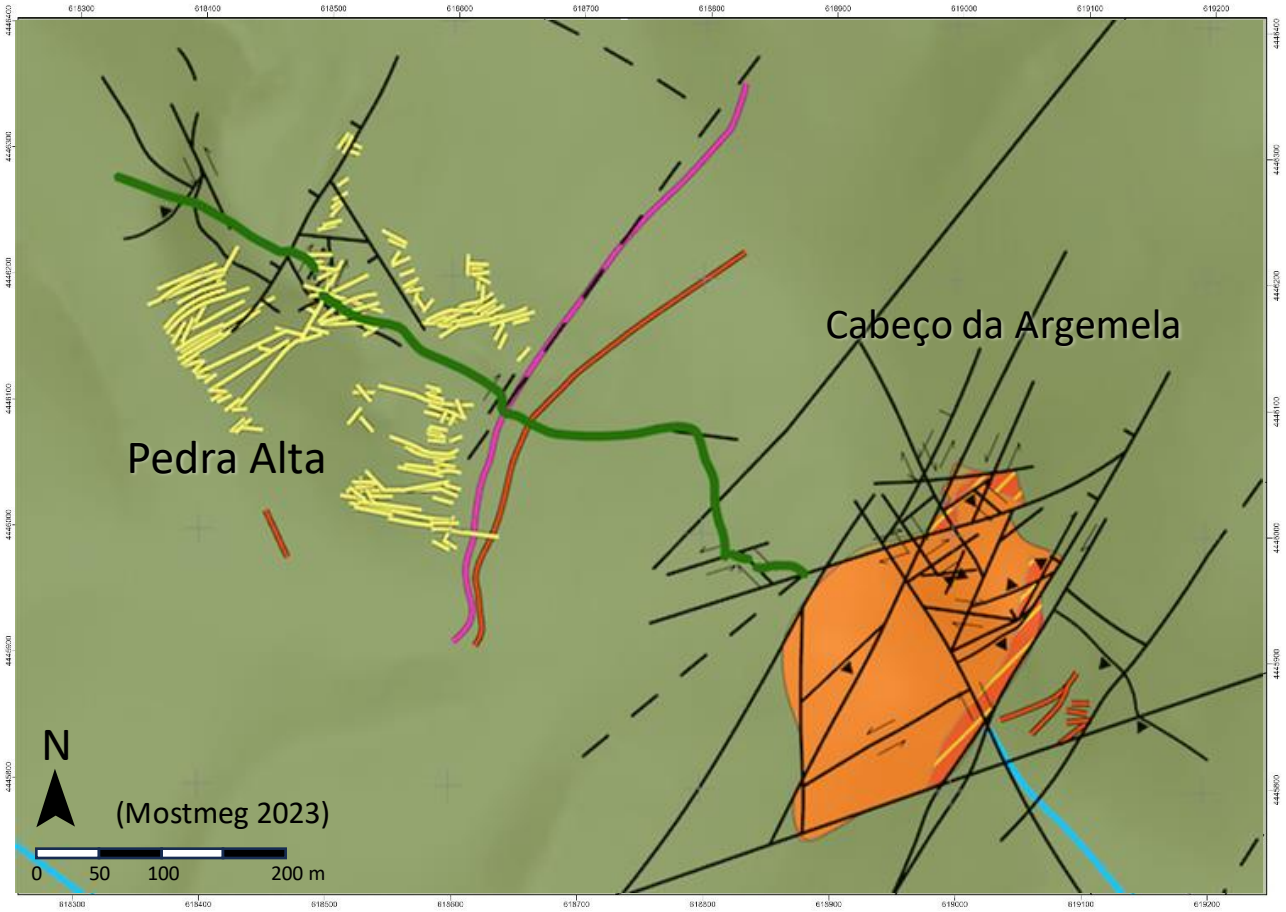
Ordovician Metasediments

Ante-Ordovician Metasediments (Beiras Group)

Tertiary deposits

(Mostmeg 2020)

ARGEMELA



Pedra Alta

Sn-Qz veins

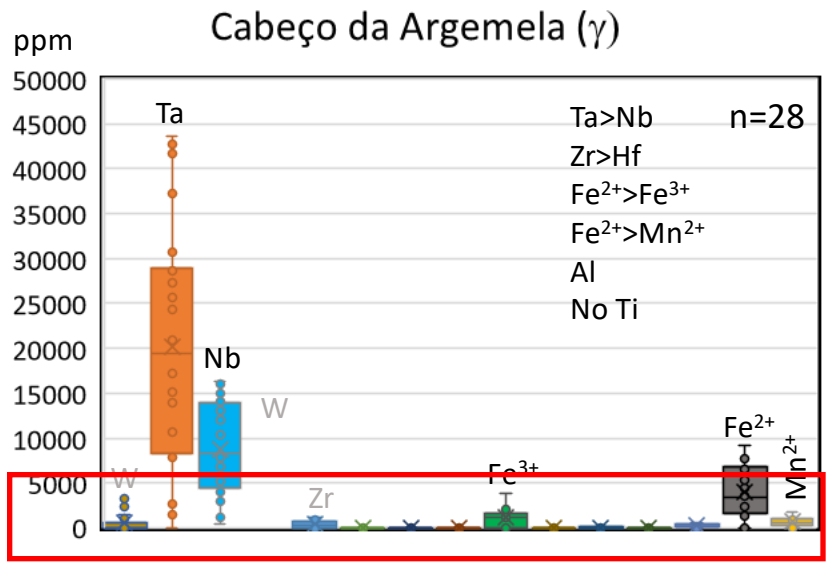
Cabeço da Argemela

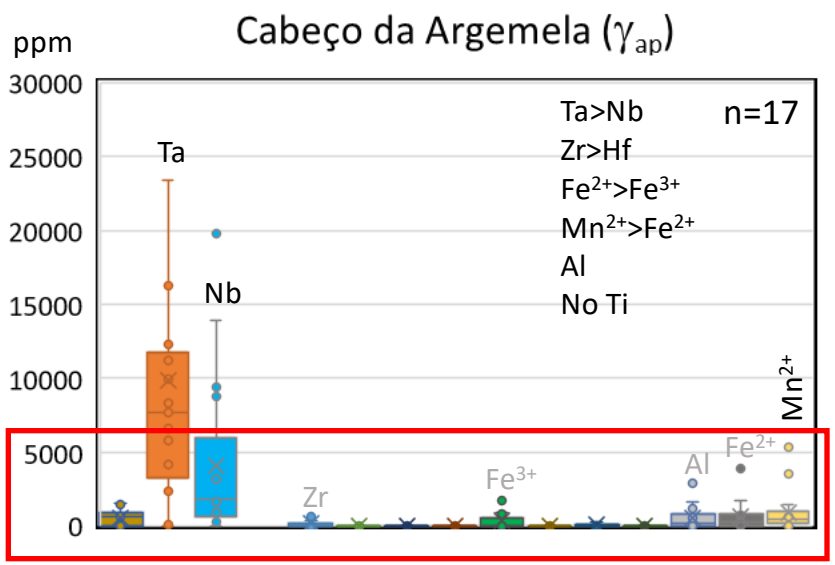
Granitic facies (γ)

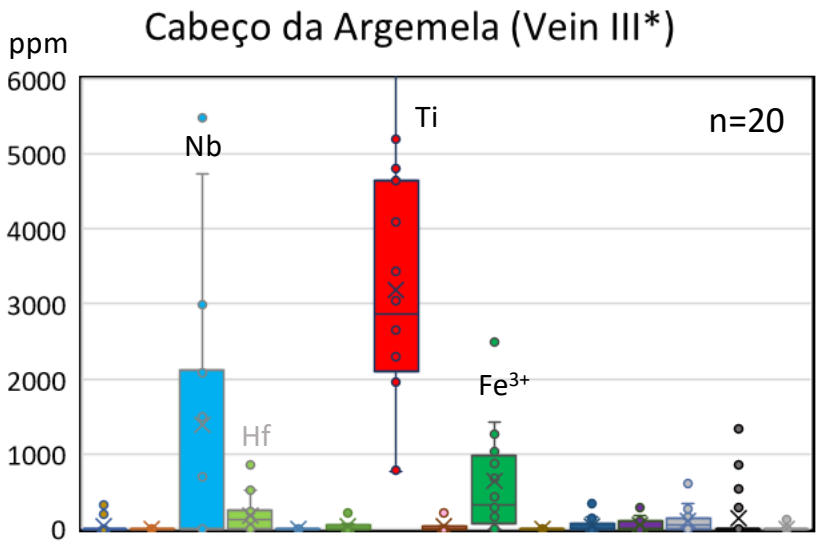
Aplitic-pegmatitic facies (γ_{ap})

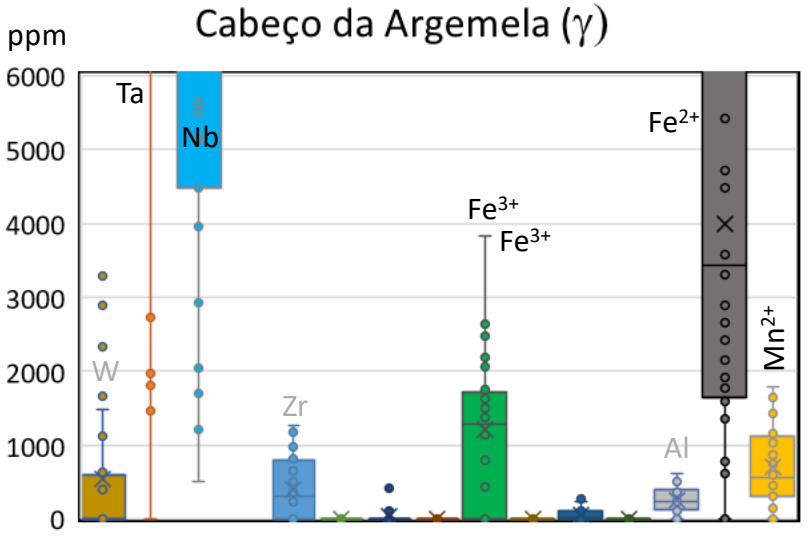
Veins (type I, II, III, III*)

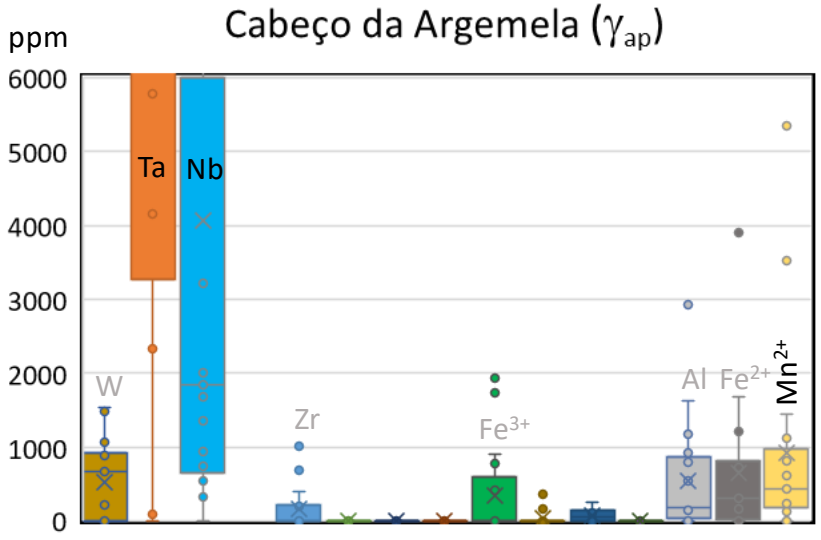
Cassiterite – Electron Microprobe Analyses (EMPA)





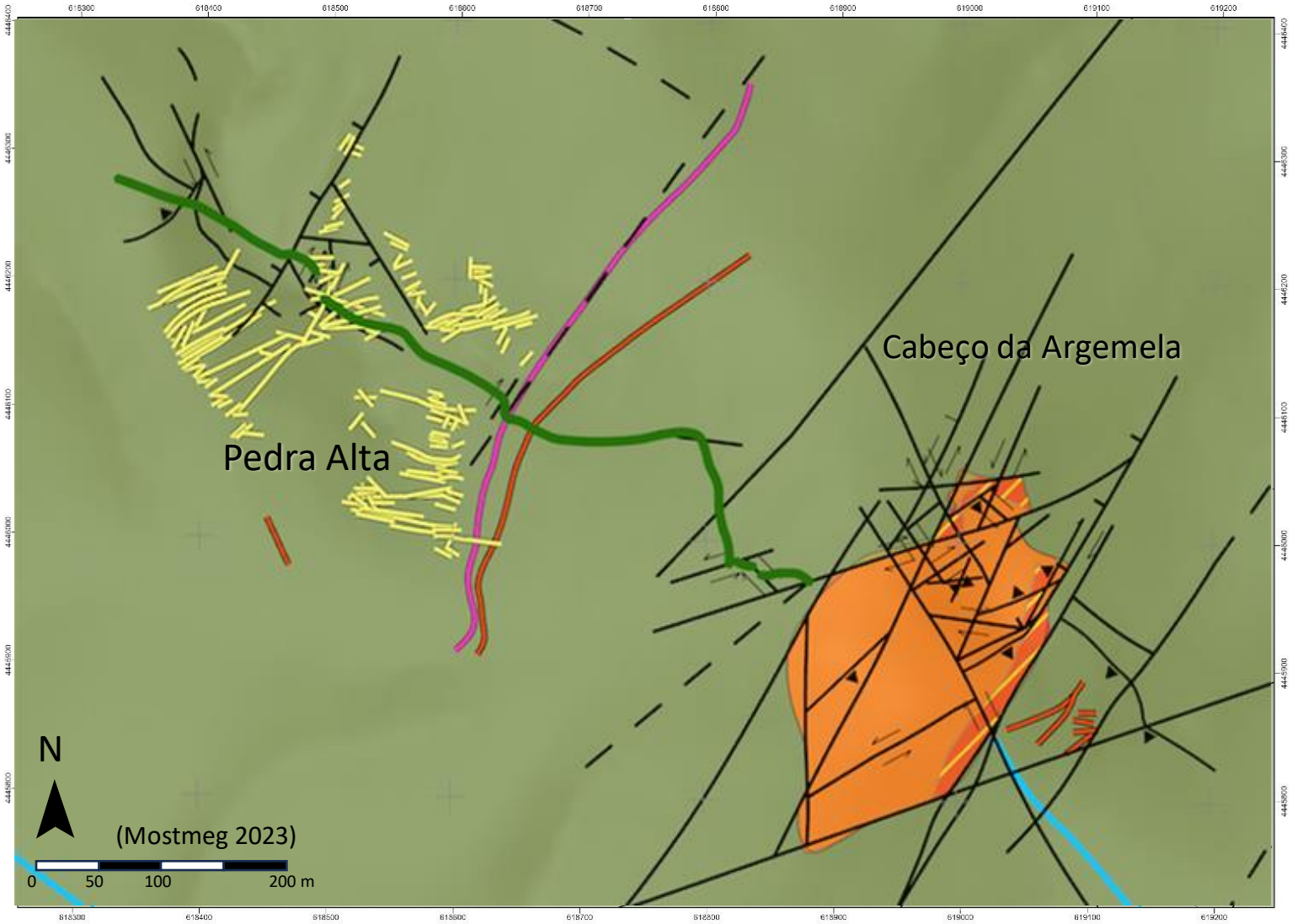


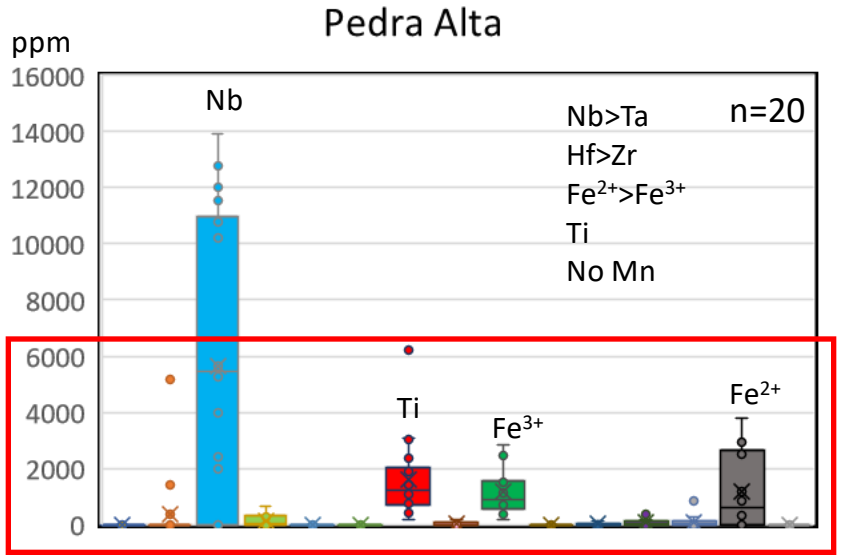


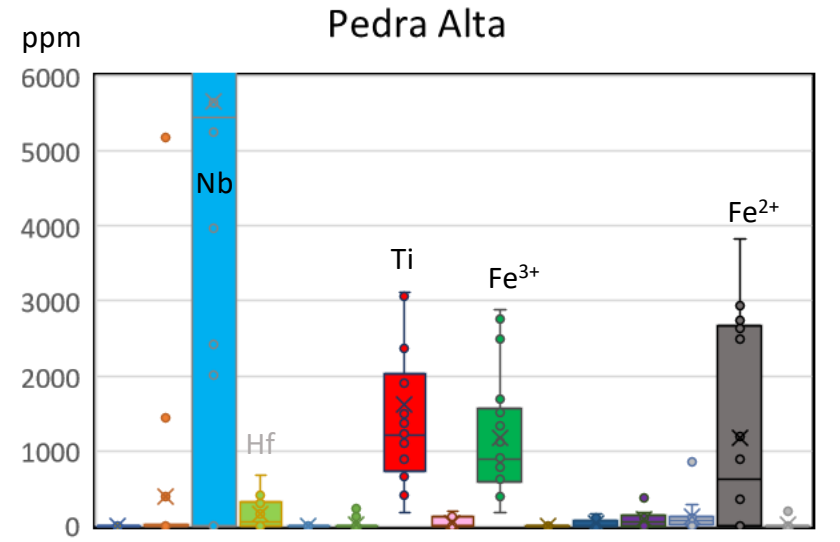


W6+ Ta5+ Nb5+ Hf4+ Zr4+ Mn4+ Ti4+ Ga3+ Fe3+ Mn3+ Cr3+ V3+ Al3+ Fe2+ Mn2+

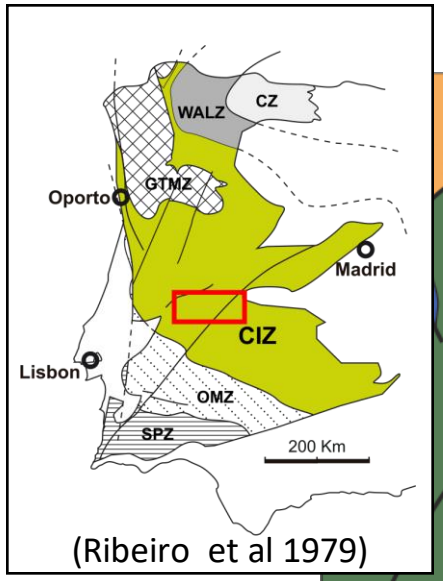
Cassiterite – Electron Microprobe Analyses (EMPA)



