Replacement of Monazite, $CePO_4$, by Florencite, $CeAl_3(PO_4)_2(OH)_6$ during Hydrothermal Alteration

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Introduction

Monazite, ideally $CePO_4$, is a wide-spread accessory mineral in igneous, metamorphic and sedimentary rocks. It is highly stable during weathering and also often during metamorphism up to granulite facies conditions and migmatization.

The stability of monazite during metamorphism, however, appears to depend on rock type and associated fluids. Monazite grows in pelitic rocks from ca. 450° C onwards, whereas in metamorphosed granitoids, primary magmatic monazite can be partly or totally replaced by apatite, allanite and epidote at the same metamorphic conditions. This kind of monazite alteration requires some addition of Ca through metamorphic fluids.

A different type of fluid-assisted monazite replacement was observed in alteration zones adjacent to Permo-Triassic lazulite ($MgAl_2(PO_4)_2(OH)_2$)-quartz veins in polymetamorphic metapelites and metapsammites of the Lower Austroalpine Grobgneis Complex, northeastern Styria, Austria. Here, monazite is largely or totally replaced by florencite, ideally $CeAl_3(PO_4)_2(OH)_6$. Florencite is a member of the crandallite group, belonging to the alunite supergroup.

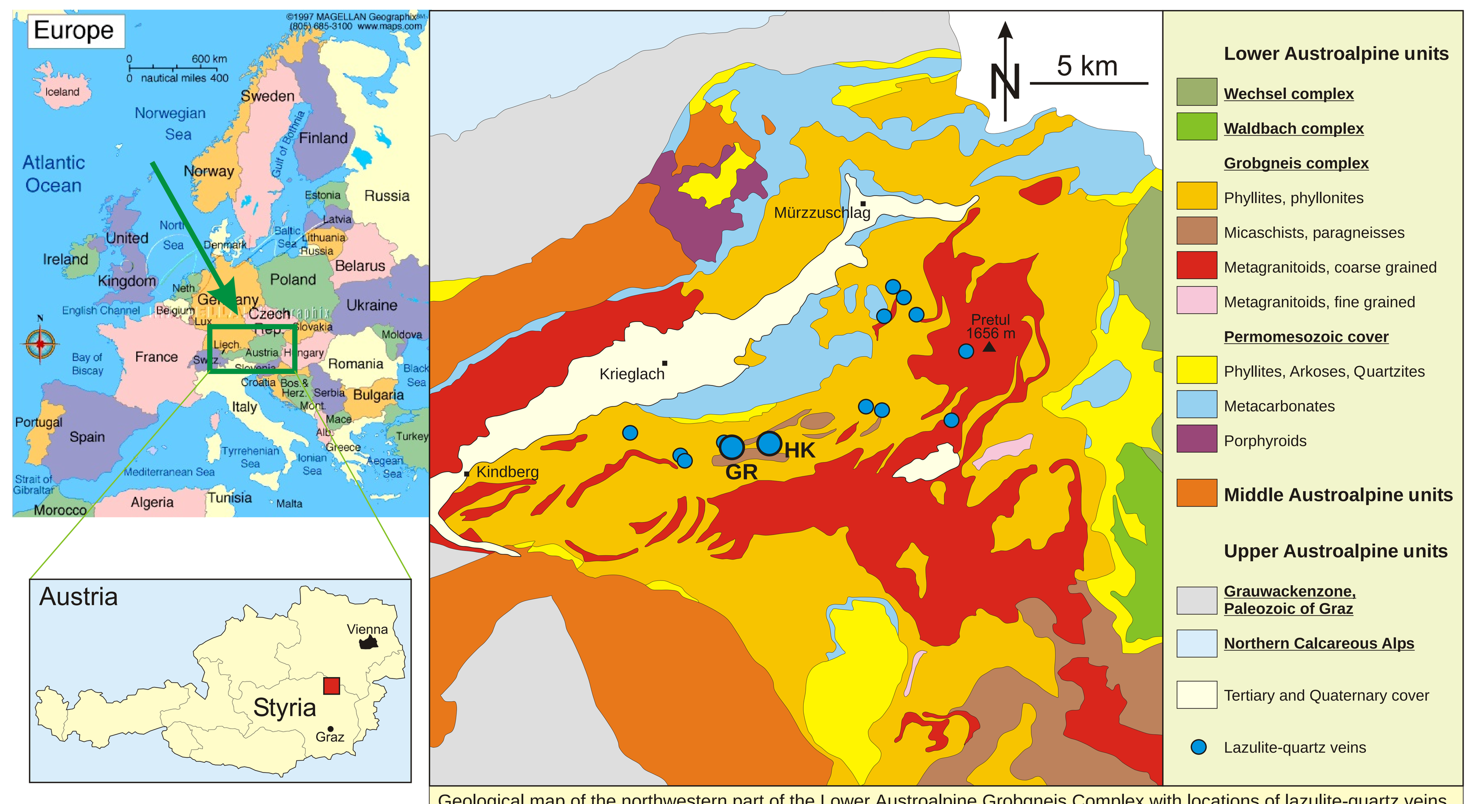
Geological Setting

