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Indications provided by  
compositional variations recorded in  
TiO<sub>2</sub> polymorphs and tourmaline

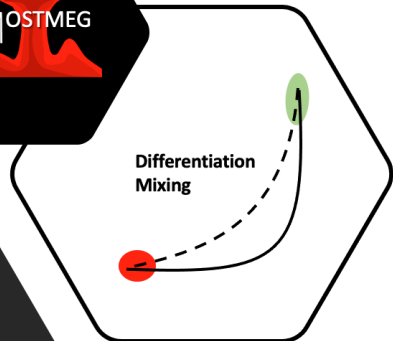
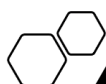
**L. Miguel Gaspar**; Nuno Grácio; Rute Salgueiro;  
Mafalda Costa; Isabel Ribeiro da Costa;  
António Mateus; Ivo Martins; Pedro Reis

# Indications provided by compositional variations recorded in TiO<sub>2</sub> polymorphs and tourmaline



## Part I

### Tourmaline



Assessment of Tourmaline Composition as a Vectoring Tool for Sn-W Deposits: The Góis-Panasqueira-Segura belt (Central Portugal)

Miguel Gaspar, Isabel R. Costa, António Mateus, Ivo Martins, and Pedro Rodrigues



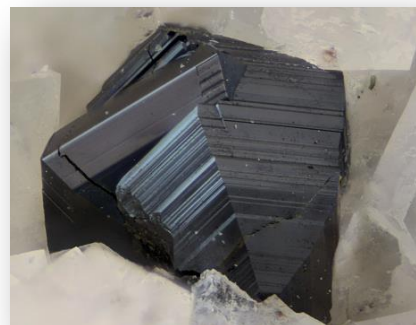
## Part II



Article

### Trace Element Geochemistry of Alluvial TiO<sub>2</sub> Polymorphs as a Proxy for Sn and W Deposits

Miguel Gaspar <sup>1,2,\*</sup>, Nuno Grácio <sup>2,3</sup>, Rute Salgueiro <sup>3</sup> and Mafalda Costa <sup>4</sup>



Rutile

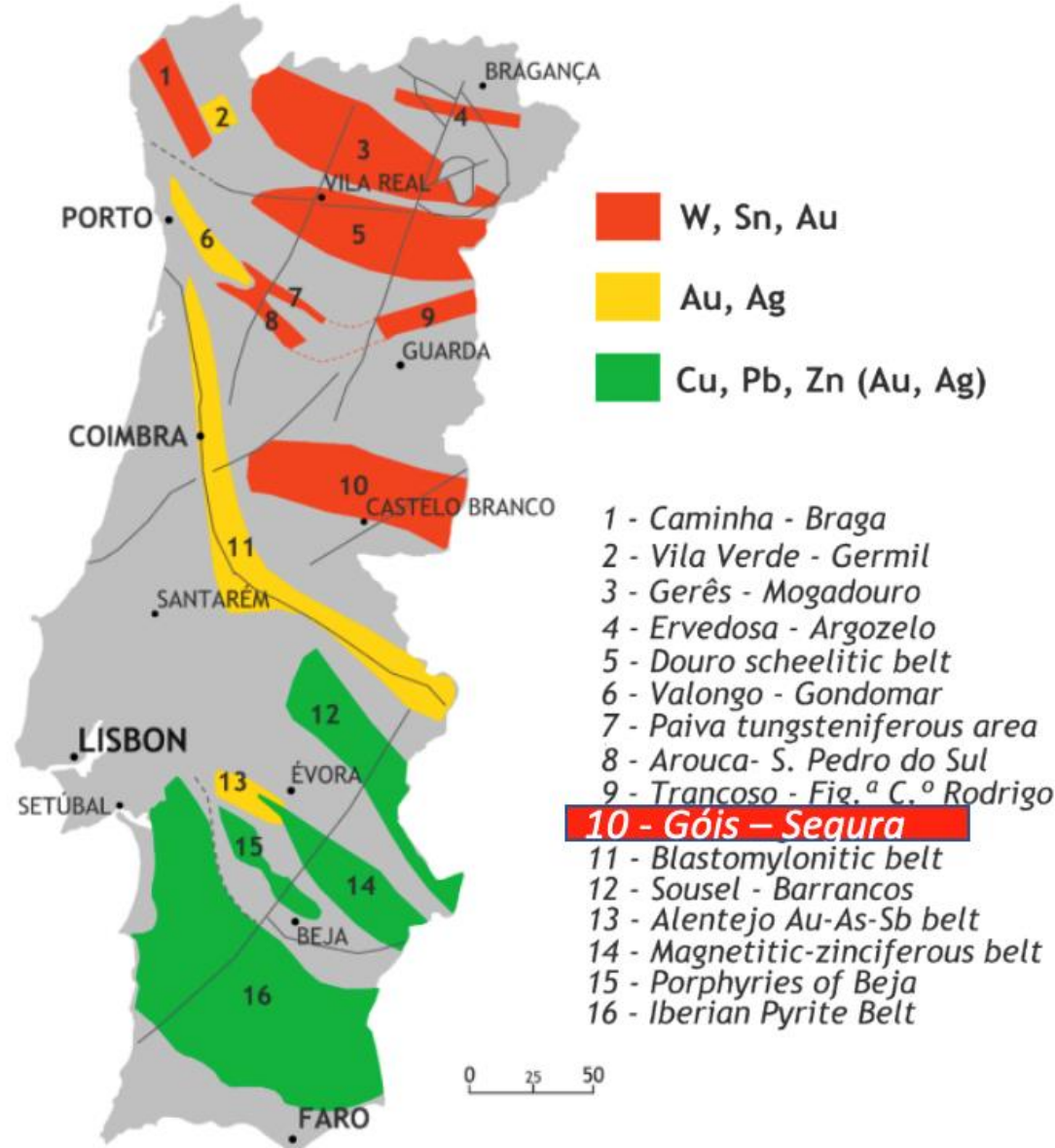
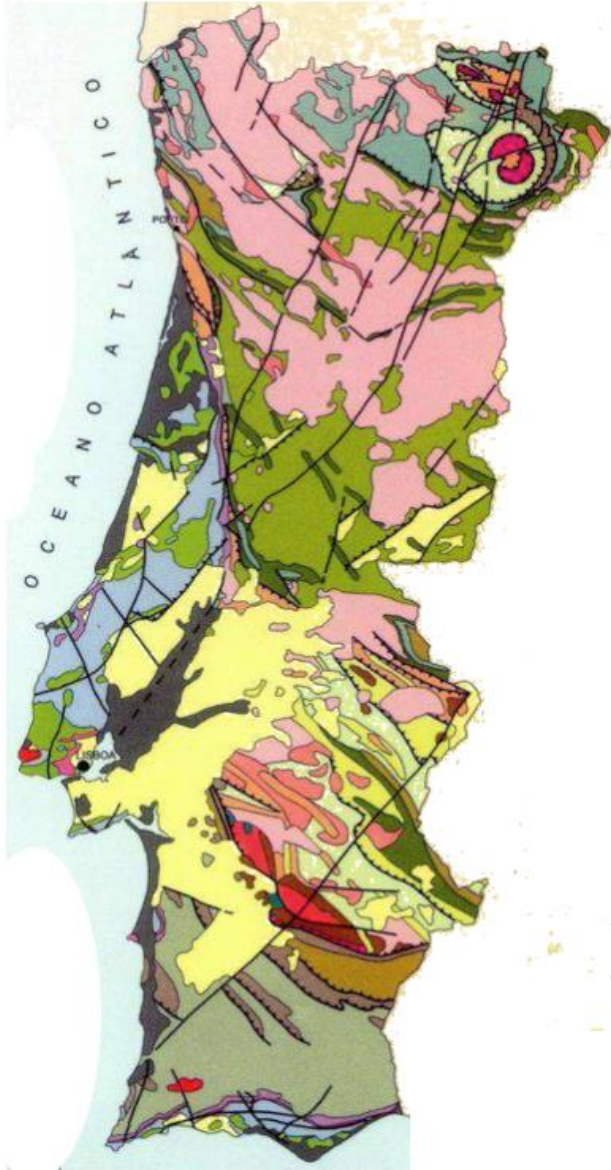


Anatase



Brookite

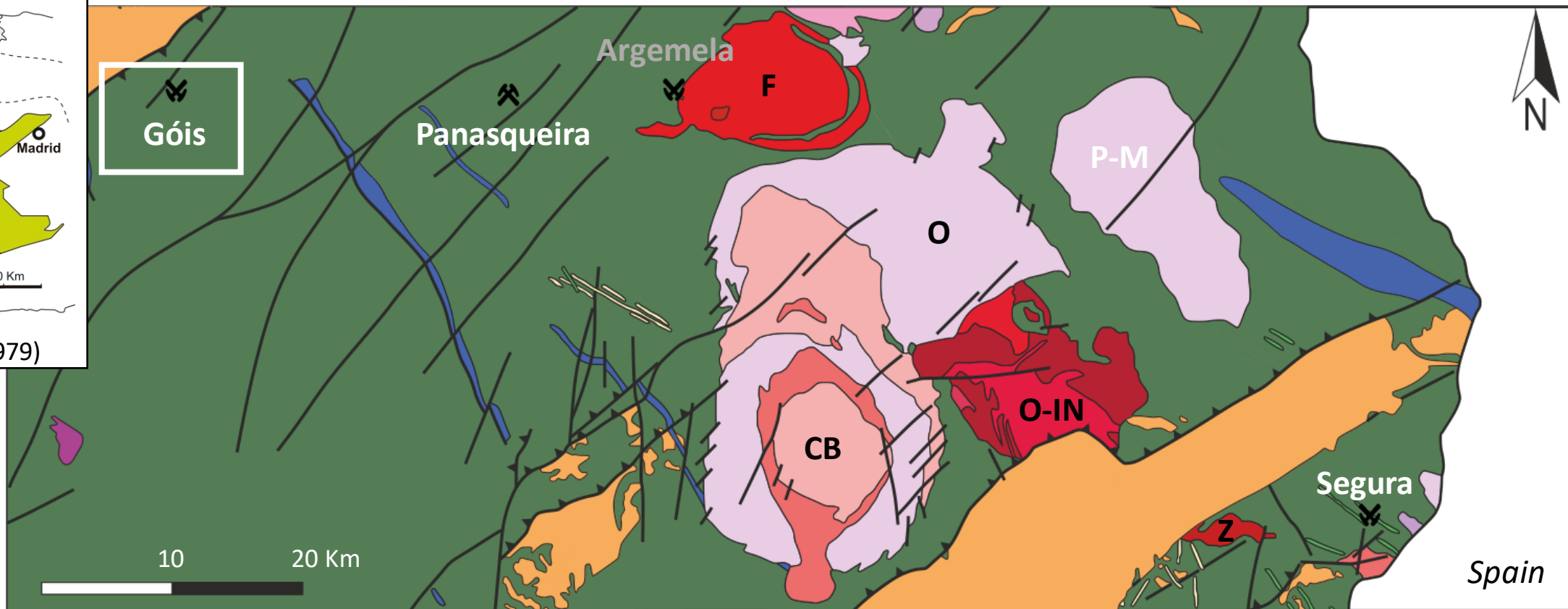
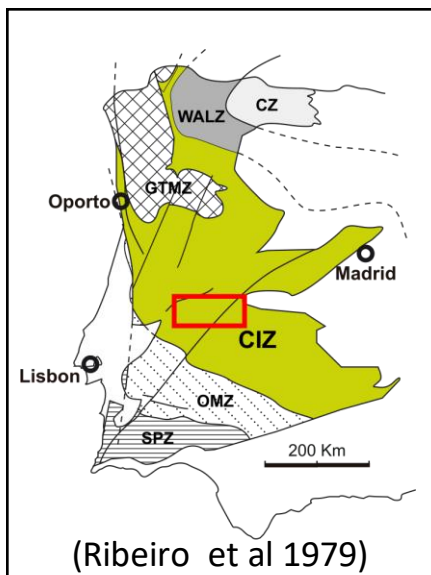
# Metallogenic belts









## Sn-W deposits

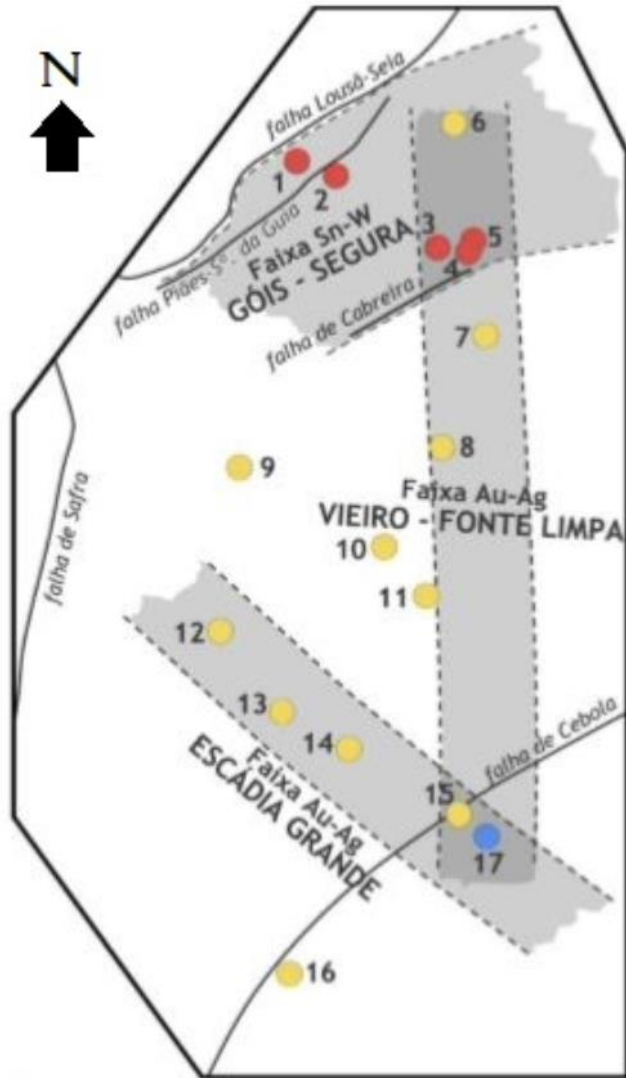
- W quartz veins
- W(Sn) quartz veins
- W skarns
- Sn(W) quartz veins
- Sn aplite-pegmatites
- Sn greisen
- Sn alluvial

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



- |   |                     |   |   |   |                   |
|---|---------------------|---|---|---|-------------------|
|  | Variscan Granites   |  | Ordovician Metasediments                        |  | Tertiary deposits |
|  | Ordovician Granites |  | Ante-Ordovician Metasediments<br>(Beiras Group) |   |                   |
|  | Cadomian Granites   |   |   |   |                   |

# Góis – Vale Pião deposit



(Manuel et al. 2017)

## Mineral occurrences

### (Sn-W)

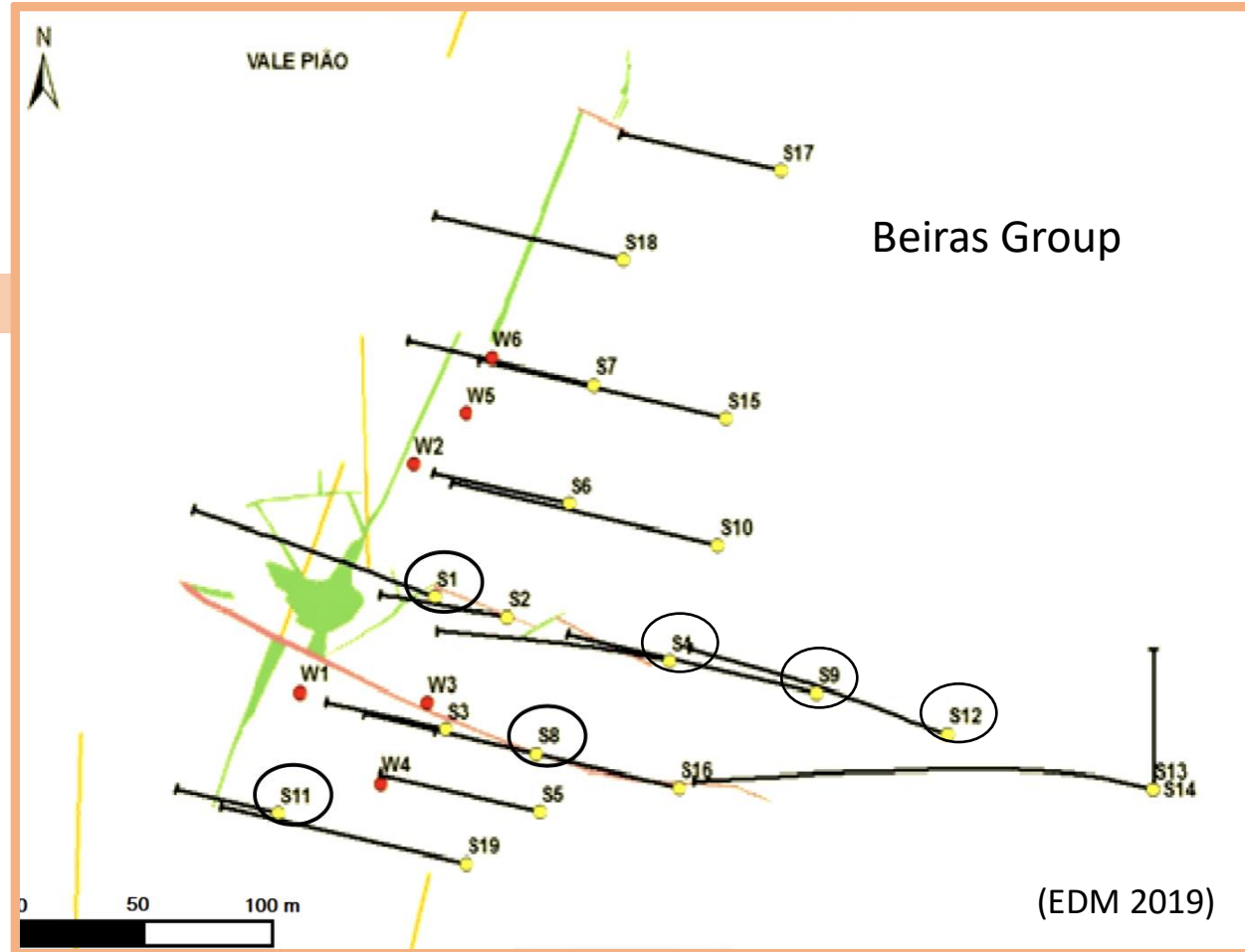
- 1 – Vale Moreiro – Casal Loureiro
- 2 – Senhora da Guia
- 3 – Rabadão
- 4 – Vale Pião**
- 5 – Barroca de Amiães

### (Au-Ag)

- 6 – Vieiro
- 7 – Cadafaz
- 8 – Corterredor
- 9 – Cerdeira
- 10 – Mestras
- 11 – Cabeçadas
- 12 – Escádia Grande
- 13 – Roda Cimeira
- 14 – Roda Fundeira
- 15 – Fonte Limpa
- 16 – Alvares

### (Sb-Au)

- 17 – Vale Torto

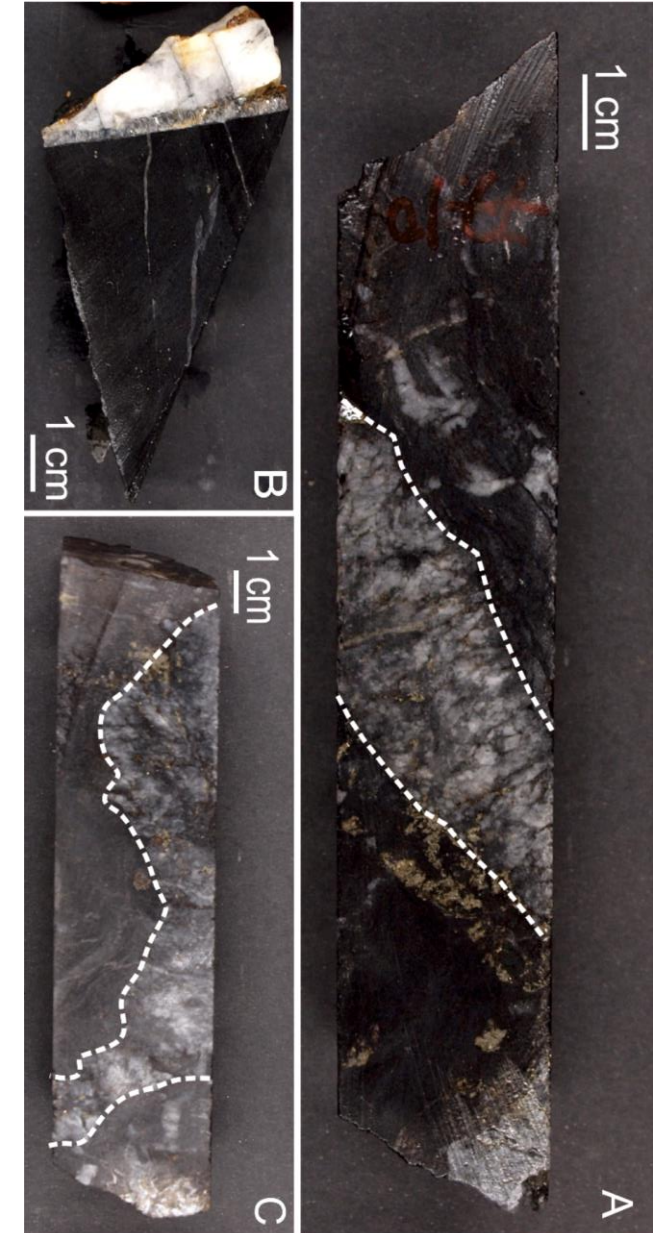
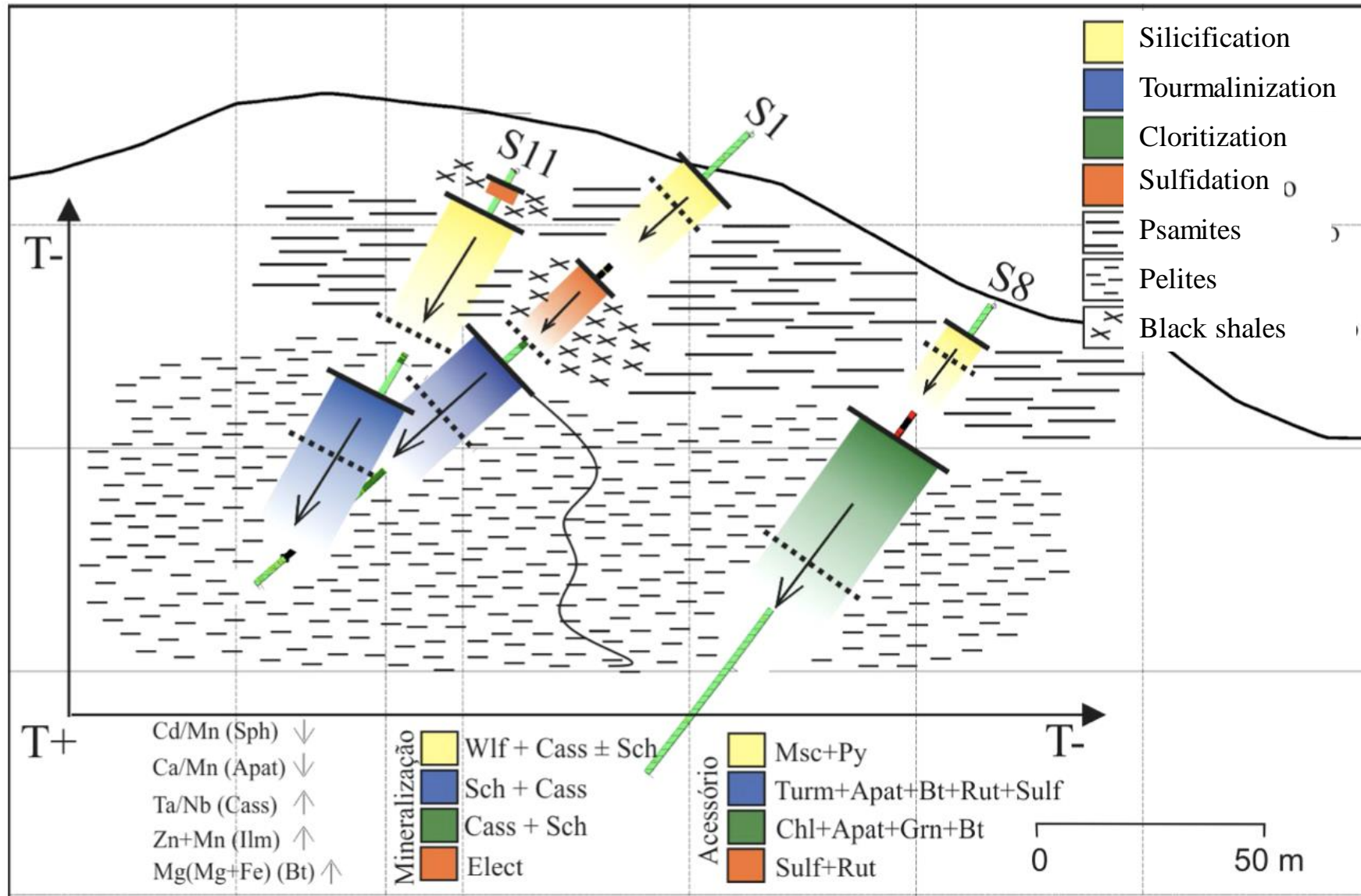


■ Breccias – Woframite/Scheelite

○ Studied core

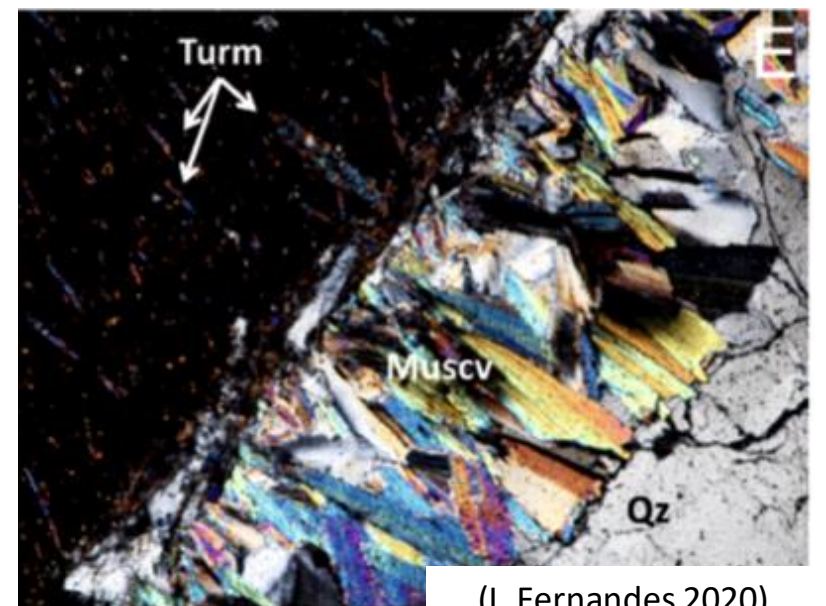
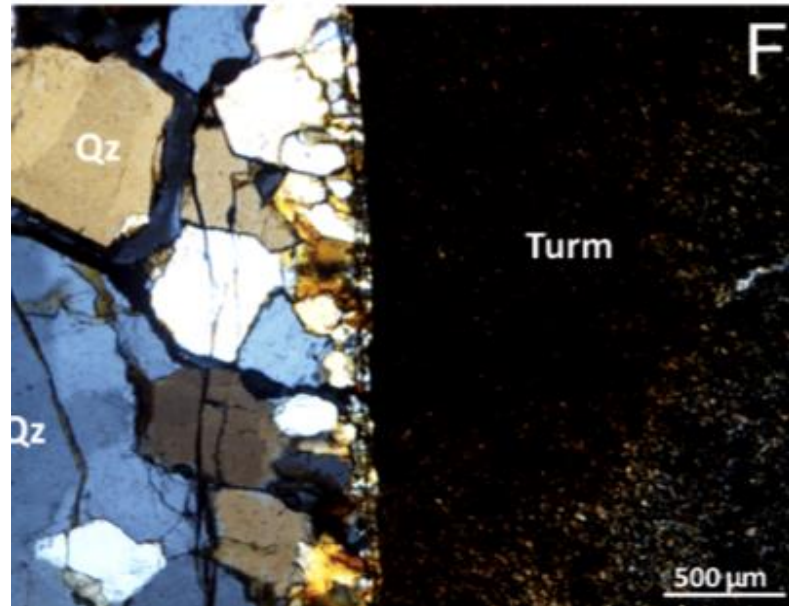
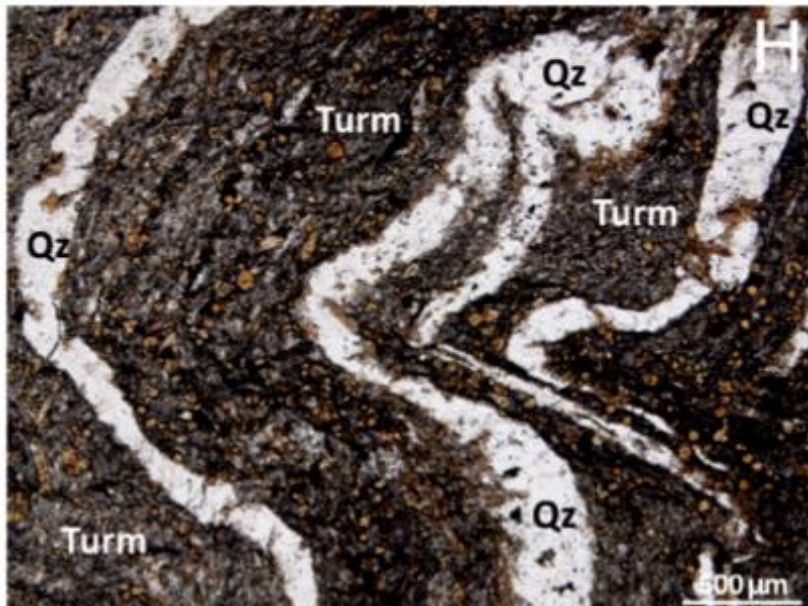
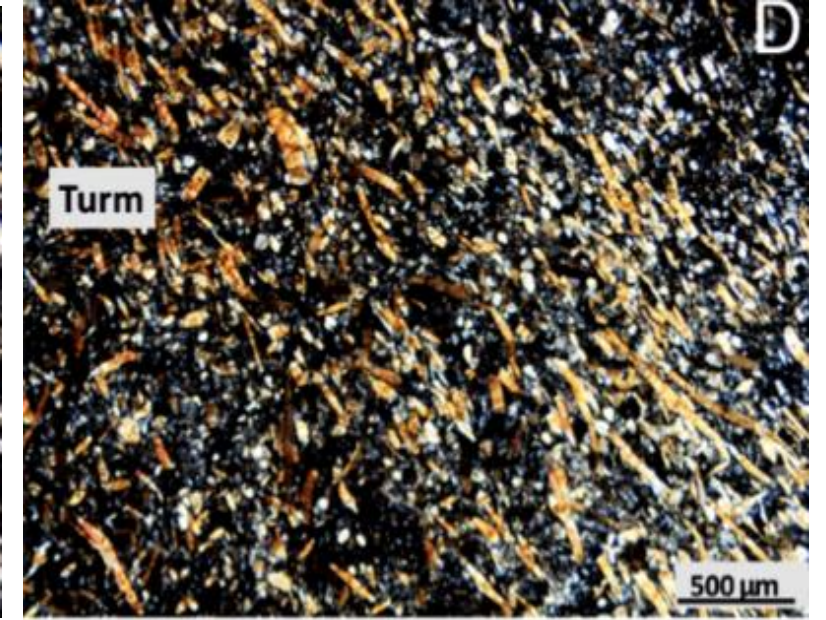
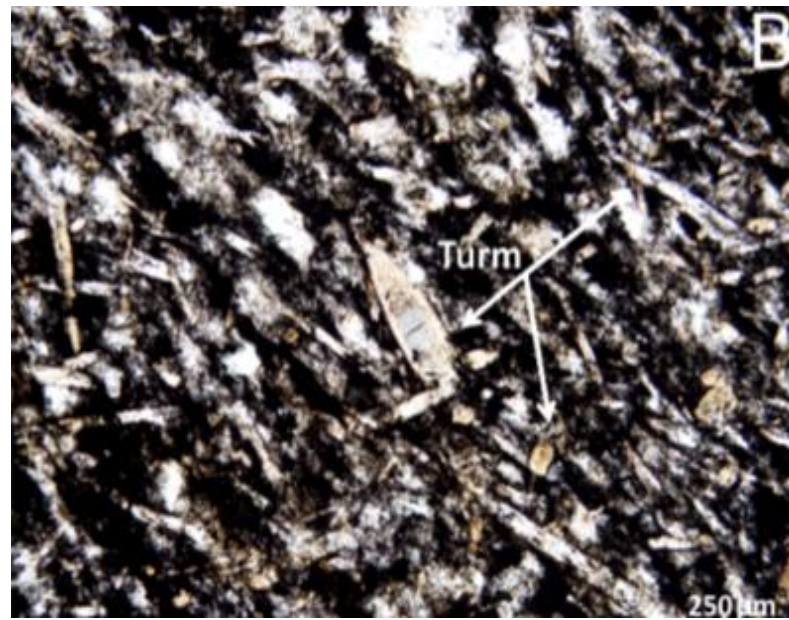
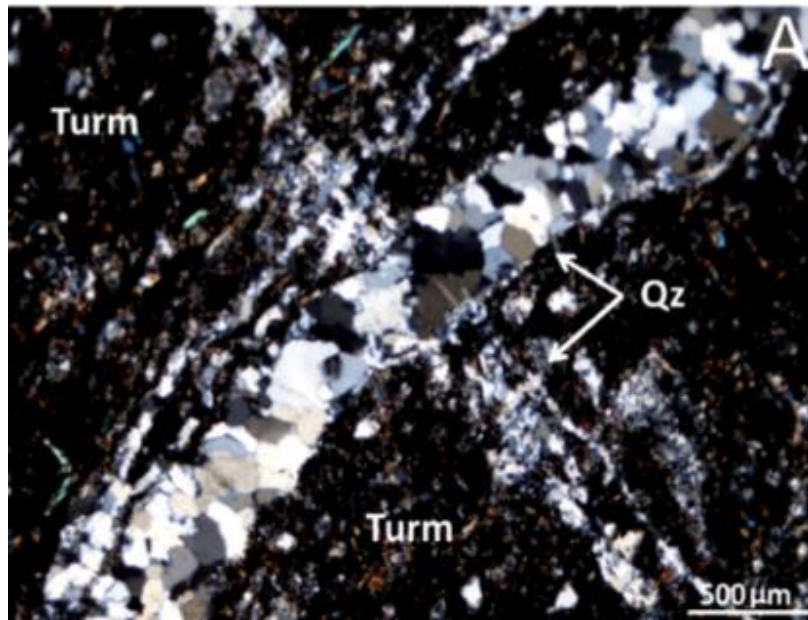
— Quartz – Wolframite – Cassiterite veins

