Seminary of dept. Mineralogy, Petrology and Economic Geology
Faculty of Natural Sciences
Comenius University

Remobilization and fractionation of rare lithophile elements under post-magmatic, hydrothermal to supergene conditions

Remobilizácia a frakcionácia vzácnych litofilných prvkov v post-magmatických, hydrotermálnych až supergénnych podmienkach

Martin Ondrejka, Peter Bačík, Pavel Uher, Marián Putiš,

Alexandra Molnárová, Štefan Ferenc, Tomáš Mikuš, Stanislava Milovská, Bronislava Voleková & Radek Škoda

VEGA and APVV projects linked to this topic

VEGA 1/0257/13: Accessory minerals under rock-fluid interaction conditions in magmatic and metamorphic systems - Ondrejka

VEGA 1/0467/20: Remobilisation and fractionation of rare lithophile elements under hydrothermal and supergene conditions – Ondrejka

APVV-18-0065: Light lithophile elements (Li, Be, B) in selected minerals: from crystal structure to geological processes – Bačík

My research interests:

a) Rock-fluid interaction processes, alteration-transformation of accessory minerals (e.g. monazite, xenotime, apatite, allanite, titanite, uraninite), post-magmatic to low-*T* (supergene) remobilisation and fractionation of rare lithophile elements.

b) Petrology (mineralogy, geochemistry, geochronology) of granitoids and felsic volcanics (esp. A-types=ferroan).

Selected publications linked to this topic

Lithos 142–143 (2012) 245–255
Contents lists available at SciVerse ScienceDirect
Lithos
journal homepage: www.elsevier.com/locate/lithos
ELSEVIER

Two-stage breakdown of monazite by post-magmatic and metamorphic fluids: An example from the Veporic orthogneiss, Western Carpathians, Slovakia

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Mineral Petrol (2016) 110:561–580
DOI 10.1007/s00710-016-0432-8

ORIGINAL PAPER

Fluid-driven destabilization of REE-bearing accessory minerals in the granitic orthogneisses of North Veporic basement (Western Carpathians, Slovakia)

M. Ondrejka [1] · M. Putiš [1] · P. Uher [1] · I. Schmiedt [1] · L. Pukančík [1] · P. Konečný [2]

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ELSEVIER
CrossMark

Britholite, monazite, REE carbonates, and calcite: Products of hydrothermal alteration of allanite and apatite in A-type granite from Stupné, Western Carpathians, Slovakia

Pavel Uher [a,*], Martin Ondrejka [a], Peter Bačík [a], Igor Broska [b], Patrik Konečný [c]

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Mineralogical Magazine, December 2018, Vol. 82(6), pp. 1277–1300

Minerals of the rhabdophane group and the alunite supergroup in microgranite: products of low-temperature alteration in a highly acidic environment from the Velence Hills, Hungary

Martin Ondrejka [1,*], Peter Bačík [1], Tomáš Sobocký [1], Pavel Uher [1], Radek Škoda [2], Tomáš Mikuš [3], Jarmila Luptáková [3] and Patrik Konečný [4]

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The Canadian Mineralogist
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CARBONATE-BEARING PHOSPHOHEDYPHANE–"HYDROXYLPHOSPHOHEDYPHANE" AND CERUSSITE: SUPERGENE PRODUCTS OF GALENA ALTERATION IN PERMIAN APLITE (WESTERN CARPATHIANS, SLOVAKIA)

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Mineralogical Magazine

Hellandite-(Y)–hingganite-(Y)–fluorapatite retrograde coronae: a novel type of fluid-induced dissolution-reprecipitation breakdown of xenotime-(Y) in the metagranites of Fabova Hoľa (Western Carpathians, Slovakia)

--Manuscript Draft--

	Hellandite-(Y)–hingganite-(Y)–fluorapatite retrograde coronae: a novel type of fluid-induced dissolution-reprecipitation breakdown of xenotime-(Y) in the metagranites of Fabova Hoľa (Western Carpathians, Slovakia)
	Y-B-Be silicates in a retrograde coronae around xenotime
	Article
	Pete Williams - Special issue
	hellandite-(Y); hingganite-(Y); Y-B-Be silicate; xenotime breakdown; dissolution-reprecipitation; reaction coronae; metagranite, Fabova Hoľa; Western Carpathians; Slovakia
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	Marián Putiš, Prof.
	Peter Bačík, PhD
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	Bronislava Voleková, PhD
	Stanislava Milovská, PhD
	Libor Pukančík, MSc

Rock-fluid interaction processes including rare lithophile elements

Be, Cs, Rb, Sc, Ln, Y, Nb, Ta, Zr, Hf, U and Th

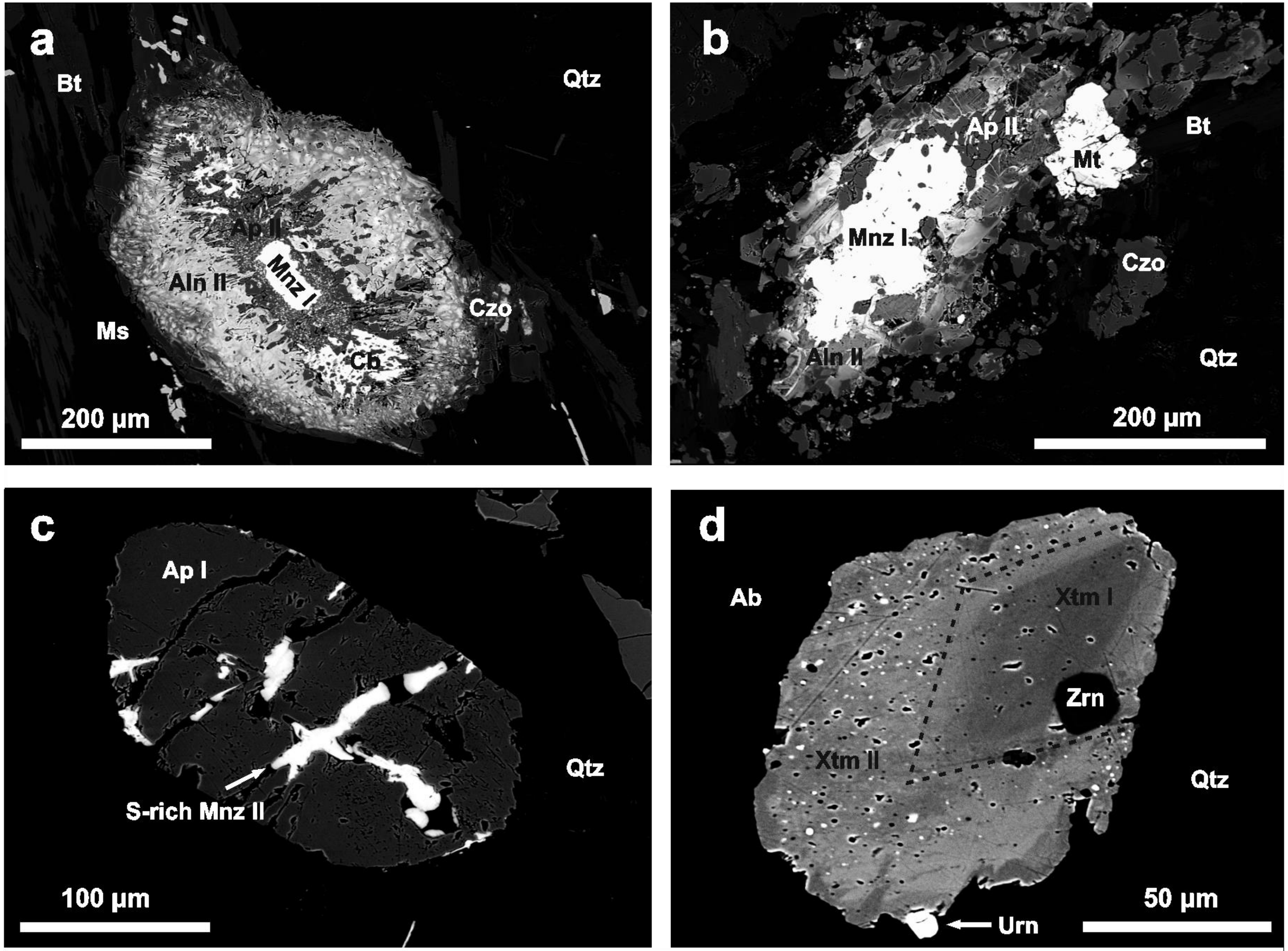
In-situ dissolution–reprecipitation: destabilization of the primary mineral phase and subsequent precipitation of newly-formed and stable mineral phase.