The Grobgneis Complex is part of the Austroalpine nappe pile at the eastern end of the Alps. It belongs to the Lower Austroalpine units and covers an area of ca. 2000 km^2, east and west of the underlying Wechsel- and Waldbach Complex. The Grobgneis Complex consists of a polymetamorphic basement, comprising phyllites, phyllonites, mica schists, paragneisses and voluminous Carboniferous to Permian granitoid intrusions, and a Permo-Triassic, parautochthonous cover sequence, comprising phyllites, metaarcoses ("Verrucano", Permian), porphyroids, quartzites ("Semmeringquarzit", Scythian) and various metacarbonates (Triassic-Jurassic).

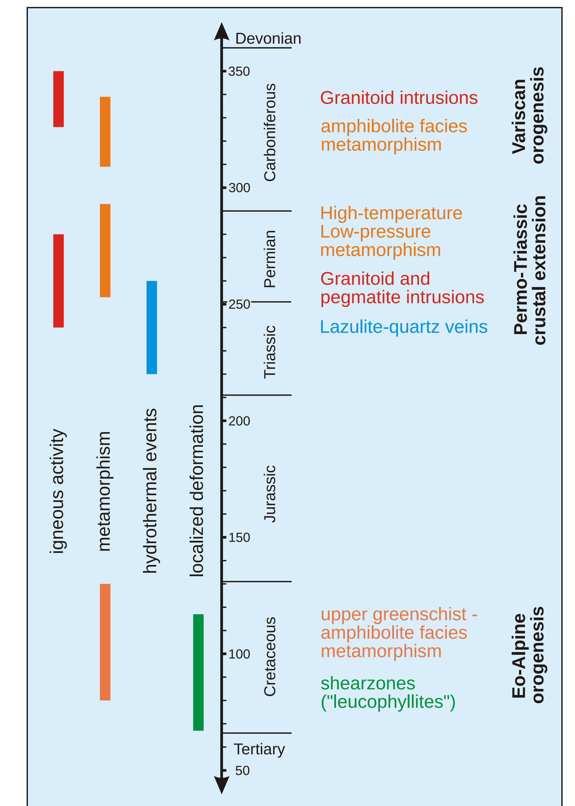
Three metamorphic events can be distinguished, based on petrological and geochronological data:
- A Variscan (340-310 Ma) amphibolite facies metamorphism (garnet + staurolite).
- An only locally observed Permian (280-240 Ma) HT-LP metamorphism (andalusite + sillimanite + biotite).
- An Eo-Alpine (100-80 Ma) greenschist to lower amphibolite facies overprint (chloritoid + chlorite + garnet ± staurolite ± kyanite).

For the Permian and Eo-Alpine event, metamorphic conditions seem to increase from north to south.

A conspicuous feature of the northern part of Grobgneis Complex is the occurrence of abundant hydrothermal lazulite-quartz veins. In most places, they are found as up to several m^2 large, loose blocks, and only a few outcrops are known, eg. Höllkogel (HK) and Granegg, GR. These outcrops were studied in more detail, because the relationships between veins, host rocks and alteration can be readily observed.



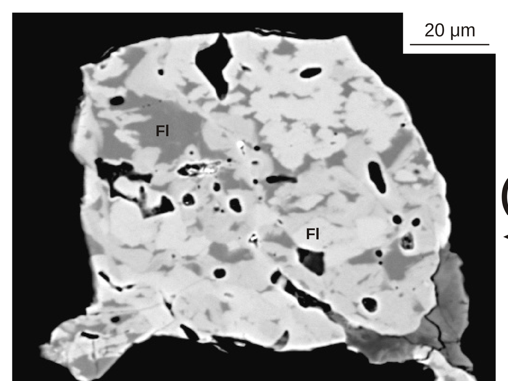
Geological map of the northwestern part of the Lower Austroalpine Grobgneis Complex with locations of lazulite-quartz veins. Source: Cornelius (1936), modified.