# Góis – Vale Pião deposit



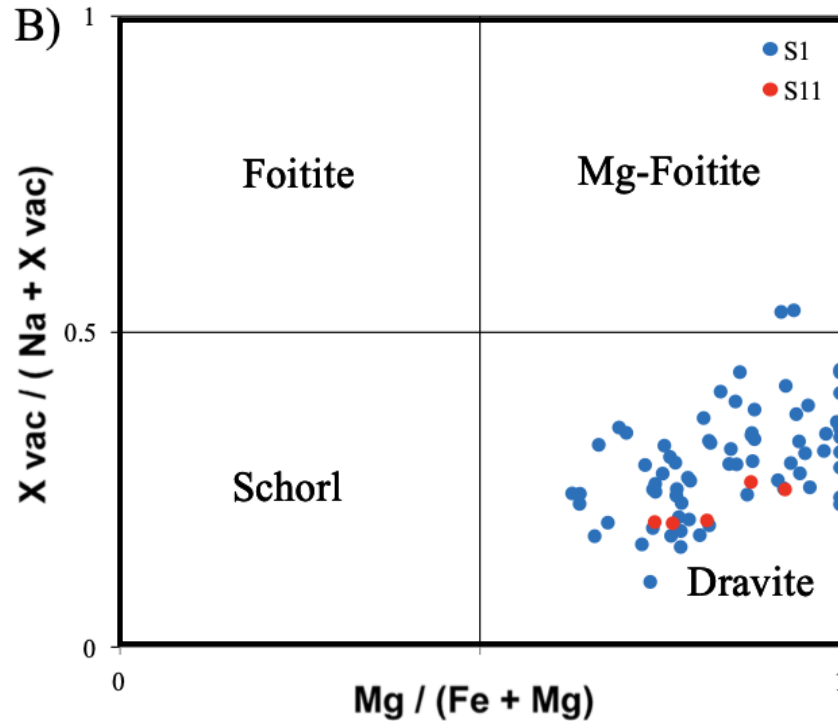
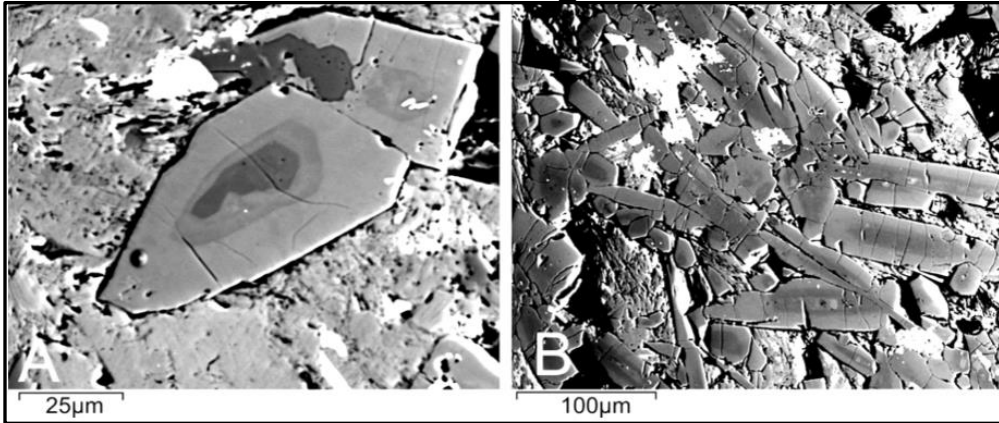
(I. Fernandes 2020)

# Góis – Vale Pião Tourmaline

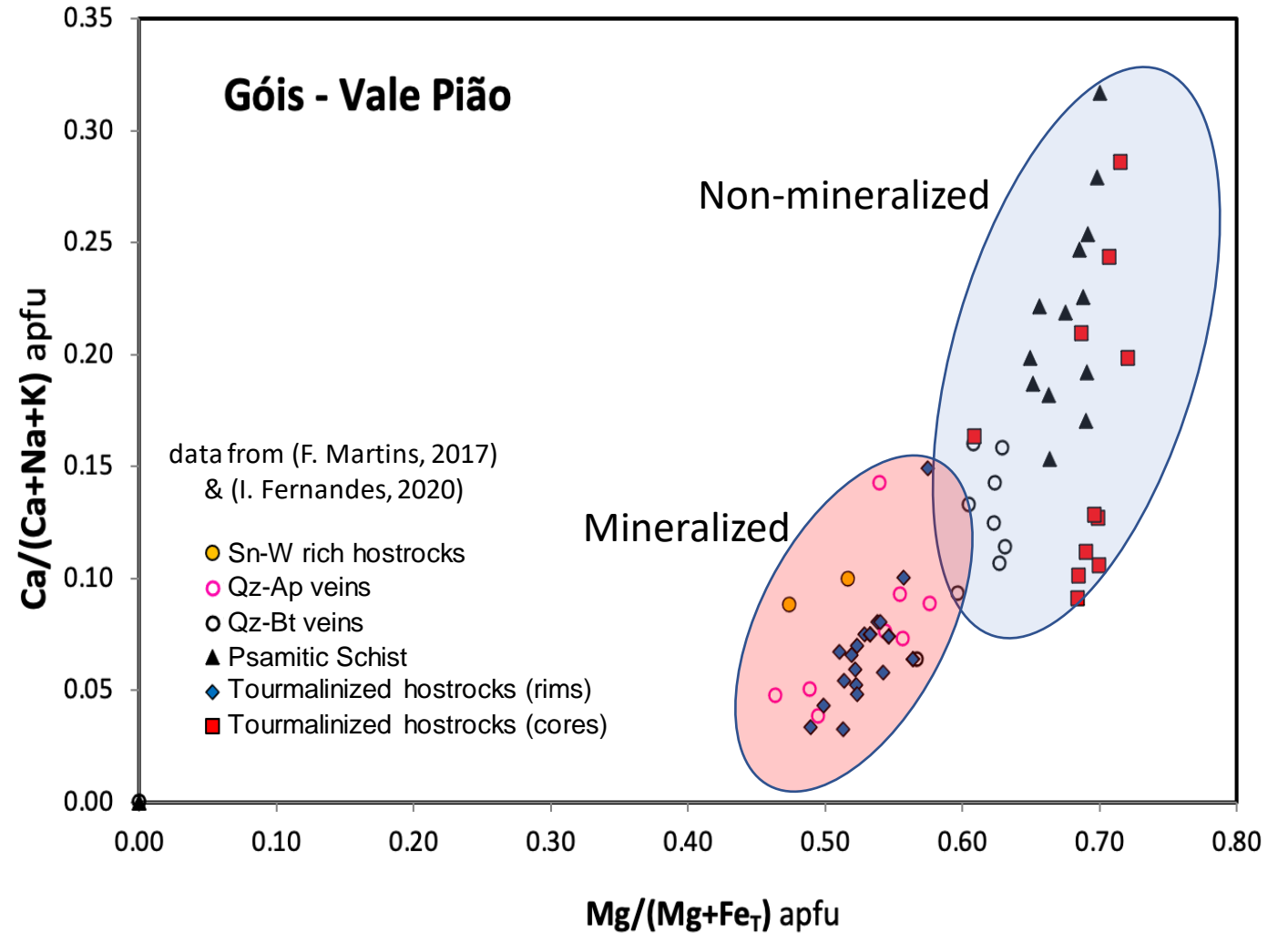


# Góis – Vale Pião Tourmaline

BSE images

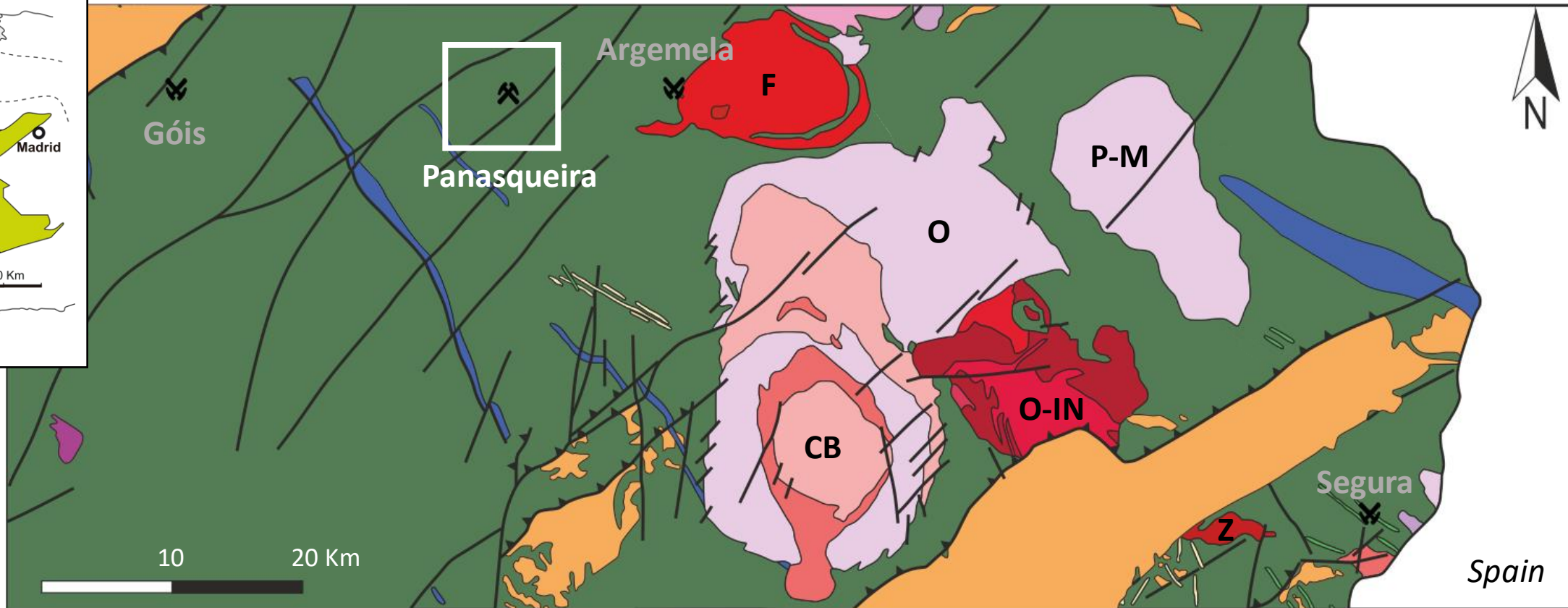
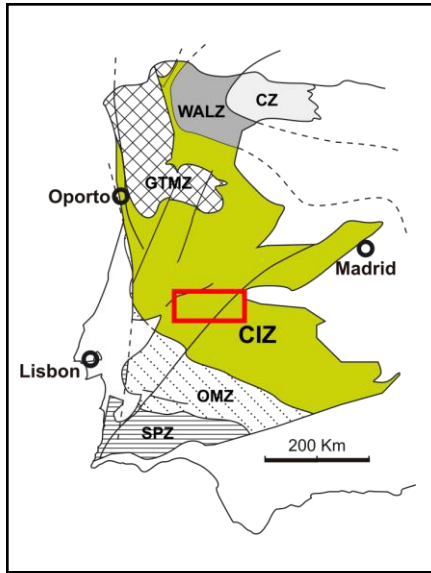








## Tourmaline Composition



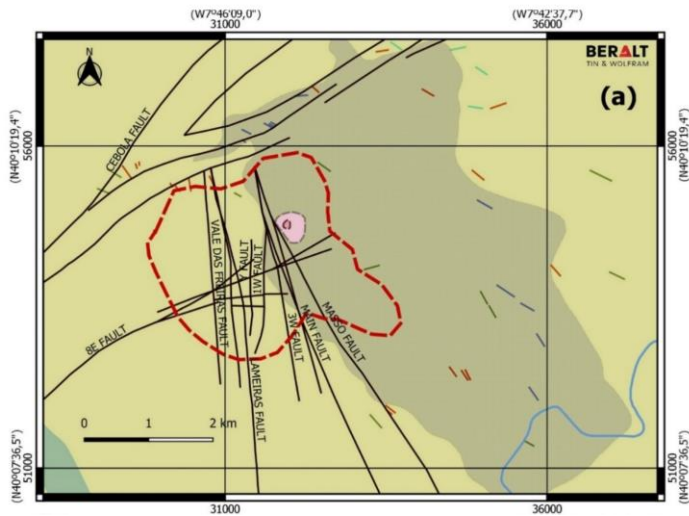


# Góis-Panasqueira-Segura Sn-W belt (Central Portugal)

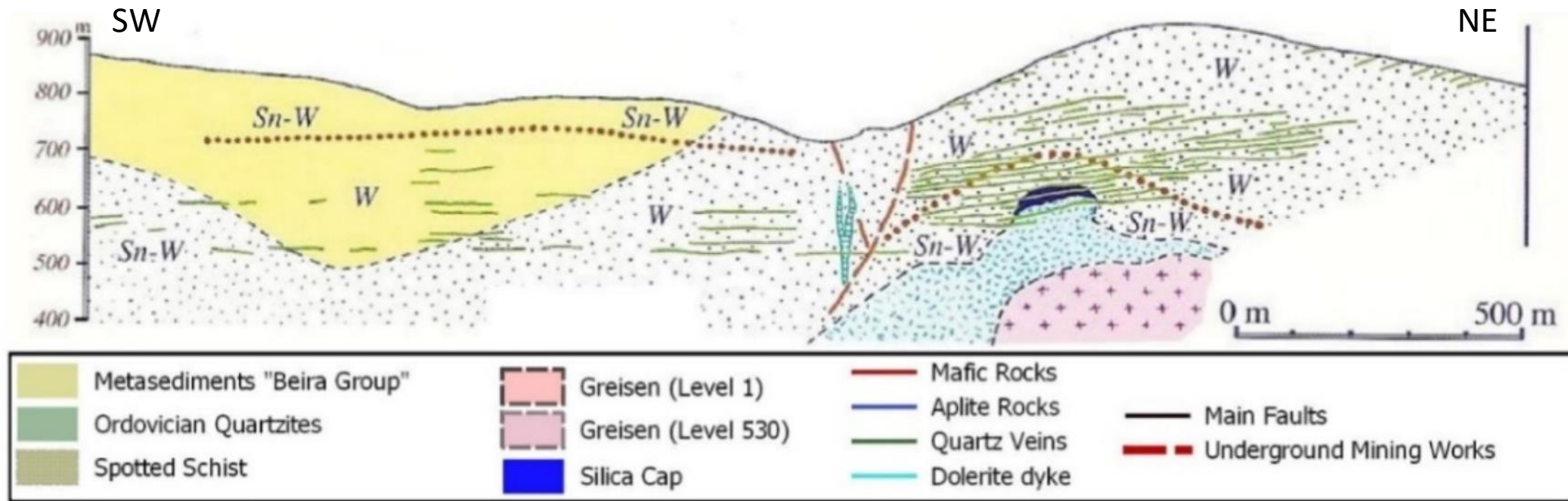


- |   |   |   |
|---|---|---|
|  Variscan Granites   |  Ordovician Metasediments                        |  Tertiary deposits |
|  Ordovician Granites |  Ante-Ordovician Metasediments<br>(Beiras Group) |   |
|  Cadomian Granites   |   |   |

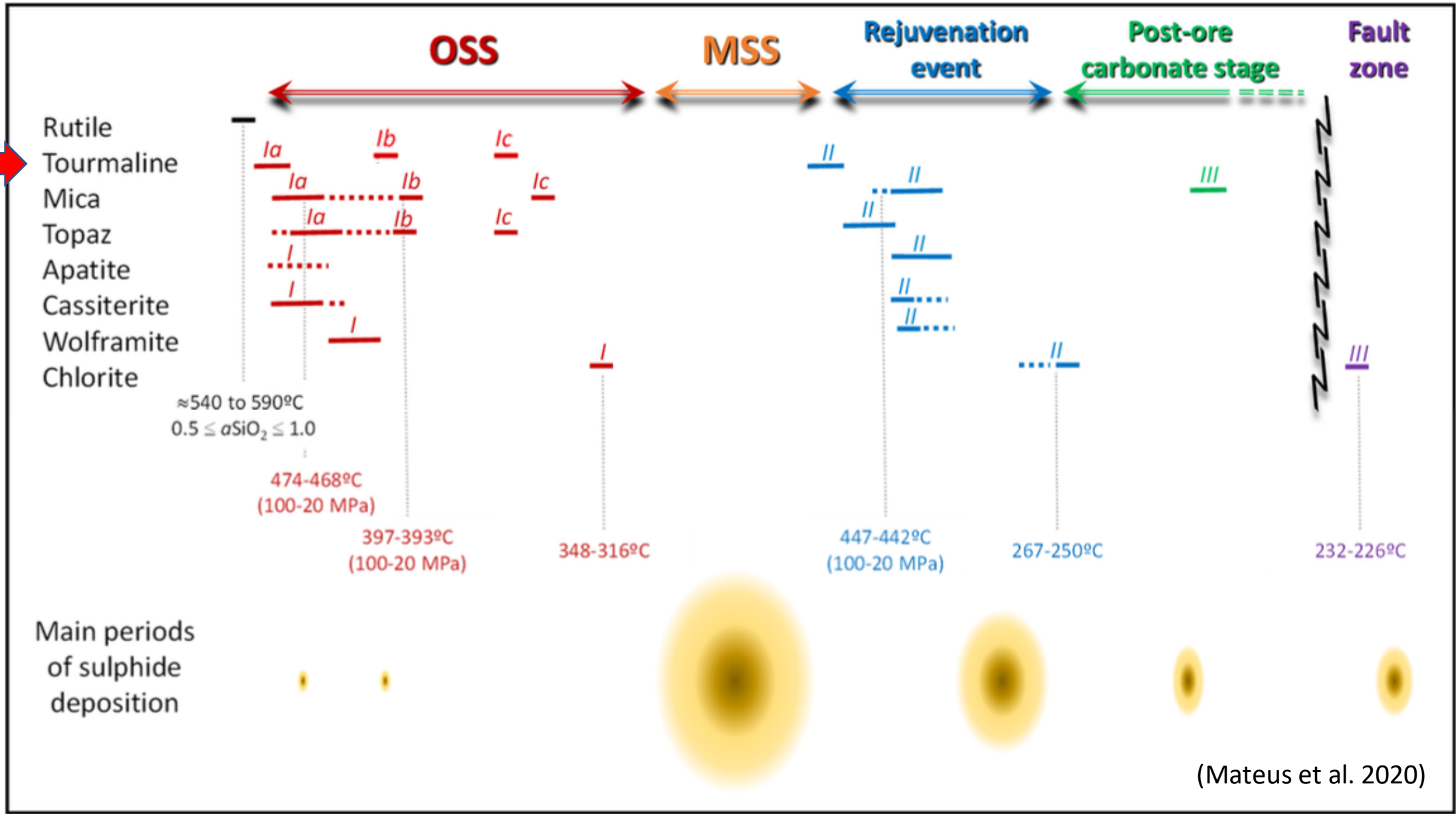
# Panasqueira W-Sn-(Cu) deposit



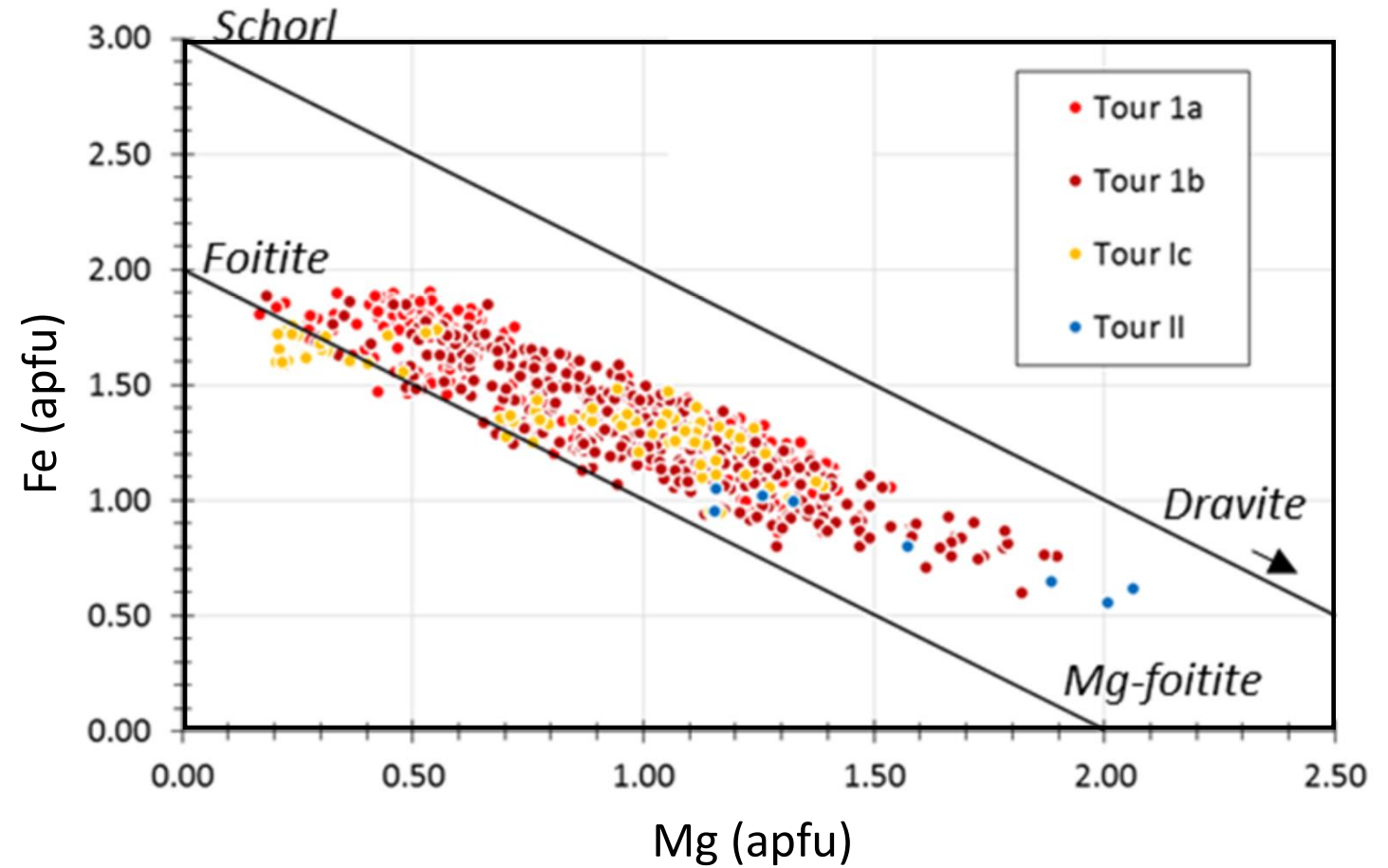
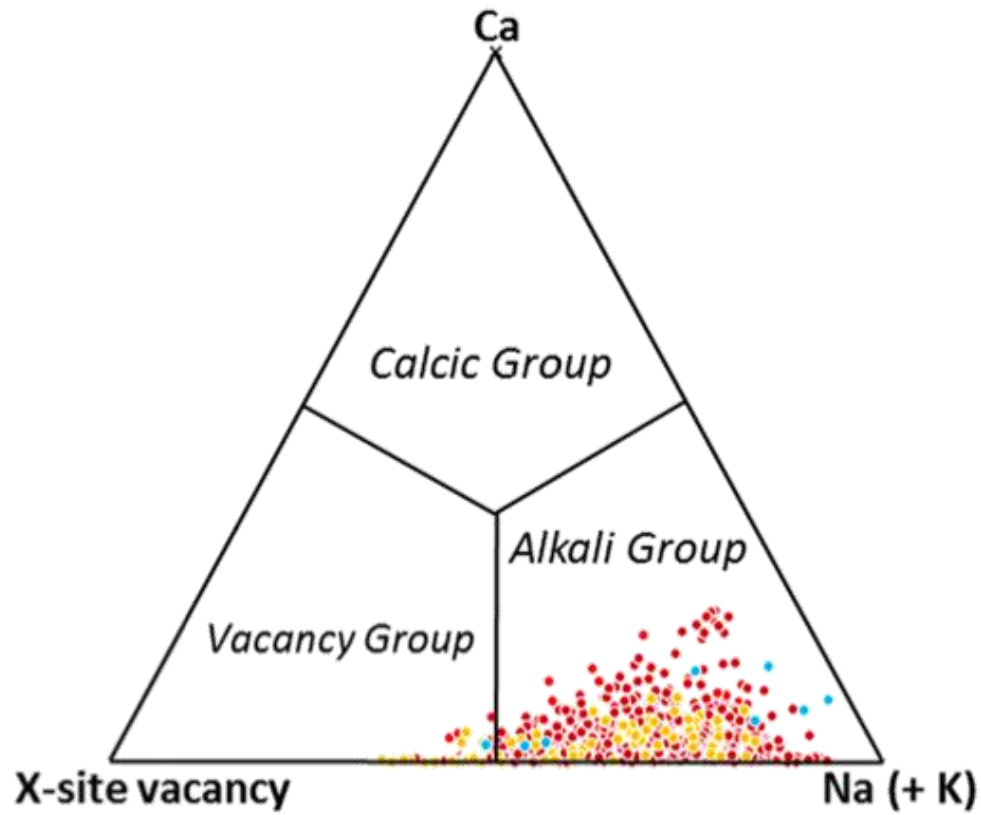
- W quartz veins
- W(Sn) quartz veins
- Sn(W) quartz veins
- Sn greisen



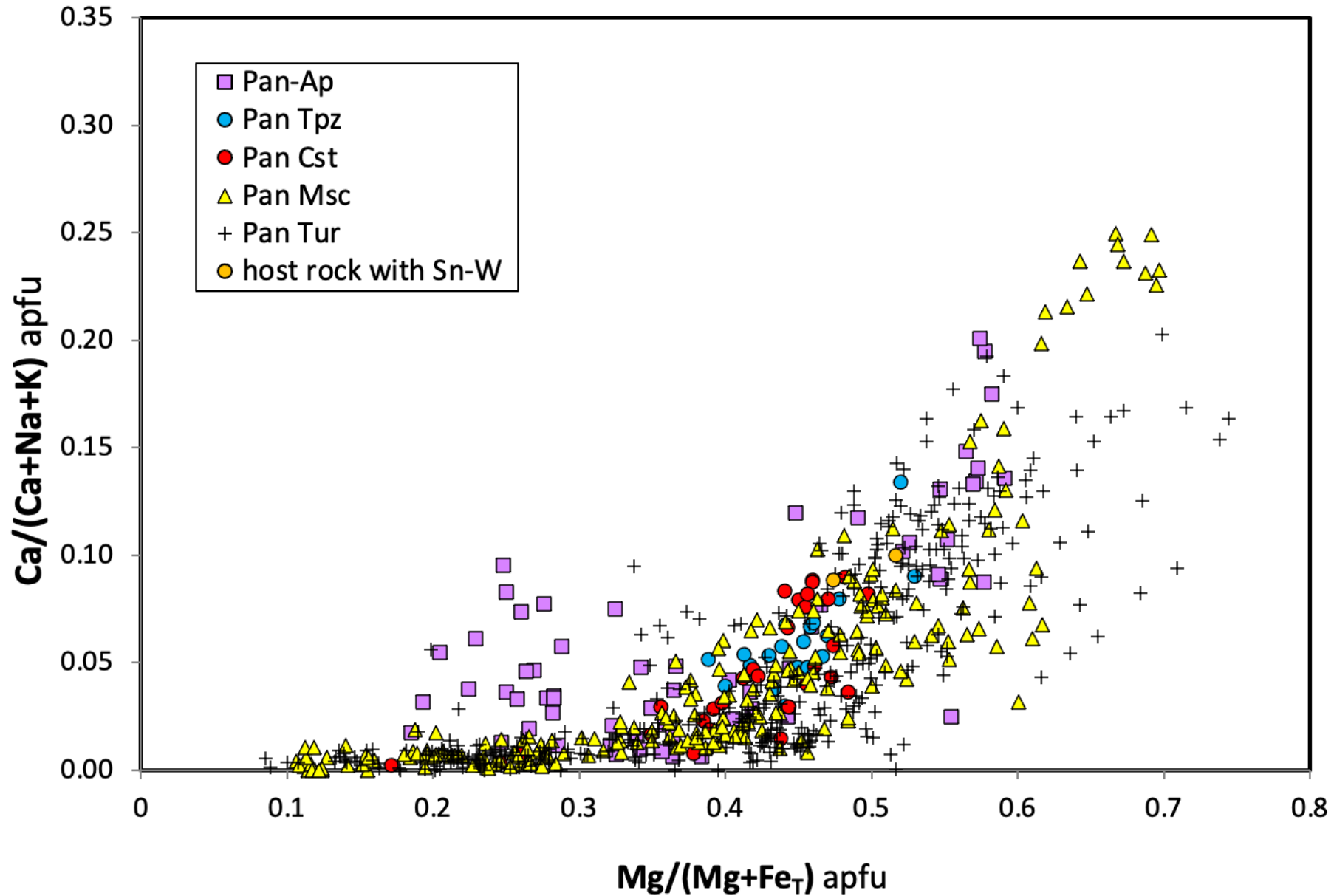
# Simplified paragenetic sequence of Panasqueira deposit



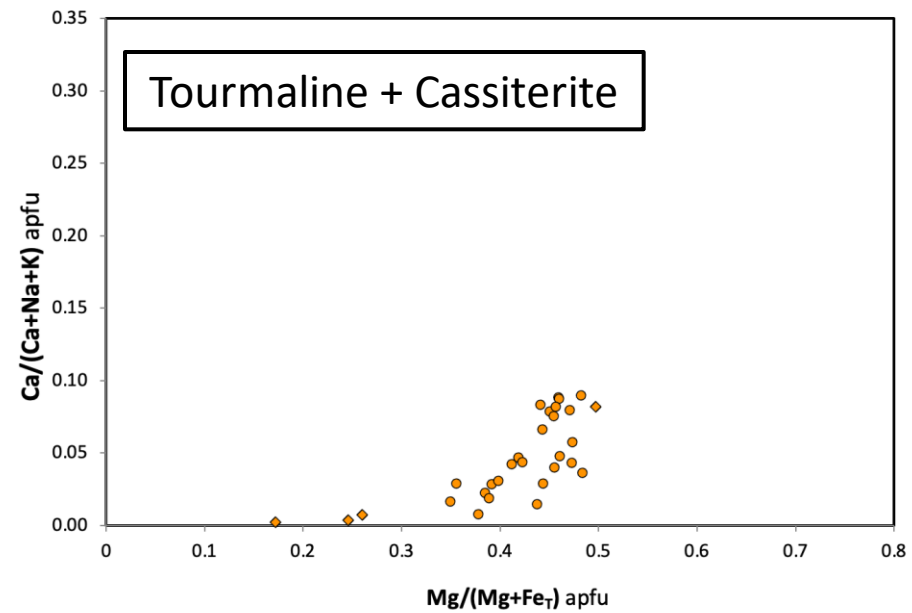
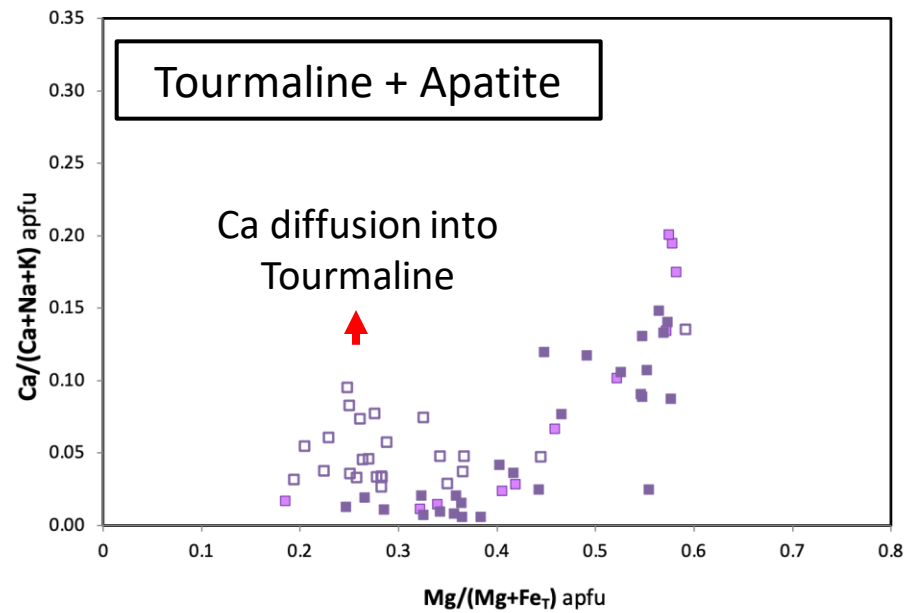
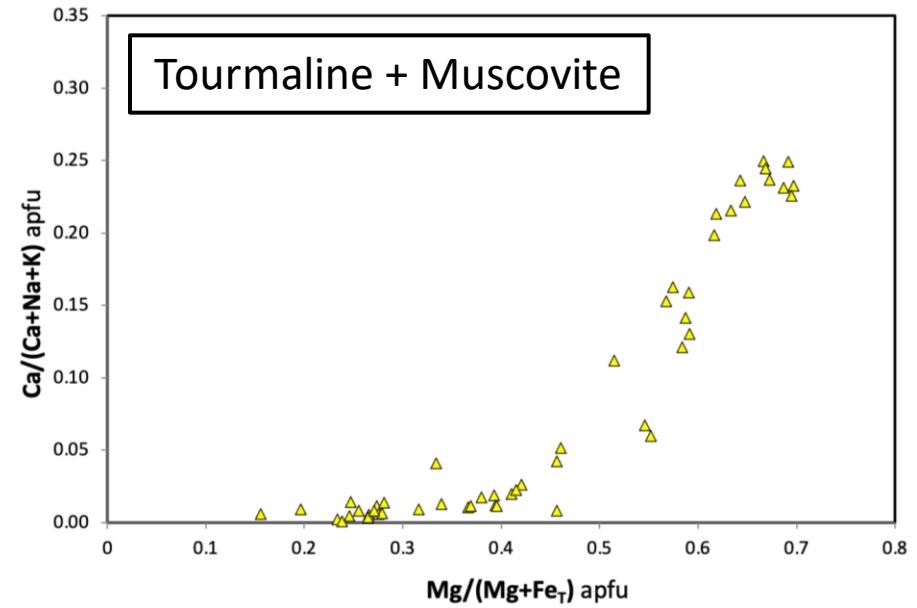
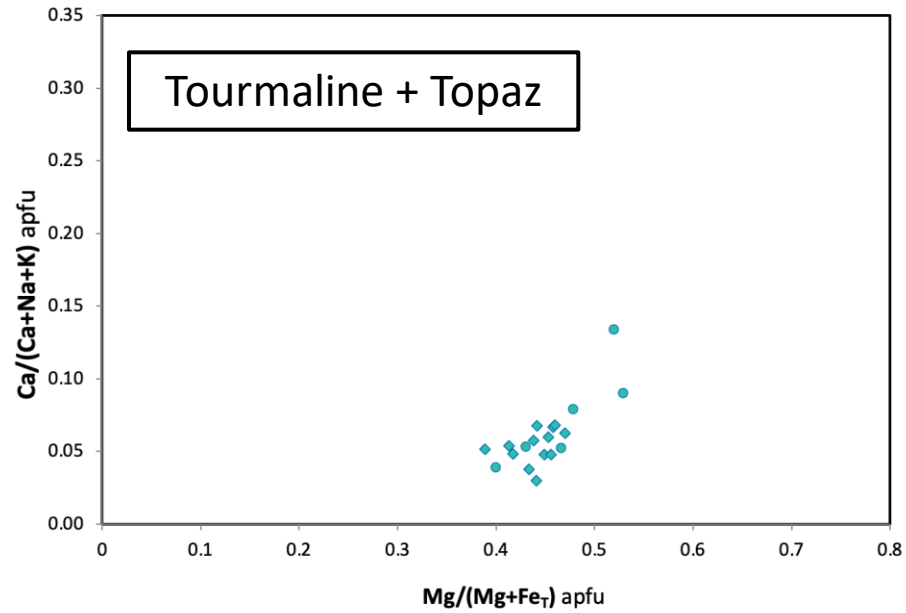
# Panasqueira tourmaline