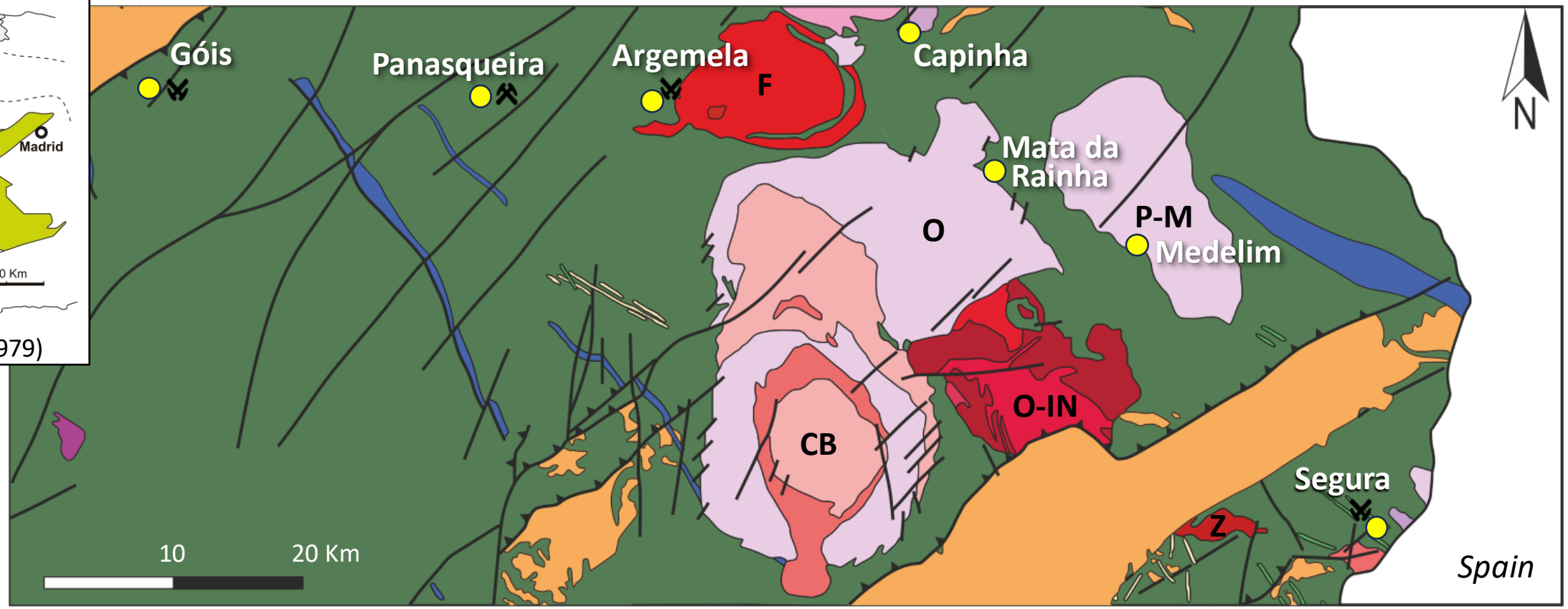




Góis-Panasqueira-Segura Sn-W belt (Central Portugal)



(Ribeiro et al 1979)



Variscan Granites

Ordovician Granites

Cadomian Granites

Ordovician Metasediments

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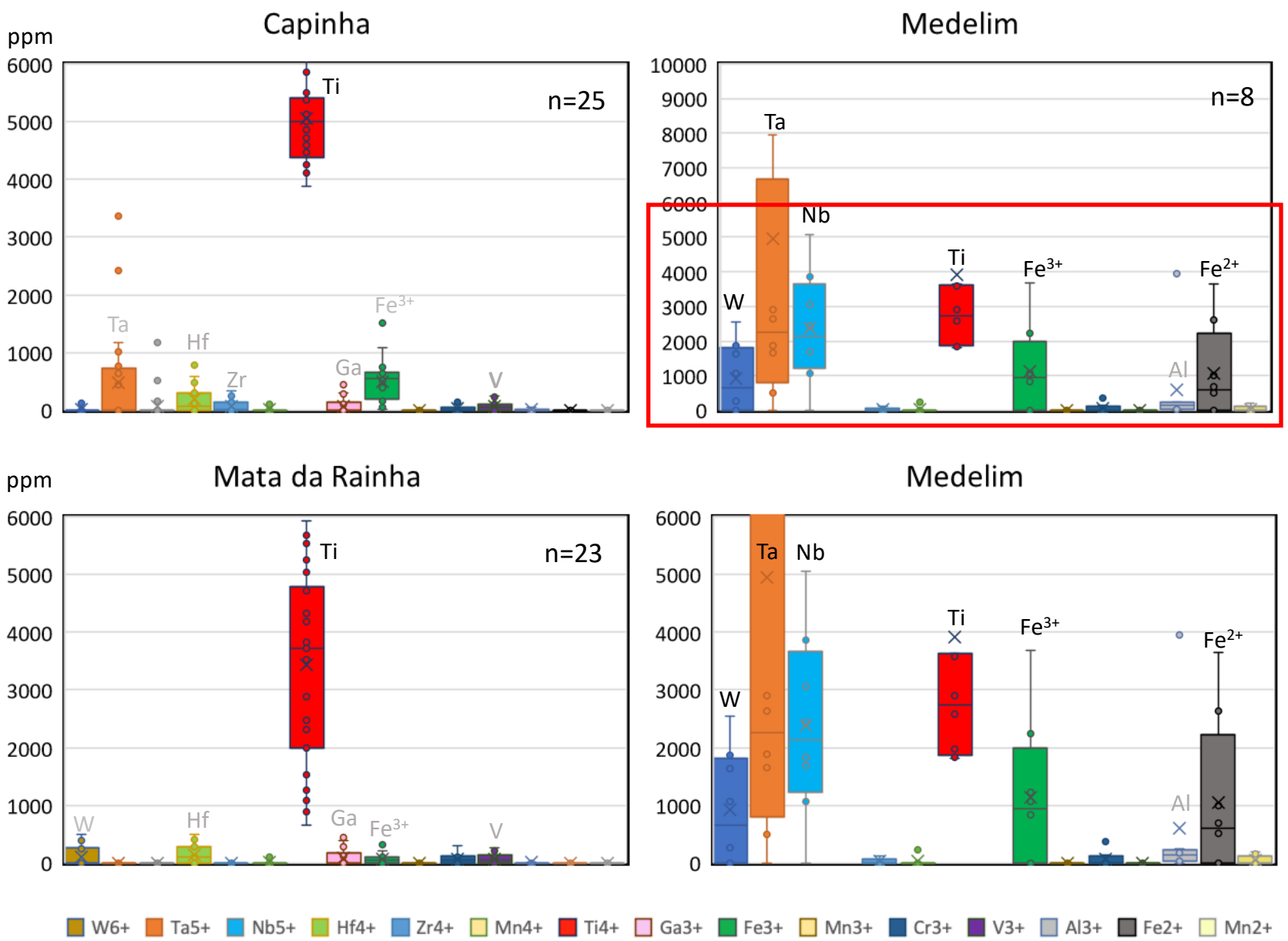
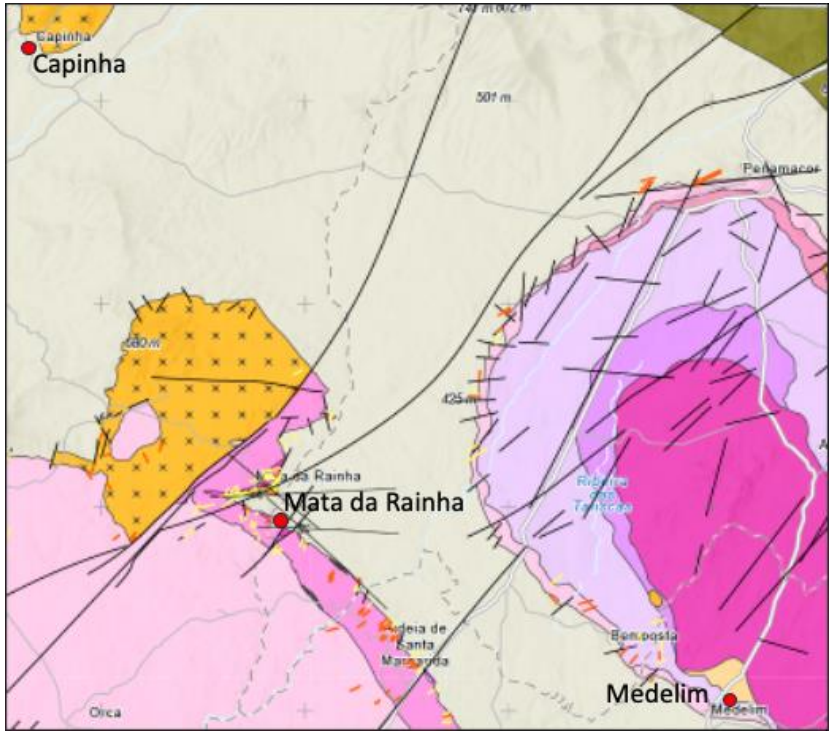
(Mostmeg 2020)

Cassiterite – Electron Microprobe Analyses (EMPA)





Capinha

Concessão 761 - Caberna e Quinta da Caverna de Baixo

Peri-botholithic Wlf +Css Qz veins

Mata da Rainha

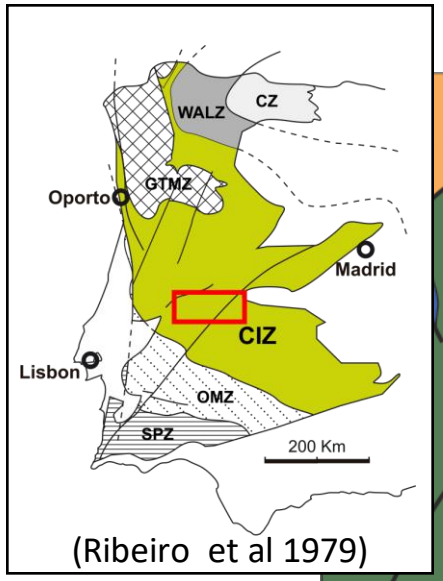
Peri-botholithic Wlf + Css Qz veins

(± Tourmaline)

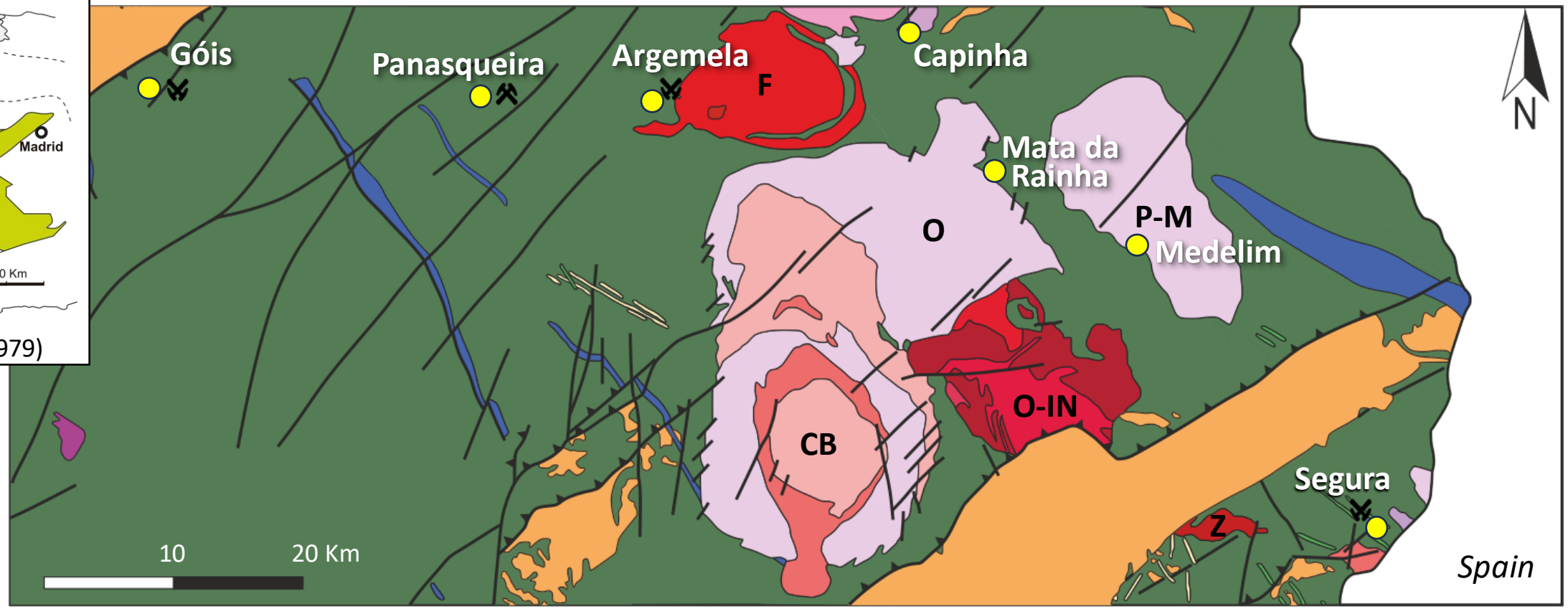
Medelim

Most differentiated facies of the Penamacor-Monsanto pluton

Góis-Panasqueira-Segura Sn-W belt (Central Portugal)



(Ribeiro et al 1979)



Variscan Granites

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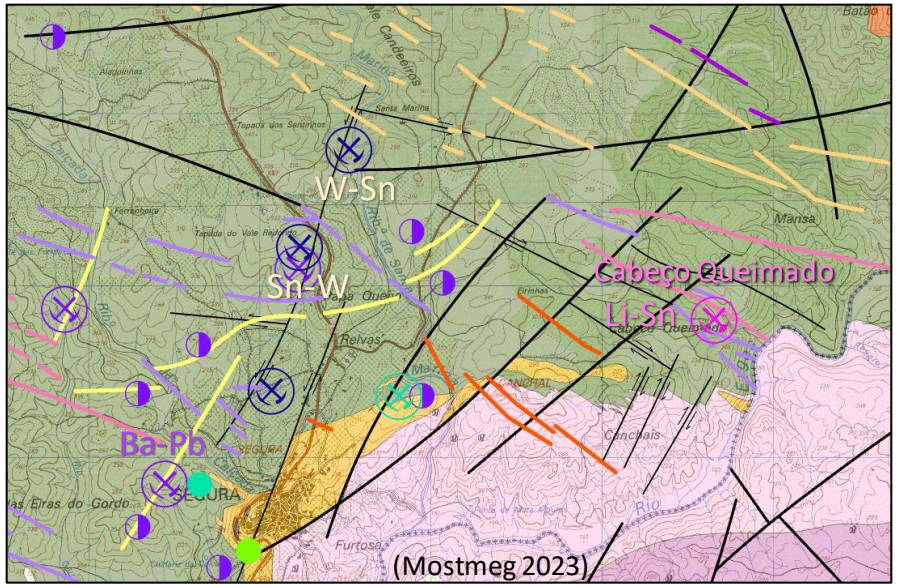
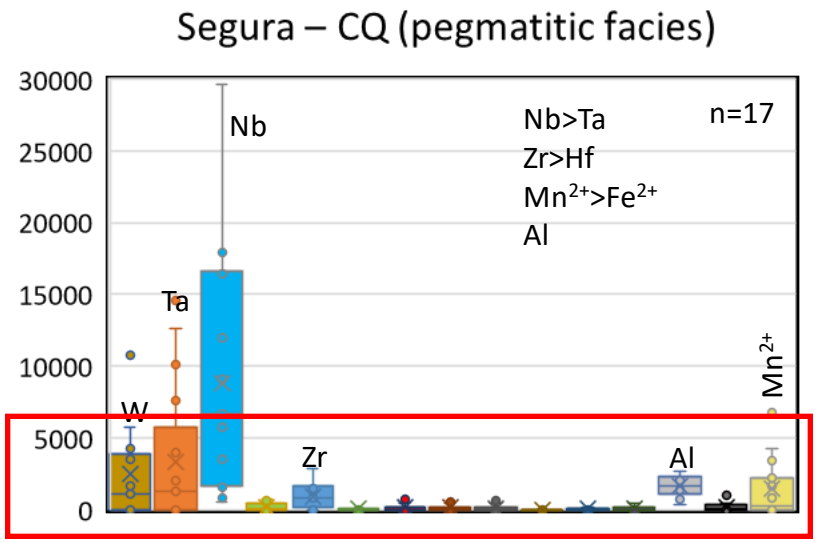
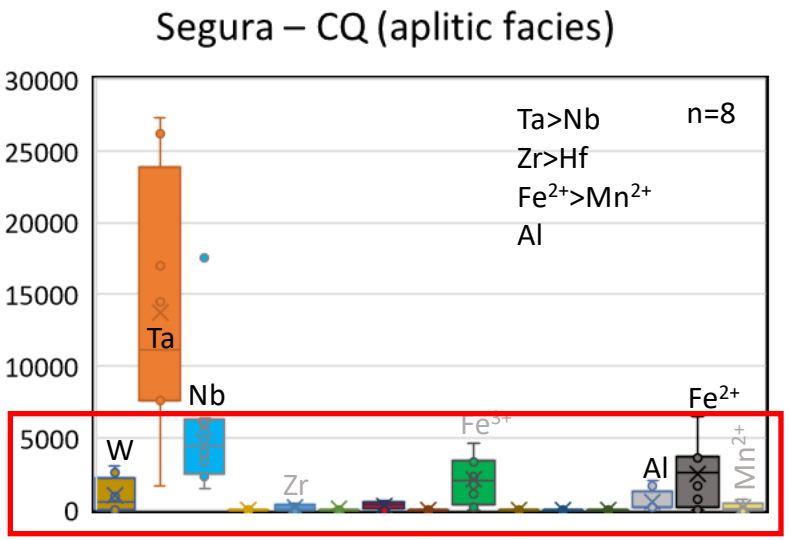
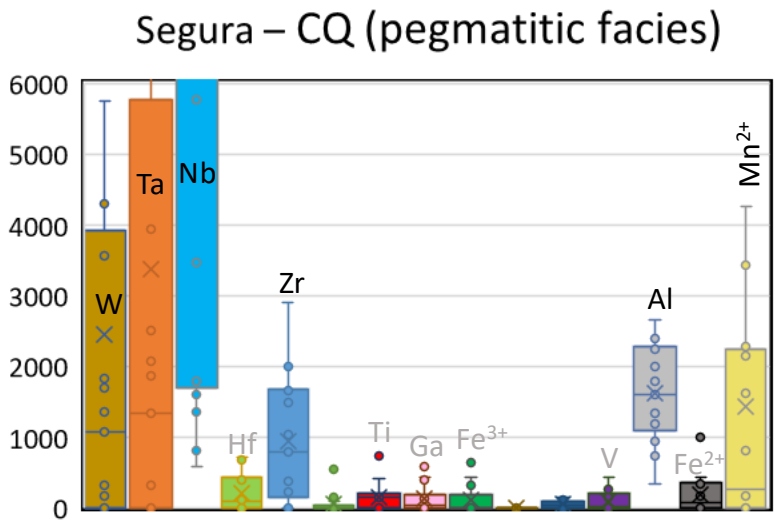
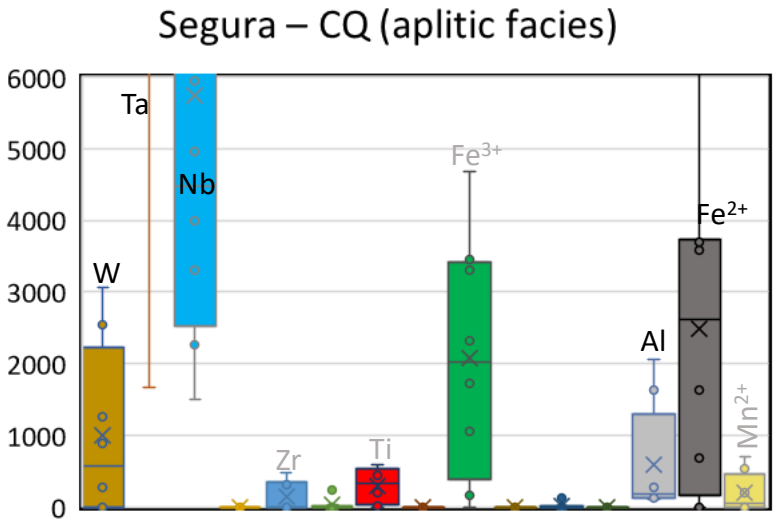
Cassiterite – Electron Microprobe Analyses (EMPA)