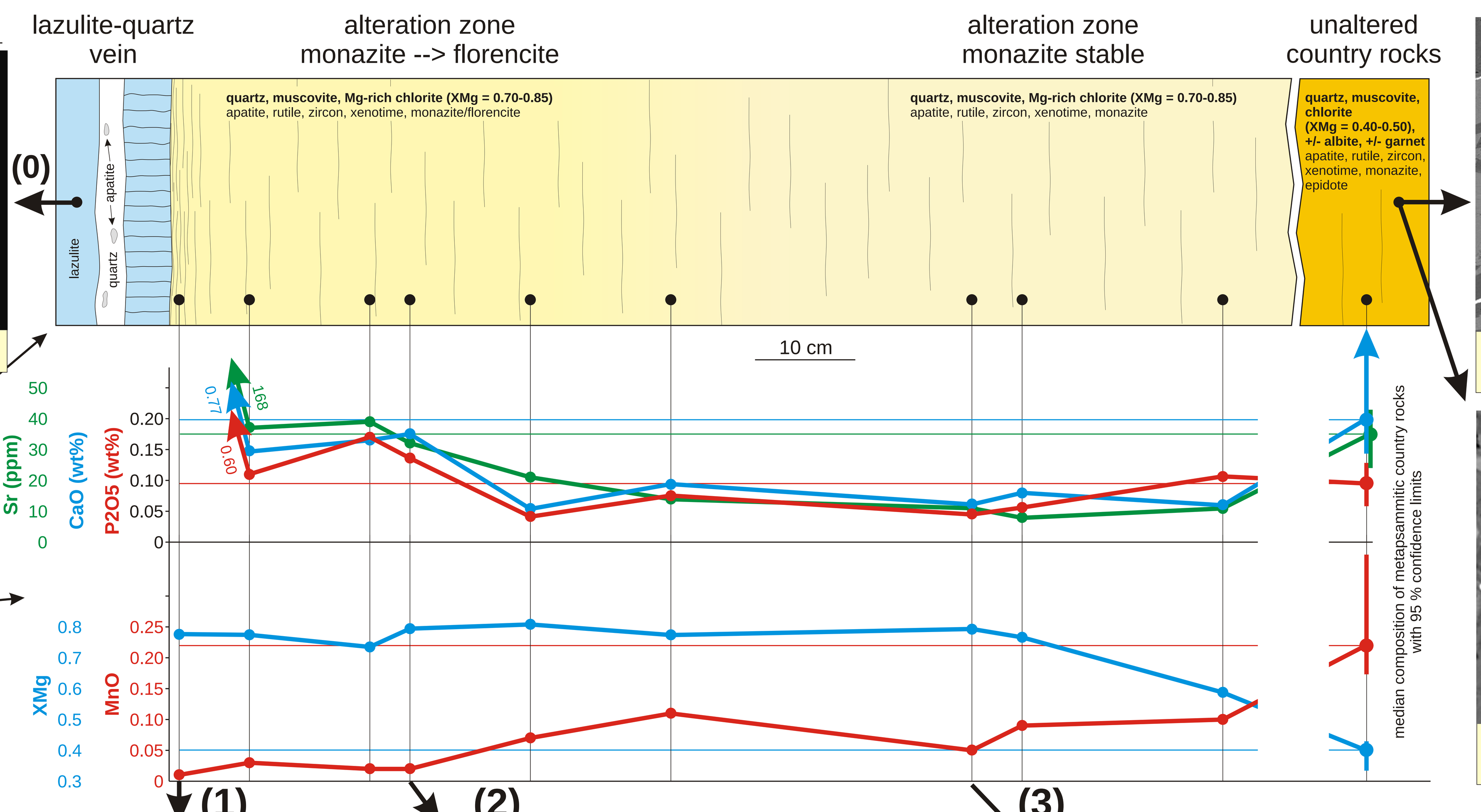
Endogenic geological events recorded in the Grobgneis Complex, based on petrological and geochronological data.

Petrography of Monazite Replacement by Florencite

Metapsammitic host rock

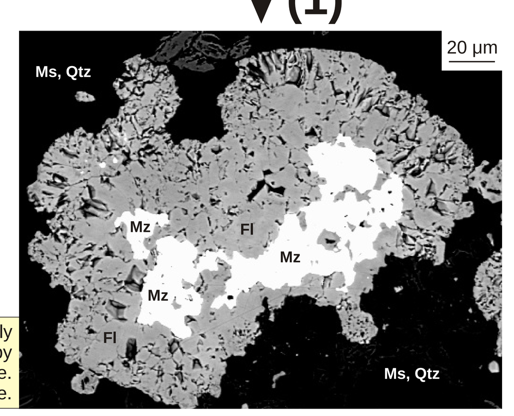


Typical patchily zoned florencite in a lazulite-rich domain of the lazulite-quartz vein. BSE image.

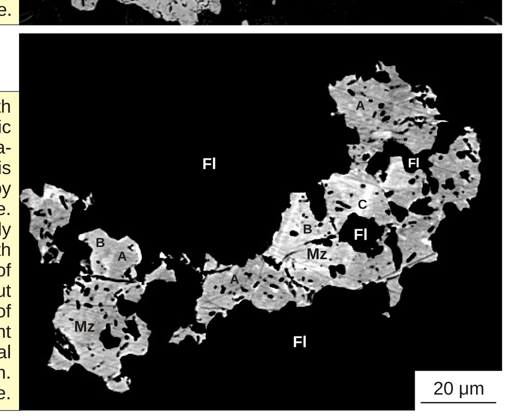


Petrographic and chemical characteristics of an alteration zone in metapsammitic country rocks. Outcrop at Höllkogel (HK).

