The retrograde hydration of the granitoid continental crust as seen from epidote-bearing veins: Trace elements and microstructures

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Why epidote?

1) Range of micro- and meso-structures providing insight into different deformation extents and regimes **in the same host rock**.
2) Geochemically diverse and heterogeneous nominally hydrous mineral phase → **potential fluid tracer**.

Study areas:

1) Central Aar Granite, Aar Massif (Fig. 1): Variscan calcalcaline granodiorite, with widespread shear zones related to Alpine deformation (Wehrens et al., 2017).
2) Albula Granite, Albula Pass (Fig. 2): Variscan to post-Variscan calcalcaline granodiorite, slightly deformed by Alpine deformation (Froitzheim & Eberli, 1997).

Determining if the several epidote structures are geochemically related could isolate **more than one hydration events** of the granitoid continental crust, or indicate that only one occurred.

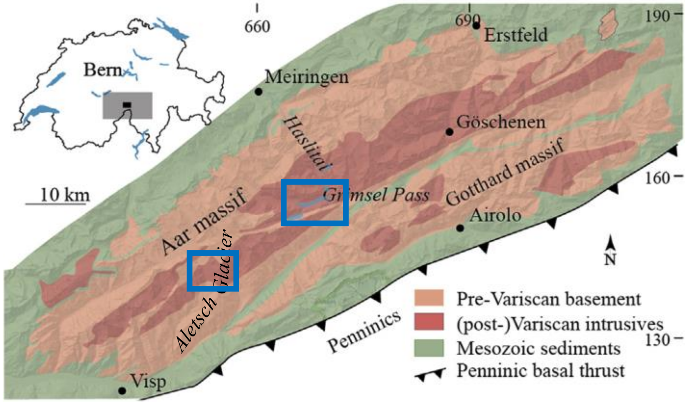

Fig. 1 – Aar Massif with sampling localities at Grimsel Pass and Aletsch Glacier (blue rectangles; modified from Wehrens at al., 2017).

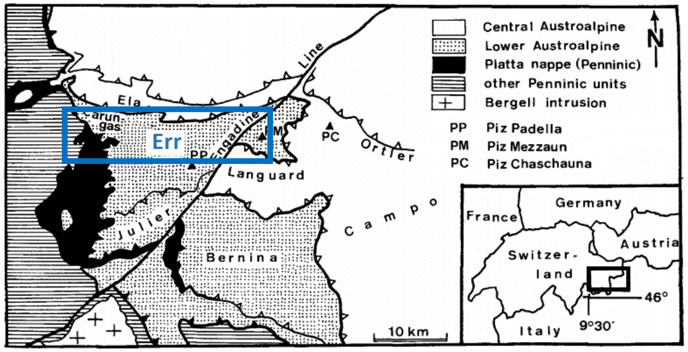

Fig. 2 – Err Nappe with sampling locality at Albula Pass (blue rectangle; modified from Froitzheim & Eberli, 1997).

2. Micro- and meso-structures

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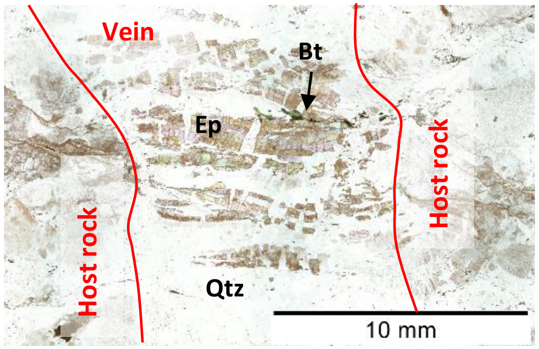


Fig. 3 – Fractured epidotes in intact epidote + quartz + local biotite vein (scan; Aar Massif).

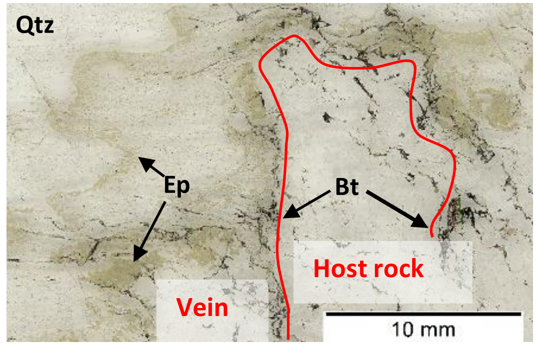


Fig. 4 – Folded epidote + quartz + biotite vein (scan; Aar Massif).

