

# Origin and metamorphic reworking of the Buca della Vena Tl-rich orebody (Alpi Apuane)

This research was supported by  
MIUR-SIR 2014 project "THALMIGEN"

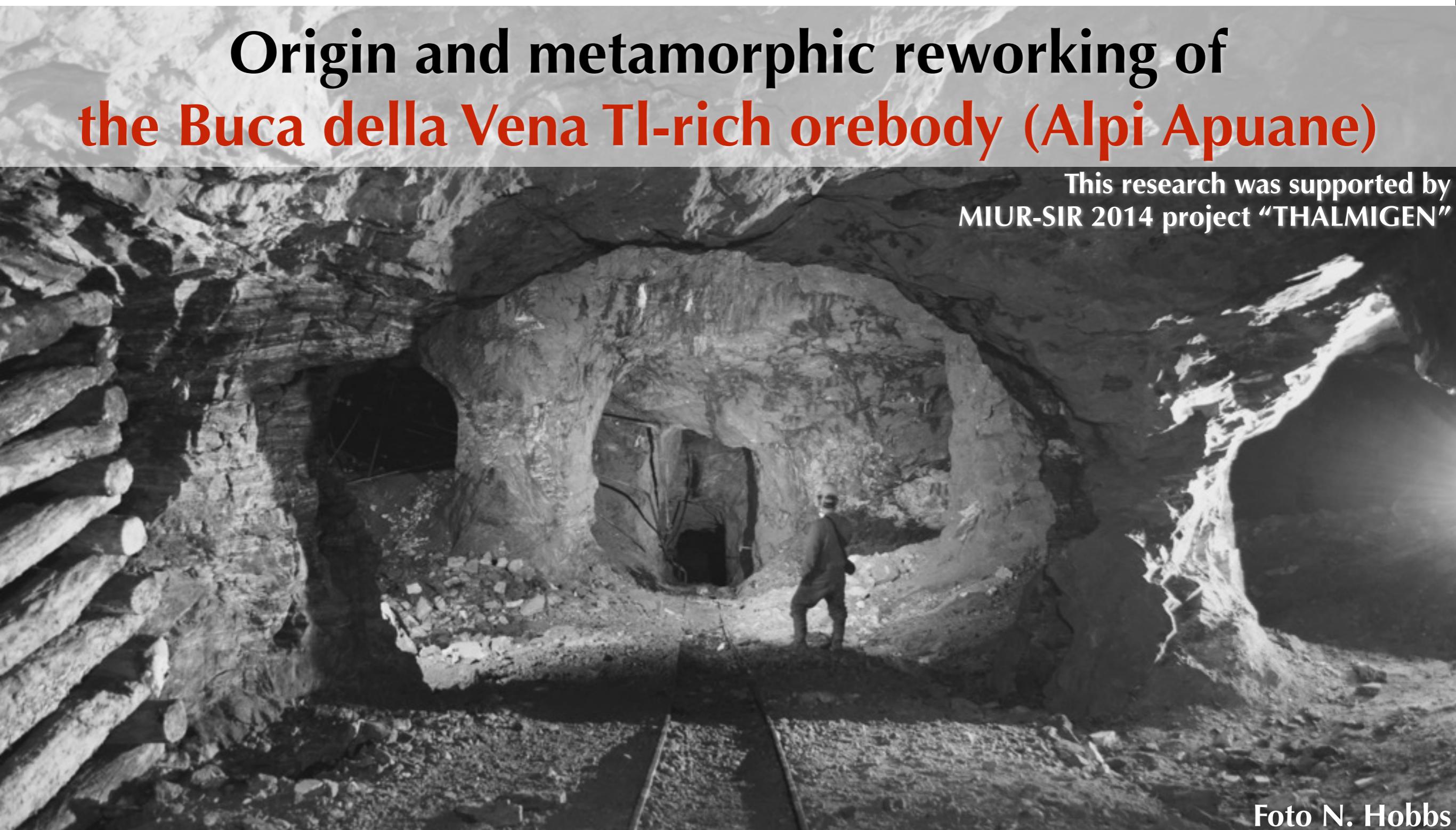


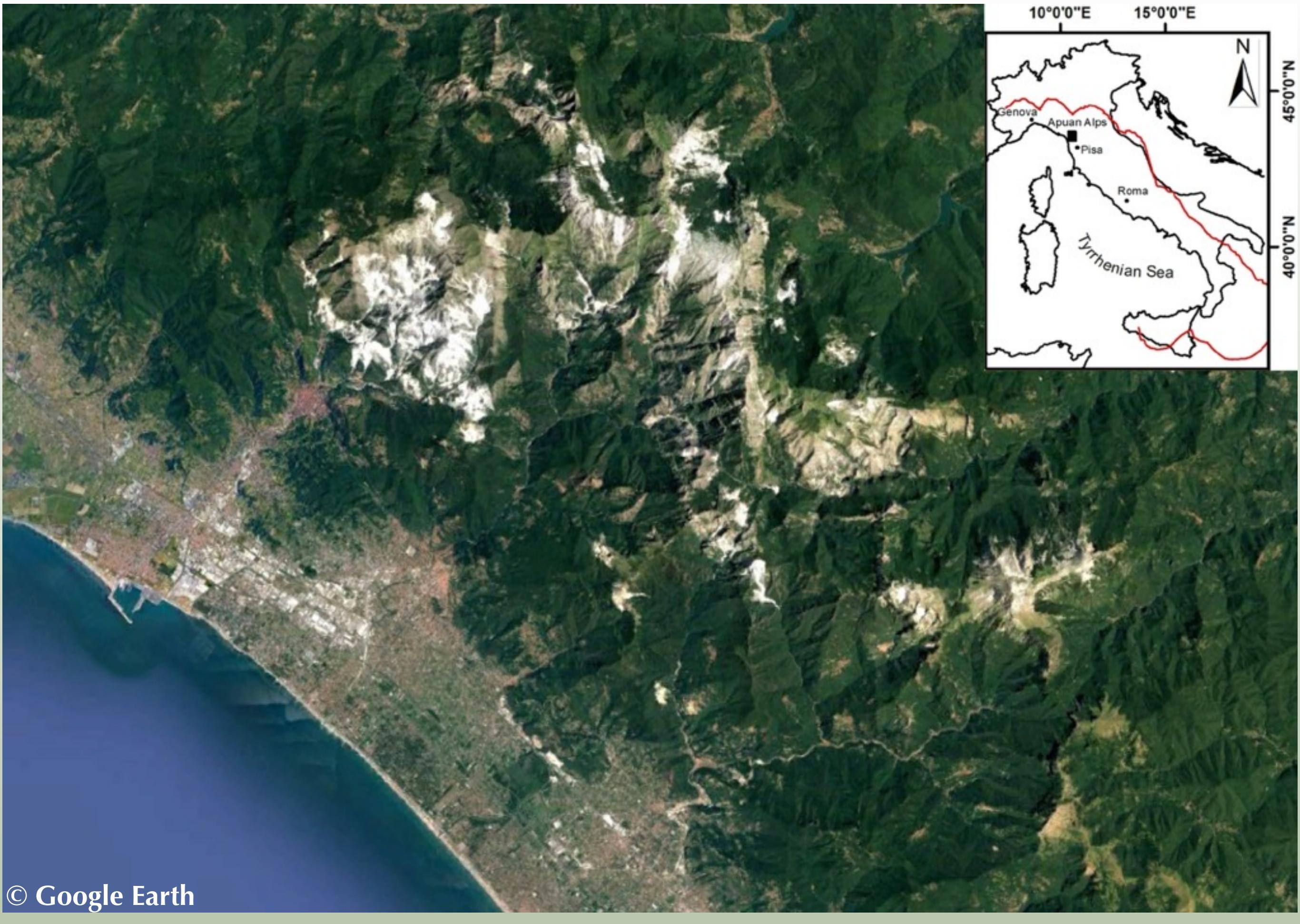
Foto N. Hobbs

Simone Vezzoni - [vezzoni@dst.unipi.it](mailto:vezzoni@dst.unipi.it)  
D. Pieruccioni, A. Dini, G. Molli, C. Biagioni



DIPARTIMENTO DI SCIENZE DELLA TERRA  
UNIVERSITÀ DI PISA

# Alpi Apuane



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Buca della Vena

# Buca della Vena



**Main features (pre-2007)**

**Size:**

**180000-300000 t**

**Mineralogy:**

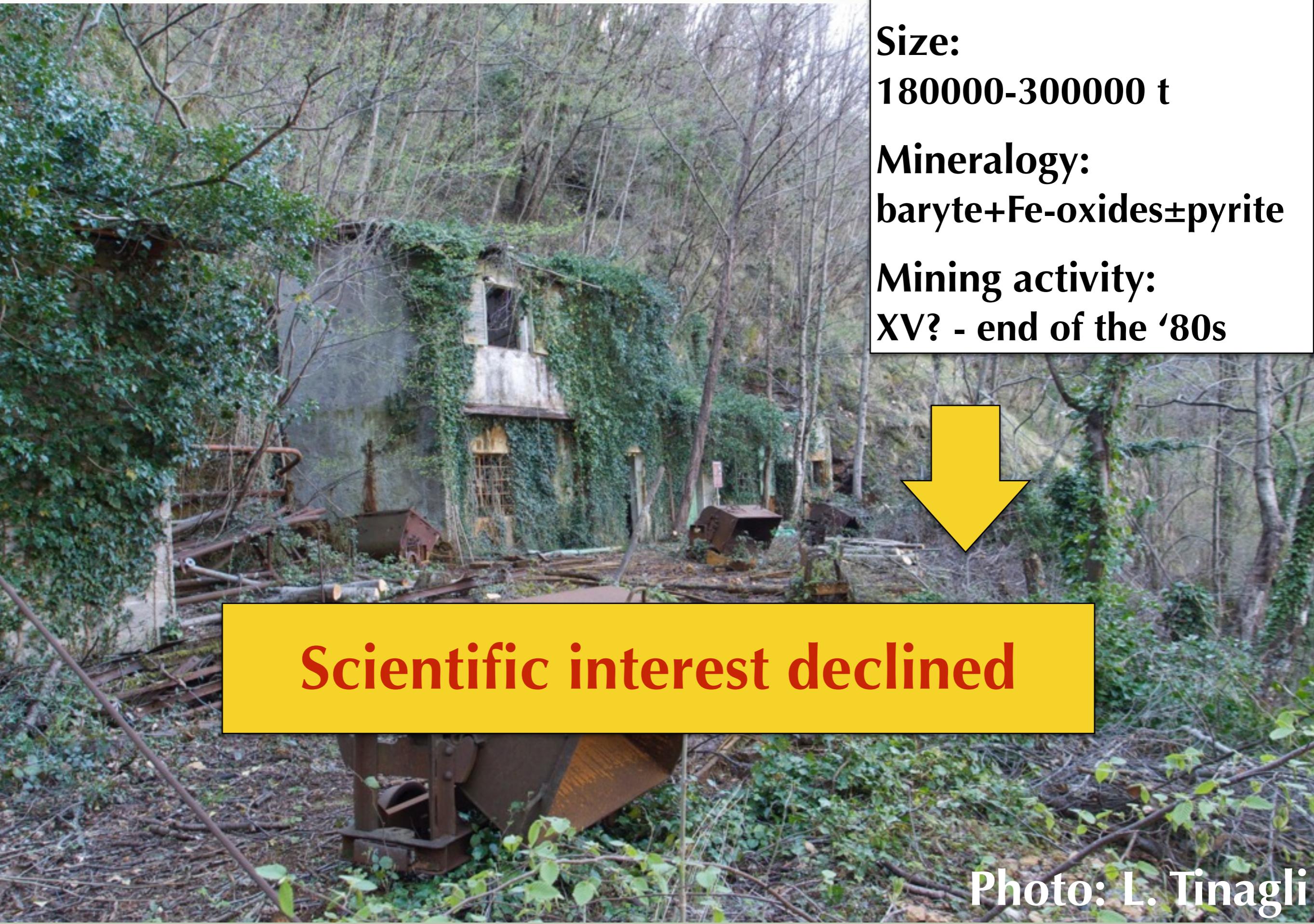
**baryte+Fe-oxides±pyrite**

**Mining activity:**

**XV? - end of the '80s**

**Photo: L. Tinagli**

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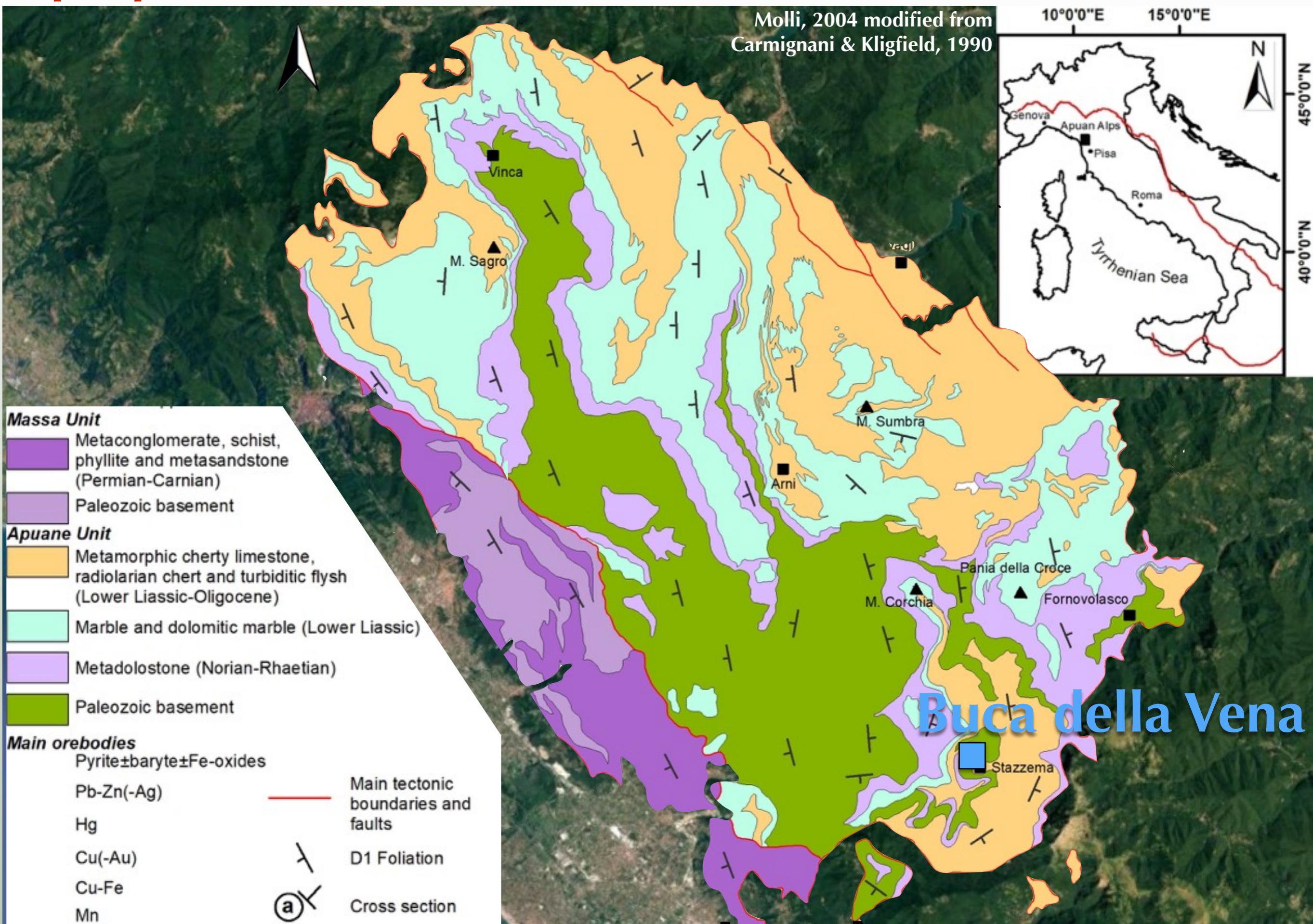
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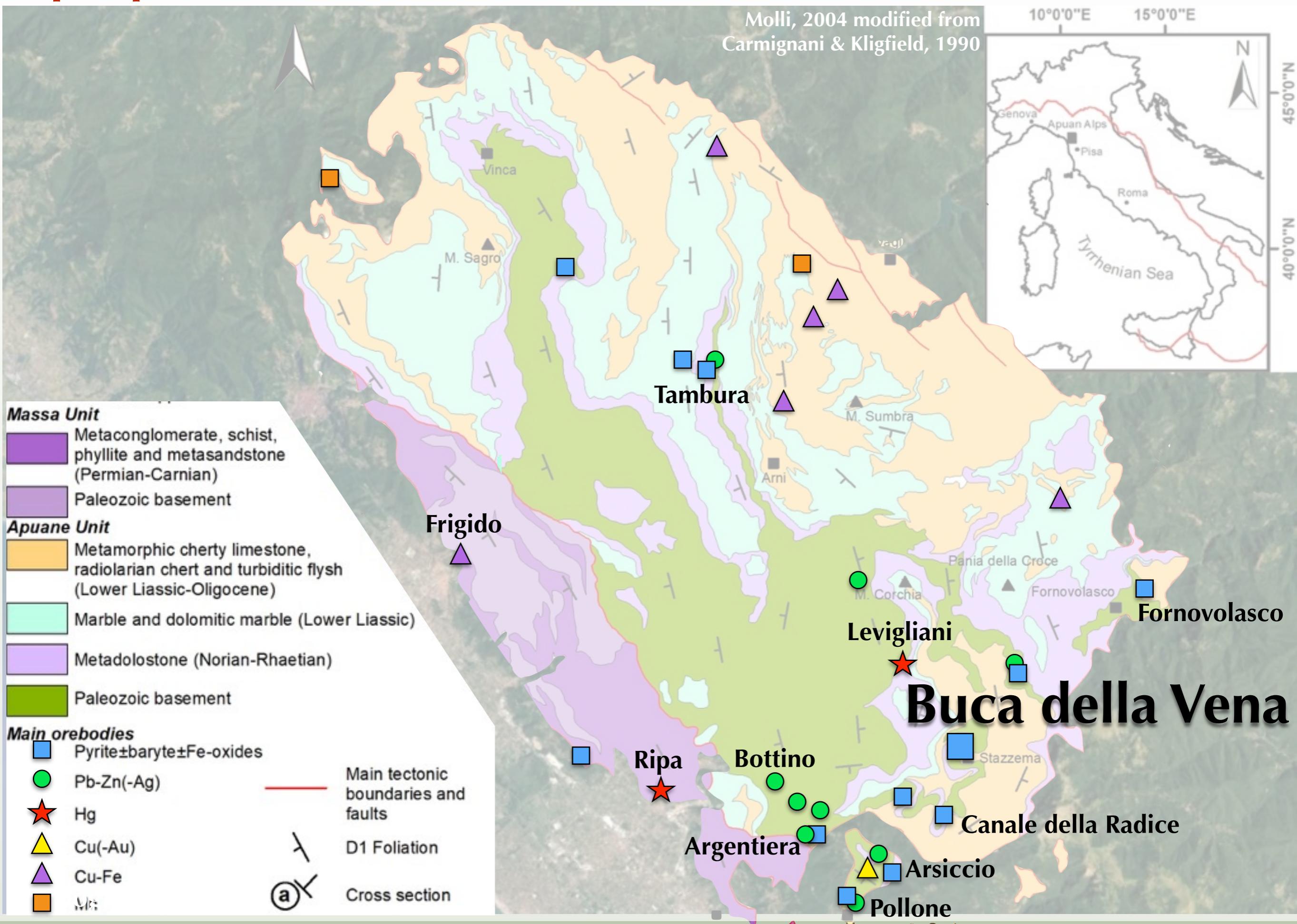
**Scientific interest declined**