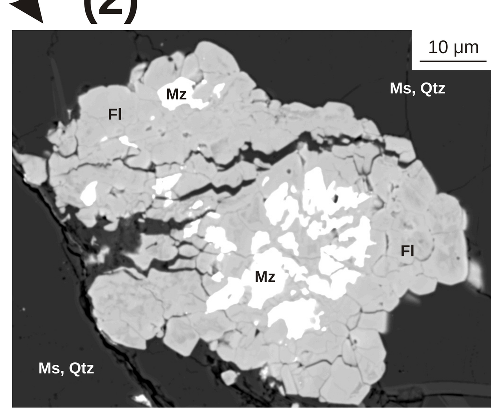
This alteration zone is composed of quartz, muscovite, Mg-rich chlorite (XMg = 0.70-0.85), apatite, rutile, zircon, xenotime, and monazite/florencite. Replacement of monazite by florencite is restricted to the proximal part.



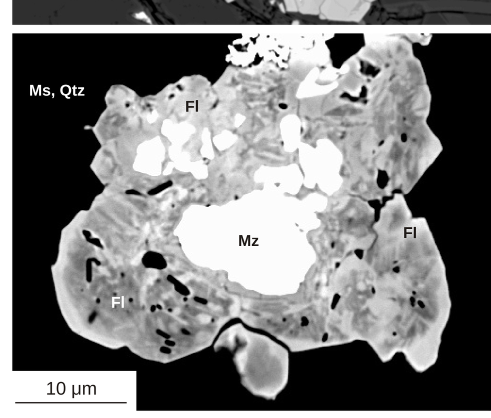
Monazite partly replaced by florencite. BSE-image.



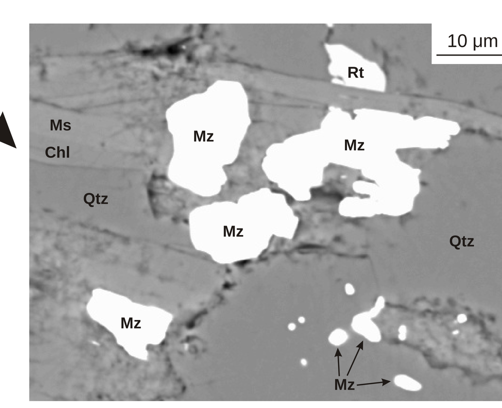
Monazite with concentric zoning in Th,Ca-content is replaced by florencite. Note the sharply cut growth zones of monazite without signs of significant compositional modification. BSE-image.



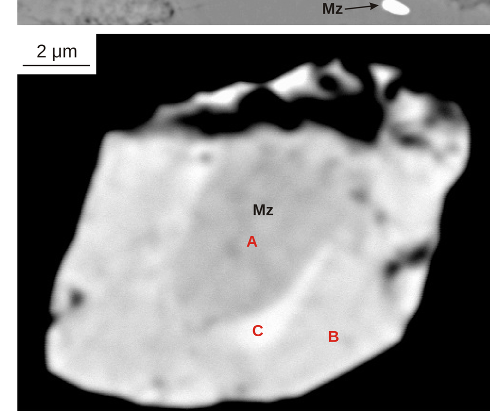
Monazite is partly replaced by florencite. Florencite is broken, cracks are filled with muscovite. BSE-image.



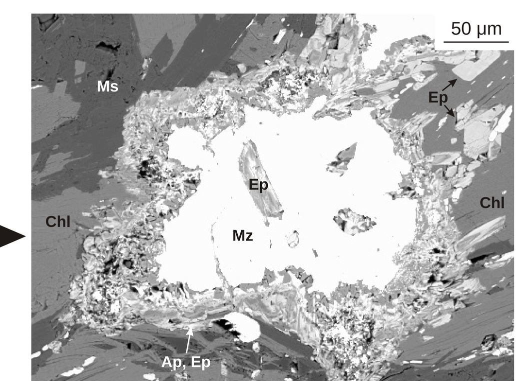
Monazite is partly replaced by florencite. Differences in BSE-contrast of florencite are due to variable Sr-, Ca- and REE-content. Darker areas are enriched in Sr and Ca. BSE-image.



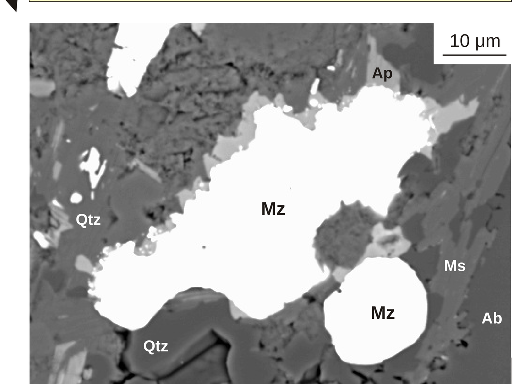
Fresh monazite crystals in association with quartz, muscovite and Mg-rich chlorite. BSE-image.