Epidotes in veins:

- Euhedral with recognizable growth directions ca. perpendicular to vein boundaries in intact veins (Fig. 3).
- Anhedral and re-orientated, often defining epidote clusters in folded and/or sheared veins (Fig. 4).

X_{Czo} = 0.10-0.30

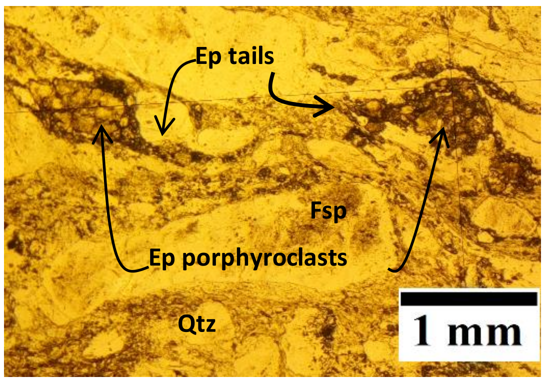


Fig. 5 – Epidote porphyroclasts and finer-grained tails (plane polarized light; Aar Massif).

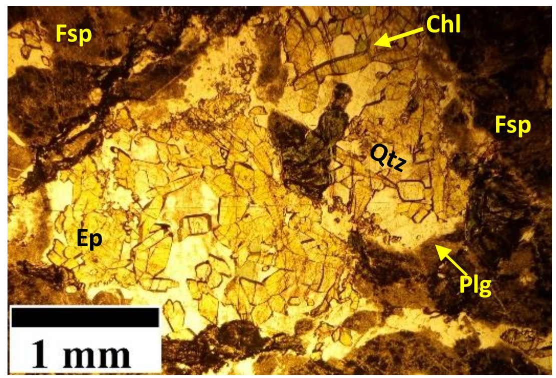


Fig. 6 – Metamorphic epidote (cross polarized light; Albula Pass).

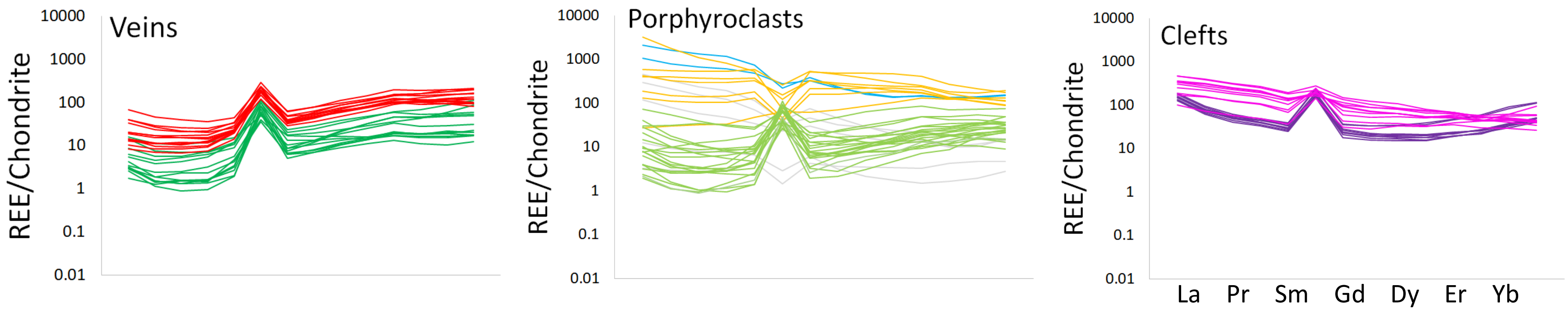
Fig. 7 – Cleft epidotes (Aar Massif).