Li-Sn Aplito-pegmatites Cerro (Cabeço) Queimado

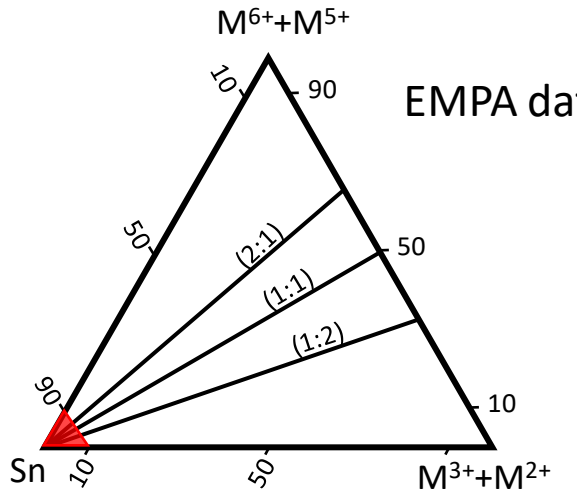
Sn-bearing aplites

Sn-(W) Veins

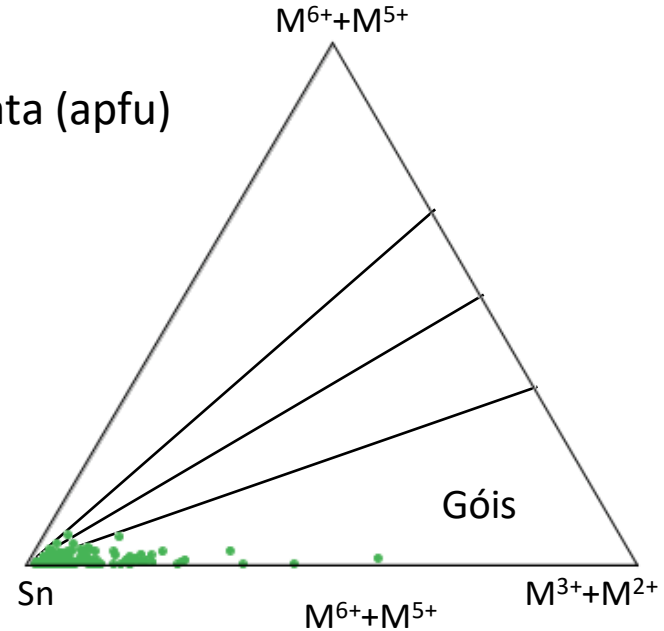
W-(Sn) Veins

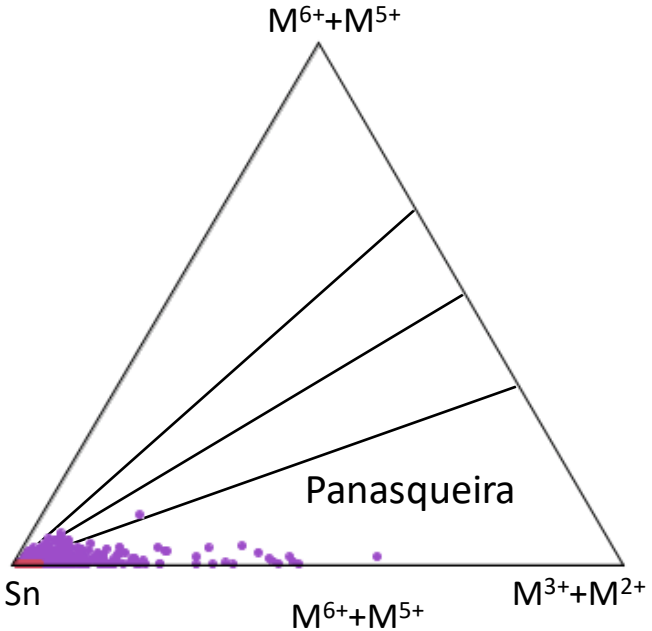
W6+ Ta5+ Nb5+ Hf4+ Zr4+ Mn4+ Ti4+ Ga3+ Fe3+ Mn3+ Cr3+ V3+ Al3+ Fe2+ Mn2+

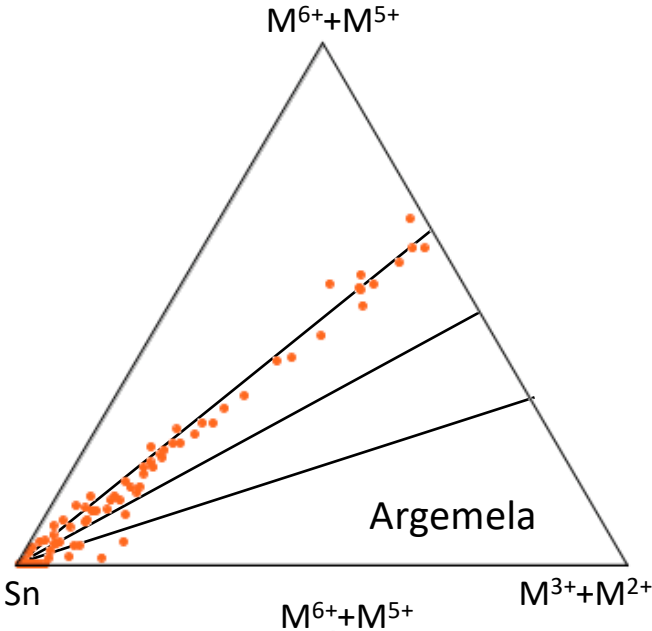
Cassiterite – Electron Microprobe Analyses (EMPA)

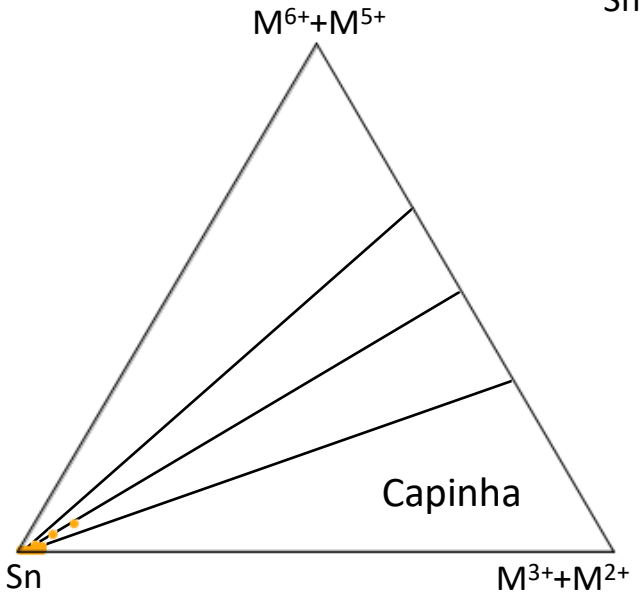


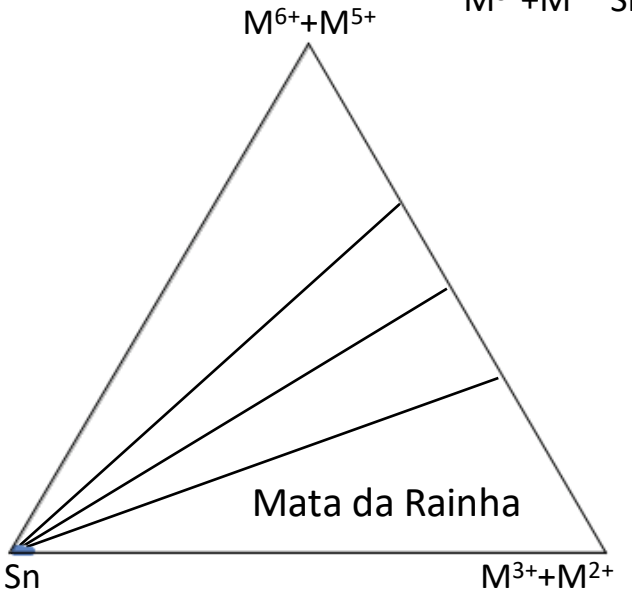
EMPA data (apfu)

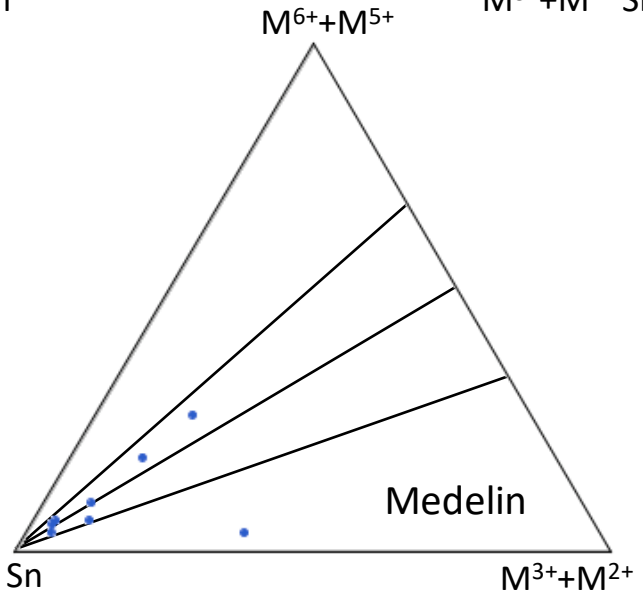


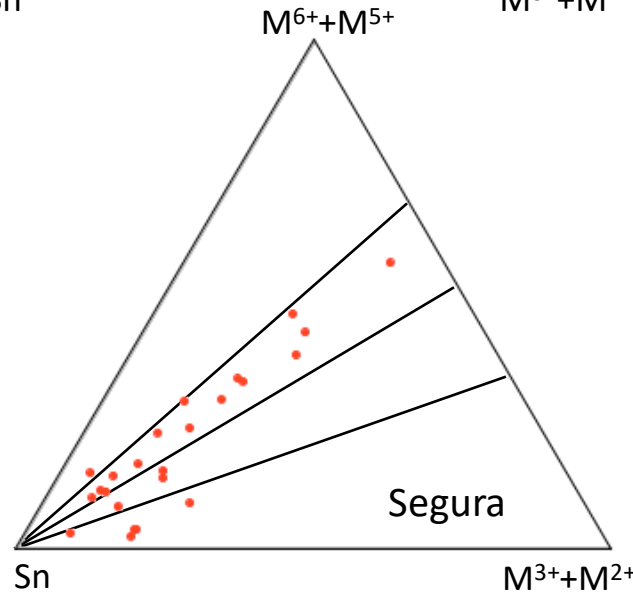










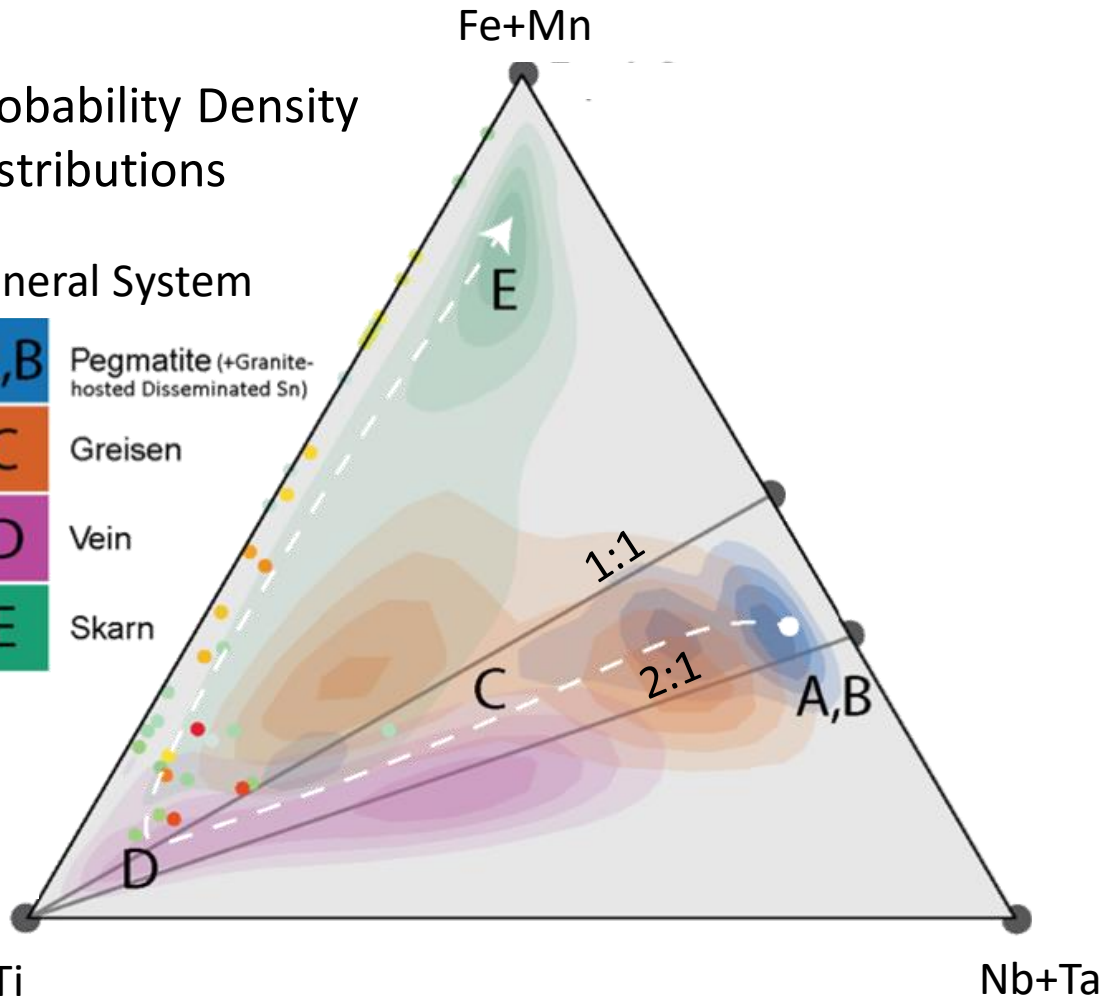


Exploration Tools – Minor Element Fingerprints

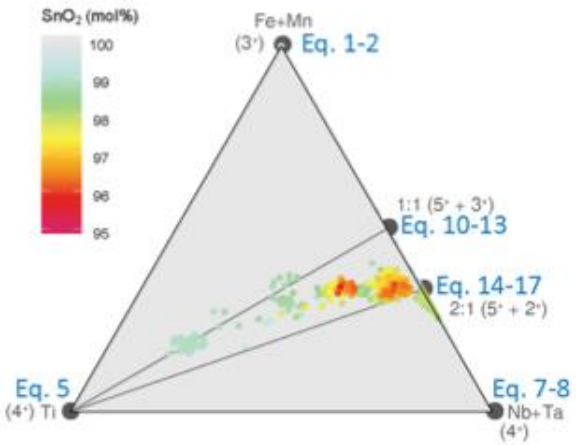
Probability Density Distributions

Mineral System

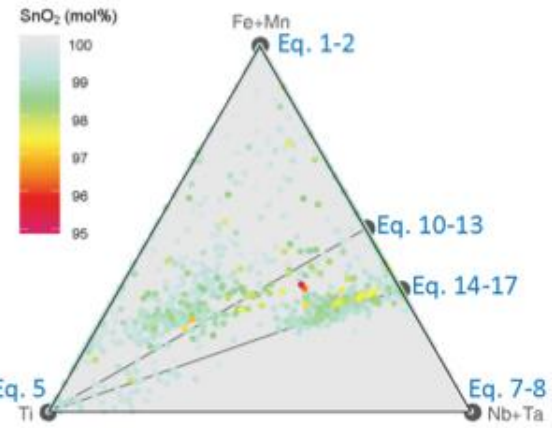
- A,B Pegmatite (+Granite-hosted Disseminated Sn)
- C Greisen
- D Vein
- E Skarn