**Photo: L. Tinagli**

# Alpi Apuane ores



# Alpi Apuane ores





Quartz, "Il Bimbo"; 21x10 cm

Photo: A. Dini

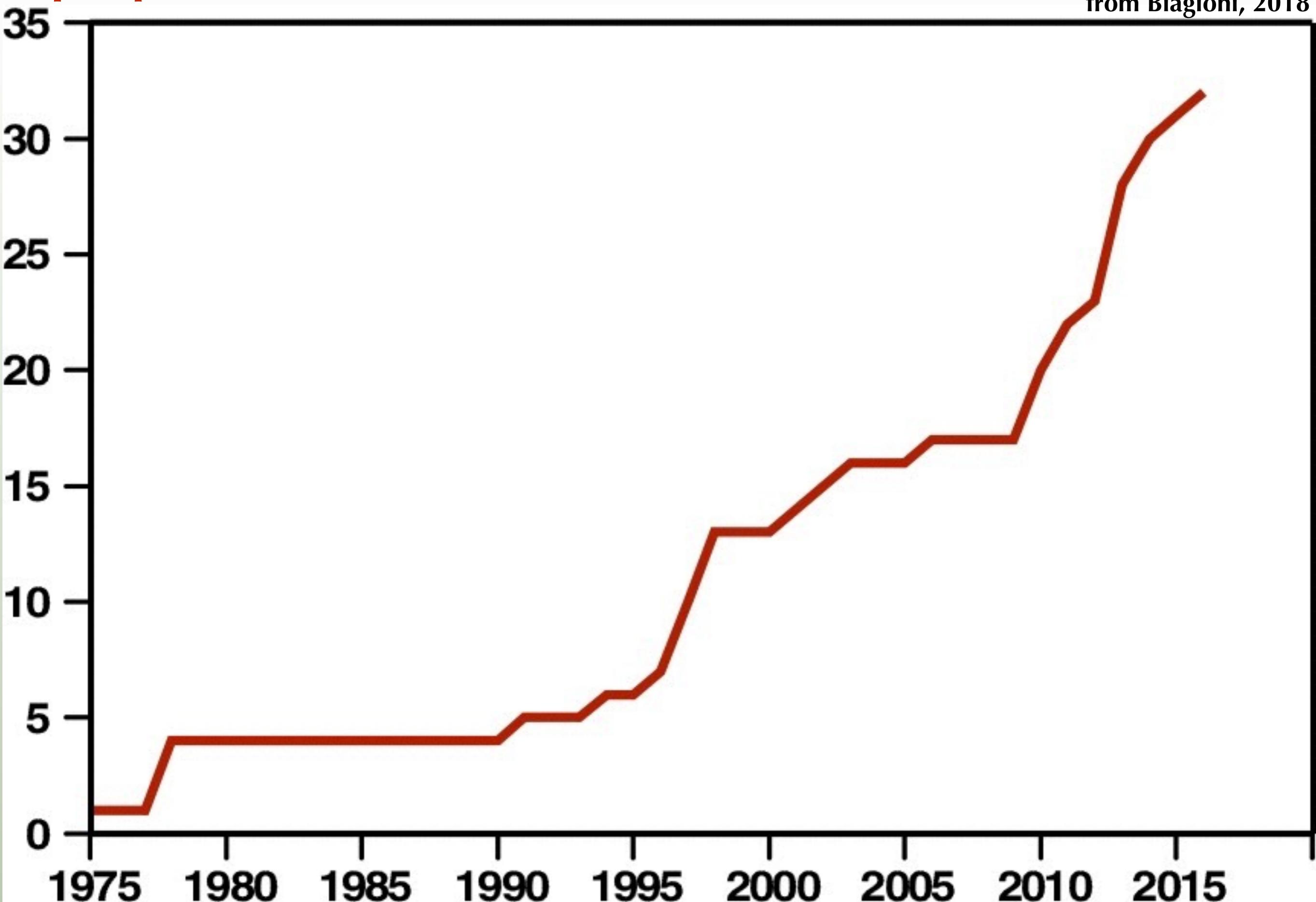


Boulangerite ( $\text{Pb}_5\text{Sb}_4\text{S}_{11}$ ), ~25x15 cm

Photo: M. Lorenzoni

# Alpi Apuane new minerals

from Biagioni, 2018



# Alpi Apuane new minerals

from Biagioni, 2018



*American Mineralogist, Volume 64, pages 1230-1234, 1979*

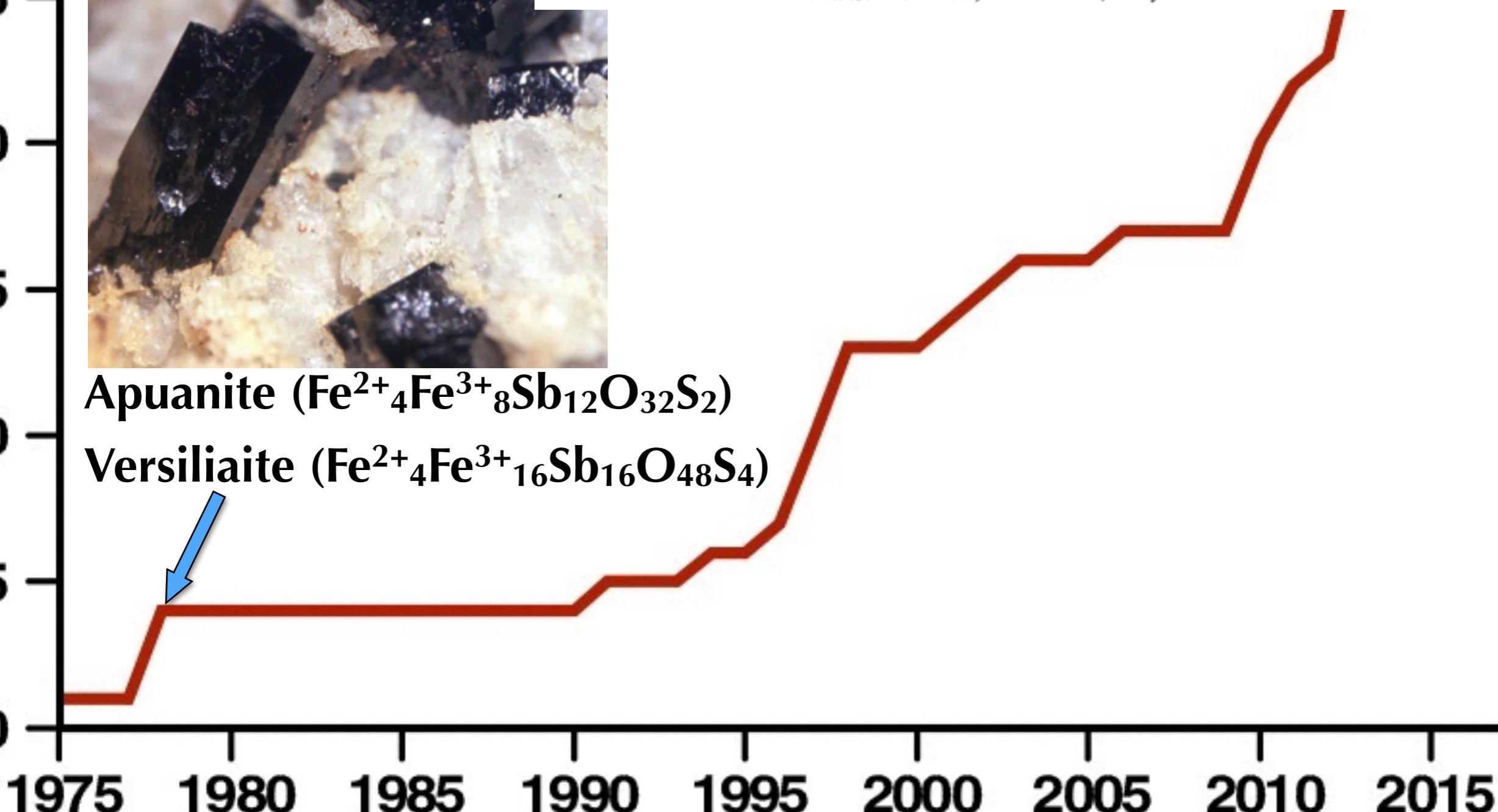
Versiliaite and apuanite, two new minerals from the Apuan Alps, Italy

MARCELLO MELLINI, STEFANO MERLINO AND PAOLO ORLANDI

*Istituto di Mineralogia e Petrografia dell'Università di Pisa  
C.N.R., Centro di Studio per la Geologia Strutturale e Dinamica dell'Appennino  
Via S. Maria 53, 56100 Pisa, Italy*

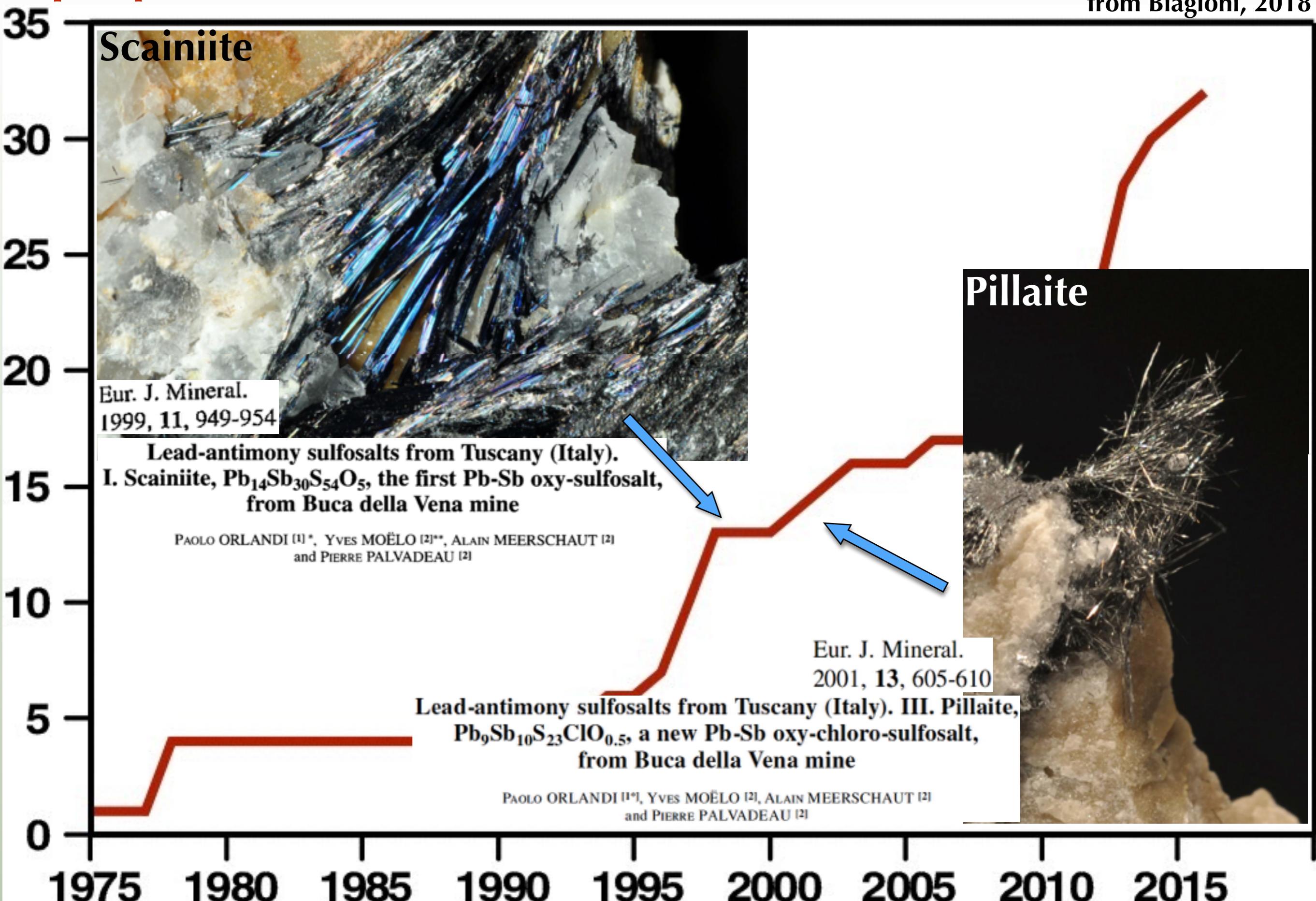
Apuanite ( $\text{Fe}^{2+}_4\text{Fe}^{3+}_8\text{Sb}_{12}\text{O}_{32}\text{S}_2$ )

Versiliaite ( $\text{Fe}^{2+}_4\text{Fe}^{3+}_{16}\text{Sb}_{16}\text{O}_{48}\text{S}_4$ )



# Alpi Apuane new minerals

from Biagioni, 2018



# Alpi Apuane new minerals

from Biagioni, 2018

35

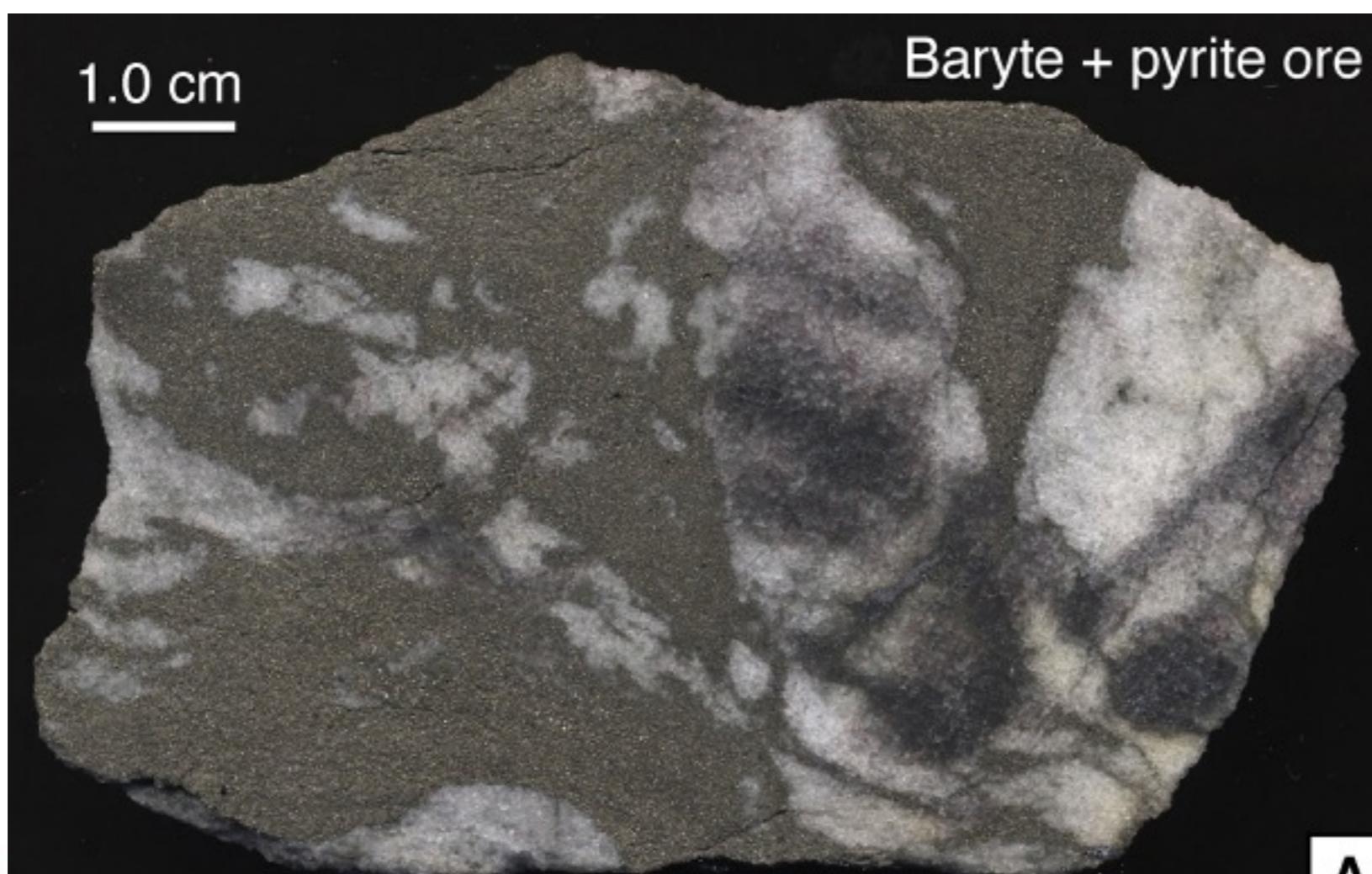
*Mineralogical Magazine, February 2014, Vol. 78(1), pp. 101–117*

Mercury-arsenic sulfosalts from the Apuan Alps (Tuscany, Italy). II. Arsiccioite,  $\text{AgHg}_2\text{TiAs}_2\text{S}_6$ , a new mineral from the Monte Arsiccio mine: occurrence, crystal structure and crystal chemistry of the routhierite isotypic series

25

C. BIAGIONI<sup>1,\*</sup>, E. BONACCORSI<sup>1</sup>, Y. MOËLO<sup>2</sup>, P. ORLANDI<sup>1,3</sup>, L. BINDI<sup>4</sup>, M. D'ORAZIO<sup>1</sup> AND S. VEZZONI<sup>1</sup>