Epidotes in host rock:

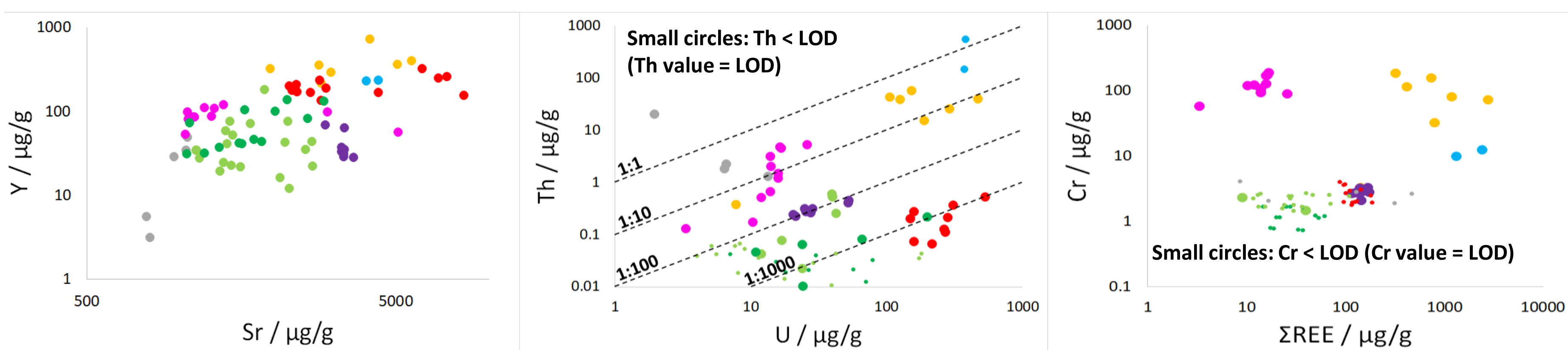
- Porphyroclasts (Fig. 5): lens-shaped clusters defined by anhedral epidote fragments, often accompanied by smaller-sized epidote grains defining tails; bound to mylonitic host rock.
- Metamorphic epidote (Fig. 6): Ep+Chl(+Alb?) assemblage, with mostly euhedral epidote grains; indicative of very low- to low-grade metamorphic conditions.
- Epidote in clefts (Fig. 7): aggregates of euhedral epidote grains crystallizing in cavities.

X_{Czo} = 0.20-0.40

2. Data - Aar Massif



All samples in plots



Red = vein A; dark green = vein B; blue = porphyroclast A; yellow = porphyroclast B; gray = porphyroclast C; light green = porphyroclast D; pink = cleft A; violet = cleft B.

- Different structures → different chondrite-normalized REE patterns, with ΣREE contents higher in most porphyroclasts than in veins and highly variable in all samples except for cleft B.
- Eu anomalies: positive in veins and clefts; negative in all porphyroclasts except for porphyroclast D.
- Porphyroclast D: overall more similar to veins than to the other porphyroclasts.
- Th/U ratios of porphyroclasts and clefts: mostly between values of 1:1 and 1:100; veins and porphyroclast D: values mostly < 1:100 and Th often < LOD.
- Cr: entirely < LOD in veins and in porphyroclast C, and mostly < LOD in porphyroclast D.