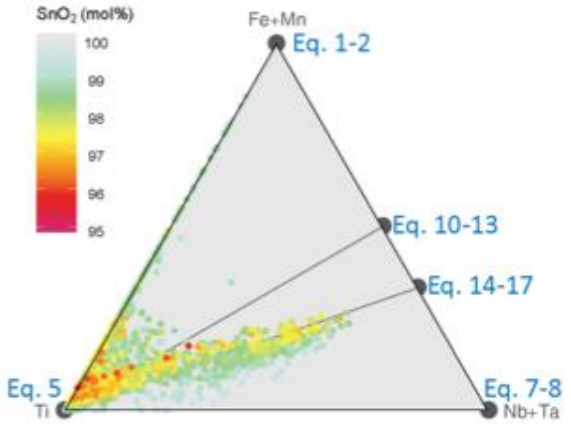
Pegmatite (A) & Granite-hosted (B)



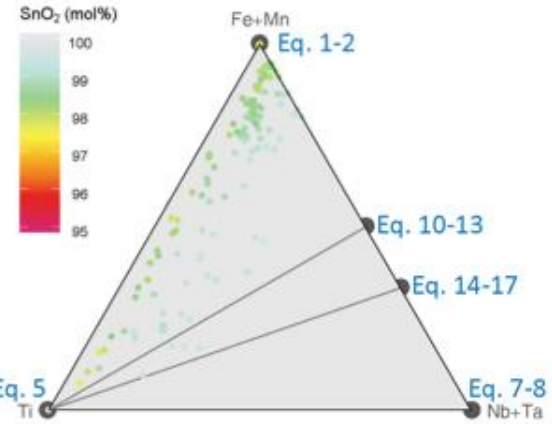
Greisen (C)



Vein-hosted (D)



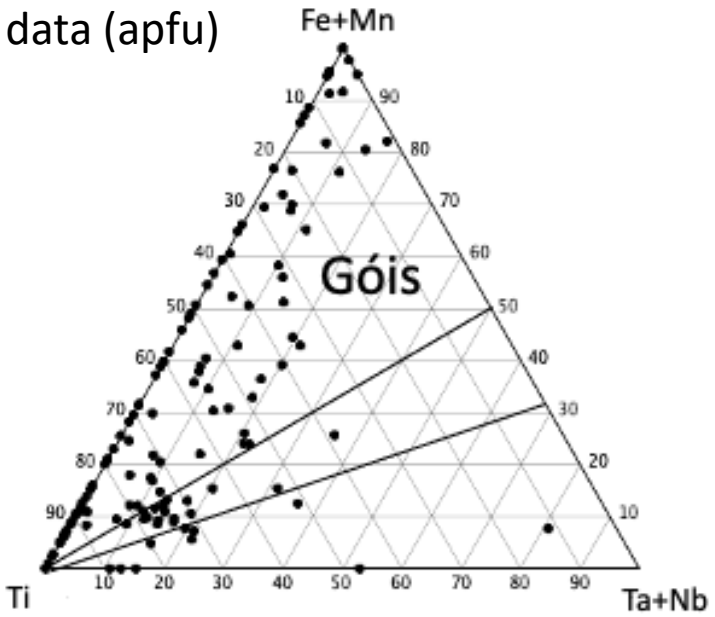
Skarn (E)

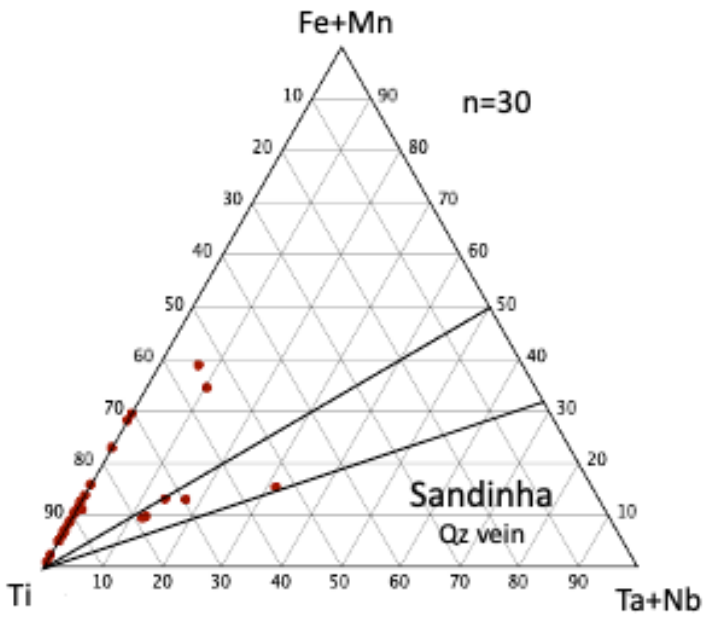


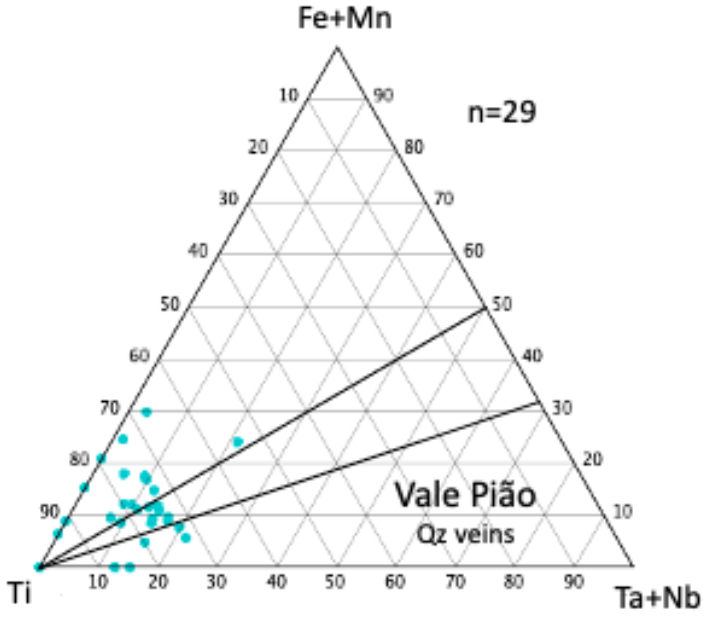
(Bennet, J.M. 2021)

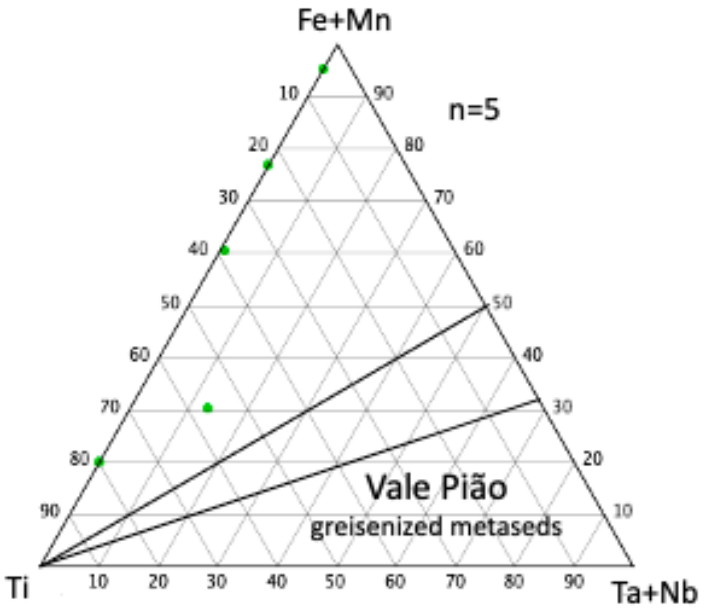
Exploration Tools – Minor Element Fingerprints

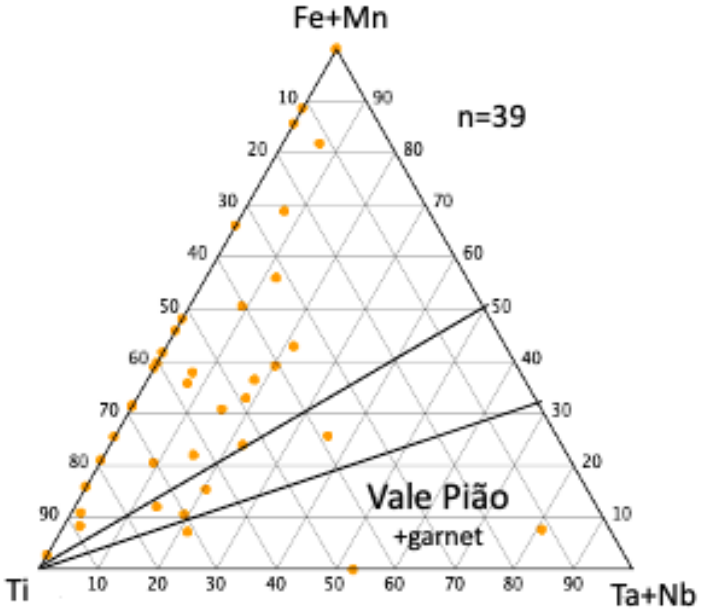
EMPA data (apfu)

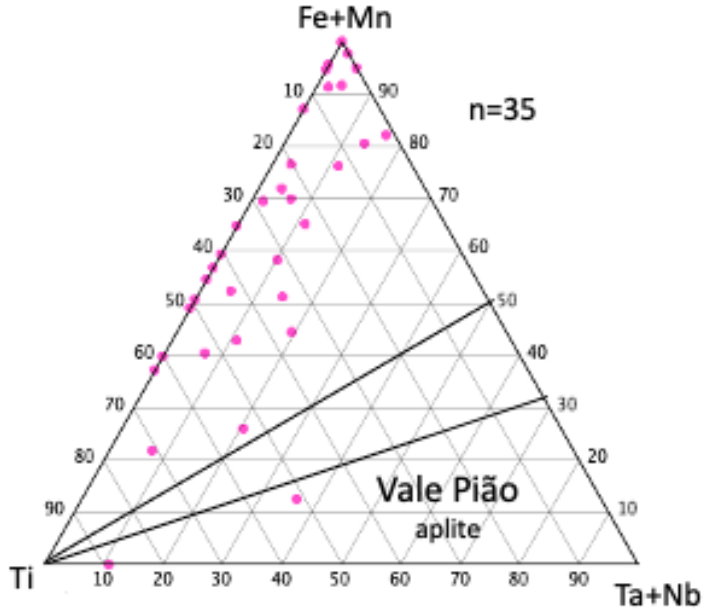






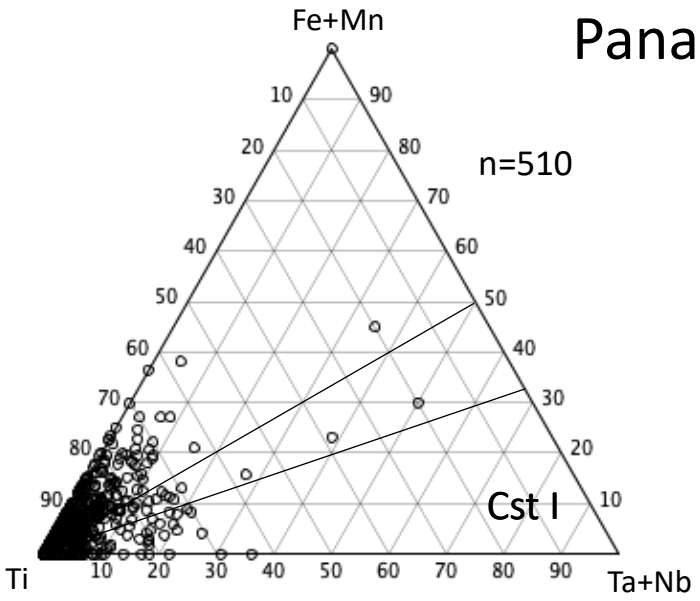


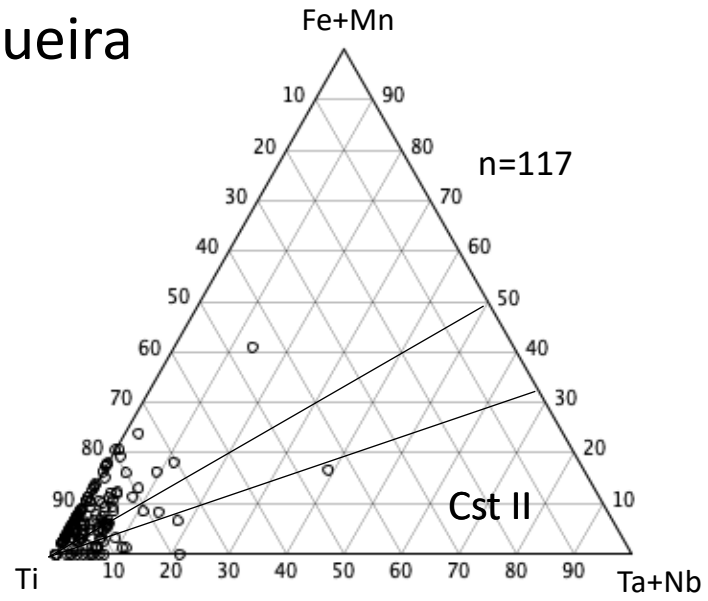


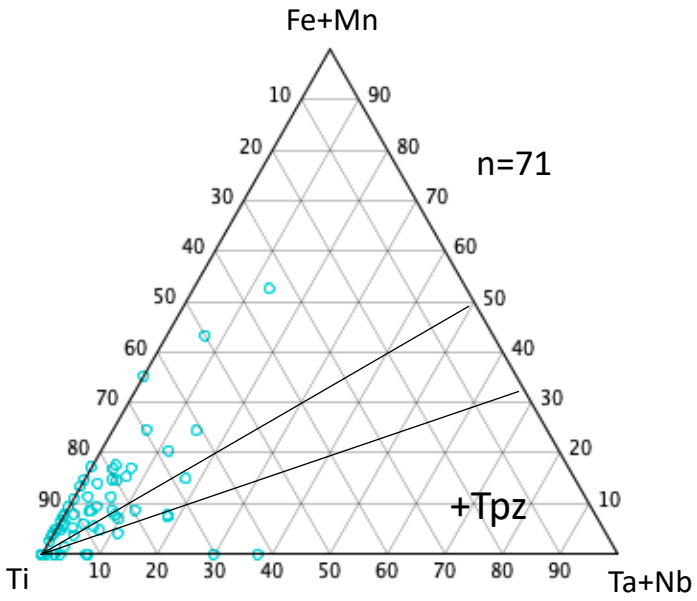


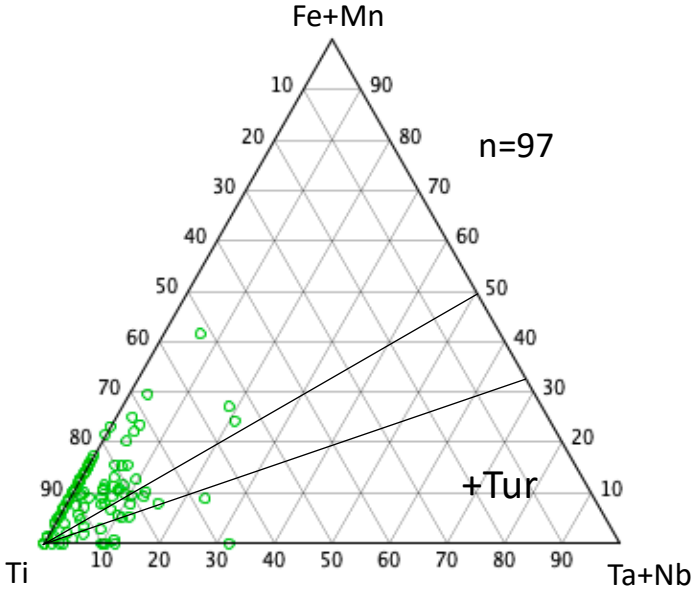
Exploration Tools – Minor Element Fingerprints