e.g. autometasomatic inclusions of secondary phases in a host mineral
- pseudomorphs
- coronae microtextures (Mnz, Xtm ...)
- secondary rims

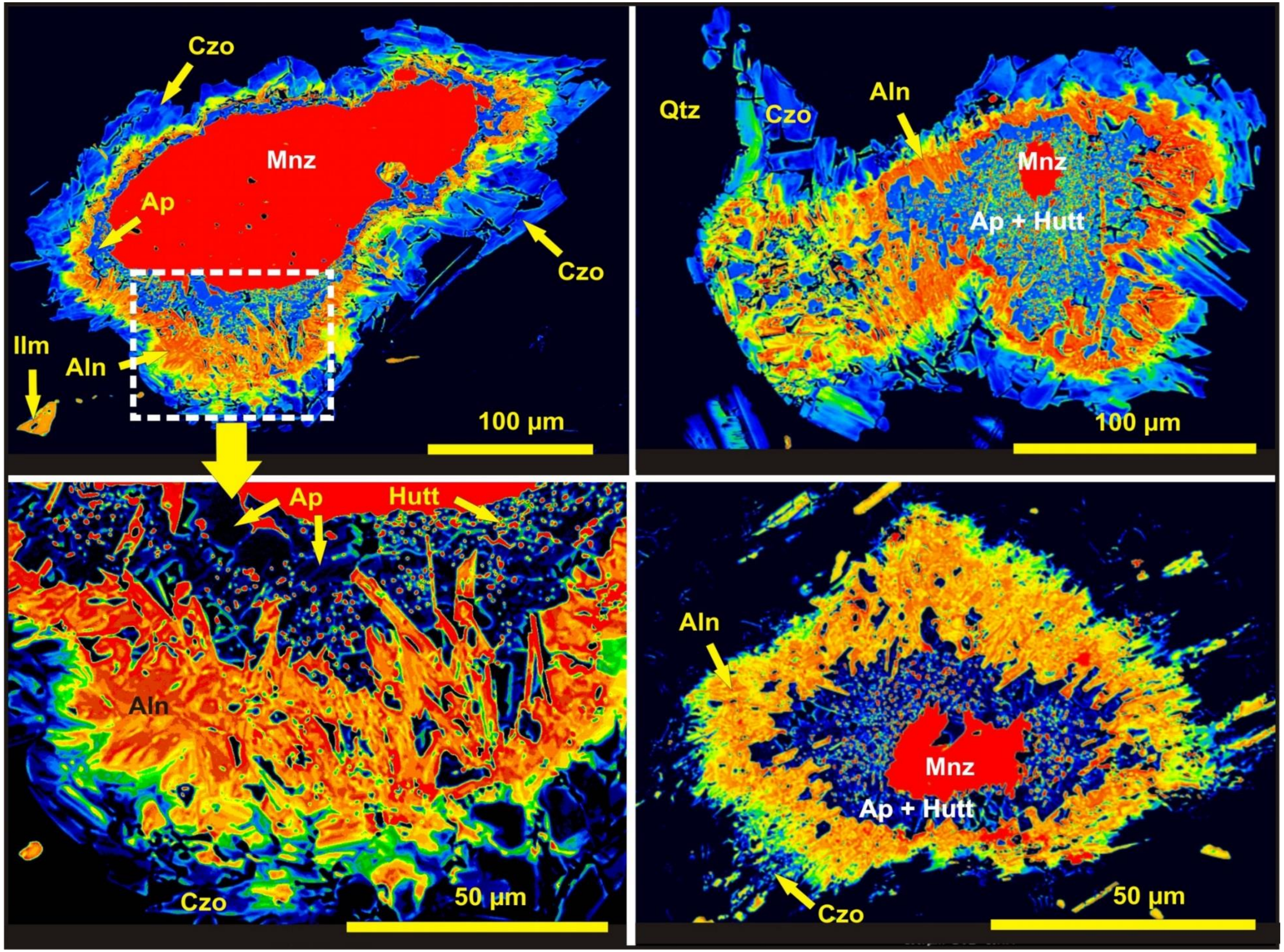
Precipitation of new mineral phases: crystallization in aqueous solutions hydrothermal fluid = a carrier of trace elements required for crystallization. The transport of chemical elements.

e.g. secondary fillings of fissures, fractures and cavities
- system of secondary veinlets
- newly-formed minerals
- impregnations

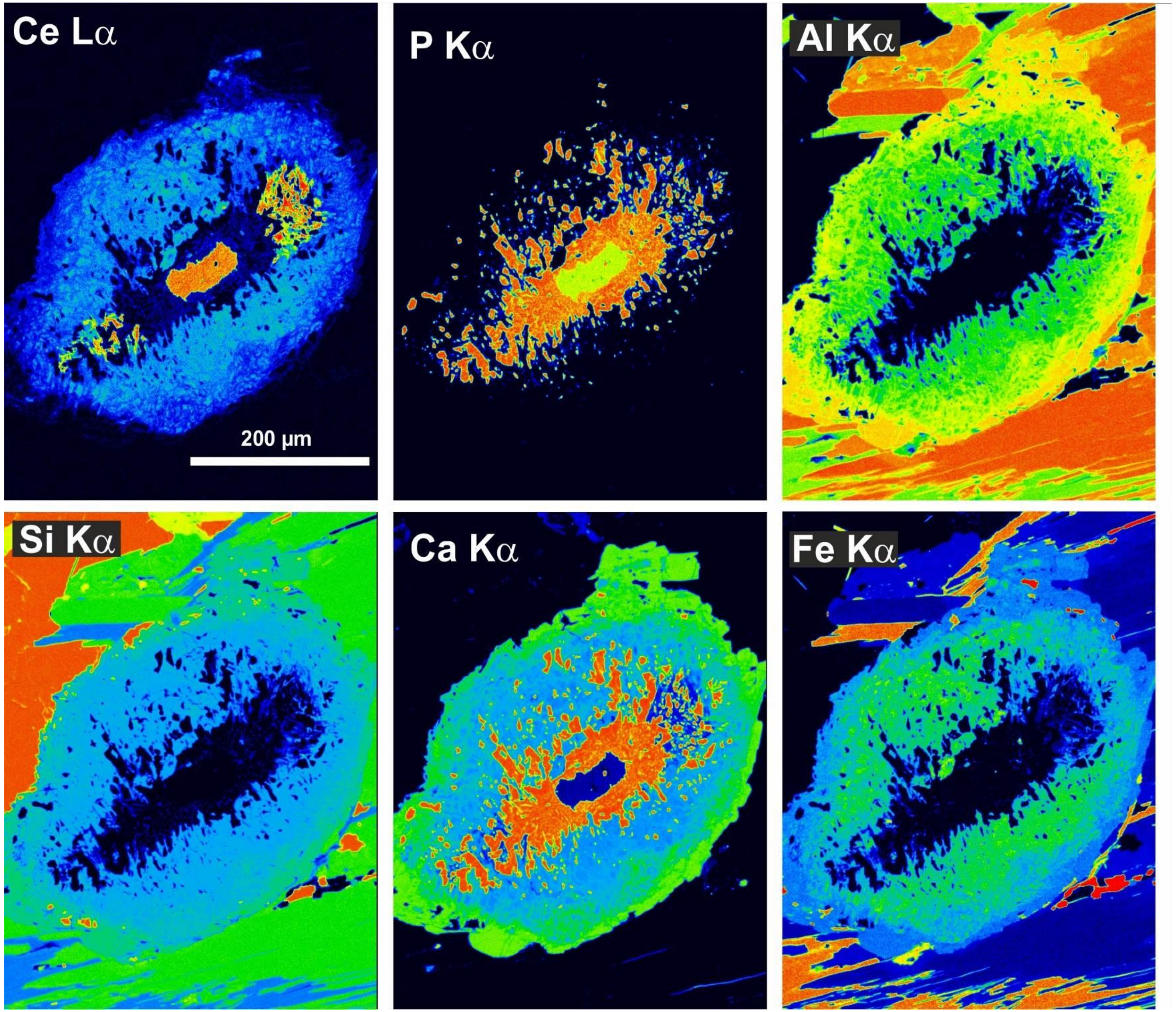
BSE – breakdown microtextures – Veporic orthogneisses

