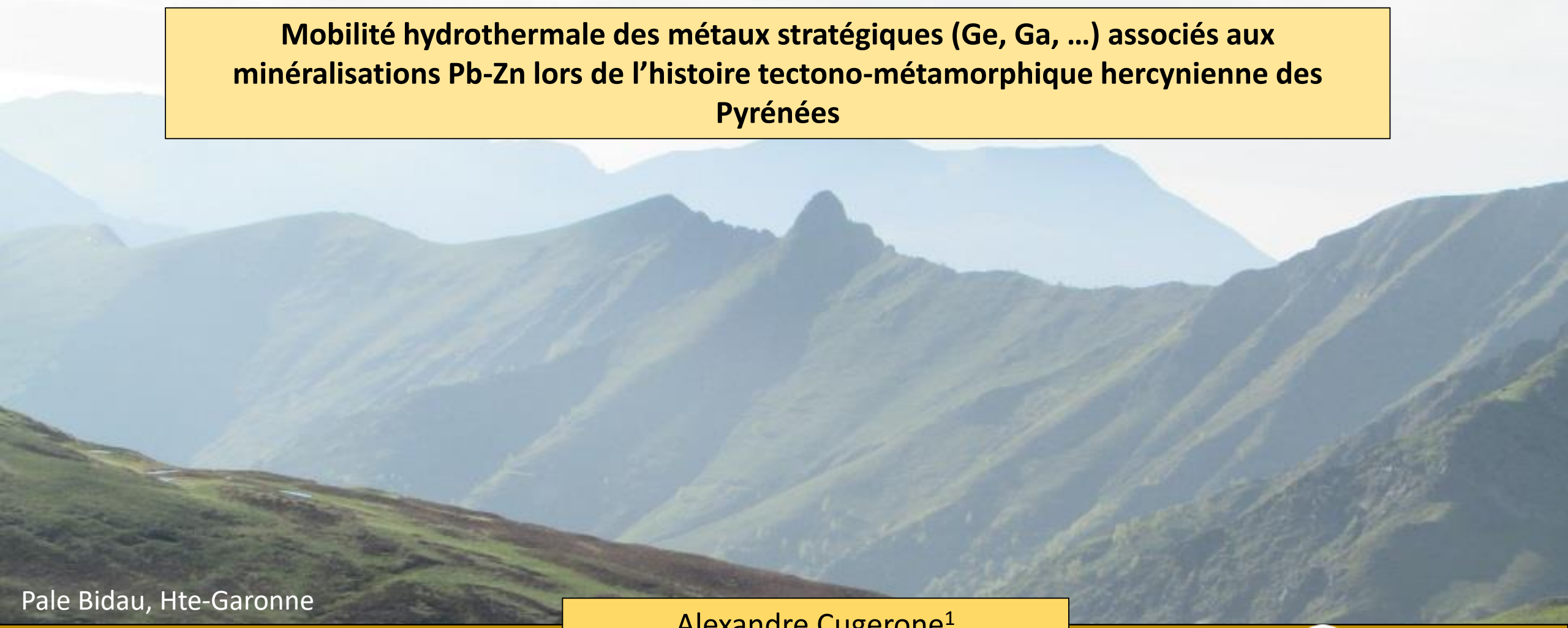
Mobilité hydrothermale des métaux stratégiques (Ge, Ga, …) associés aux minéralisations Pb-Zn lors de l'histoire tectono-métamorphique hercynienne des Pyrénées



Pale Bidau, Hte-Garonne

Alexandre Cugerone[1]

RGF 2017 1ère année de thèse post M2 RGF

***Encadrants**: Cenki-TokB.[1], ChauvetA.[1], Le Goff E.[4], Oliot E.[1], Munoz M.[1], Salvi S.[2], Béziat D.[2], Kouzmanov K.[3],*

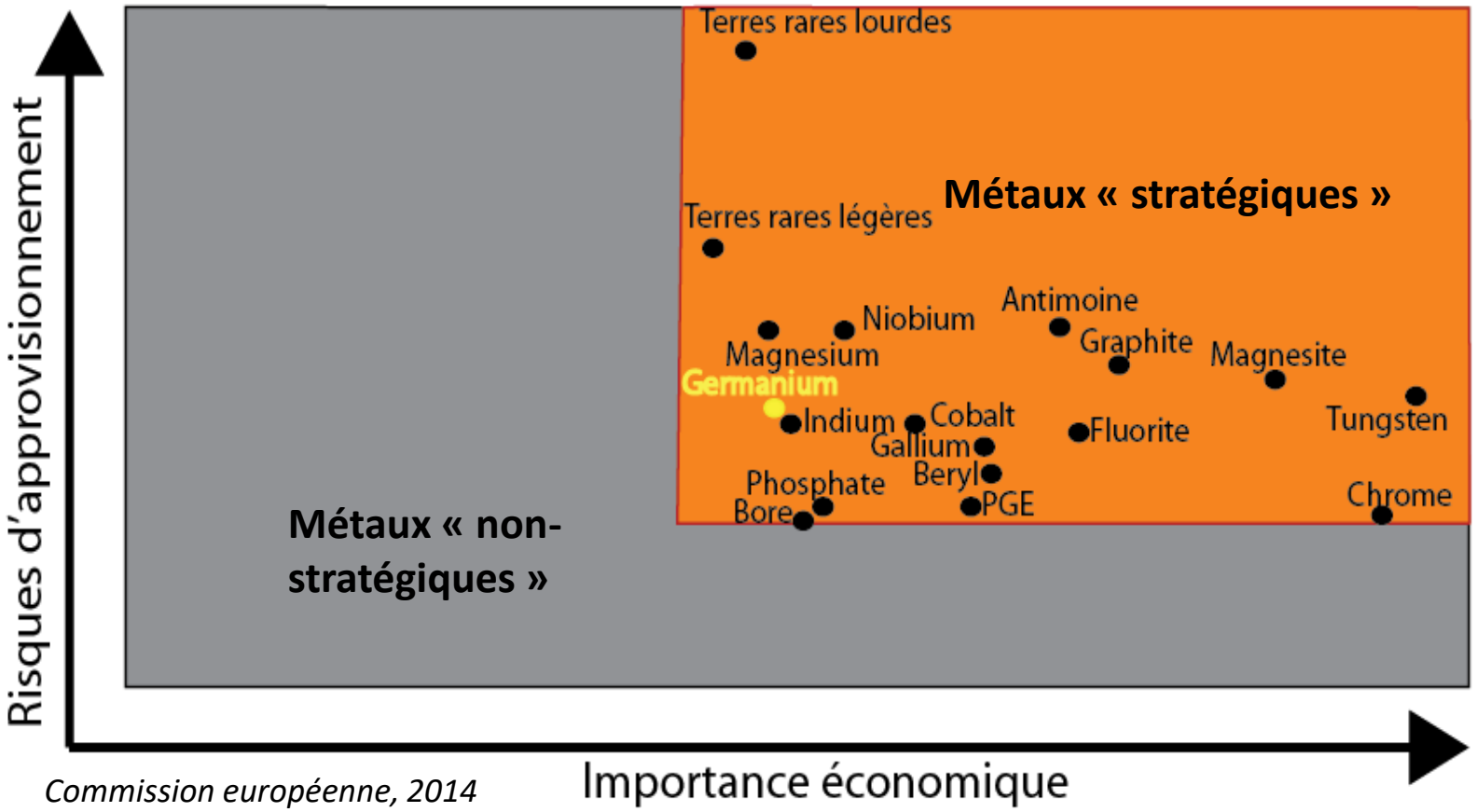
[1] *Laboratoire Géosciences Montpellier (CNRS-UMR 5243), Université de Montpellier*

[2] Géosciences Environnement Toulouse (GET)

[3] *Université de Genève*

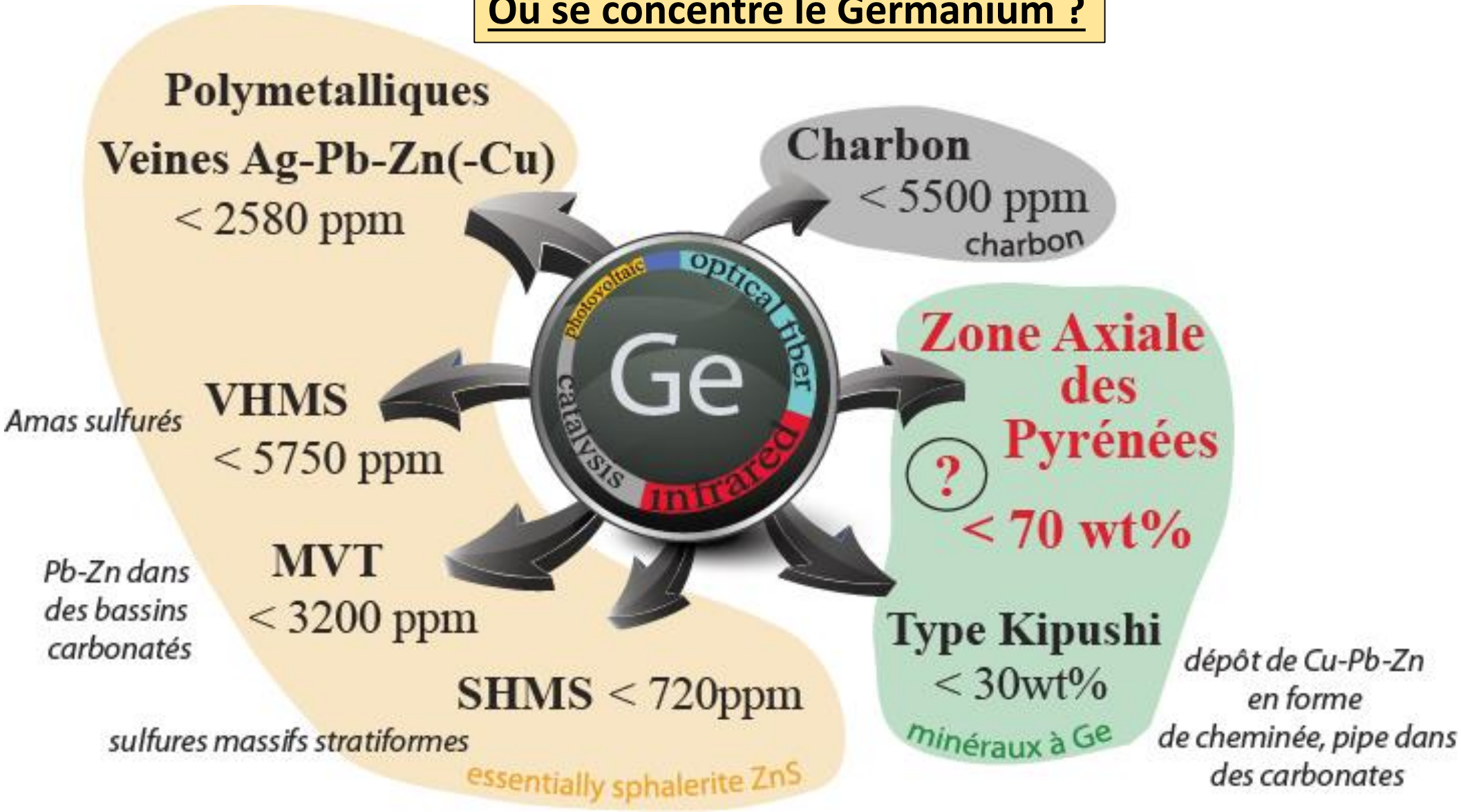
[4] *BRGM*

Pourquoi le Germanium ?