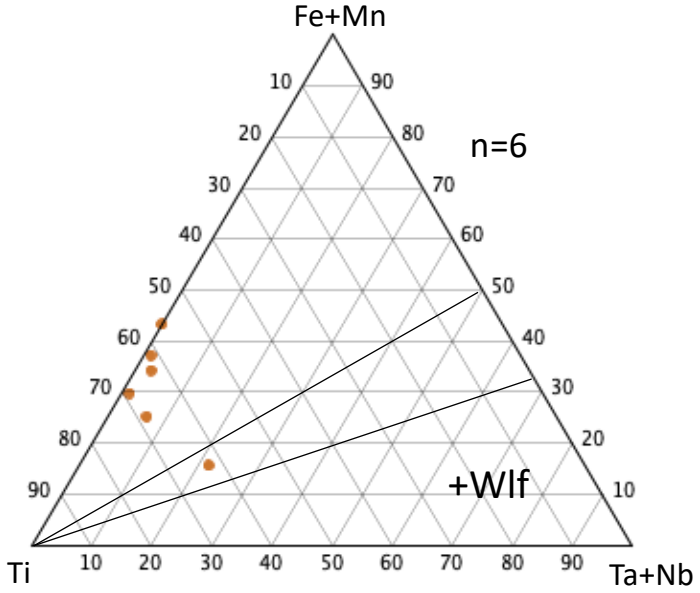
Panasqueira

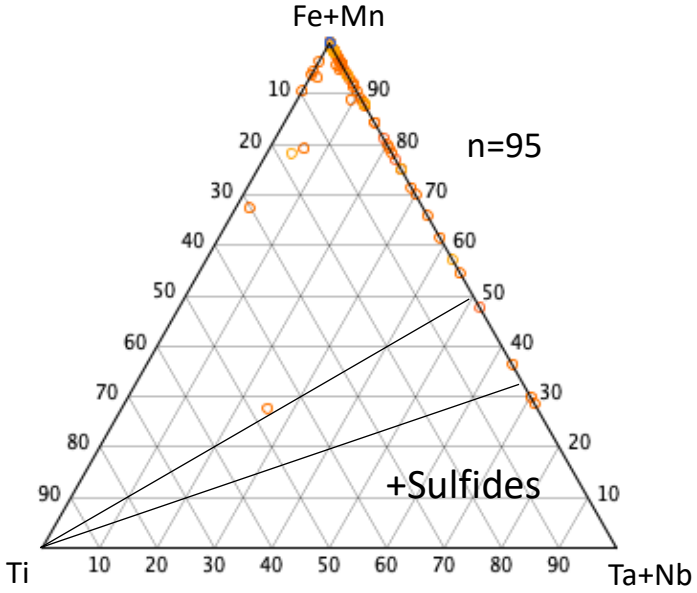




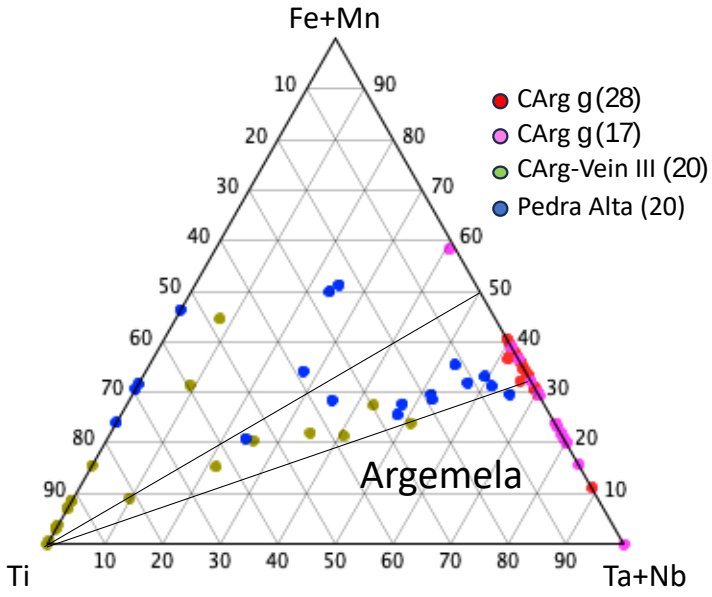


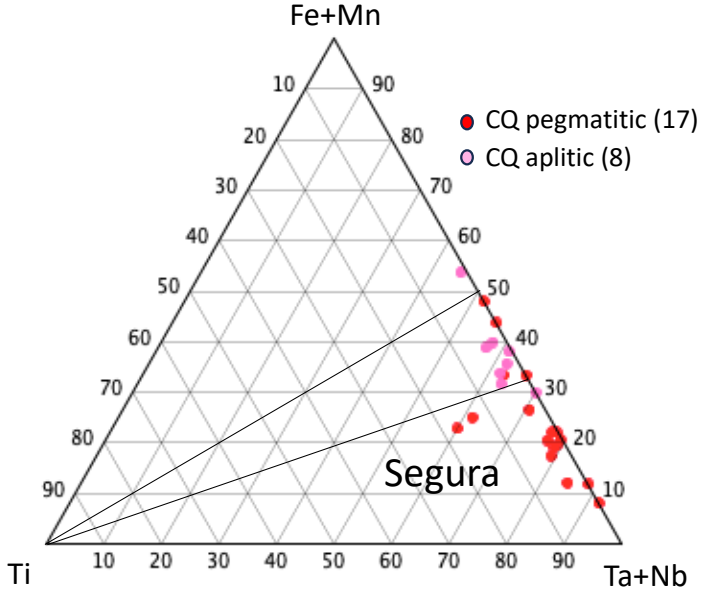


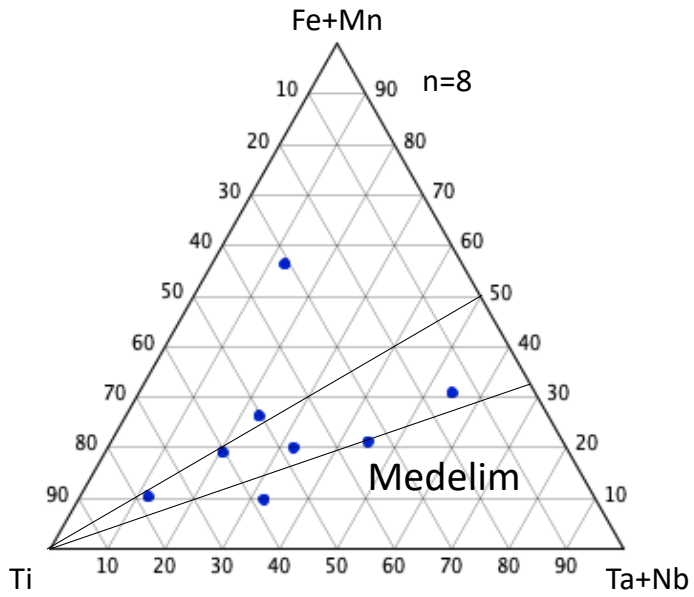


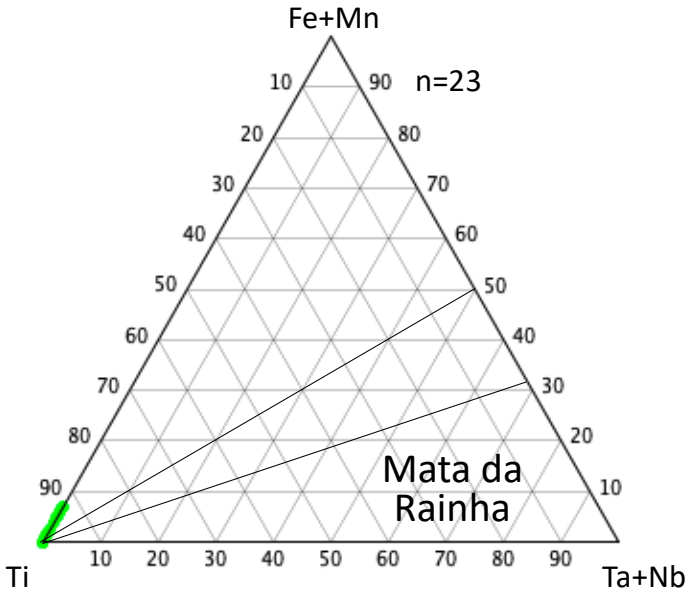


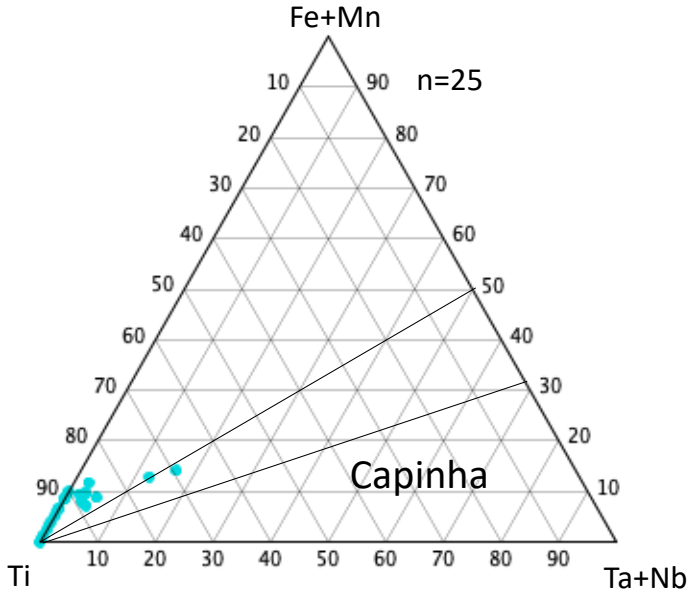
Exploration Tools – Minor Element Fingerprints



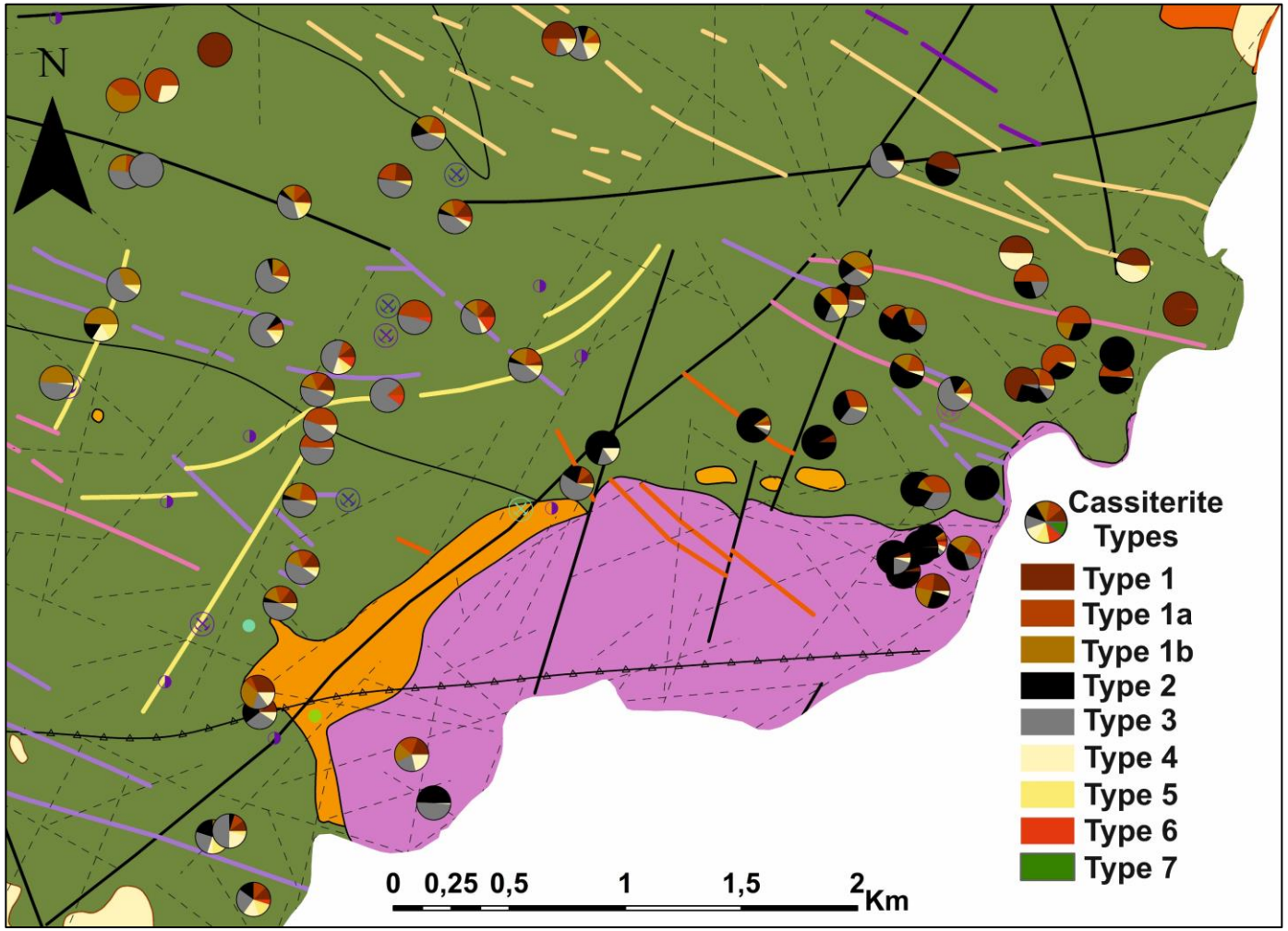


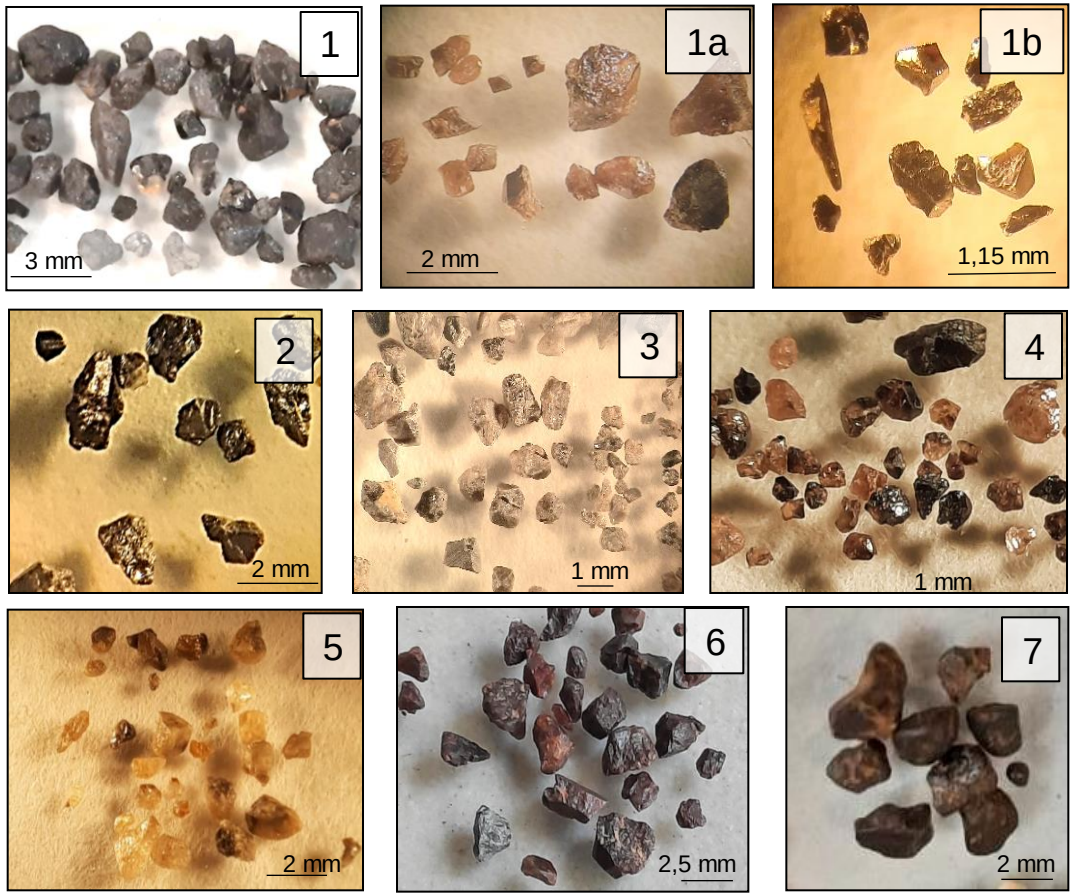






Aplication to Alluvial Cassiterite (Segura)