Strongly zoned, non-corroded monazite crystal. Th-content range from 0.5 to 13 wt.%. BSE-image.

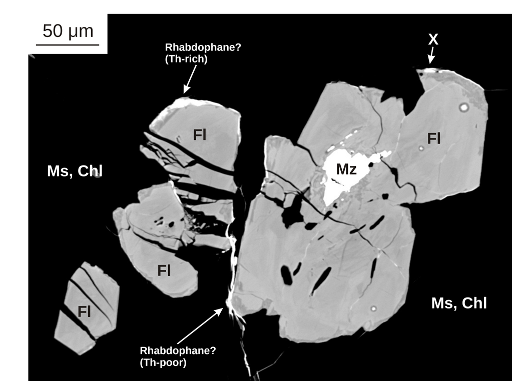


Typical replacement texture of of monazite in unaltered metapsamitic-metapelitic country rocks. Monazite is partly replaced by apatite and REE-bearing epidote. BSE-image.

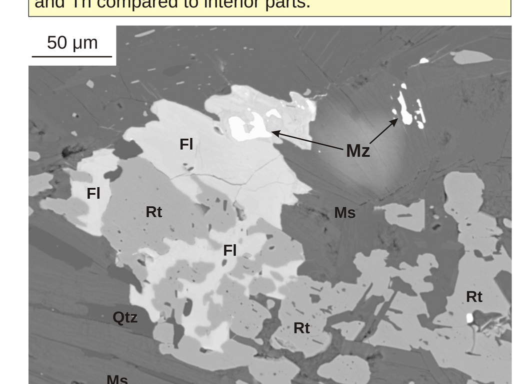


Typical replacement texture of of monazite in unaltered metapsammitic-metapelitic country rocks. Monazite is sligthly corroded by apatite. BSE-image.

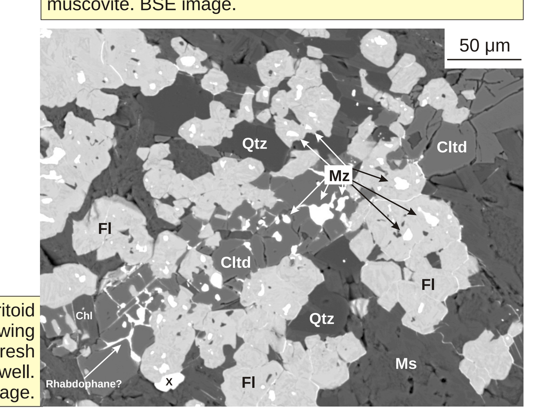
Metapelitic host rock



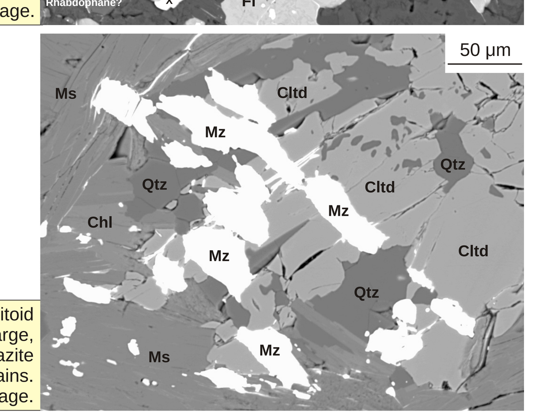
Fractured florencite with monazite relics and muscovite inclusions. Fractures in florencite are filled with muscovite. Differences in BSE contrast of florencite are due to variable Th-, Ca- and REE-content. Rims are enriched in Ca and Th compared to interior parts.



Intimate intergrowth of florencite with Eo-Alpine rutile. Age relationships between florencite and rutile are not entirely clear. Note small fresh monazite grains enclosed in muscovite. BSE image.

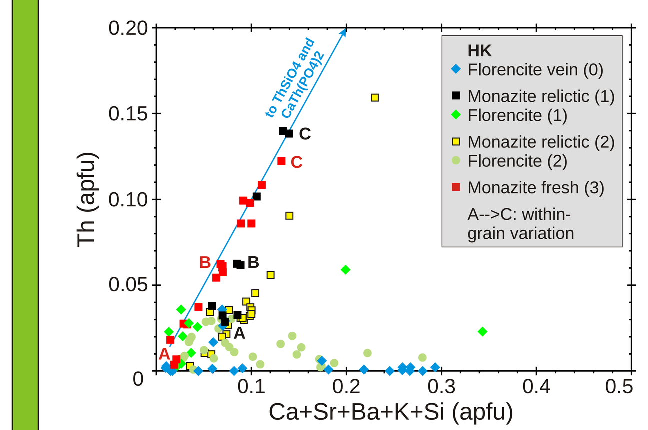


Eo-Alpine chloritoid is overgrowing florencite and fresh monazite as well. BSE-image.

