Spodumene-dominant pegmatite (Adagói)

RESSOURCES 21
International Congress
METALS FOR ELECTRIC MOBILITY
Li Ni Co Mn REE
Nancy, France, September 19 to 20, 2023
UNIVERSITÉ DE LORRAINE cnrs INRAE

Lithium and rare metal granites in Portugal

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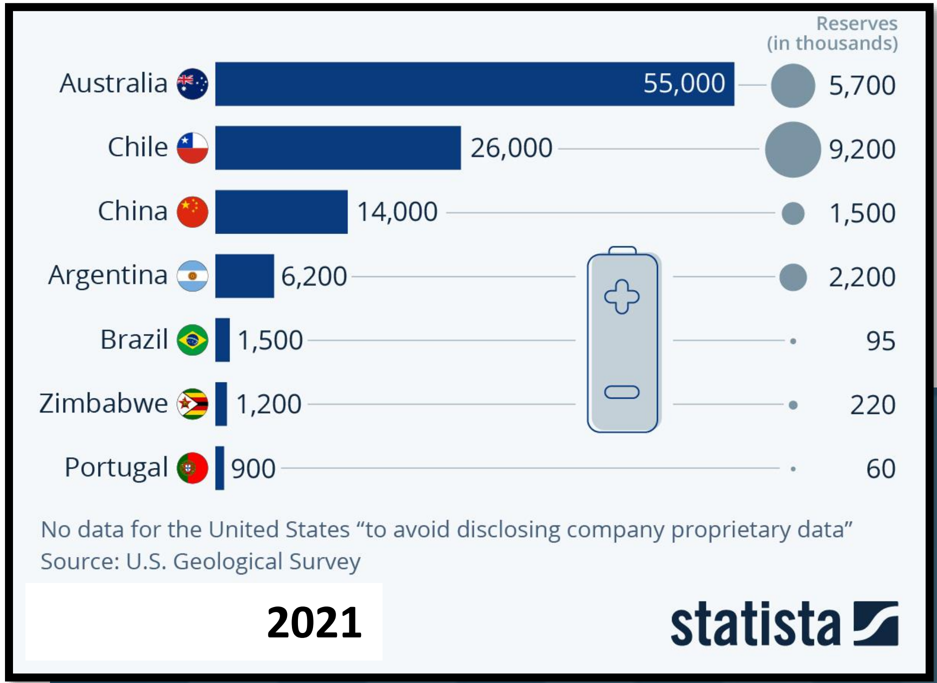
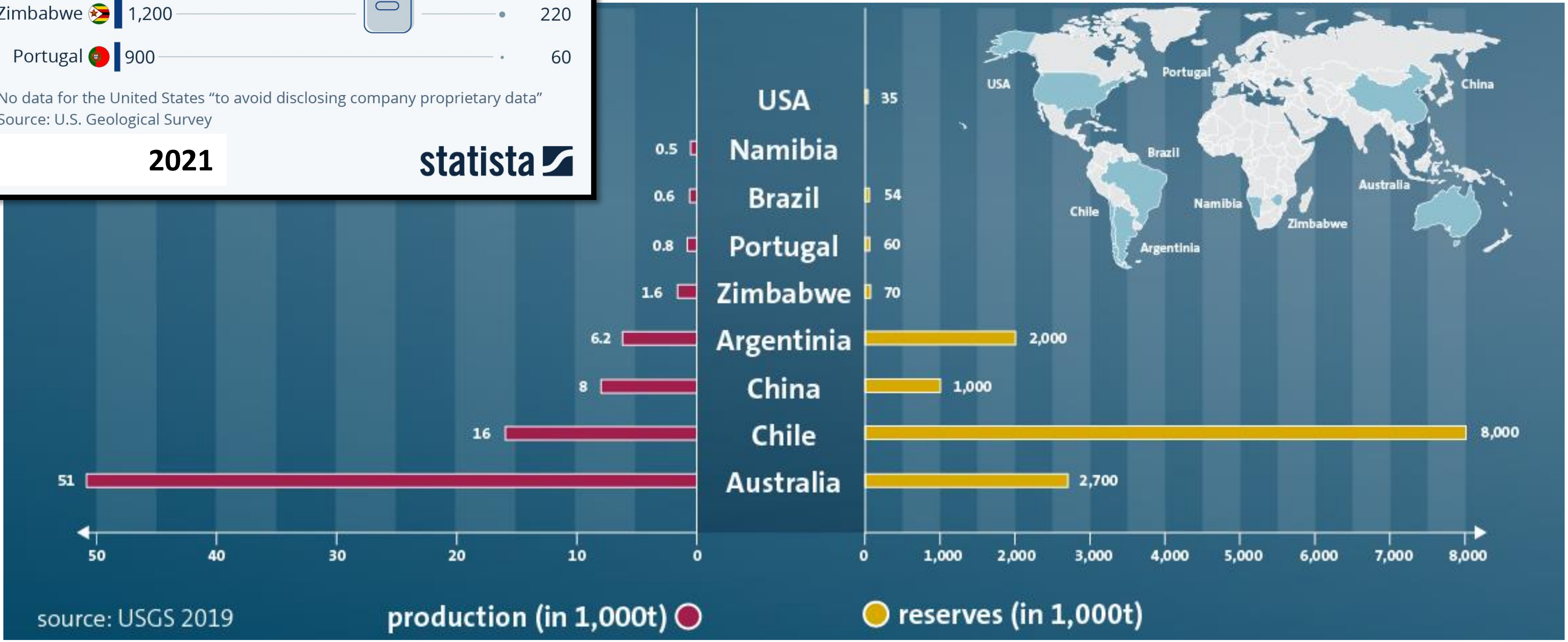
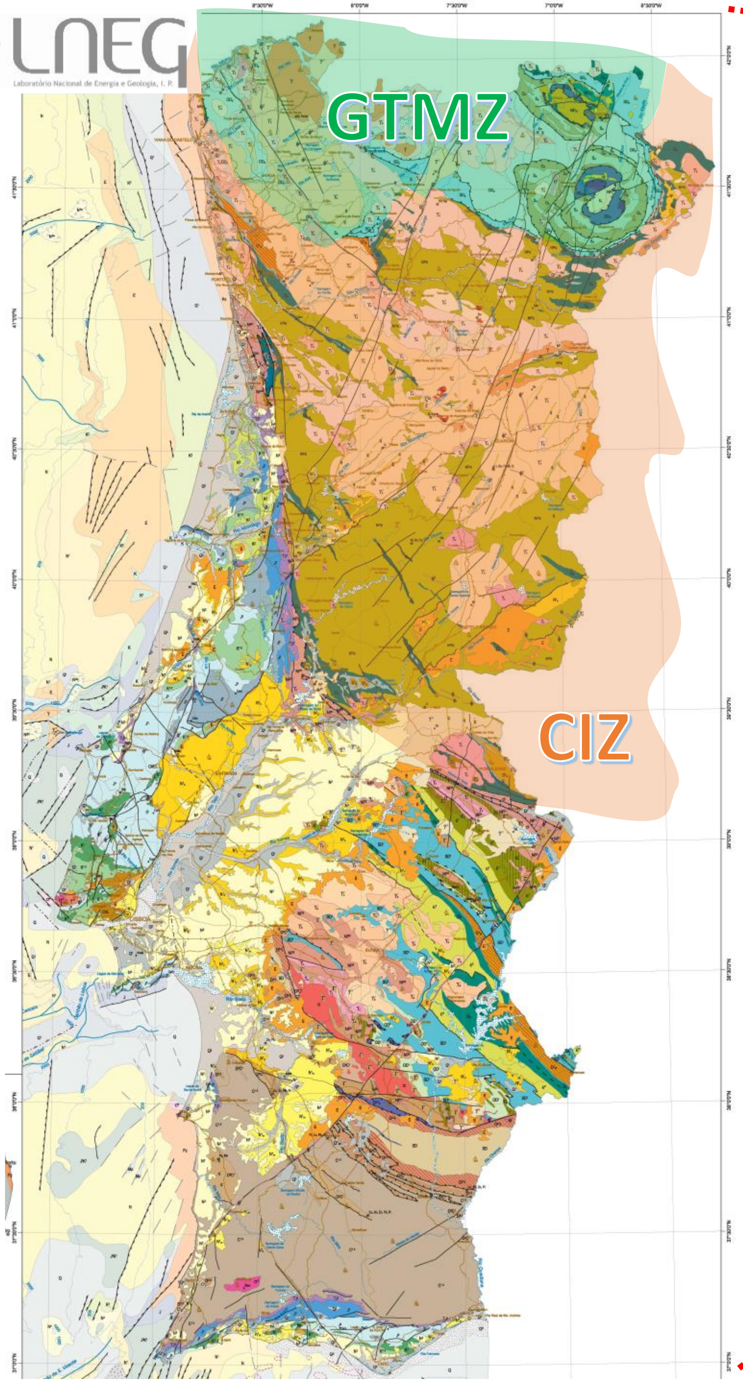
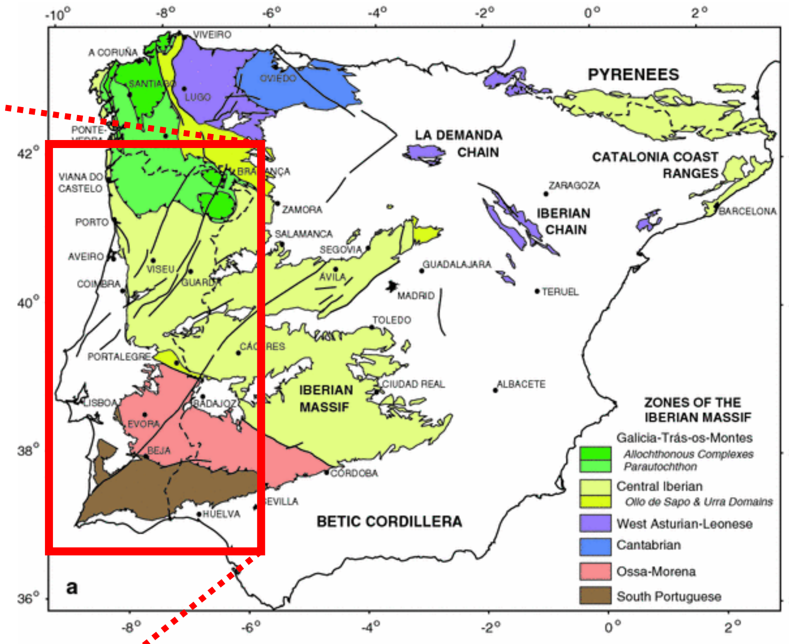
Ciências ULisboa
INSTITUTO DOM LUIZ

- Official inventory (2018): 306 kt Li-resources (in ≈71Mt of LCT aplite-pegmatite rocks); 53 kt as Li-reserves.
- Increasing these figures might be possible as implied by known exposures; but grades/tonnages and mineralogy vary significantly.