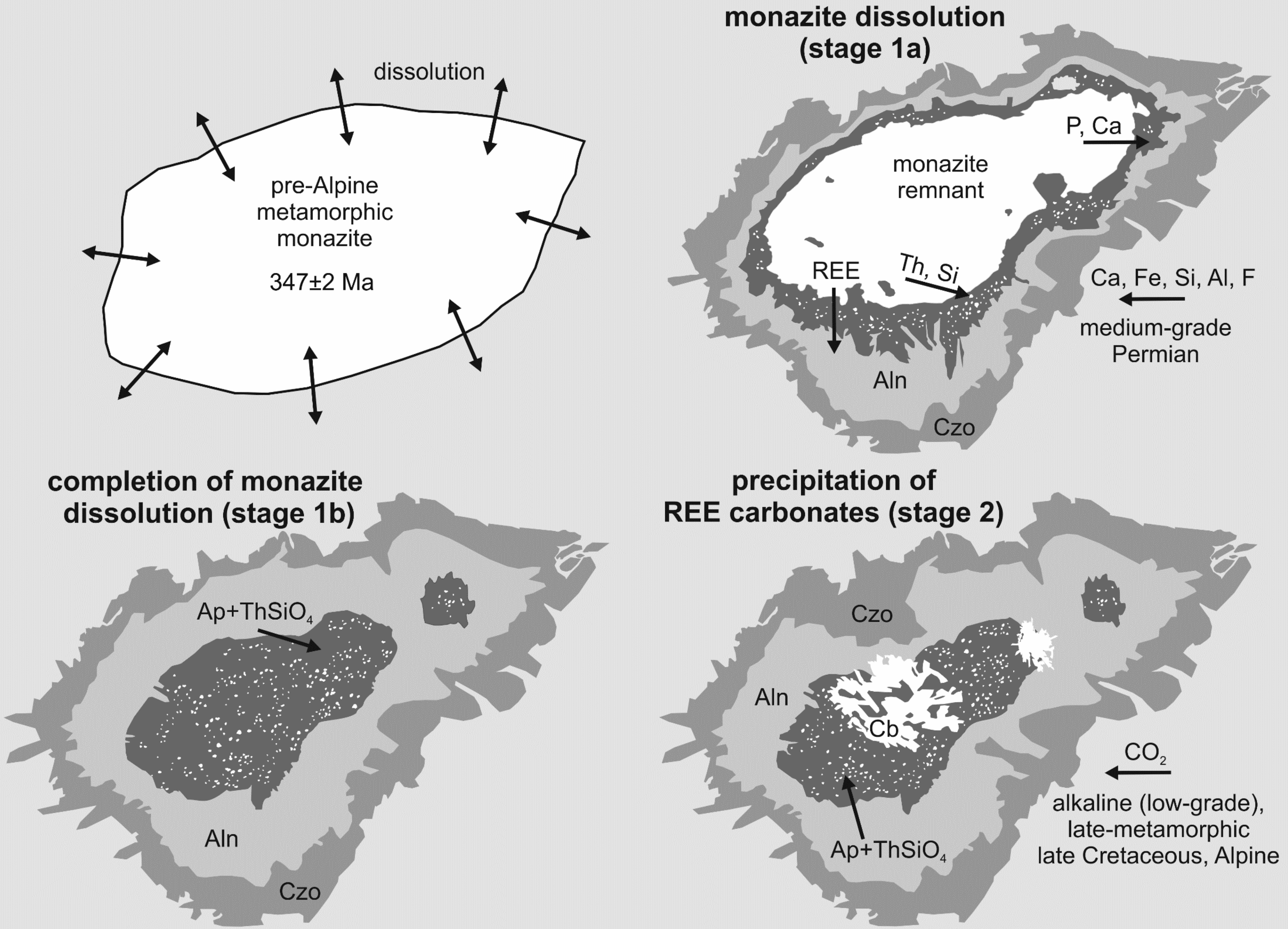


Corona formation around Mnz – Veporic orthogneisses

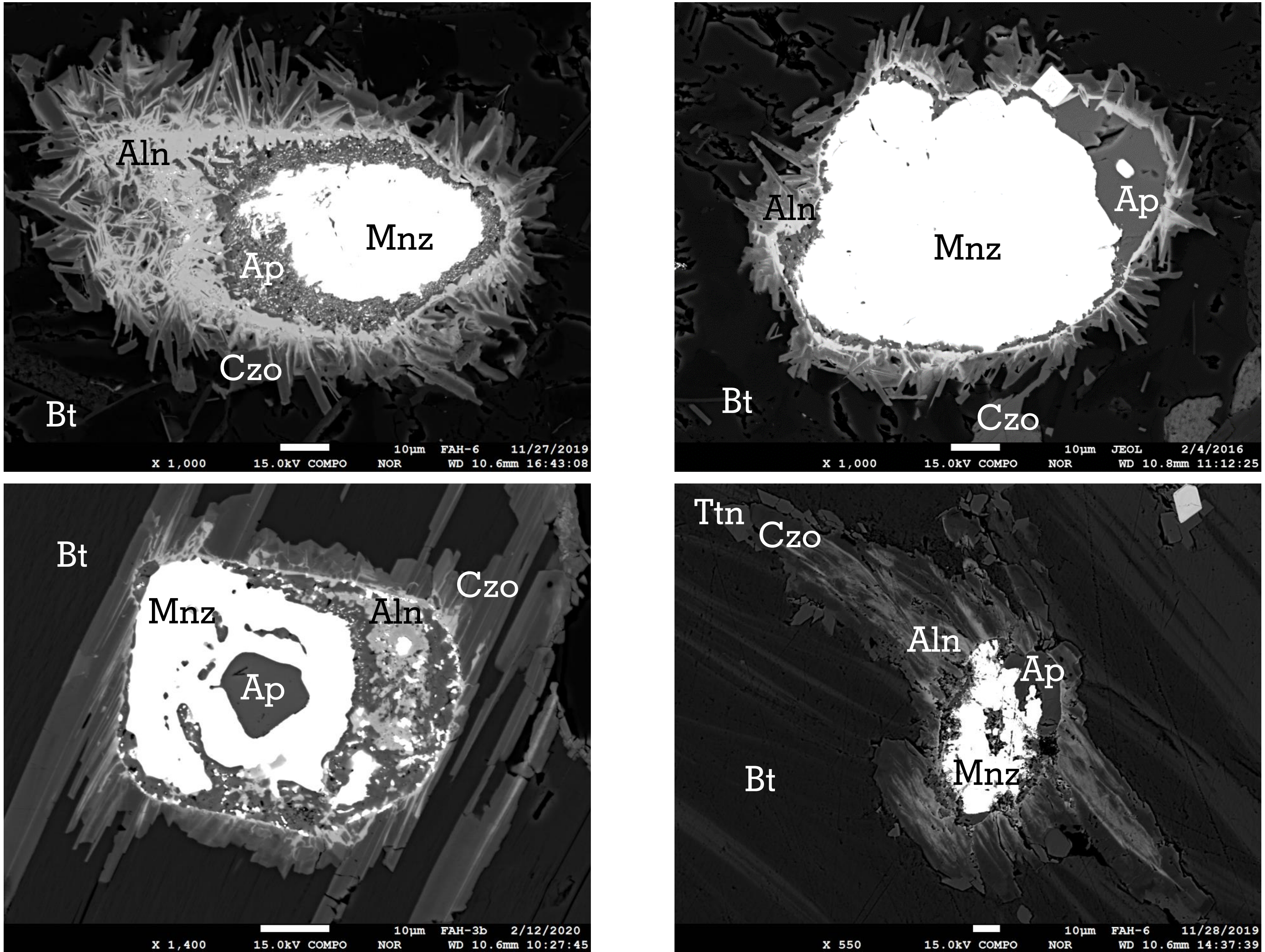


X-ray maps – Mnz corona

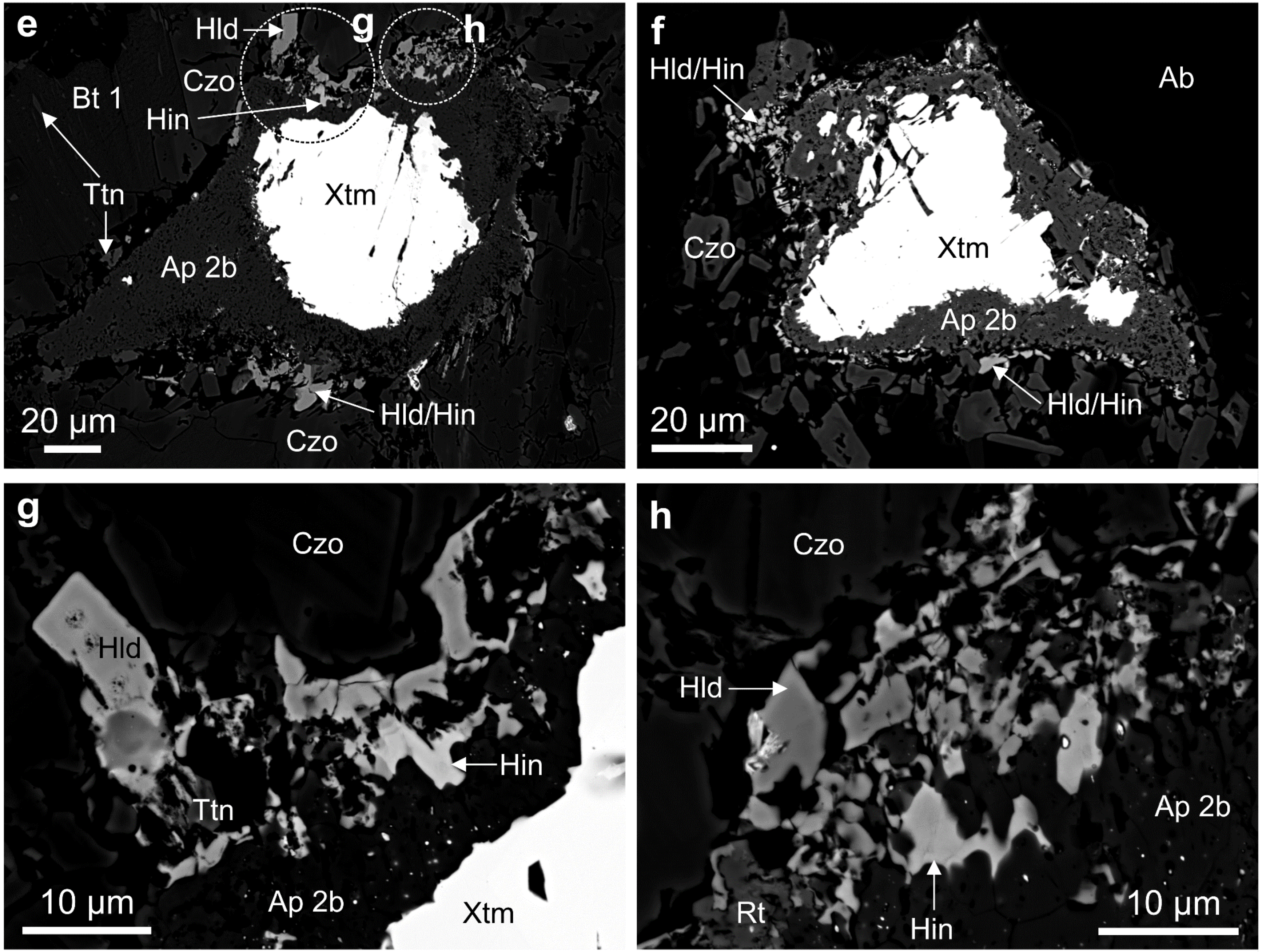



dissolution
pre-Alpine
metamorphic
monazite
347±2 Ma
monazite dissolution
(stage 1a)
P, Ca
monazite
remnant
REE
Th, Si
Ca, Fe, Si, Al, F