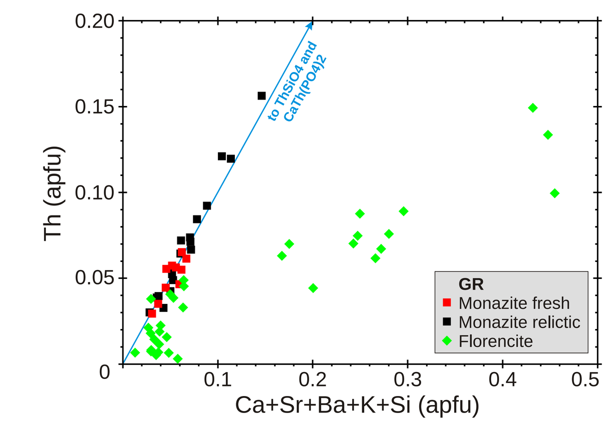


Eo-Alpine chloritoid is overgrowing large, unaltered monazite grains. BSE-image.

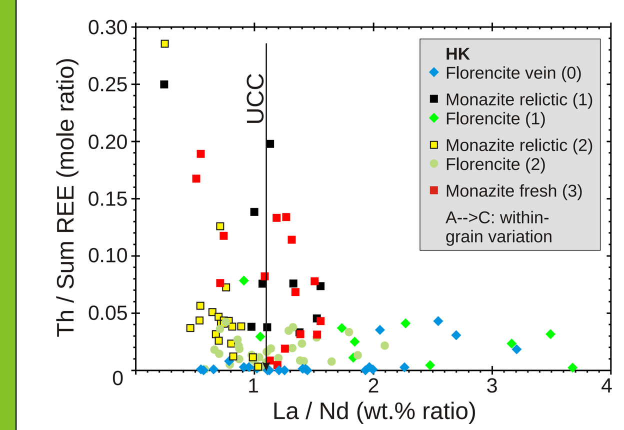
Chemistry of Monazite Replacement by Florencite



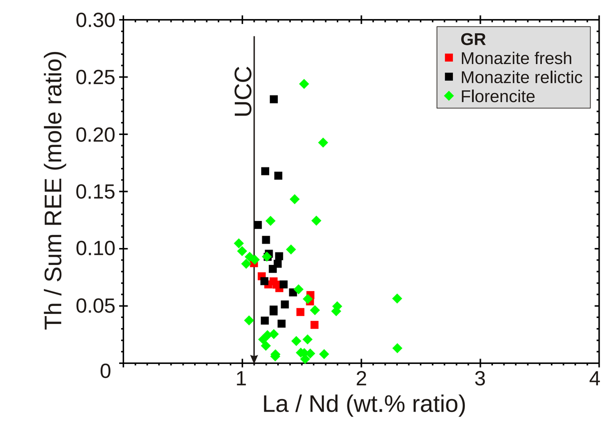
Incorporation of Th in monazite and florencite in the alteration zone at Höllkogel (HK - metapsammitic host rock). Note the highly variable Th-content within a single monazite grain. Monazites in sample (2) contain up to 1.5 wt.% SO_3. Th-content in florencite is not correlated with any mono-, di- or tetravalent element.



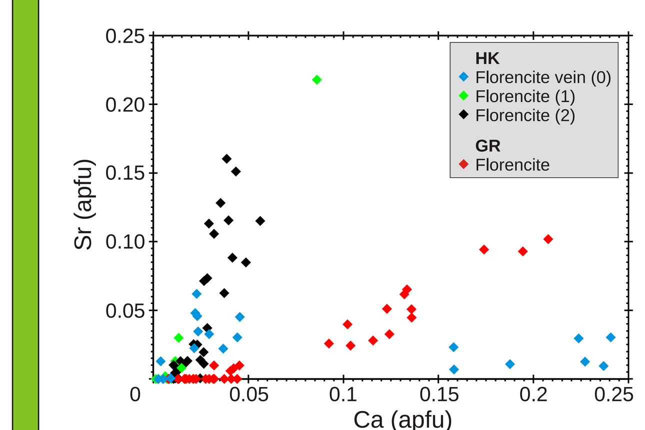
Incorporation of Th in monazite and florencite in the alteration zone at Grannegg (GR - metapelitic host rock). Th-content in florencite is positively correlated with mono-, di- and tetravalent elements.



Variation of La/Nd ratio and Th/REE ratio in monazite and florencite in the alteration zone at Höllkogel (HK - metapsammitic host rock). Some florencite analyses show a significant shift to higher La/Nd ratios compared to precursor monazite. Th/REE ratios in florencite do not reach values as high as in precursor monazite. UCC: Upper Continental Crust.



Variation of La/Nd ratio and Th/REE ratio in monazite and florencite in the alteration zone at Grannegg (GR - metapelitic host rock). Both ratios are in the same range for florencite and precursor monazite. UCC: Upper Continental Crust.