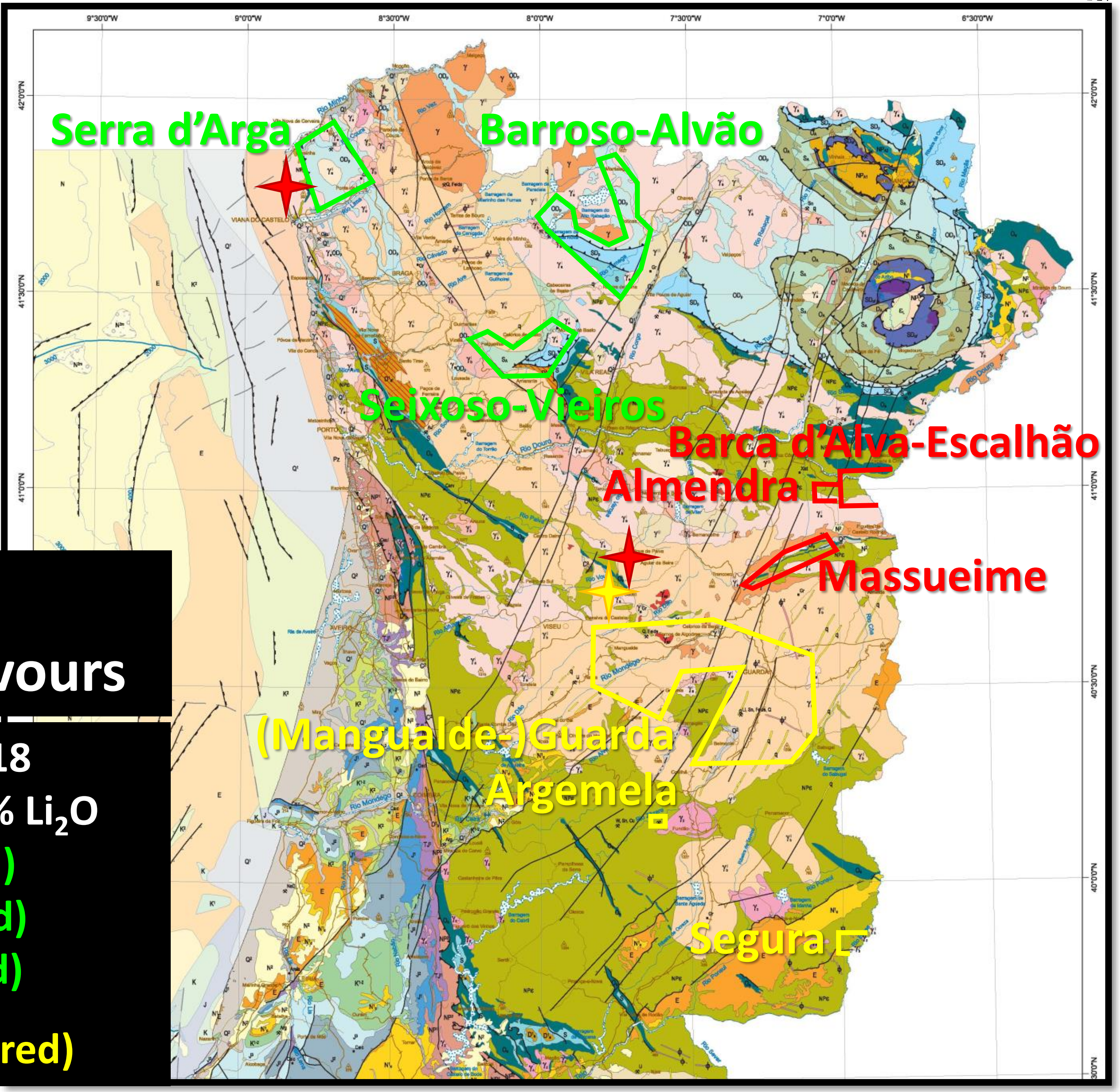




Adapted from
https://doi.org/10.1007/s00531-011-0715-6

Li-resources confined to various subtypes of LCT lodes:

- ***GTMZ*** – mostly petalite- or spodumene-dominant aplite-pegmatite bodies with poor internal differentiation, hosted in metasedimentary units of the Parautochthon.
- ***CIZ*** – mostly peri-granite (in different units of the Autochthon – Douro or Beiras Groups) or intra-granite aplite-pegmatite bodies variably enriched in Li-bearing micas and/or phosphates; occasional metasomatized leucogranite cupolas and quartz-lodes with Li-phosphates.

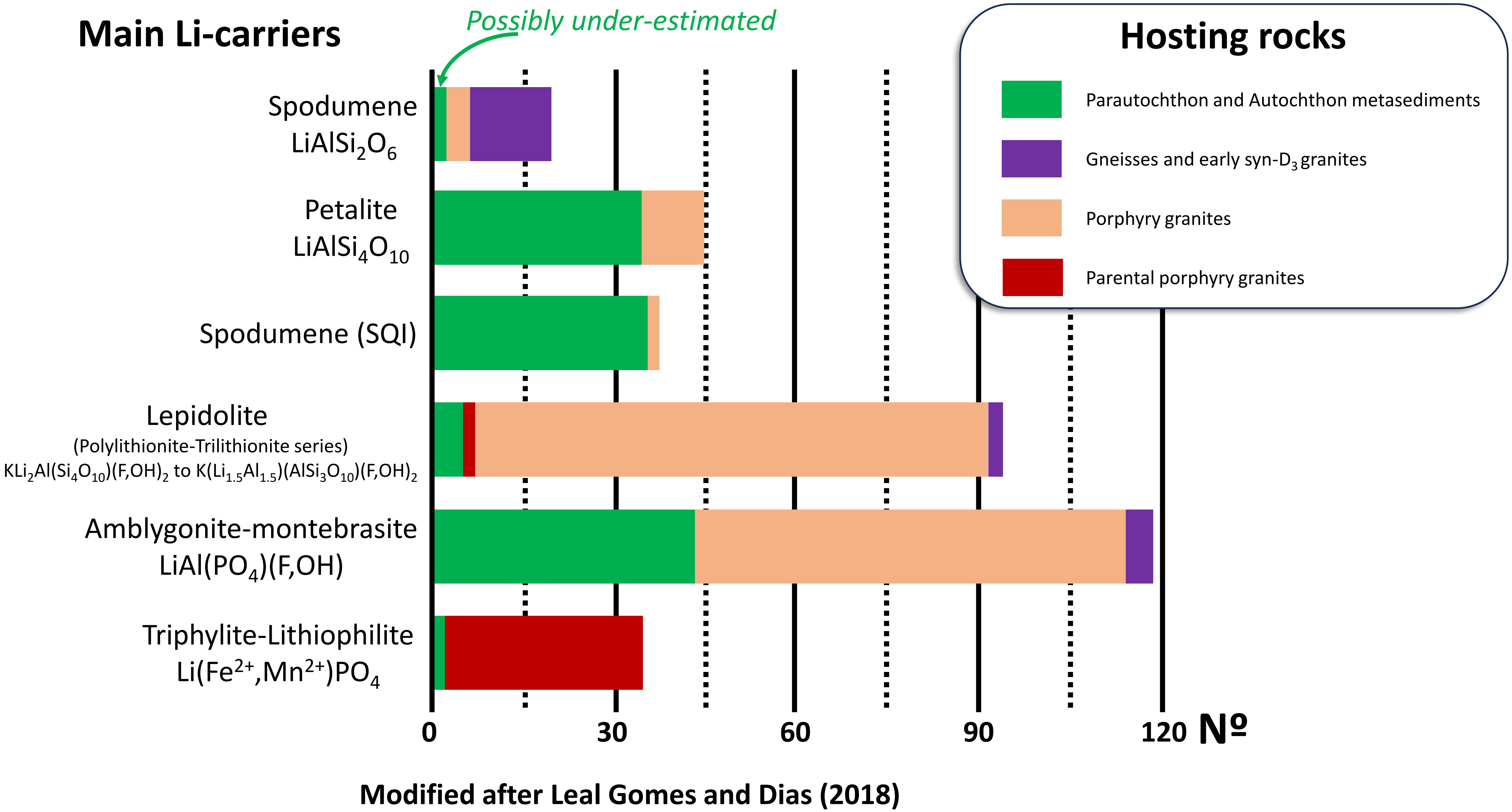


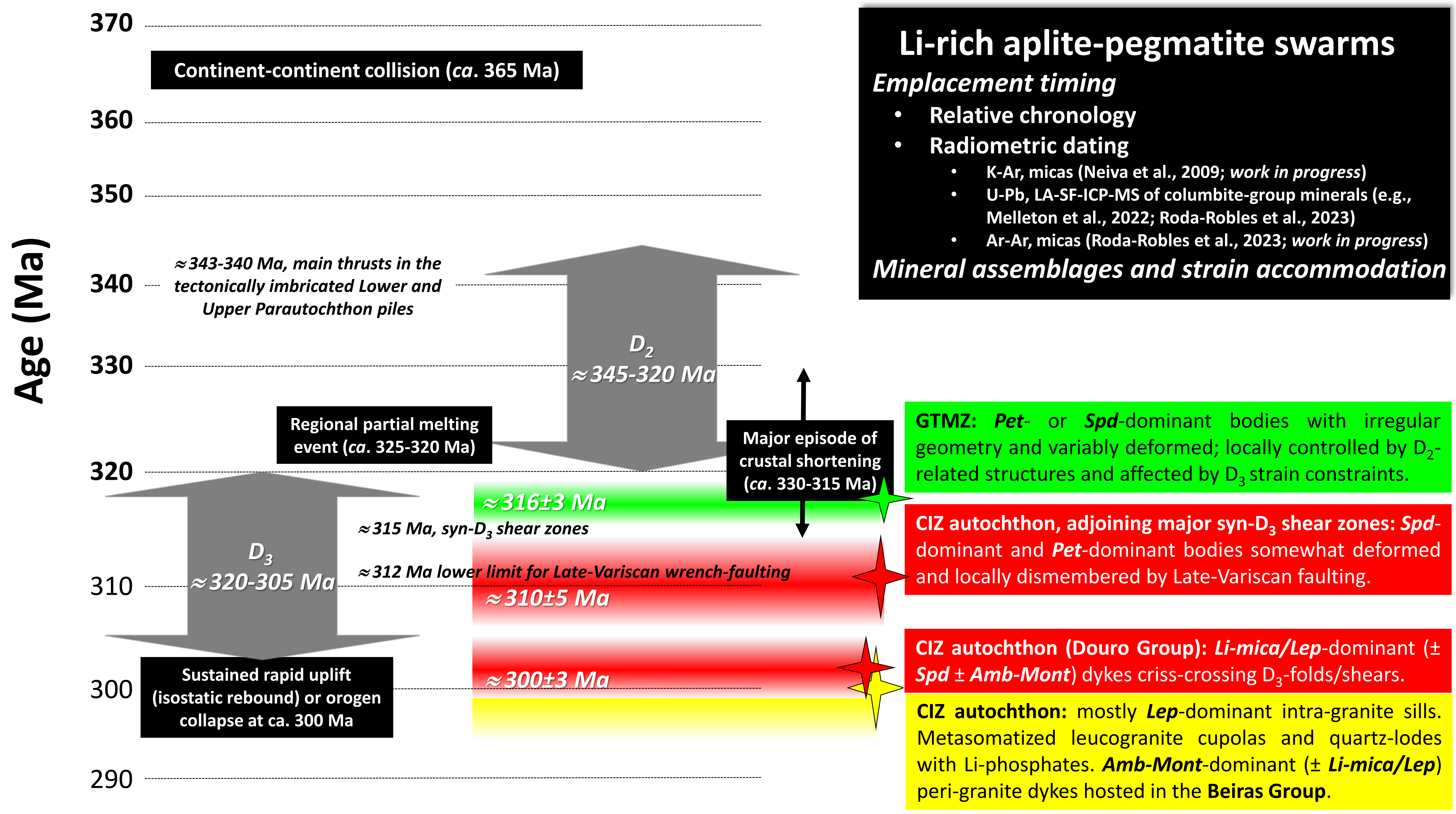
9 high potential areas for exploration/exploitation endeavours

Resources for the main 5 prospects, 2018 (excluding Argemela): 29.74 Mt @ 0.81 wt% Li_2O

- 16.80 Mt @ 0.88 wt% Li_2O (inferred)
- 12.30 Mt @ 0.68 wt% Li_2O (indicated)
- 0.64 Mt @ 1.50 wt% Li_2O (measured)

Argemela: 20.10 Mt @ 0.4 wt% Li_2O (inferred)