medium-grade
Permian
Aln
Czo
completion of monazite
dissolution (stage 1b)
Ap+ThSiO$_4$
Aln
Czo
precipitation of
REE carbonates (stage 2)
Czo
Aln
Cb
CO_2
Ap+ThSiO$_4$
alkaline (low-grade),
late-metamorphic
late Cretaceous, Alpine

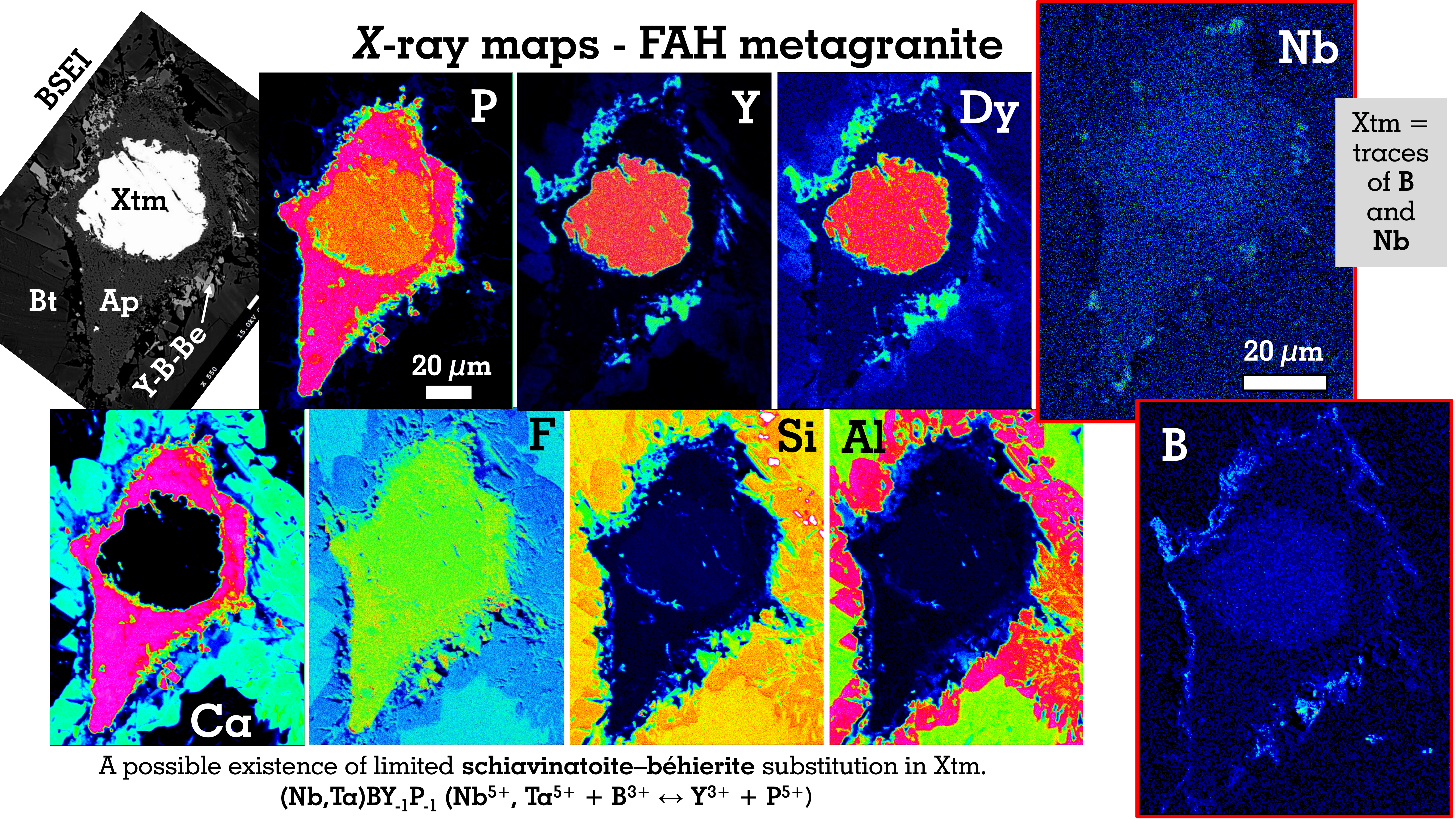
Corona around Mnz– Veporic (FAH) metagranites (mylonites)