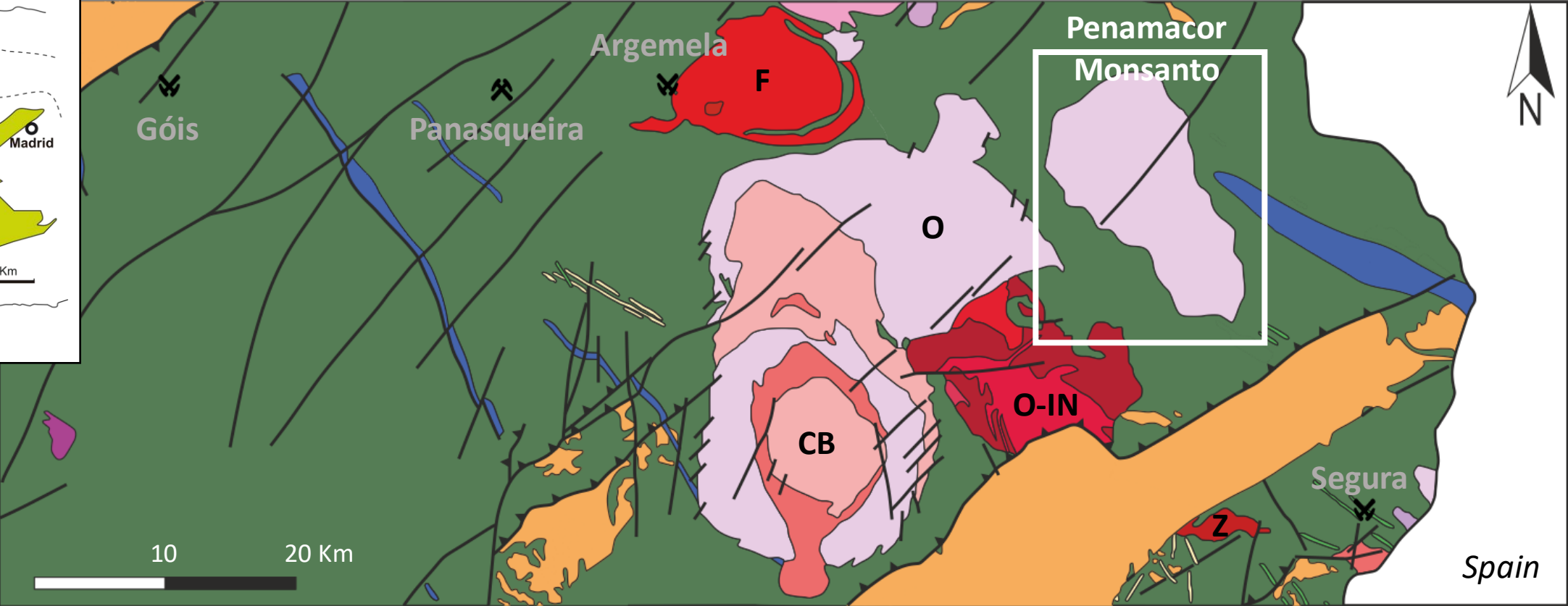
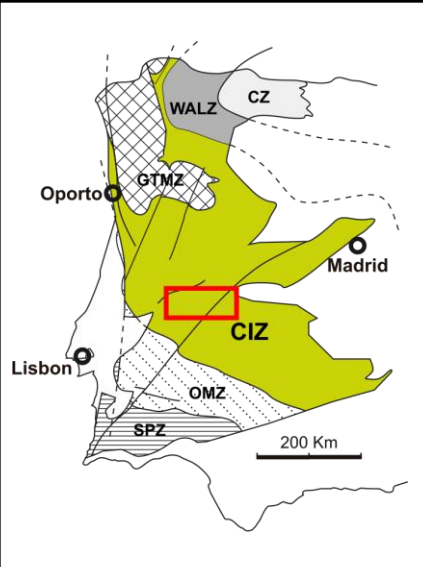
# Panasqueira tourmaline









# Panasqueira tourmaline

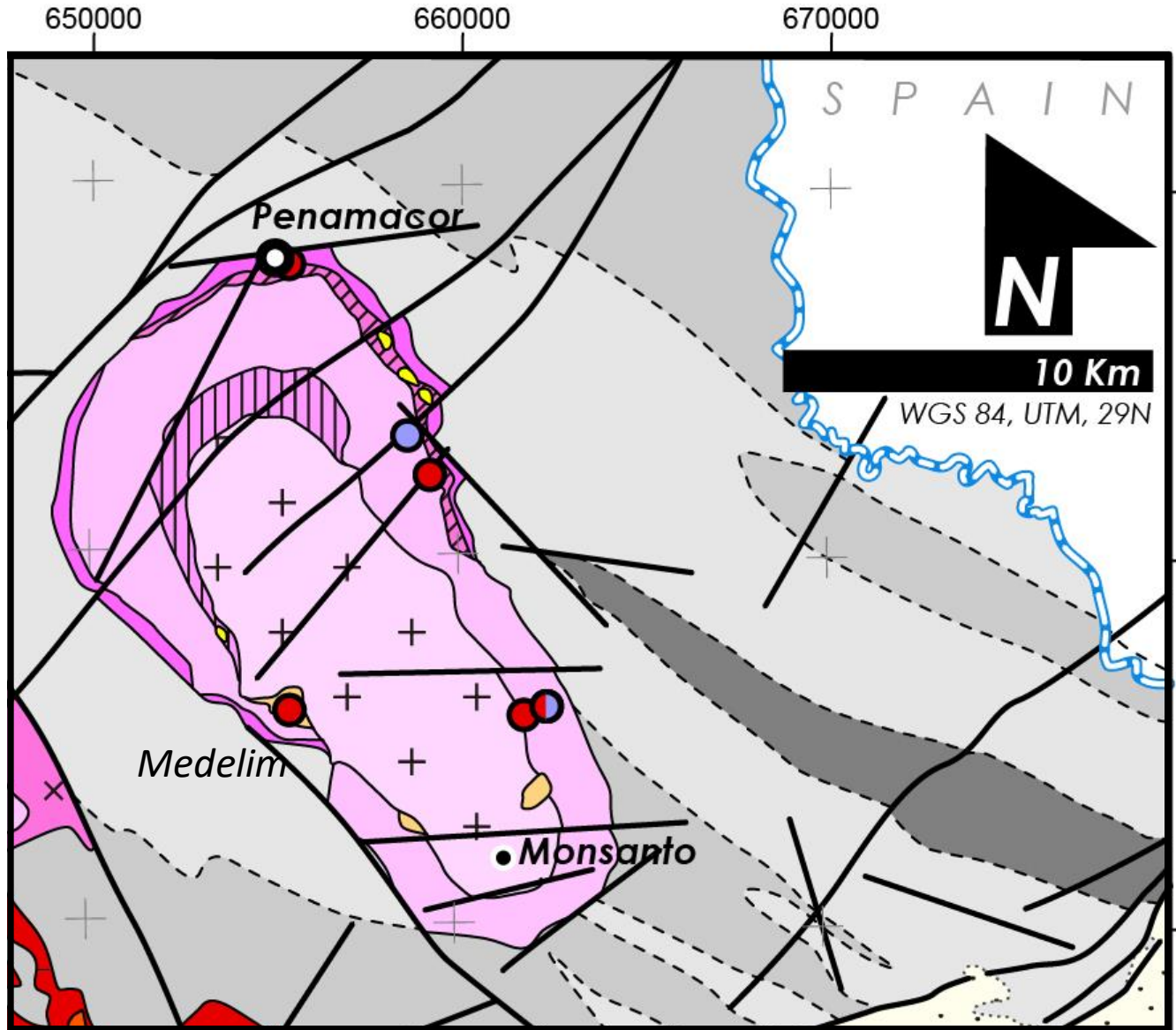


# Góis-Panasqueira-Segura Sn-W belt (Central Portugal)






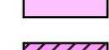

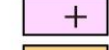

- |   |                     |   |   |   |                   |
|---|---------------------|---|---|---|-------------------|
|  | Variscan Granites   |  | Ordovician Metasediments                        |  | Tertiary deposits |
|  | Ordovician Granites |  | Ante-Ordovician Metasediments<br>(Beiras Group) |   |                   |
|  | Cadomian Granites   |   |   |   |                   |

# Penamacor-Monsanto-Medelim



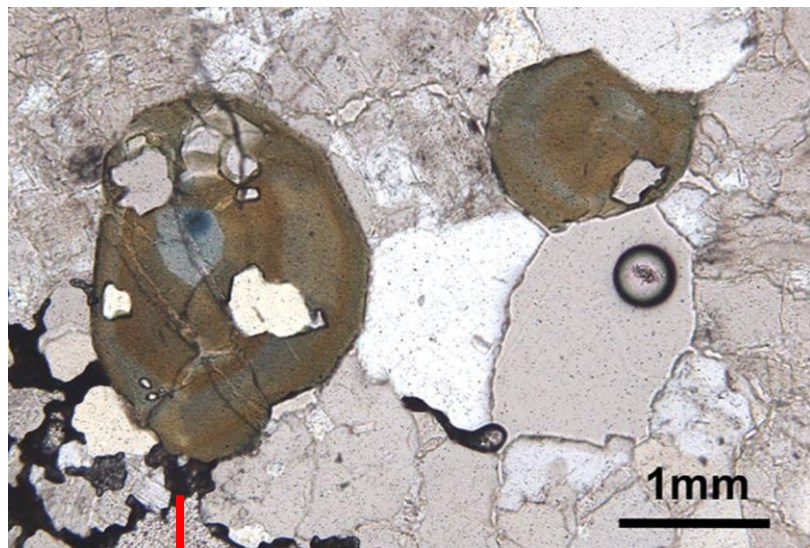
## Variscan

### Penamacor-Monsanto

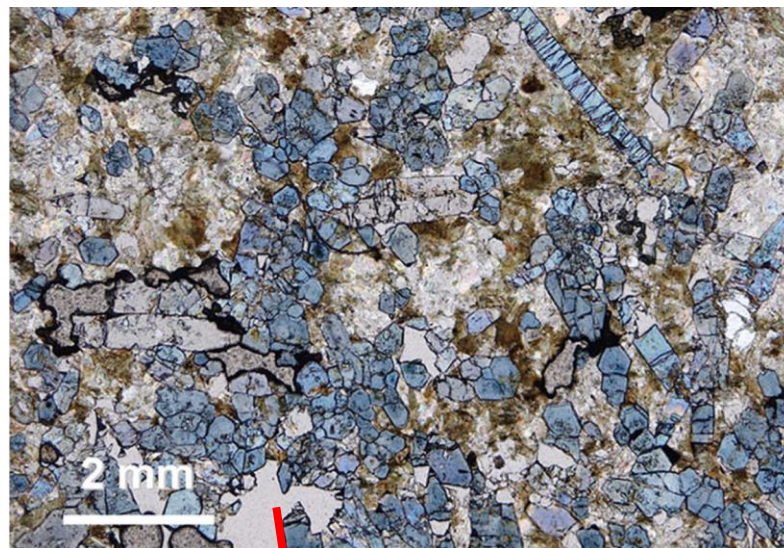
-   $G_{PM} 1$ : Medium- to coarse-grained muscovite-biotite granite
-   $G_{PM} 2$ : Medium-grained muscovite-biotite granite
-   $G_{PM} 3$ : Coarse- to medium-grained porphyritic biotite-muscovite granite
-   $G_{PM} 4$ : Medium-grained porphyritic biotite-muscovite granite
-   $G_{PM} 5$ : Coarse-grained porphyritic muscovite-biotite granite
-   $G_{PM} 6$ : Medium- to coarse-grained porphyritic
-  Pegmatite-Aplite dykes swarm



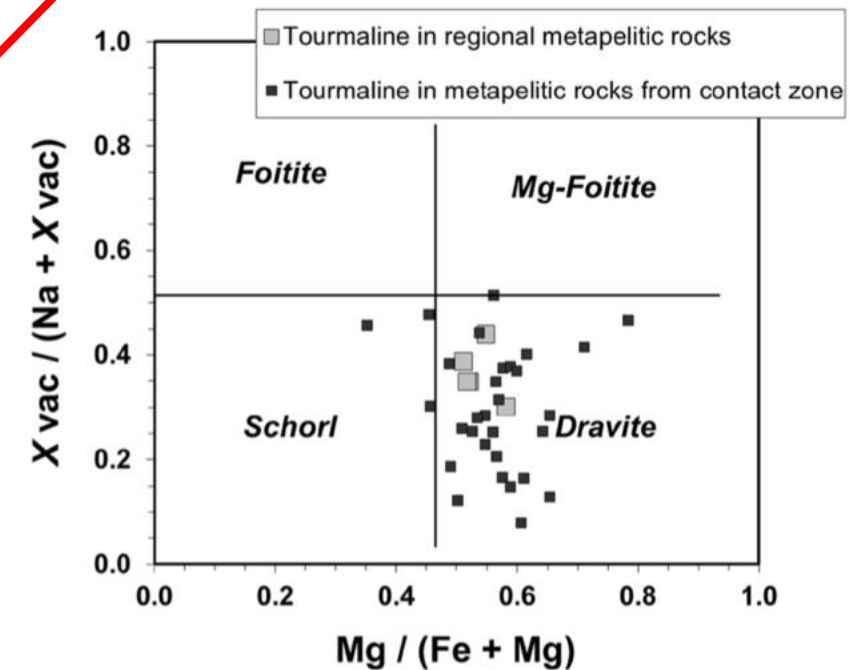
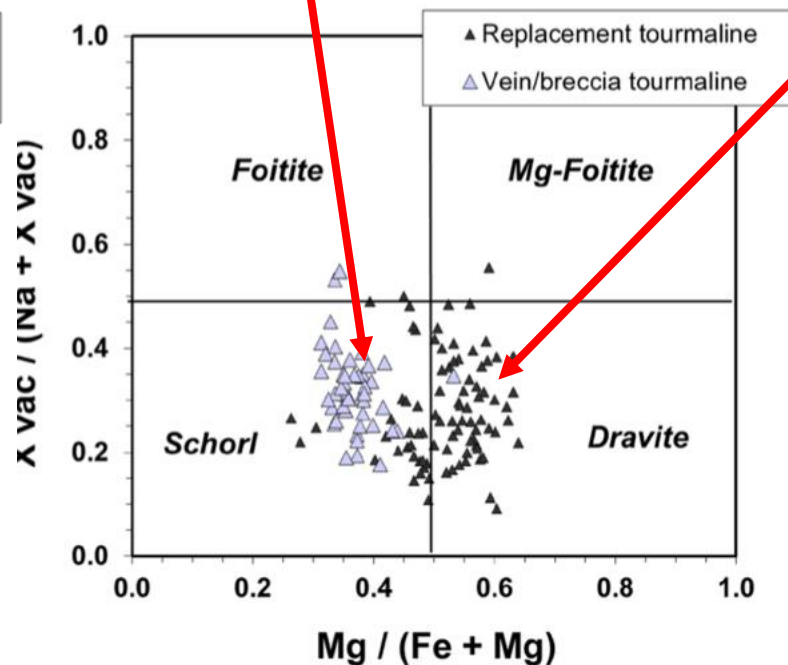
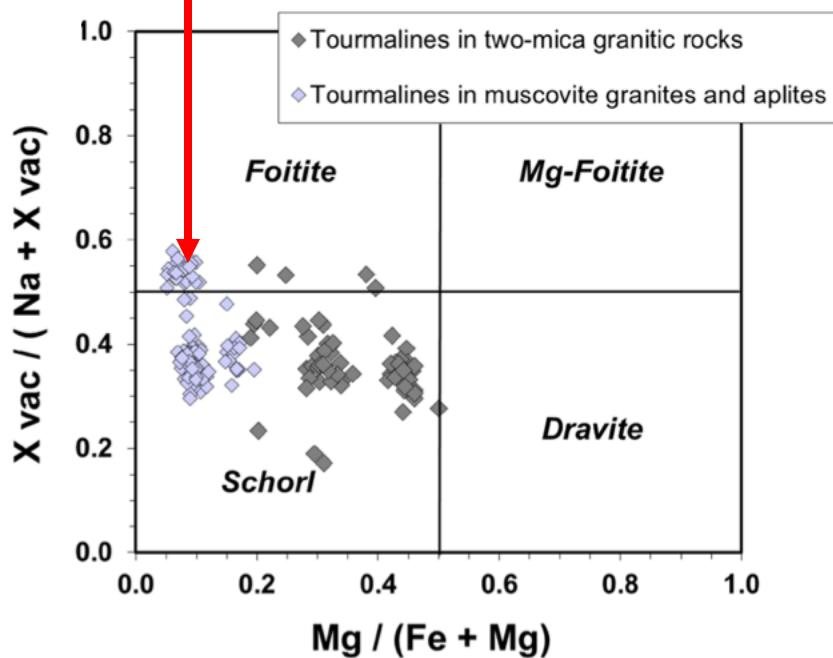
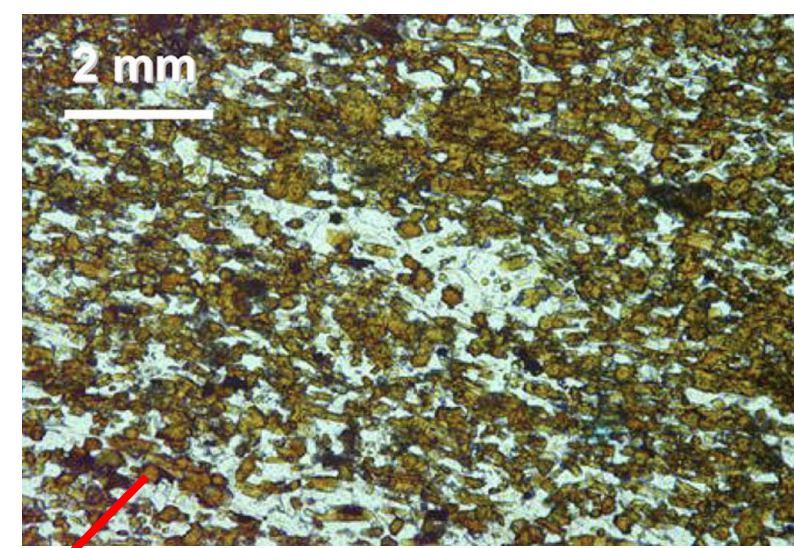
Granite



Qz vein/breccia

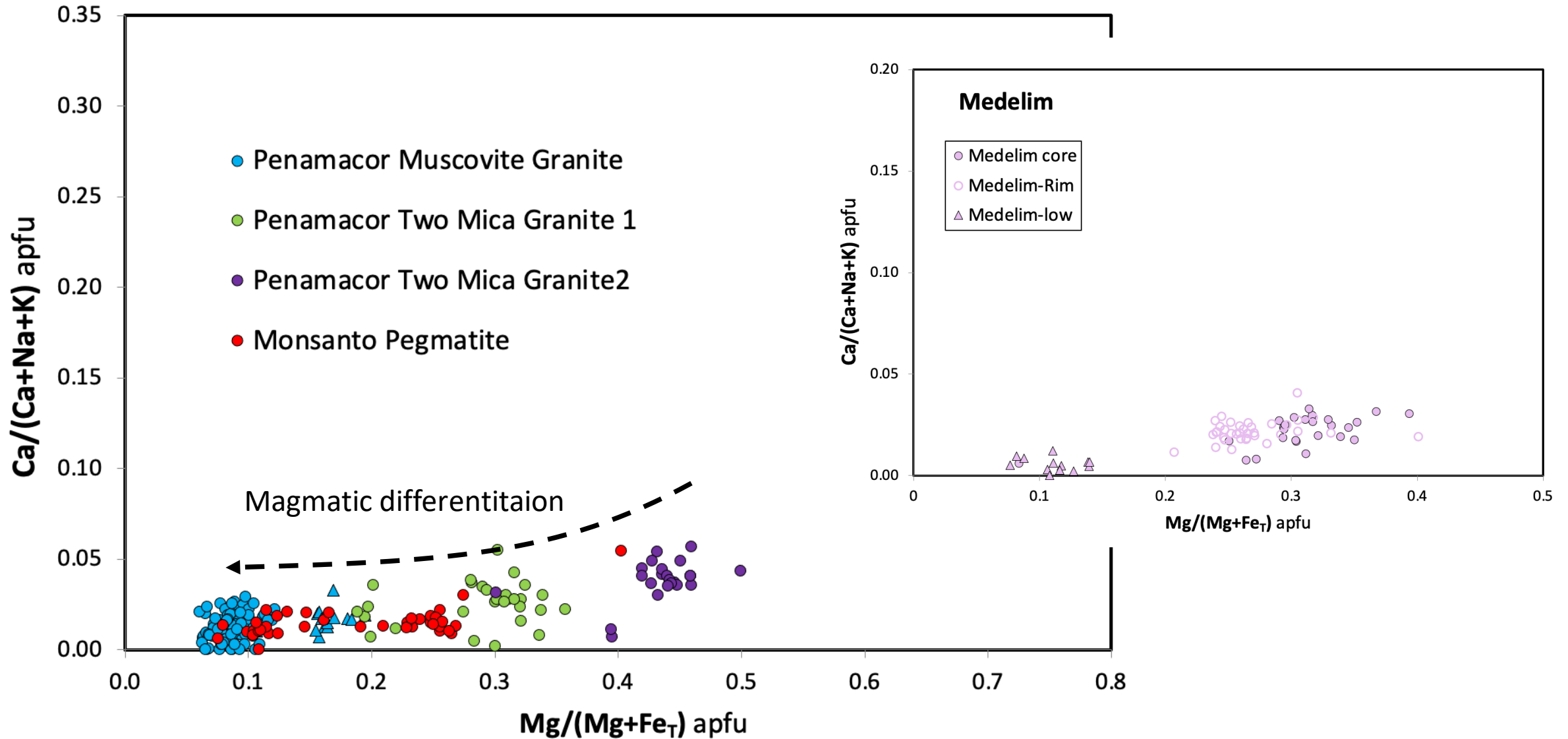


Tourmalinite

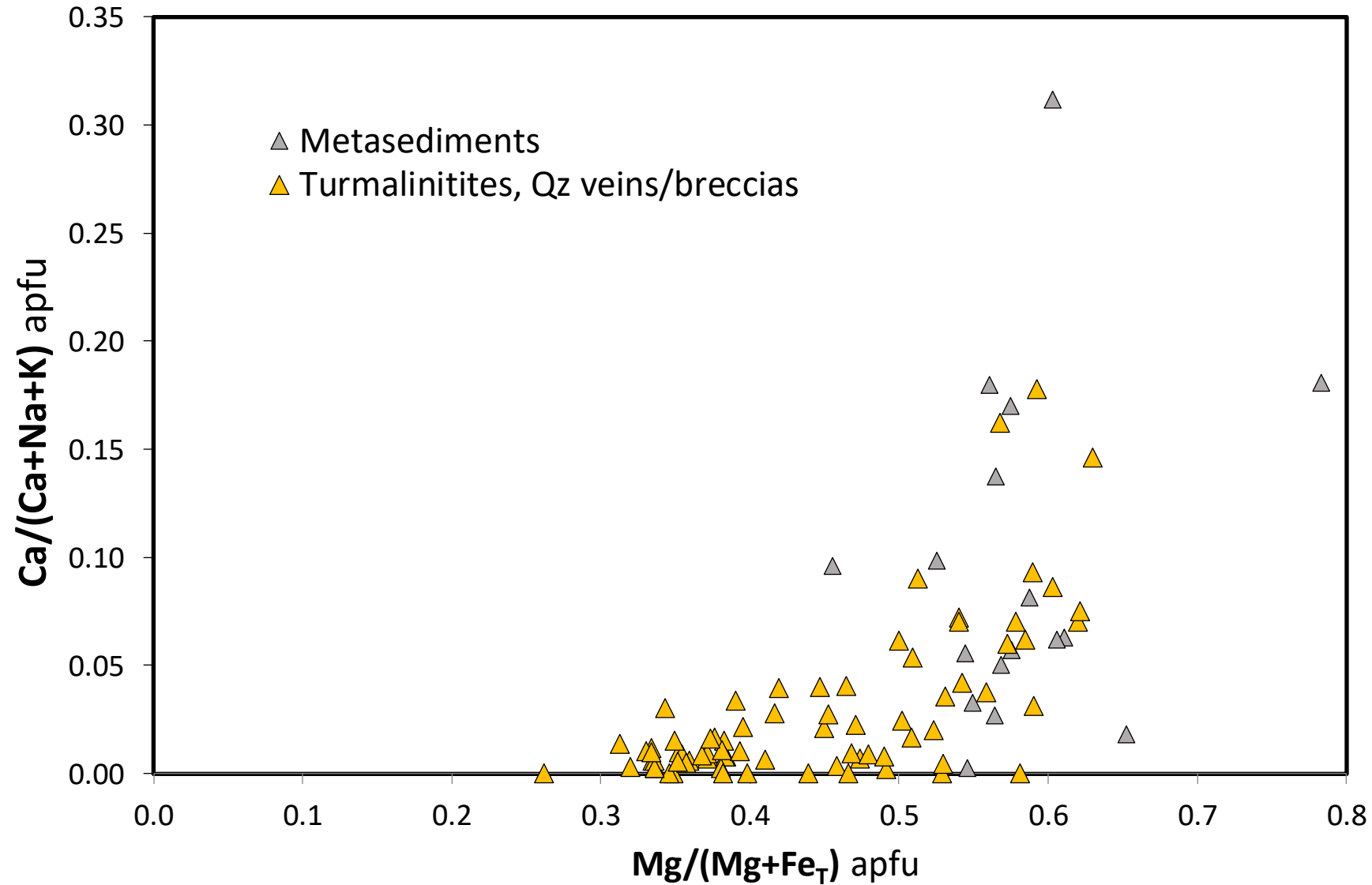


(Ribeiro da Costa et al. 2014)

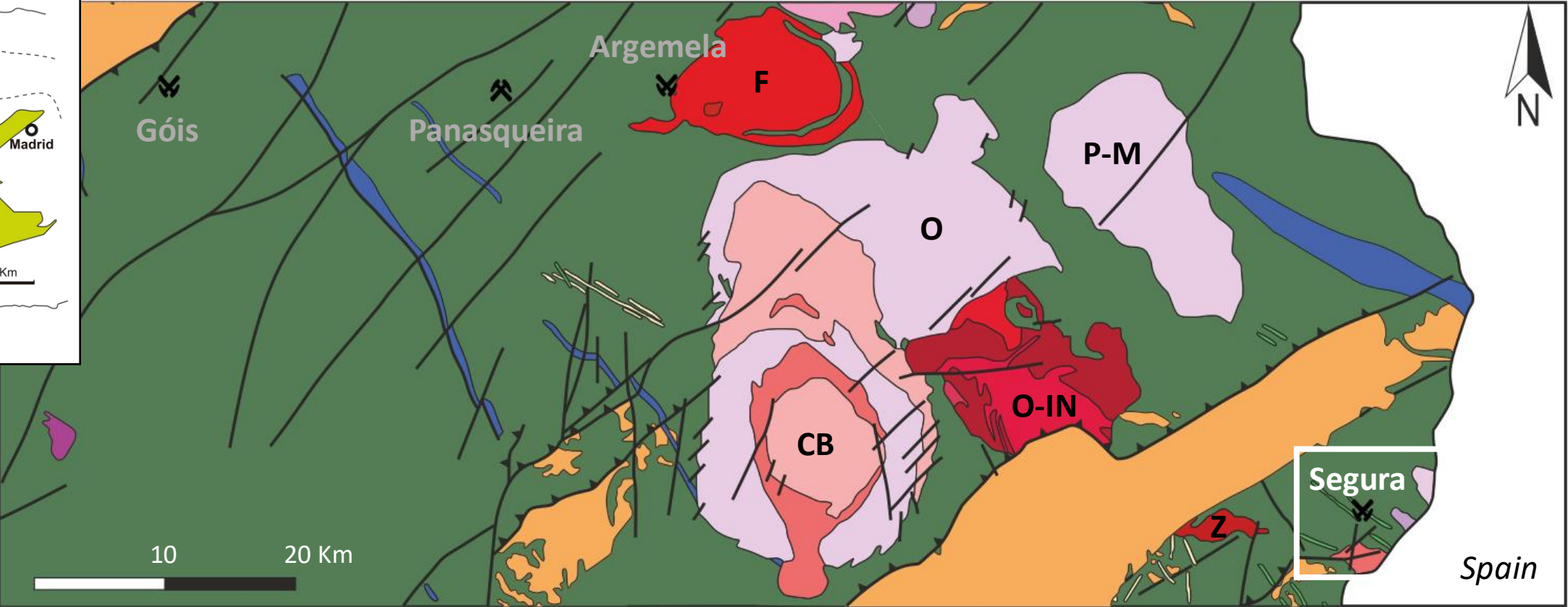
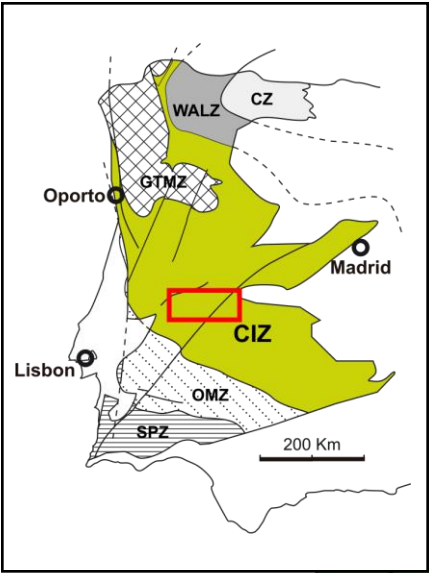
# Tourmaline from magmatic rocks



# Tourmaline from metasediments, toumalinite & breccias



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

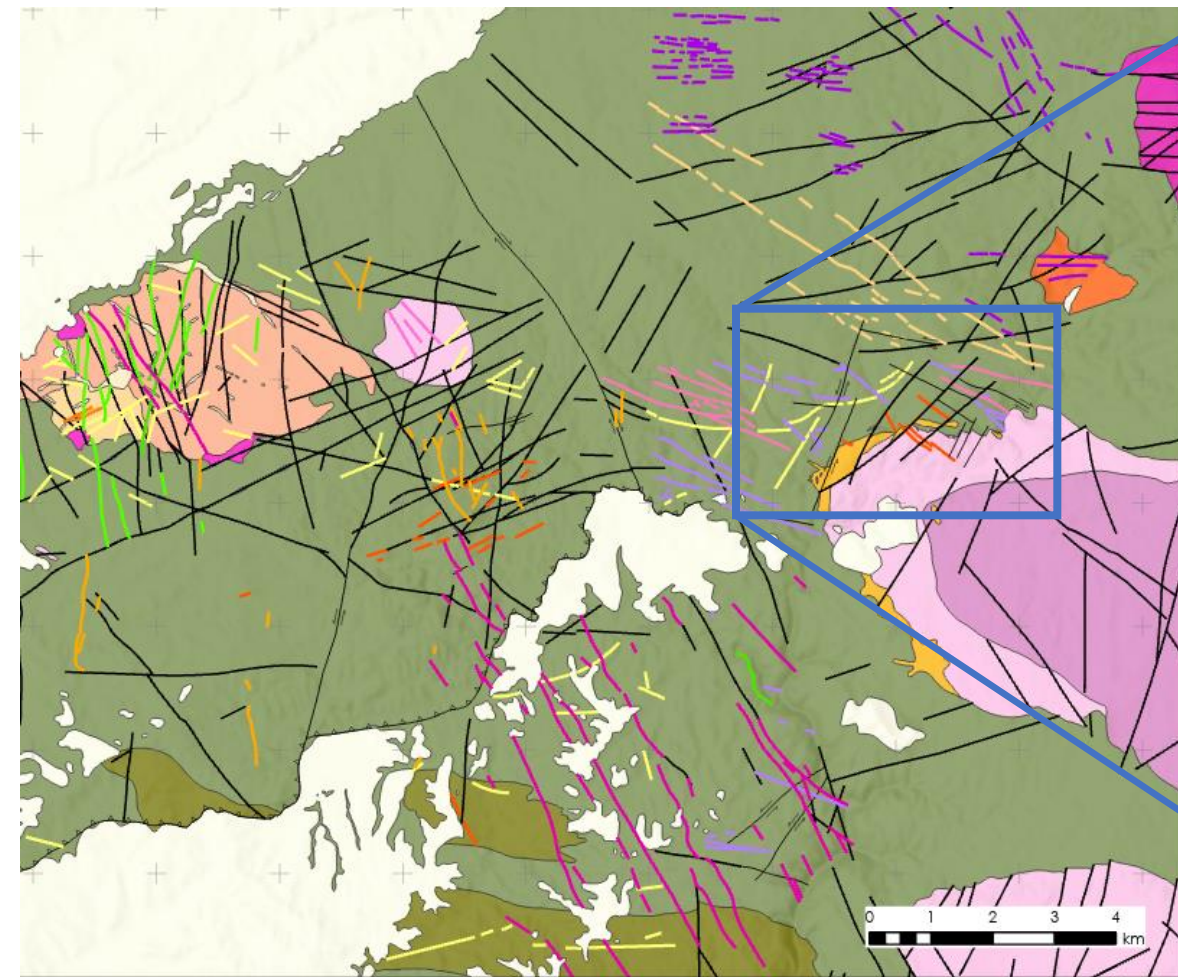


- Variscan Granites
- Ordovician Granites
- Cadomian Granites
- Ordovician Metasediments
- Ante-Ordovician Metasediments (Beiras Group)
- Tertiary deposits