20



15

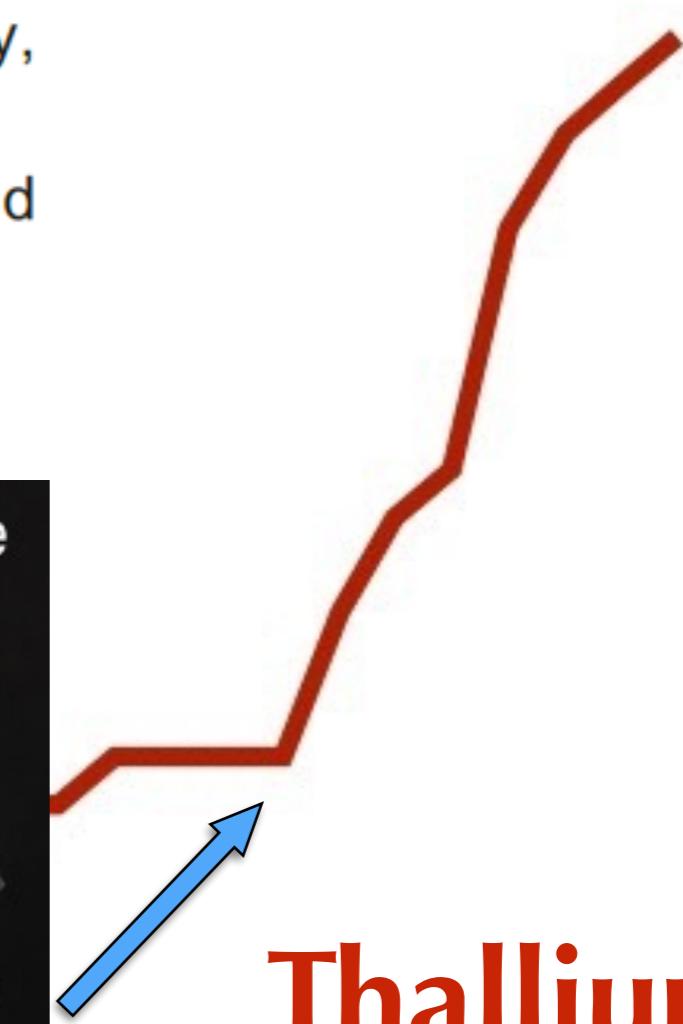
10

5

0

1975 1980 1985 1990 1995 2000 2005 2010 2015

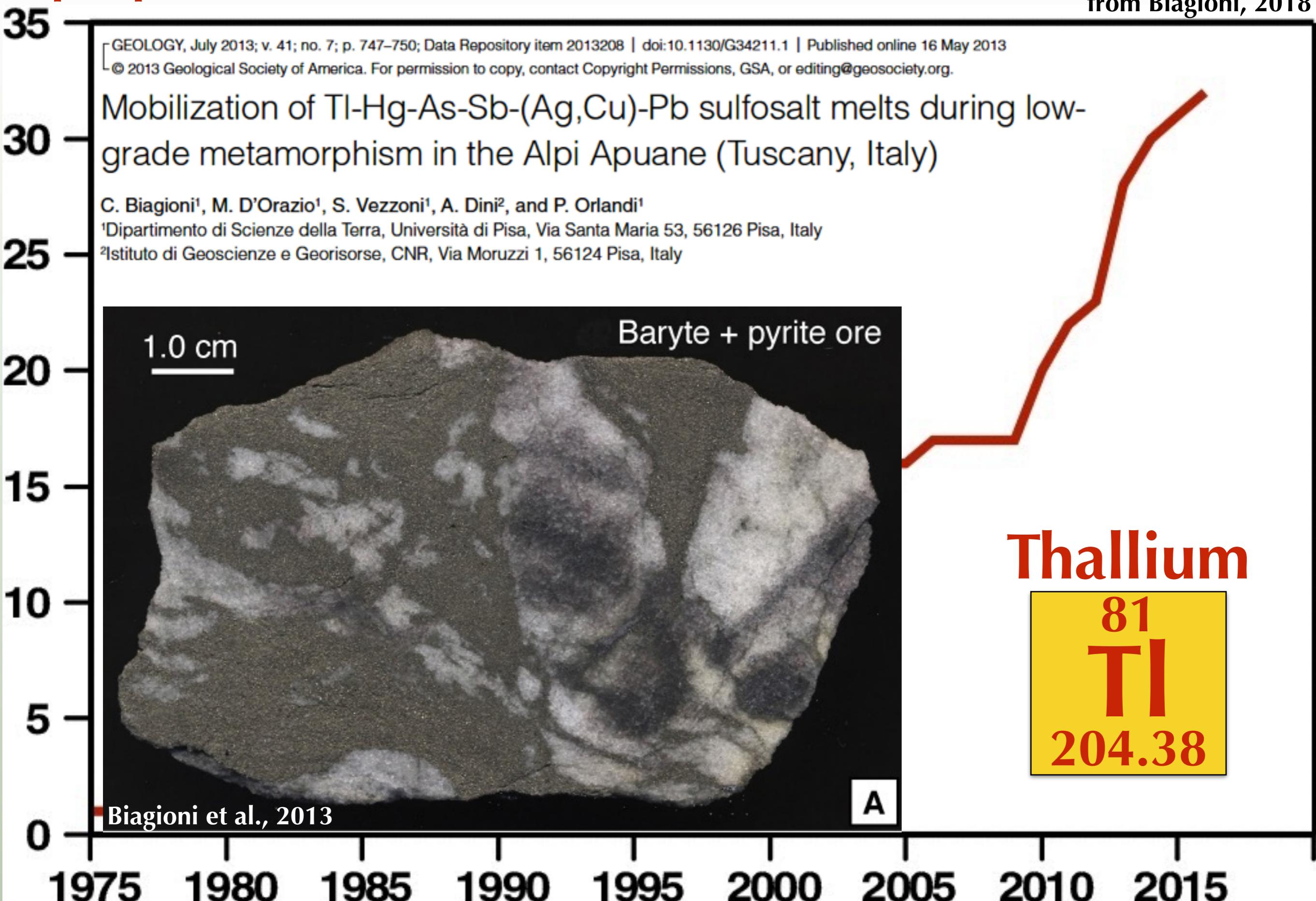
Biagioni et al., 2013



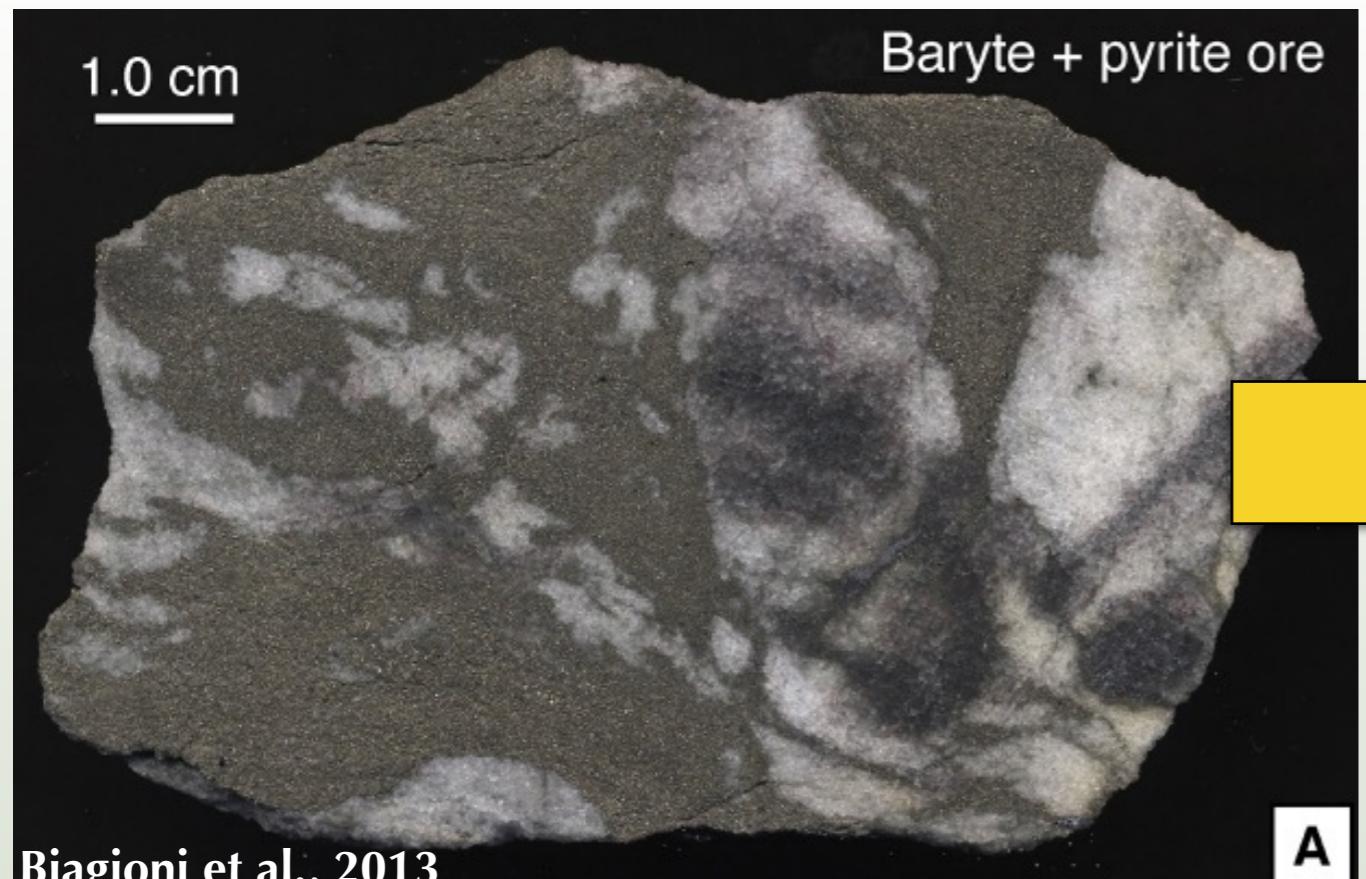
Thallium  
81  
Tl  
204.38

# Alpi Apuane new minerals

from Biagioni, 2018



# Alpi Apuane new discoveries



Biagioni et al., 2013

A

VALDICASTELLO LA SOSTANZA E' ALTAMENTE TOSSICA  
E' scoppiato l'allarme "tallio"  
Vietato usare acqua dei rubinetti

La Nazione, 4-10-2014

environment

Photo: S. Vezzoni

Mine Water Environ

DOI 10.1007/s10230-017-0485-x

**Thallium and Other Potentially Toxic Elements in the Baccatoio Stream Catchment (Northern Tuscany, Italy) Receiving Drainages from Abandoned Mines**

Martina Perotti<sup>1</sup> · Riccardo Petrini<sup>1</sup> · Massimo D'Orazio<sup>1</sup> · Lisa Ghezzi<sup>1</sup> · Roberto Giannecchini<sup>1</sup> · Simone Vezzoni<sup>1</sup>

**Science of the Total Environment 548–549 (2016) 33–42**

Human exposure to thallium through tap water: A study from Valdicastello Carducci and Pietrasanta (northern Tuscany, Italy)

Beatrice Campanella <sup>a,b</sup>, Massimo Onor <sup>a</sup>, Alessandro D'Ulivo <sup>a</sup>, Roberto Giannecchini <sup>c</sup>, Massimo D'Orazio <sup>c</sup>, Riccardo Petrini <sup>c</sup>, Emilia Bramanti <sup>a,\*</sup>

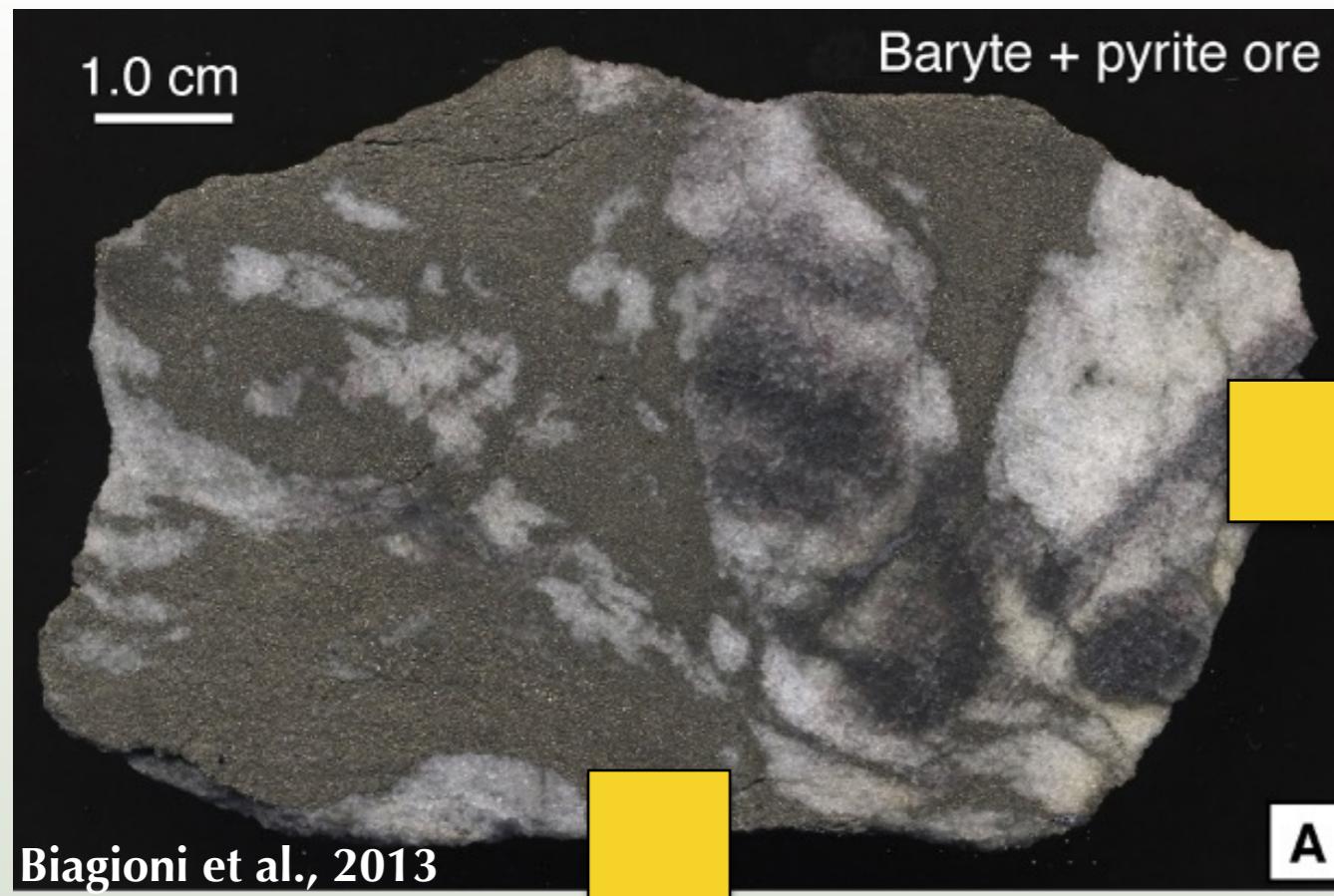
**Journal of Geochemical Exploration 197 (2019) 84–92**

Groundwater and potentially toxic elements in a dismissed mining area: Thallium contamination of drinking spring water in the Apuan Alps (Tuscany, Italy)

Lisa Ghezzi<sup>a,\*</sup>, Massimo D'Orazio<sup>a</sup>, Marco Doveri<sup>b</sup>, Matteo Lelli<sup>b</sup>, Riccardo Petrini<sup>a</sup>, Roberto Giannecchini<sup>a</sup>

...

# Alpi Apuane new discoveries



As, Sb, Hg, Tl, Pb, Bi...

Miner Deposita (2017) 52:687–707  
DOI 10.1007/s00126-016-0697-1

Thallium-rich pyrite ores from the Apuan Alps, Tuscany, Italy:  
constraints for their origin and environmental concerns

Massimo D'Orazio<sup>1</sup> · Cristian Biagioni<sup>1</sup> · Andrea Dini<sup>2</sup> · Simone Vezzoni<sup>1</sup>

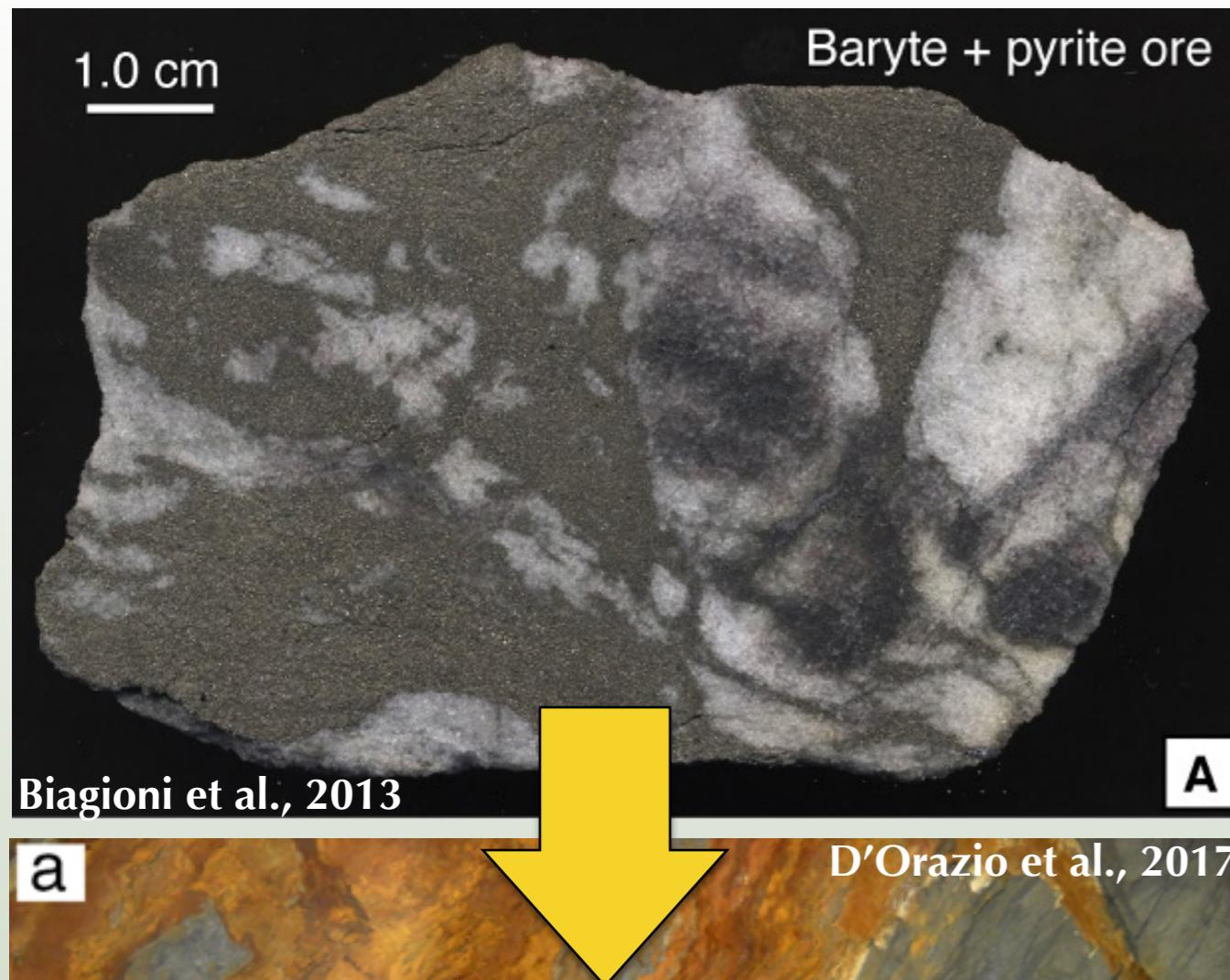
Ore Geology Reviews 102 (2018) 59–105

Textural and trace element evolution of pyrite during greenschist facies  
metamorphic recrystallization in the southern Apuan Alps (Tuscany, Italy):  
Influence on the formation of Tl-rich sulfosalt melt

Luke L. George<sup>a</sup>, Cristian Biagioni<sup>a,\*</sup>, Massimo D'Orazio<sup>a</sup>, Nigel J. Cook<sup>b</sup>

ore geochemistry

# Alpi Apuane new discoveries



# Permian magmatism

JOURNAL OF MAPS

2018, VOL. 14, NO. 2, 357–367

Geology and tectonic setting of the Fornovolasco area, Alpi Apuane (Tuscany, Italy)