Corona around Xtm– Veporic (FAH) metagranites (mylonites)



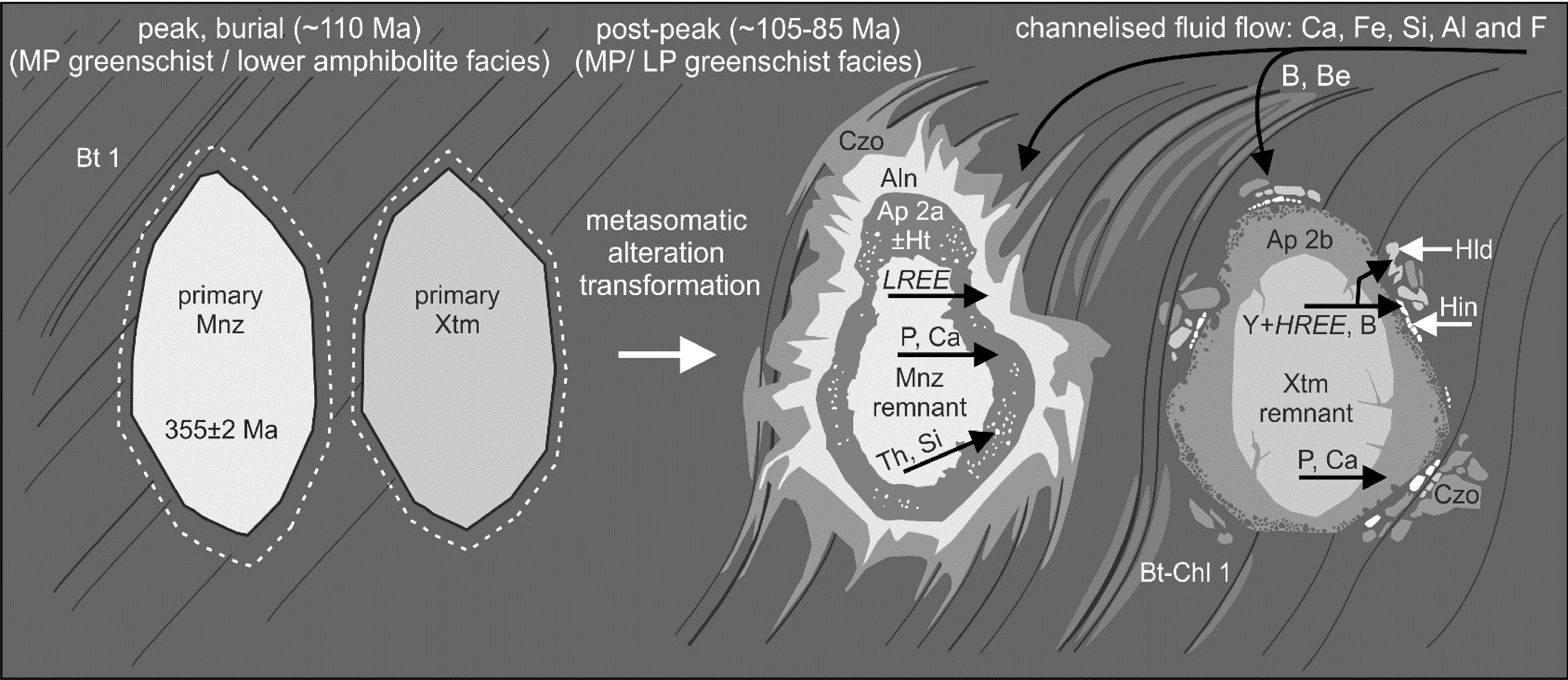
X-ray maps - FAH metagranite



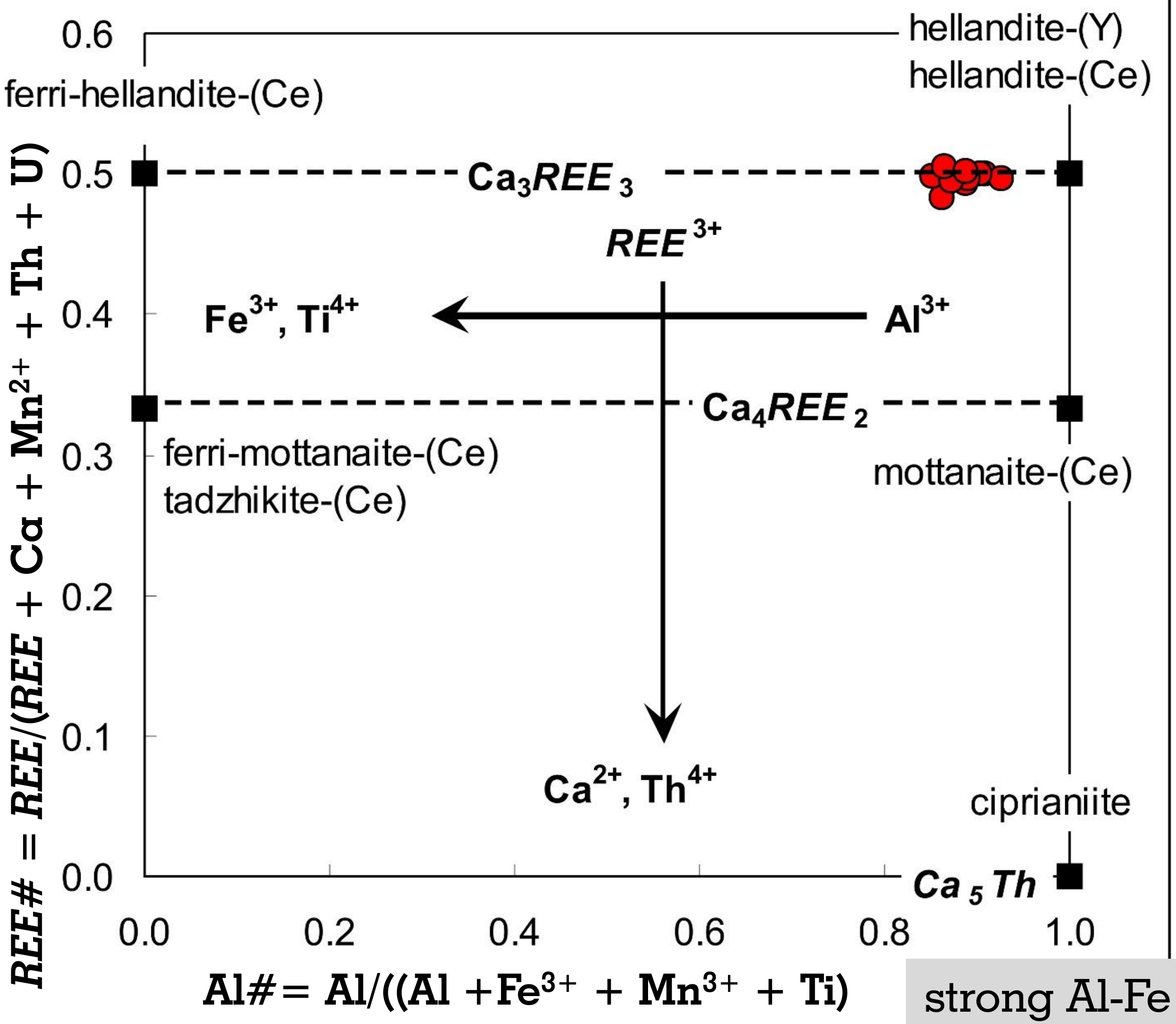
A possible existence of limited **schiavinatoite–béhierite** substitution in Xtm.