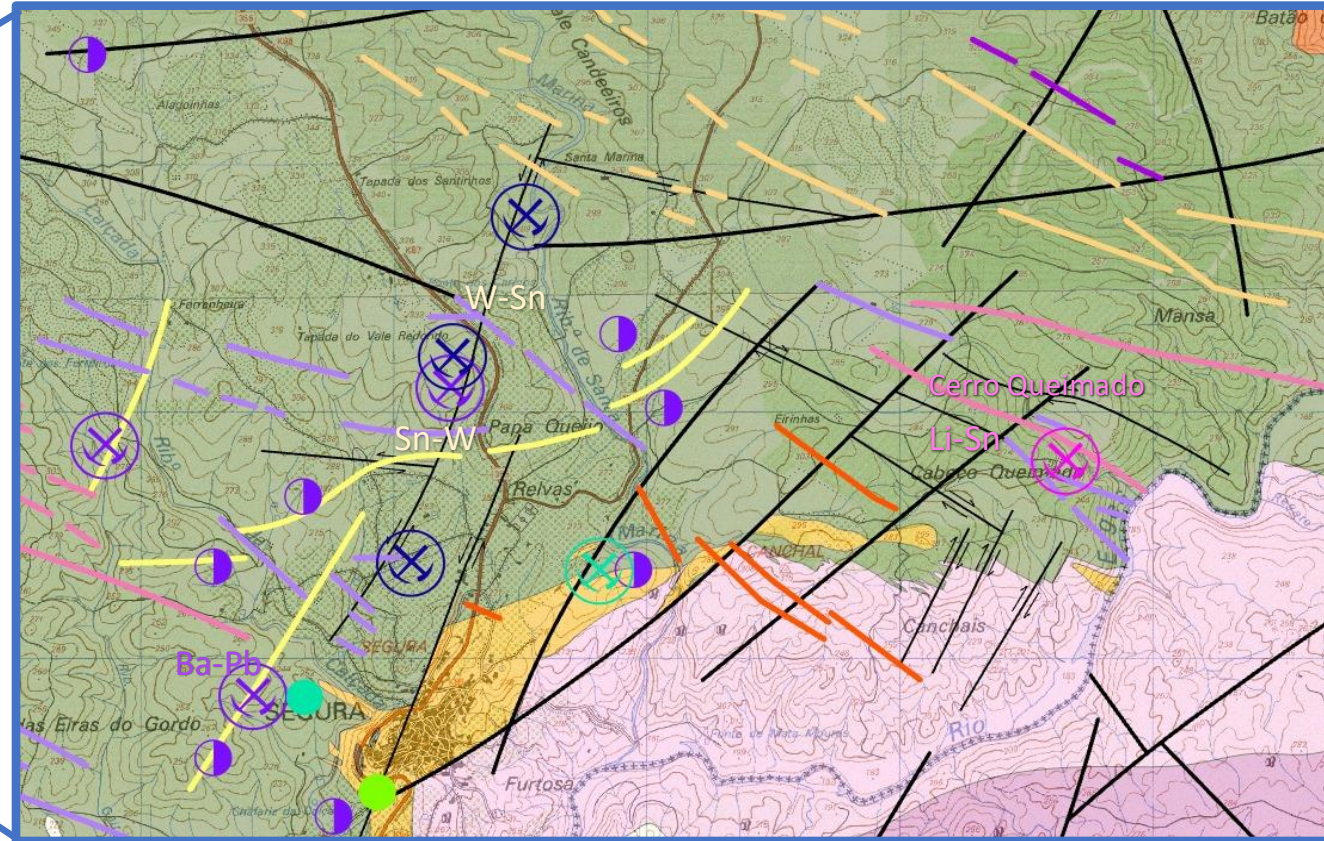
(MOSTMEG 2020)

# Segura-Zebreira-Salvaterra do Extremo

New data (MOSTMEG)



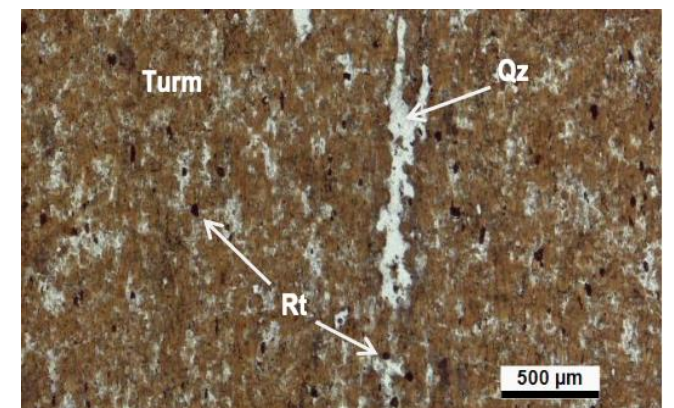
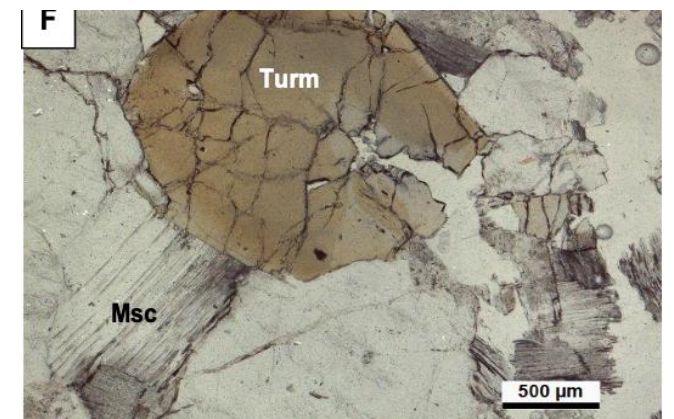
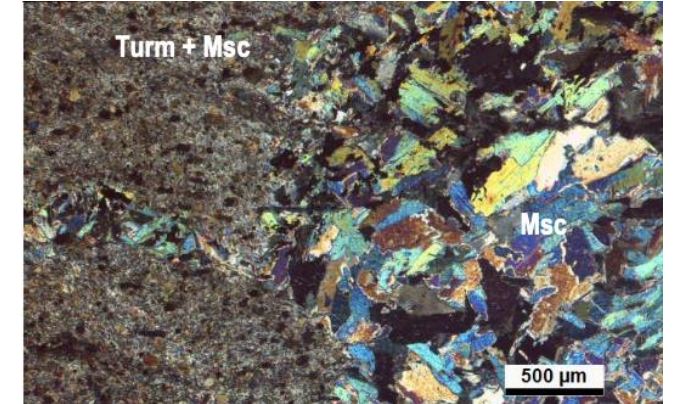
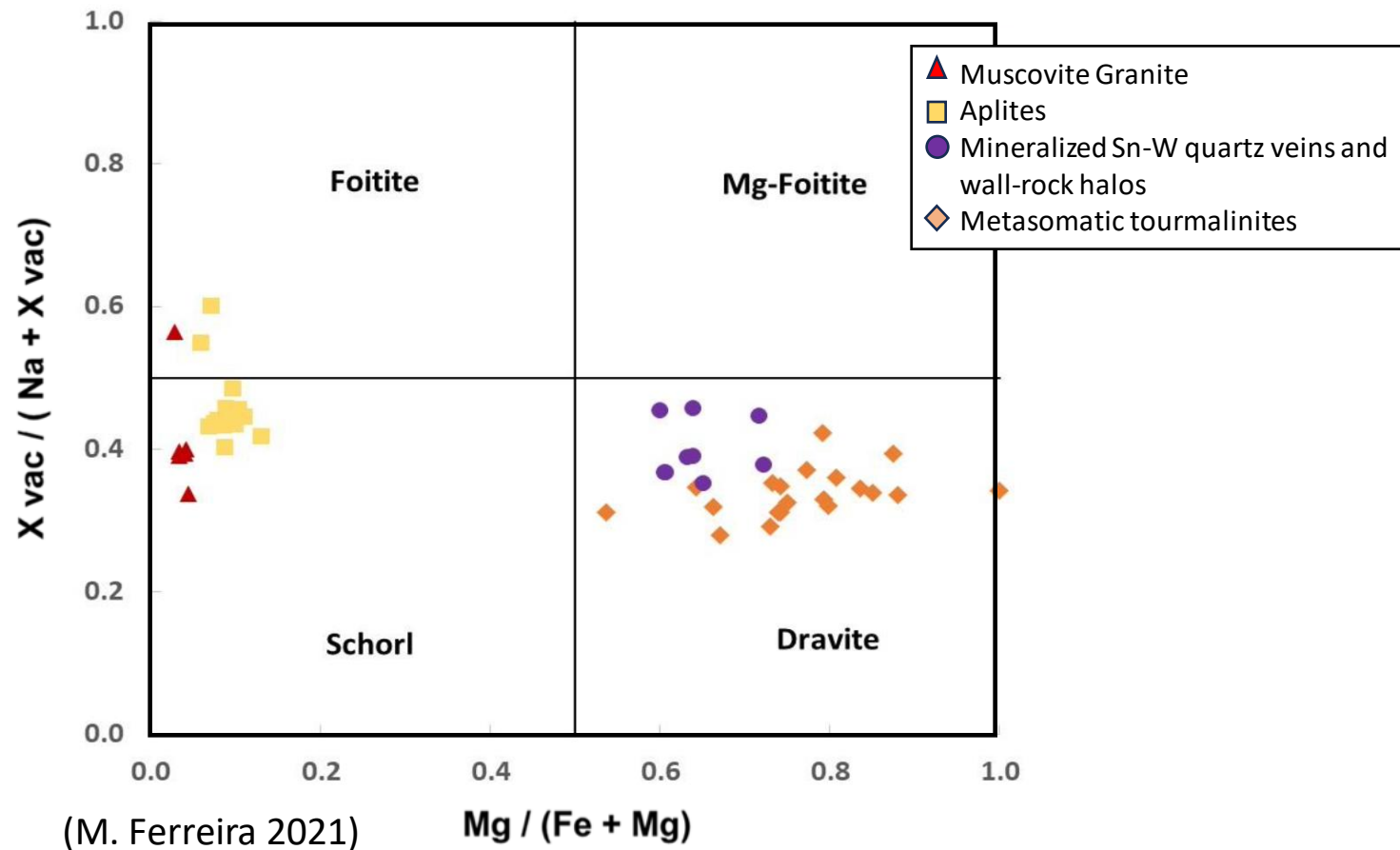
(MOSTMEG 2023)



(MOSTMEG 2023)

# Segura

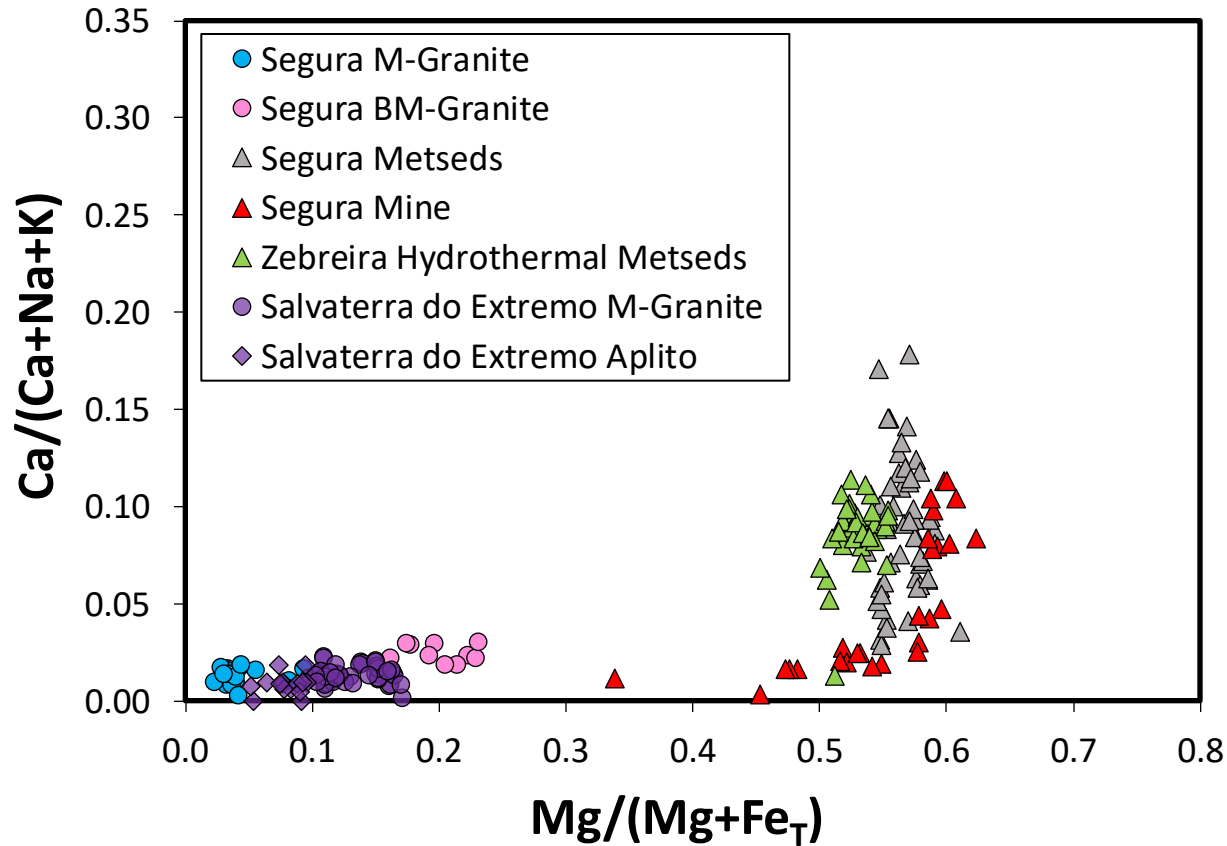
Sub-horizontal Sn-W quartz vein system similar to Panasqueira



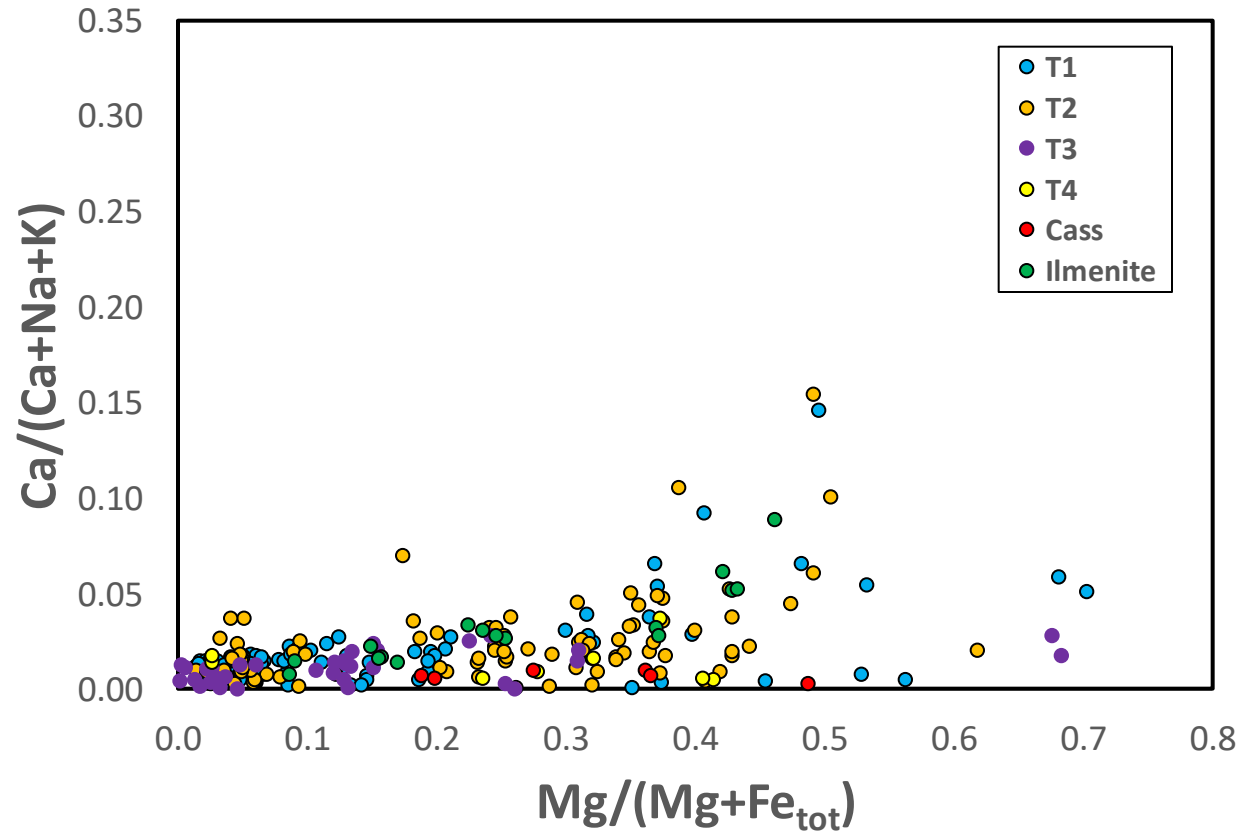
# Segura-Zebreira-Salvaterra do Extremo



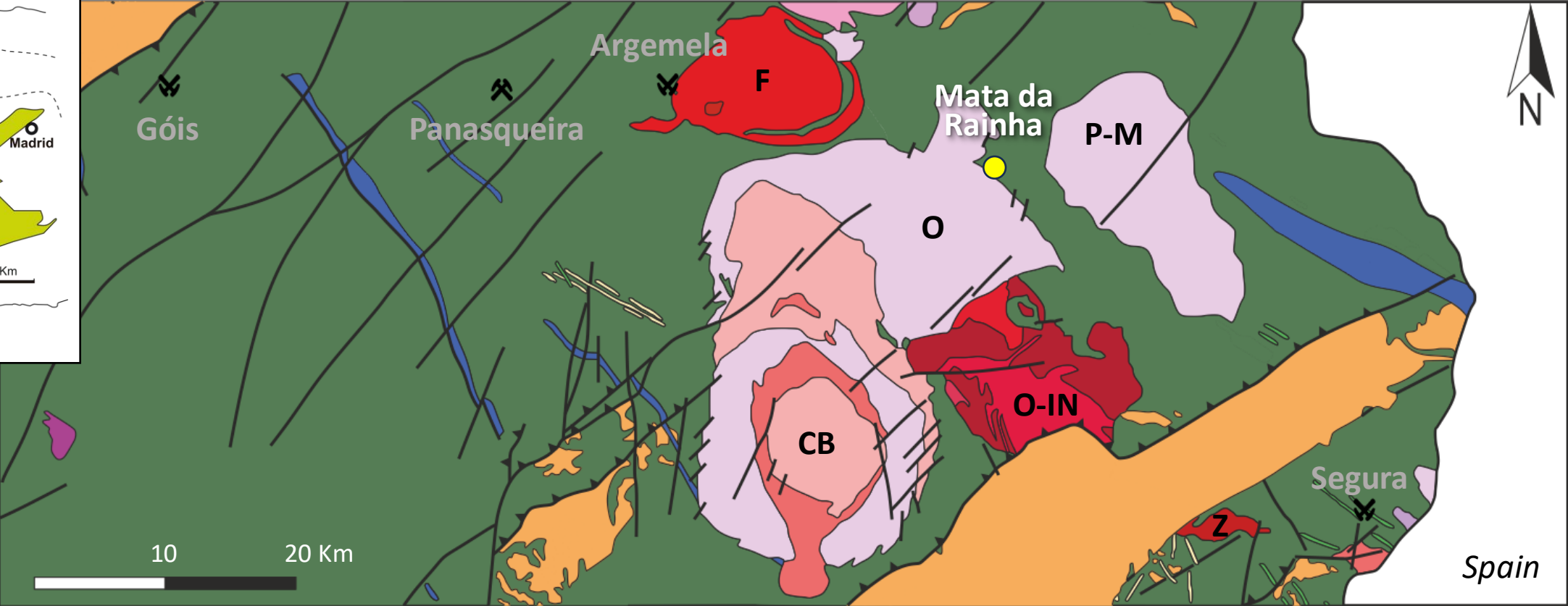
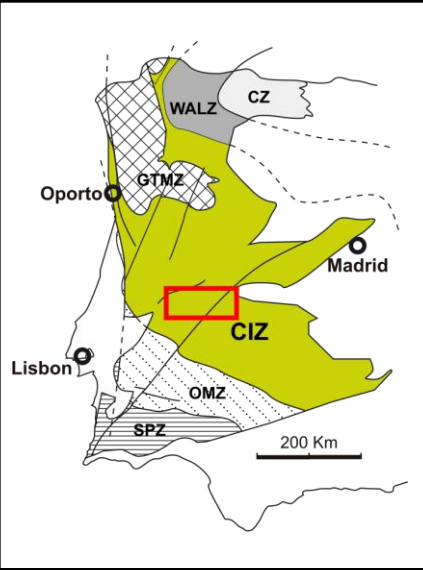
## Segura-Zebreira-Salvaterra do Extremo



## Alluvial tourmaline from Segura



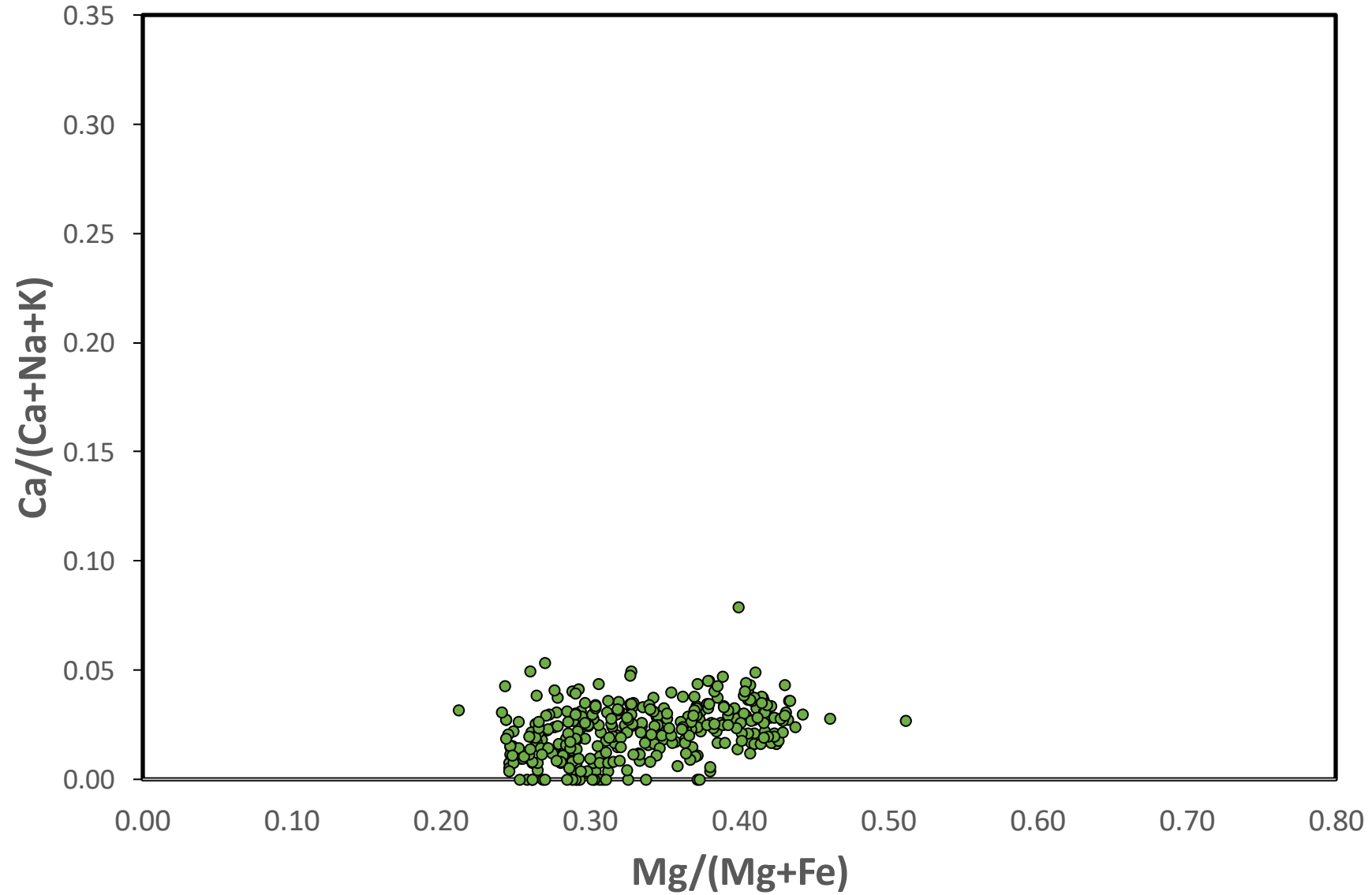
# Góis-Panasqueira-Segura Sn-W belt (Central Portugal)



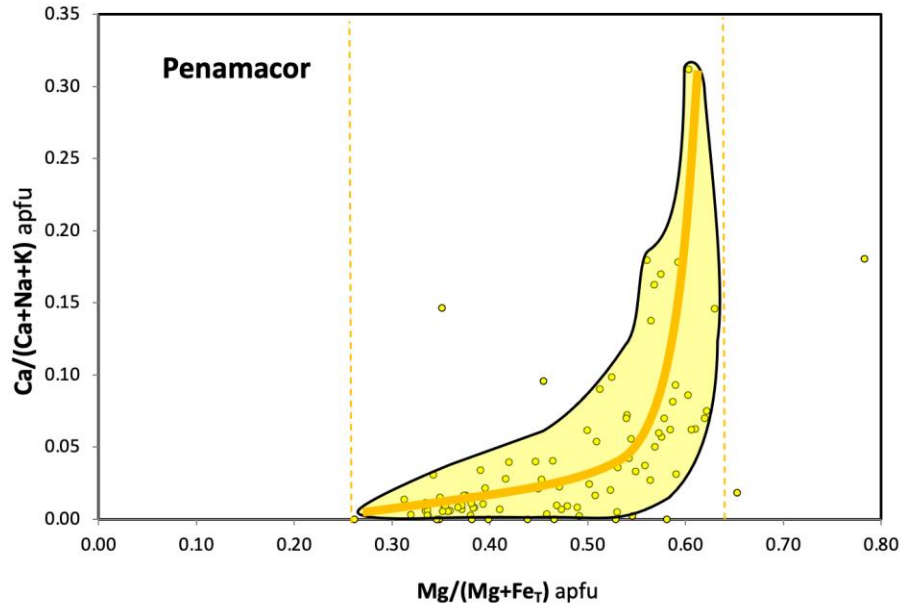
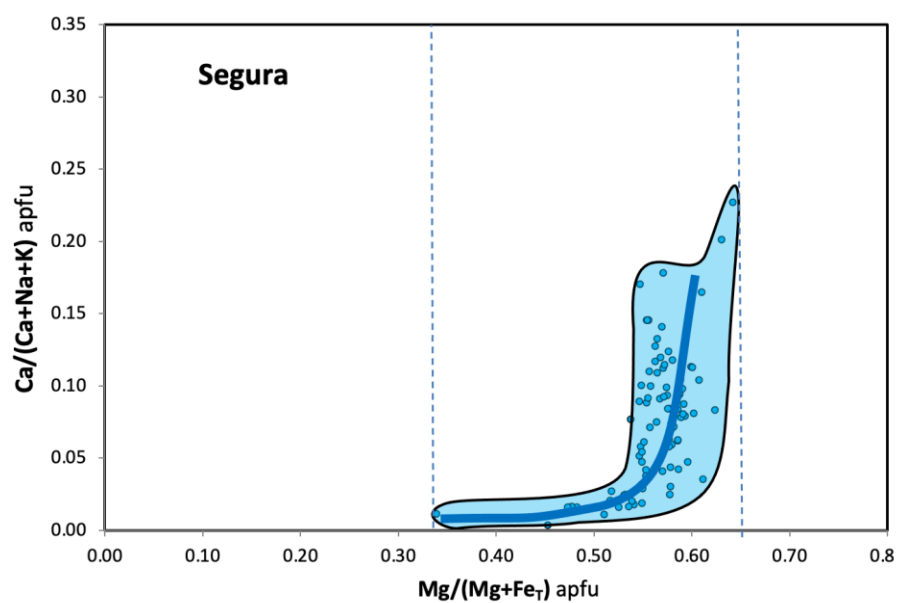
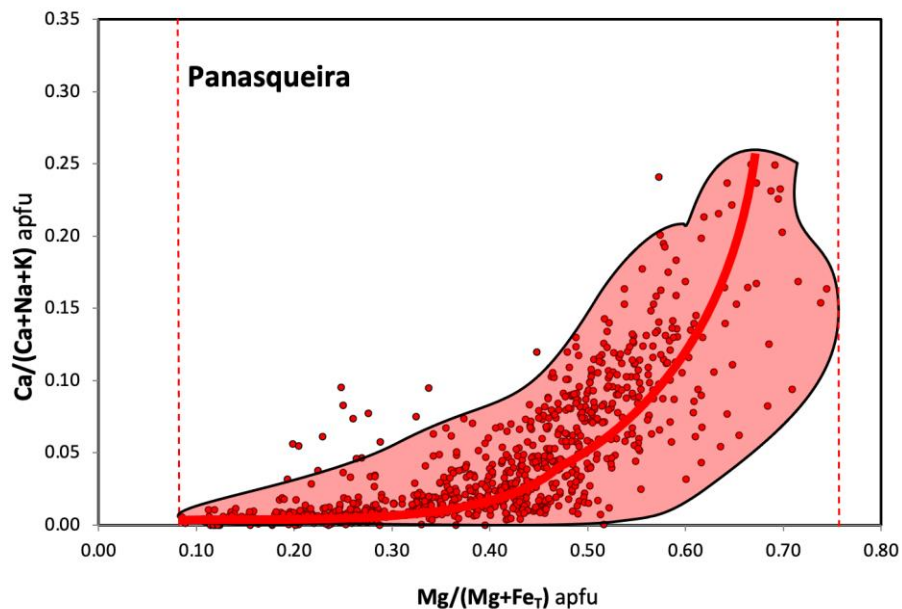
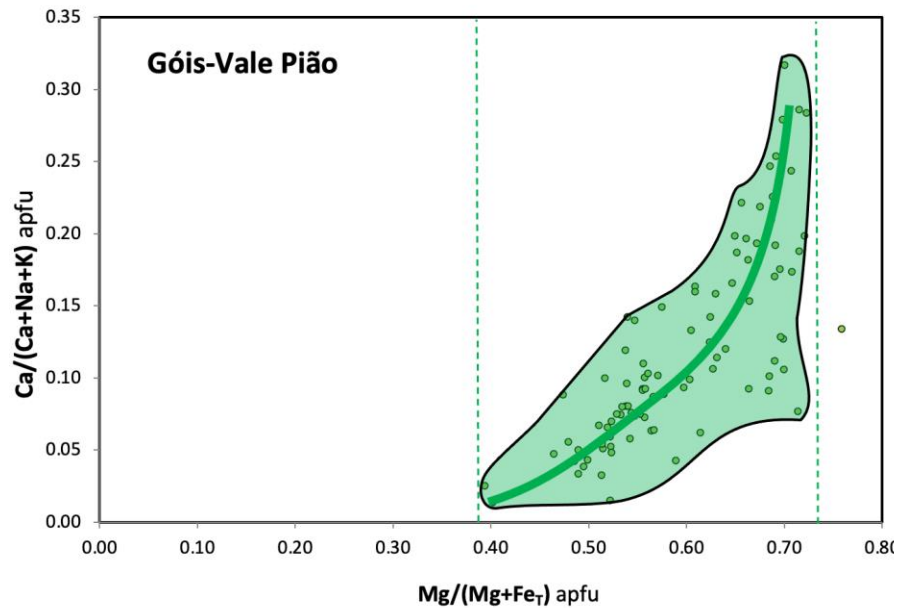
- Variscan Granites
- Ordovician Granites
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- Ordovician Metasediments
- Ante-Ordovician Metasediments (Beiras Group)
- Tertiary deposits



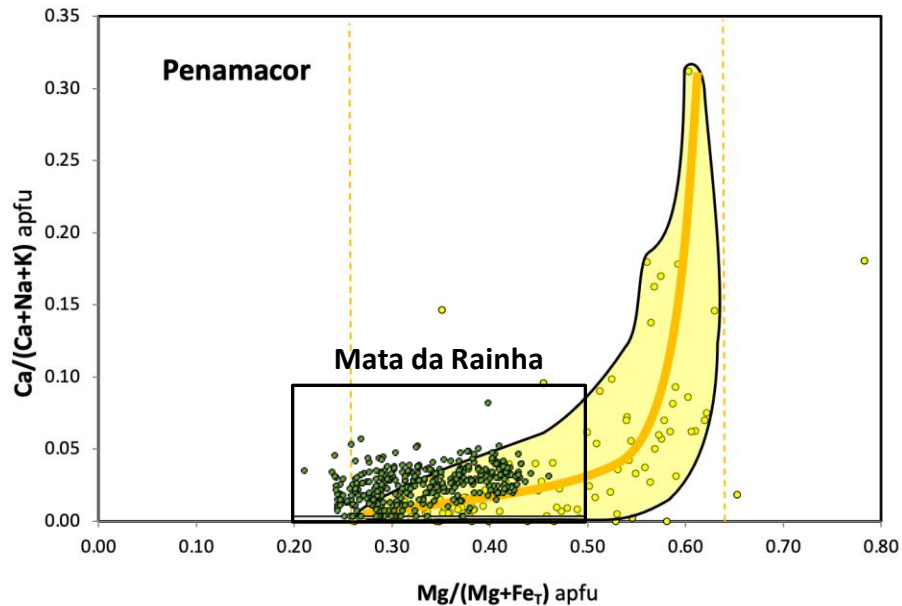
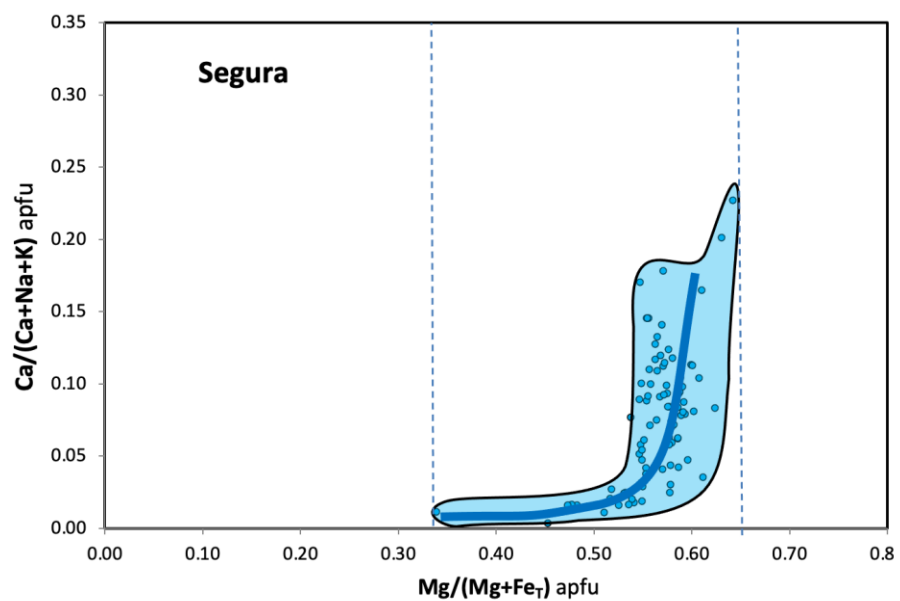
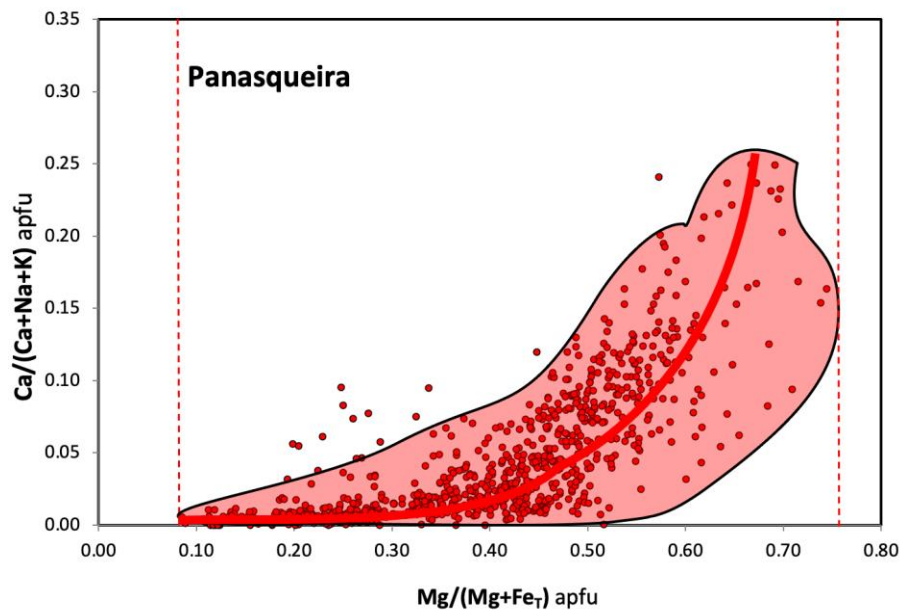
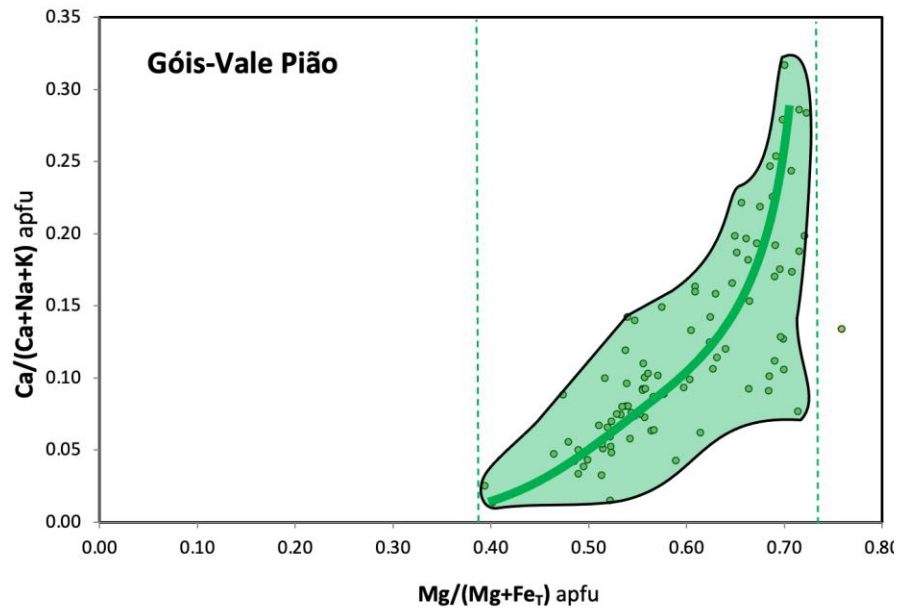
# Mata da Rainha