Diego Pieruccioni , Yuri Galanti , Cristian Biagioni and Giancarlo Molli

Lithos 318–319 (2018) 104–123

Evidence of Permian magmatism in the Alpi Apuane metamorphic complex (Northern Apennines, Italy): New hints for the geological evolution of the basement of the Adria plate

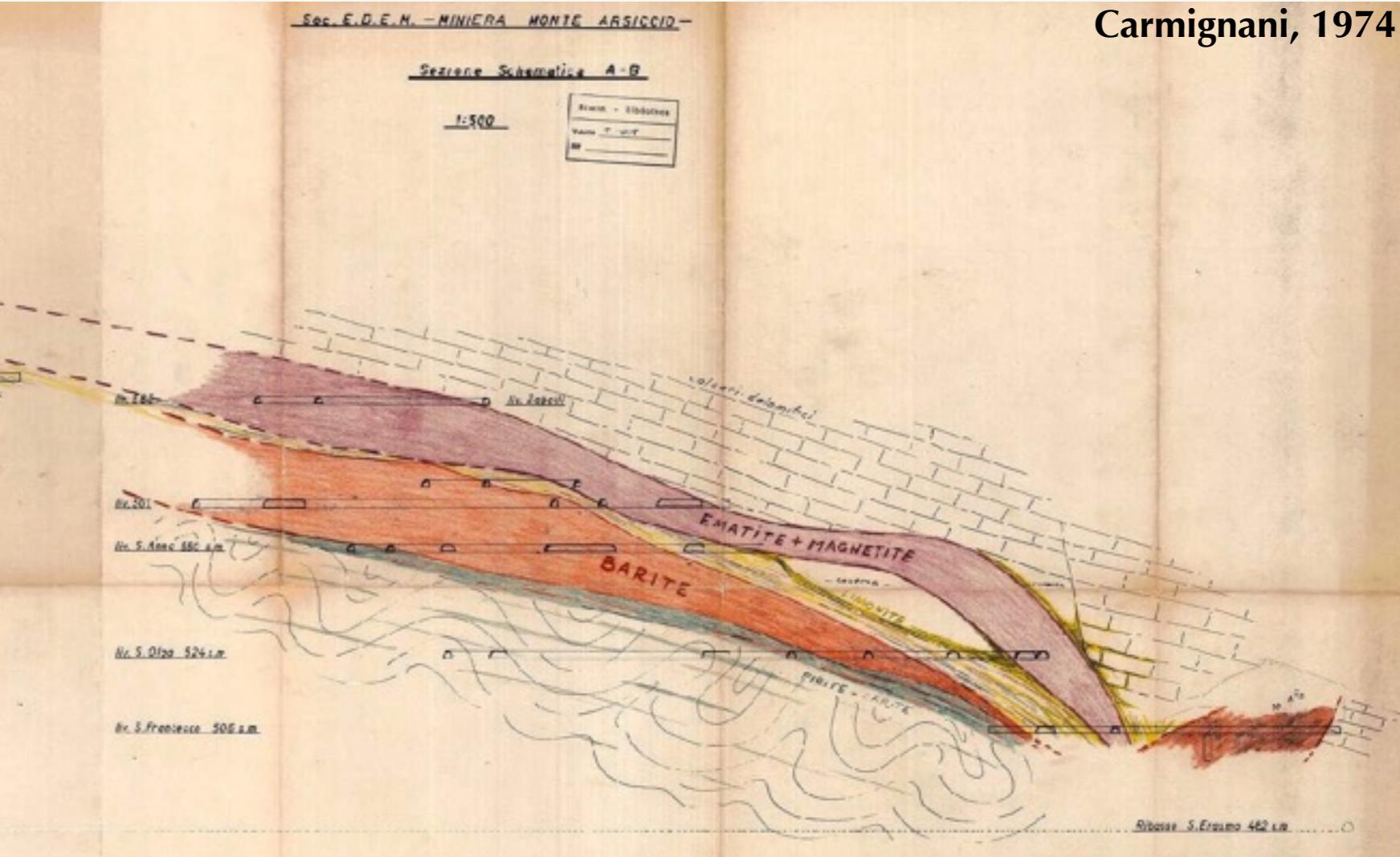
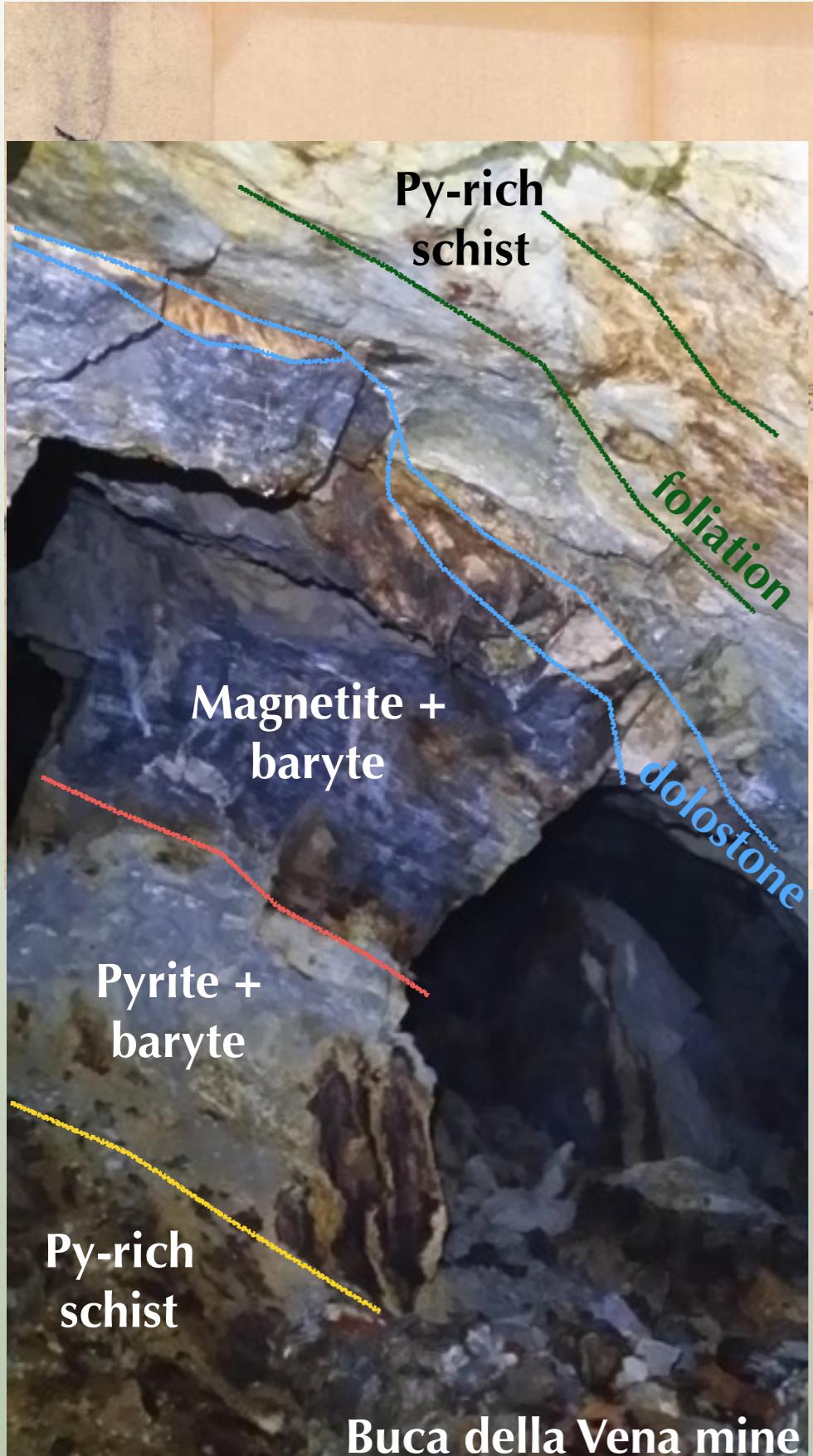
Simone Vezzoni <sup>a</sup>, Cristian Biagioni <sup>a,\*</sup>, Massimo D'Orazio <sup>a</sup>, Diego Pieruccioni <sup>a</sup>, Yuri Galanti <sup>a</sup>, Maurizio Petrelli <sup>b,c</sup>, Giancarlo Molli <sup>a</sup>

Vezzoni et al., 2018



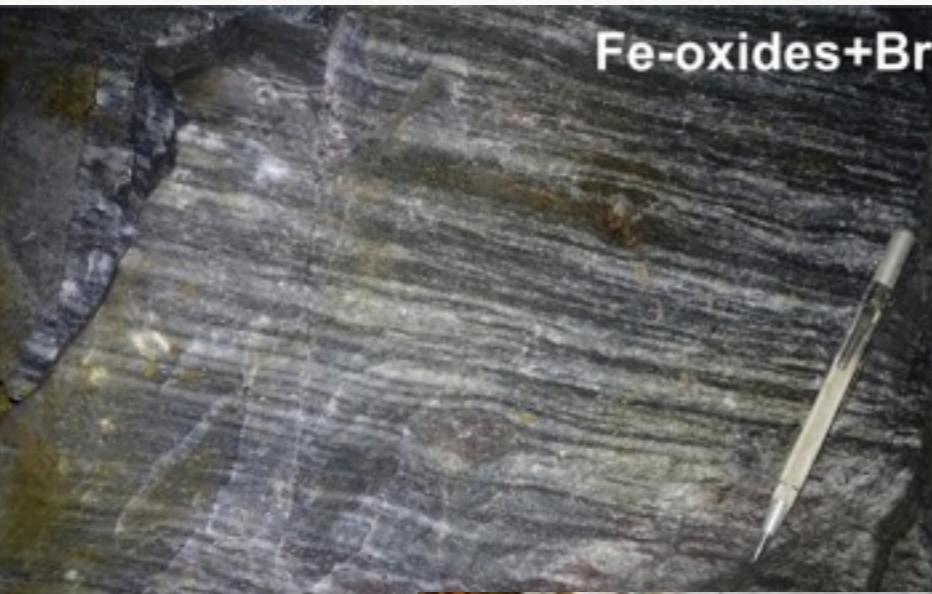
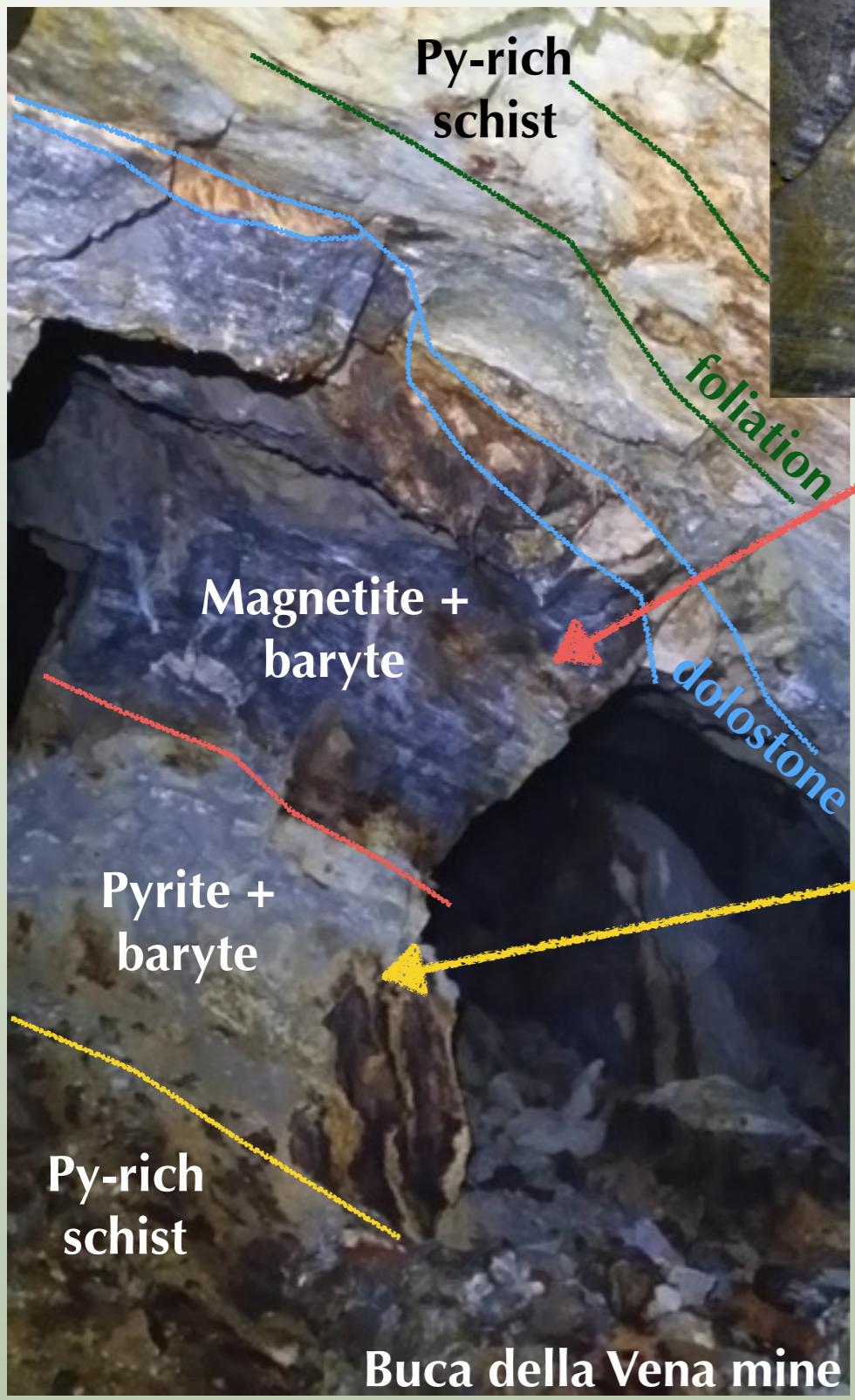
# Baryte, pyrite, and Fe-oxides orebodies

## Main features: 1. stratiform;



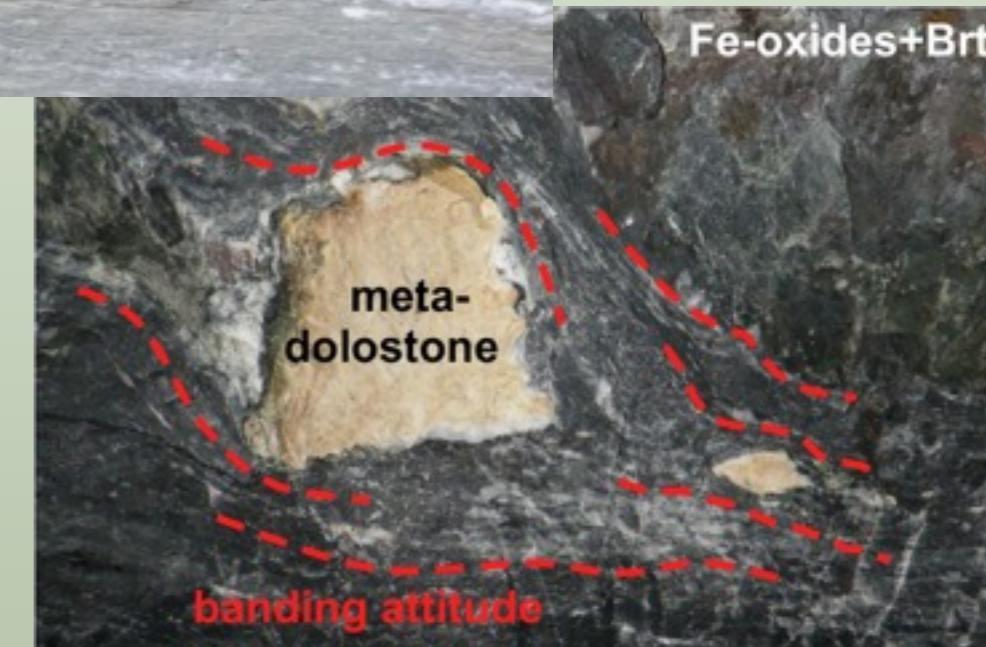
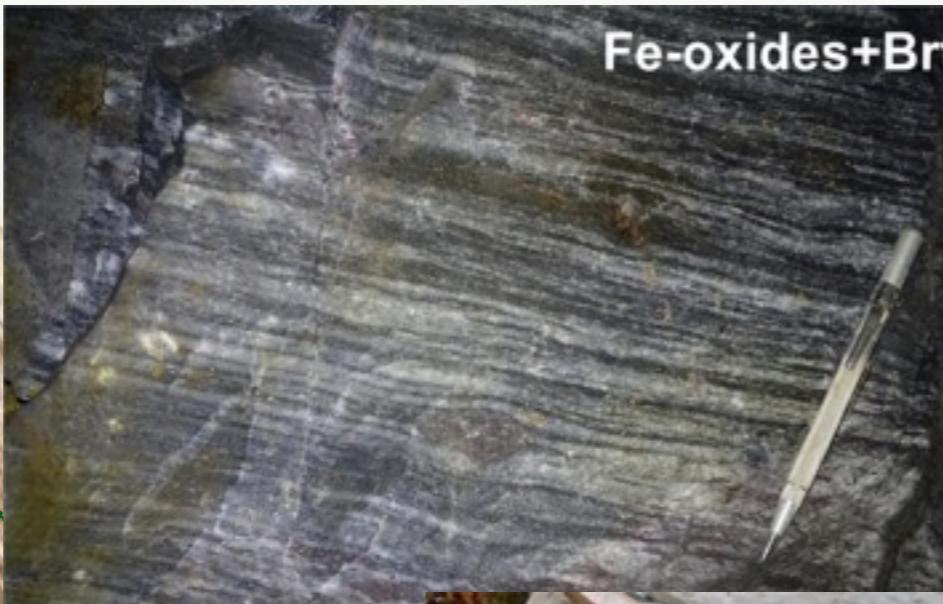
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# Baryte, pyrite, and Fe-oxides orebodies

Main features: 1. stratiform; 2. zoned; 3. with metacarbonate lenses.



# Baryte, pyrite, and Fe-oxides orebodies

## Genetic models:

### Metamorphic, epigenetic

e.g., Carmignani et al., 1972; 1975; 1976

- Origin:  
**Hydrothermal(-metasomatic)**  
related to the intrusion of an early-orogenic Apenninic plutonic body

- Age:  
**Miocene**

- Evidences:
  1. Ore bodies location;
  2. No lithostratigraphic control;
  3. Ore zoning (“hot point”).

### Pre-metamorphic, syngenetic

e.g., Cortecci et al., 1985; Ciarapica et al., 1985; Orberger et al., 1986; Benvenuti et al., 1986; Cortecci et al., 1992; Costagliola et al., 1998

- Origin:  
**Sedimentary(-hydrothermal?) proto-ore** partly remobilized during the metamorphism

- Age:  
**Silurian-Devonian or Middle-Upper Triassic**

- Evidences:
  1. Lithostratigraphic control;
  2. Ore bodies morphology;
  3. Ore texture;
  4. S, C e O isotopic composition.