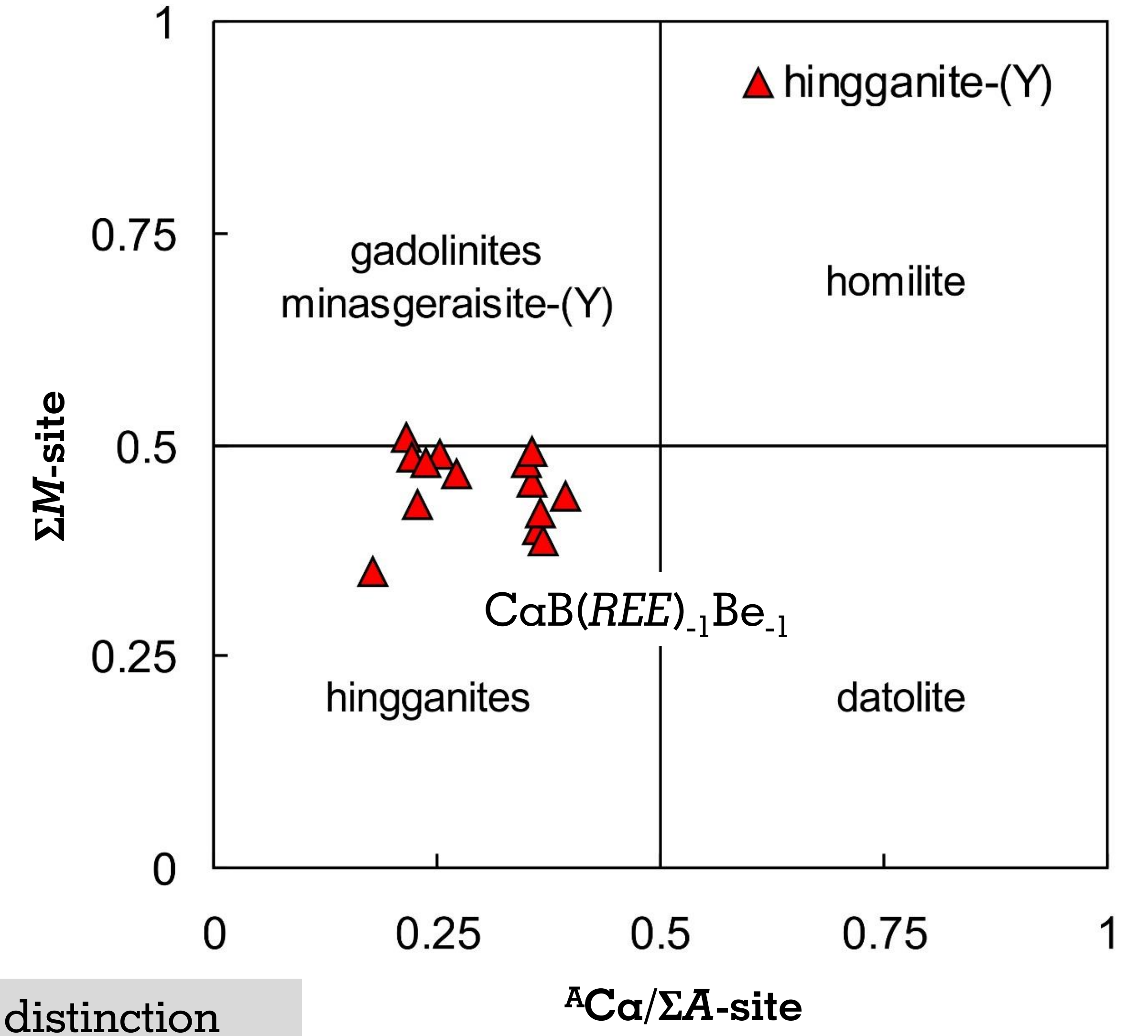
$(Nb,Ta)BY_{-1}P_{-1}$ (Nb^{5+}, Ta^{5+} + B^{3+} ↔ Y^{3+} + P^{5+})

Coronae around Mnz and Xtm – FAH metagranites (mylonites)



Crystal-chemistry of Y-B-Be silicates (FAH metagranite)





Ideal formula of hellandite-(Y)

[$(Ca,REE)_4Y2Al\square_2(B_4Si_4O_{22})(OH)_2$]

Oberti et al. 2019

strong Al-Fe distinction

hellandite-(Y) : Al>>Fe^{3+}

hingganite-(Y): Al<<Fe^{2+}

limited $Fe^{3+}Al_{-1}$

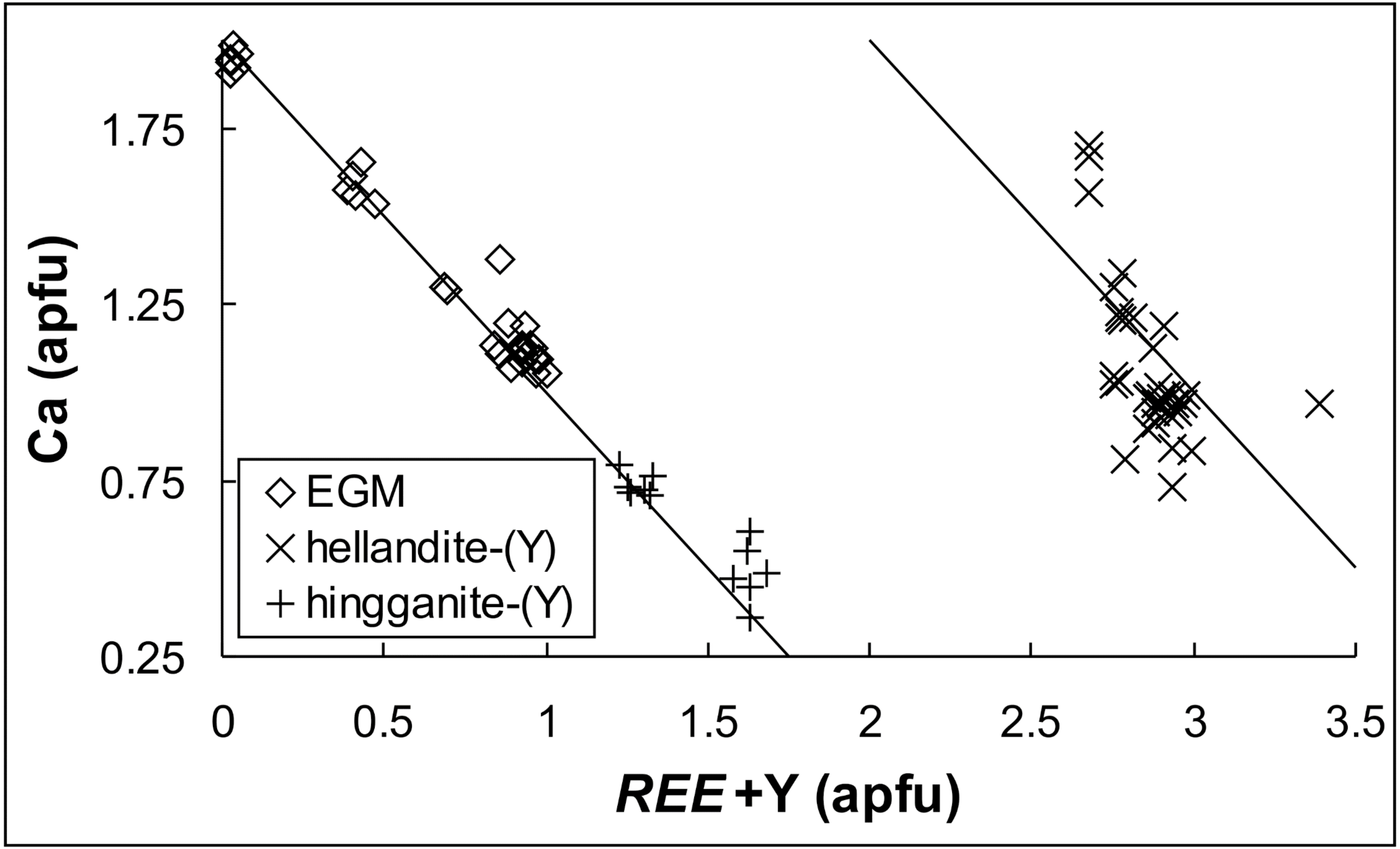
Ideal formula of hingganite(Y)