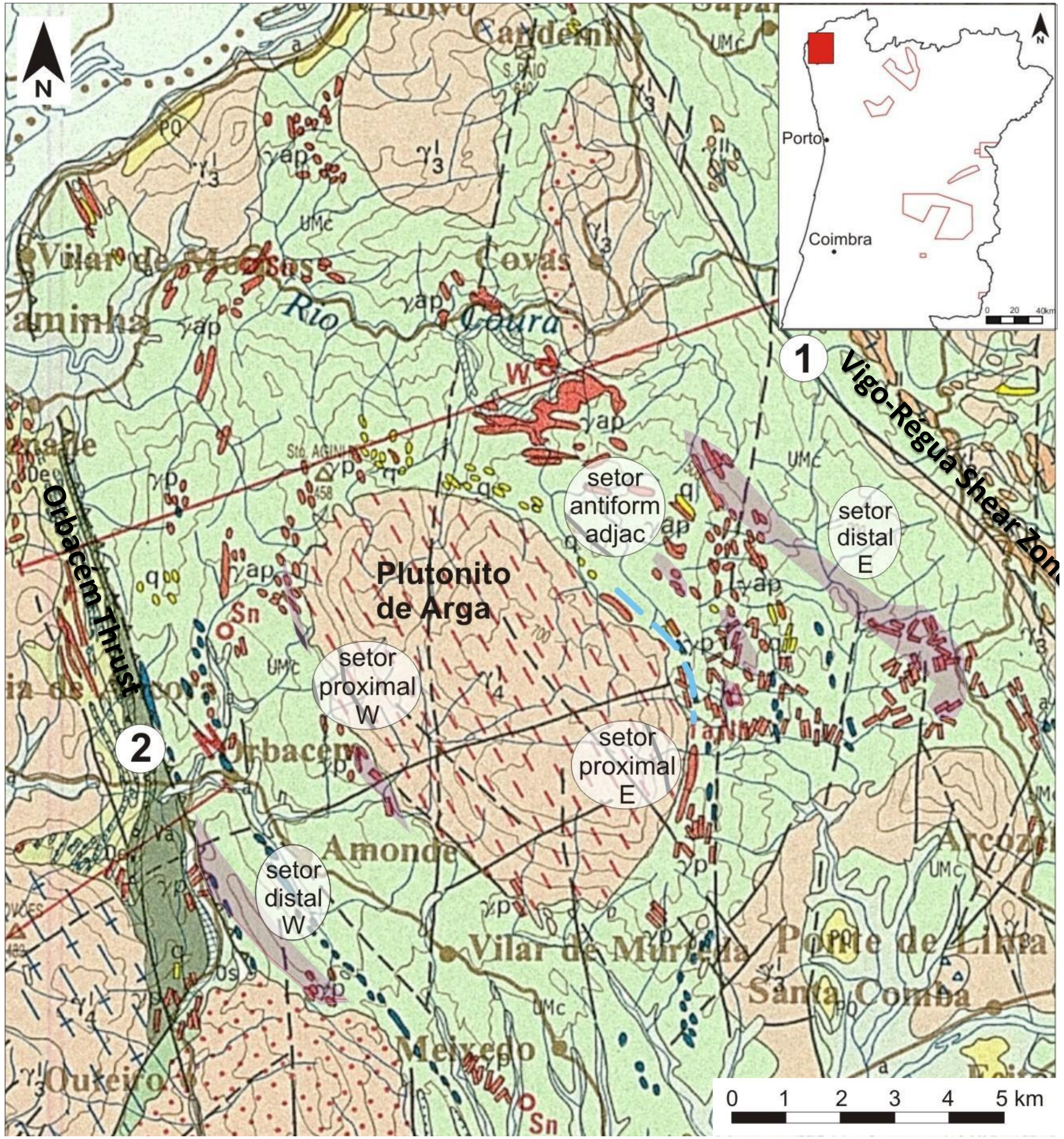

Main Li-carriers
Possibly under-estimated
Spodumene
$LiAlSi_2O_6$
Petalite
$LiAlSi_4O_{10}$
Spodumene (SQI)
Lepidolite
(Polylithionite-Trilithionite series)
$KLi_2Al(Si_4O_{10})(F,OH)_2$ to $K(Li_{1.5}Al_{1.5})(AlSi_3O_{10})(F,OH)_2$
Amblygonite-montebrasite
$LiAl(PO_4)(F,OH)$
Triphylite-Lithiophilite
$Li(Fe^{2+},Mn^{2+})PO_4$
0
30
60
90
120
Nº
Hosting rocks
Parautochthon and Autochthon metasediments
Gneisses and early syn-D_3 granites
Porphyry granites
Parental porphyry granites
Modified after Leal Gomes and Dias (2018)



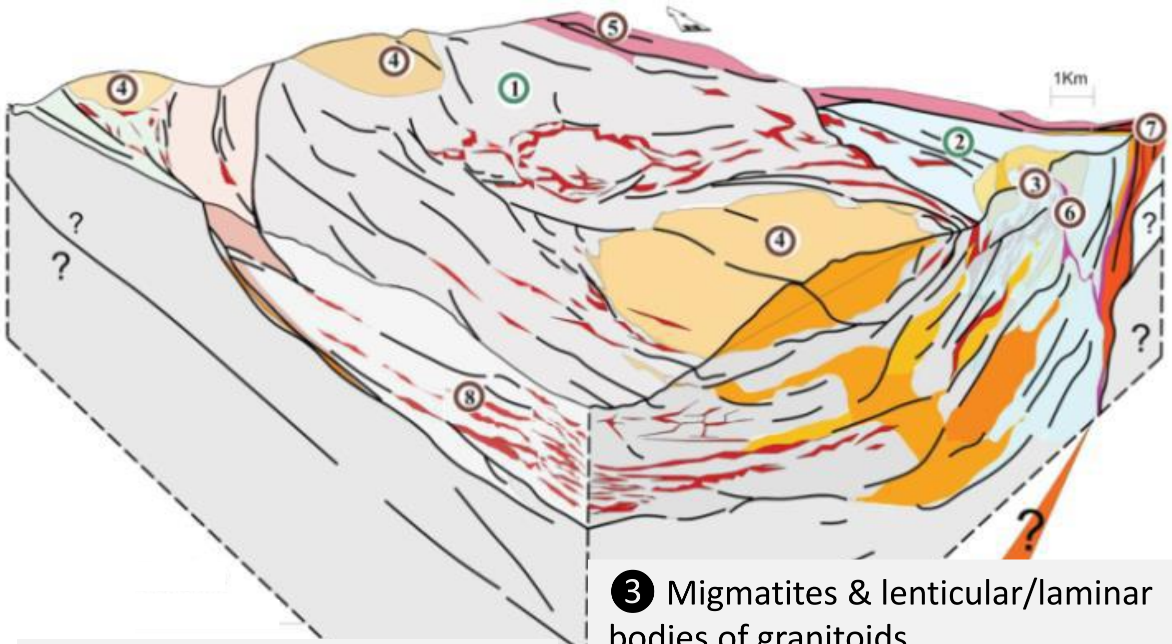
Age (Ma)
370
360
350
340
330
320
310
300
290
Continent-continent collision (ca. 365 Ma)
≈343-340 Ma, main thrusts in the tectonically imbricated Lower and Upper Parautochthon piles
D$_2$
≈345-320 Ma
Regional partial melting event (ca. 325-320 Ma)
Major episode of crustal shortening (ca. 330-315 Ma)
D$_3$
≈320-305 Ma
≈316±3 Ma
≈315 Ma, syn-D$_3$ shear zones
≈312 Ma lower limit for Late-Variscan wrench-faulting
≈310±5 Ma
≈300±3 Ma
Sustained rapid uplift (isostatic rebound) or orogen collapse at ca. 300 Ma
Li-rich aplite-pegmatite swarms
Emplacement timing
• Relative chronology
• Radiometric dating
• K-Ar, micas (Neiva et al., 2009; work in progress)
• U-Pb, LA-SF-ICP-MS of columbite-group minerals (e.g., Melleton et al., 2022; Roda-Robles et al., 2023)
• Ar-Ar, micas (Roda-Robles et al., 2023; work in progress)
Mineral assemblages and strain accommodation
GTMZ: Pet- or Spd-dominant bodies with irregular geometry and variably deformed; locally controlled by D$_2$-related structures and affected by D$_3$ strain constraints.
CIZ autochthon, adjoining major syn-D$_3$ shear zones: Spd-dominant and Pet-dominant bodies somewhat deformed and locally dismembered by Late-Variscan faulting.
CIZ autochthon (Douro Group): Li-mica/Lep-dominant (± Spd ± Amb-Mont) dykes criss-crossing D$_3$-folds/shears.
CIZ autochthon: mostly Lep-dominant intra-granite sills. Metasomatized leucogranite cupolas and quartz-lodes with Li-phosphates. Amb-Mont-dominant (± Li-mica/Lep) peri-granite dykes hosted in the Beiras Group.

Aplite-pegmatite bodies hosted in Parautochthon metasediments

Serra d'Arga



Leal Gomes (1995, 2005); Leal Gomes and Dias (2018)



SILURIAN

❶ Metasediments, locally incorporating volcanogenic and exhalative components.

❷ Metasedimentary-exhalative succession.

❸ Migmatites & lenticular/laminar bodies of granitoids.

❹ Early syn-D_3 two-mica peraluminous granites.

❺ Hybridised granites.

❻ Granodioritic facies.

❼ Syn- to late-D_3 granites (emplacement controlled by the Vigo-Régua Shear Zone).

❽ Aplite-pegmatite bodies (irregular geometry; controlled by D_2-related structures and affected by D_3).

Qz + Kf (± Ab)
+ Pet + Spd
± Ms ± Amb/Mont ± Cst ± Ta(-Nb) oxides

Aplite-pegmatite bodies hosted in Parautochthon metasediments

Serra d'Arga

Kf (± Ab) + Qz + Pet

(Pet → Euc + 3Qz)

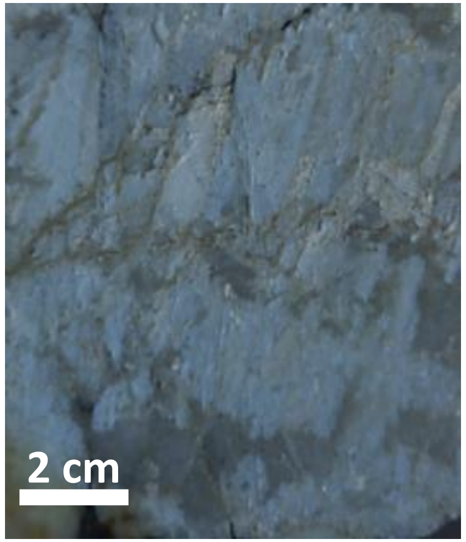
Pet → Spd + 2Qz (= SQI)

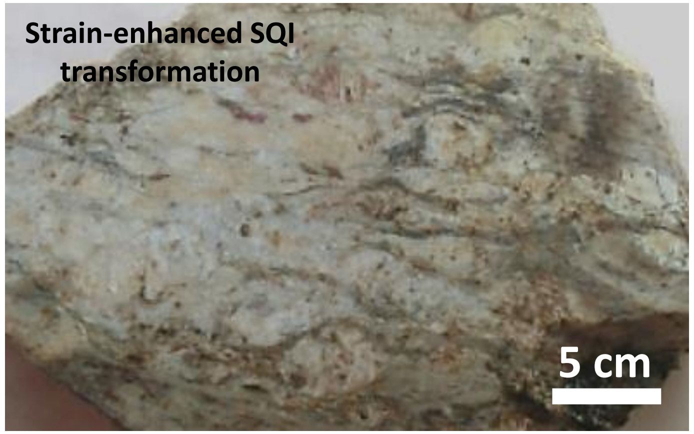
(Spd → Bk)

Spd + H^+ + H_2O = Ck + SiO_2 (kaolinite or illite ± montmorillonite)

TIME

SQI pseudomorphic transformation of petalite (palisade texture)