3. Data - Albula Pass

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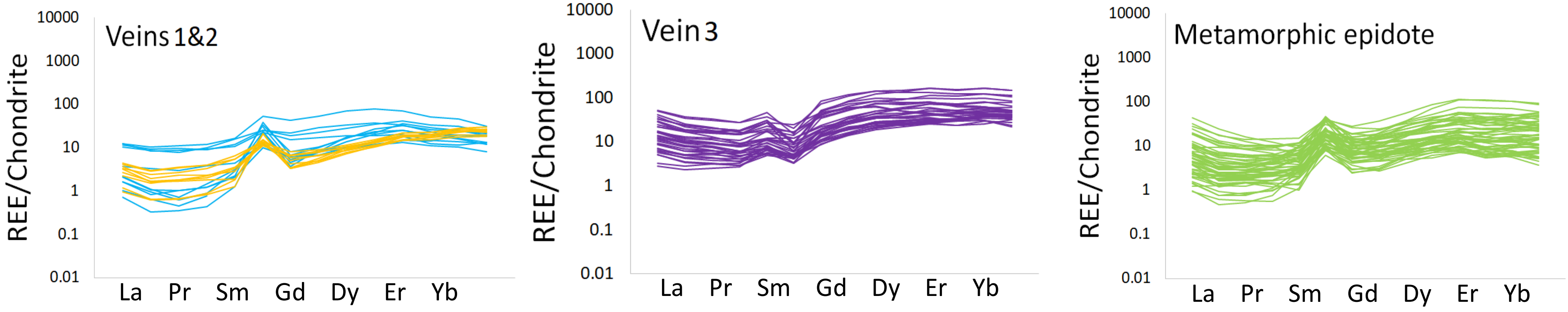
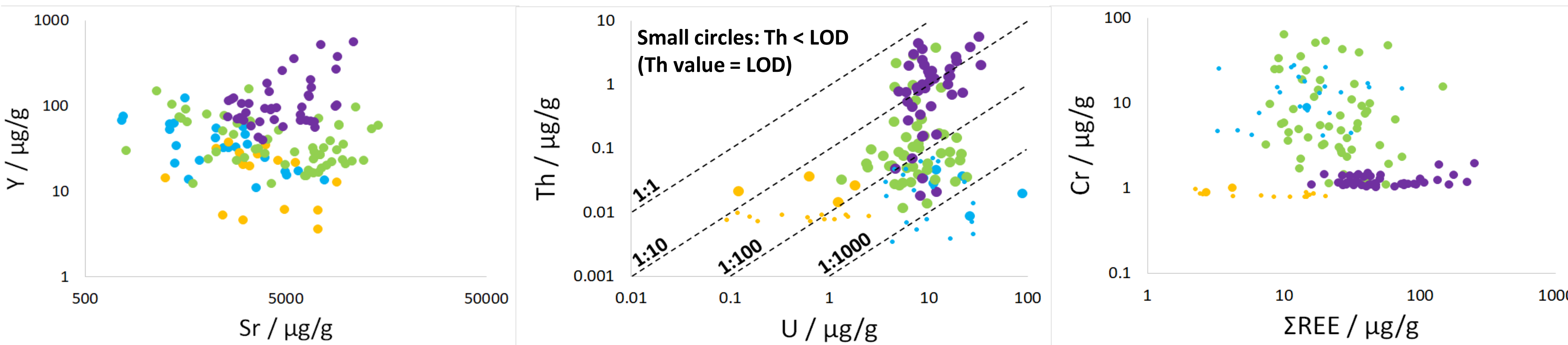


All samples in plots



Blue = vein A; yellow = vein B; violet = vein C; light green = metamorphic epidote.

- All samples: overall similar chondrite-normalized REE patterns.
- Vein C: only sample displaying negative Eu anomalies.
- Vein A, vein B and metamorphic epidote: overlapping clusters in Y/Sr and Th/U plots, and similar ΣREE contents; vein C overlaps only partially with the other samples.
- Most of Th/U values of vein C: around 1:10; mostly < 1:10 in the other samples, often with Th < LOD.
- Metamorphic epidote: higher Cr than vein C; Cr is mostly < LOD in the other two veins, with the only analyses > LOD similar to metamorphic epidote for vein A, and similar to vein C for vein B.

4. Final remarks

Aar Massif samples:

- Chondrite-normalized REE patterns can be linked to the different microstructures: the fact that the porphyroclasts, despite having endured deformation events, retain a distinct geochemical signal argues that **epidote does not geochemically reset during deformation**.
- The latter point is supported by the distinct clusters in Y/Sr, Th/U and Cr/ΣREE defined by most samples.
- The fact that there exist differences in porphyroclasts C and D with respect to the other porphyroclasts in the Aar Massif samples might be indicative of **separate events of epidote formation**, or might reflect the **effects of co-crystallizing mineral phases**.

Albula samples:

- All values are similar among vein A, vein B and metamorphic epidote if values are > LOD.
- Vein C is different in that it displays negative Eu anomalies and forms distinct clusters in Y/Sr, Th/U and Cr/ΣREE.
- All differences can be due to a **role of co-crystallizing mineral phases** or to **two separate events of epidote formation**, with **one linked to the very low- to low-grade metamorphic event** that affected the area.

Overall remarks:

- ΣREE contents are highly variable (few to hundreds of µg/g) in epidotes of both study areas.
- Chondrite-normalized REE patterns of veins are **overall LREE-depleted relative to HREE**, as opposed to the high-REE member of the epidote group (i.e. allanite); such trends have been reported in vein epidotes from other localities, and chondrite-normalized REE patterns of the majority of non-vein samples are consistent with a commonly observed LREE-enrichment (see Frei et al., 2004 for a comprehensive review).
- **High variability of Th/U ratios in veins** (values from ca. 1/10 to < 1/1000) with Th mostly < LOD indicates that the fluid carried U more efficiently than Th; this might be accounted for by the higher solubility of U^{6+} than U^{4+}.
- A **role of oxidation states** might be invoked also to explain Cr contents mostly below LOD in all veins.