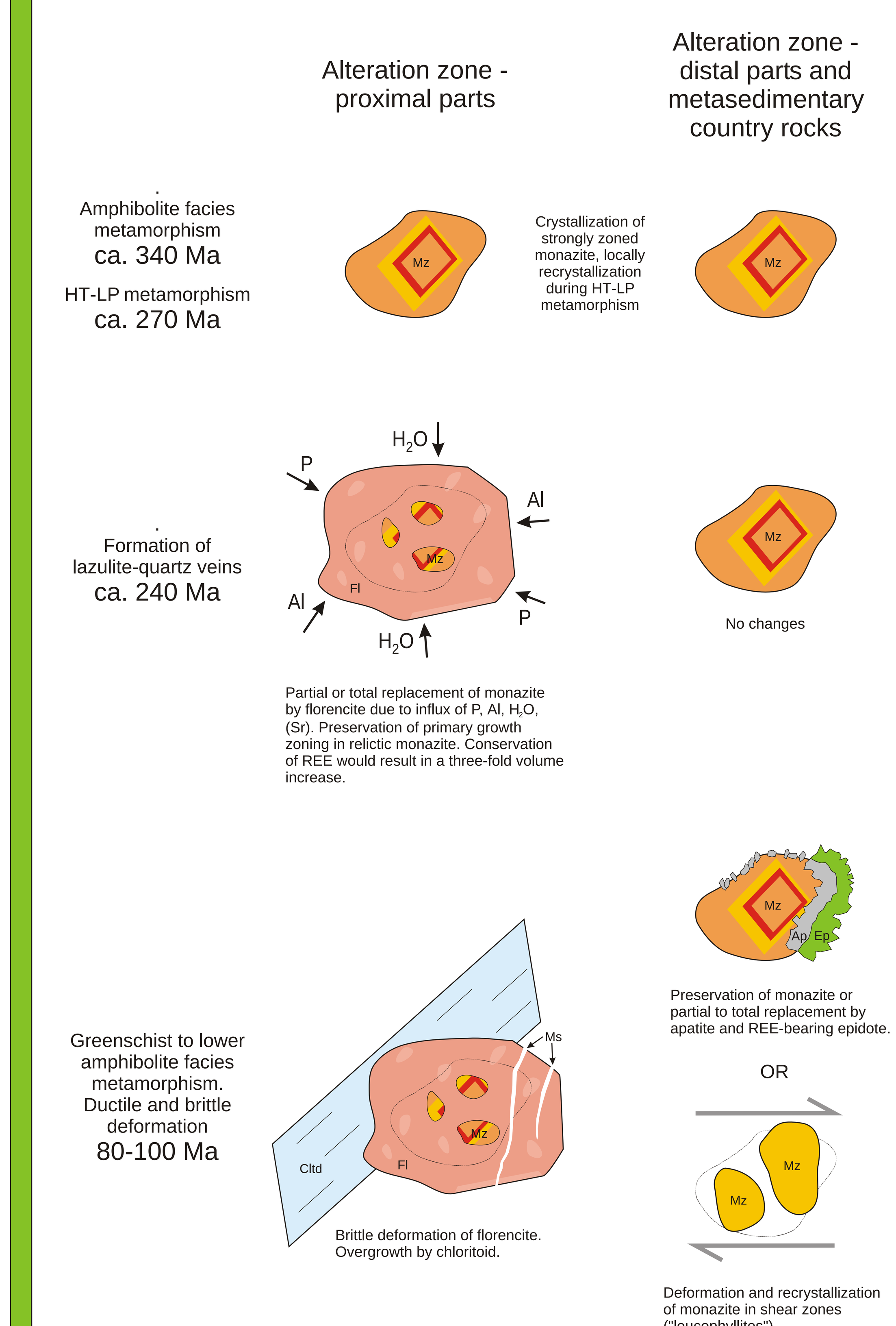


Content of divalent cations in florencite. Sr- and Ca-contents are different for the alteration zones studied and florencite in lazulite-quartz veins itself.

Monazite
(LREE,Th,Ca)(P,Si)O_4

Florencite
(LREE,Th,Ca,Sr)$Al_3(PO_4)_2(OH)_6$

Conceptual Model of Monazite and Florencite Formation and Behavior in the Studied Region



Partial or total replacement of monazite by florencite due to influx of P, Al, H_2O, (Sr). Preservation of primary growth zoning in relictic monazite. Conservation of REE would result in a three-fold volume increase.