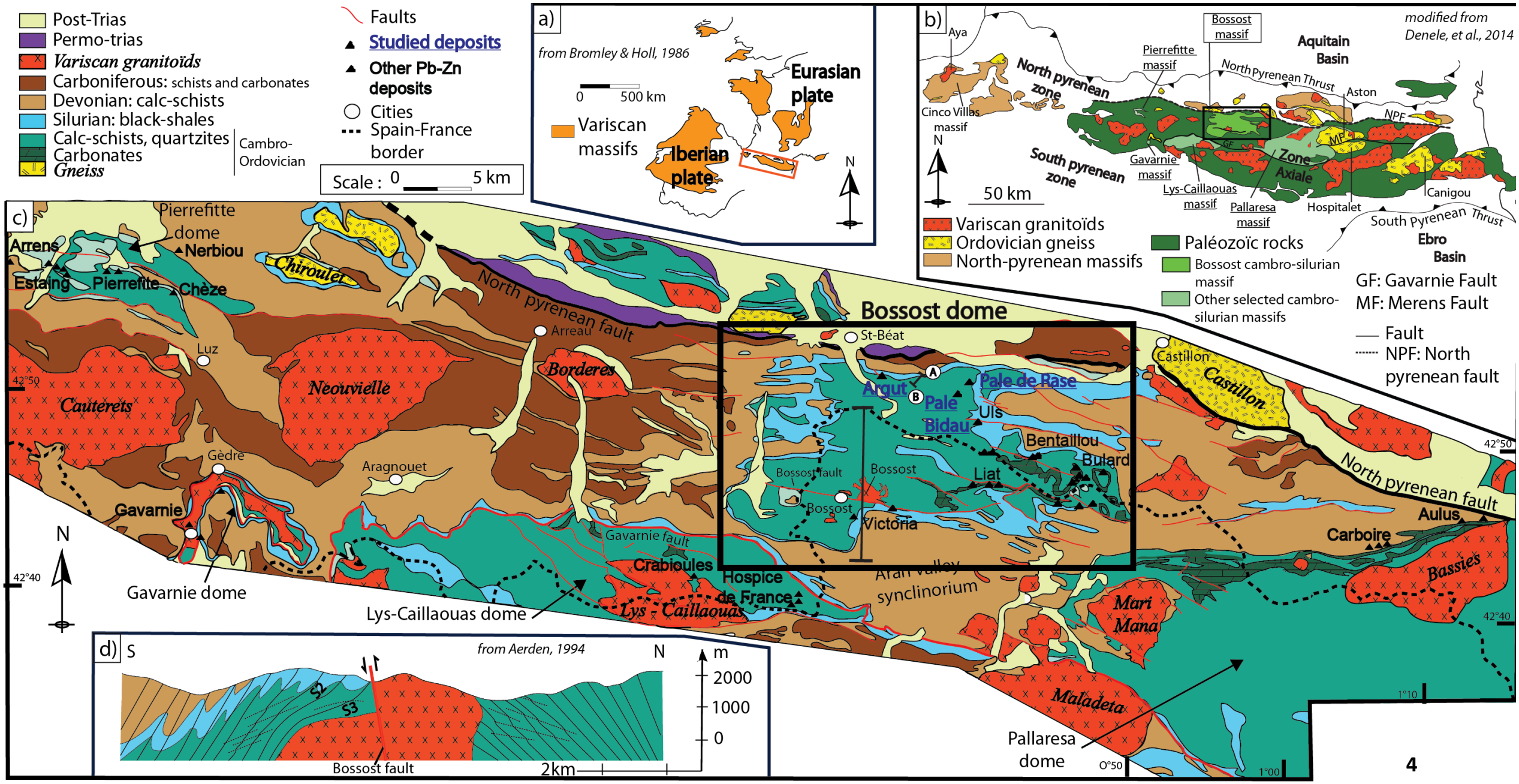


Commission européenne, 2014

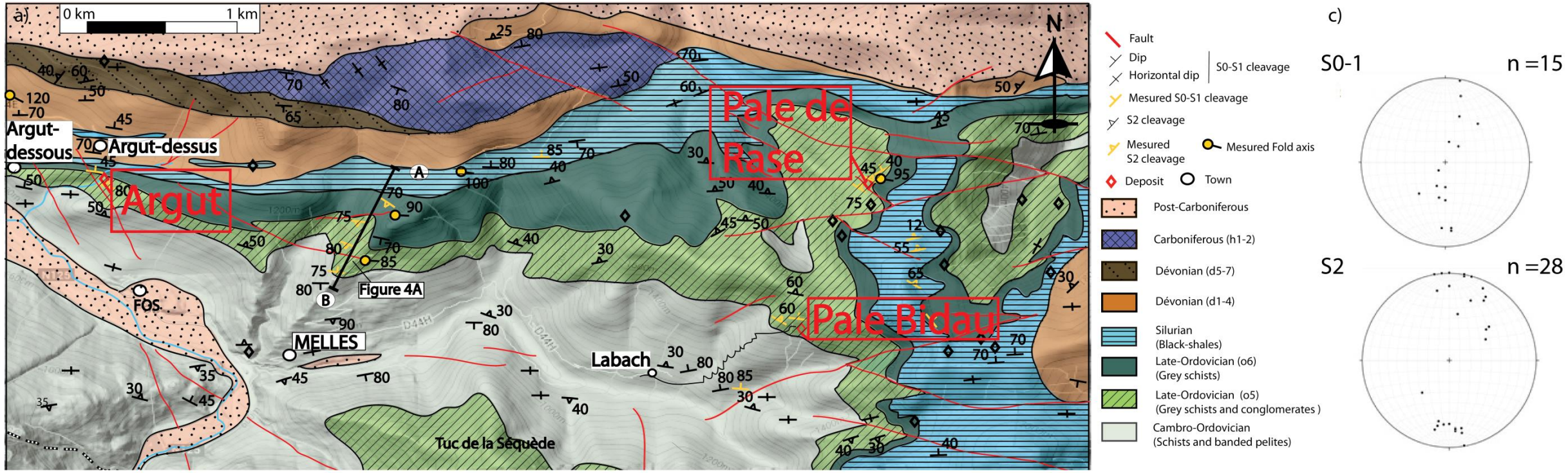
Où se concentre le Germanium ?

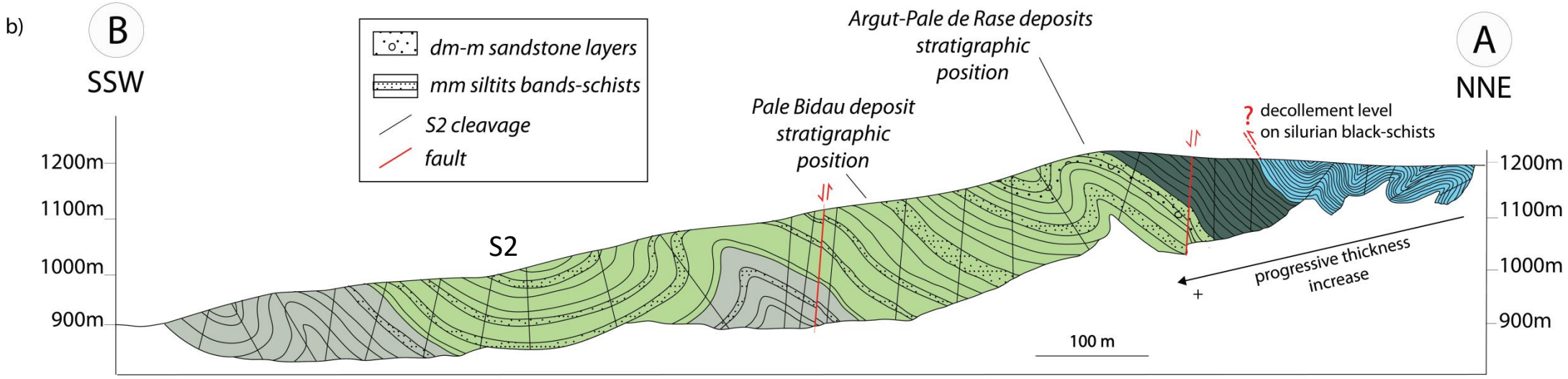


Zone d'étude: Zone Axiale des Pyrénées



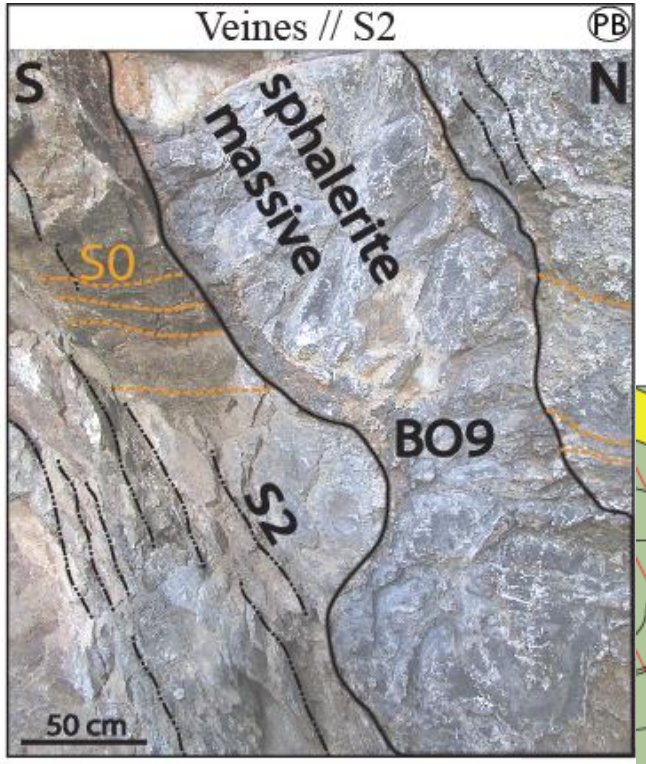
Nord du dome de Bossost



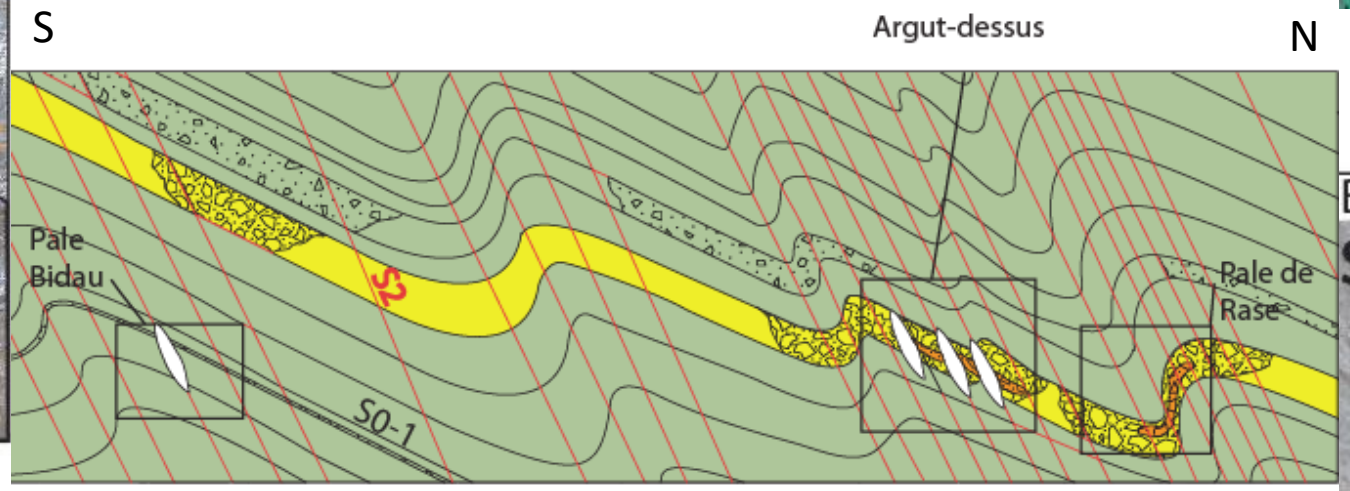


Synthèse structurale

2 types de minéralisation



Pale Bidau



minéralisation stratiforme : sphalerite, galena, pyrite

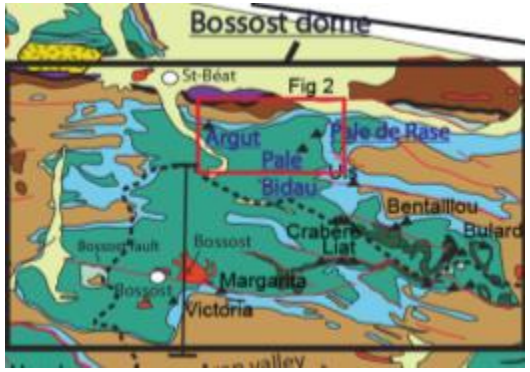
minéralisation en veines : sphalerite, galena, pyrite