[$Y_2\square Be_2Si_2O_8(OH)_2$]

Bačík et al. 2017

general trend of Ca–*REE*+Y substitution

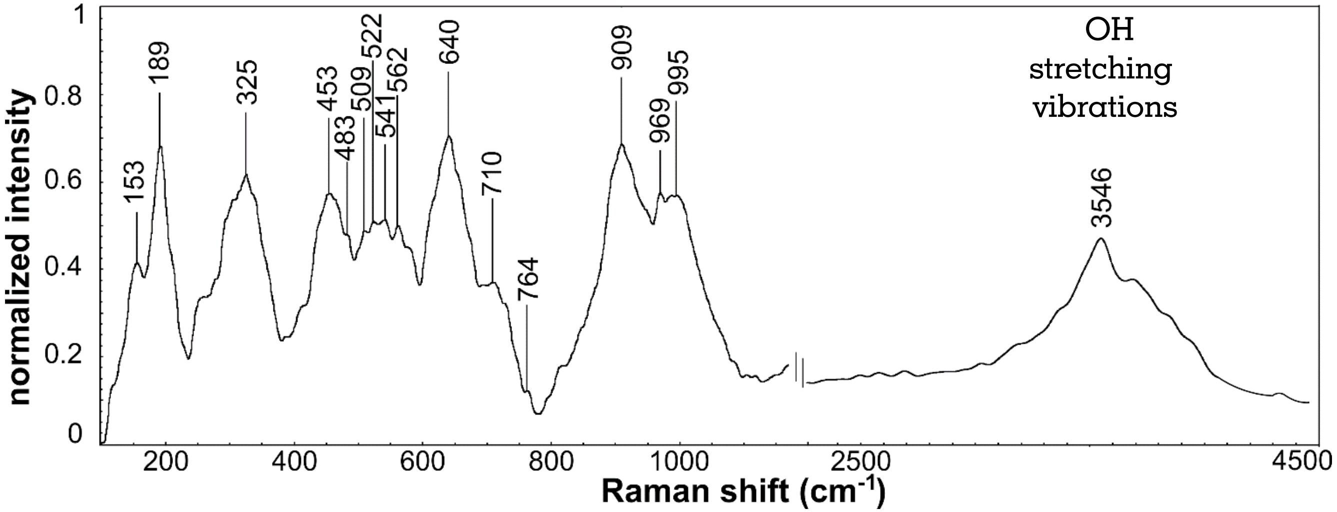
Fluid chemistry occurred during hydrothermal alteration of Mnz and Xtm. It was substantially controlled by the activity of Ca



Raman spectra of Y-B-Be silicates

hingganite-(Y)
[$Y_2\square Be_2Si_2O_8(OH)_2$]

gadolinite supergroup

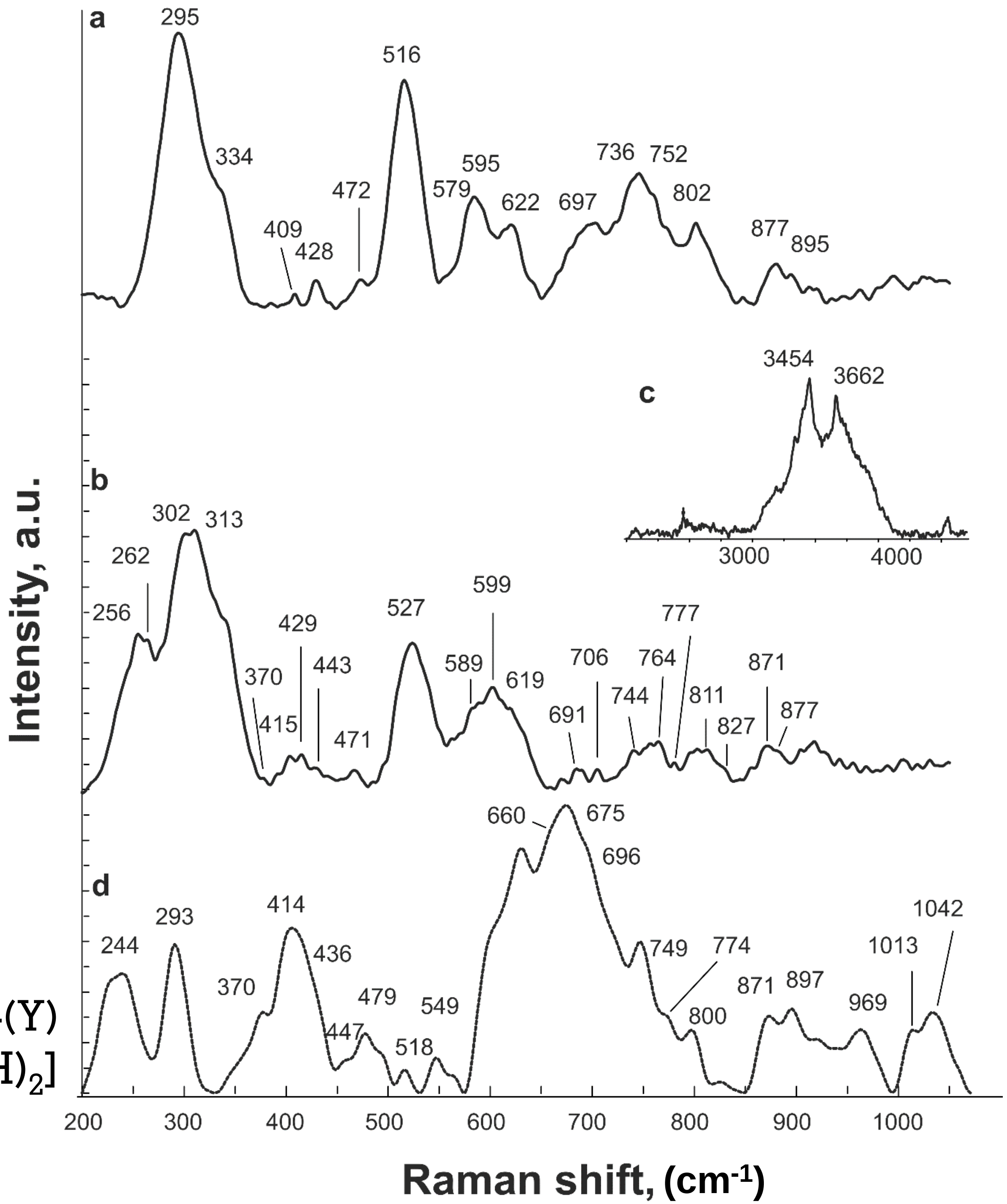


bending modes of Si-O and Be-O,
stretching vibrations of *REE*-O
and Fe-O,
lattice vibrations

stretching
vibrations
of *Si-O and Be-O*

hellandite group

hellandite-(Y)
[$(Ca,REE)_4Y2Al\square_2(B_4Si_4O_{22})(OH)_2$]



Conclusions – part I.

Variscan arc granites are not a favorable environment for magmatic borosilicate minerals and **high B activity was recognized only in Alpine overprinted rocks**.

The localized occurrence of Y-B-Be silicate minerals in the Variscan metagranites, which formed in reaction coronae during post-peak Alpine metamorphism, suggests a **high activity of B and Be in the transformations**.

Possible sources of light elements

Boron and Be were probably mobilized during the Alpine mylonitization from common rock-forming minerals, esp. Ms and Plg (low contents but high modal abundances).