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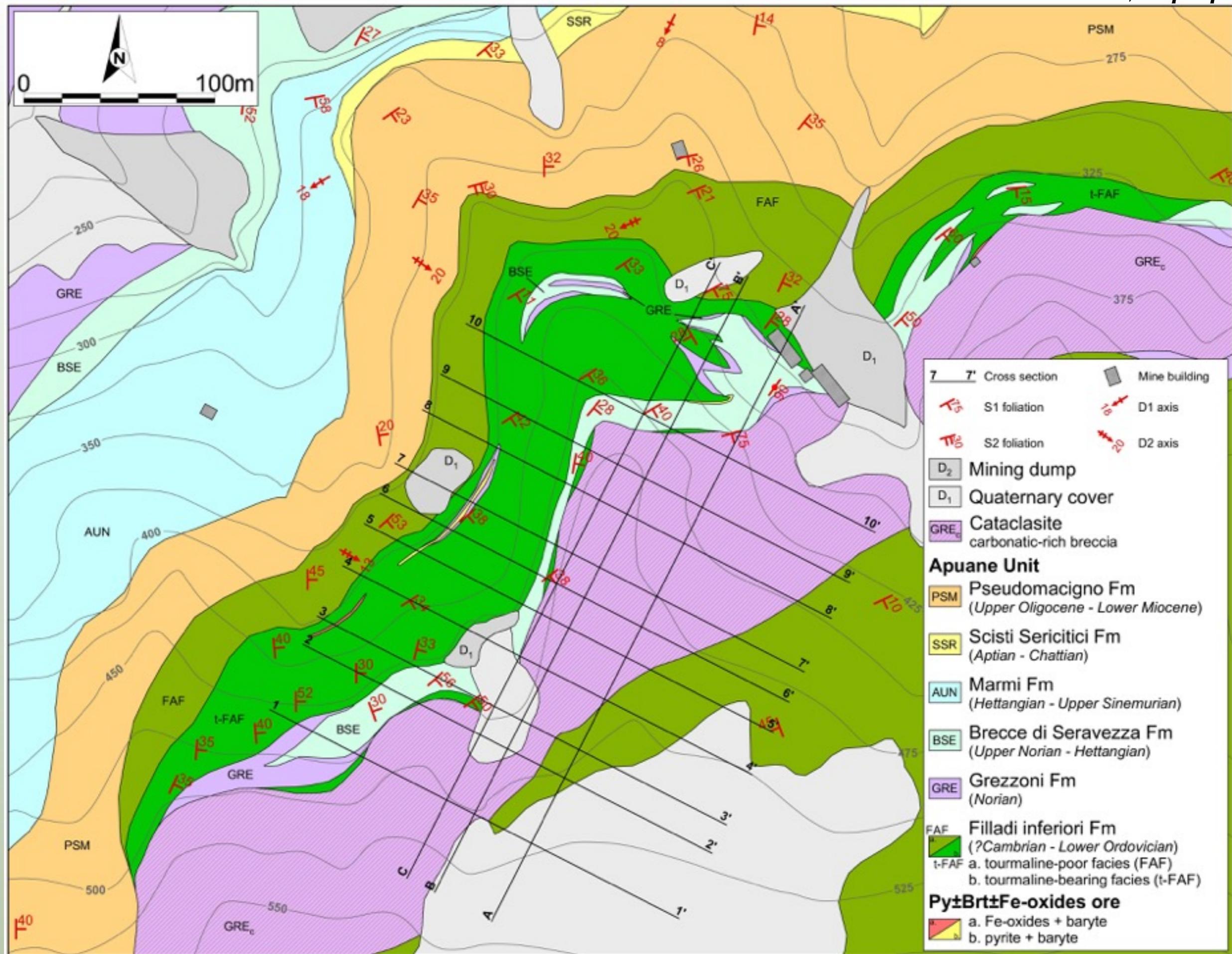
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# Buca della Vena geological map

Vezzoni et al., *in prep.*



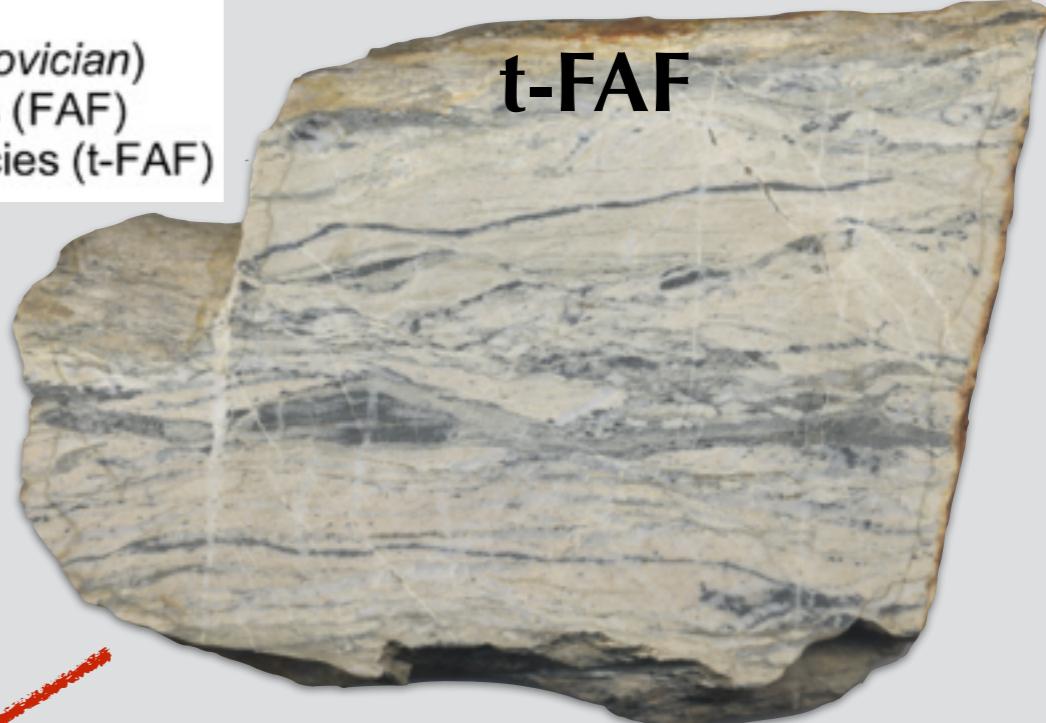
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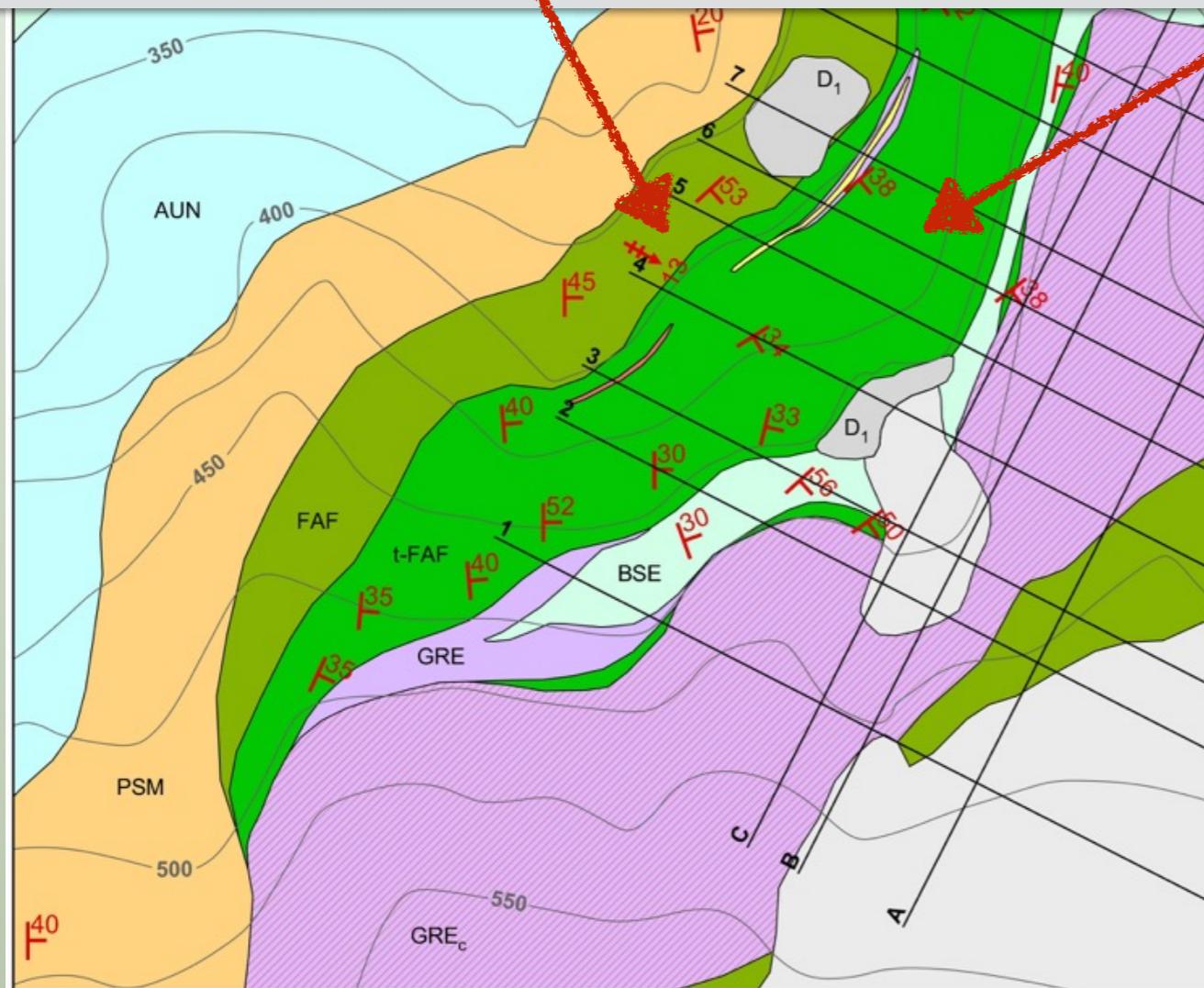
FAF



t-FAF



tourmalinized



Atti Soc. Tosc. Sci. Nat., Mem., Serie A, 125 (2018)  
pagg. 69-80, fig. 4; tab. 1; doi: 10.2424/ASTSN.M.2018.24

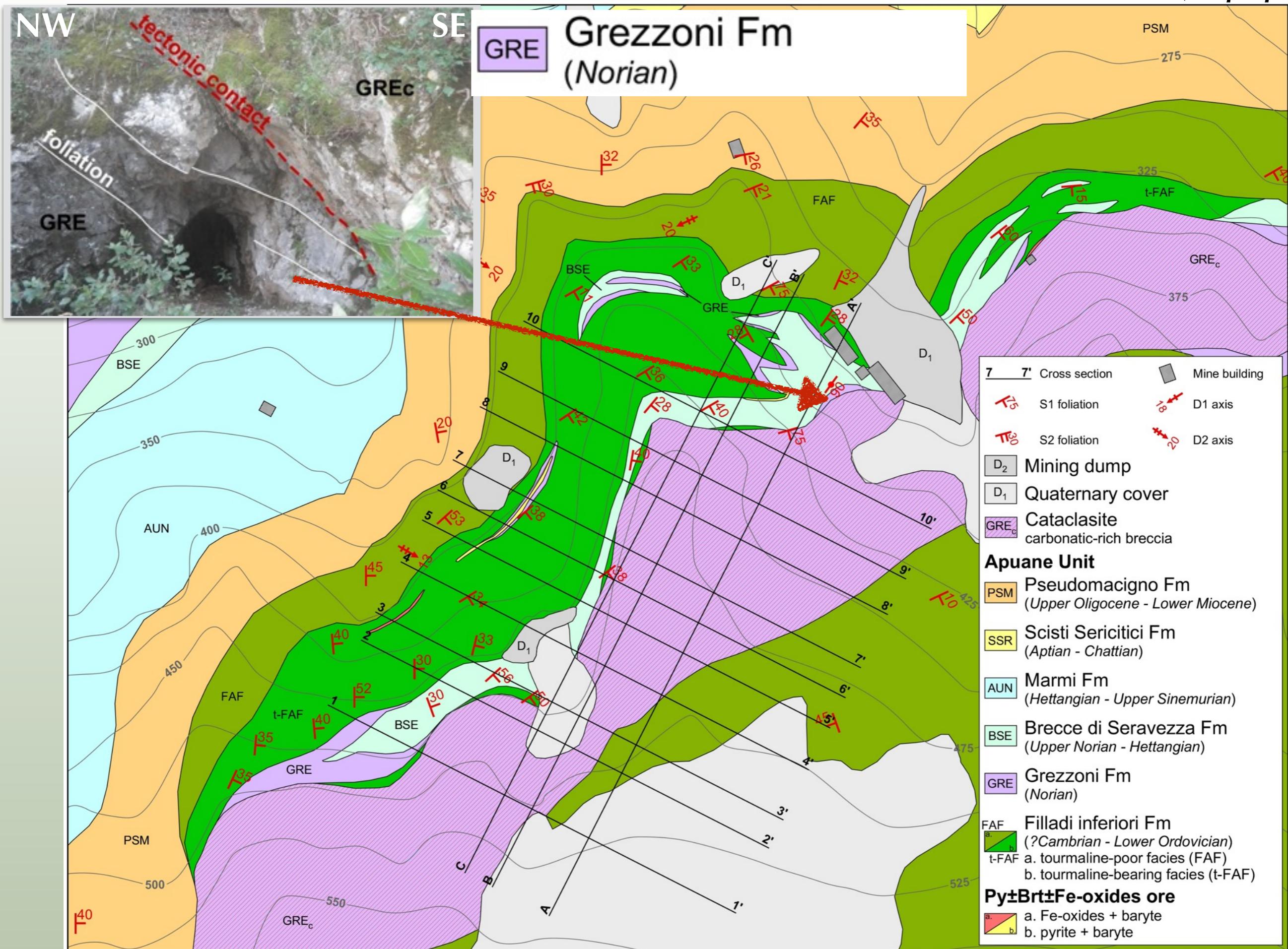
DIEGO PIERUCCIONI <sup>(1)</sup>, SIMONE VEZZONI <sup>(1)</sup>, MAURIZIO PETRELLI <sup>(2)(3)</sup>

A PETROGRAPHIC AND U-PB GEOCHRONOLOGICAL APPROACH  
TO THE RECONSTRUCTION OF THE PRE-ALPINE HISTORY  
OF ALPI APUANE (TUSCANY)

SSR	Scisti Sericitici Fm (Aptian - Chattian)
AUN	Marmi Fm (Hettangian - Upper Sinemurian)
BSE	Brecce di Seravezza Fm (Upper Norian - Hettangian)
GRE	Grezzonini Fm (Norian)
FAF	Filladi inferiore Fm a. tourmaline-poor facies (FAF) b. tourmaline-bearing facies (t-FAF)
Py±Brt±Fe-oxides ore	a. Fe-oxides + baryte b. pyrite + baryte