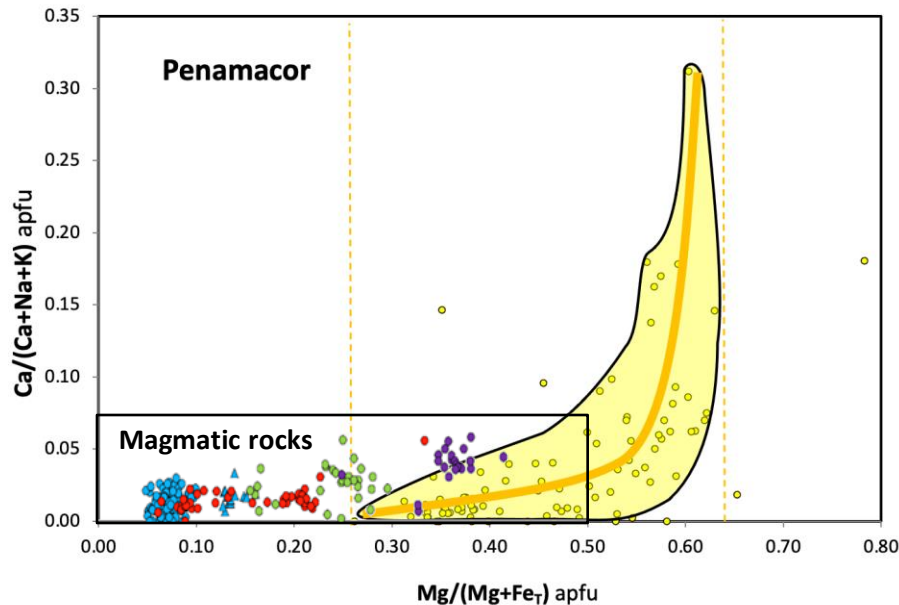
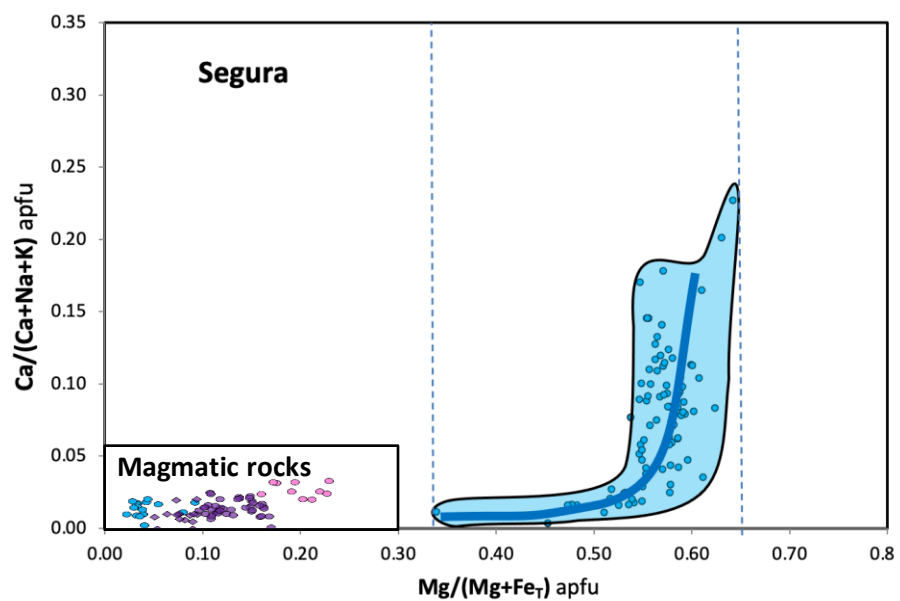
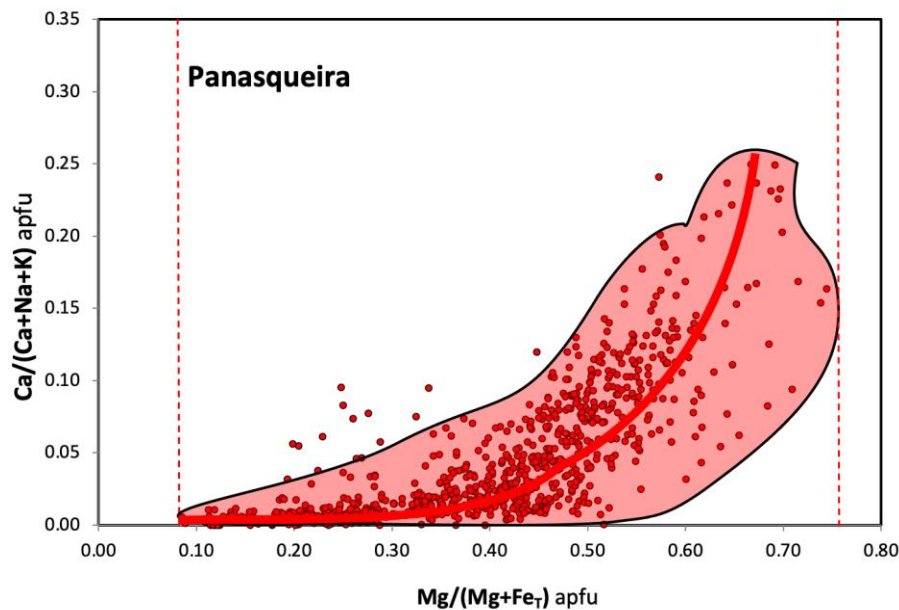
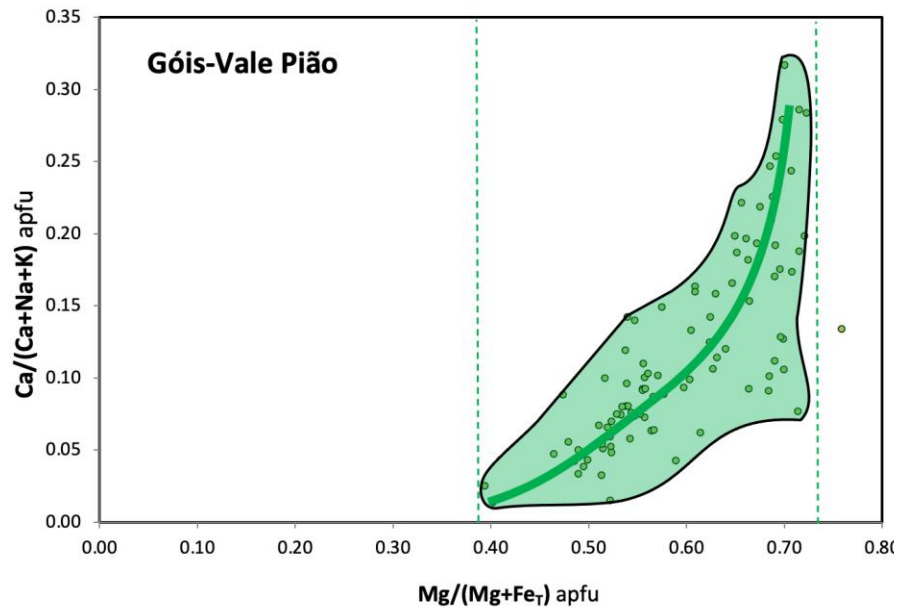
# Summarizing



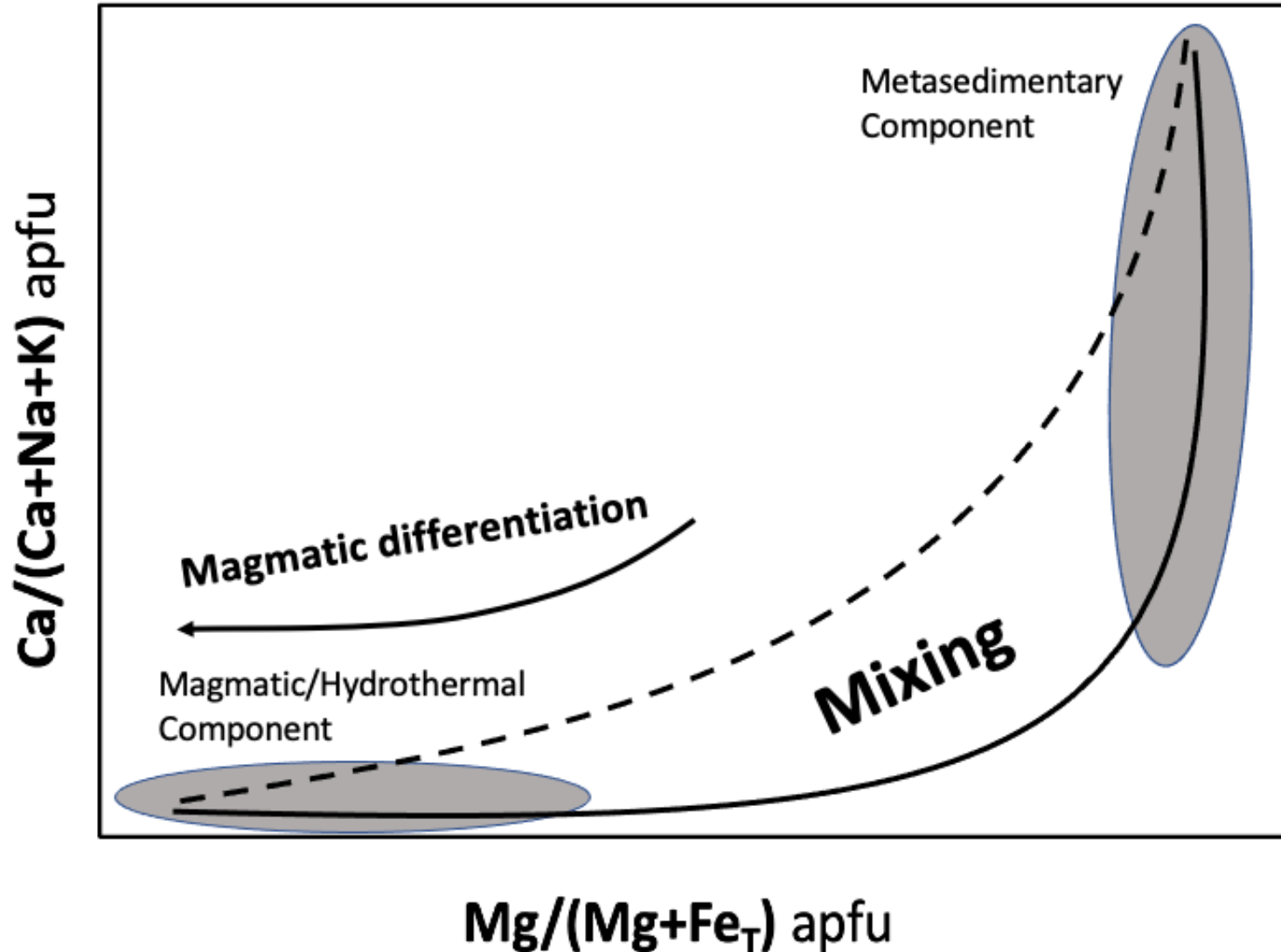
# Summarizing



# Summarizing



# Assessment of Tourmaline Composition as a Vectoring Tool for Sn-W Deposits



# Assessment of Tourmaline Composition as a Vectoring Tool for Sn-W Deposits

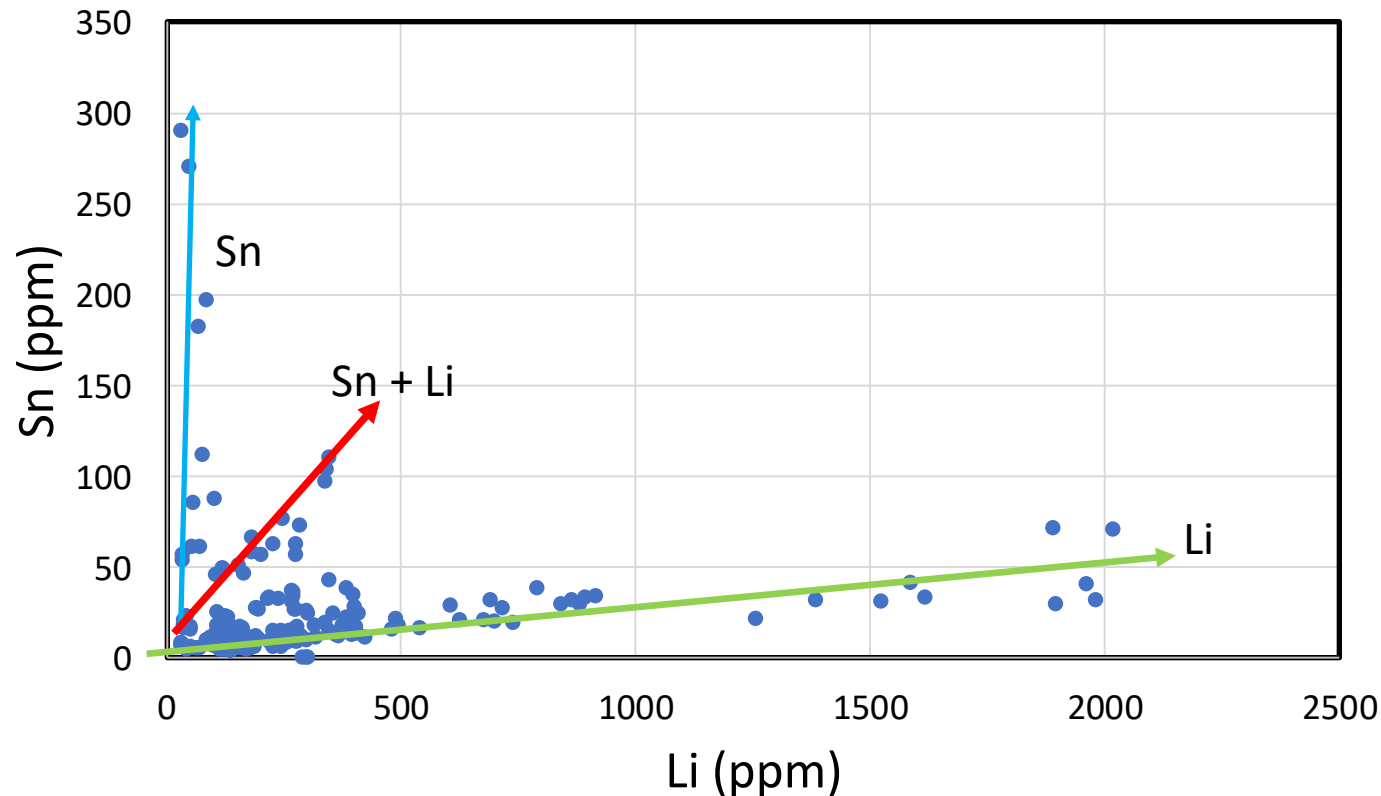


What about minor and trace elements?

# Assessment of Tourmaline Composition as a Vectoring Tool for Sn-W Deposits

What about minor and trace elements?

Alluvial Tourmaline from Segura (LA-ICPMS)



Comeback in June!

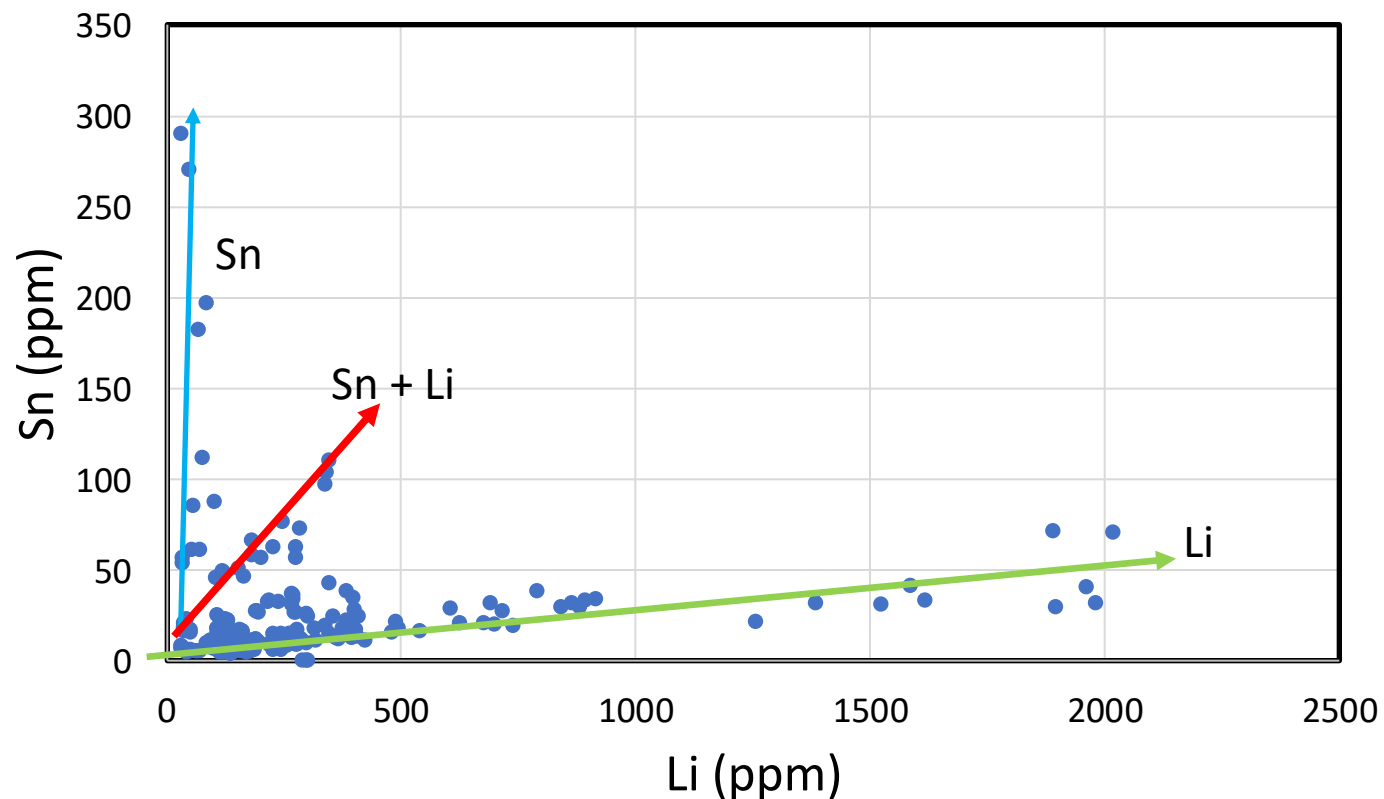


# Assessment of Tourmaline Composition as a Vectoring Tool for Sn-W Deposits



What about minor and trace elements?

Alluvial Tourmaline from Segura (LA-ICPMS)





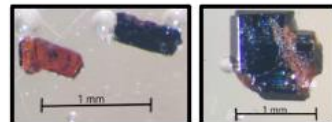
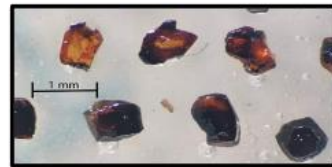
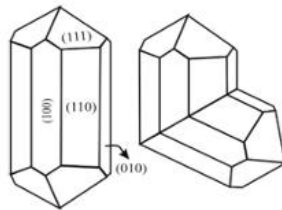
Article

## Trace Element Geochemistry of Alluvial TiO<sub>2</sub> Polymorphs as a Proxy for Sn and W Deposits

Miguel Gaspar <sup>1,2,\*</sup>, Nuno Grácio <sup>2,3</sup>, Rute Salgueiro <sup>3</sup> and Mafalda Costa <sup>4</sup>

Rutile

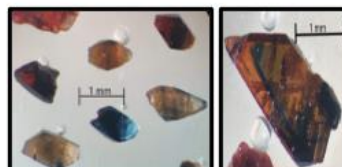
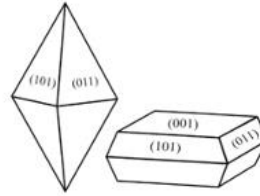
(4/m2/m2/m)



n=695

Anatase

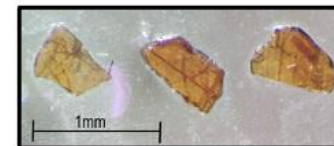
(4/m2/m2/m)



n=1125

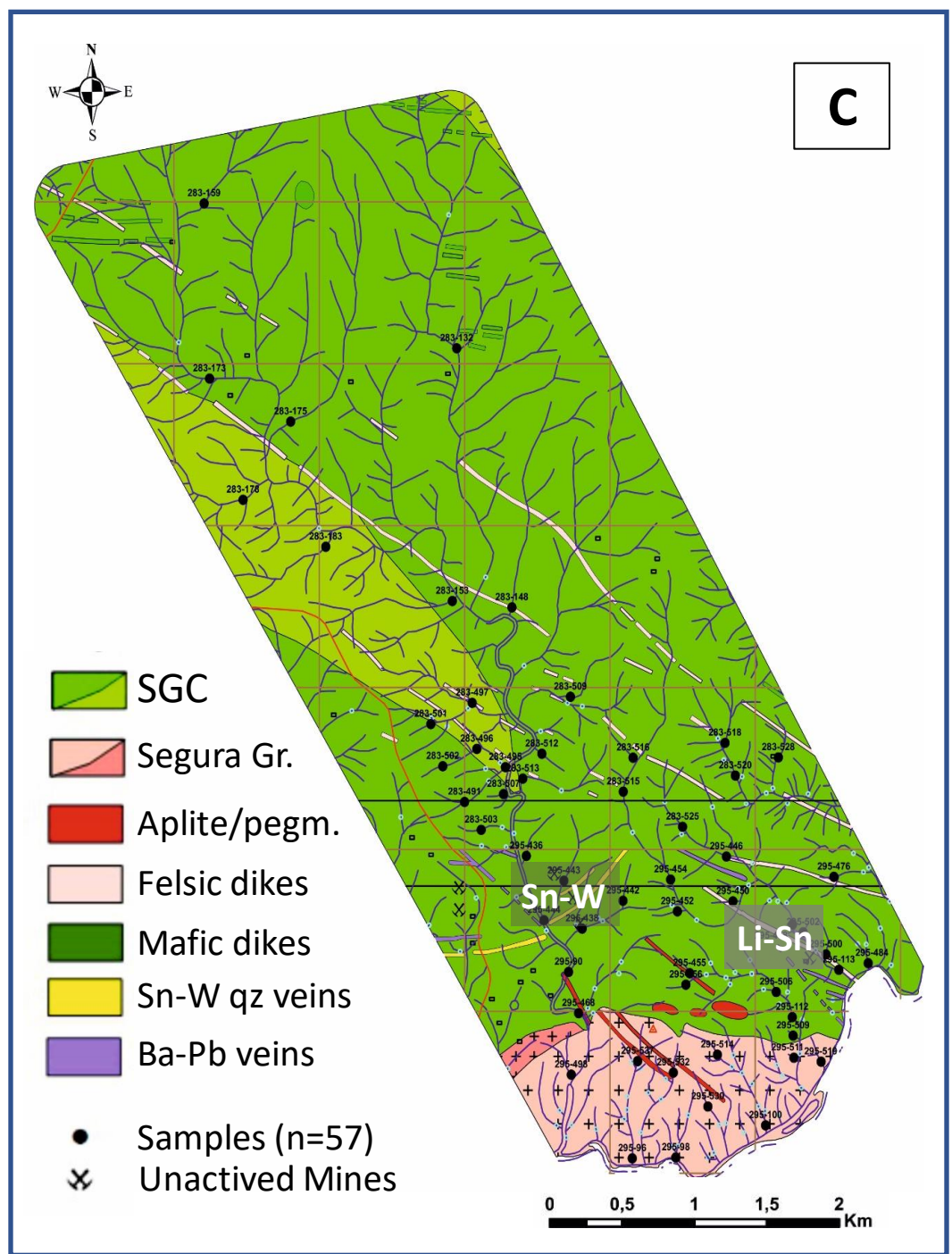
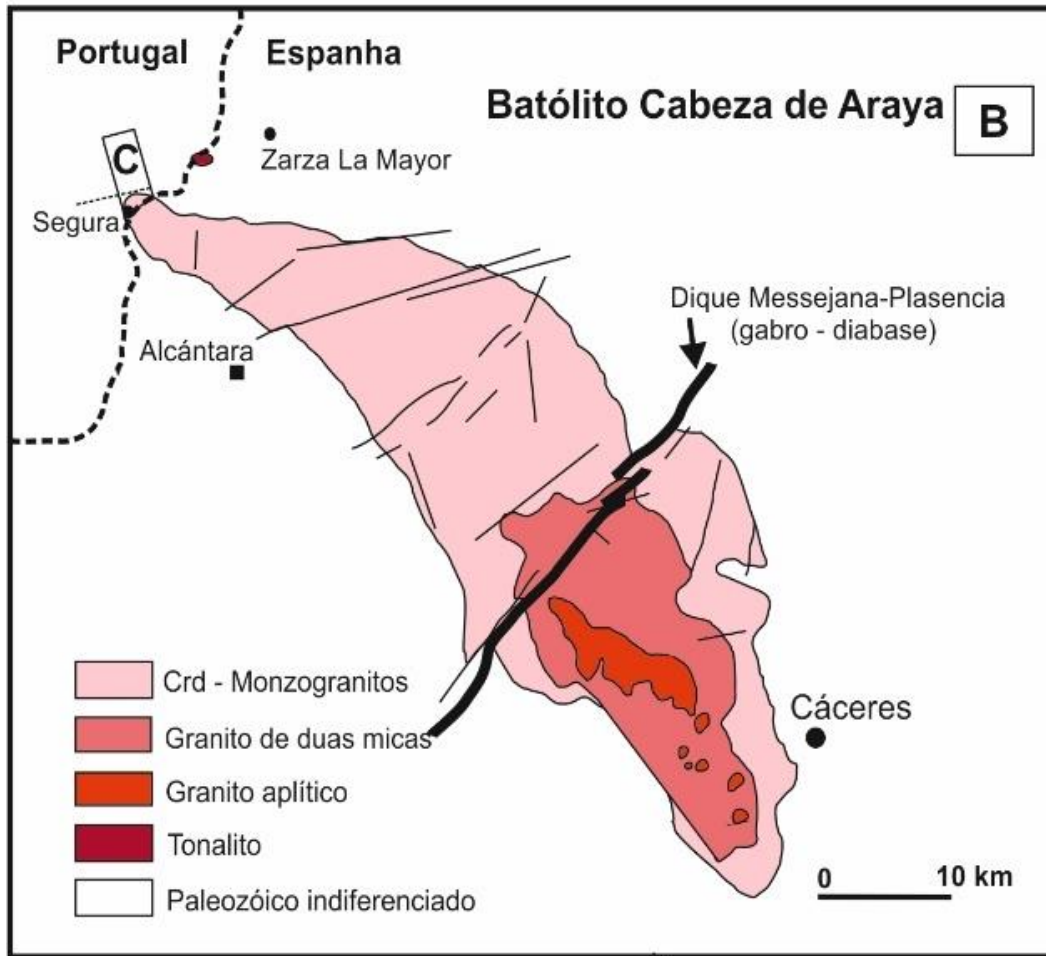
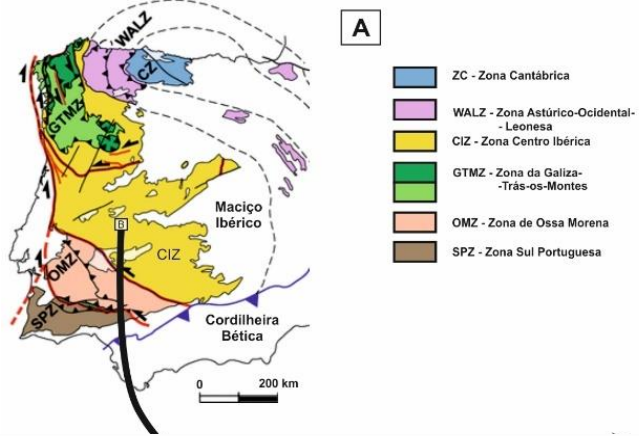
Brookite

(2/m2/m2/m)