Niveau porteur des minéralisations: conglomerate-sandstone or schist

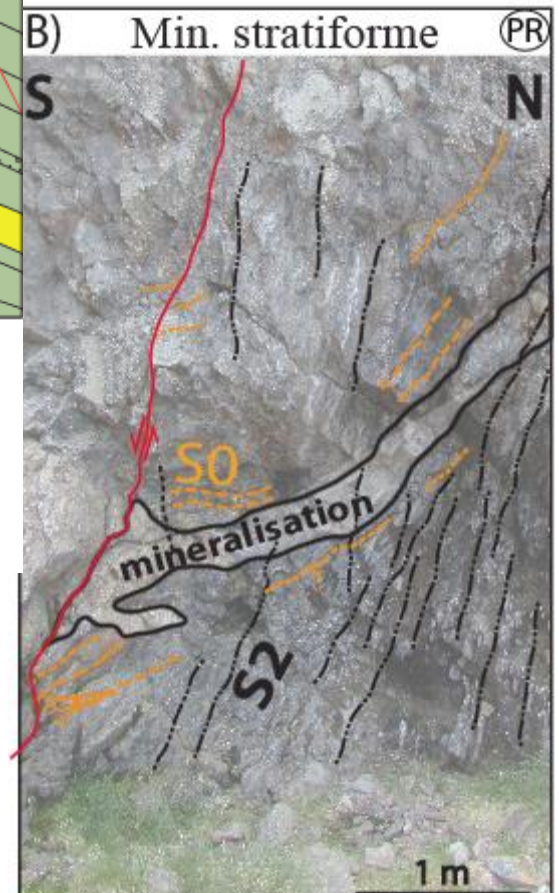
Niveau à conglomérats/siltites

Ordovician-Sup (o5) schistes gris

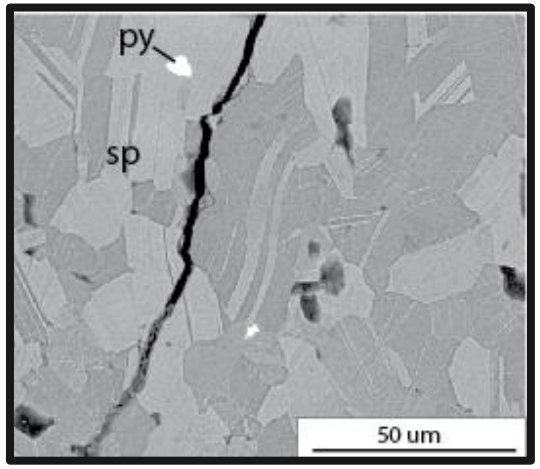
250 m Echelle horizontale



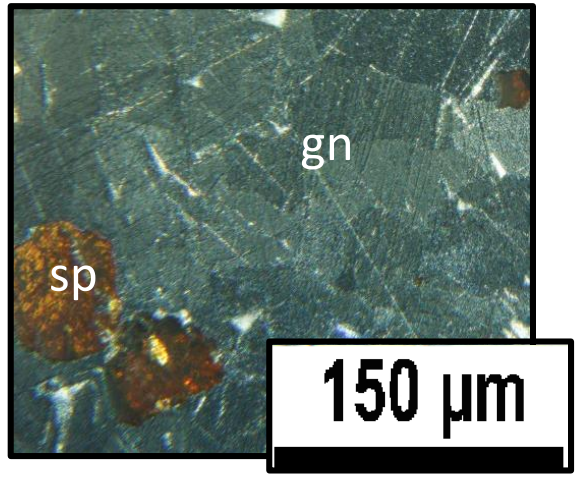
Pale de Rase



Microstructures

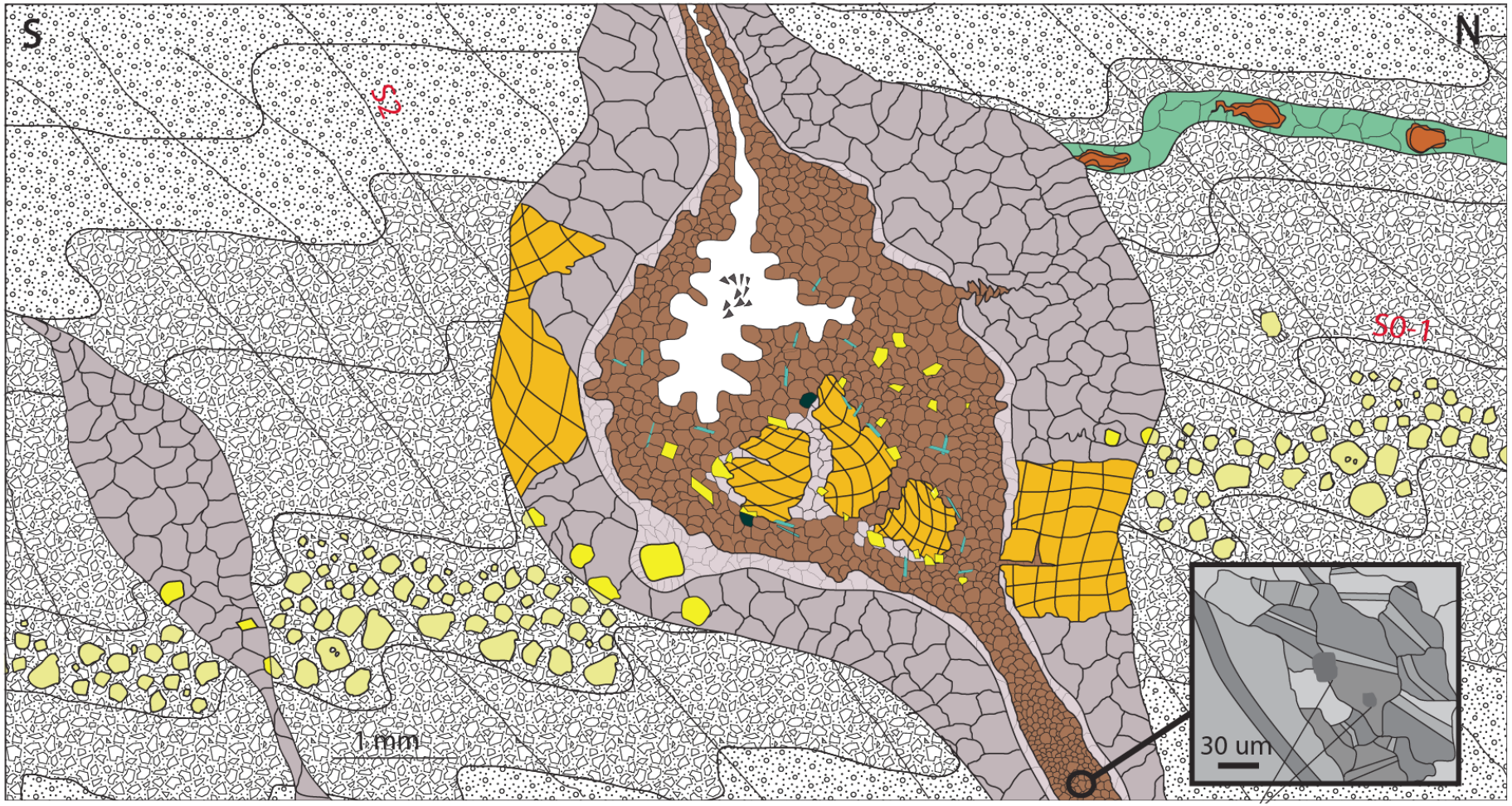


Sphalerite ZnS



Galène PbS *Etched with thiourea-HCl solution*

→Texture granoblastique



Minéralisation à Ge

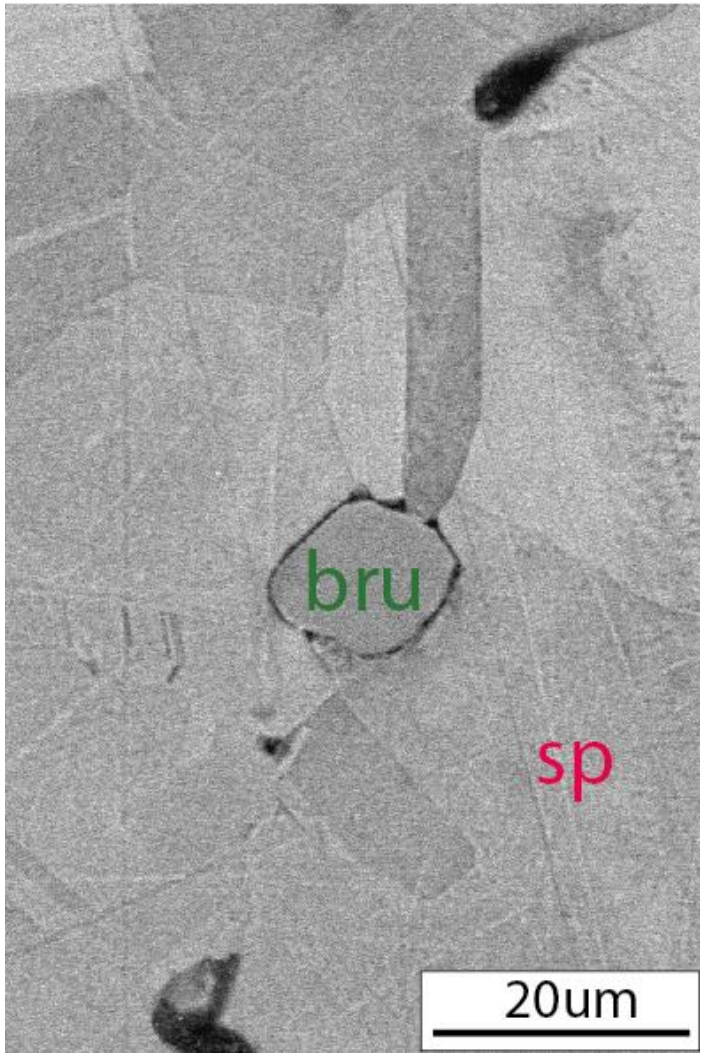
Host rocks
- Thin beds (calc-schists-siltstones)
- Coarse beds (Lutites-micro-conglomerates)

Primary stratiform mineralization
- Sphalerite with quartz boundaries
- Pyrite (framboid relicts)
- Quartz

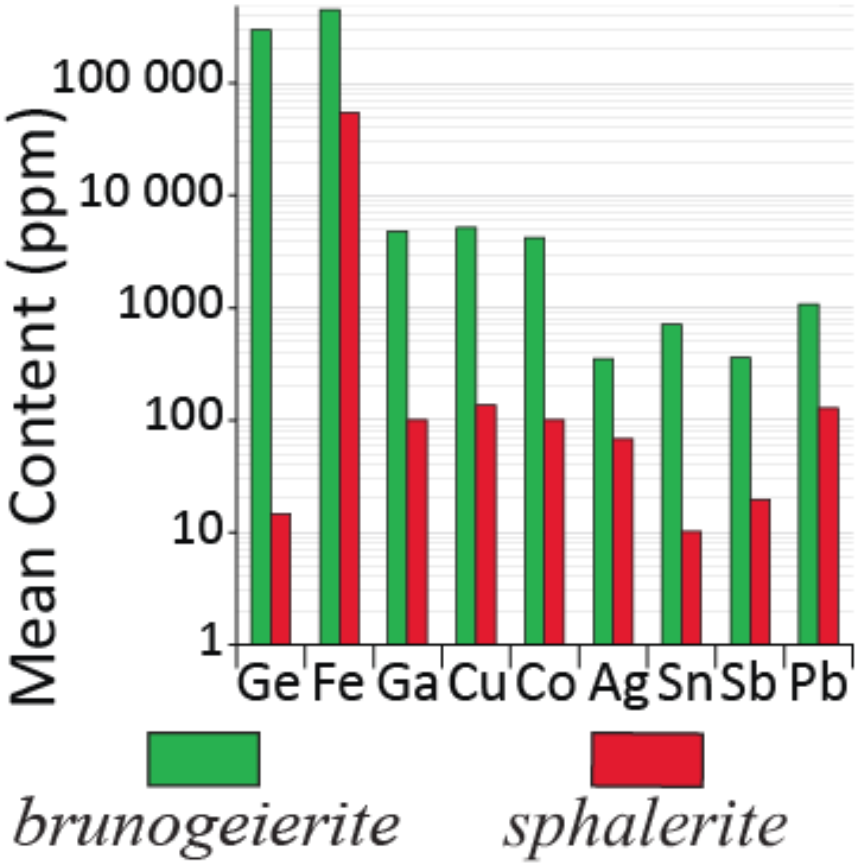
Secondary vein mineralization
- Main Qtz 1
- Overgrowth Qtz
- Carbonate
- Sphalerite
- Galena
- Pyrite-Chalcopyrite-Arsenopyrite
- Graphite
- Muscovite