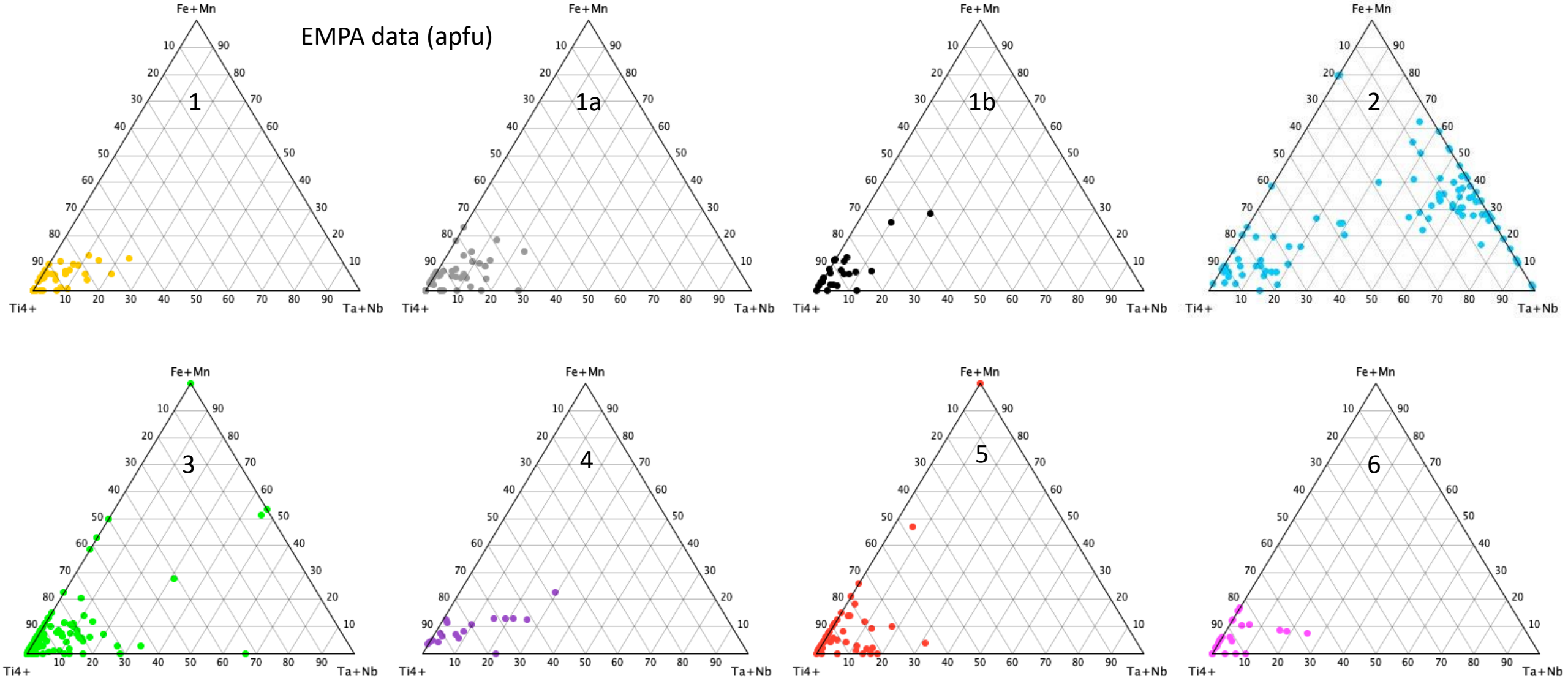


2.5 cm mounts

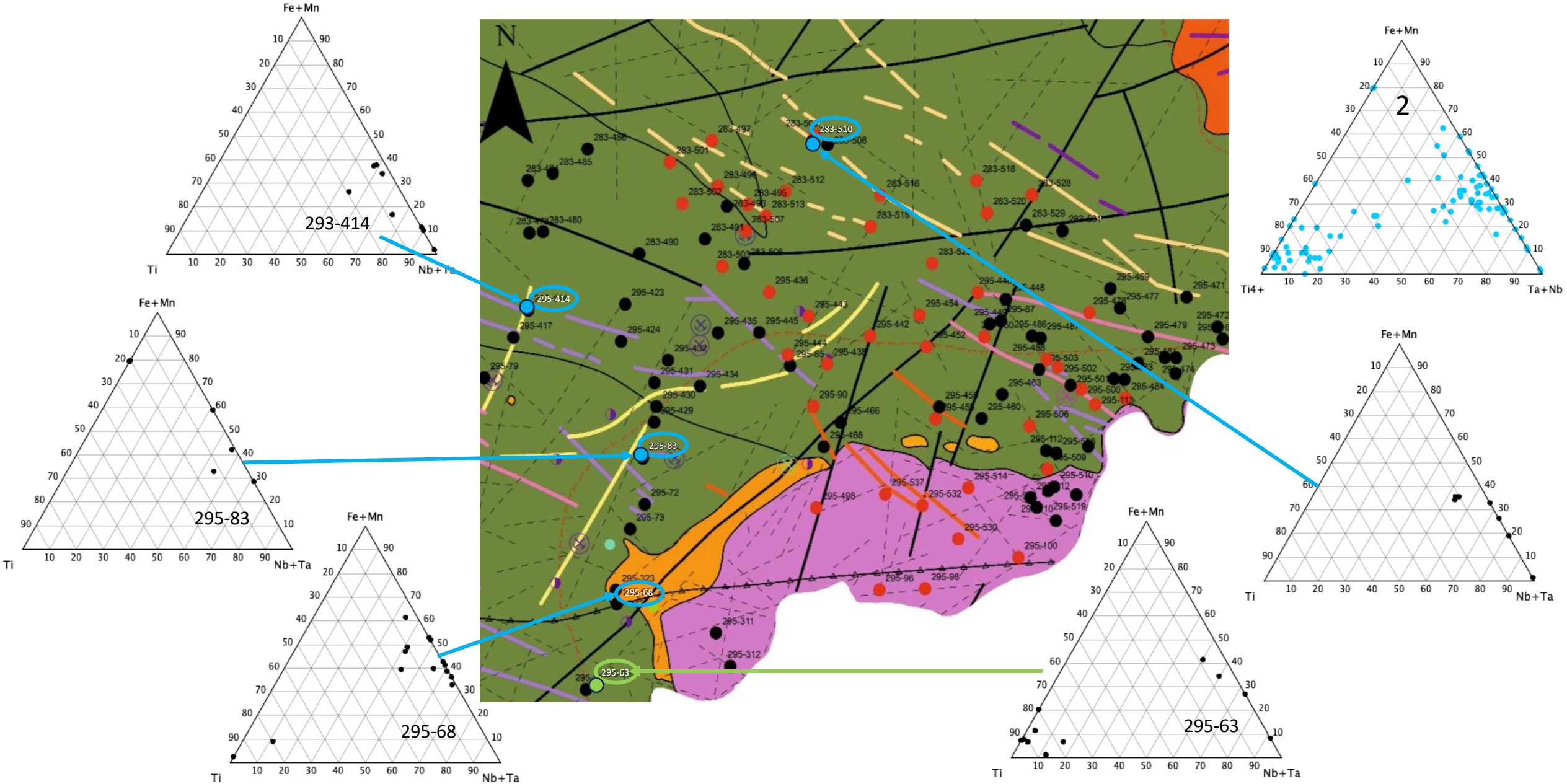
Alluvial samples can have multiple sources

Aplication to Alluvial Cassiterite (Segura)

EMPA data (apfu)



Aplication to Alluvial Cassiterite (Segura)



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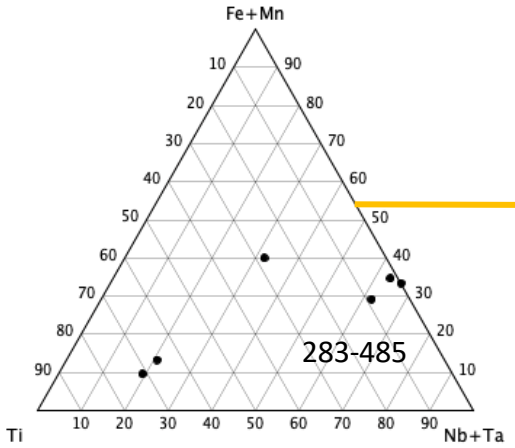
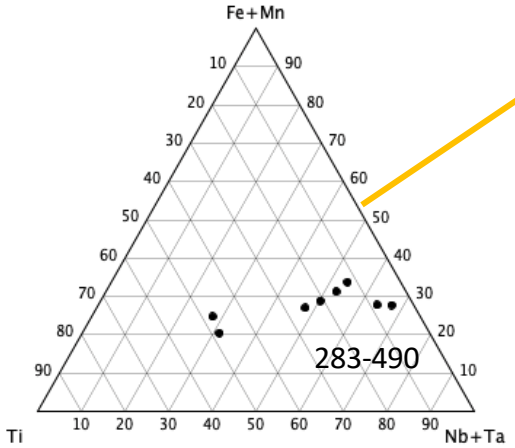
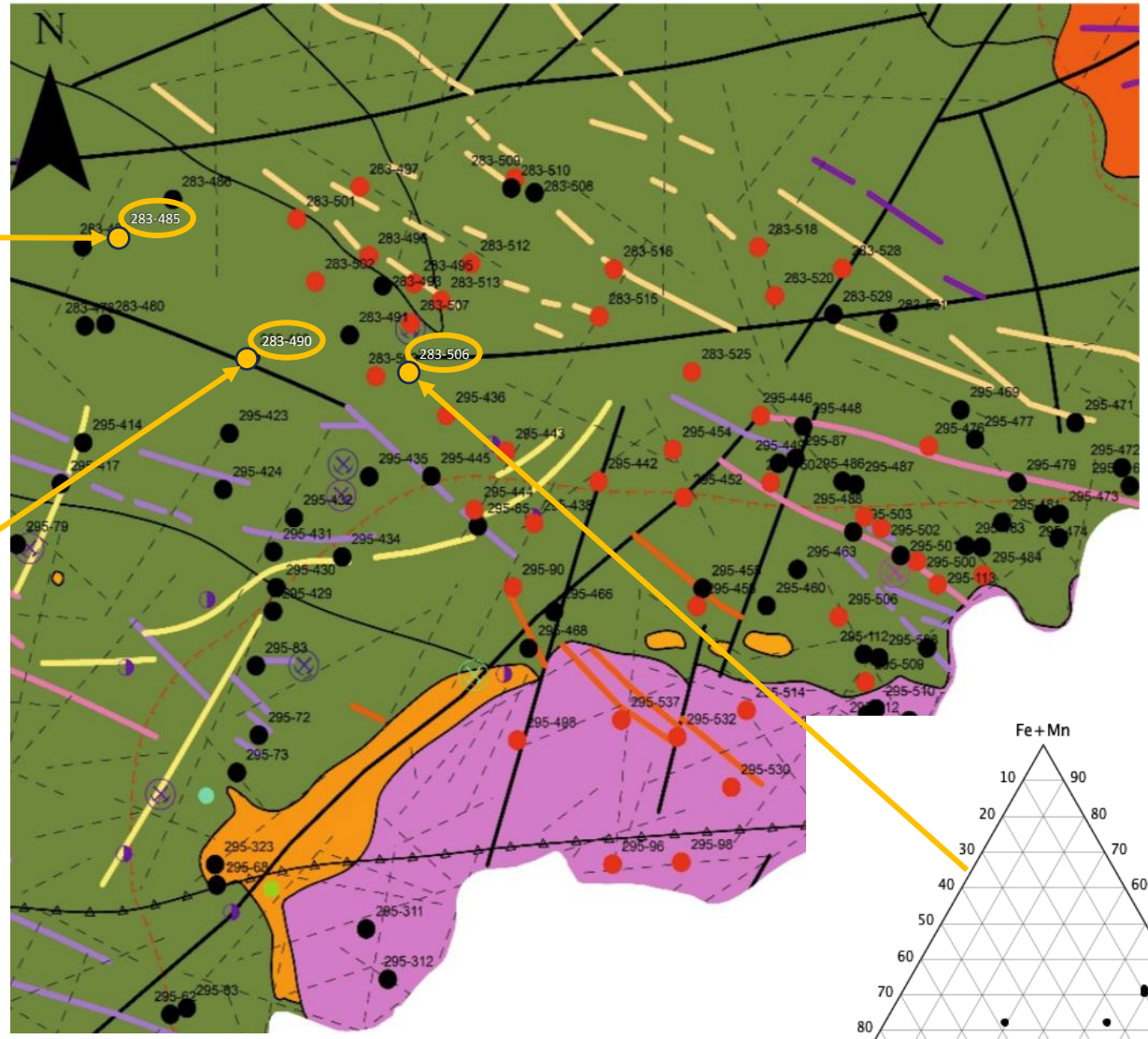
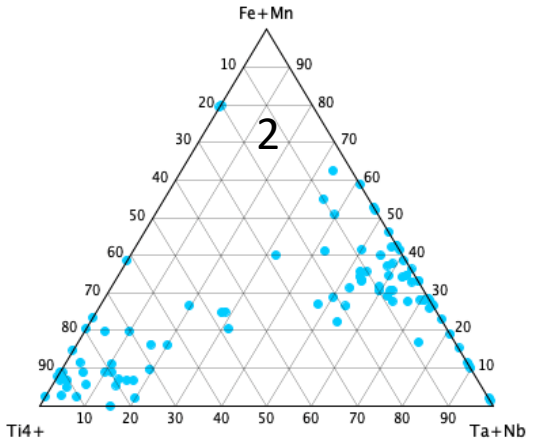
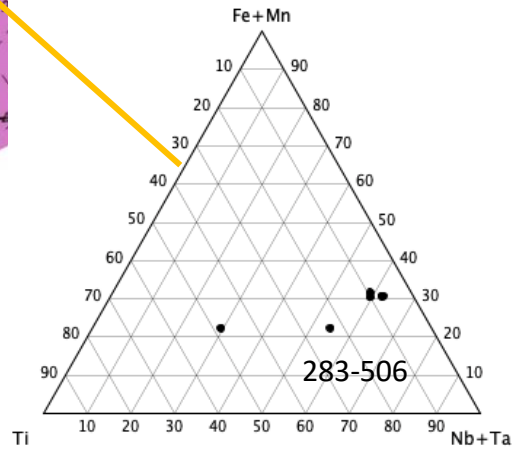


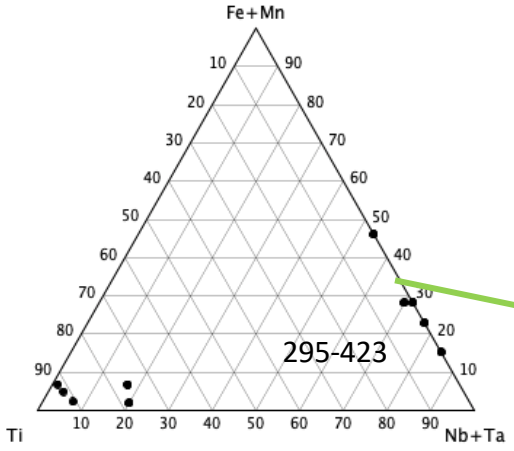


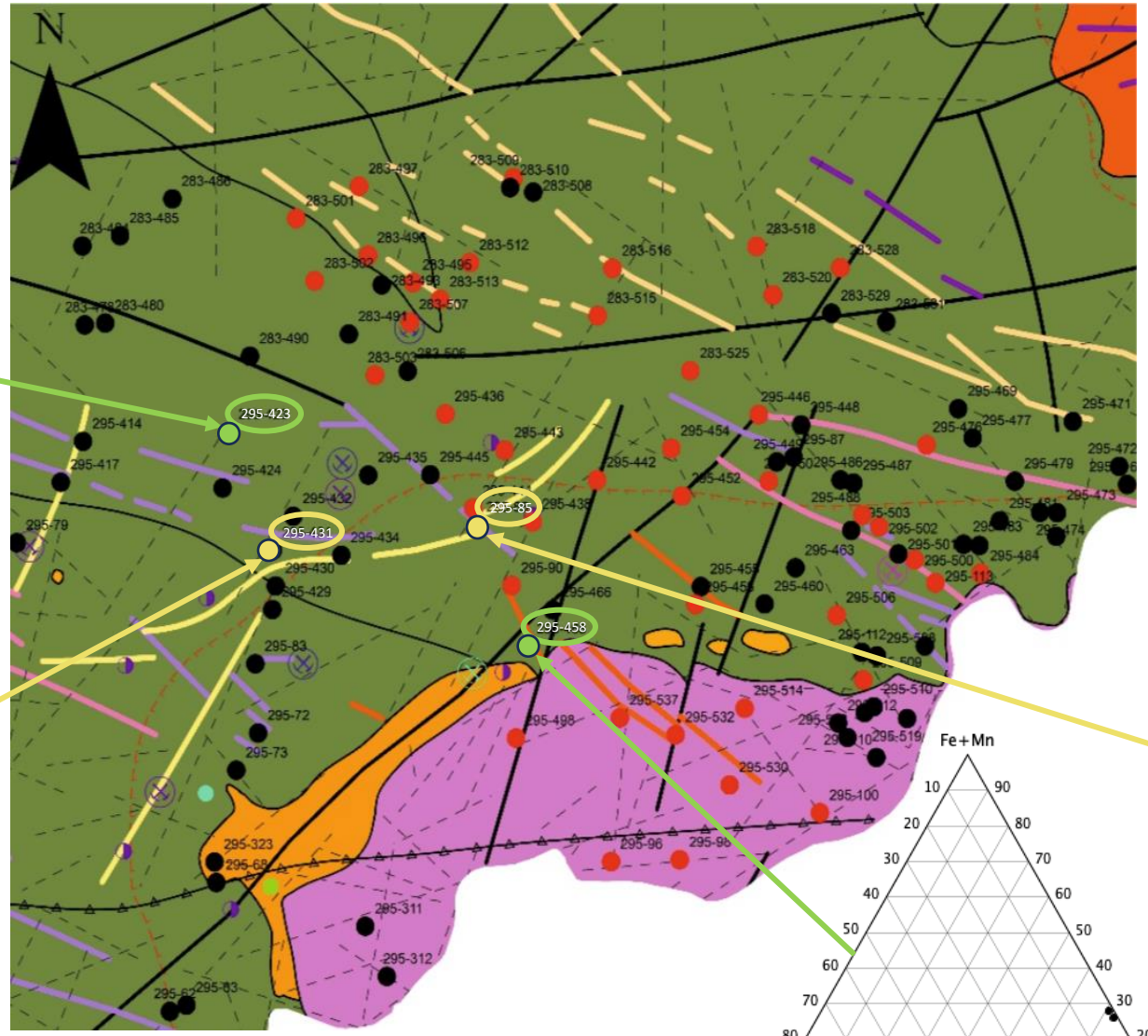


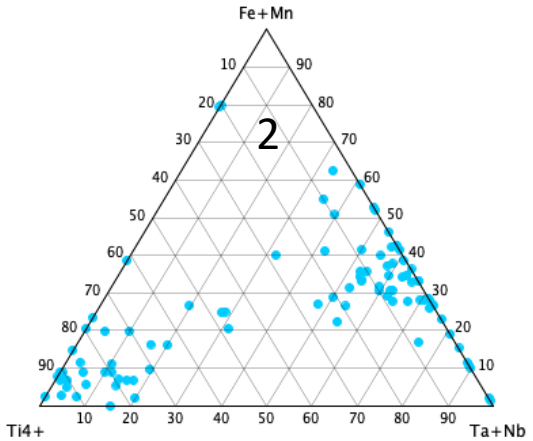


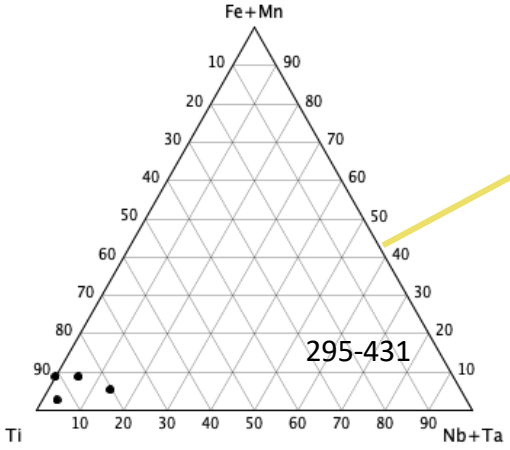


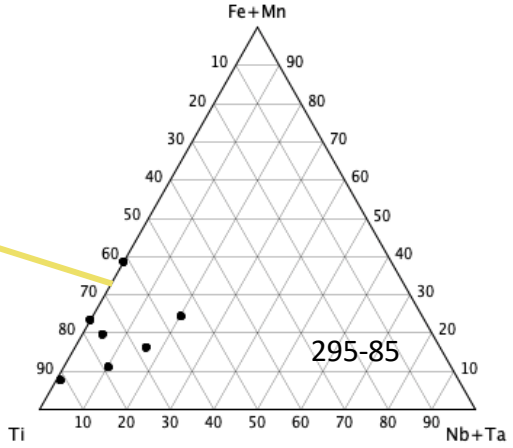
Aplication to Alluvial Cassiterite (Segura)