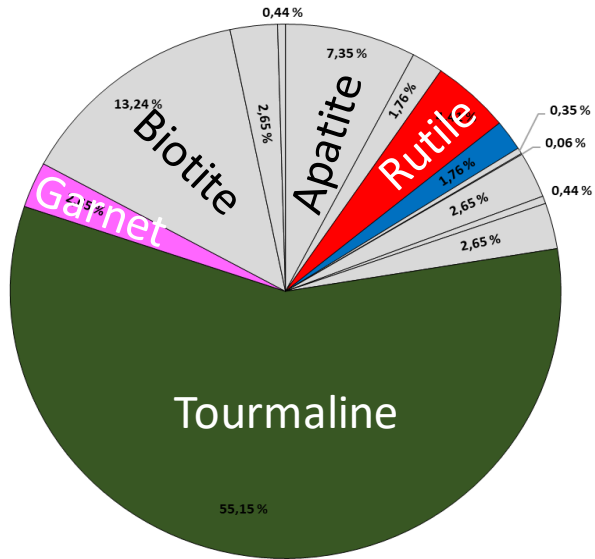
n=295

# Geological Setting

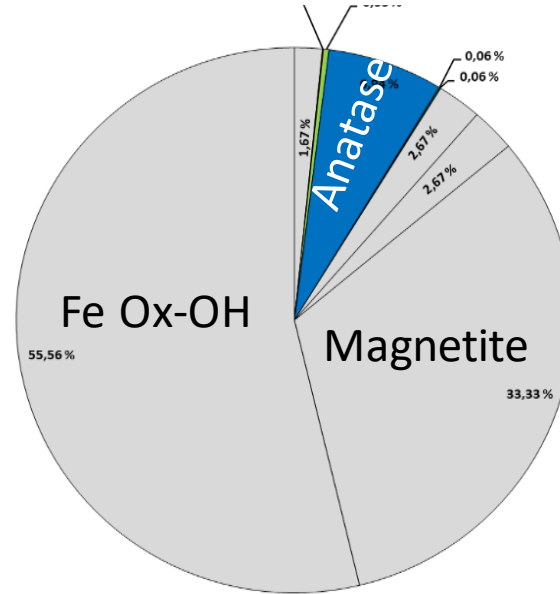


# Alluvial Heavy Mineral Associations

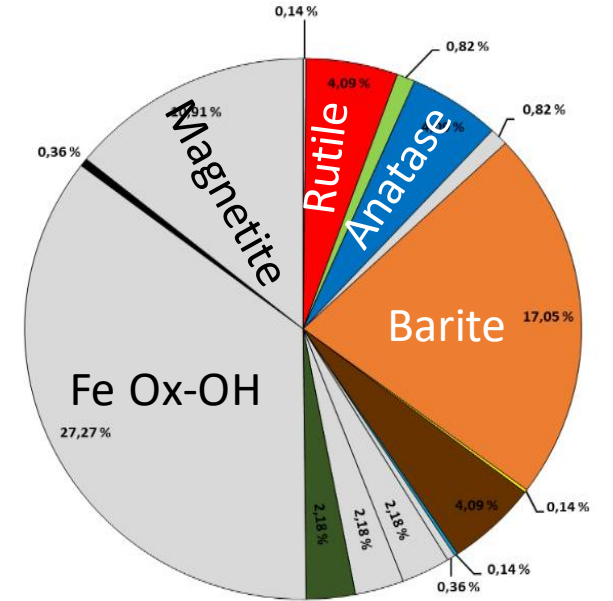
## Granite



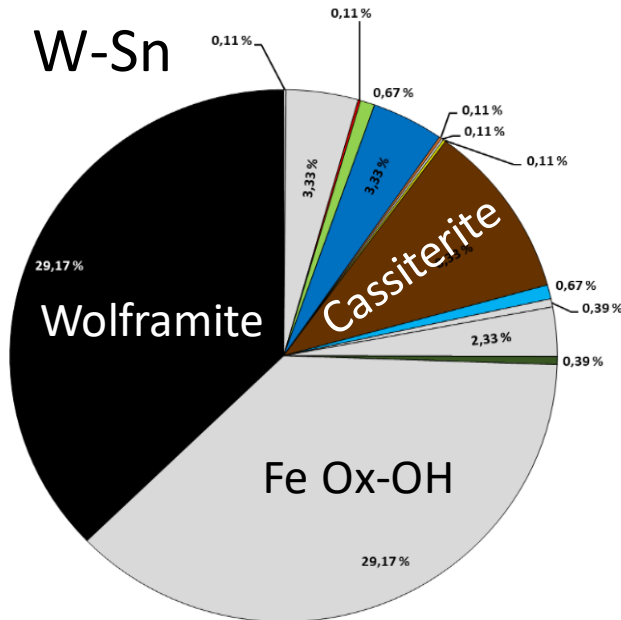
## SGC metasediments



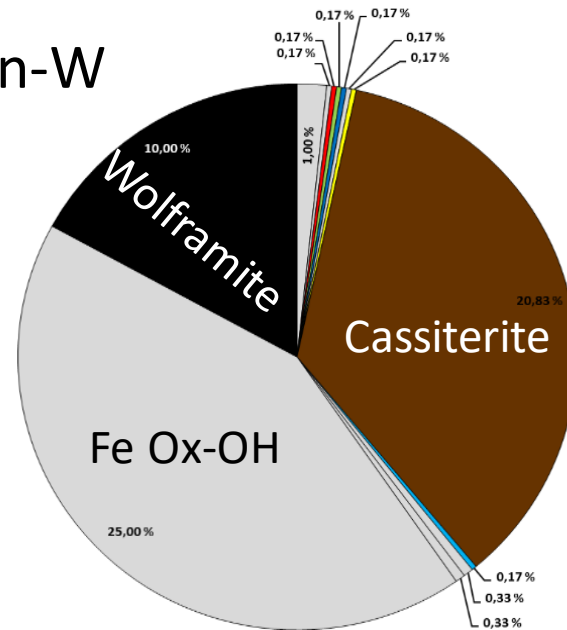
## Ba-Pb



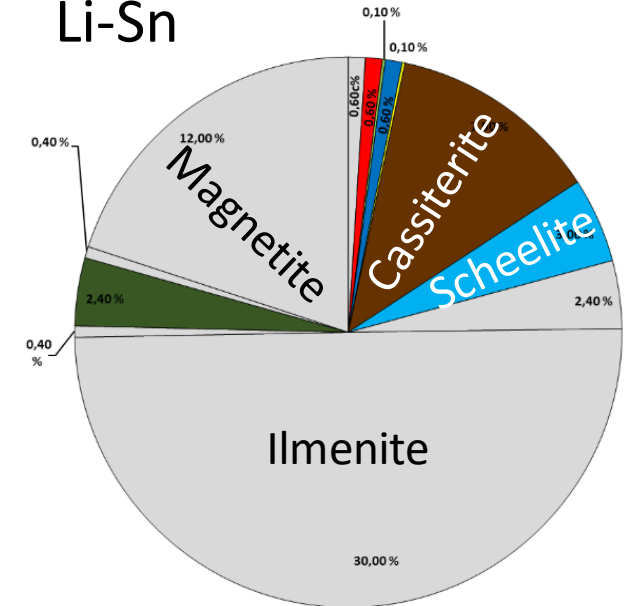
## W-Sn



## Sn-W

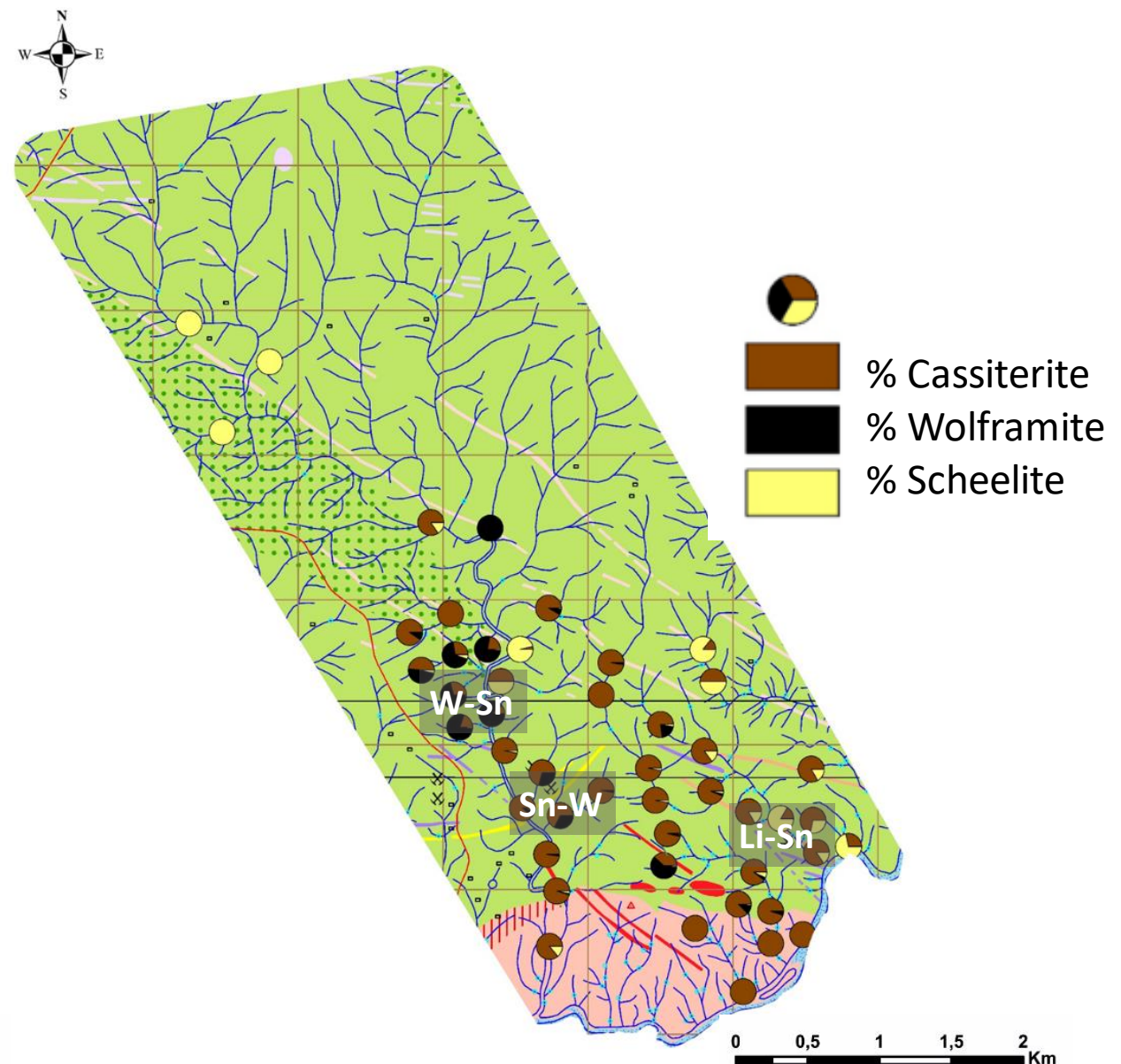
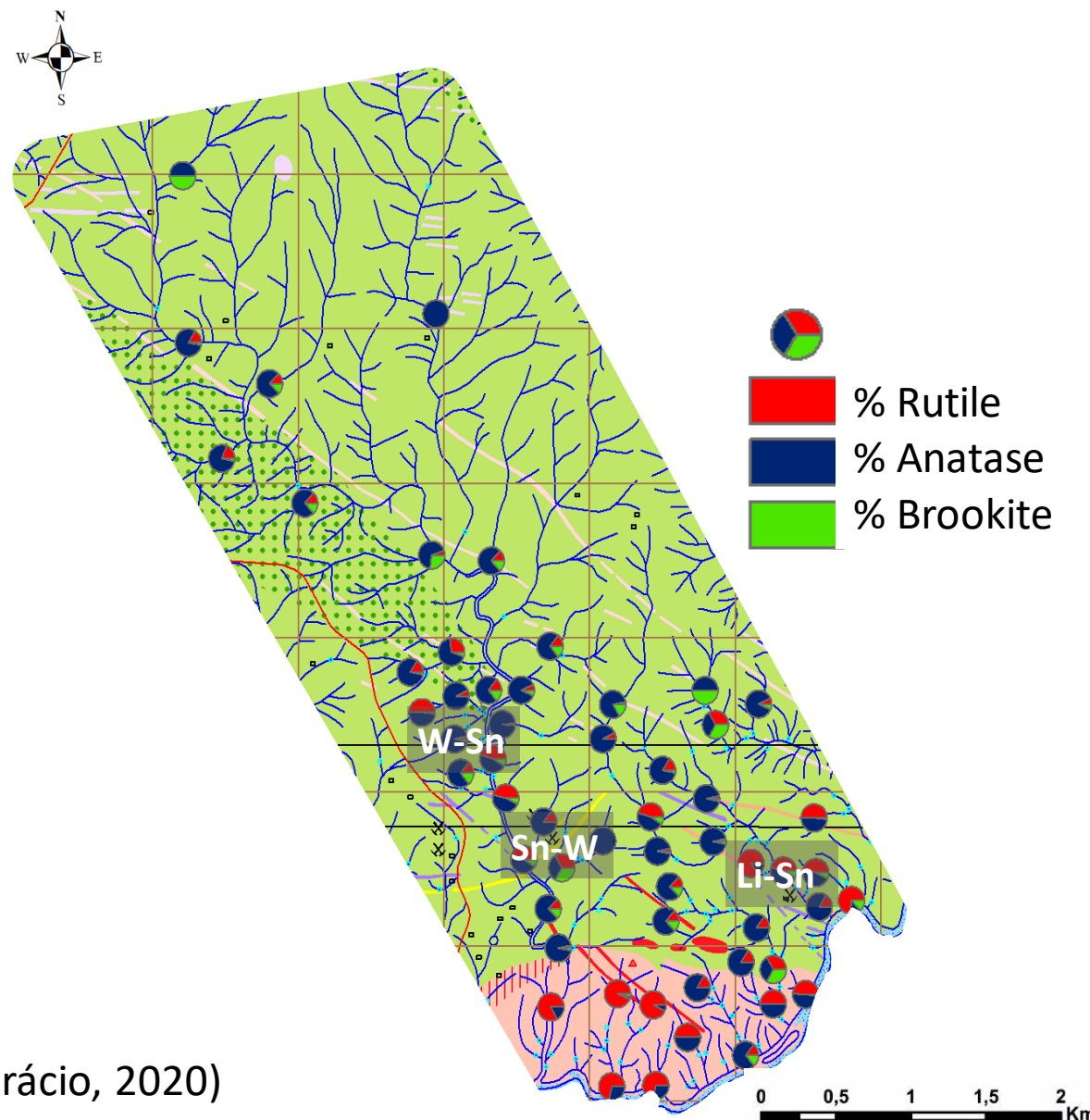


## Li-Sn



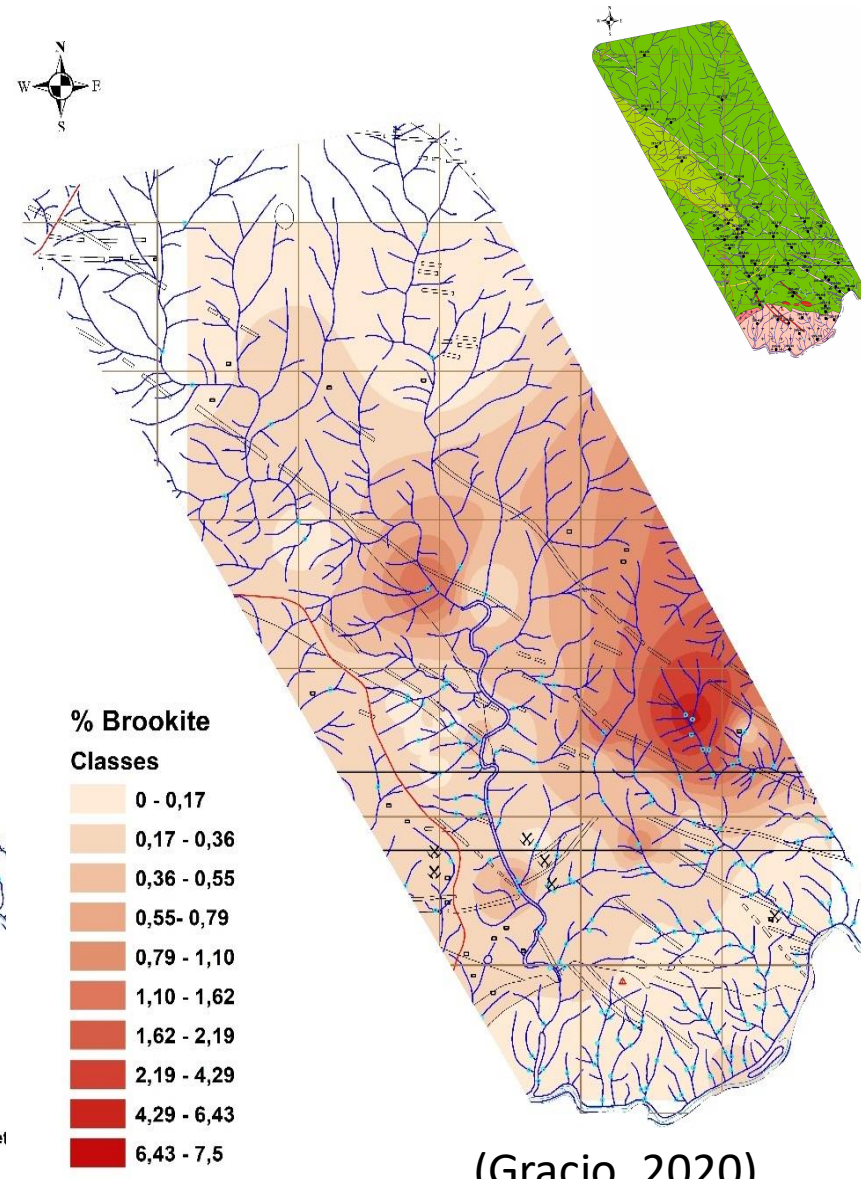
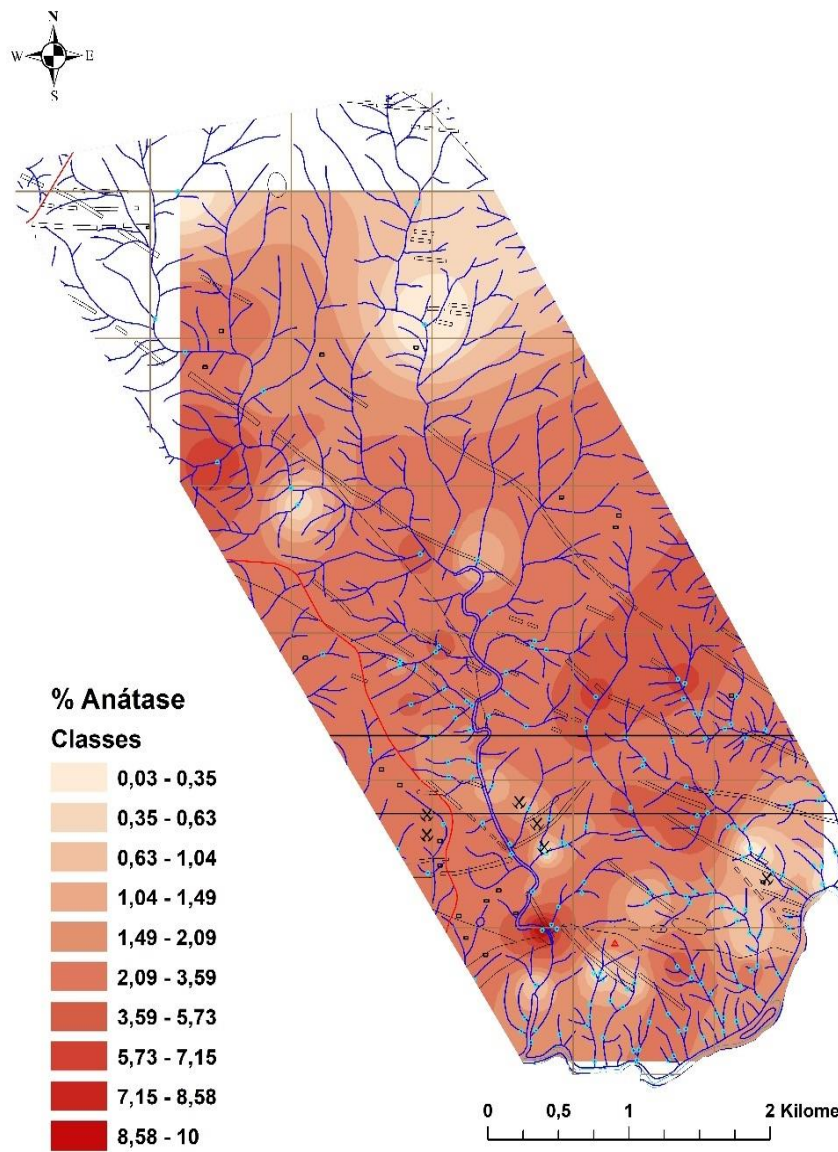
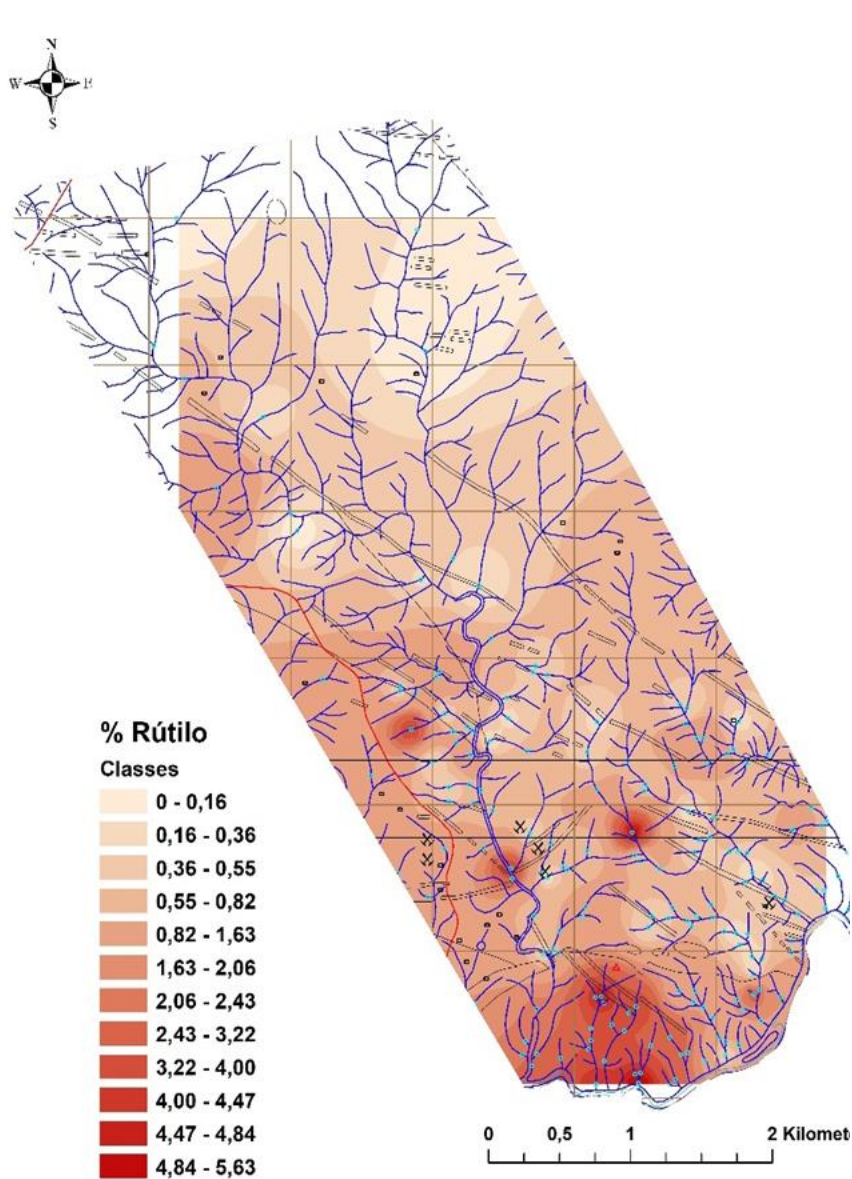
(Grácio, 2020)

# Alluvial heavy mineral relative abundance maps



(Grácio, 2020)

# Alluvial heavy mineral relative abundance maps



(Gracio, 2020)

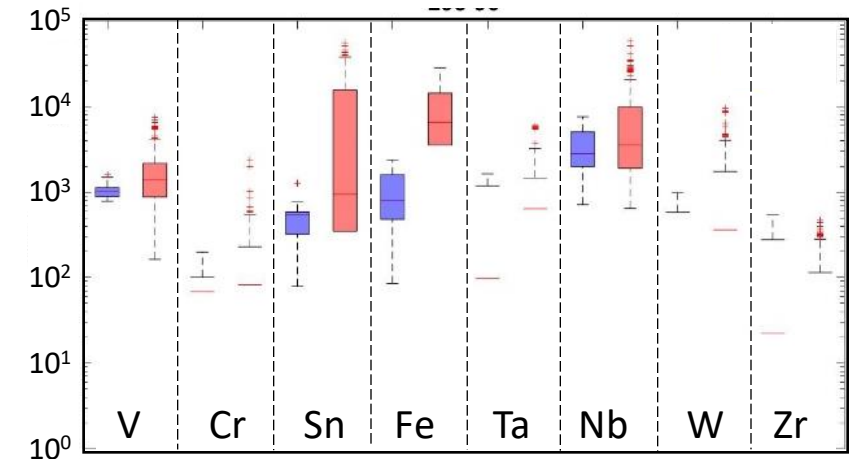
# Trace elements in TiO<sub>2</sub> minerals – EMP data

## Trace element geochemistry of rutile and anatase EMP data

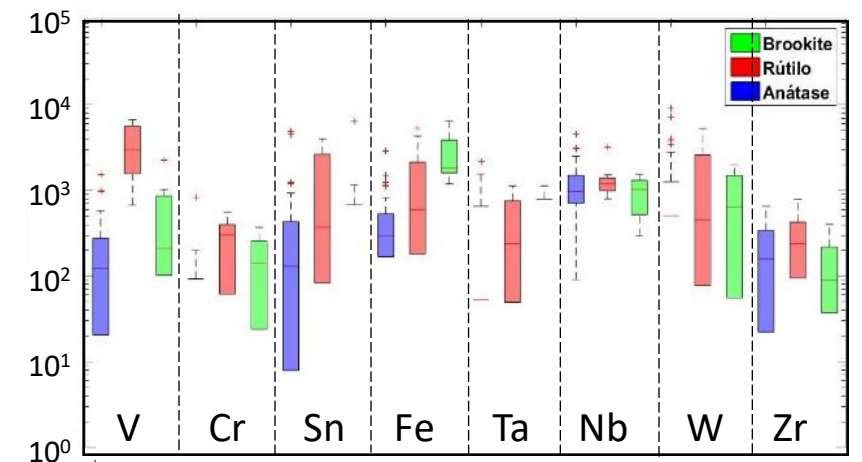
	V	Cr	Fe	Sn	Nb	Ta	W	Zr
<b>Rútilo (ppm)</b>								
Mínimo	< 205	< 196	< 194	< 350	< 312	< 1199	< 1212	< 279
Máximo	10937	4201	29258	55665	85347	19139	57173	1577
Média	1712	168	5882	4462	5723	890	5126	68
Mediana	1271	0	4508	882	3845	0	1491	0
Desvio Padrão	1388	370	5196	7900	6269	1990	8898	163
<b>Anátase (ppm)</b>								
Mínimo	< 198	< 196	< 188	< 354	< 302	< 1143	< 1103	< 270
Máximo	5289	1006	17699	4892	12296	16895	10523	992
Média	754	23	472	85	1575	261	694	99
Mediana	877	0	894	0	1139	0	0	0
Desvio Padrão	545	88	280	387	1510	833	1566	193

(Grácio, 2020)

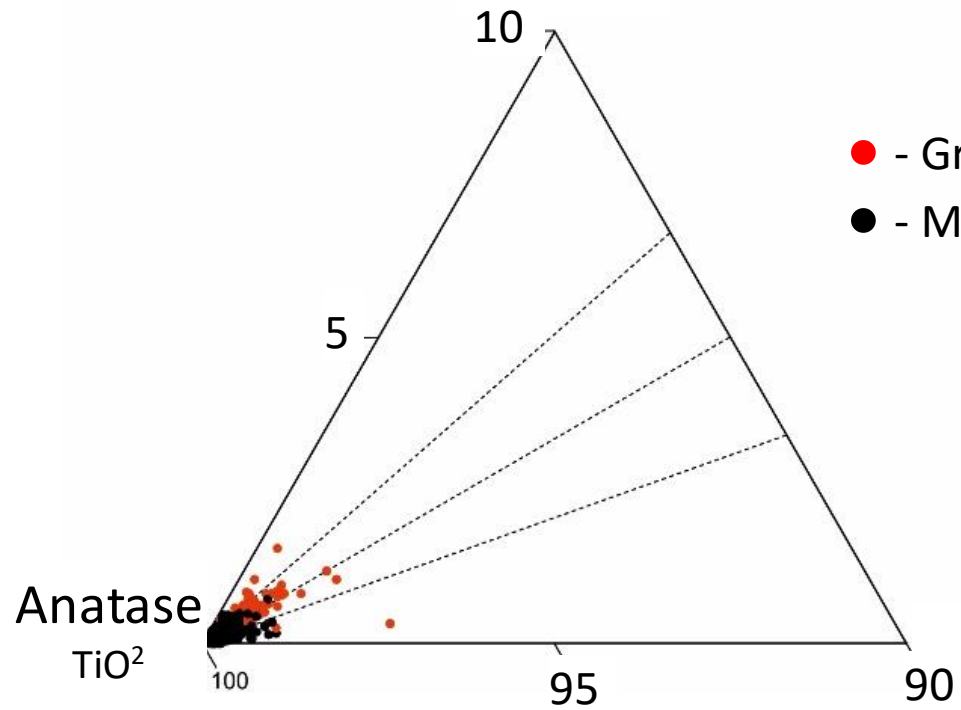
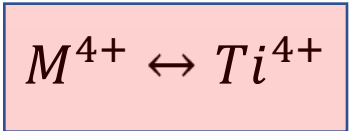
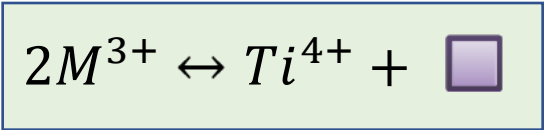
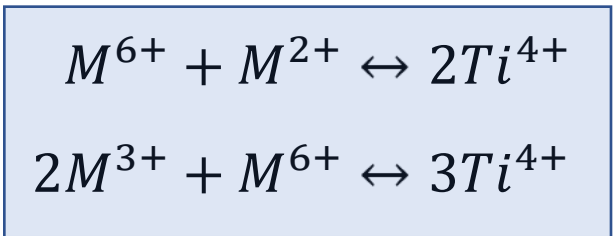
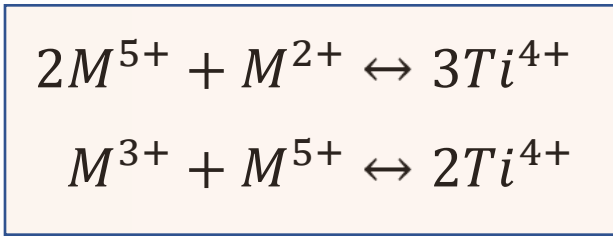
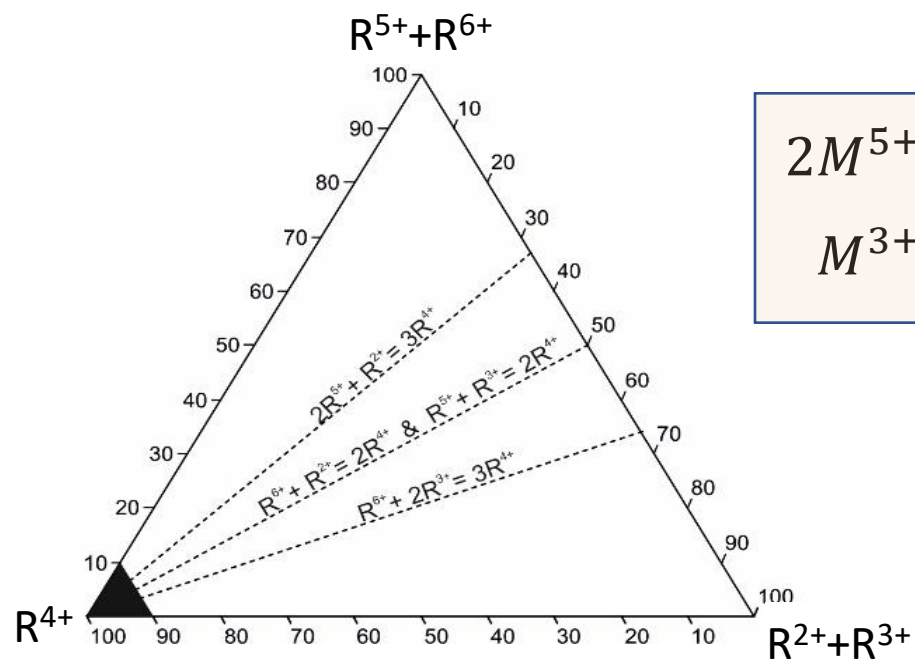
### Granites