Bru : Brunogéiérite $(Ge)Fe^{2+}_2O_4$

Sp: Sphalerite ZnS



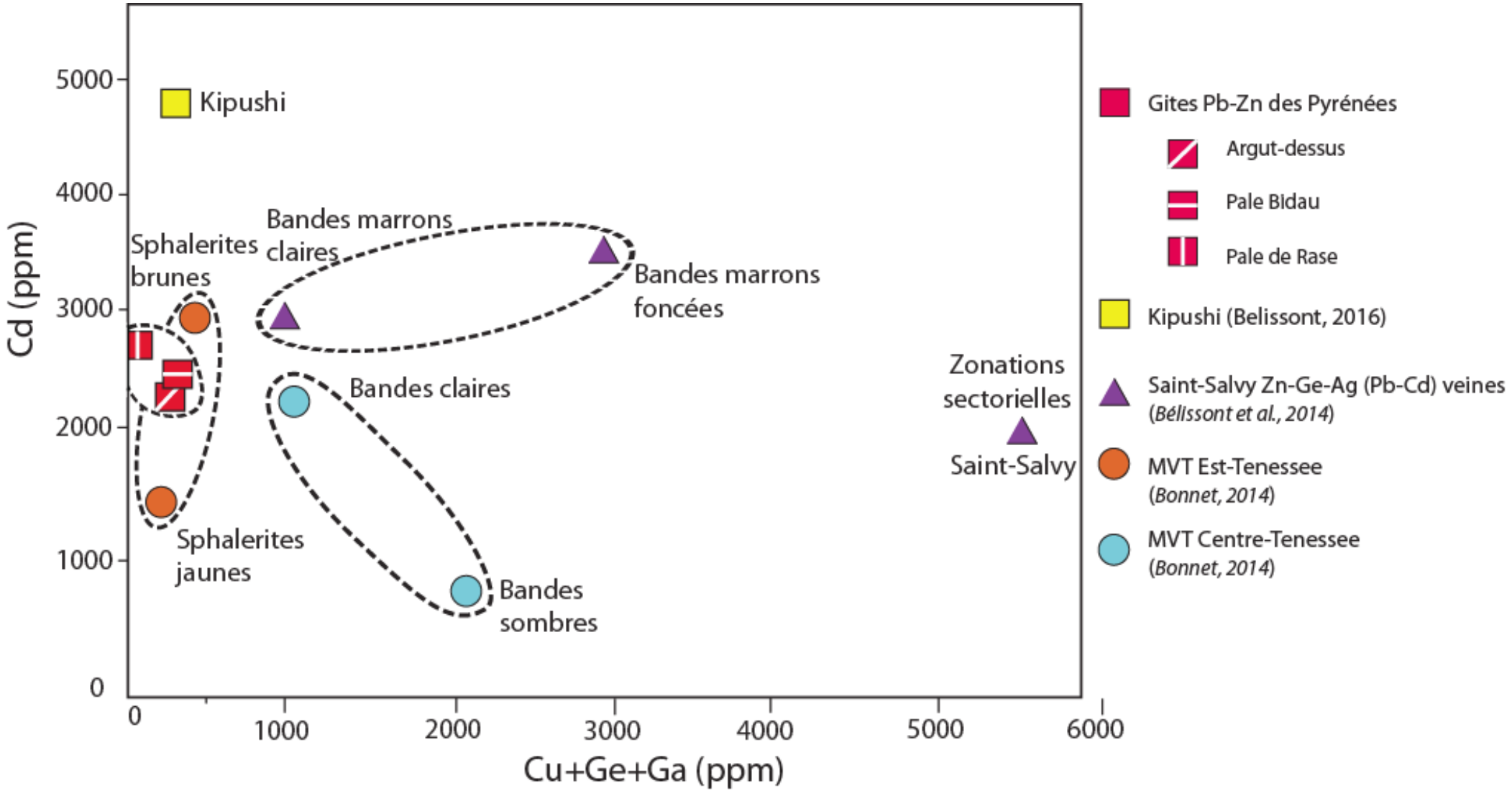
Géochimie: LA-ICP-MS



Ge sphalerite: 15 ppm
brunogeierite: 29%wt

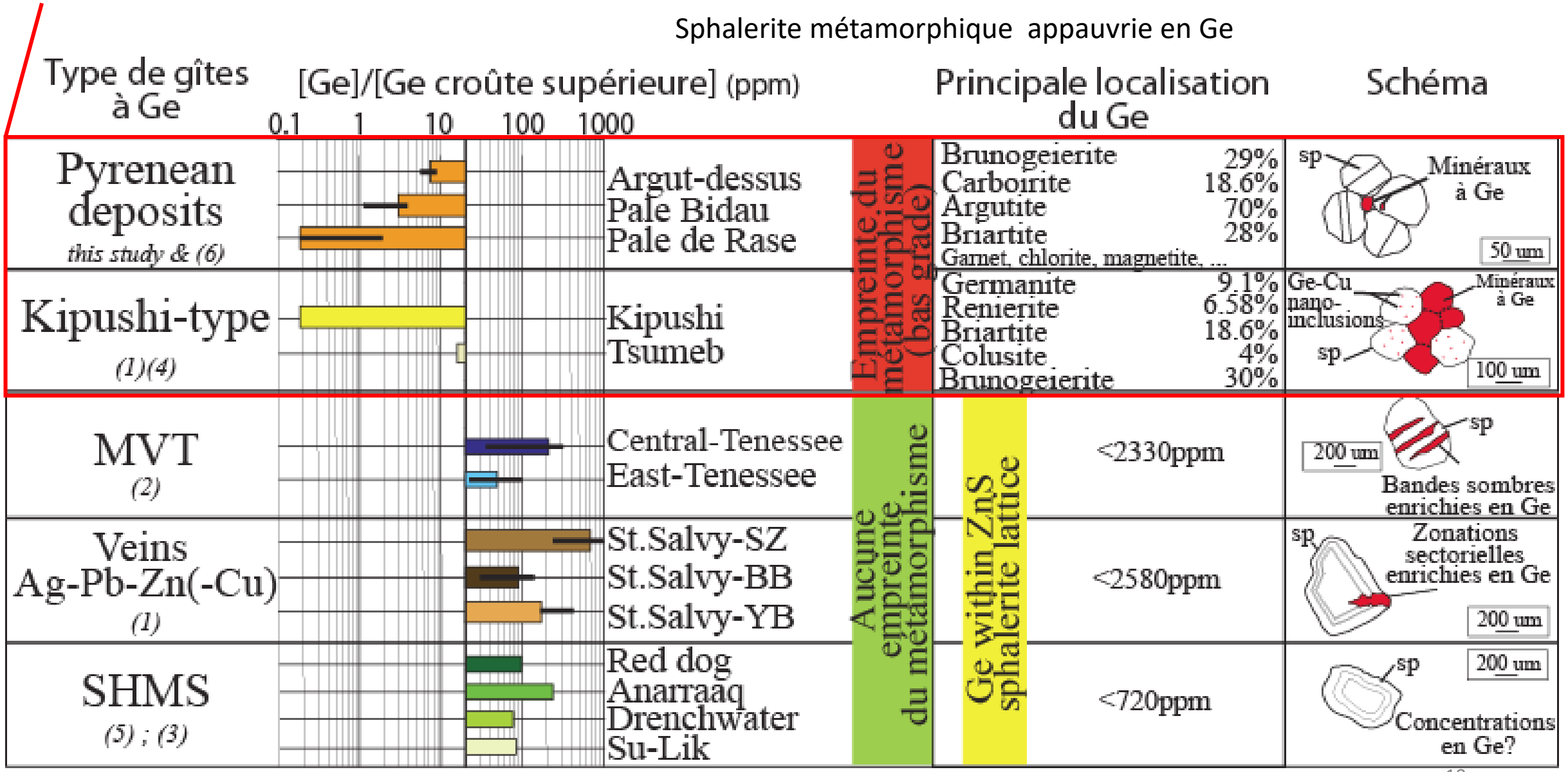
Géochimie: LA-ICP-MS

Comparaison de différents gîtes à Ge dans le monde



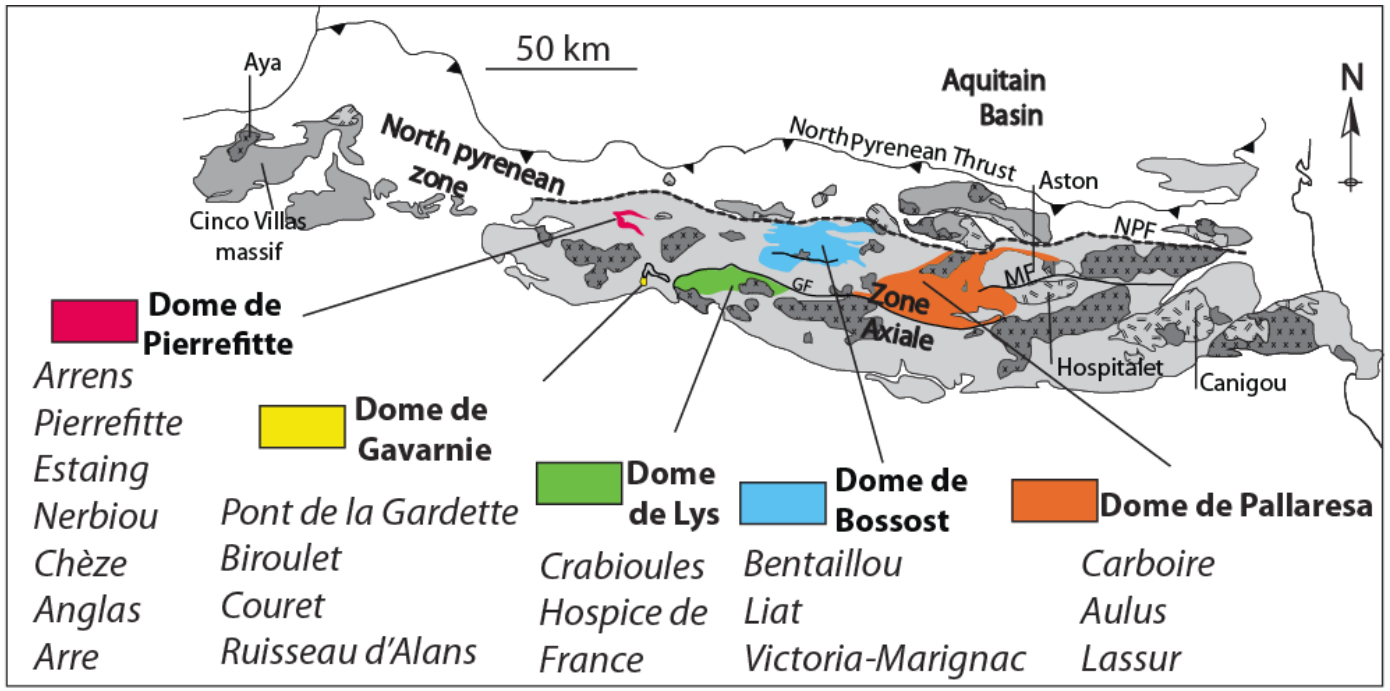
Minéralisations métamorphisées (<schiste vert) présentent uniquement des concentrations à Ge concentrées >%