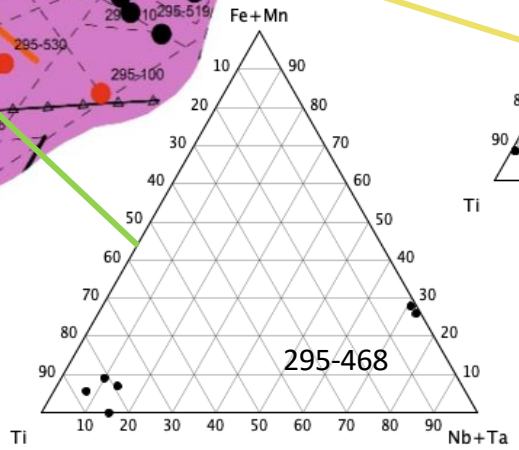




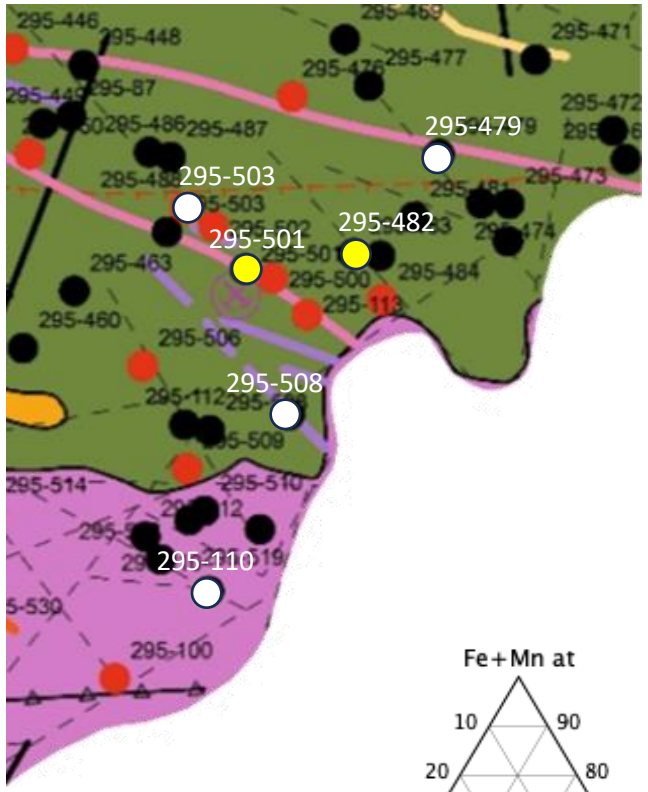




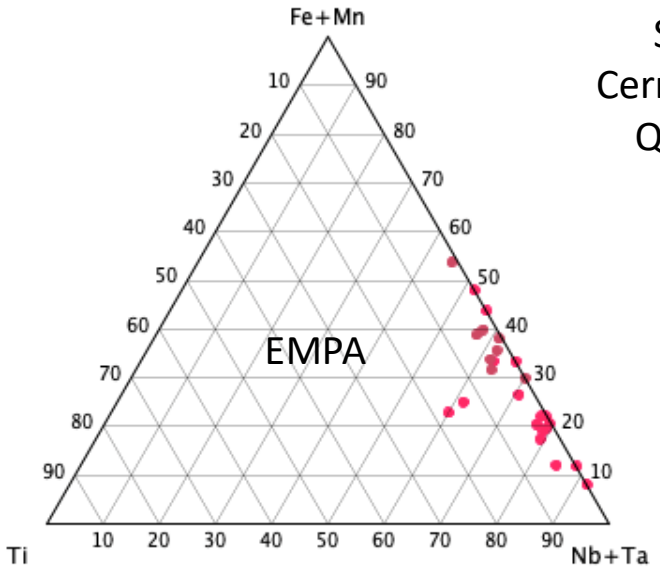


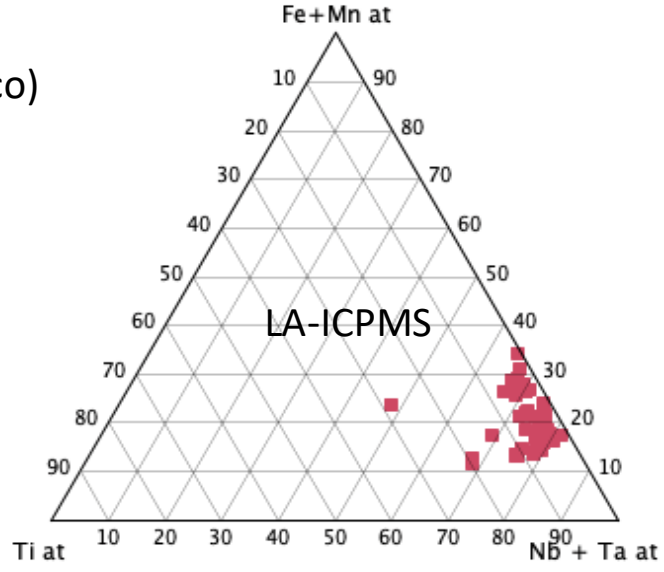


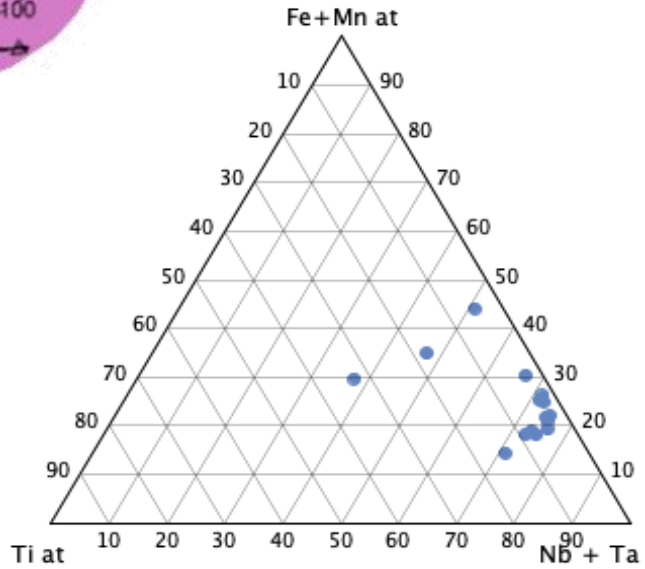
Cassiterite – LA-ICPMS Analyses

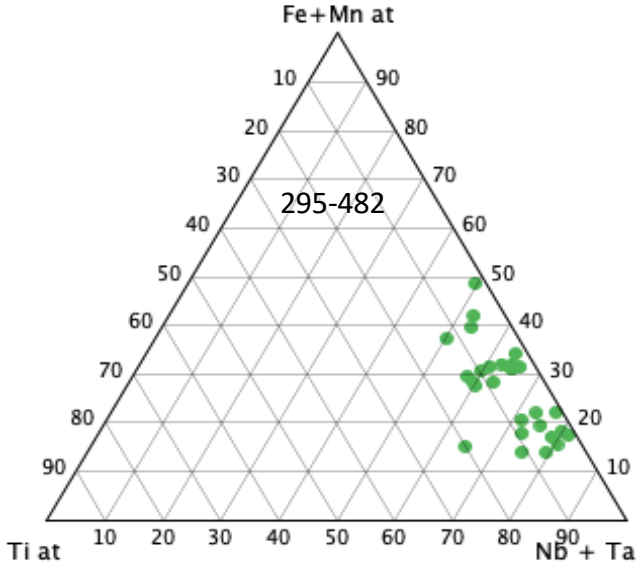


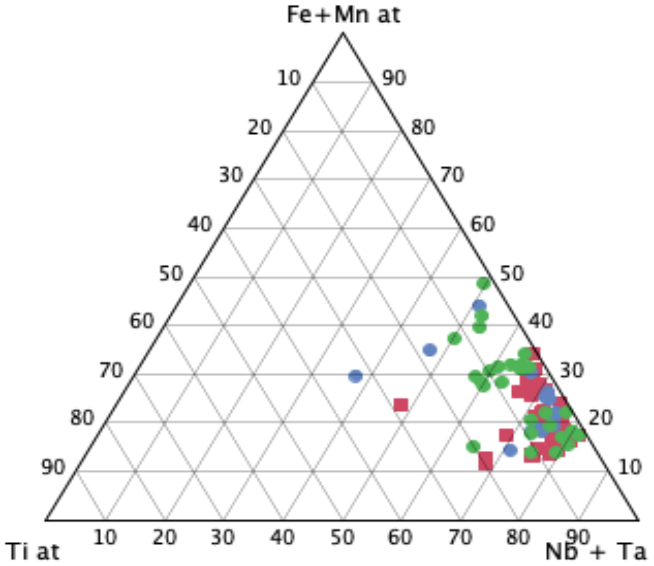
SEGURA
Cerro (Cabeço)
Queimado



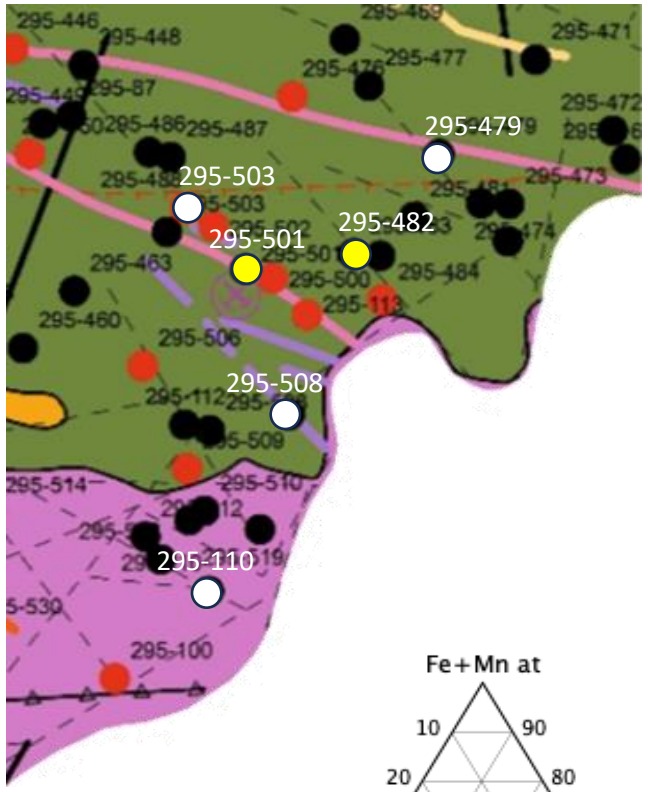


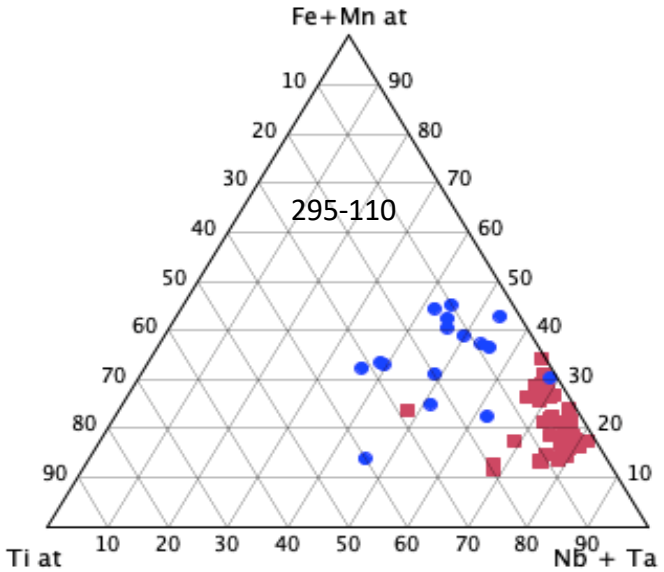


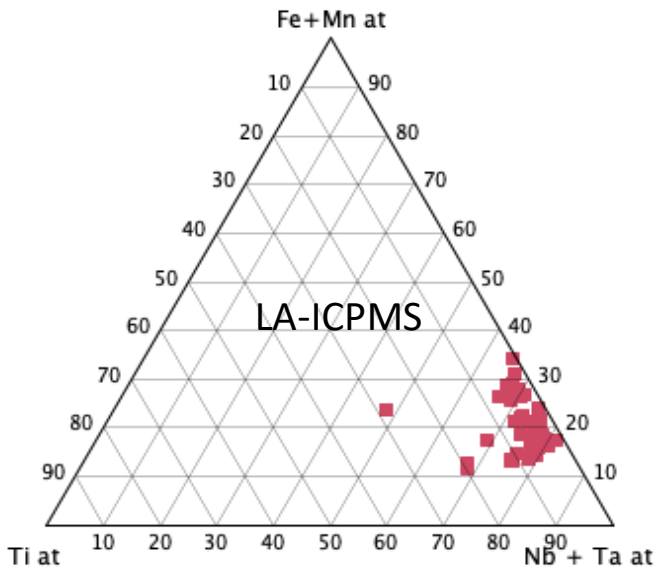


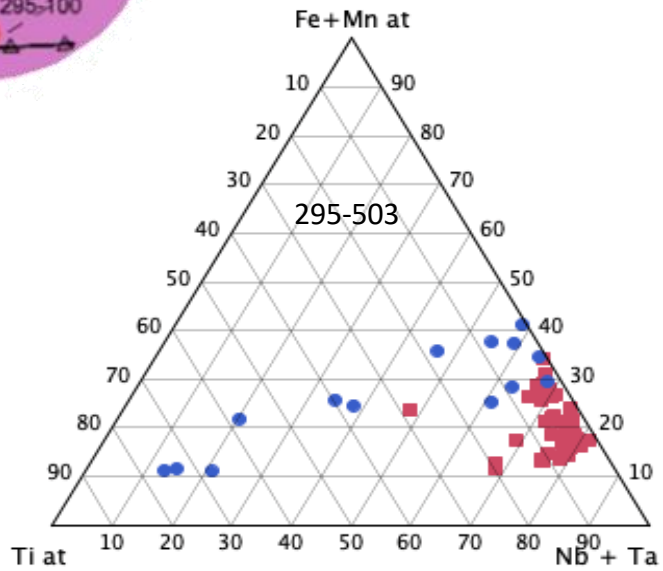


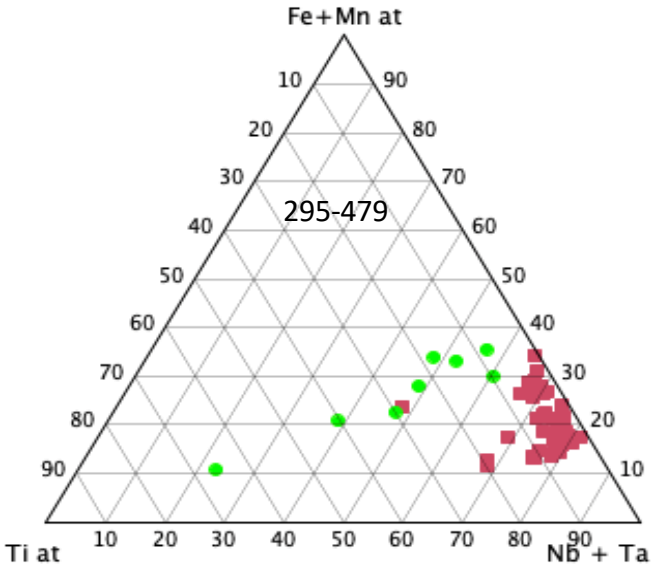
Cassiterite – LA-ICPMS Analyses

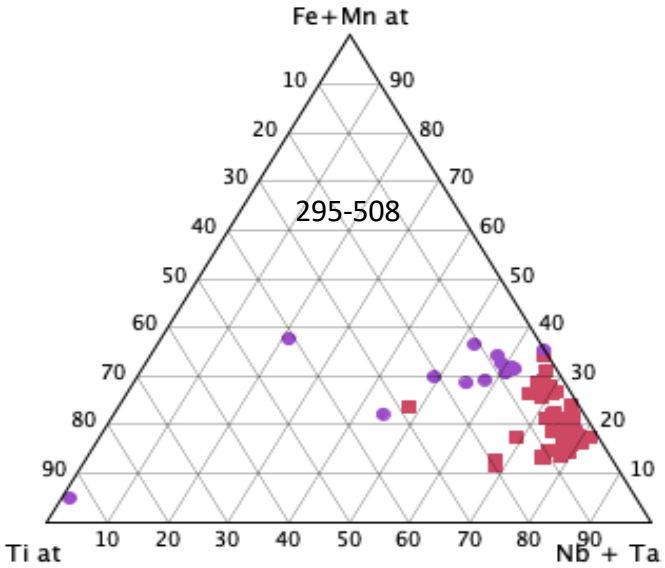




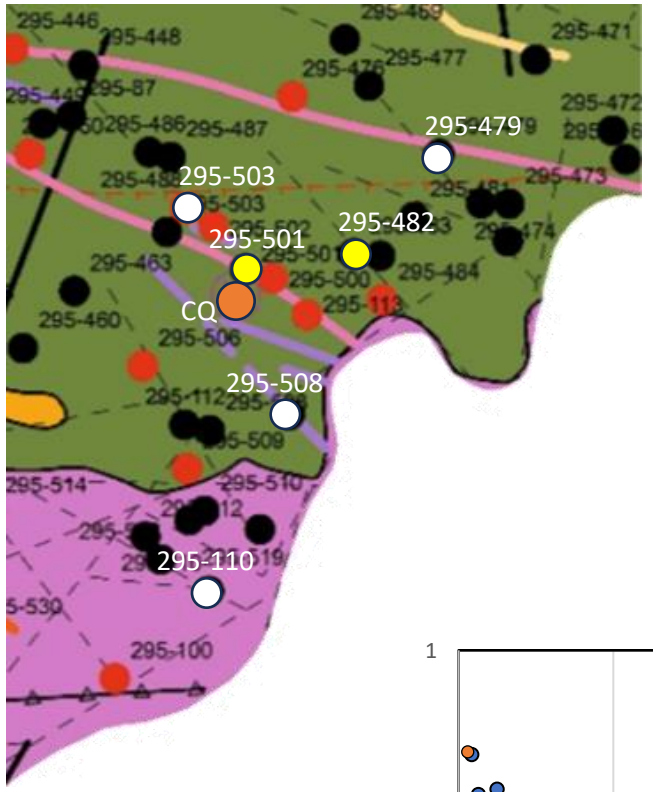


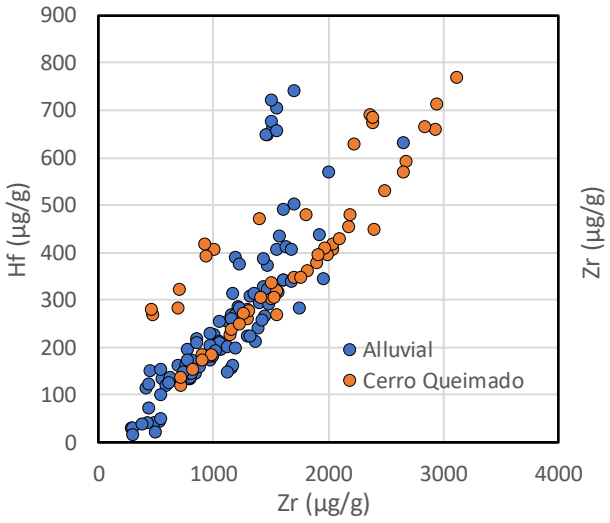


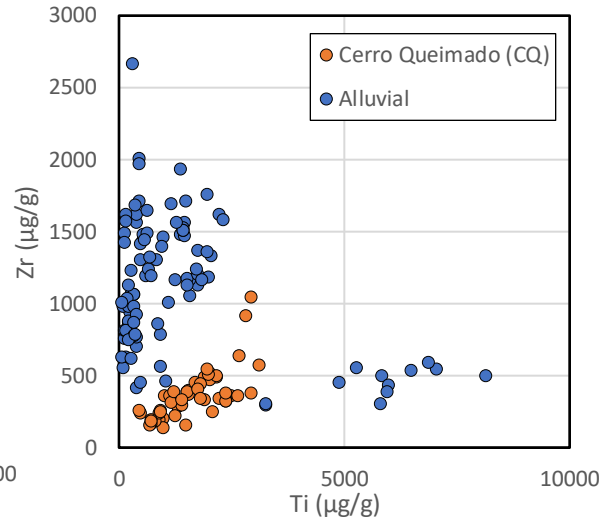


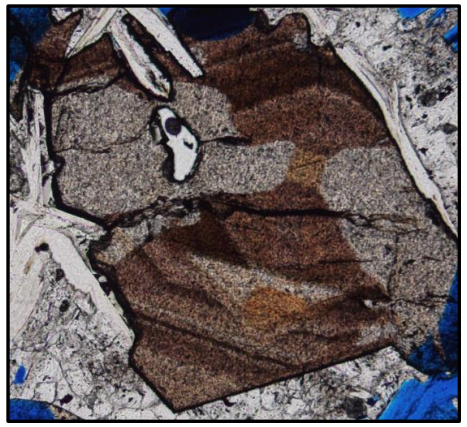


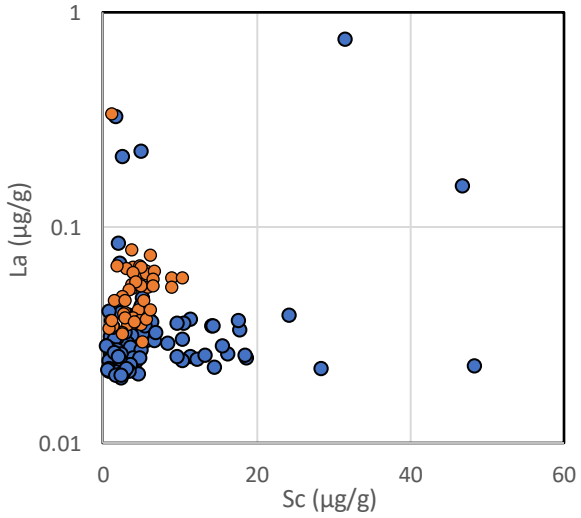
Cassiterite – LA-ICPMS Analyses (trace elements)