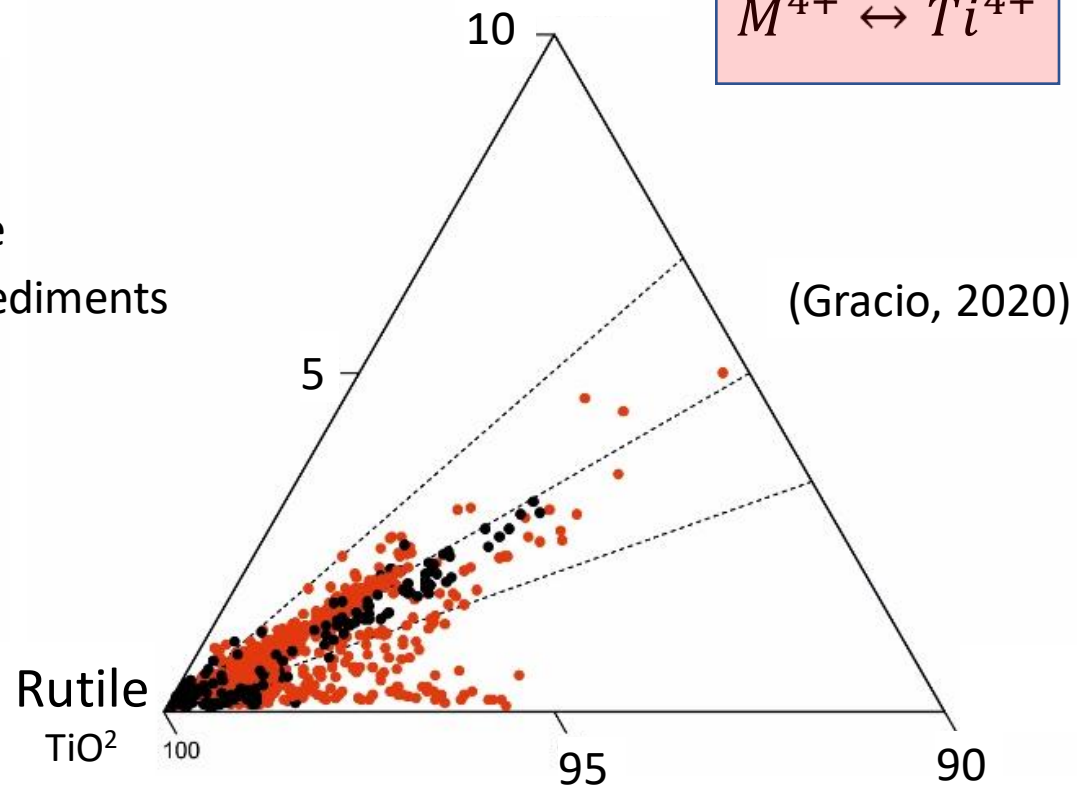
### Mineralized Zones



# Trace Element Substitution Mechanisms

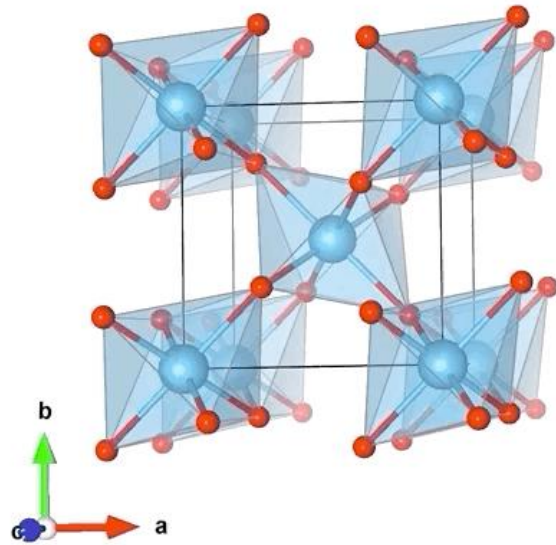


- - Granite
- - Metasediments



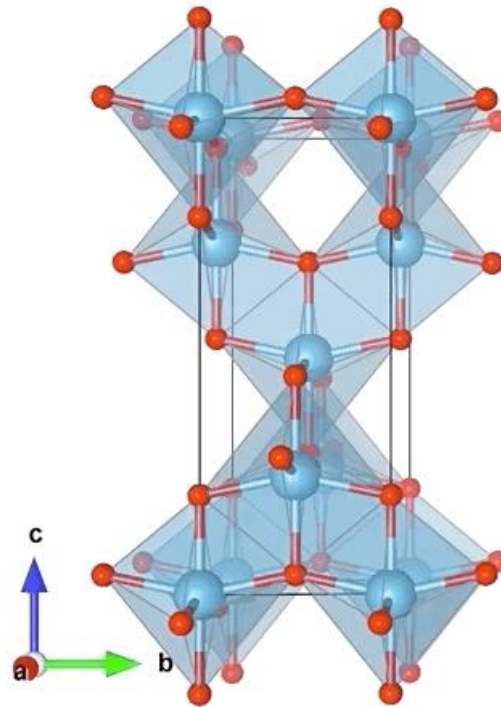
# TiO<sub>2</sub> Polymorph structures

## Rutile



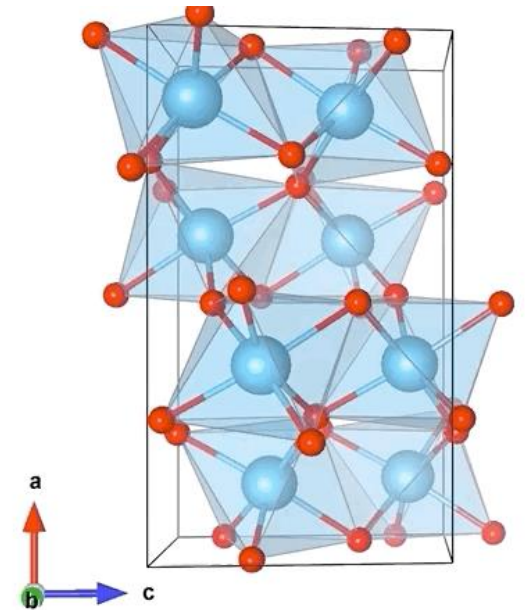
2 OSE

## Anatase



4 OSE

## Brookite



3 OSE

Effective Ionic Radii (Å)  
in VI coordination

0.58

0.59

0.60

Ti<sup>4+</sup> (VI)  
0.605

0.62

V<sup>3+</sup>

Nb<sup>5+</sup> Fe<sup>3+</sup>

0.64

0.65

0.66

0.69

Sn<sup>4+</sup>

0.69

0.72

0.75

0.77

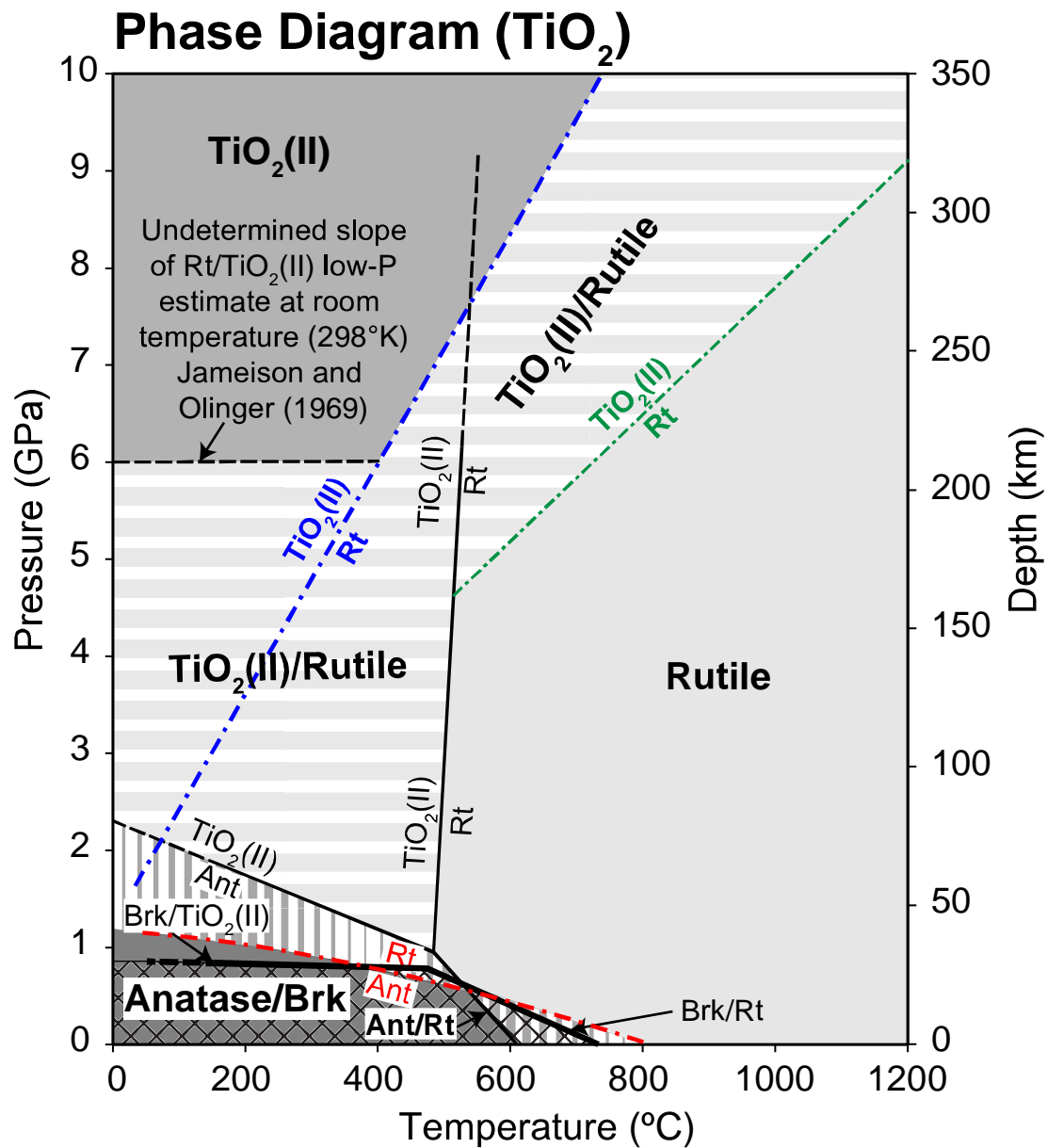
Fe<sup>2+</sup>

0.82

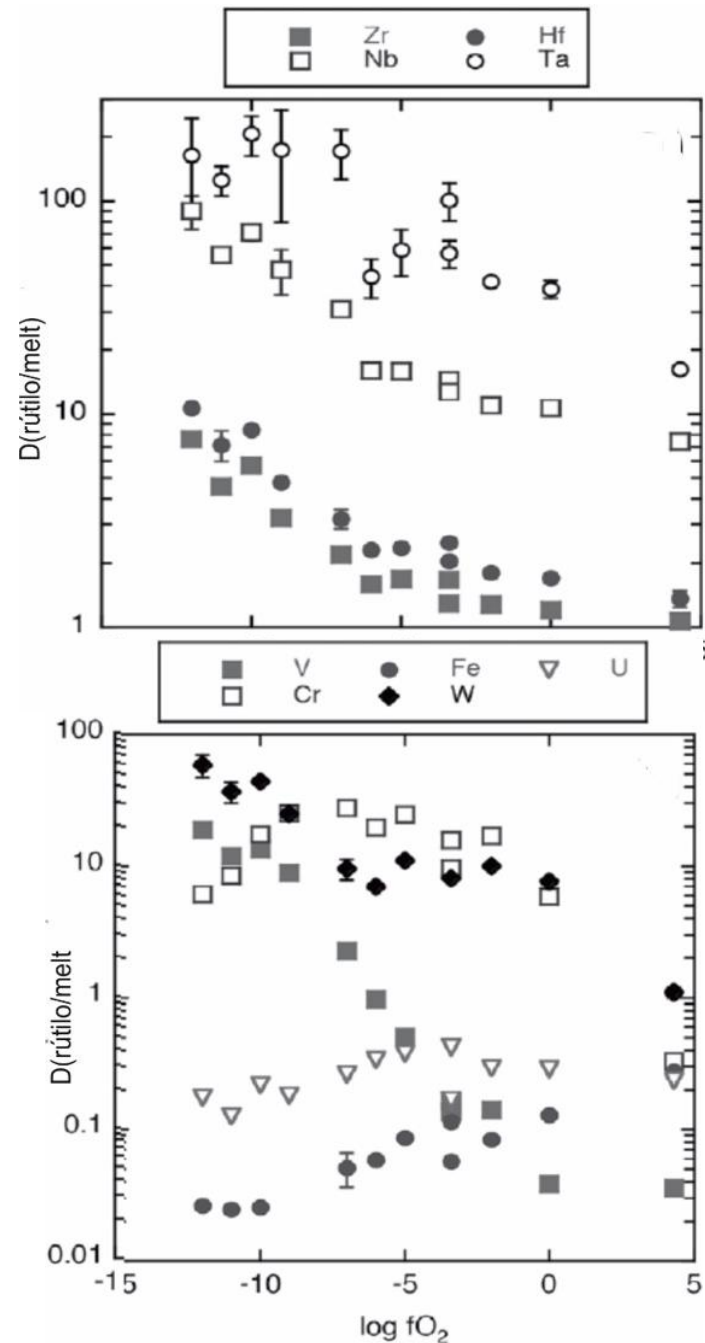
Mn<sup>2+</sup>



# TiO<sub>2</sub> Polymorph Stability Primary vs. Secondary



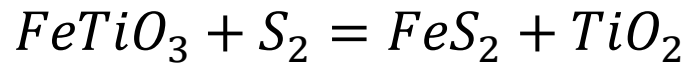
(Plavsa et al., 2017)



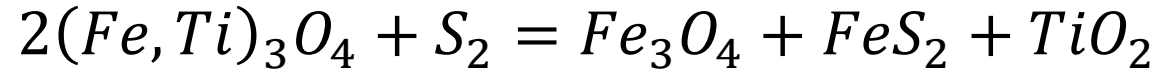
(Mallmann et al., 2014)

## Alteration of Ti-rich phases

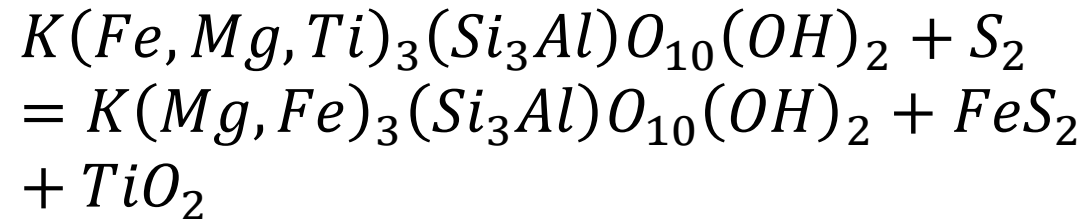
Ilmenite



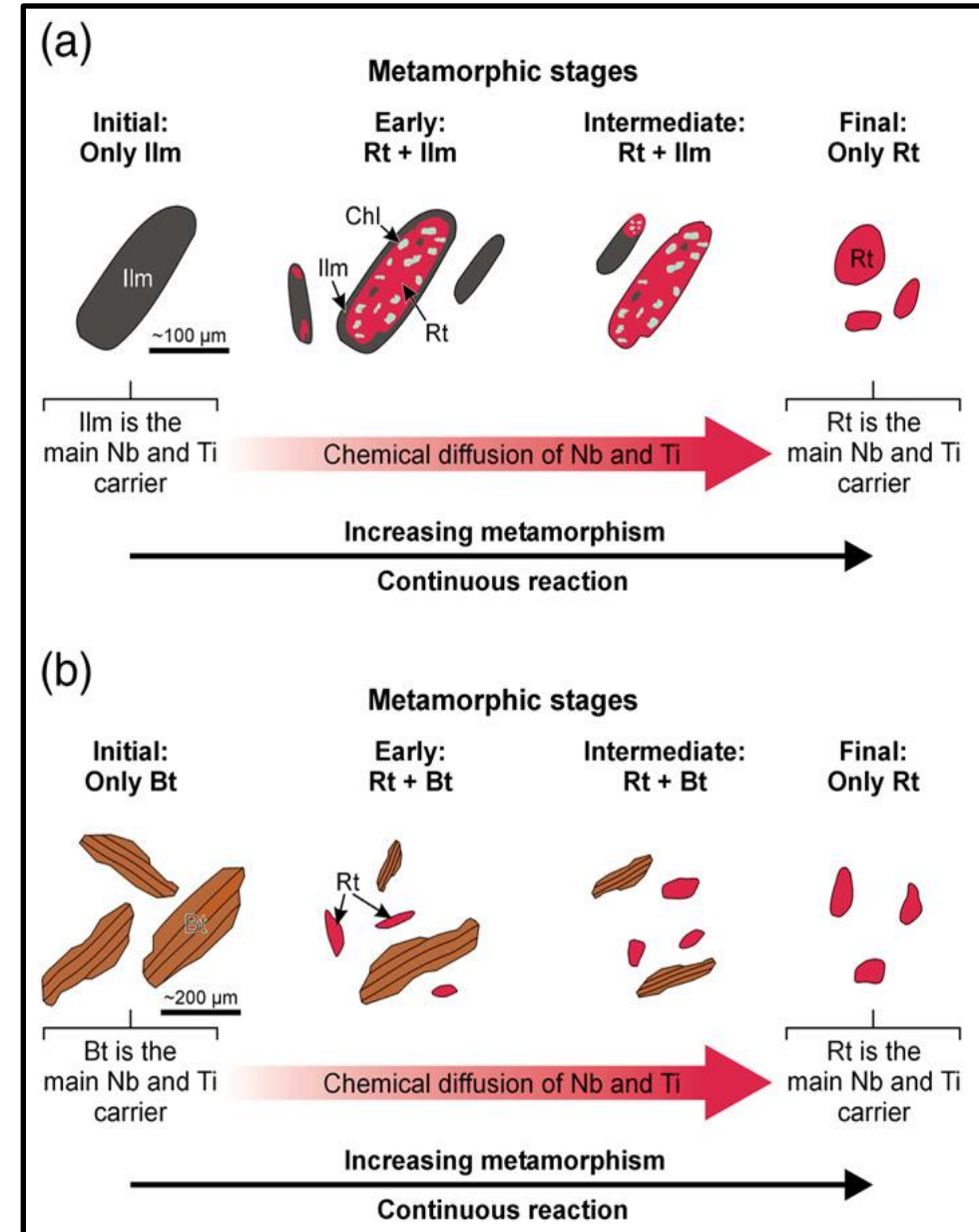
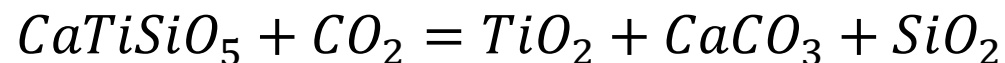
Ti-magnetite



Biotite

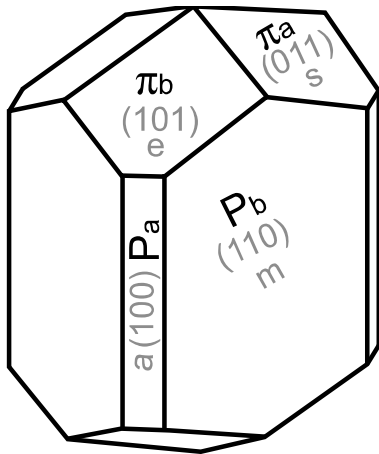


Titanite

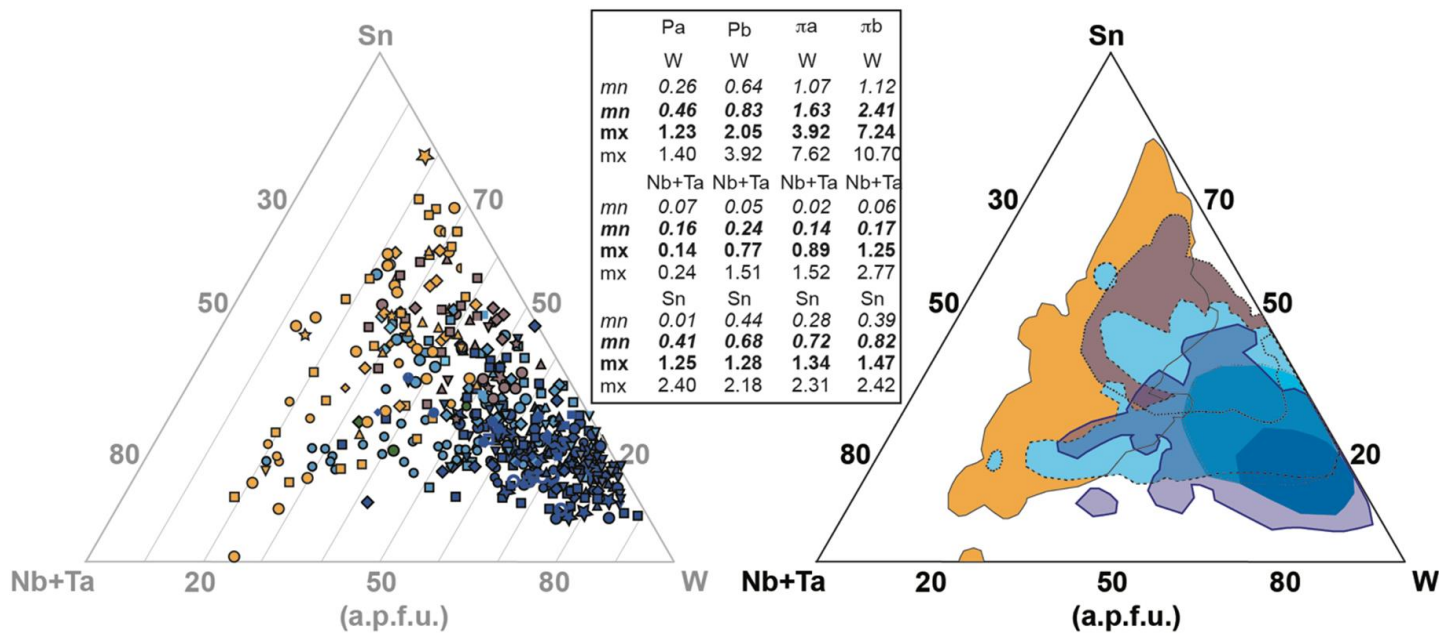
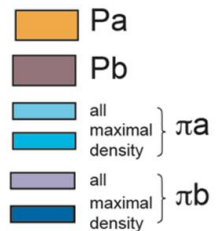


After Meinhold (2010)

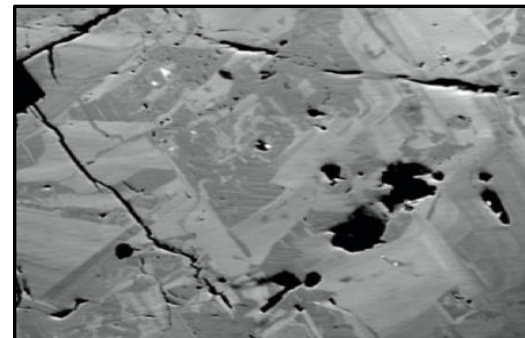
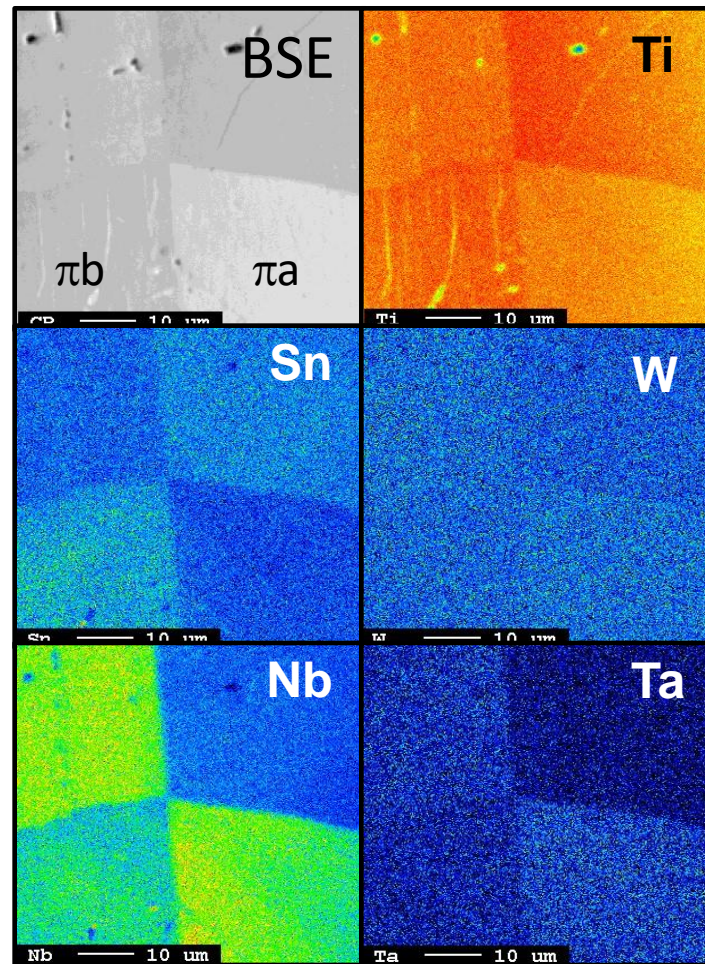
# Rutile Crystal Forms Controlling Trace Elements



Carocci et al. (2019)  
Rutile – Panasqueira deposit



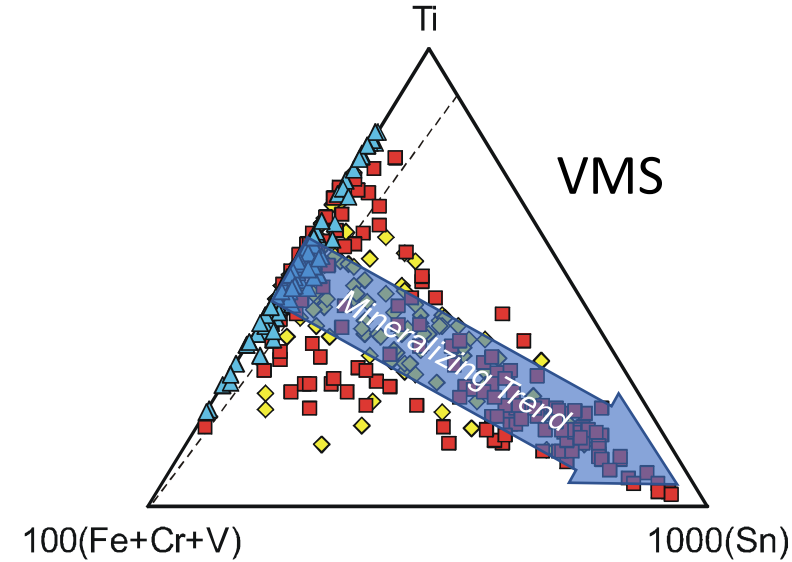
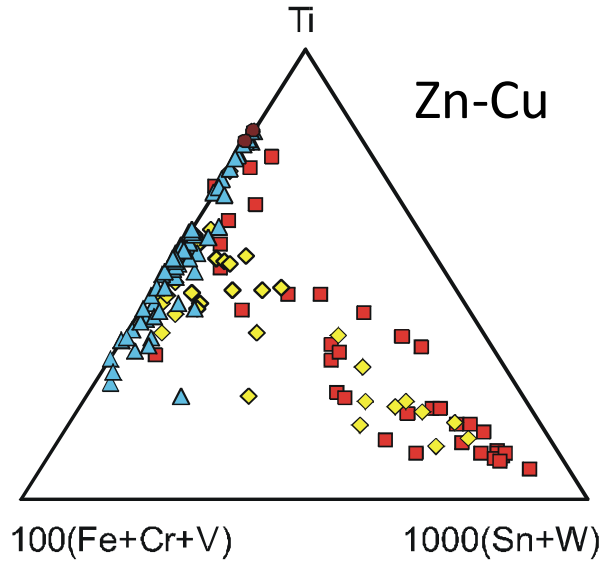
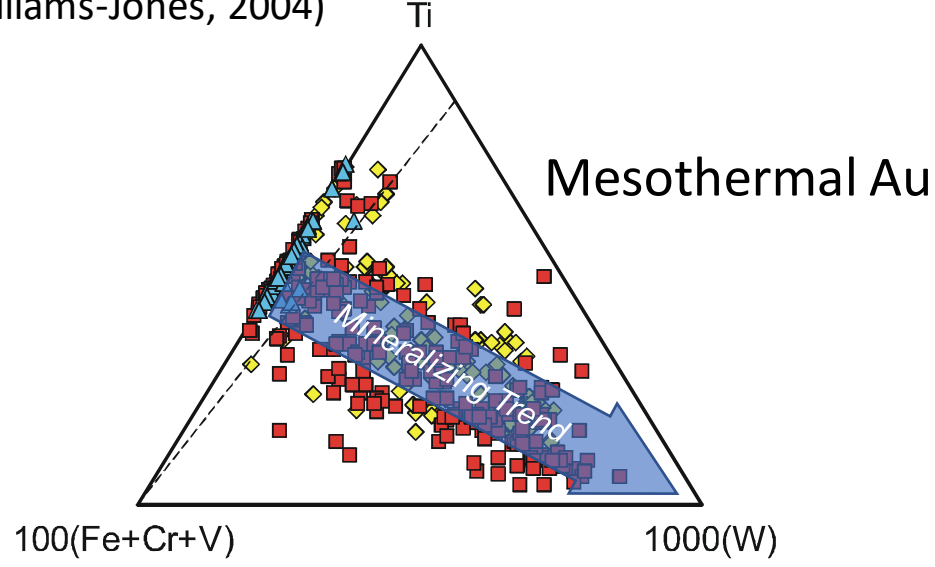
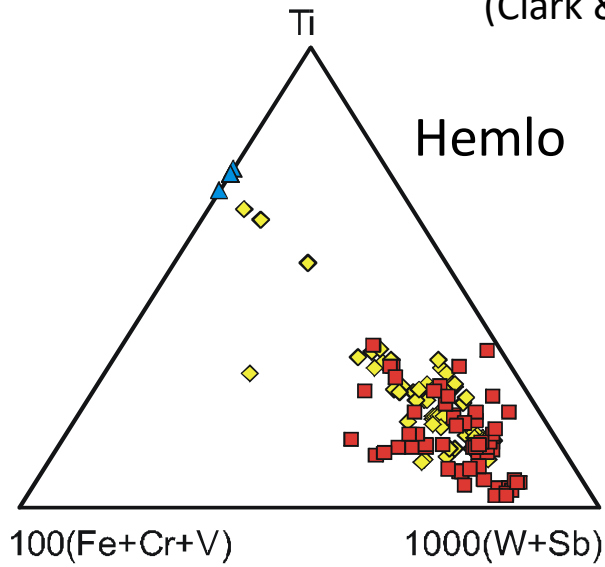
Grácio (2020)



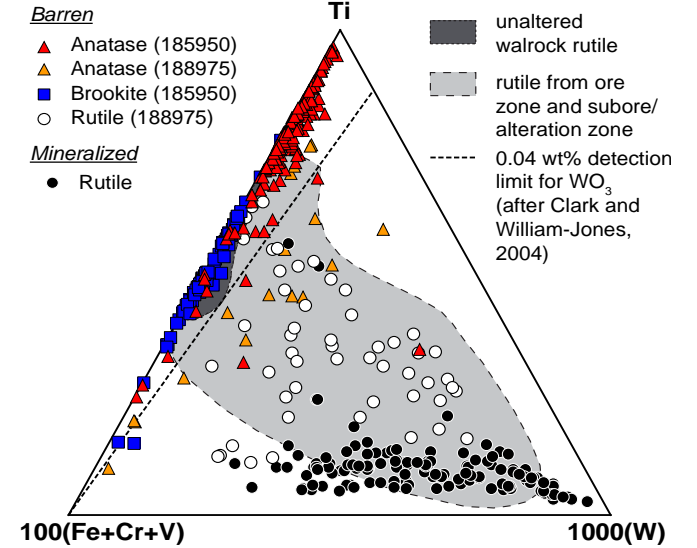
(Grácio, 2020)

# Exploration Tools – Trace Element Vectoring/Fingerprints

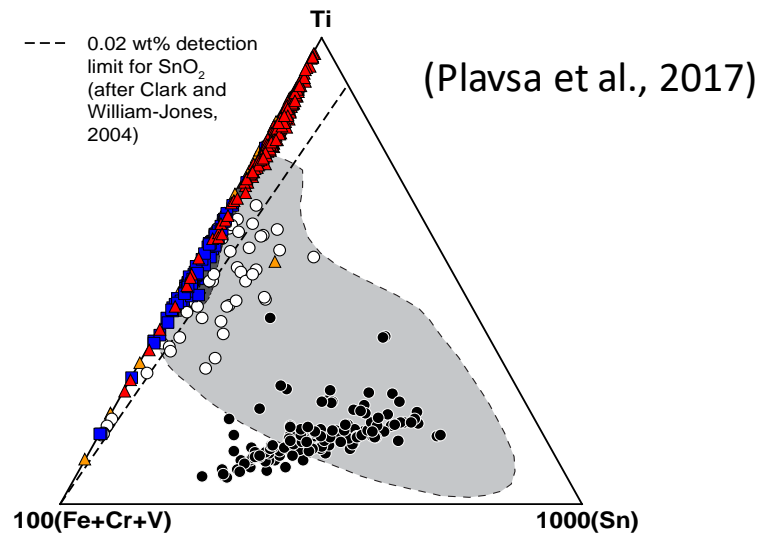
(Clark & Williams-Jones, 2004)



## b) Mesothermal Au deposits



## c) Base metal deposits



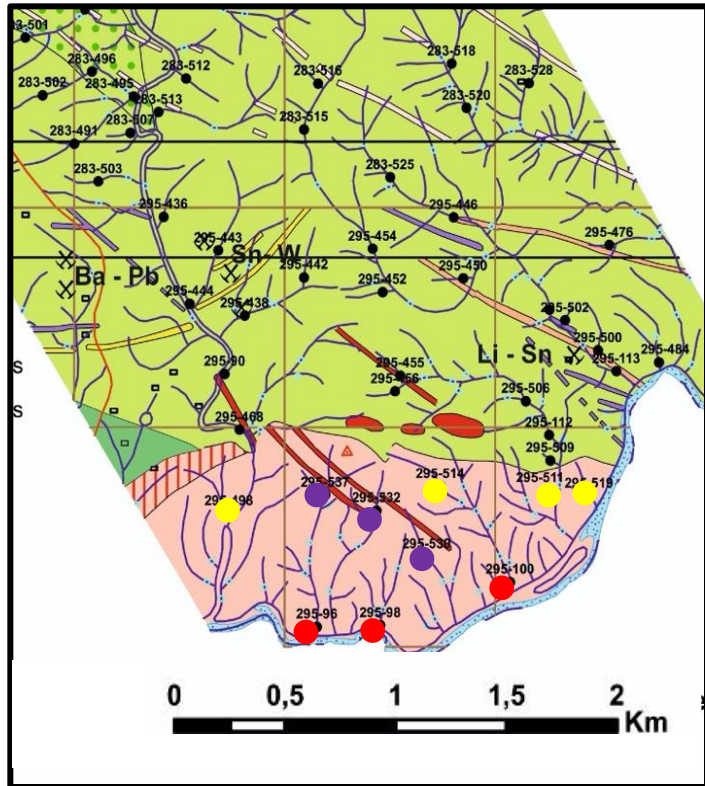
# Exploration Tools – Trace Element Fingerprints

Internal Zone

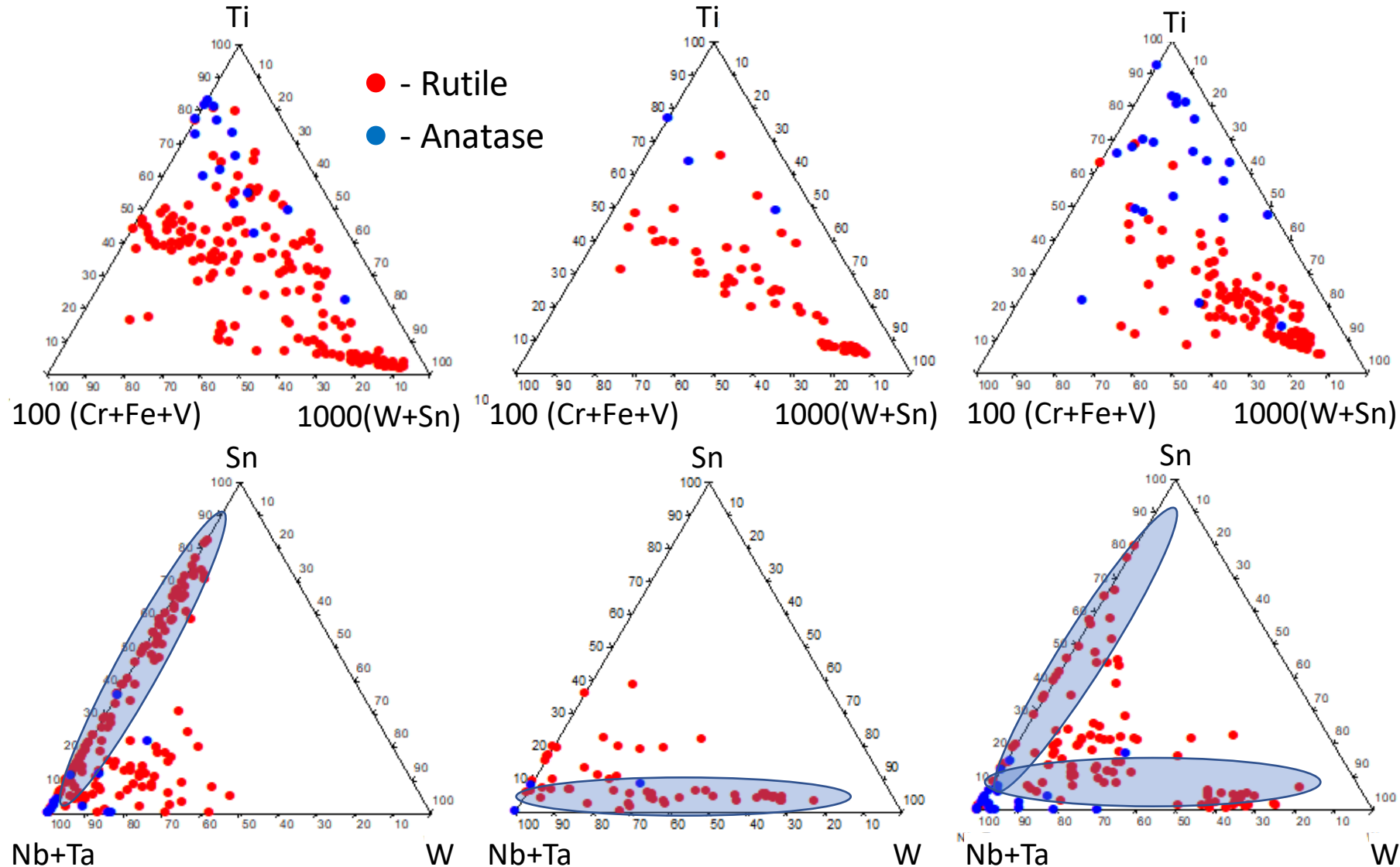
Border Zone

Aplitic-rich Zone

## Granites

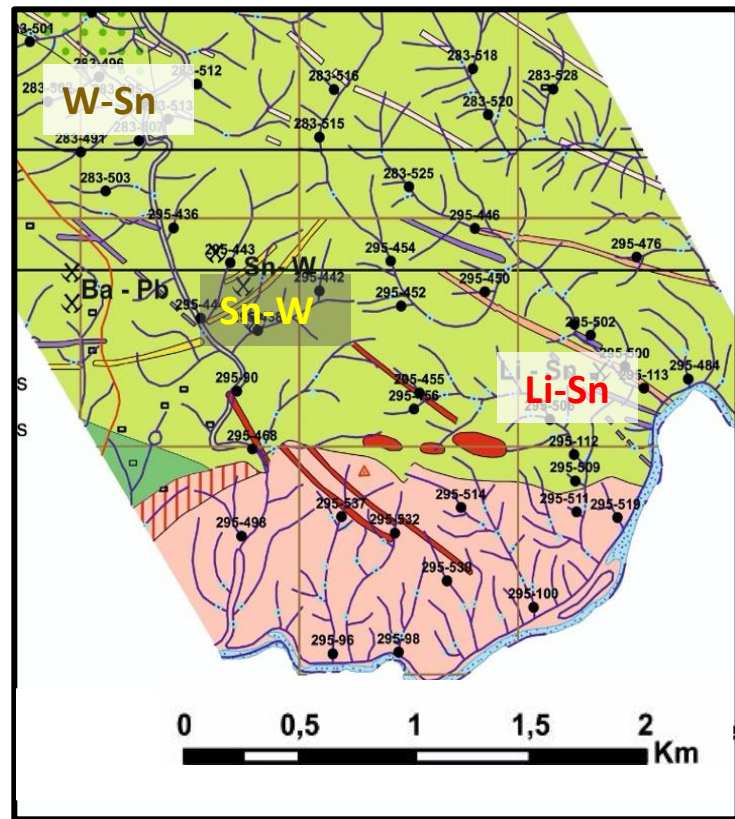


(Gracio, 2020)