Sphalerite métamorphique appauvrie en Ge



Cugerone, et al., en cours de publication

Perspective de la thèse



Terrains dans différents gites Pb-Zn

Structurale - Echantillonage

Inclusion fluides

Gangue - Sphalerite

Fluides minéralisateurs à Ge dans les Pyrénées

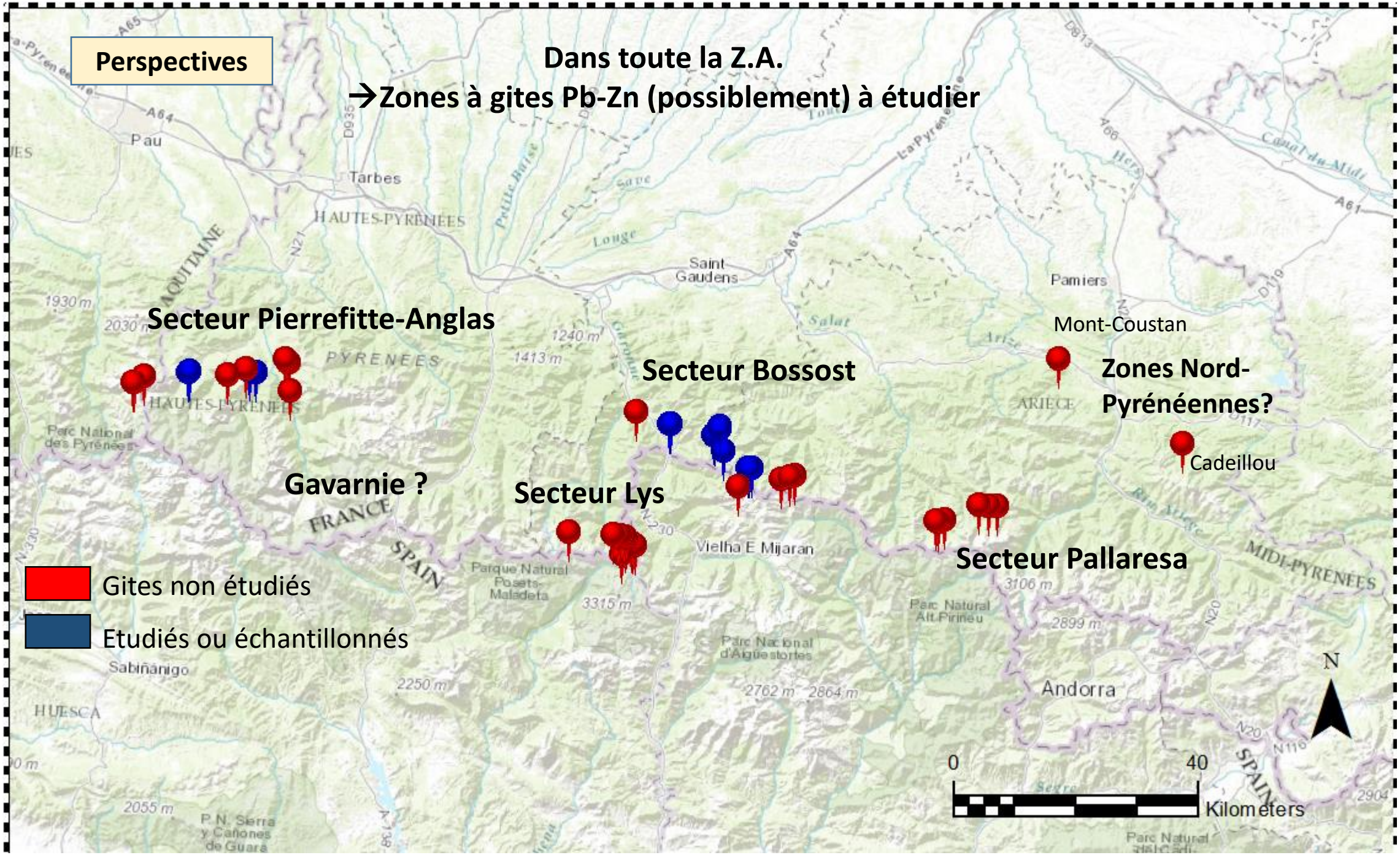
Geochimie

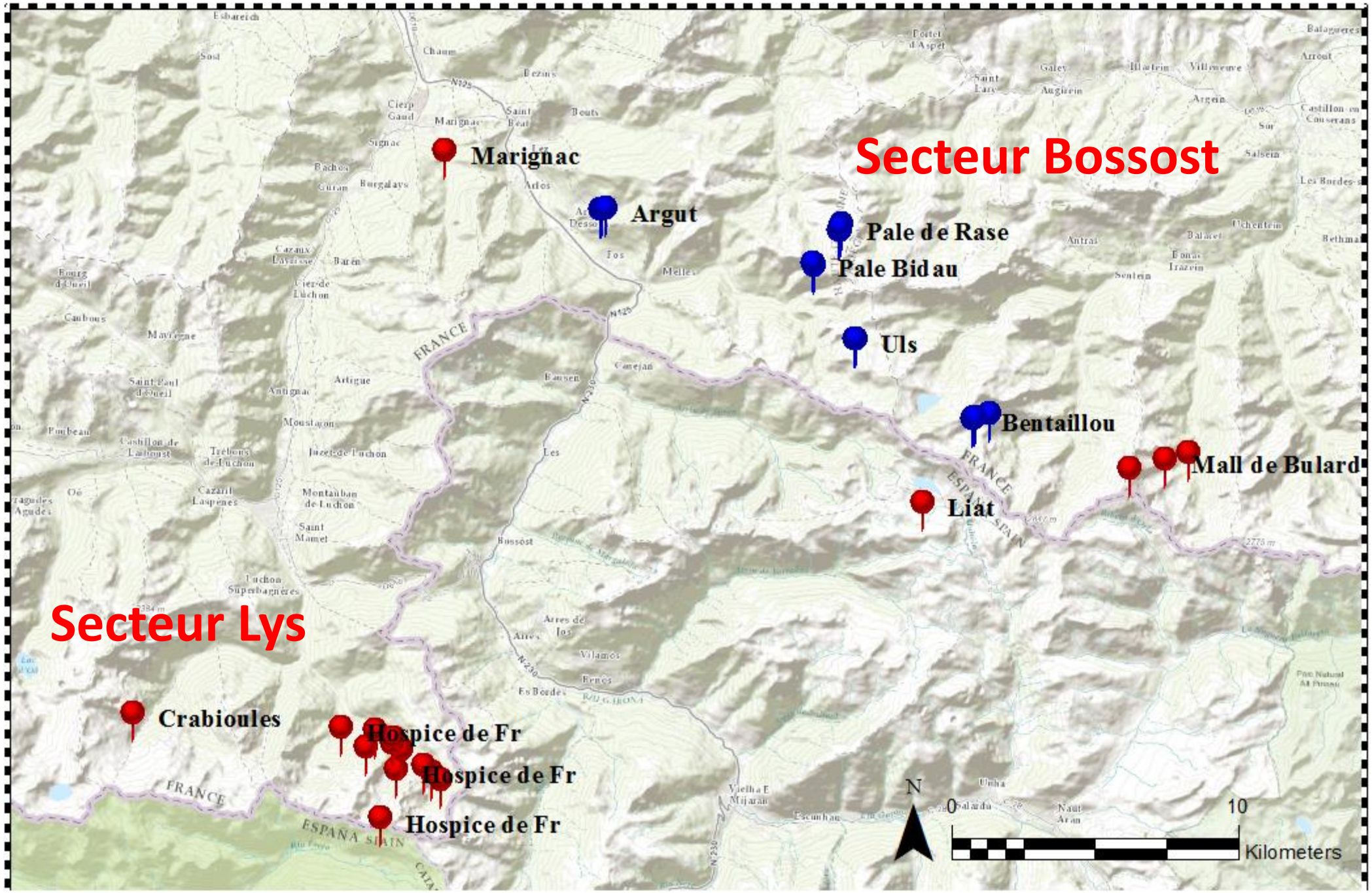
QEMSCAN - EPMA - LA-ICP-MS - (XANES-µXRF)

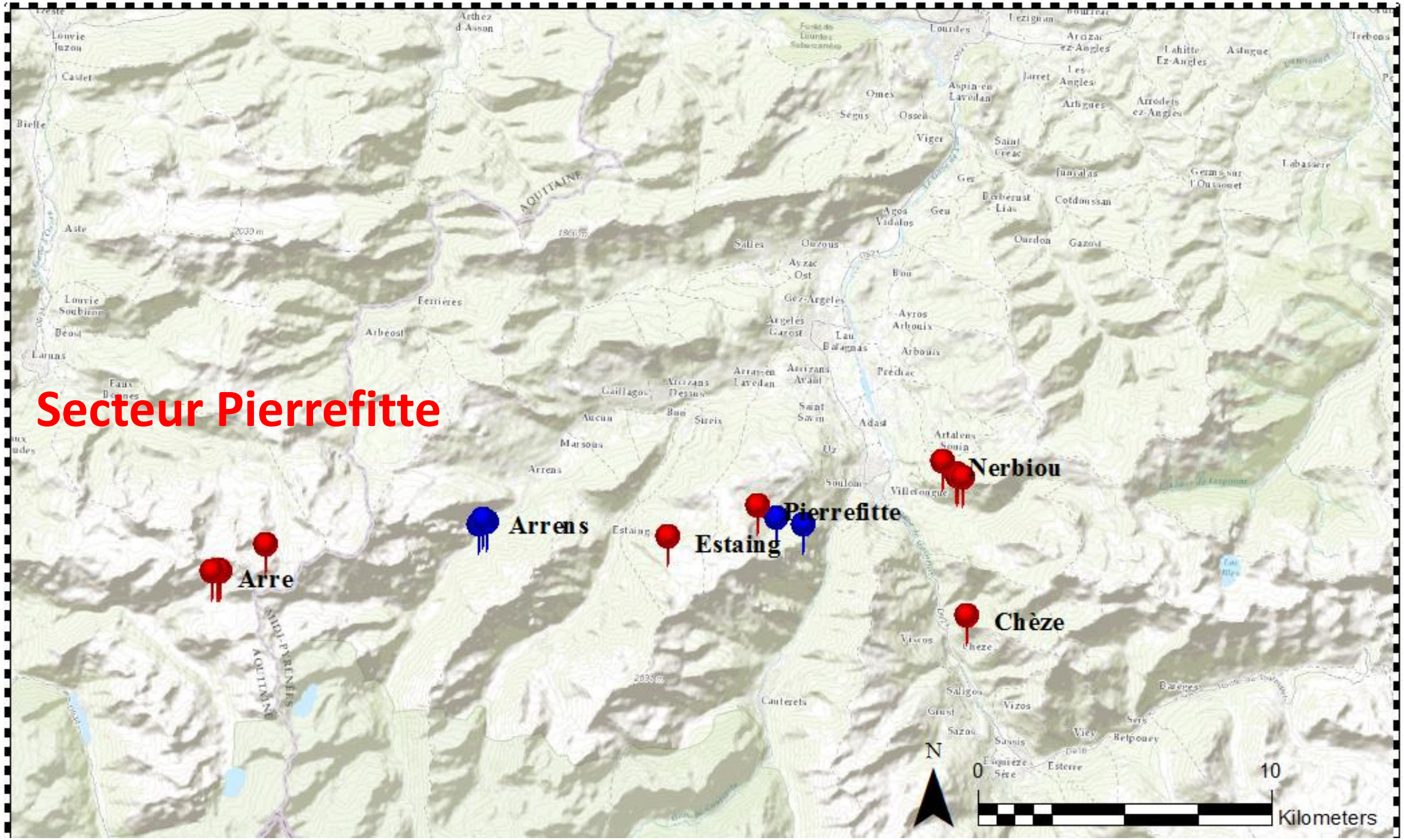
Microstructures

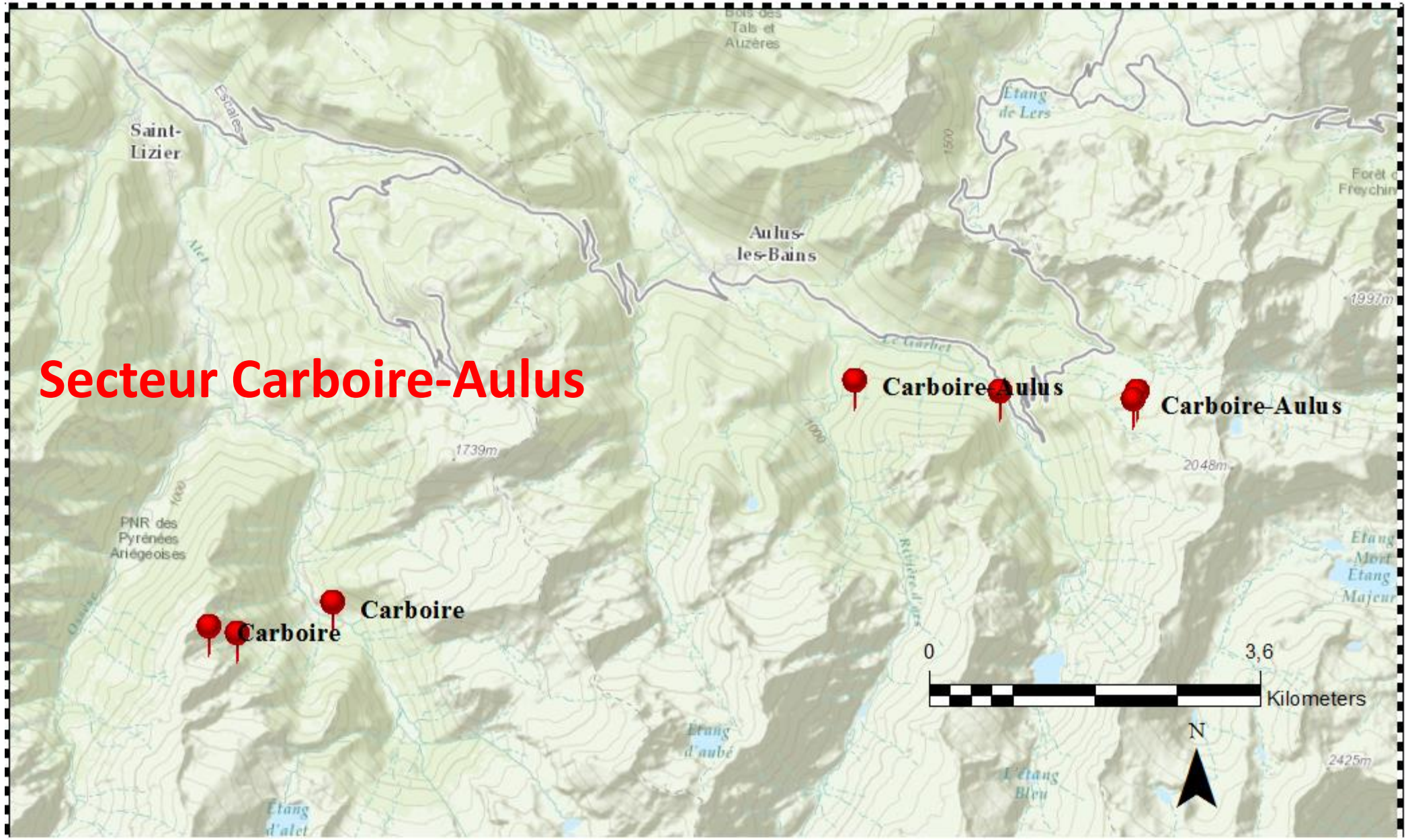
Microscopie - MEB - SEM-CL - NIR spectroscopy - EBSD