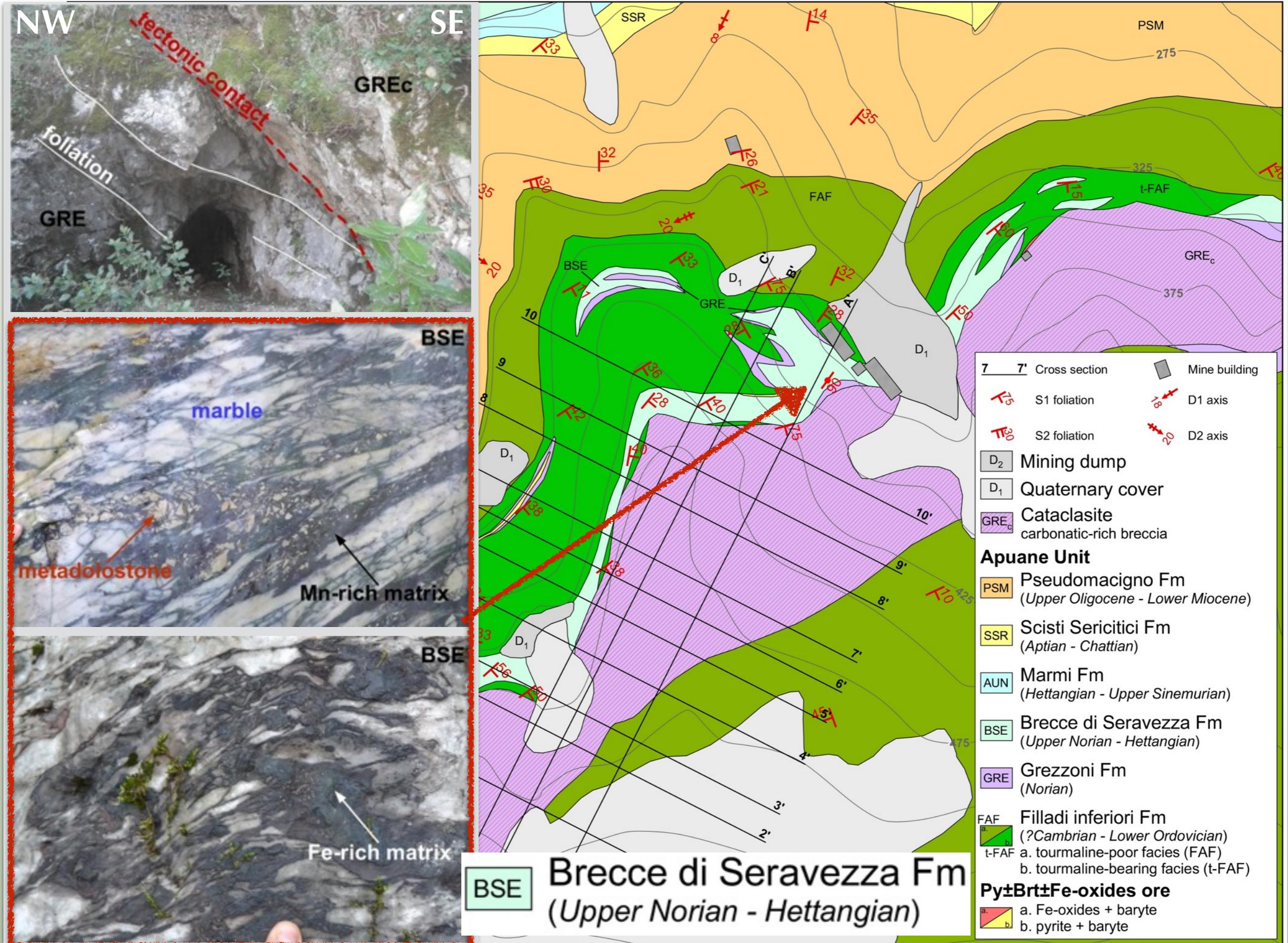
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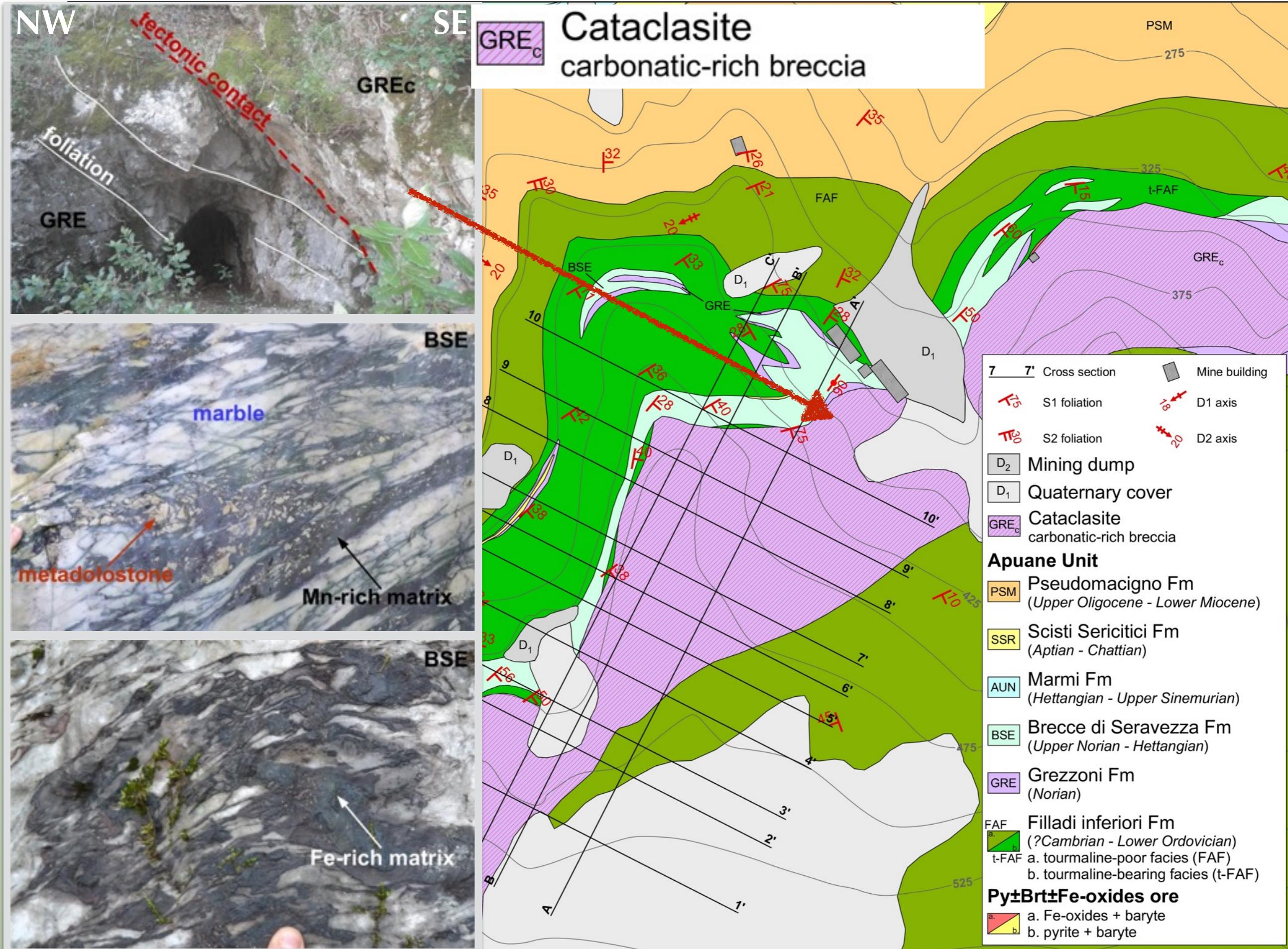
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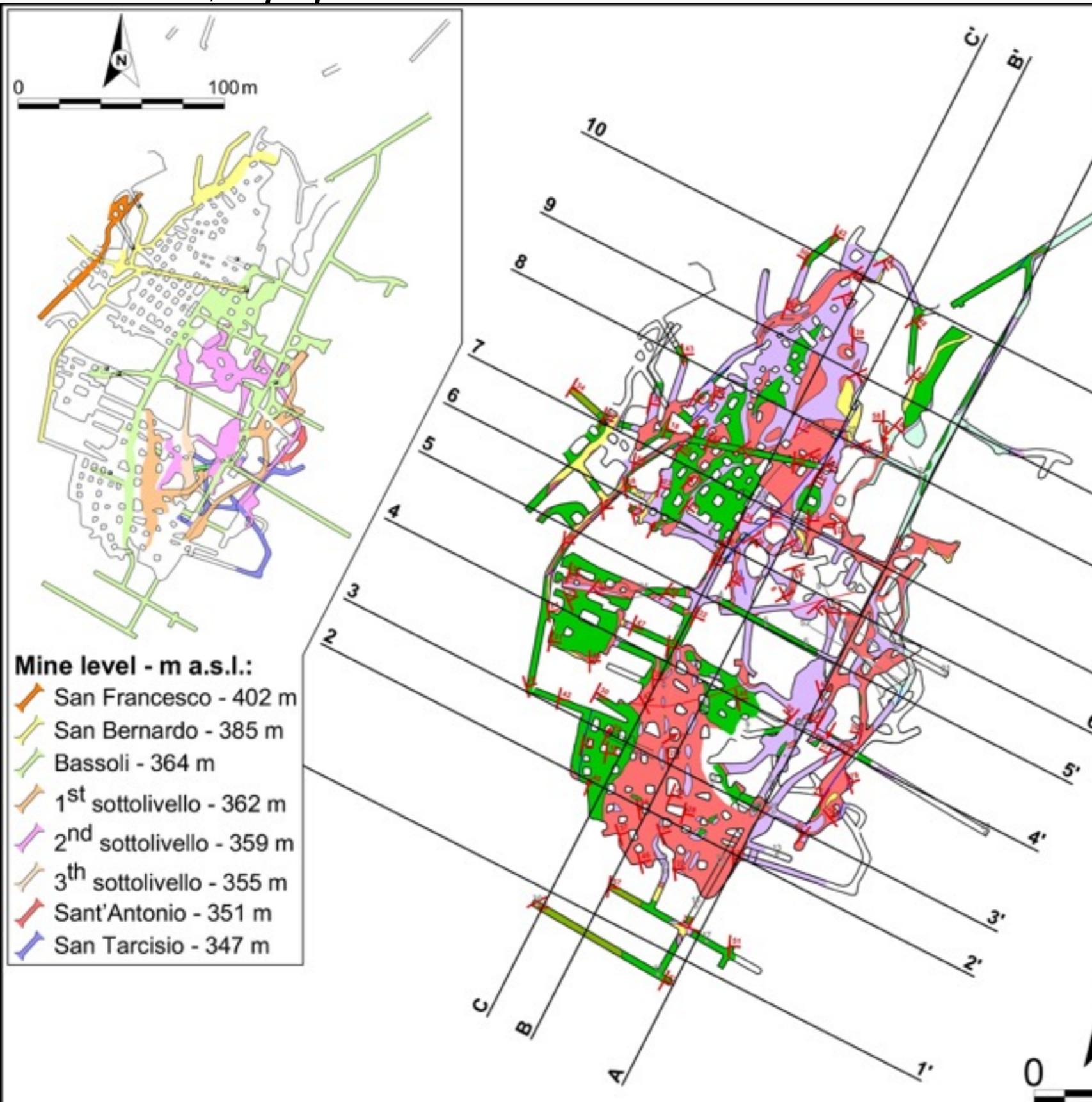
Vezzoni et al., *in prep.*



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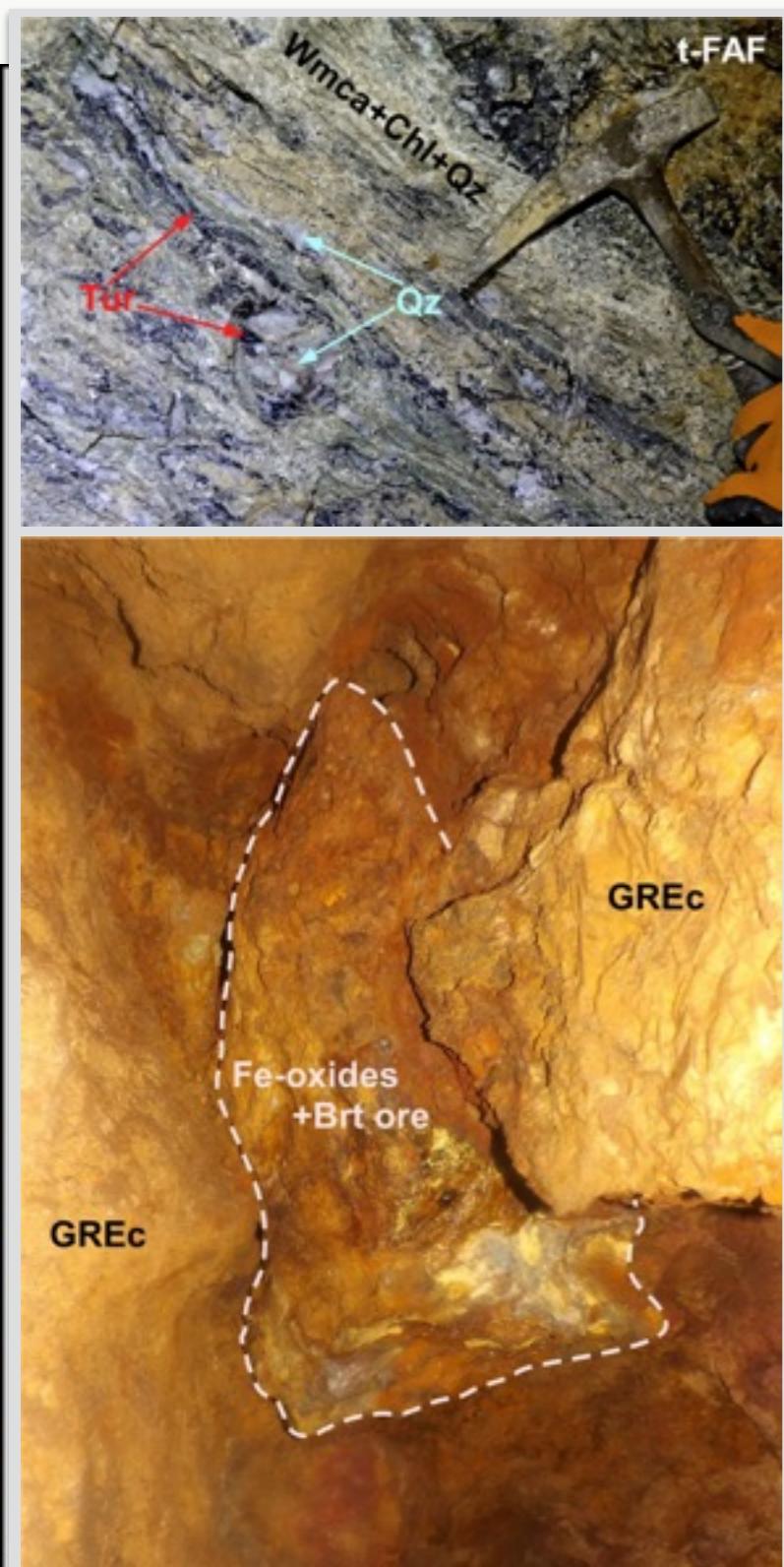
Fe-oxides+Brt

Vezzoni et al., *in prep.*



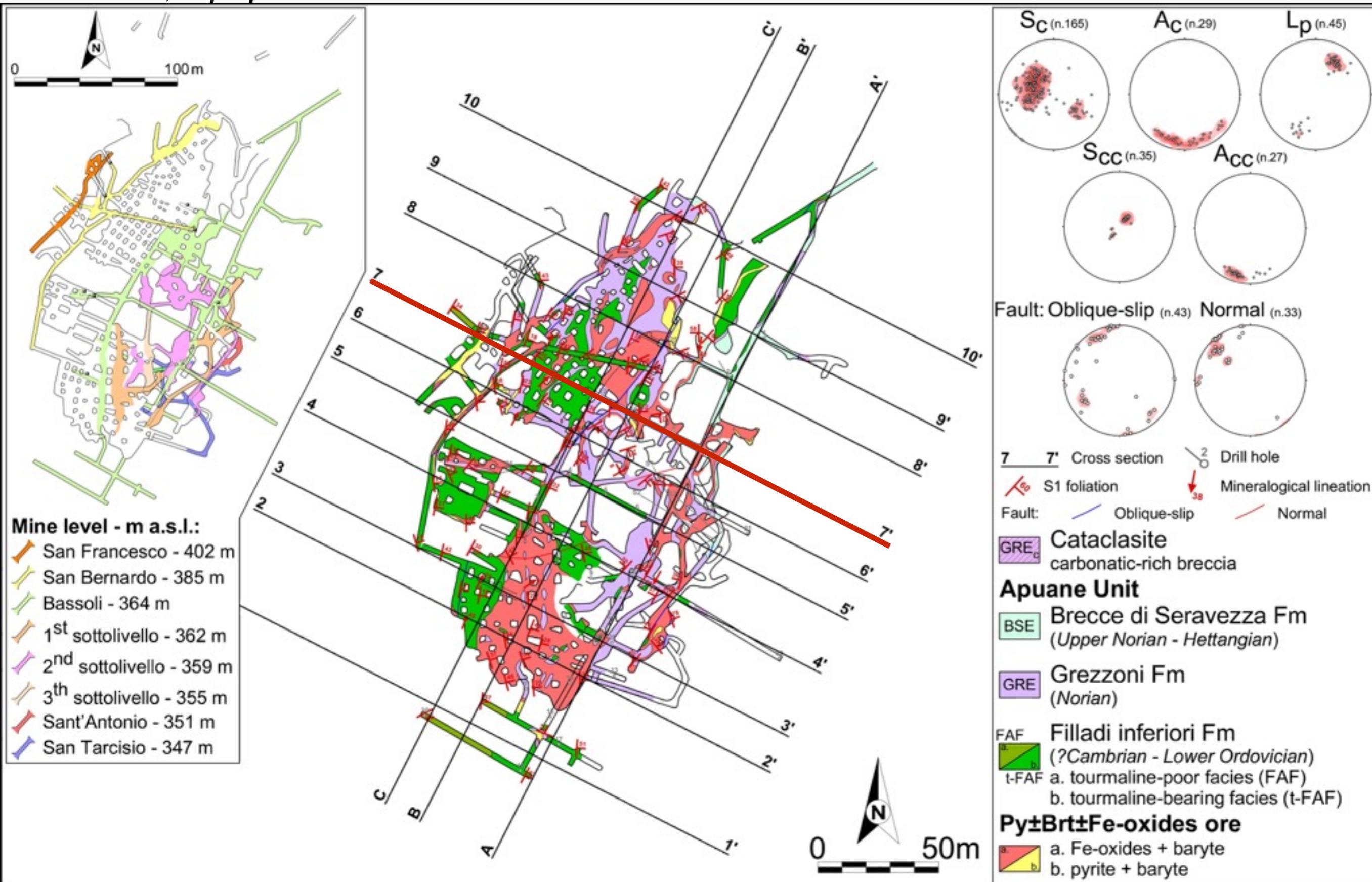
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Fe-oxides+Brt



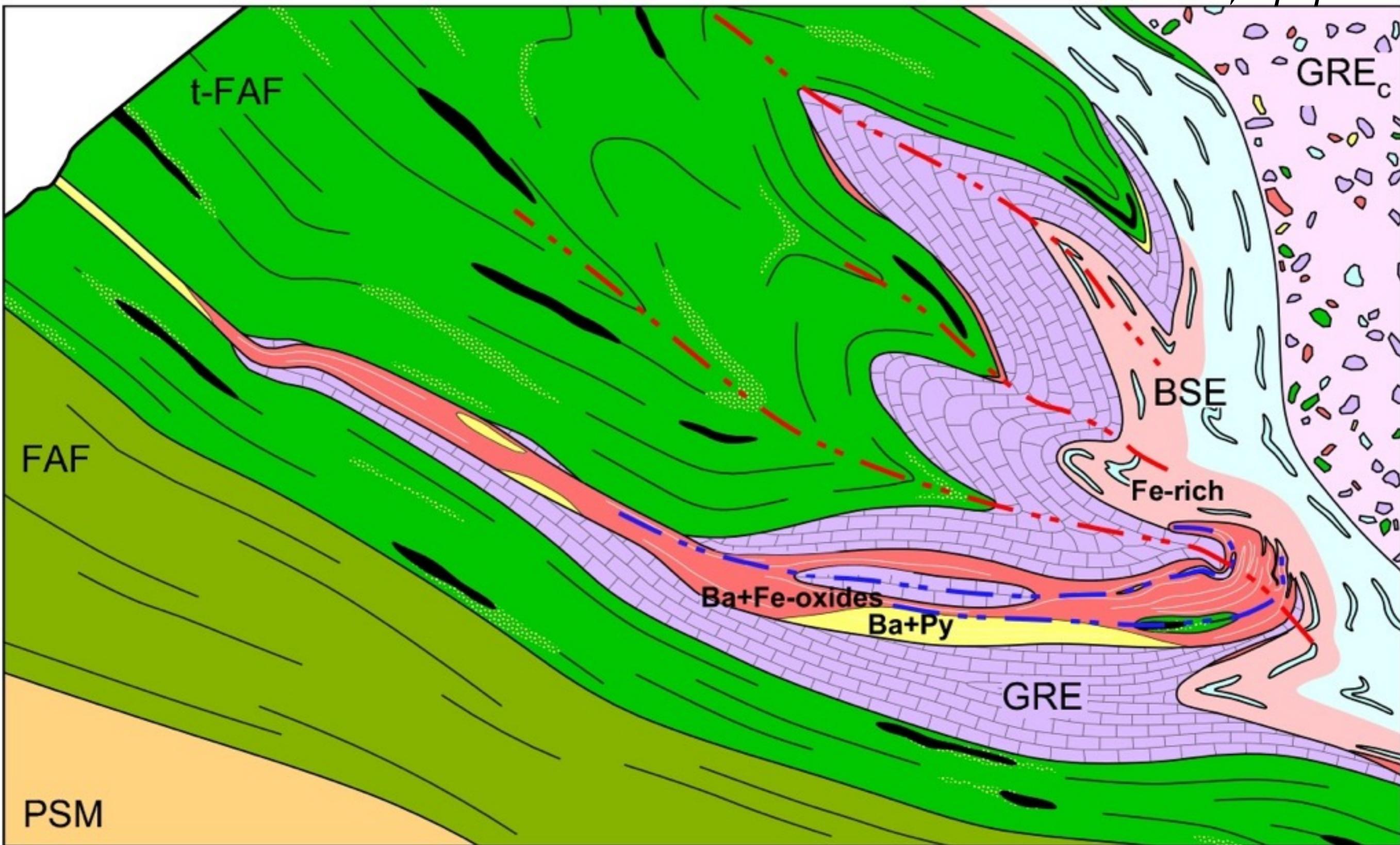
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Vezzoni et al., *in prep.*