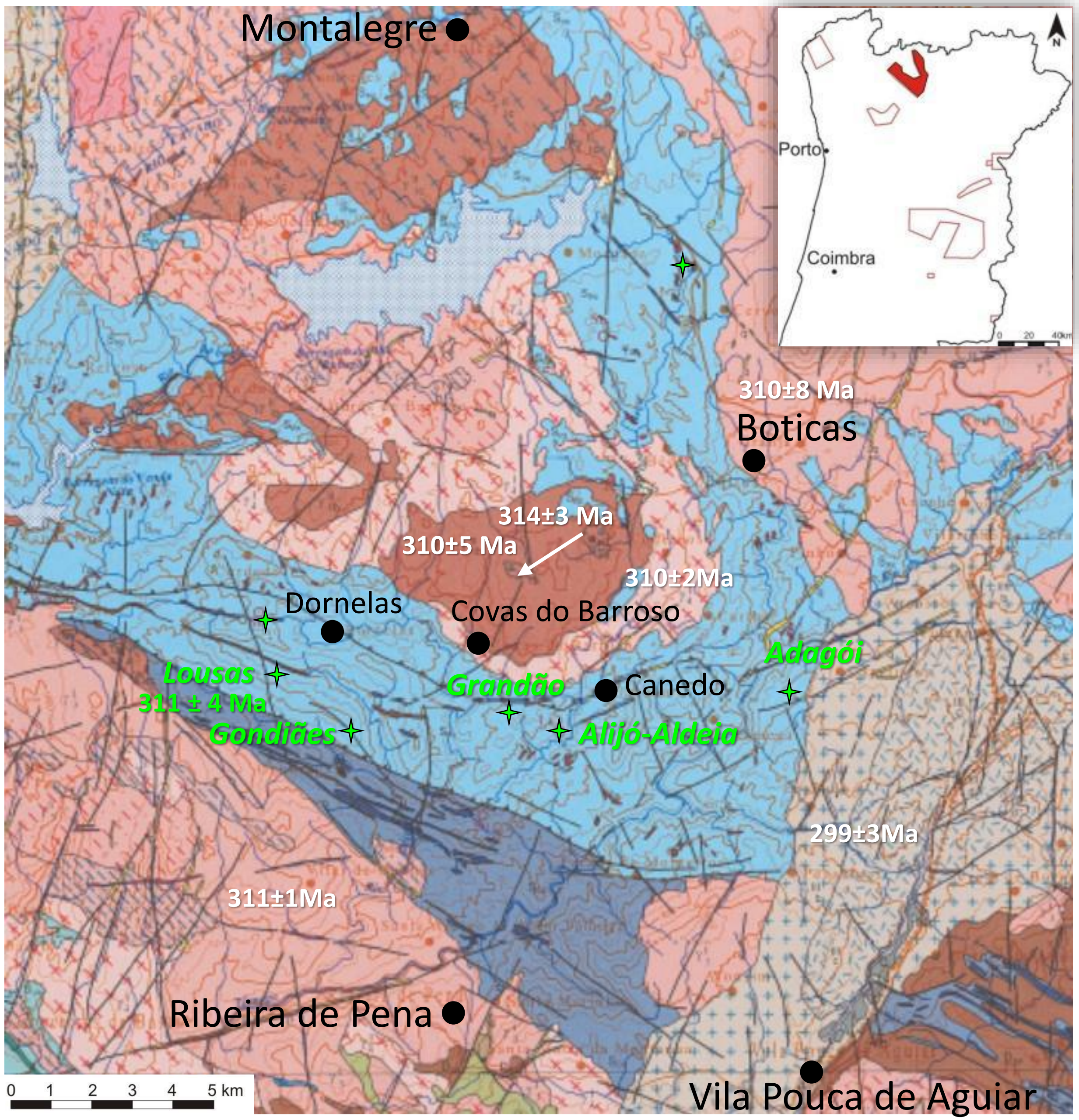


Petalite (Pet) = $LiAlSi_4O_{10}$
Spodumene (Spd) = $LiAlSi_2O_6$
Eucryptite (Euc) = $LiAlSiO_4$

Bikitaite (Bk)= $LiAlSi_2O_6 \cdot H_2O$
Cookeite (Ck) = $(LiAl_4\square)[AlSi_3O_{10}](OH)_8$

Aplite-pegmatite bodies hosted in Parautochthon metasediments

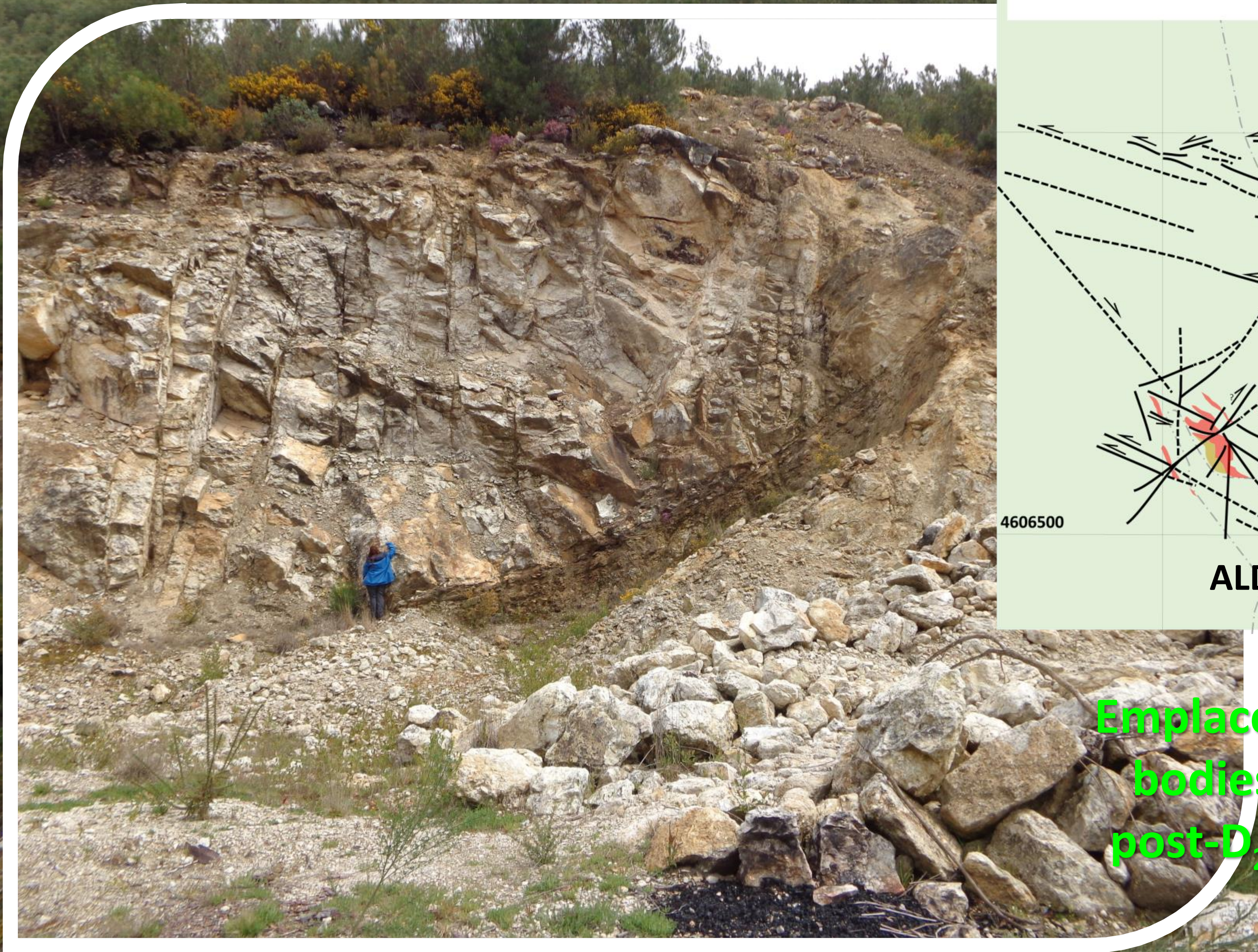
Barroso-Alvão

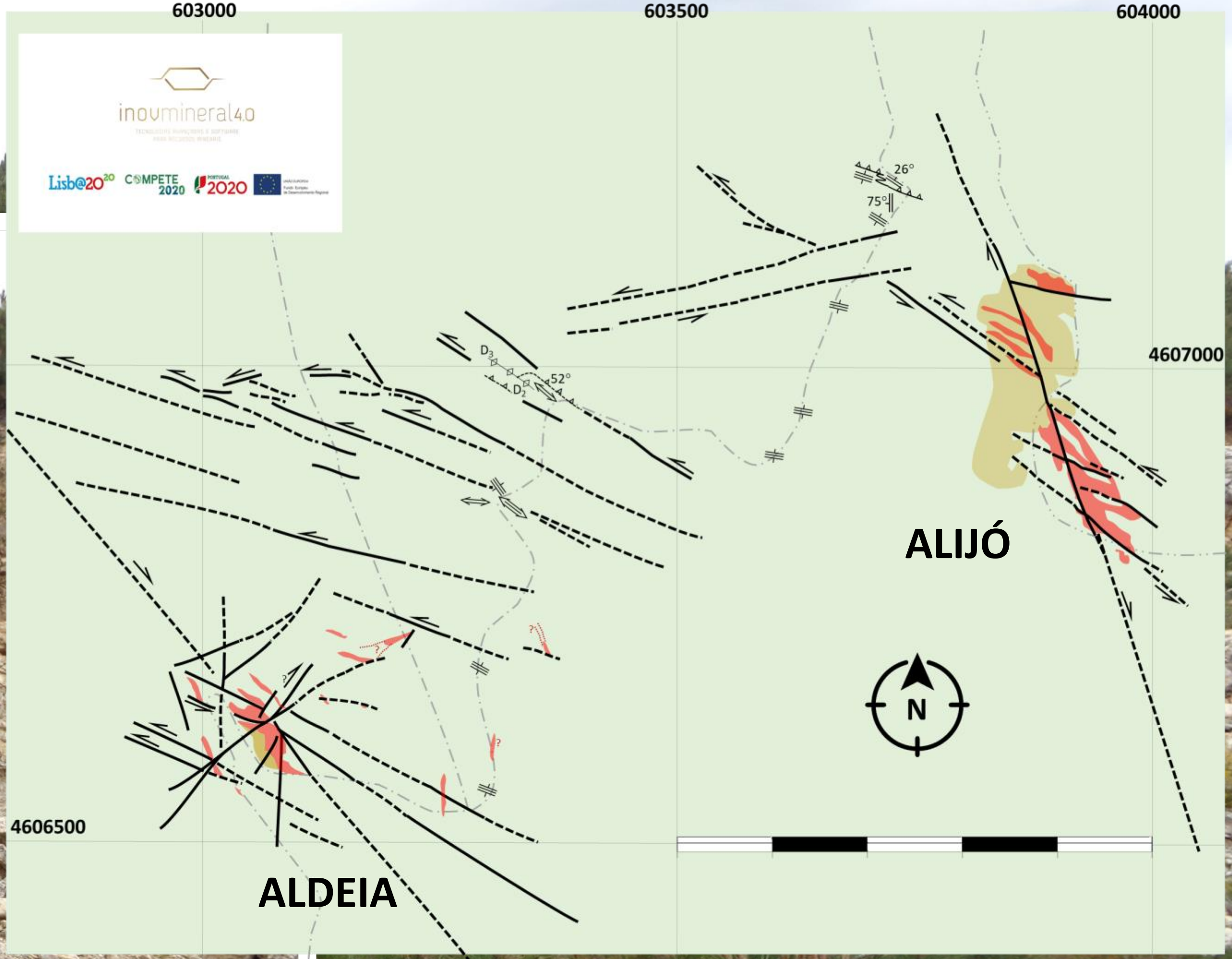


- Charoy et al., 1992, 2001;
- Farinha and Lima, 2000;
- Lima, 2000;
- Noronha et al., 2006;
- Bobos et al. 2007;
- Martins, 2009;
- Martins and Lima, 2011;
- Martins et al., 2011;
- Dias et al., 2019

(Rare Lep-bearing lodes)

ALDEIA main body (*Spd-dominant*)





Emplacement of Li-rich (aplite-)pegmatite bodies should be placed in the late- to post-D_2 timeframe, clearly preceding D_3.