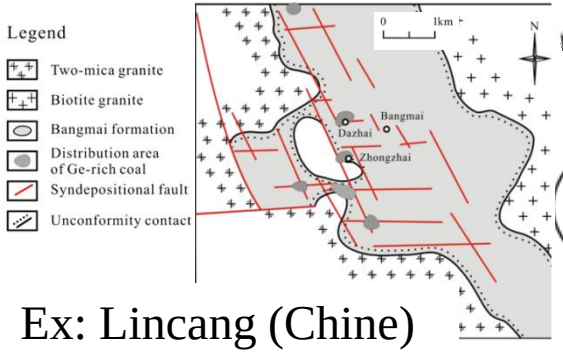
Merci pour votre attention


Perspectives
Dans toute la Z.A.
→Zones à gites Pb-Zn (possiblement) à étudier
Secteur Pierrefitte-Anglas
Secteur Bossost
Gavarnie ?
Secteur Lys
Secteur Pallaresa
Mont-Coustan
Zones Nord-Pyrénéennes?
Cadeillou
Gites non étudiés
Etudiés ou échantillonnés
Pau
Tarbes
HAUTES-PYRENEES
Saint Gaudens
Pamiers
ARIEGE
PYRENEES
FRANCE
SPAIN
Vielha E Mijaran
Andorra
MIDI-PYRENEES
Parque Natural Posets-Maladeta
Parc National d'Aigüestortes
Parc Natural Alt Pirineu
Sabiñanigo
HUESCA
P.N. Sierra y Cañones de Guara
Parc National des Pyrénées
N
0
40
Kilometers


Secteur Bossost
Marignac
Argut
Pale de Rase
Pale Bidau
Uls
Bentaillou
Mall de Bulard
Liat
Secteur Lys
Crabioules
Hospice de Fr
Hospice de Fr
Hospice de Fr
FRANCE
ESPAÑA SPAIN
N
0
10
Kilometers


Secteur Pierrefitte
Nerbiou
Pierrefitte
Arrens
Estaing
Arre
Chèze
N
0
10
Kilometers


Secteur Carboire-Aulus
Saint-Lizier
Aulus-les-Bains
Carboire-Aulus
Carboire-Aulus
Carboire
Carboire
PNR des Pyrénées Ariégeoises
1739m
2048m
1997m
2425m
Étang de Lers
Étang d'aubé
Étang d'alet
L'étang Bleu
Étang Mort
Étang Majeur
0
3,6
Kilometers
N

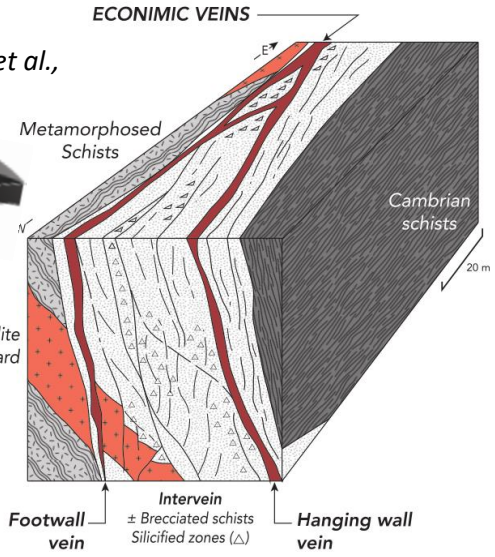


Ex: Lincang (Chine)

Qi, et al., 2011

Charbon et lignite
Bassin houiller
C ▲ 5500 ppm

Ex: Saint-Salvy (France) *Cassard et al., 1993*



Veins Ag-Pb-Zn(-Cu)
Filons minéralisés
ZnS ▲ 2580 ppm

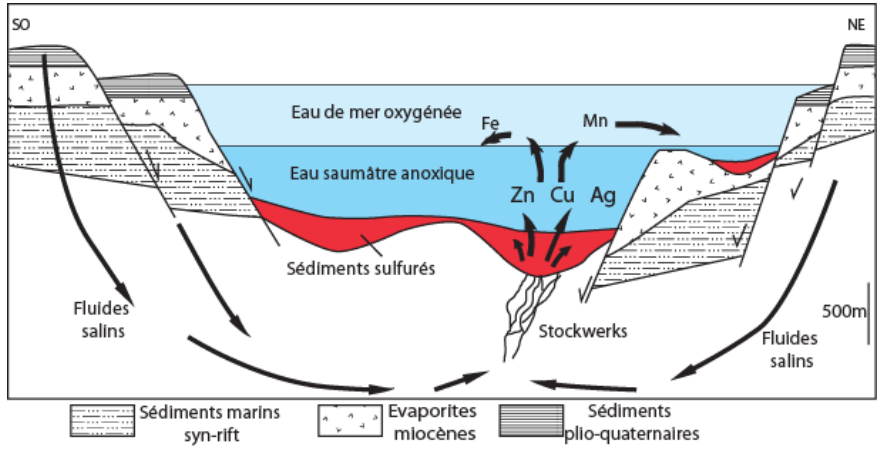
Volcanic Hosted massive sulphide (VHMS)
Volcanisme sous-marin
ZnS ou $CuFeS_2$ ▲ 5750 ppm

Pyrenean Axial Zone
?
Ge-minerals ▲ 70 %

Type Mississippi-Valley (MVT)
Fluides de bassin - épigénétique
ZnS ▲ 3200 ppm

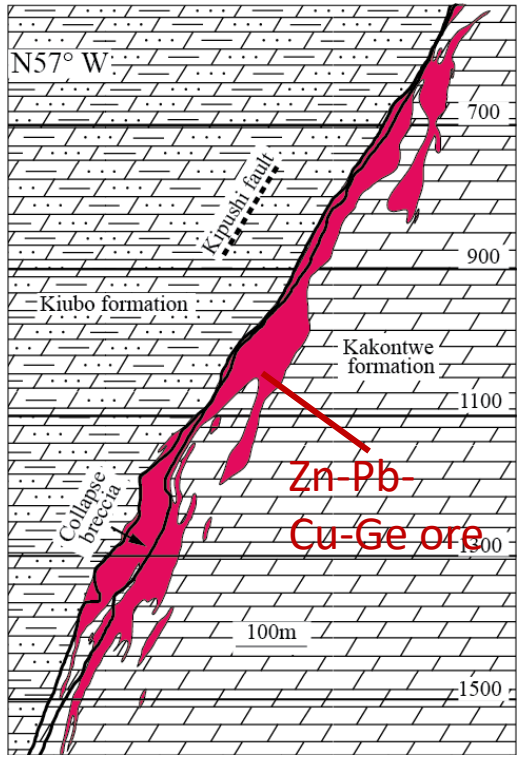
Sediment-hosted massive sulphide (SHMS)
Fluides de bassin - syngenetique
ZnS ▲ 720ppm

Kipushi-type
corps bréchiques minéralisés
Ge-minerals ▲ 30%

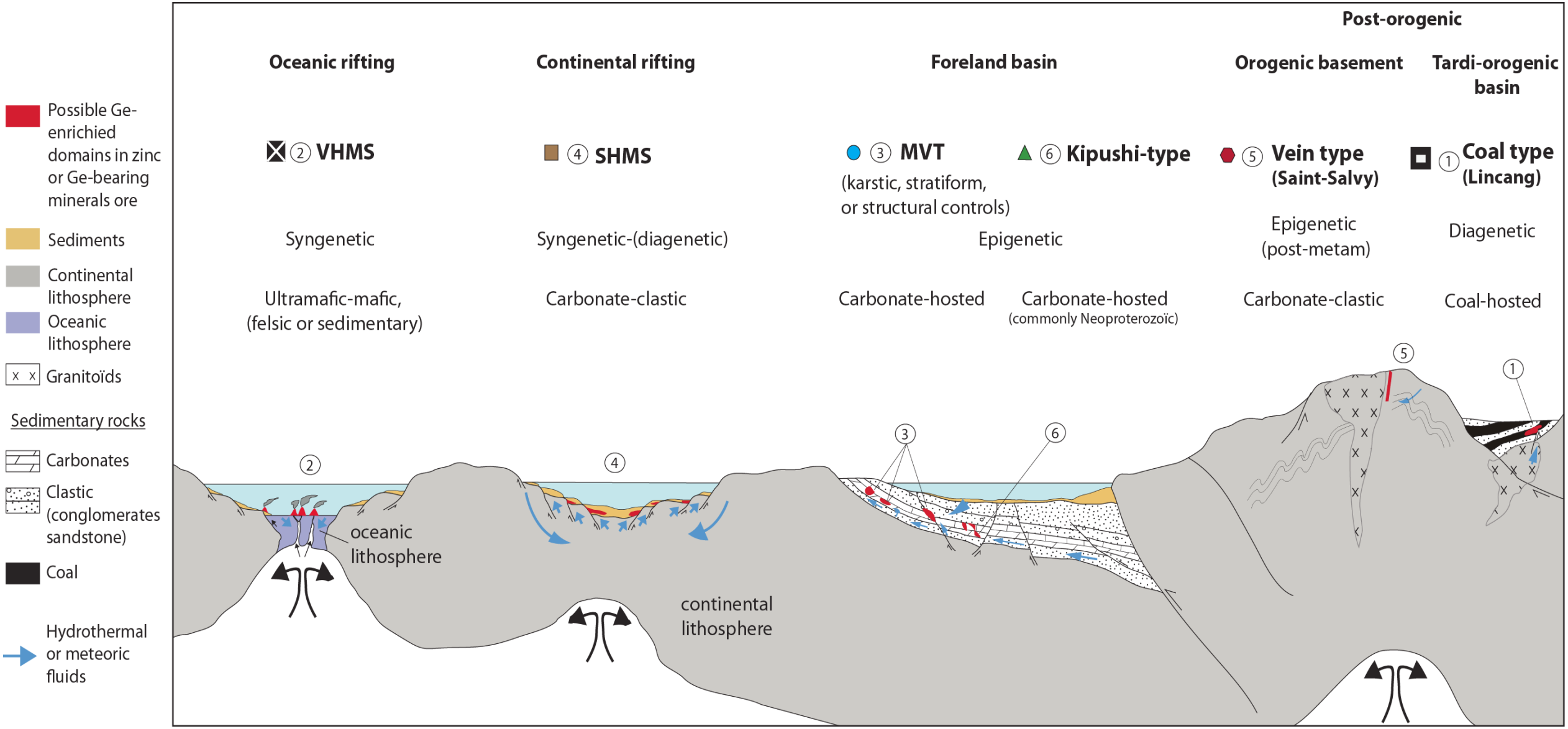


Ex type : Mer Rouge

Ex type : Kipushi (R.D. Congo)