# Exploration Tools – Trace Element Fingerprints

## Sn-W Mineralized

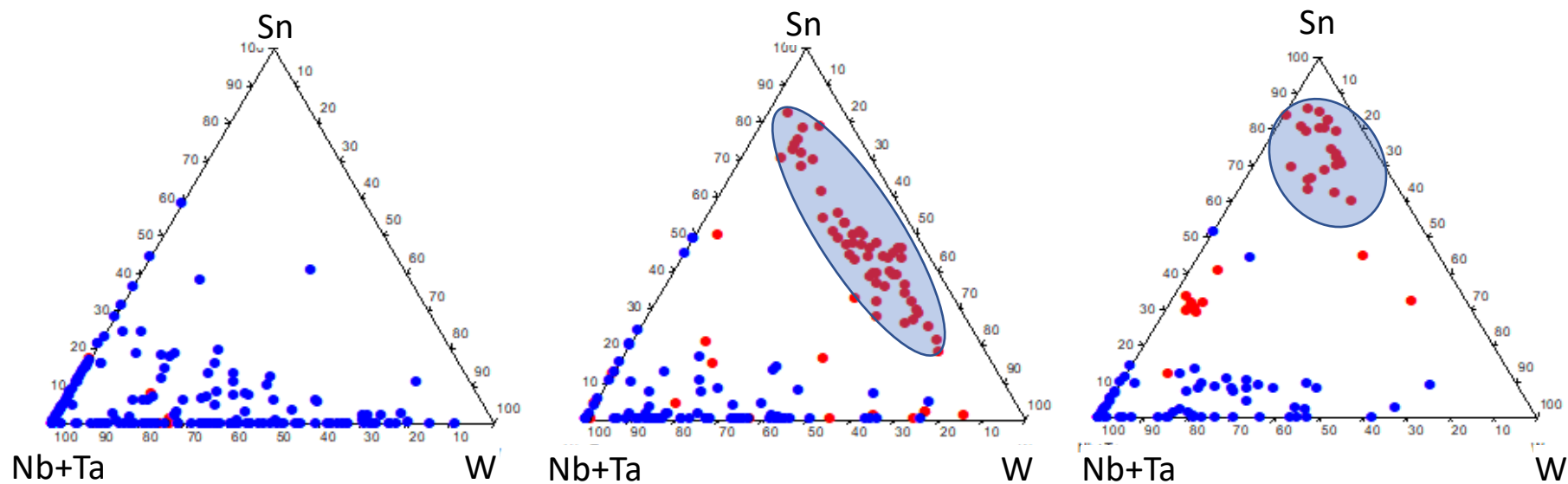
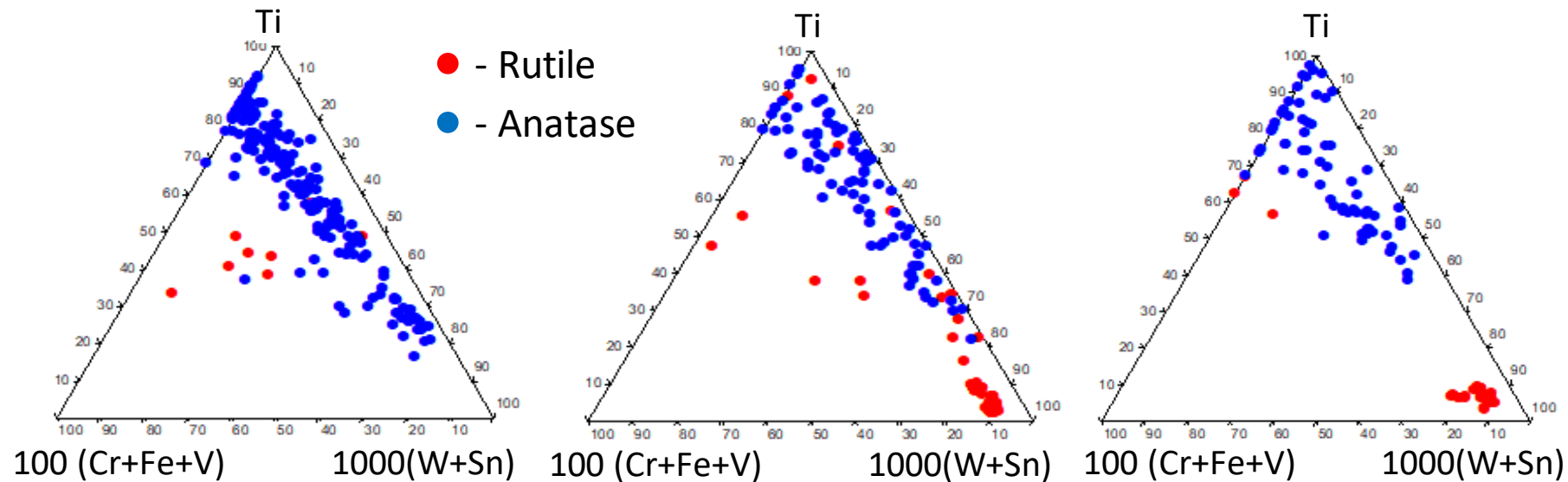


(Gracio, 2020)

**Sn ± W**

**W ± Sn**

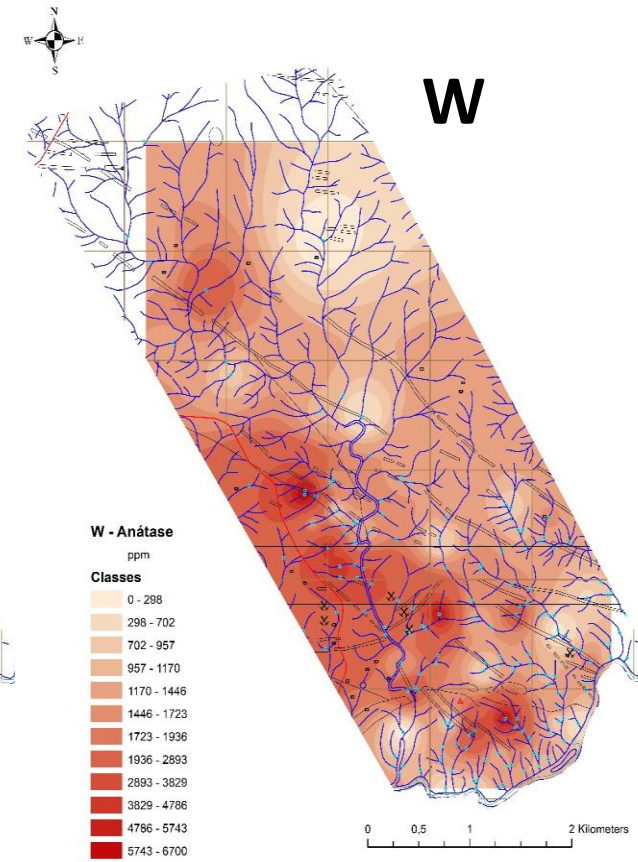
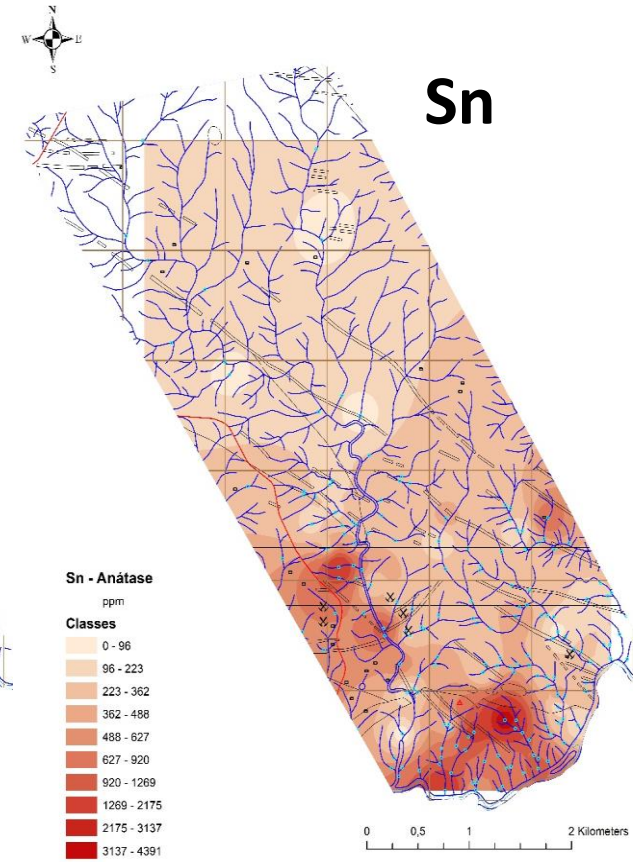
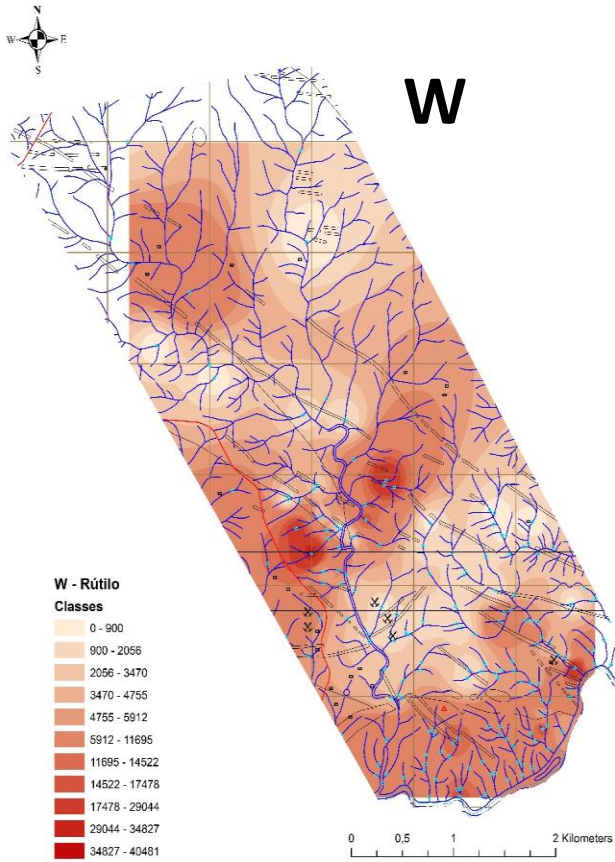
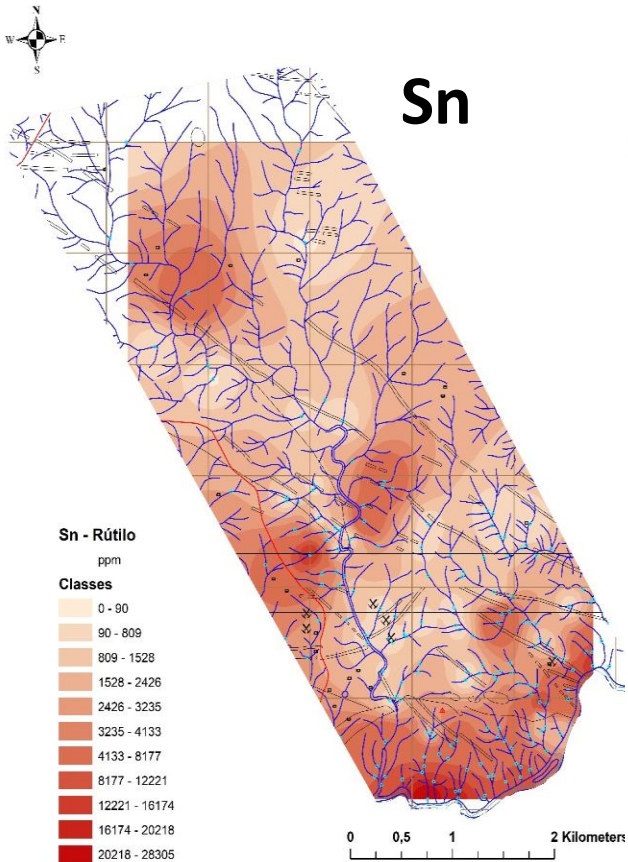
**Li ± Sn**



# Exploration Tools – Trace Element Abundance Maps

## Rutile

## Anatase

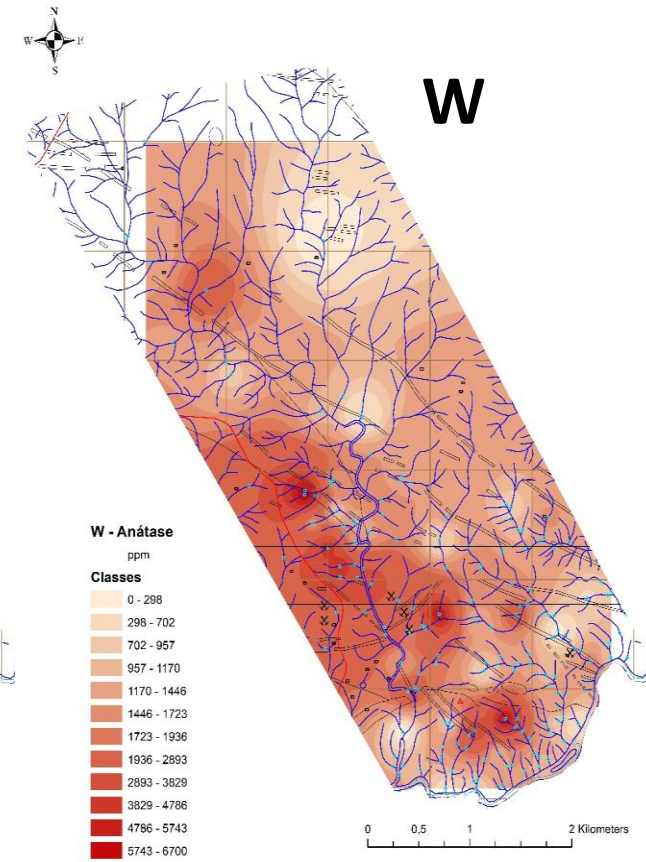
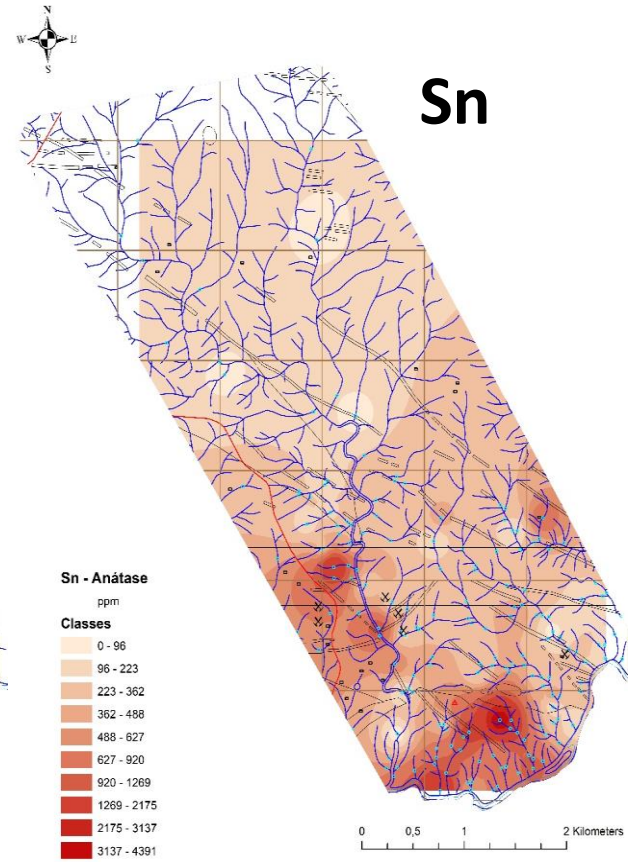
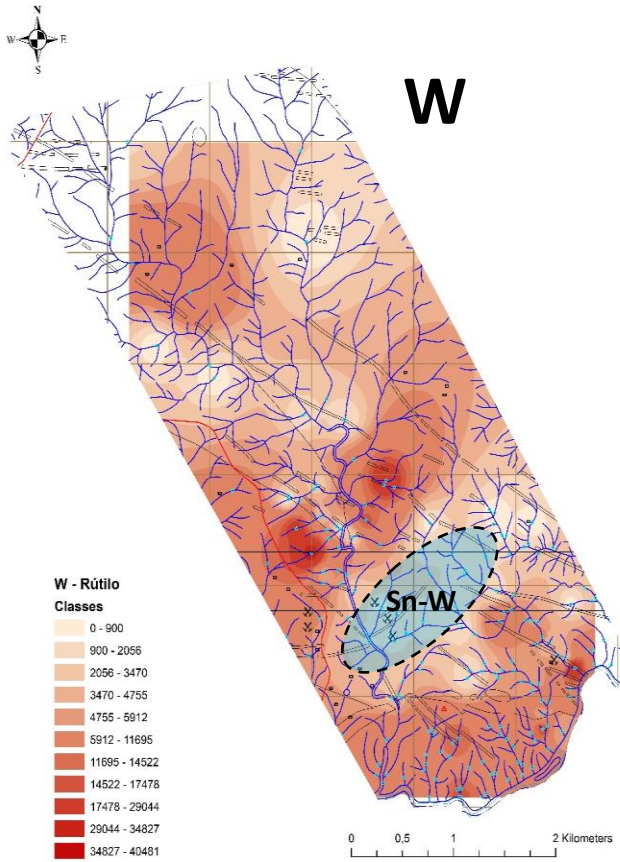
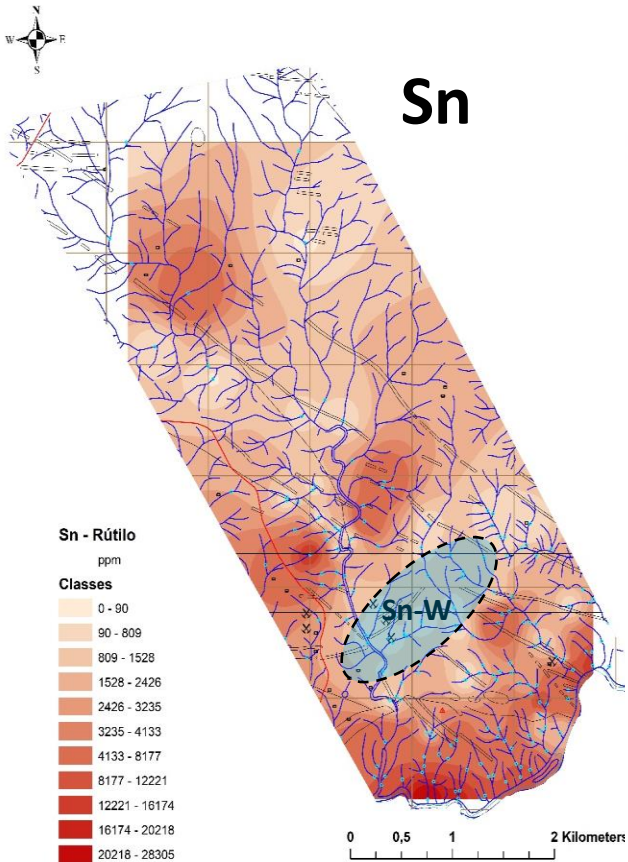


(Gracio, 2020)

# Exploration Tools – Trace Element Abundance Maps

Rutile

Anatase



(Gracio, 2020)



# Exploration Tools – Trace Element Abundance Maps

## Rutile

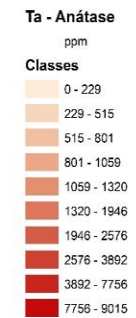
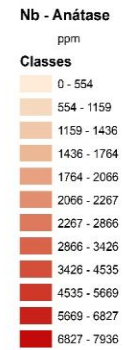
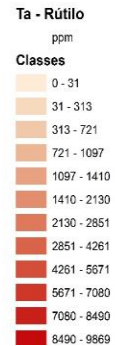
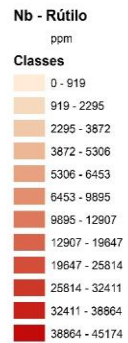
## Anatase

**Nb**

**Ta**

**Nb**

**Ta**

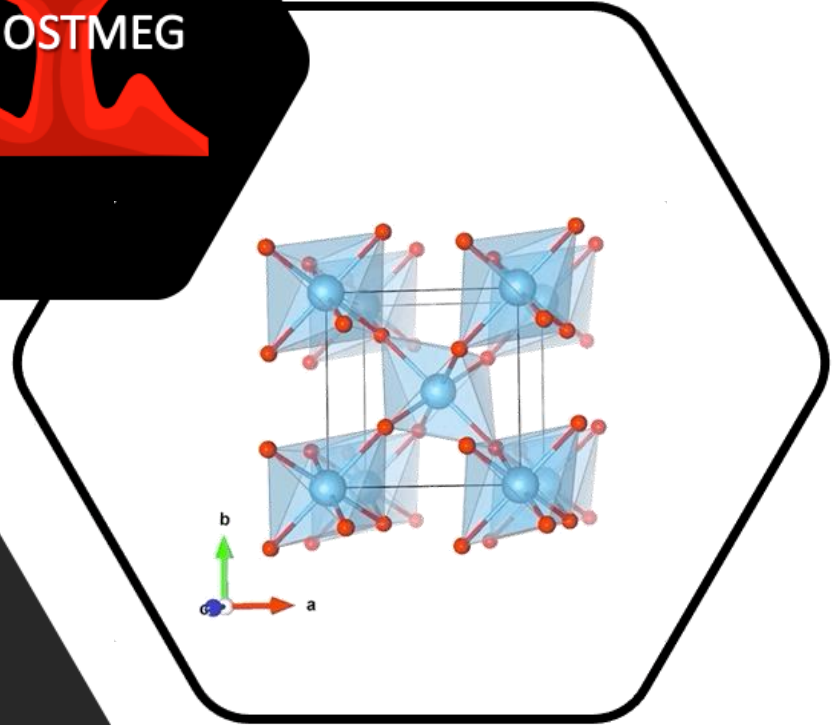
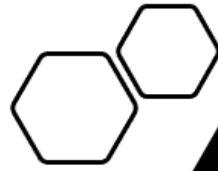


(Gracio, 2020)

# Take Home Messages

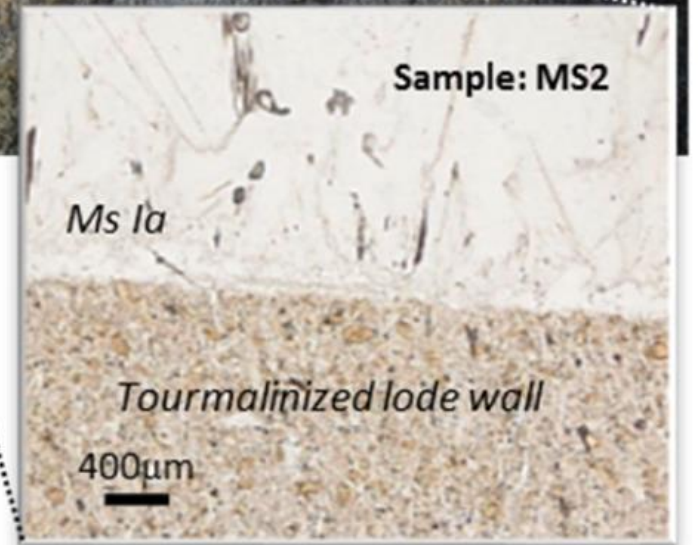
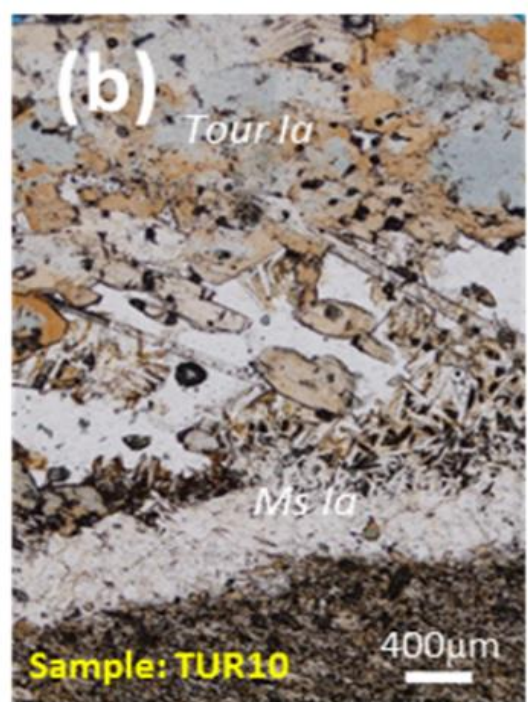
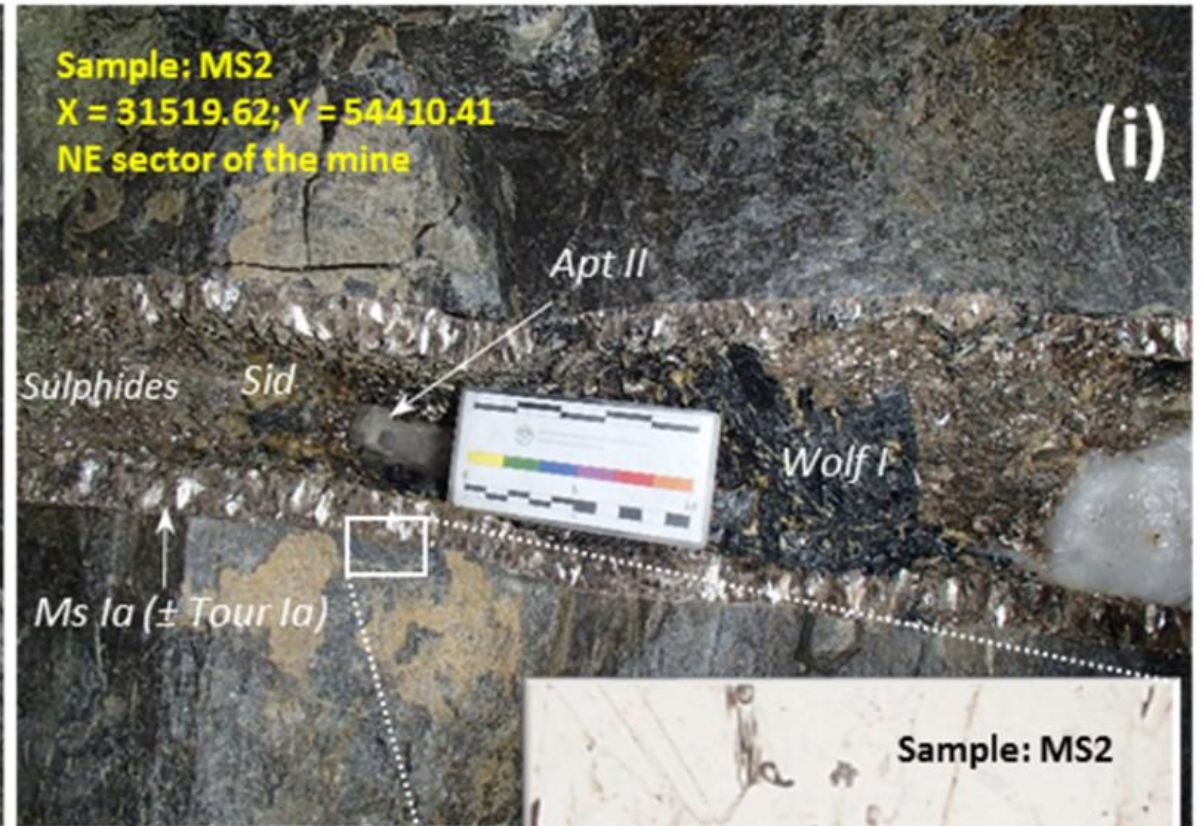


- ❖ Alluvial heavy mineral associations are a good proxy for local geology and mineralized areas.
- ❖ Alluvial heavy mineral abundance maps can pinpoint orebodies & unravel metamorphic and metasomatic processes related to the installation of productive intrusives.
- ❖ Alluvial rutile & anatase trace element geochemistry are an excellent exploration tool for Sn and W deposits:
  - Sn-rich and W-rich primary magmatic rutile can be used as a proxy for specialized and productive Sn & W granites;
  - Primary hydrothermal rutile & anatase, precipitated from mineralizing fluids, can be either enriched or depleted in HFSE depending on their relative position in the paragenetic sequence in respect to cassiterite (Sn), wolframite (W) and scheelite (W), or other HFSE forming minerals.



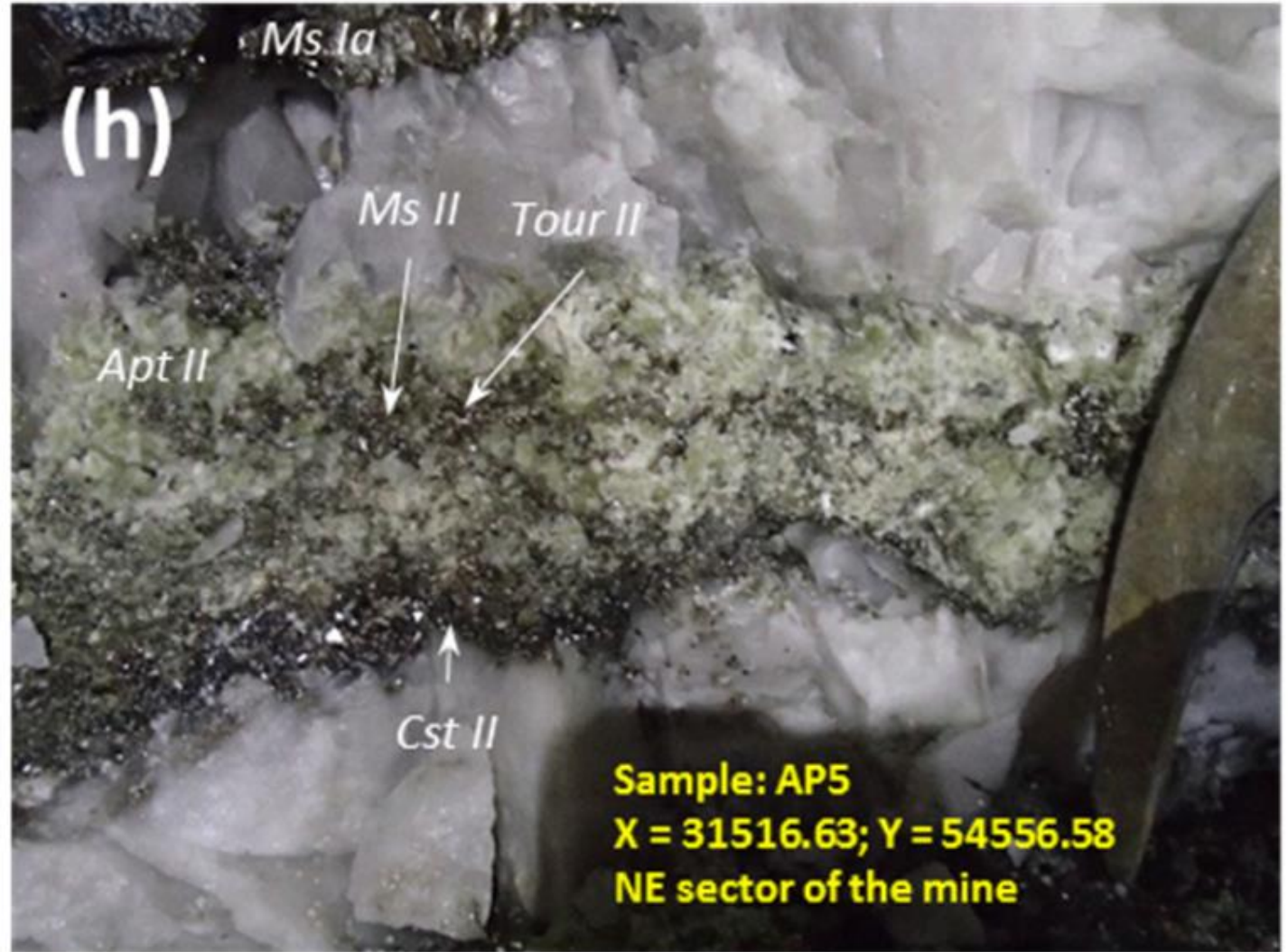
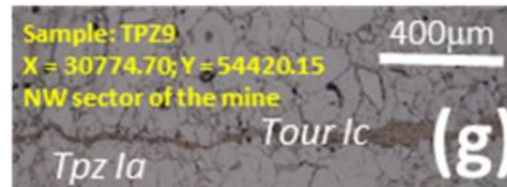
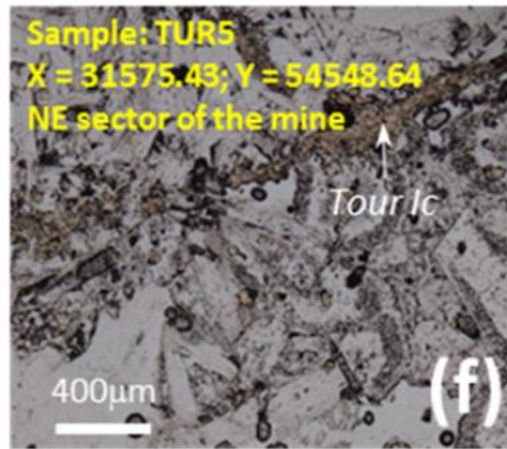
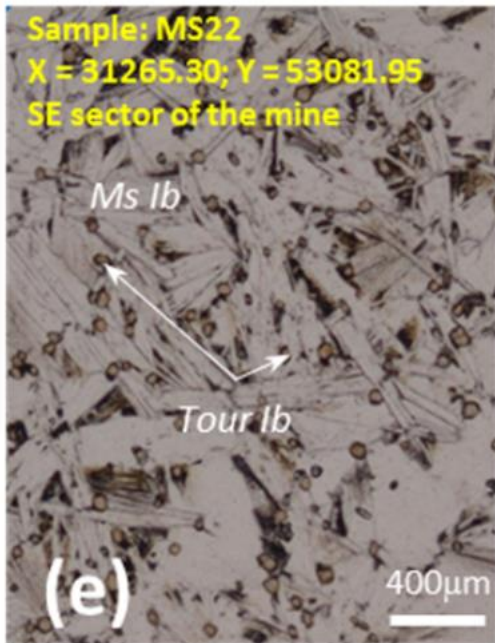
To be continued... Part III in about 5-10 min! Stay tuned! There will be coffee afterwards!

# Panasqueira tourmaline



**Tourmaline (Ia)** selvages of quartz lodes intergrown with Ms(Ia) preceding Wfm(I) and Cass(I) metasomatic halos

# Panasqueira tourmaline



**Tourmaline Ib** – Intergrown with MS(II)  
Thin selvages with Tpz

**Tourmaline Ic** – veinlet structures

**Tourmaline II** – in selvages and reopening of Qz veins with Cst II and Ap II (OSS2)