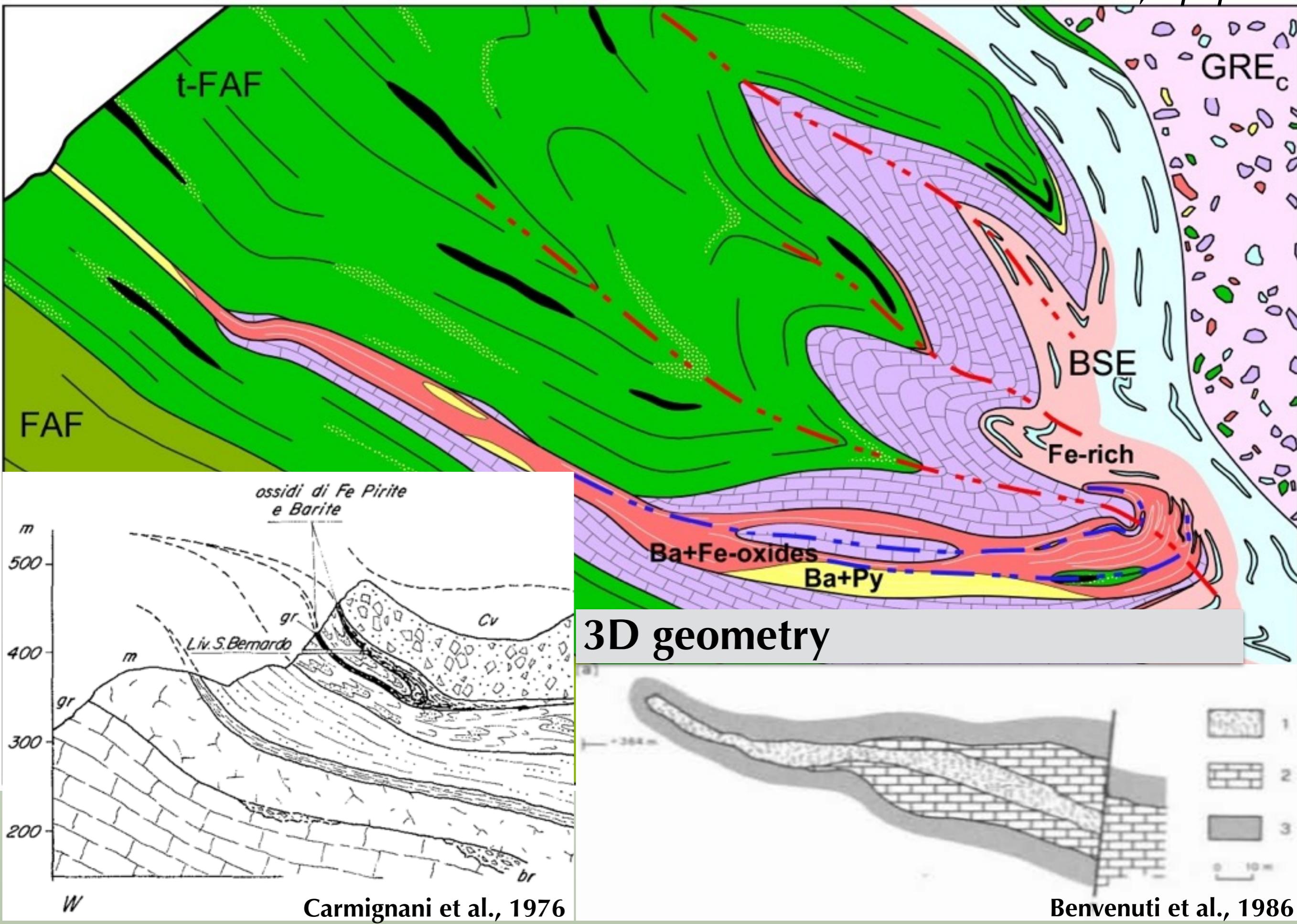
# Buca della Vena geological section

Vezzoni et al., *in prep.*



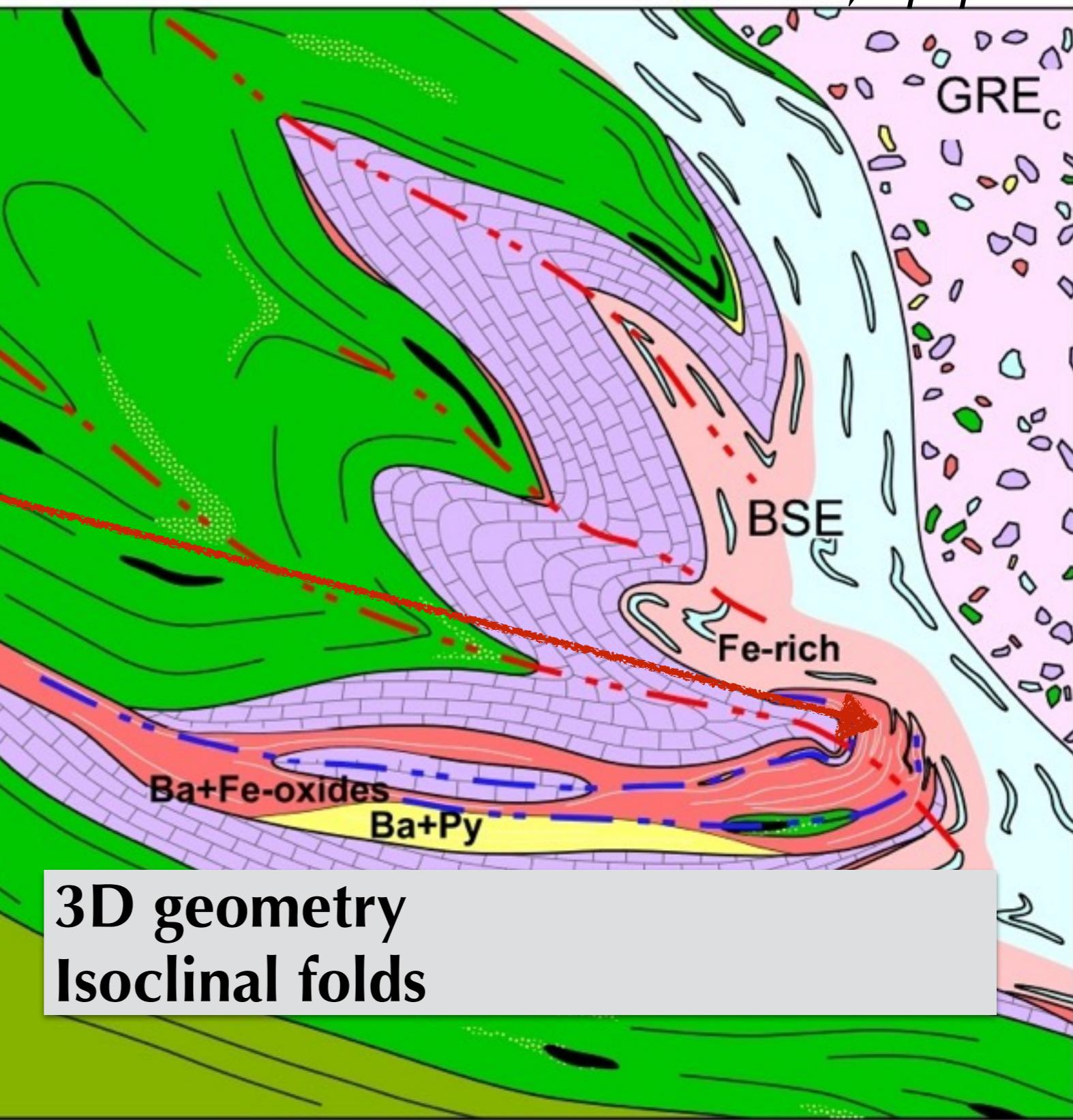
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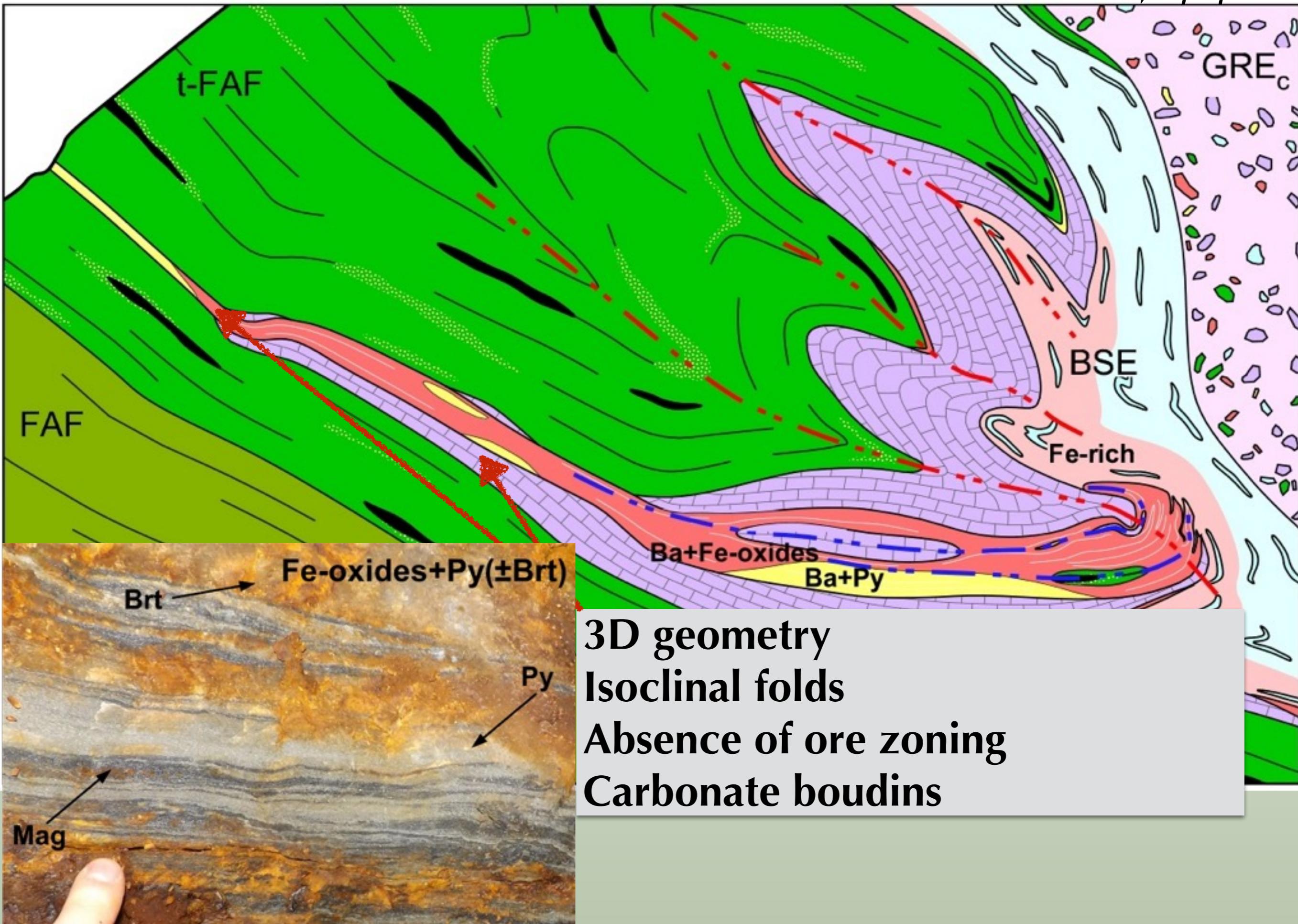
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Vezzoni et al., *in prep.*



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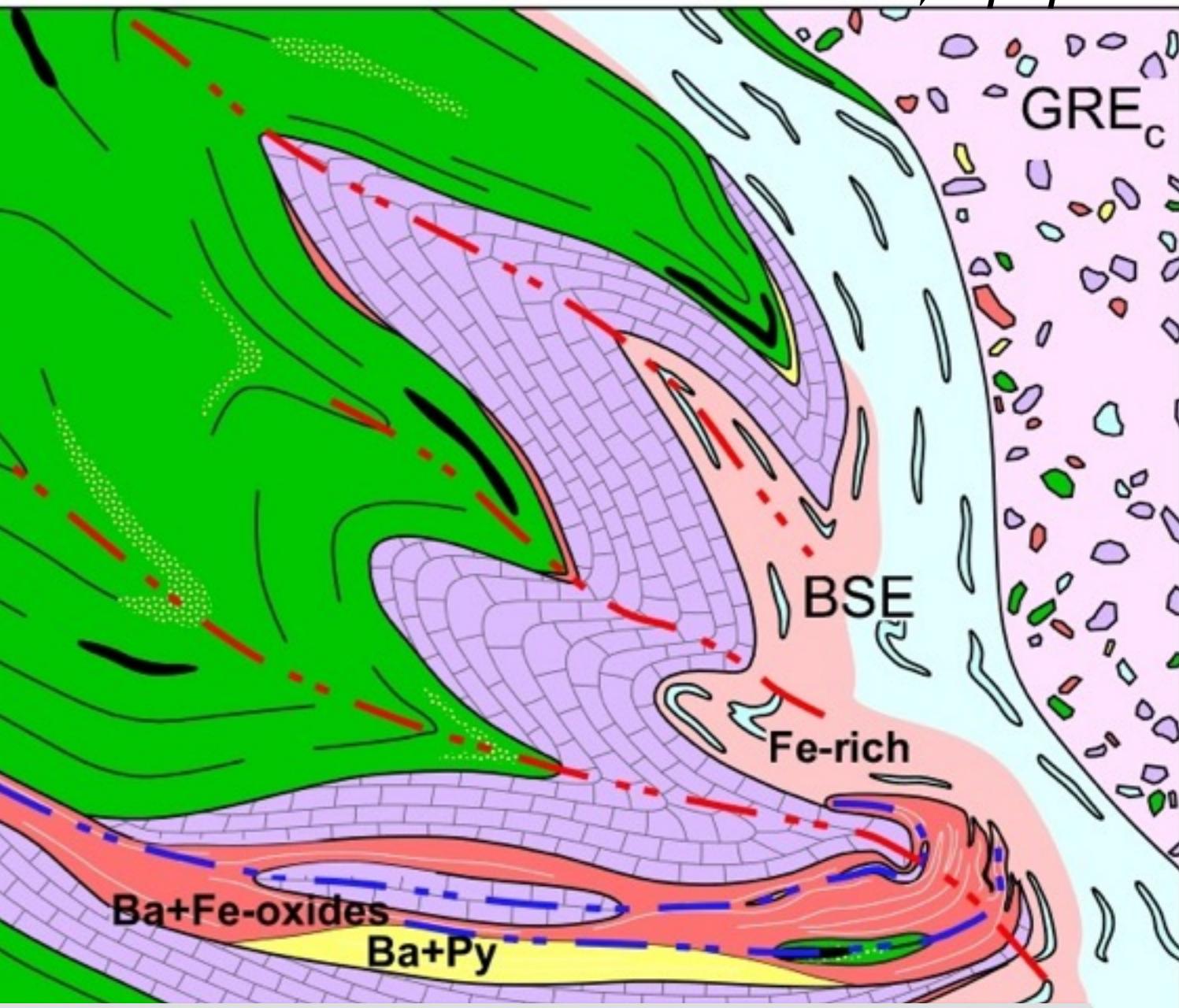
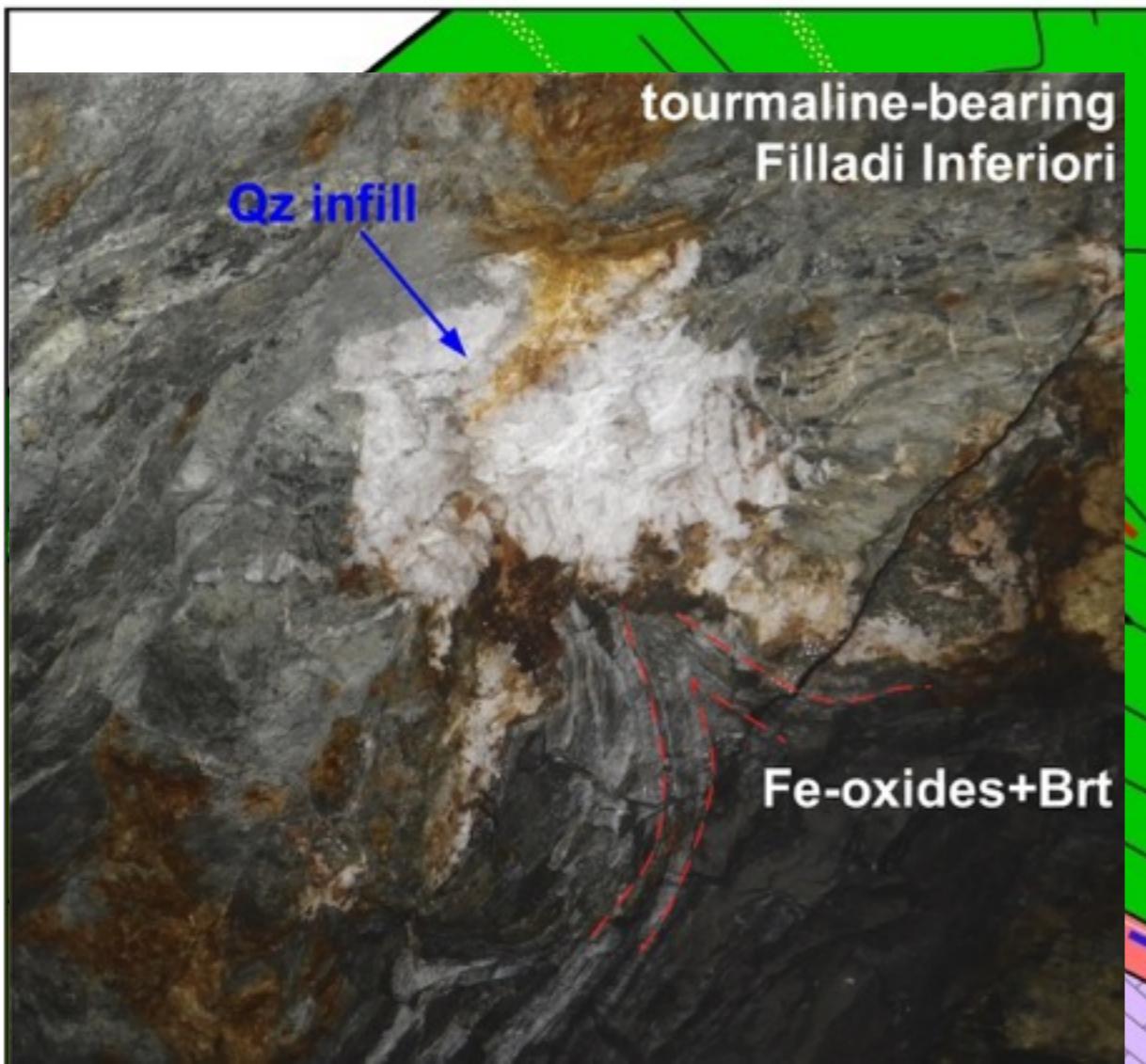
Vezzoni et al., *in prep.*



3D geometry  
Isoclinal folds  
Absence of ore zoning  
Carbonate boudins

# Buca della Vena geological section

Vezzoni et al., *in prep.*



**3D geometry  
Isoclinal folds  
Absence of ore zoning  
Carbonate boudins  
Rheology ores vs. carbonate/schist  
No metasomatism**

# Alpi Apuane Tl-district

## baryte/pyrite and baryte/Fe-oxides (area%) ~ 1

Data from image analysis (Vezzoni et al., *in prep.*) and XRF (D'Orazio et al., 2017)