Barroso-Alvão

Spd-dominant bodies (TYPE 1)

First crystallization stage

- Qz (± Ab I) + Kf + (Ms I) ± beryl ± apatite ± Fe-Mn(-Li) phosphates

Second crystallization stage (significant Na-enrichment)

- Spd II + Ab II + Qz II + Ms II ± Mont ± Ta(-Nb) oxides
- [Pet II, after Spd – ***TYPE 2***]

Late metasomatic/hydrothermal processes

- Secondary phosphates ± cookeite ± clay minerals

Adagói

Thin film of Pet around Spd

Aplite-pegmatite bodies hosted in Parautochthon metasediments

Barroso-Alvão

Pet-dominant bodies (TYPE 3)

First crystallization stage

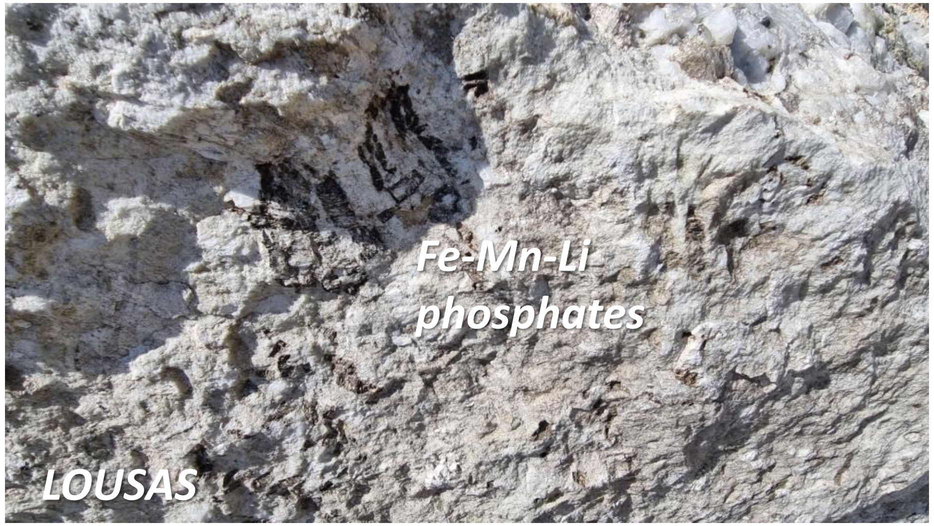
- Qz + Kf + Pet ± Spd (incipient SQI) ± Cst ± Ta(-Nb) oxides

Second crystallization stage (significant Na-enrichment)

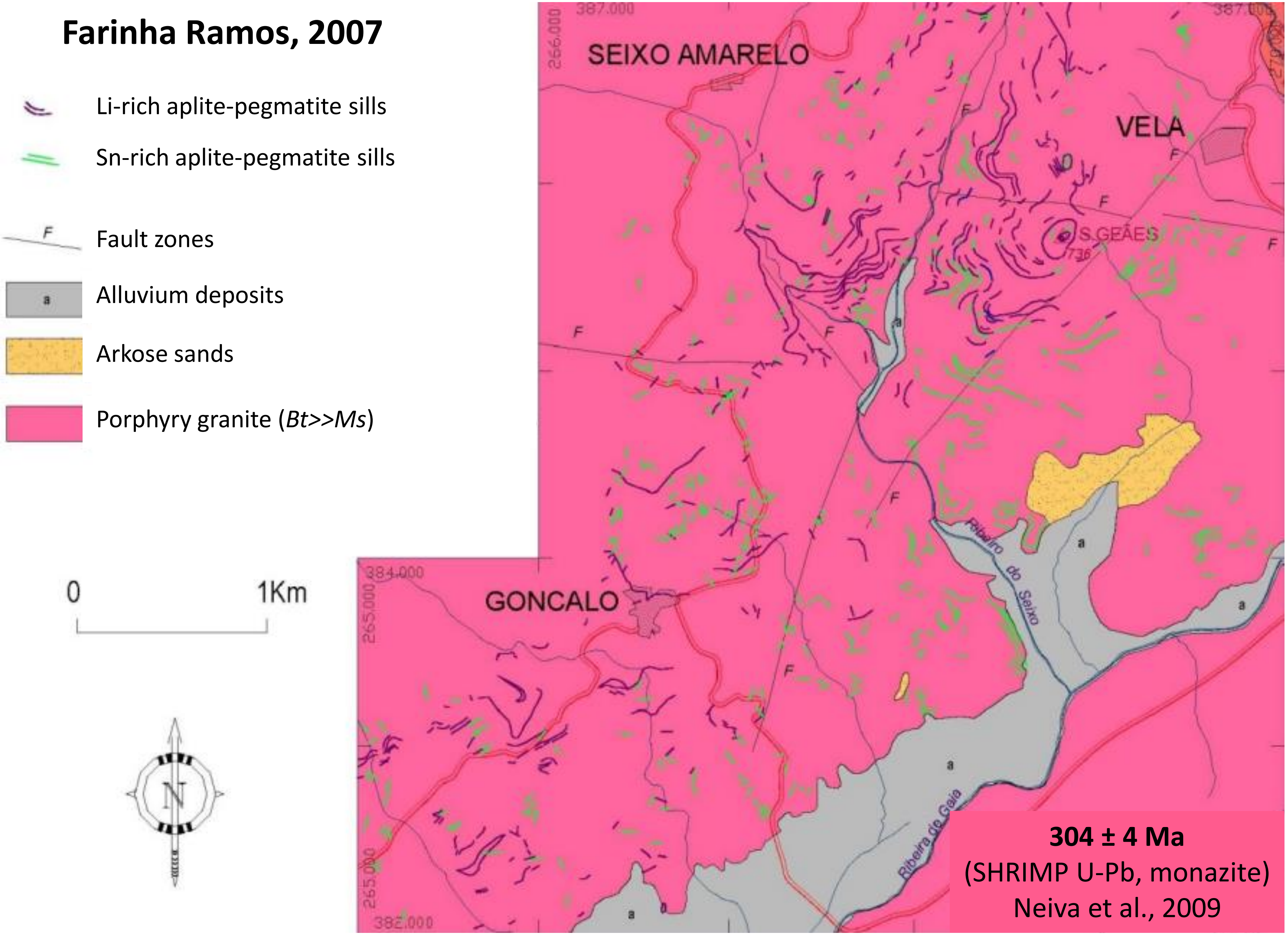
- Ab II + Qz II (± Spd) + Ms II ± Euc ± Fe-Mn-Li phosphates
- [strain-enhanced SQI → Spd ↑ = ***TYPE 4***]

Late metasomatic/hydrothermal processes

- Secondary phosphates ± cookeite ± clay minerals



Farinha Ramos, 2007



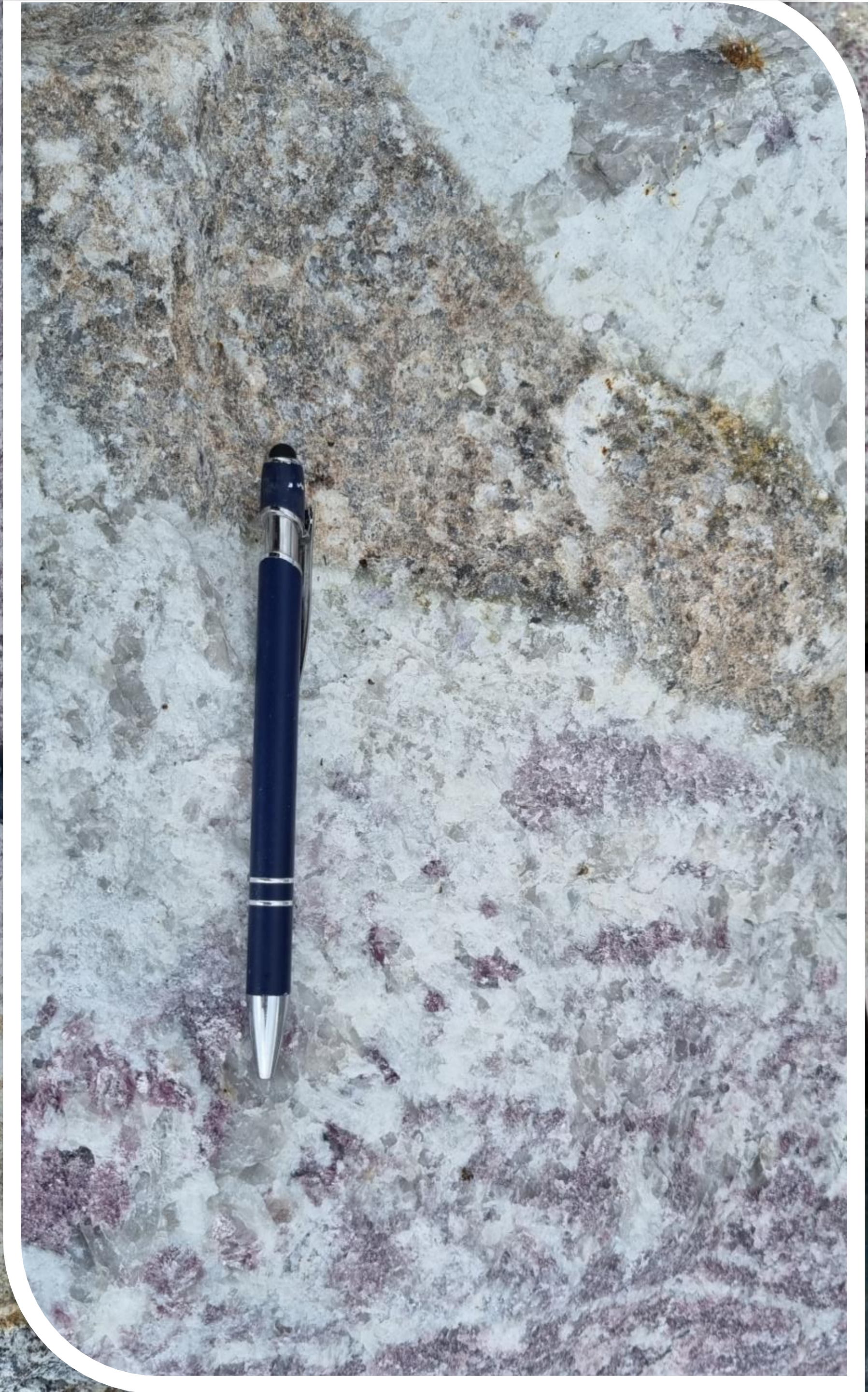
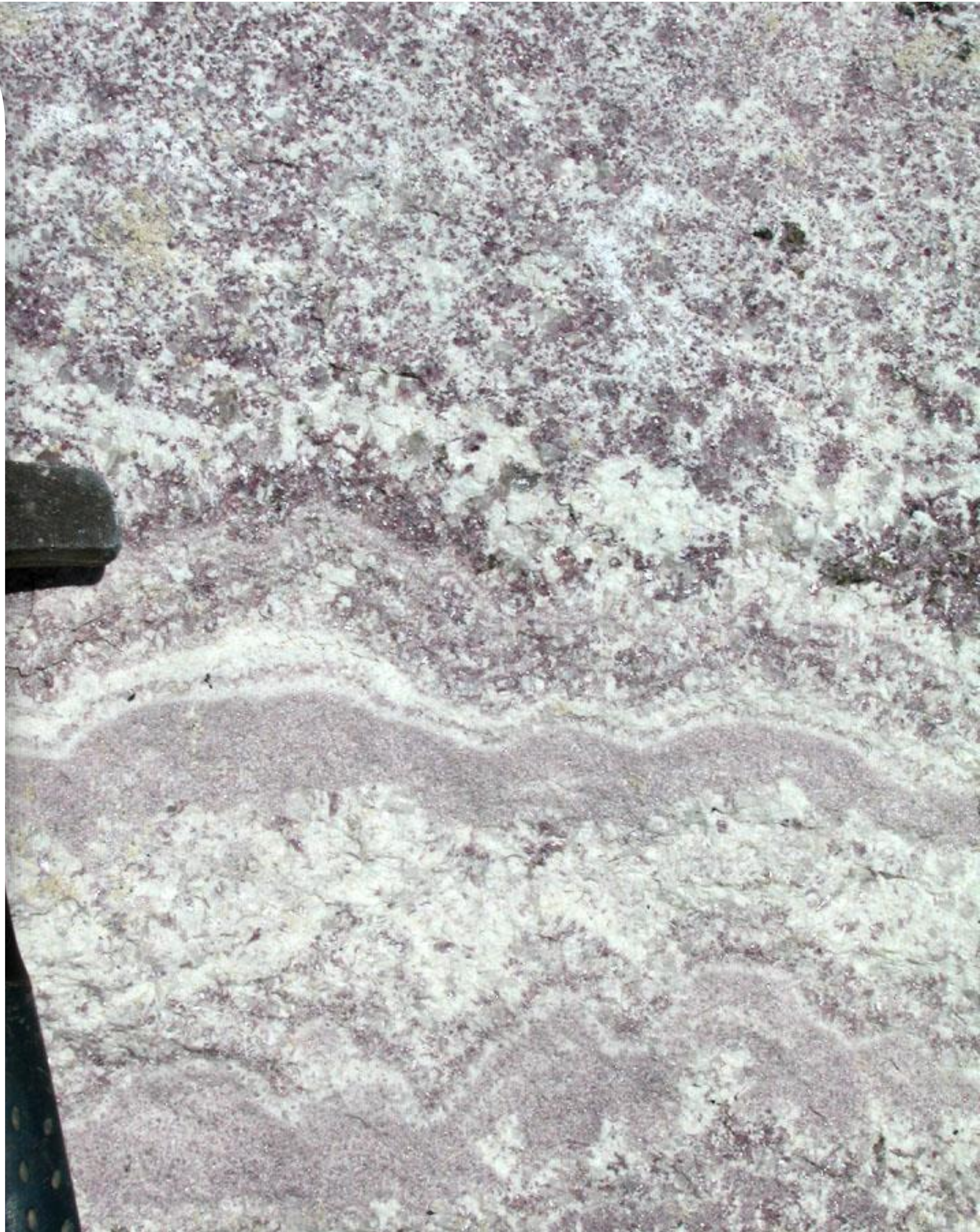
Lepidolite-rich pegmatites:

- 301±3 Ma (Ar-Ar, *Ms*)
- 270-277 Ma (K-Ar, *Lep*).

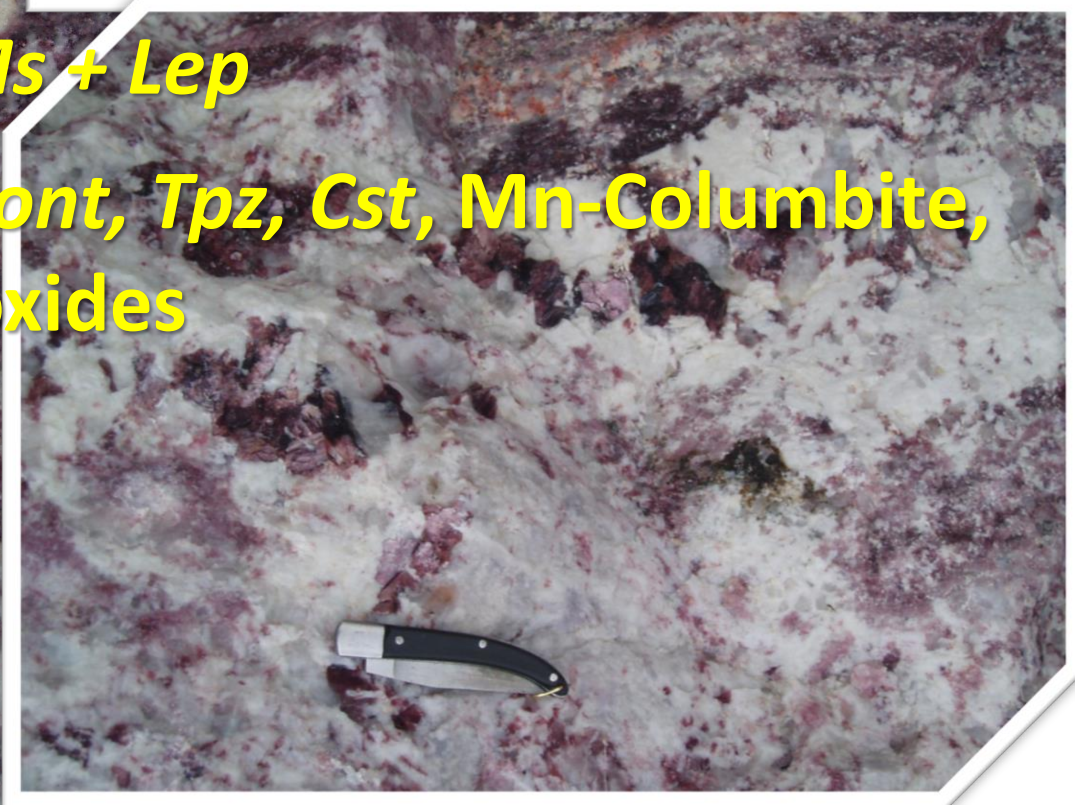
Parental, highly differentiated (volatile enriched), Fráguas granite (to the East):

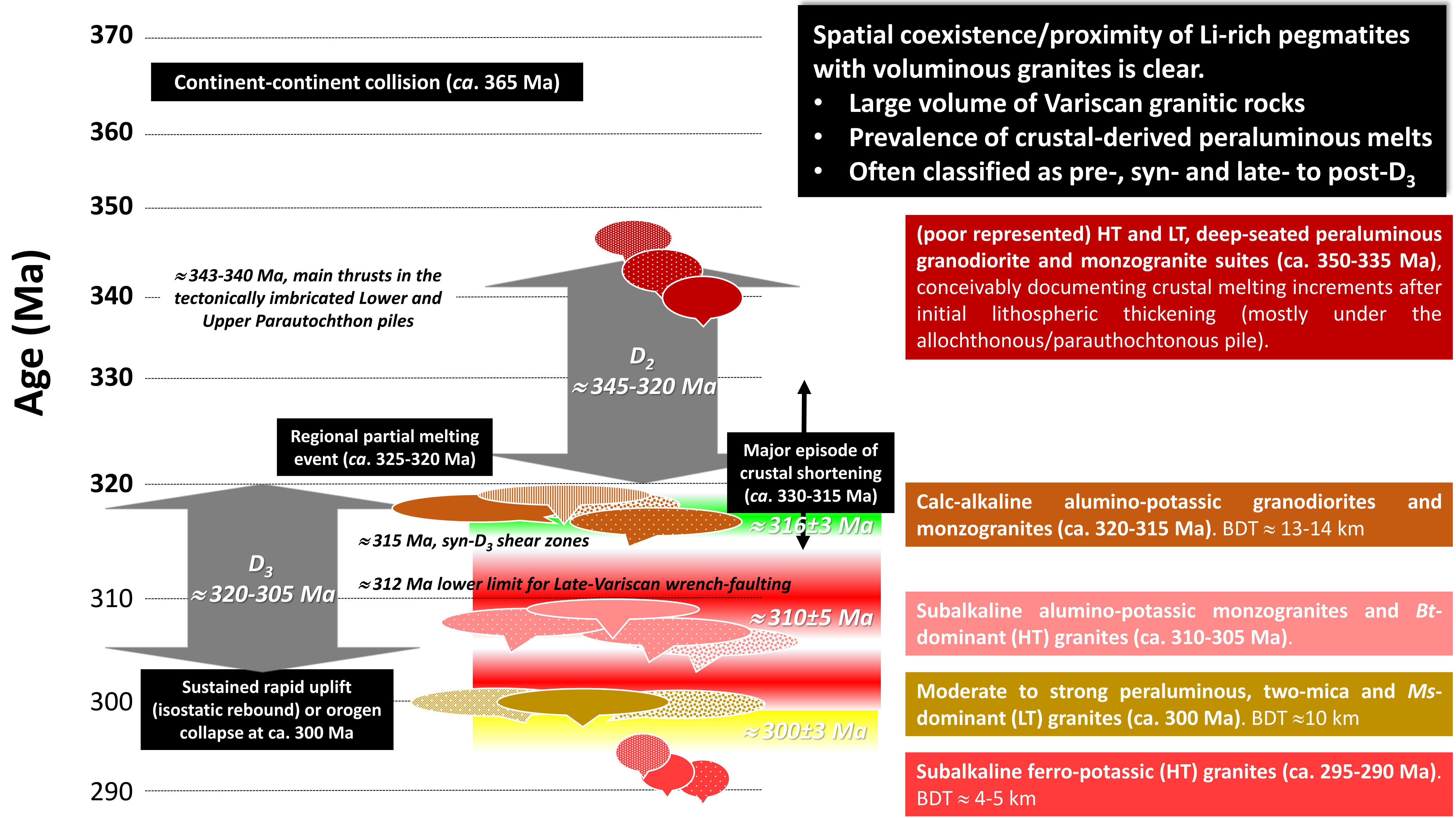
- 300±1 Ma (SHRIMP U-Pb, zircon)
- 301±2 Ma (SHRIMP U-Pb, monazite)

Neiva et al., 2011

- Li-rich sills more evolved than those bearing *Cst*
- Complex, banded, sometimes zoned
- No evidence of significant intracrystalline deformation
- Main: *Qz + Ab + K-f + Ms + Li-Ms + Lep*
- Accessory: *Ambly-Mont, Na-Mont, Tpz, Cst*, Mn-Columbite, microlite, Al-phosphates, Mn-oxides
- Traces: zircon, monazite
- Sporadic: torbernite, autunite