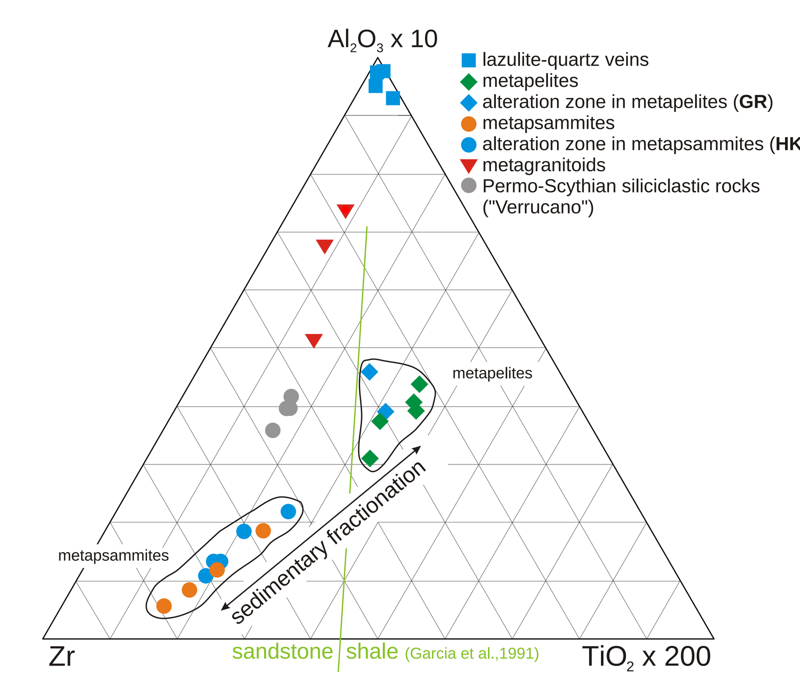
No changes

Brittle deformation of florencite. Overgrowth by chloritoid.

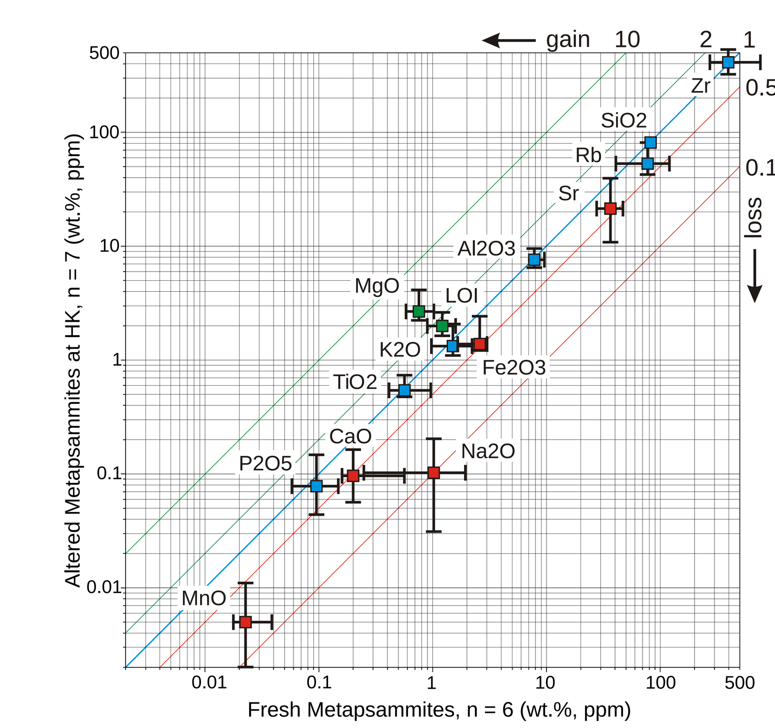
Preservation of monazite or partial to total replacement by apatite and REE-bearing epidote.

Deformation and recrystallization of monazite in shear zones ("leucophyllites").

Chemical Characterization of Host Rocks and Alteration Zones



Chemical comparison of alteration zones with host rocks. Lazulite-quartz veins with alteration zones occur both in metapsammites and metapelites. These rock types are clearly discernible by characteristic Zr/Ti-ratios. Ratios of typical "immobile" elements remained virtually unchanged during the alteration process.



Isocon-diagram for the alteration zone in metapsammitic rocks at Höllkogel (HK). Assuming Ti and Zr as immobile elements, Na, Mn, and Fe are significantly depleted, whereas Mg is ca. 3-fold enriched in the alteration zone compared with unaltered metapsammitic country rocks. Volume change is not significant. Error bars represent 95 % confidence limits.

Summary and Conclusions

Aluminium and phosphorus are major elements in lazulite-quartz veins, and breakdown of monazite to florencite in the alteration zones can be most probably related to the hydrothermal fluids associated with vein formation. This interpretation is supported by the occurrence of accessory florencite as the sole LREE-bearing mineral in the lazulite-quartz veins itself, suggesting instability of monazite, and stability of florencite, in the vein forming fluids.

Assuming constant REE, this type of monazite alteration would result in a ca. three-fold volume increase by addtion of Al, P and H_2O. However, some fractionation and transport of REE and Th may have occurred.

Distal parts of the alteration zones and unaltered country rocks contain monazites with total Pb ages between 360 and 250 Ma. These monazites are usually fresh or can be partly replaced by apatite and REE-bearing epidote. This replacement can be related to the Eo-Alpine greenschist to lower amphibolite facies overprint of the area. Florencite remained stable during this metamorphic event.