Modified from Kampunzu, et al., 2009

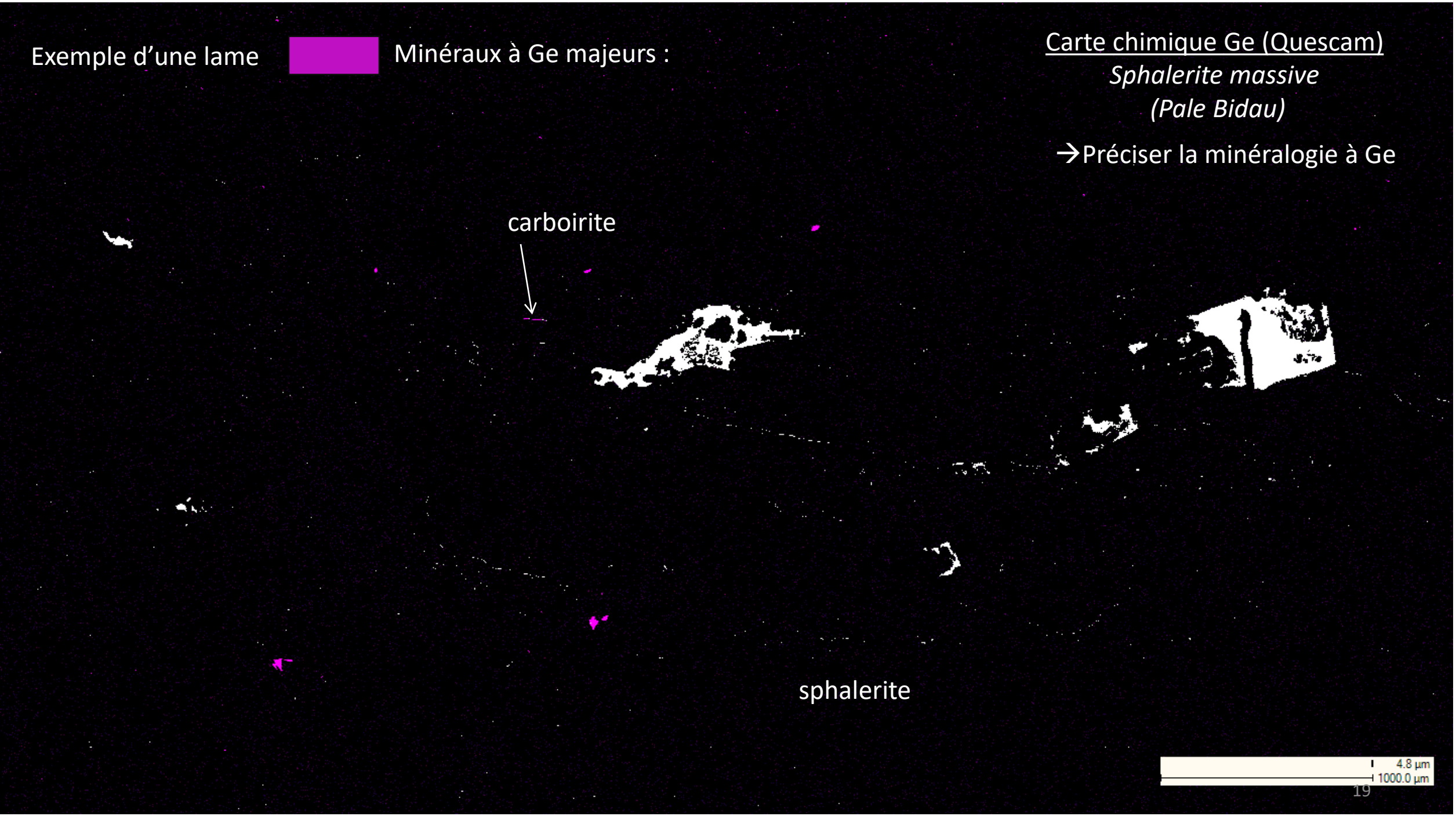

Post-orogenic
Oceanic rifting
Continental rifting
Foreland basin
Orogenic basement
Tardi-orogenic basin
Possible Ge-enrichied domains in zinc or Ge-bearing minerals ore
Sediments
Continental lithosphere
Oceanic lithosphere
Granitoïds
Sedimentary rocks
Carbonates
Clastic (conglomerates sandstone)
Coal
Hydrothermal or meteoric fluids
② VHMS
④ SHMS
③ MVT
(karstic, stratiform, or structural controls)
⑥ Kipushi-type
⑤ Vein type (Saint-Salvy)
① Coal type (Lincang)
Syngenetic
Syngenetic-(diagenetic)
Epigenetic
Epigenetic (post-metam)
Diagenetic
Ultramafic-mafic, (felsic or sedimentary)
Carbonate-clastic
Carbonate-hosted
Carbonate-hosted (commonly Neoproterozoïc)
Carbonate-clastic
Coal-hosted
oceanic lithosphere
continental lithosphere

Exemple d'une lame

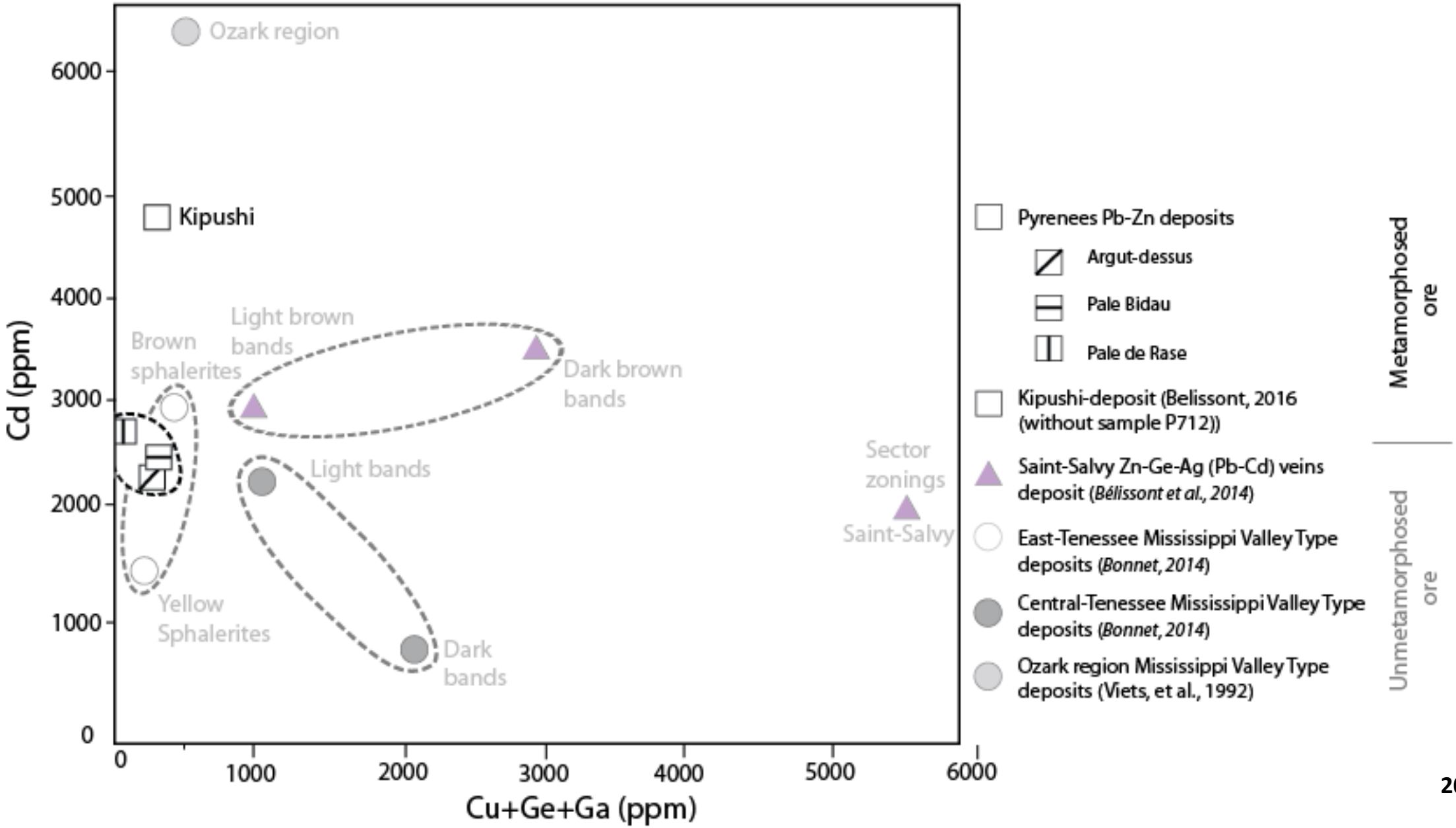
Minéraux à Ge majeurs :

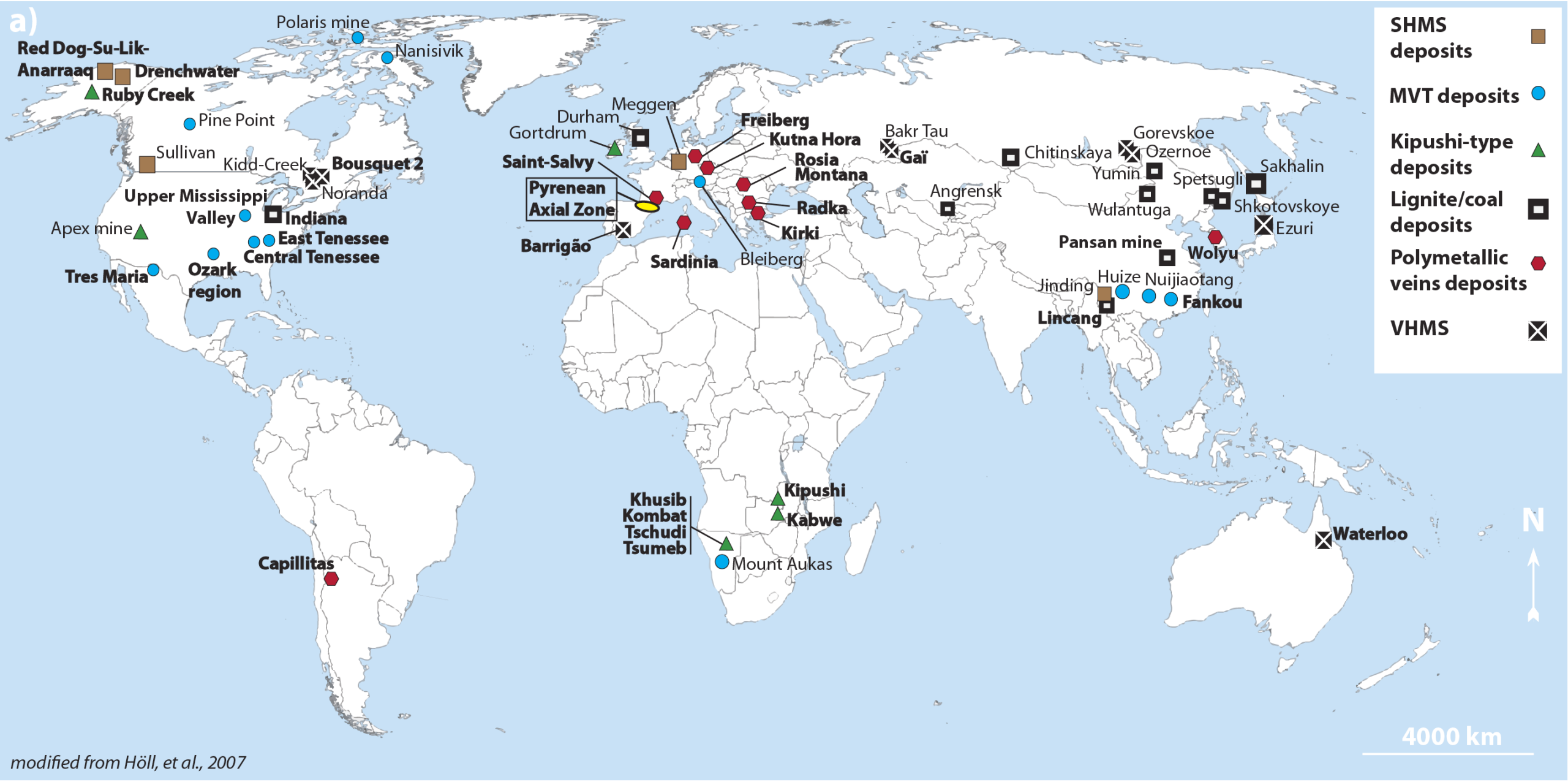
Carte chimique Ge (Quescam)
Sphalerite massive
(Pale Bidau)