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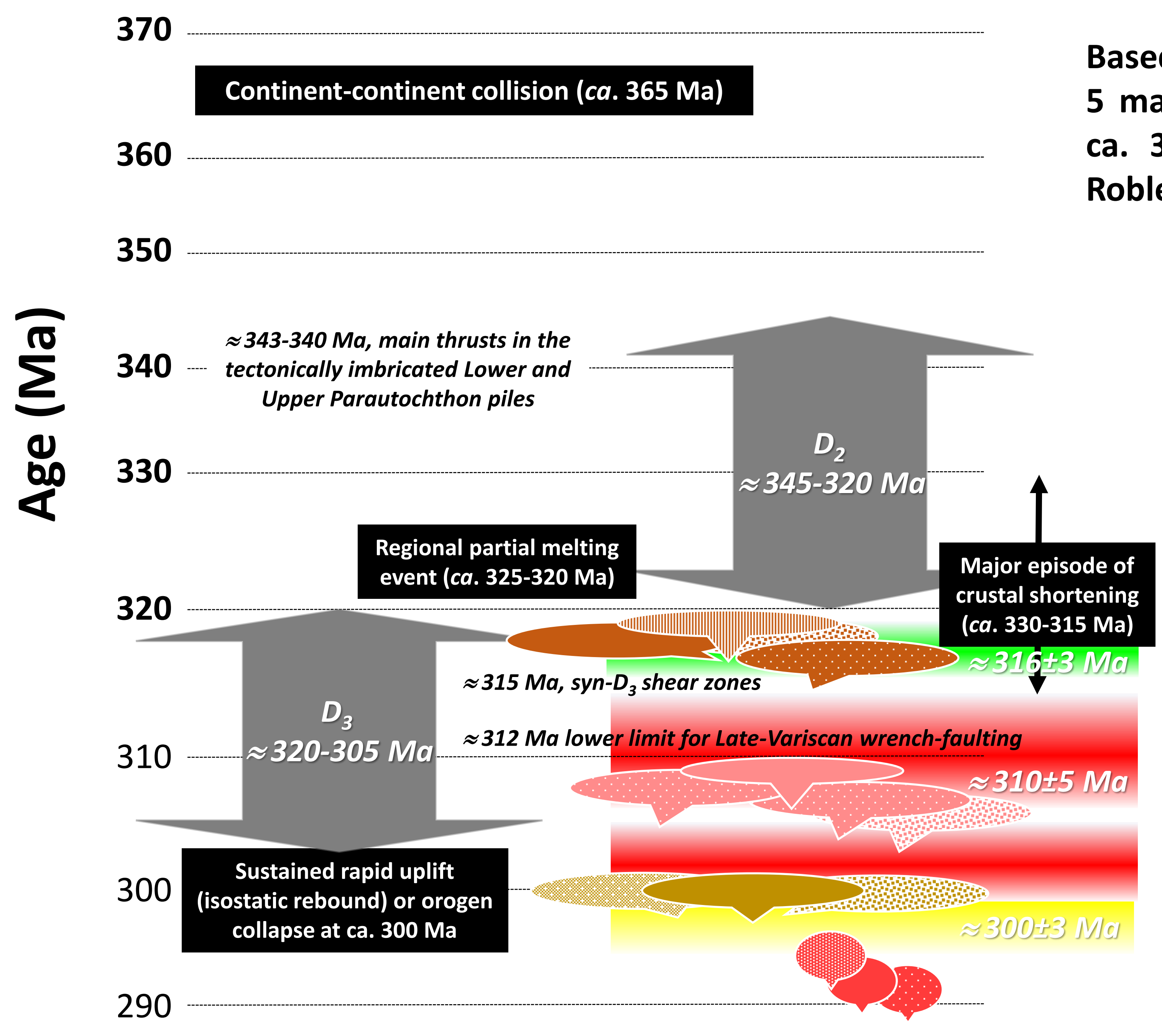
Continent-continent collision (ca. 365 Ma)
≈343-340 Ma, main thrusts in the tectonically imbricated Lower and Upper Parautochthon piles
D_2 ≈345-320 Ma
Regional partial melting event (ca. 325-320 Ma)
Major episode of crustal shortening (ca. 330-315 Ma)
≈316±3 Ma
≈315 Ma, syn-D_3 shear zones
D_3 ≈320-305 Ma
≈312 Ma lower limit for Late-Variscan wrench-faulting
≈310±5 Ma
Sustained rapid uplift (isostatic rebound) or orogen collapse at ca. 300 Ma
≈300±3 Ma
Spatial coexistence/proximity of Li-rich pegmatites with voluminous granites is clear.
• Large volume of Variscan granitic rocks
• Prevalence of crustal-derived peraluminous melts
• Often classified as pre-, syn- and late- to post-D_3
(poor represented) HT and LT, deep-seated peraluminous granodiorite and monzogranite suites (ca. 350-335 Ma), conceivably documenting crustal melting increments after initial lithospheric thickening (mostly under the allochthonous/parauthochtonous pile).
Calc-alkaline alumino-potassic granodiorites and monzogranites (ca. 320-315 Ma). BDT ≈ 13-14 km
Subalkaline alumino-potassic monzogranites and Bt-dominant (HT) granites (ca. 310-305 Ma).
Moderate to strong peraluminous, two-mica and Ms-dominant (LT) granites (ca. 300 Ma). BDT ≈10 km
Subalkaline ferro-potassic (HT) granites (ca. 295-290 Ma). BDT ≈ 4-5 km



Based on petrographic and geochemical features, 5 main granite suites were emplaced during the ca. 320-295 Ma period (Villaseca, 2011; Roda-Robles et al., 2018):

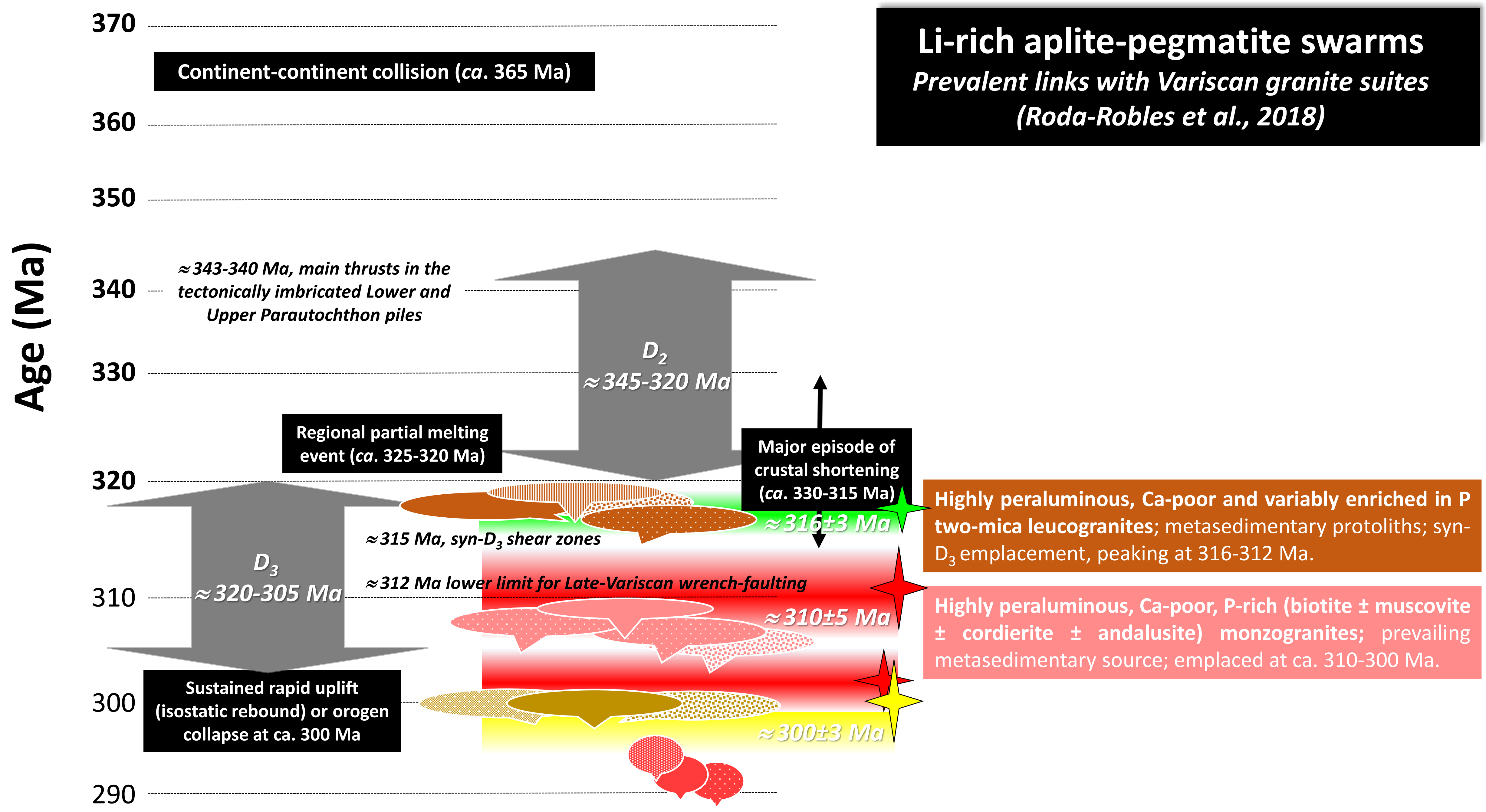
(*) Moderately to low peraluminous granites, with features at the limit between S- and I-type granites, with emplacement ages of 319–299 Ma.

Highly peraluminous, Ca-poor and variably enriched in P two-mica leucogranites; metasedimentary protoliths; syn-D_3 emplacement, peaking at 316-312 Ma. Minor (*)

Highly peraluminous, Ca-poor, P-rich (biotite ± muscovite ± cordierite ± andalusite) monzogranites; prevailing metasedimentary source; emplaced at ca. 310-300 Ma.

P-poor, moderately peraluminous granites, mostly crystallized at 308–299 Ma, coupled with (*)

I-type granites including metaluminous to low peraluminous amphibole-bearing biotite-granodiorites.



Li-rich aplite-pegmatite swarms
Prevalent links with Variscan granite suites
(Roda-Robles et al., 2018)
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D2 ≈345-320 Ma
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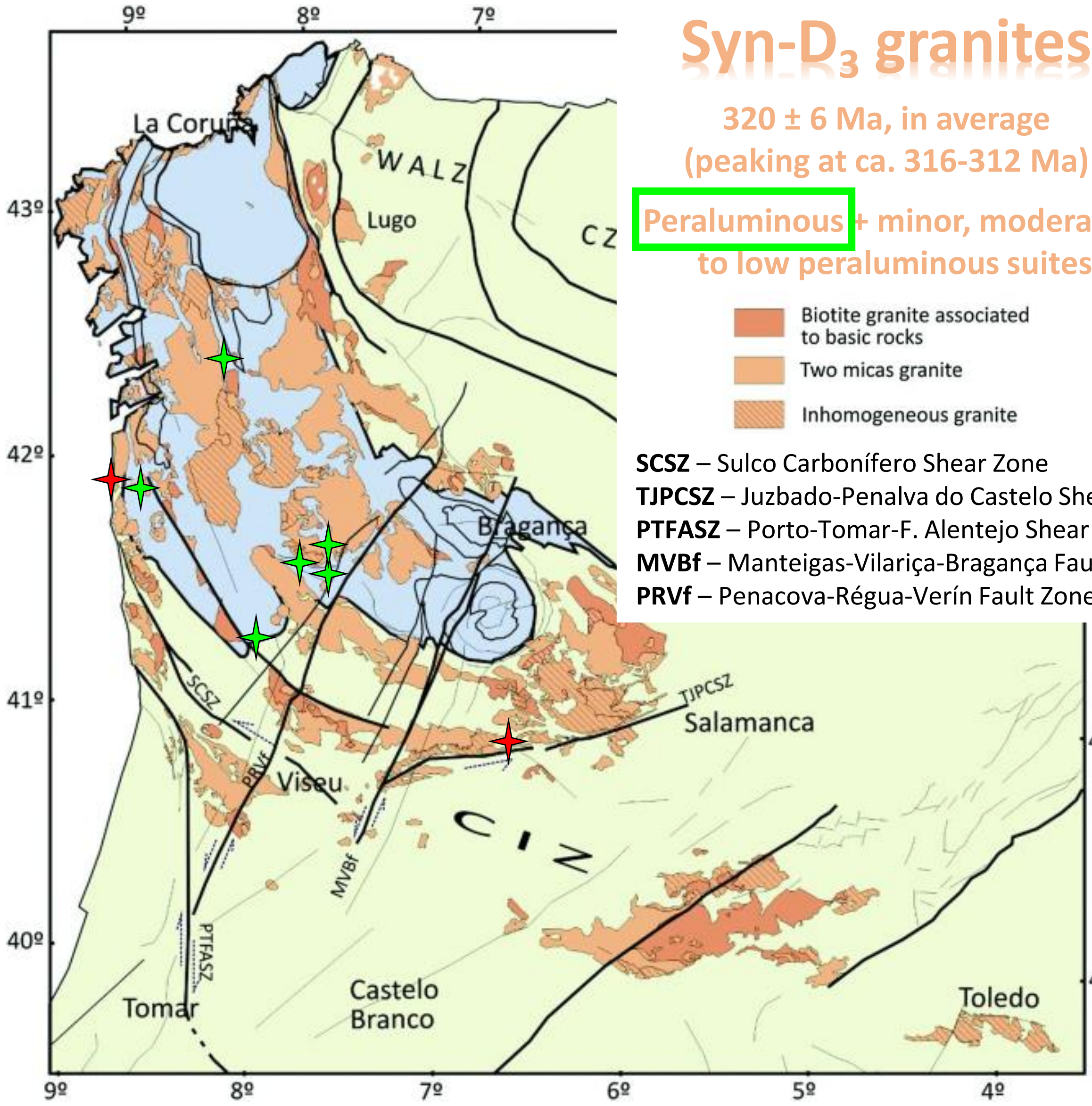