Ore type:	V (m <sup>3</sup> )	d (t/m <sup>3</sup> )	Tonnage (t)
baryte + pyrite	11000	4.75	53000
baryte + Fe-oxides	52000	4.85	252000
<b>Buca della Vena mine</b>			305000

# Alpi Apuane Tl-district

Ore deposits:	<b>BDV</b>	<b>M. Arsiccio</b>	<b>Pollone</b>	<b>CDR</b>	<b>Fornovolasco</b>	<b>AA district</b>
	Massive pyrite					
Mined ore (t)						
Reserves (t)						
Tl-grade ( $\mu\text{g/g}$ )	-	77 <sup>1</sup>	-	675 <sup>1</sup>	871 <sup>1</sup>	
Tl-mined ore (t)						
Tl-reserves (t)						
	Mixed baryte + pyrite					
Mined ore (t)						
Reserves (t)						
Tl-grade ( $\mu\text{g/g}$ )	103 <sup>1</sup>	185 <sup>1</sup>	180 <sup>1</sup>	-	-	
Tl-mined ore (t)						
Tl-reserves (t)						
	Mixed baryte + Fe-oxides					
Mined ore (t)						
Reserves (t)						
	Fe-oxides/hydroxides					
Mined ore (t)						
Reserves (t)						

<sup>1</sup> D'Orazio et al., 2017

# Alpi Apuane Tl-district

Ore deposits:	<b>BDV</b>	<b>M. Arsiccio</b>	<b>Pollone</b>	<b>CDR</b>	<b>Fornovolasco</b>	<b>AA district</b>
	Massive pyrite					
Mined ore (t)	-					
Reserves (t)	-					
Tl-grade ( $\mu\text{g/g}$ )	-	77 <sup>1</sup>	-	675 <sup>1</sup>	871 <sup>1</sup>	
Tl-mined ore (t)	-					
Tl-reserves (t)	-					
	Mixed baryte + pyrite					
Mined ore (t)	-					
Reserves (t)	53000 <sup>2</sup>					
Tl-grade ( $\mu\text{g/g}$ )	103 <sup>1</sup>	185 <sup>1</sup>	180 <sup>1</sup>	-	-	
Tl-mined ore (t)	-					
Tl-reserves (t)	5.5					
	Mixed baryte + Fe-oxides					
Mined ore (t)	149000 <sup>2</sup>					
Reserves (t)	103000 <sup>2</sup>					
	Fe-oxides/hydroxides					
Mined ore (t)	-					
Reserves (t)	-					

<sup>1</sup> D'Orazio et al., 2017

<sup>2</sup> Vezzoni et al., *in prep.*

# Alpi Apuane Tl-district

Ore deposits:	<b>BDV</b>	<b>M. Arsiccio</b>	<b>Pollone</b>	<b>CDR</b>	<b>Fornovolasco</b>	<b>AA district</b>
Massive pyrite						
Mined ore (t)	-	29600	-	36000	-	65600
Reserves (t)	-	-	-	48780 <sup>3</sup>	30000 <sup>4</sup>	78780
Tl-grade ( $\mu\text{g/g}$ ) <sup>1</sup>	-	77 <sup>1</sup>	-	675 <sup>1</sup>	871 <sup>1</sup>	
Tl-mined ore (t)	-	2.5	-	24.5	-	27.0
Tl-reserves (t)	-	-	-	33.0	26.0	59.0
Mixed baryte + pyrite						
Mined ore (t)	-	340000	174000	-	-	514000
Reserves (t)	53000 <sup>2</sup>	110000 <sup>5</sup>	-	-	-	163000
Tl-grade ( $\mu\text{g/g}$ ) <sup>1</sup>	103 <sup>1</sup>	185 <sup>1</sup>	180 <sup>1</sup>	-	-	
Tl-mined ore (t)	-	63	31.5	-	-	94.5
Tl-reserves (t)	5.5	20.5	-	-	-	26.0
Mixed baryte + Fe-oxides						
Mined ore (t)	149000 <sup>2</sup>	250000	-	-	-	399000
Reserves (t)	103000 <sup>2</sup>	90000 <sup>5</sup>	-	-	-	193000
Fe-oxides/hydroxides						
Mined ore (t)	-	76500	-	14500	-	91000
Reserves (t)	-	-	-	96000 <sup>3</sup>	-	96000

<sup>1</sup> D'Orazio et al., 2017

<sup>2</sup> Vezzoni et al., *in prep.*

<sup>3</sup> Galli, 1956

<sup>4</sup> Cortese, 1923

<sup>5</sup> Ercole Martina, 1969

Data from “Relazione sul Servizio Minerario ...”

**AA district - Tl > 206.5 t (Reserves 85 t)**

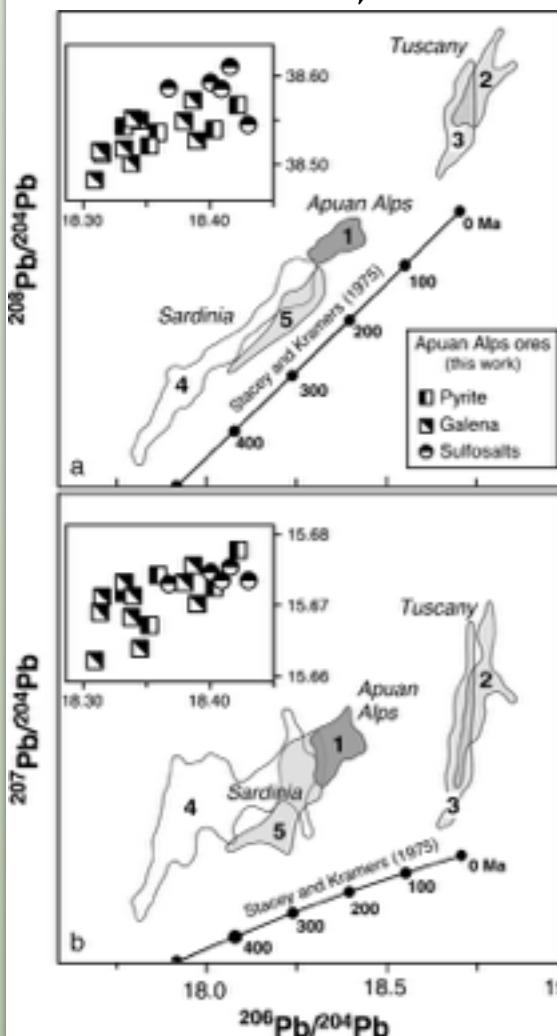
# Conclusion

## Buca della Vena is an exceptional geosite

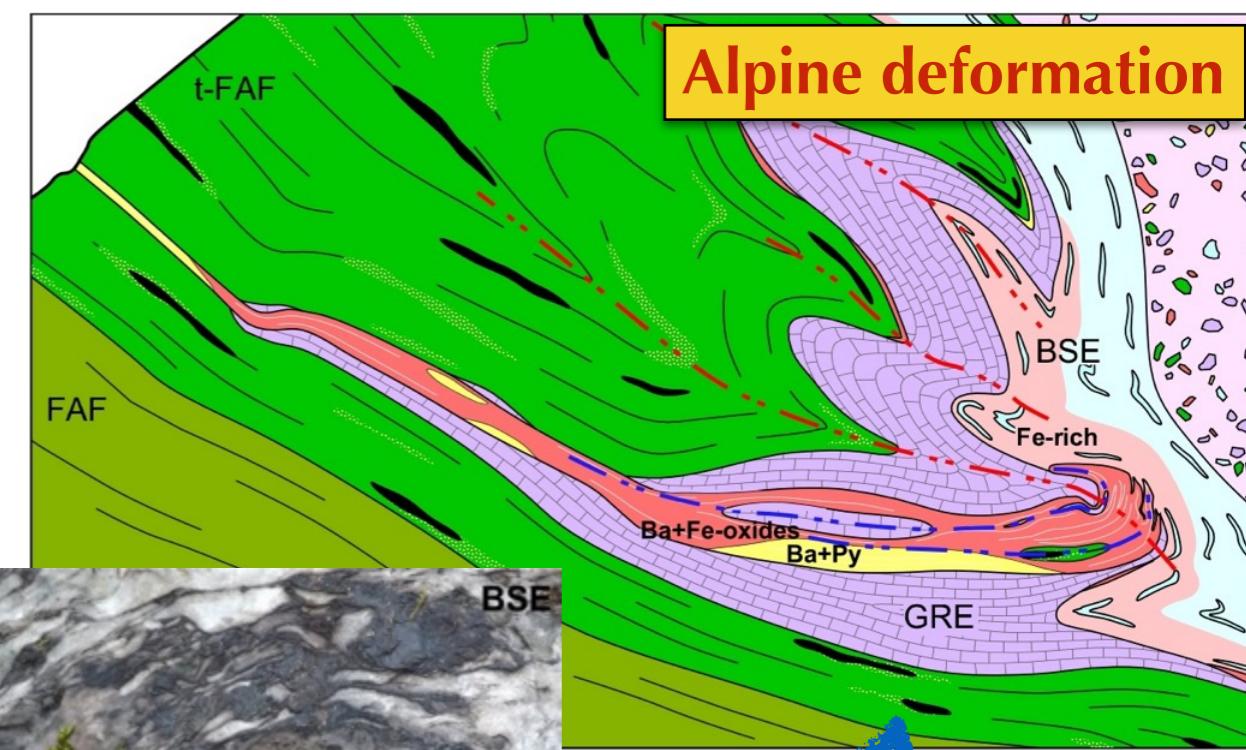
1. The actual ore setting was acquired during Alpine tectono-metamorphic event
2. The proto-ore suffered partial exhumation and supergene alteration (Upper Trias-Lower Jurassic)
3. The field geology integrated with petrography, geochemistry, isotopic data point to an hydrothermal proto-ore related to the Permian magmatism

⇒ AA is a world-class Tl-district

D'Orazio et al., 2017



+As, Sb, Hg, Tl, Bi...  
Hydrothermal system



Supergene alteration

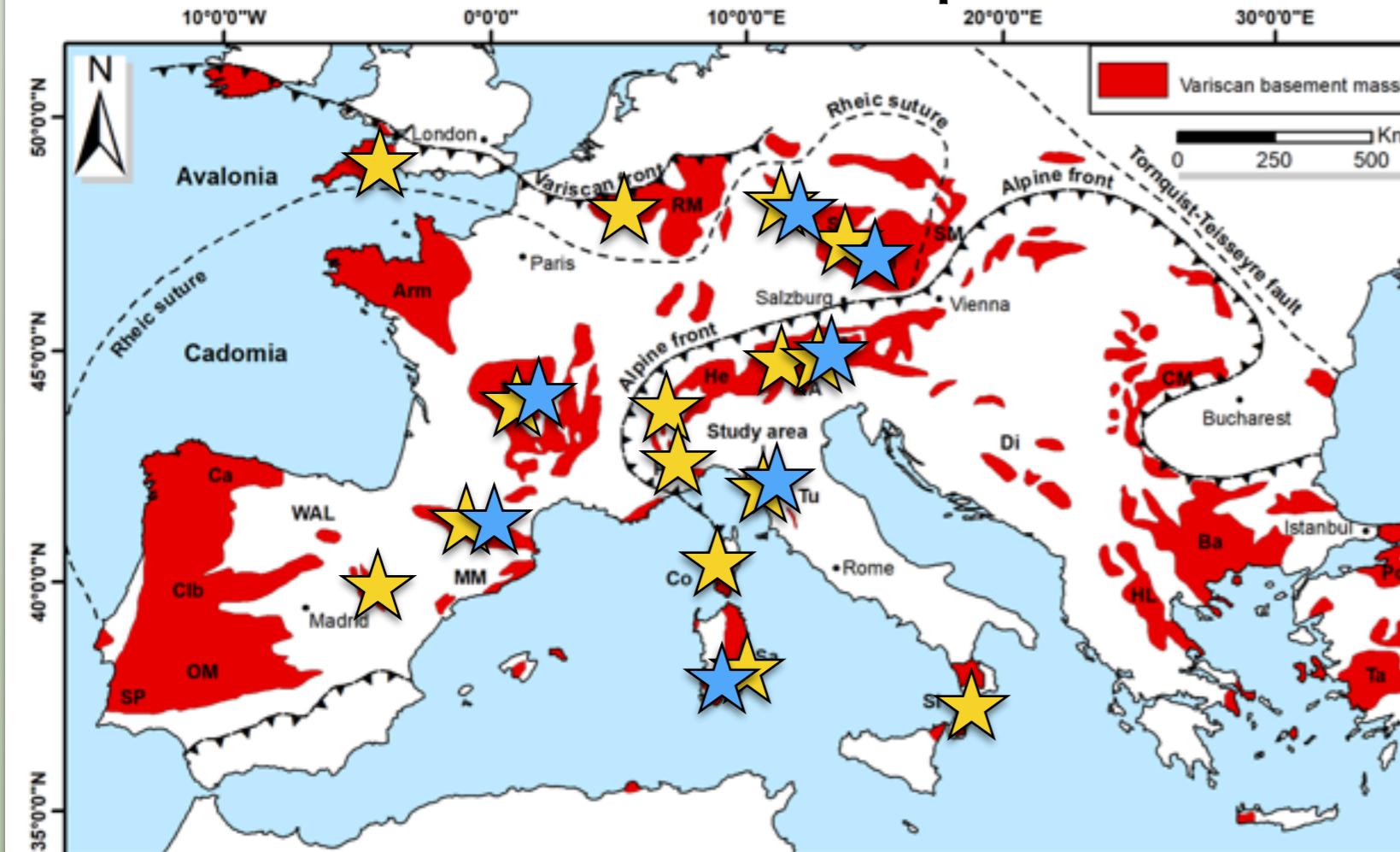
# Conclusion

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Distribution of pre-Mesozoic Units



Franke, 1989; Martínez-Catalán, 1990; Neubauer, 2014;  
Ribeiro & Sanderson, 1996; von Raumer et al. 2002, 2013

### Permian events

#### ★ Magmatism

e.g., Buzzi et al., 2008; Cabanis et al., 1990; Cassinis et al., 2008; Dallagiovanna et al., 2009; Deroin & Bonin, 2003; Finger et al., 2003; Forster et al., 1999; Gaggero et al., 2007; Lago et al., 2004; Marignac & Cuney, 1999; McCann et al., 2006; Ronca et al., 1999; Traversa et al., 2003; Visonà et al., 2007; ...

#### ★ Ores

e.g., Ackerman et al., 2017; Boni et al., 2015; Cabral et al., 2017; Cugeroni et al., 2018; De Capitani et al., 1999; Harlaux et al., 2018; Kopp et al., 2012; Marignac & Cuney, 1999; Melcher & Onuk, 2019; Nadoll et al., 2019; Ostendorf et al., 2019; ...

# Conclusion

**Field-based studies are crucial to constrain original setting, genesis and fate of orebodies**

**Relevant implications**  
e.g., natural vs anthropic environmental pollution

**Ore deposits are “geological gyms” for students**

## Buca della Vena: la Via del Ferro delle Alpi Apuane

Sabato 25 maggio 2019

Buca della Vena (Cardoso, LU) è uno dei più importanti geositi minerari delle Alpi Apuane, sia da un punto di vista storico che scientifico.

L'escursione, in mezzo a boschi e scorci panoramici sulle Alpi Apuane, guiderà alla scoperta delle passate attività minerarie con l'occasione di "toccare con mano" le mineralizzazioni qui coltivate.

Ritrovo - Piazza Europa,  
Pontestazzemese ore 9:00

Difficoltà - media

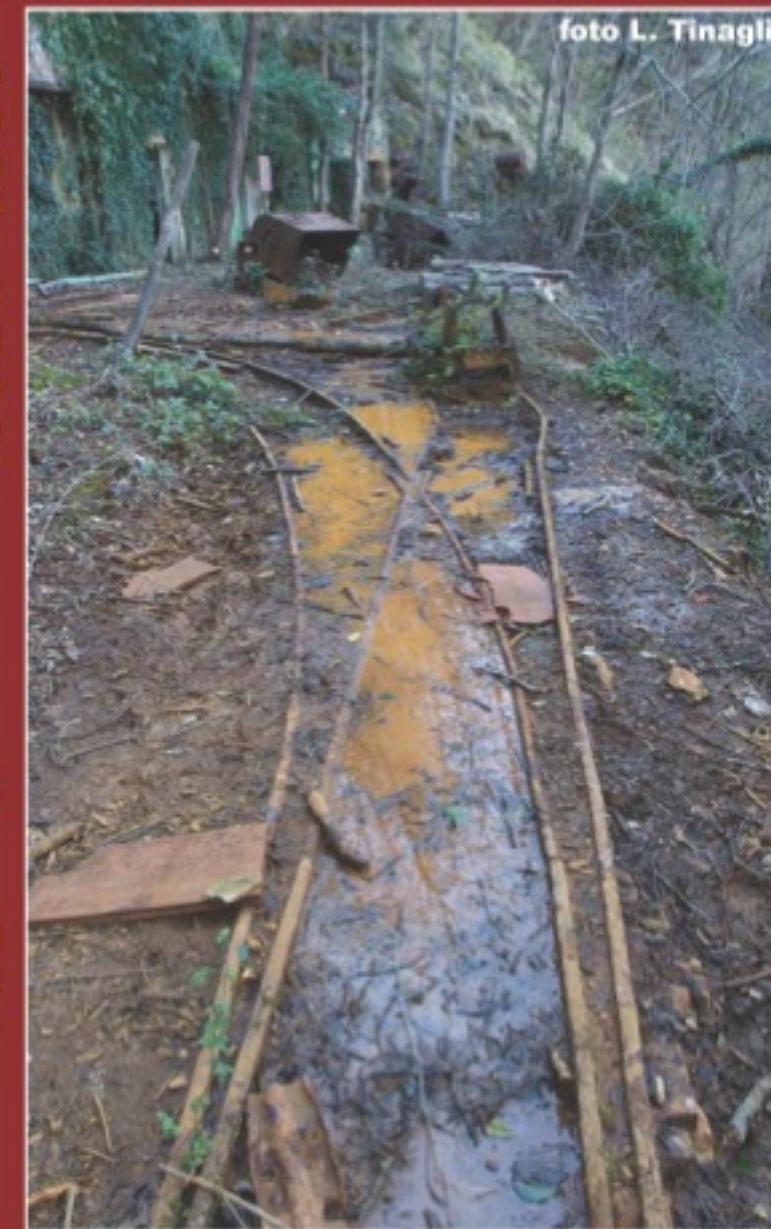
Rientro previsto - ore 15:00

Prenotazione obbligatoria entro mercoledì 22 maggio  
costo assicurazione CAI - 8 euro

Nome, Cognome, data di nascita ed eventuale iscrizione al CAI dovranno essere inviati tramite mail a:

[Simone.Vezzoni@igg.cnr.it](mailto:Simone.Vezzoni@igg.cnr.it)

Pranzo al sacco presso  
Osservatorio Astronomico  
“Alpi Apuane” (Stazzema)



con il patrocinio di:



in collaborazione con:





## METHODOLOGY FOR ESTABLISHING THE EU LIST OF **CRITICAL RAW MATERIALS**

- Guidelines •