→Préciser la minéralogie à Ge

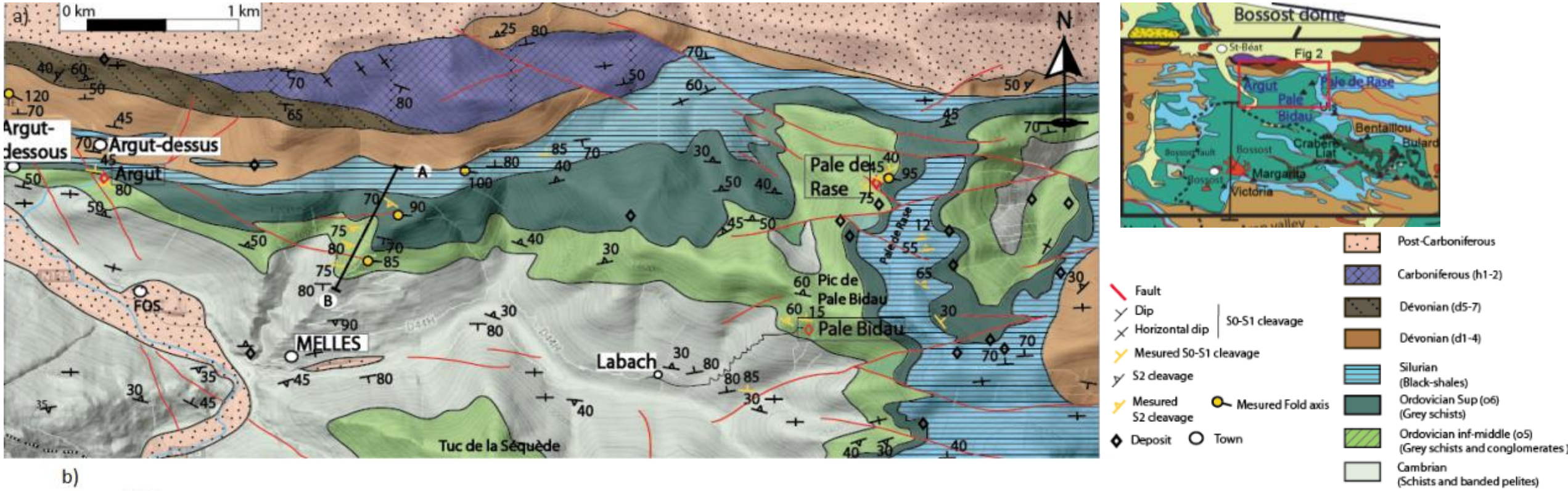


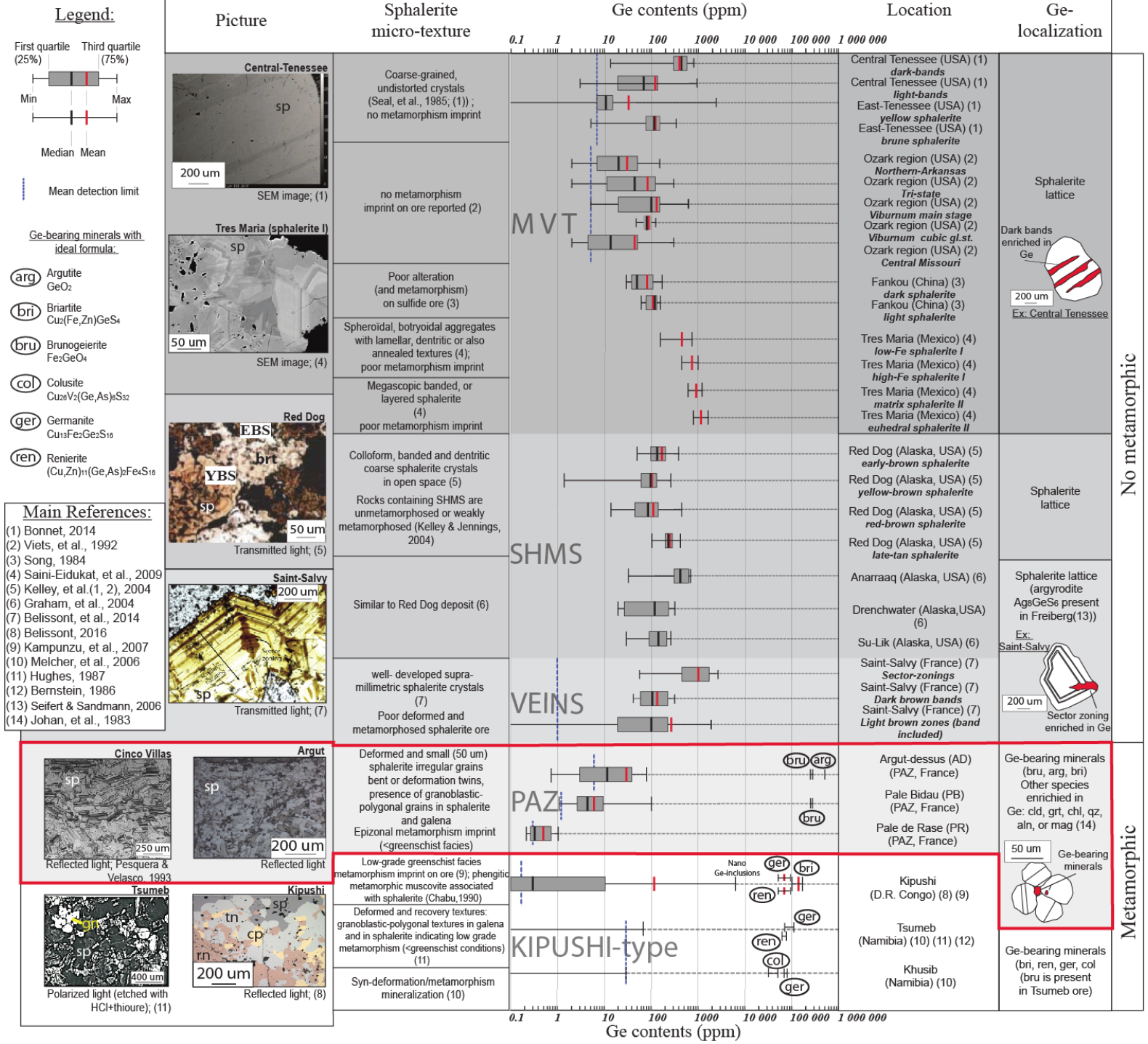
Comparaison des concentrations en Cu+Ge+Ga dans des sphalérites





modified from Höll, et al., 2007


a)
0 km
1 km
N
Argut-dessous
Argut-dessus
Argut
Pale de Rase
Pic de Pale Bidau
Pale Bidau
Labach
MELLES
FOS
Tuc de la Séquède
A
B
Bossost dome
St-Béat
Fig 2
Argut
Pale de Rase
Pale Bidau
Bentaillou
Bulard
Bossost
Crabère Liat
Margarita
Victoria
Fault
Dip
Horizontal dip
S0-S1 cleavage
Mesured S0-S1 cleavage
S2 cleavage
Mesured S2 cleavage
Mesured Fold axis
Deposit
Town
Post-Carboniferous
Carboniferous (h1-2)
Dévonian (d5-7)
Dévonian (d1-4)
Silurian (Black-shales)
Ordovician Sup (o6) (Grey schists)
Ordovician inf-middle (o5) (Grey schists and conglomerates)
Cambrian (Schists and banded pelites)
b)
B
SSW
A
NNE
dm-m sandstone layers
mm siltits bands-schists
S2 cleavage
fault
Argut-Pale de Rase deposits stratigraphic position
Pale Bidau deposit stratigraphic position
? decollement level on silurian black-schists
progressive thickness increase
1200m
1100m
1000m
900m


Legend:
First quartile (25%)
Third quartile (75%)
Min
Max
Median
Mean
Mean detection limit
Ge-bearing minerals with ideal formula:
arg Argutite GeO2
bri Briartite Cu2(Fe,Zn)GeS4
bru Brunogeierite Fe2GeO4
col Colusite Cu26V2(Ge,As)6S32
ger Germanite Cu13Fe2Ge2S16
ren Renierite (Cu,Zn)11(Ge,As)2Fe4S16
Main References:
(1) Bonnet, 2014
(2) Viets, et al., 1992
(3) Song, 1984
(4) Saini-Eidukat, et al., 2009
(5) Kelley, et al.(1, 2), 2004
(6) Graham, et al., 2004
(7) Belissont, et al., 2014
(8) Belissont, 2016
(9) Kampunzu, et al., 2007
(10) Melcher, et al., 2006
(11) Hughes, 1987
(12) Bernstein, 1986
(13) Seifert & Sandmann, 2006
(14) Johan, et al., 1983
Picture
Sphalerite micro-texture
Ge contents (ppm)
Location
Ge-localization
0.1
1
10
100
1000
10 000
100 000
1 000 000
Central-Tenessee
sp
200 um
SEM image; (1)
Tres Maria (sphalerite I)
sp
50 um
SEM image; (4)
Red Dog
EBS
brt
YBS
sp
50 um
Transmitted light; (5)
Saint-Salvy
200 um
sp
Transmitted light; (7)
Cinco Villas
sp
250 um
Reflected light; Pesquera & Velasco, 1993
Argut
sp
200 um
Reflected light
Tsumeb
gn
sp
400 um
Polarized light (etched with HCl+thioure); (11)
Kipushi
sp
tn
cp
rn
200 um
Reflected light; (8)
Coarse-grained, undistorted crystals (Seal, et al., 1985; (1)) ; no metamorphism imprint
no metamorphism imprint on ore reported (2)
Poor alteration (and metamorphism) on sulfide ore (3)
Spheroïdal, botryoidal aggregates with lamellar, dentritic or also annealed textures (4); poor metamorphism imprint
Megascopic banded, or layered sphalerite (4) poor metamorphism imprint
Colloform, banded and dentritic coarse sphalerite crystals in open space (5)
Rocks containing SHMS are unmetamorphosed or weakly metamorphosed (Kelley & Jennings, 2004)
Similar to Red Dog deposit (6)
well- developed supra-millimetric sphalerite crystals (7) Poor deformed and metamorphosed sphalerite ore
Deformed and small (50 um) sphalerite irregular grains bent or deformation twins, presence of granoblastic-polygonal grains in sphalerite and galena Epizonal metamorphism imprint (<greenschist facies)
Low-grade greenschist facies metamorphism imprint on ore (9); phengitic metamorphic muscovite associated with sphalerite (Chabu,1990)
Deformed and recovery textures: granoblastic-polygonal textures in galena and in sphalerite indicating low grade metamorphism (<greenschist conditions) (11)
Syn-deformation/metamorphism mineralization (10)
MVT
SHMS
VEINS
PAZ
KIPUSHI-type
bru
arg
bru
Nano Ge-inclusions
ger
bri
ren
ger
ren
col
ger
Central Tenessee (USA) (1) dark-bands
Central Tenessee (USA) (1) light-bands
East-Tenessee (USA) (1) yellow sphalerite
East-Tenessee (USA) (1) brune sphalerite
Ozark region (USA) (2) Northern-Arkansas
Ozark region (USA) (2) Tri-state
Ozark region (USA) (2) Viburnum main stage
Ozark region (USA) (2) Viburnum cubic gl.st.
Ozark region (USA) (2) Central Missouri
Fankou (China) (3) dark sphalerite
Fankou (China) (3) light sphalerite
Tres Maria (Mexico) (4) low-Fe sphalerite I
Tres Maria (Mexico) (4) high-Fe sphalerite I
Tres Maria (Mexico) (4) matrix sphalerite II
Tres Maria (Mexico) (4) euhedral sphalerite II
Red Dog (Alaska, USA) (5) early-brown sphalerite
Red Dog (Alaska, USA) (5) yellow-brown sphalerite
Red Dog (Alaska, USA) (5) red-brown sphalerite
Red Dog (Alaska, USA) (5) late-tan sphalerite
Anarraaq (Alaska, USA) (6)
Drenchwater (Alaska,USA) (6)
Su-Lik (Alaska, USA) (6)
Saint-Salvy (France) (7) Sector-zonings
Saint-Salvy (France) (7) Dark brown bands
Saint-Salvy (France) (7) Light brown zones (band included)
Argut-dessus (AD) (PAZ, France)
Pale Bidau (PB) (PAZ, France)
Pale de Rase (PR) (PAZ, France)
Kipushi (D.R. Congo) (8) (9)
Tsumeb (Namibia) (10) (11) (12)
Khusib (Namibia) (10)
Sphalerite lattice
Dark bands enriched in Ge
200 um
Ex: Central Tenessee
Sphalerite lattice
Sphalerite lattice (argyrodite Ag8GeS6 present in Freiberg(13))
Ex: Saint-Salvy
200 um
Sector zoning enriched in Ge
Ge-bearing minerals (bru, arg, bri) Other species enrichied in Ge: cld, grt, chl, qz, aln, or mag (14)
50 um
Ge-bearing minerals
Ge-bearing minerals (bri, ren, ger, col (bru is present in Tsumeb ore)
No metamorphic
Metamorphic
Ge contents (ppm)