Syn-D_3 granites

320 ± 6 Ma, in average
(peaking at ca. 316-312 Ma)

Peraluminous + minor, moderately to low peraluminous suites

- Biotite granite associated to basic rocks
- Two micas granite
- Inhomogeneous granite

SCSZ – Sulco Carbonífero Shear Zone
TJPCSZ – Juzbado-Penalva do Castelo Shear Zone
PTFASZ – Porto-Tomar-F. Alentejo Shear Zone
MVBf – Manteigas-Vilariça-Bragança Fault Zone
PRVf – Penacova-Régua-Verín Fault Zone

Post-D_3 granites

Meta- to low peraluminous ca. 308-295 Ma

- Biotite granites and Two Micas (*)

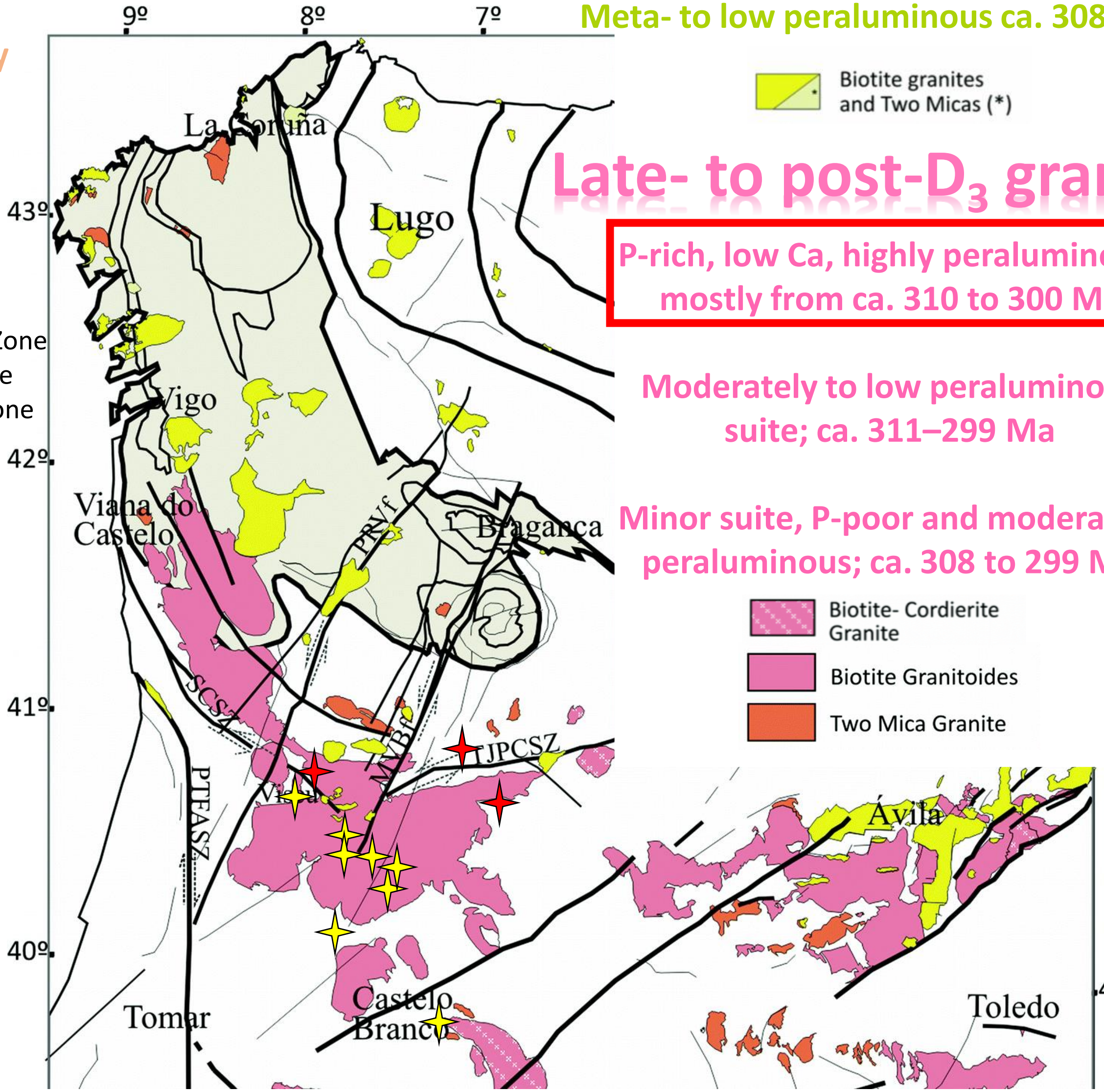
Late- to post-D_3 granites

P-rich, low Ca, highly peraluminous; mostly from ca. 310 to 300 Ma

Moderately to low peraluminous suite; ca. 311–299 Ma

Minor suite, P-poor and moderately peraluminous; ca. 308 to 299 Ma

- Biotite- Cordierite Granite
- Biotite Granitoides
- Two Mica Granite



Adapted from Ribeiro et al. (2020) Variscan Magmatism. In: C. Quesada and J. T. Oliveira (eds.), The Geology of Iberia: A Geodynamic Approach, Regional Geology Reviews, vol. 2, Springer Nature Switzerland AG 2019, 497-526, doi.org/10.1007/978-3-030-10519-8_13

Indisputable identification of parental granites (to which the highly differentiated, rare metal enriched, residual melts are related) is confirmed only in few aplite-pegmatite swarms.

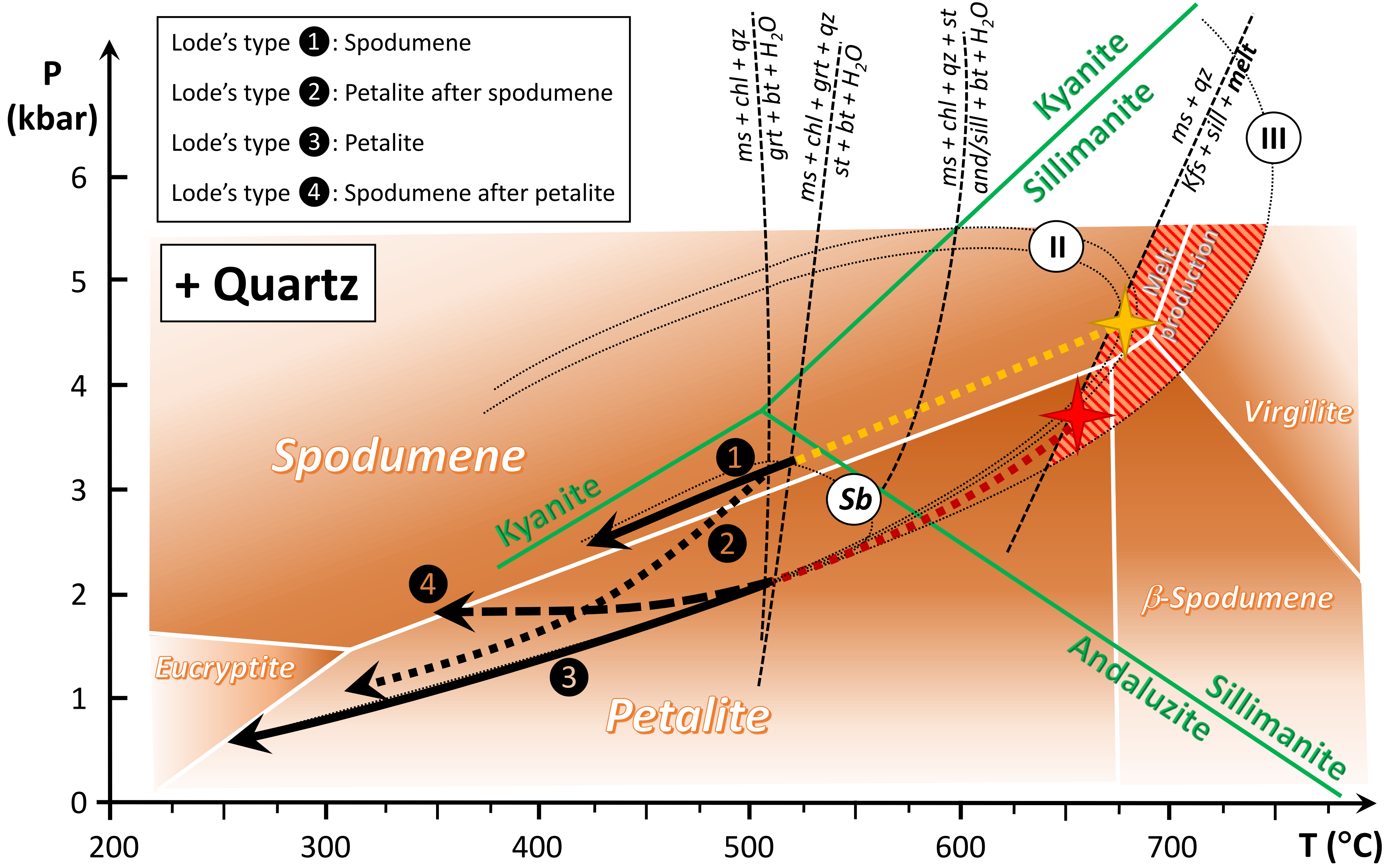
Mostly in CIZ, triphylite-lithiophilite enriched pegmatites (e.g., Mesquitela), and lepidolite-dominant and amblygonite/montebrasite-dominant lodes (e.g., Gonçalo-Seixo Amarelo, Argemela, Segura).

The involvement of **successive injections of independent batches of melts** resulting from **low melting rates** of metasediments (and metavolcanic rocks), cannot be discarded.

Specially in GTMZ, petalite- or spodumene-dominant lodes (e.g., Serra d'Arga and Barroso-Alvão).

Aplite-pegmatite bodies hosted in Parautochthon metasediments

Barroso-Alvão



Conclusions

- **Investment in exploration endeavours and mineral research must continue to suitably characterize the Portuguese resources and delimit reserves supporting an added-value chain for Li-products, including those for battery production.**
- **Inspection of the factors ruling the morphological diversity, tonnage and spatial distribution of Li-rich bodies is paramount.**
- **Also significant is the assessment of conditions controlling the relative abundance of spodumene/petalite, amblygonite/montebrasite or lepidolite, along with other minerals that could provide important by-products (Nb, Ta, Sn, Be, Cs).**
- **Several overviews on these issues already exist, but comprehensive studies are lacking for many aplite-pegmatite fields, thus hindering a correct management of these increasingly important mineral resources.**

Acknowledgements

ERA-MIN2 MOSTMEG

ERA-MIN2
RESEARCH & INNOVATION PROGRAMME ON RAW MATERIALS TO FOSTER CIRCULAR ECONOMY

ERA-MIN Joint Call 2019 (EU Horizon 2020 ERA-NET Co-fund Project ERA-MIN2, Grant agreement Nº 730238)

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Lisb@20[20] COMPETE 2020 PORTUGAL 2020

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Thank you so much for your attention!

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Lepidolite-rich pegmatite (Gonçalo)