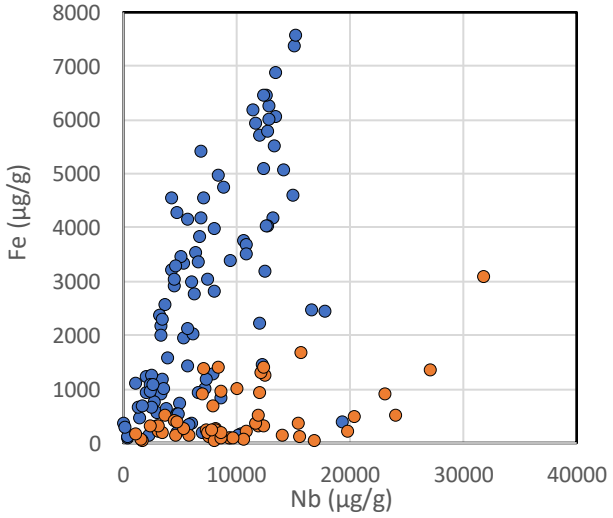




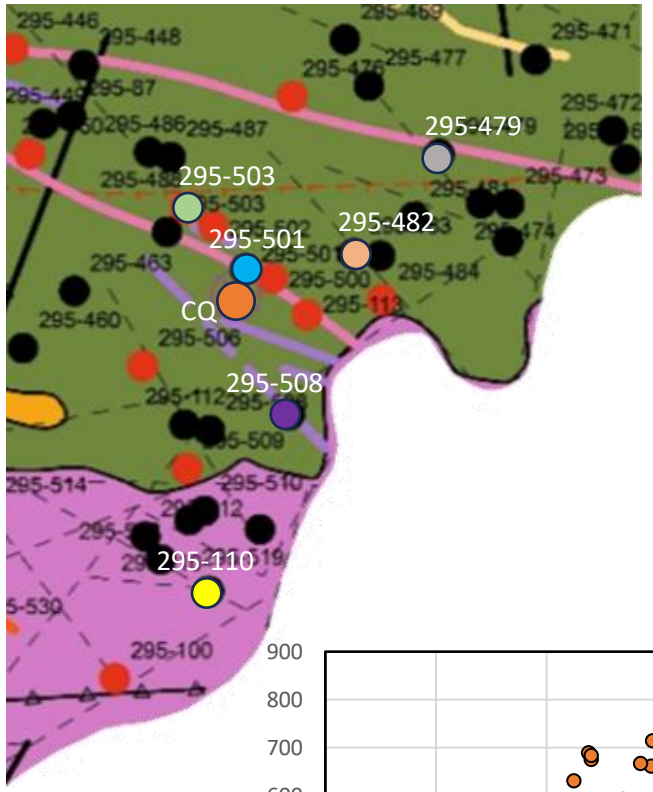


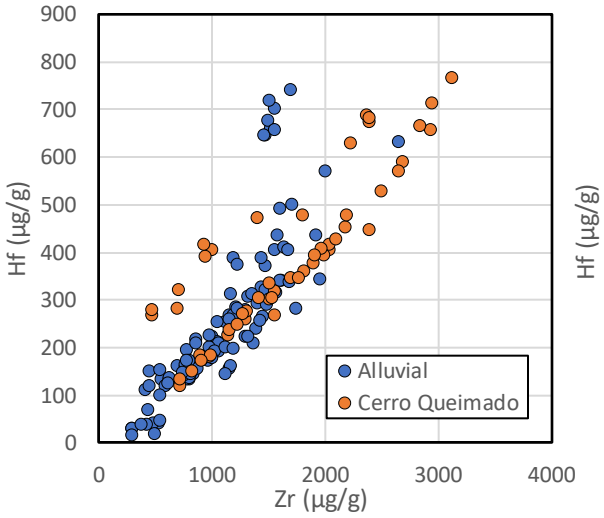


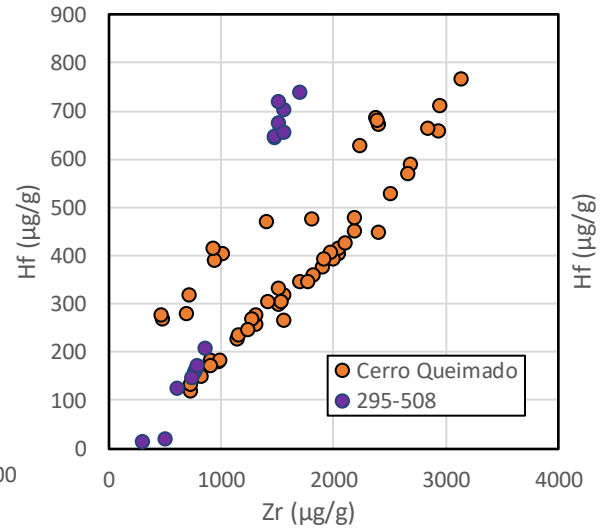


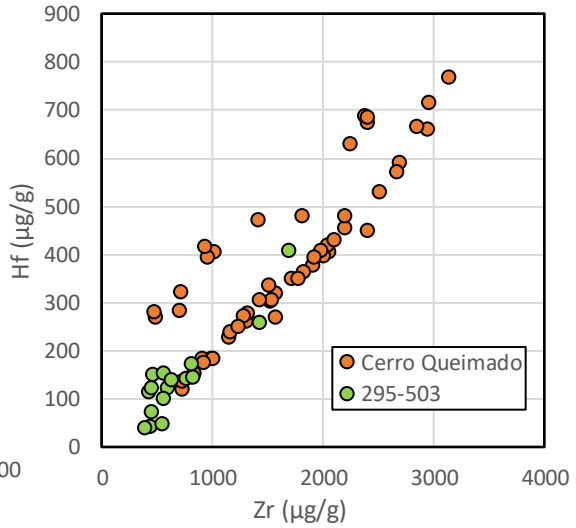


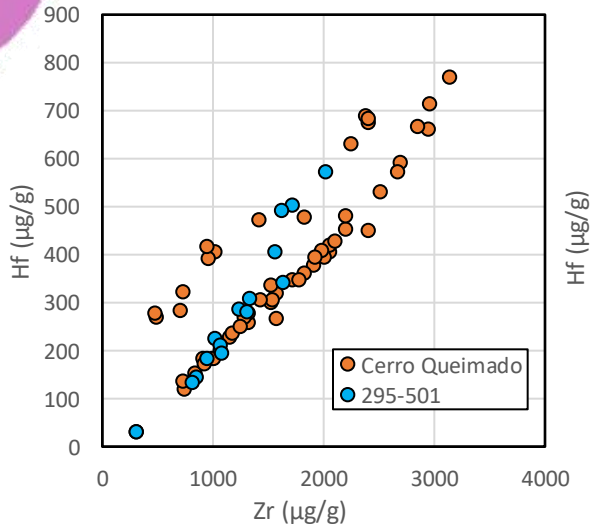
Cassiterite – LA-ICPMS Analyses (trace elements)

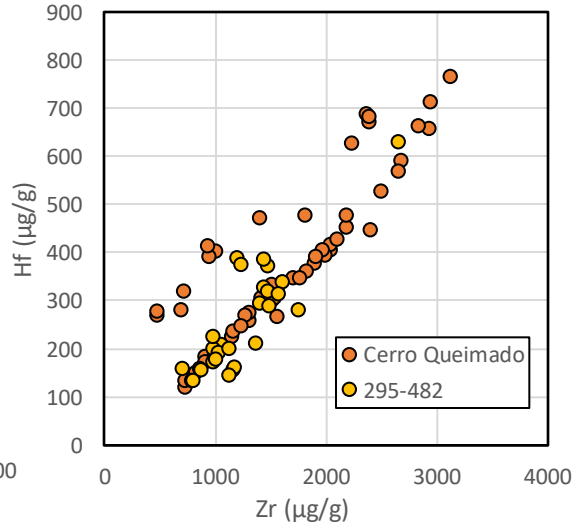


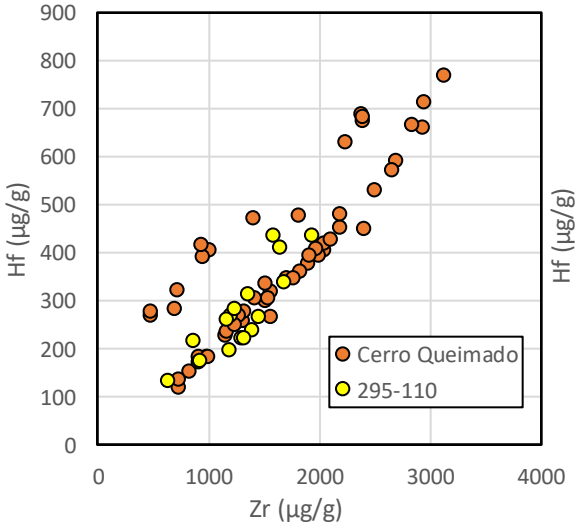


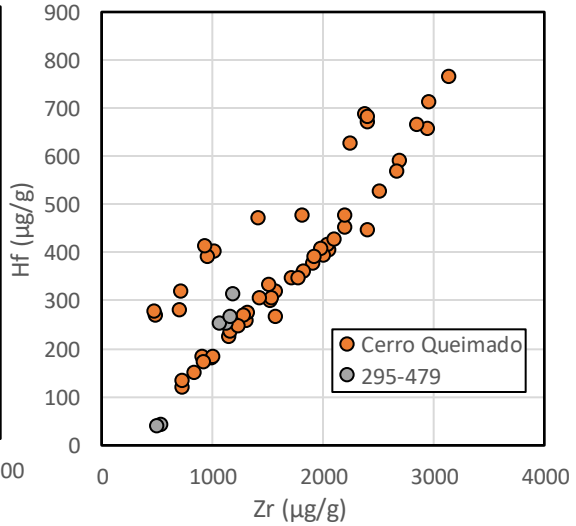










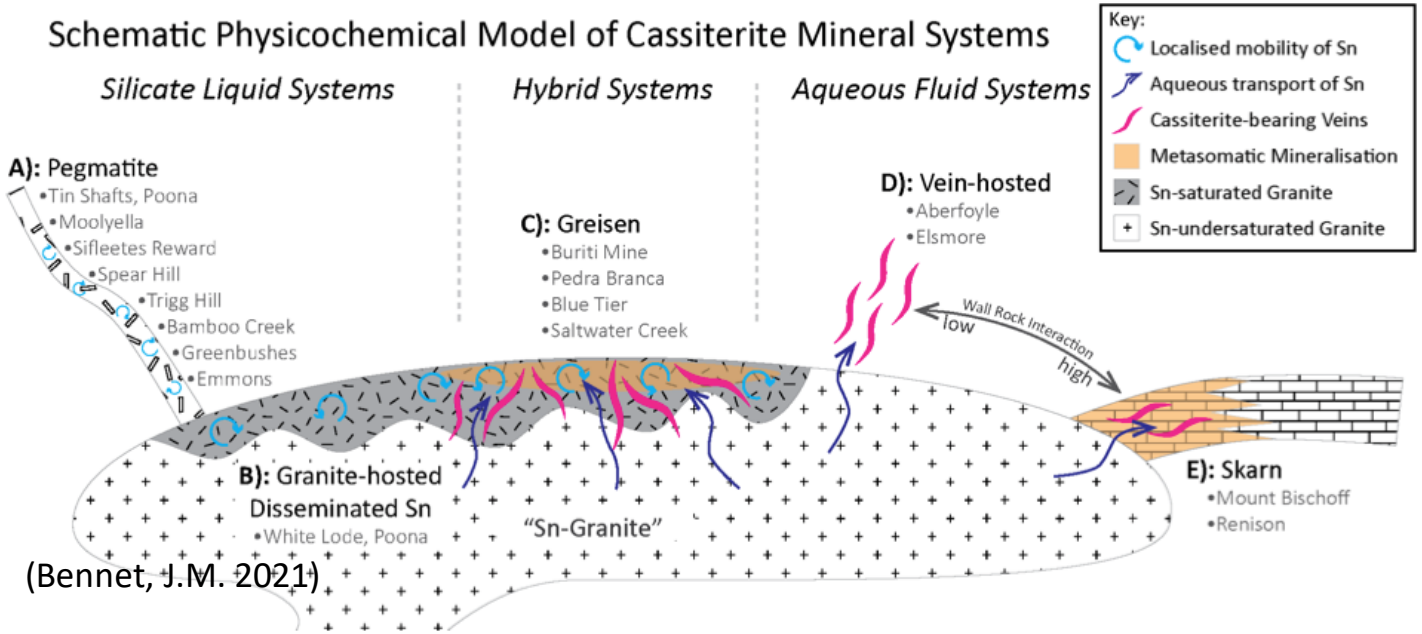


Wrap Up

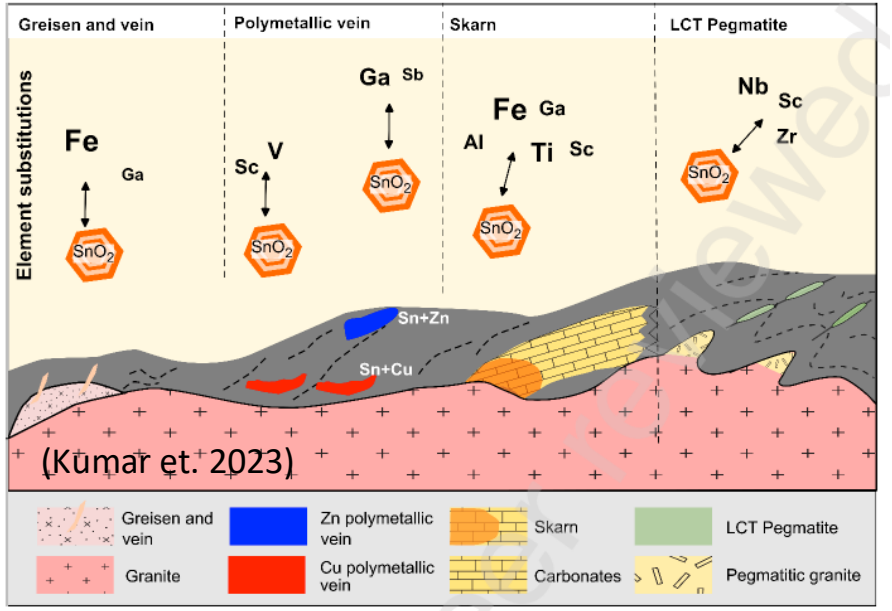
- Cassiterite minor and trace element are excellent fingerprints and can discriminate among disctint cassiterite Mineral systems.

- A multi-approach is needed to fully understand the physicochemical history of cassiterite: petrography, Imaging (CL and X-ray mapping))/EPM/LA-ICPMS.

- Alluvial cassiterite can be a good exploration starting approach



(Bennet, J.M. 2021)



(Kumar et. 2023)