A **source of B** could be the **altered xenotime-(Y)** itself, which contains **traces of B.**
Incorporation of B into the xenotime-(Y) structure: **(Nb,Ta)BY$_{-1}$P$_{-1}$ (Nb^{5+}, Ta^{5+} + B^{3+} ↔ Y^{3+} + P^{5+}).**
(a possible xenotime-(Y)–schiavinatoite–béhierite solid solution)

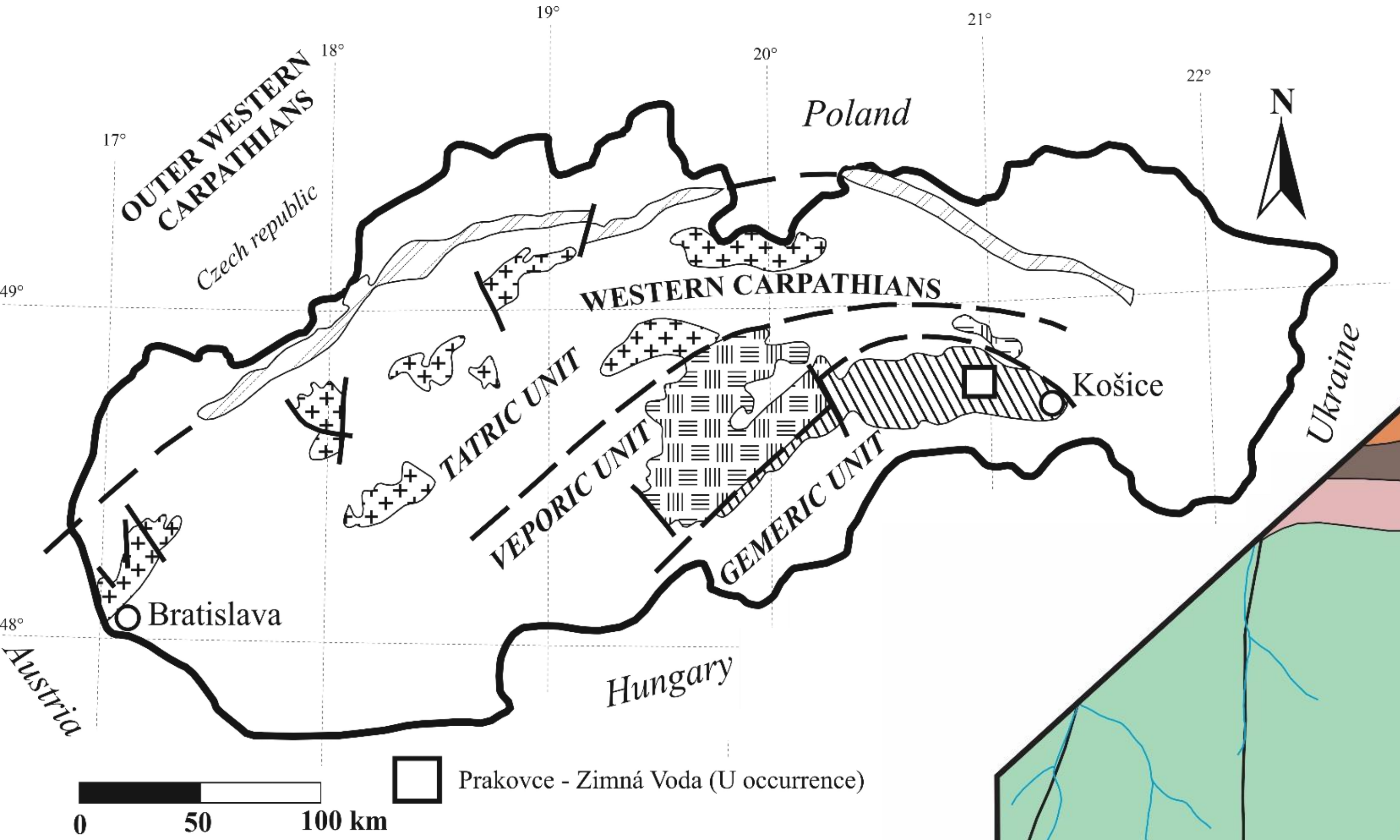
orthoborates with zircon-xenotime type crystal structure: schiavinatoite $NbBO_4$ and béhierite $TaBO_4$)

Xtm: Nb (~0.1 wt.%), Ta = b.d.l.

The **principal source of B** in the metagranites **is external**, most probably from widespread Permian magmatic rocks in the area, e.g., tourmaline-rich Klenovec granite and/or other volcanic rocks.

Formation of **Hld** and **Hin** in the Fabova Hoľa metagranite may have resulted from the **localized heterogeneity and Y-B-Be saturated environment** occurring in the proximity of the altered Xtm only, instead of the more common EGM or tourmaline, which was documented in metagranites in broader vicinity of the FAH-3 sample.

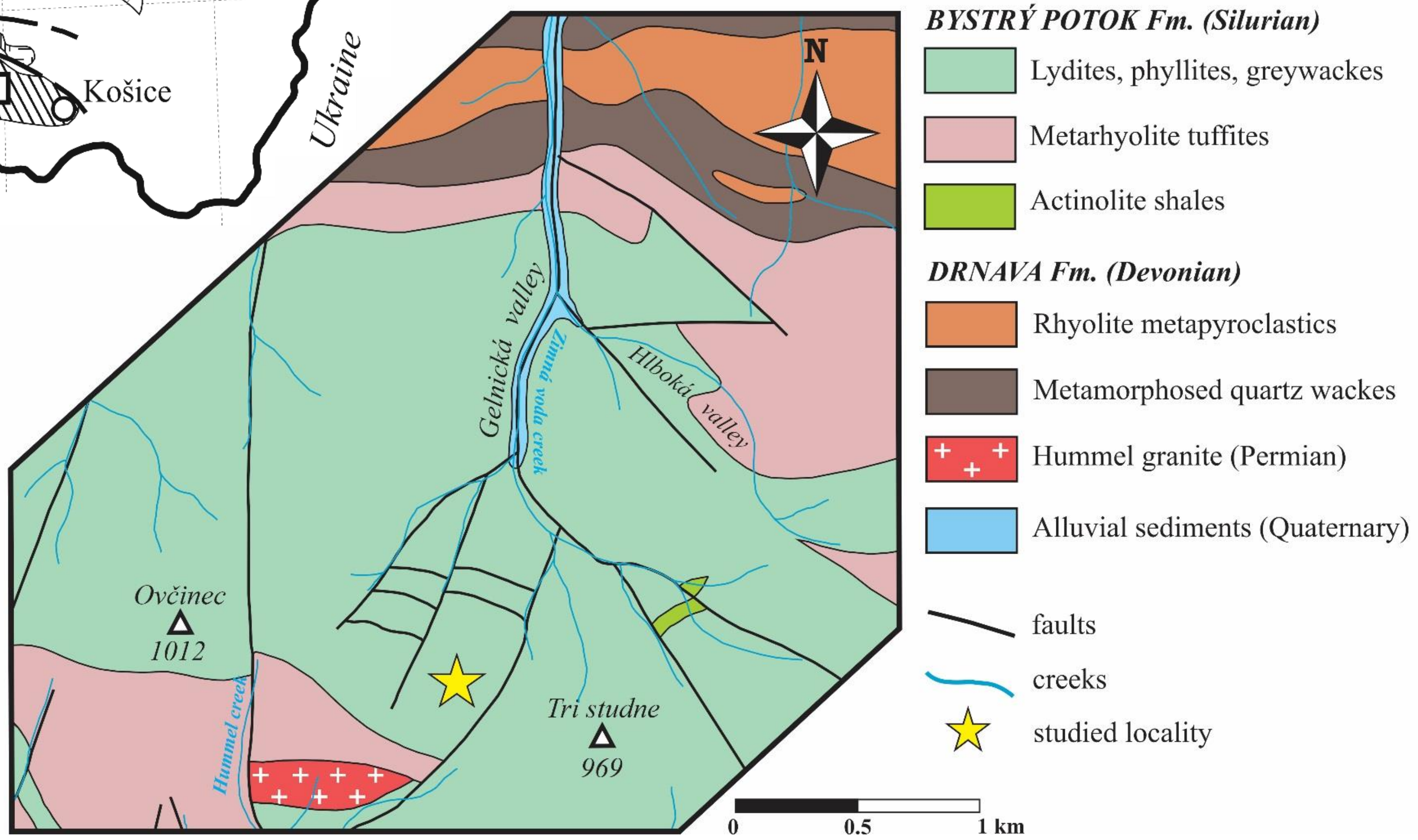
Selective Gd (MREE) supersaturation during low-temperature alteration of U-REE-Au ores



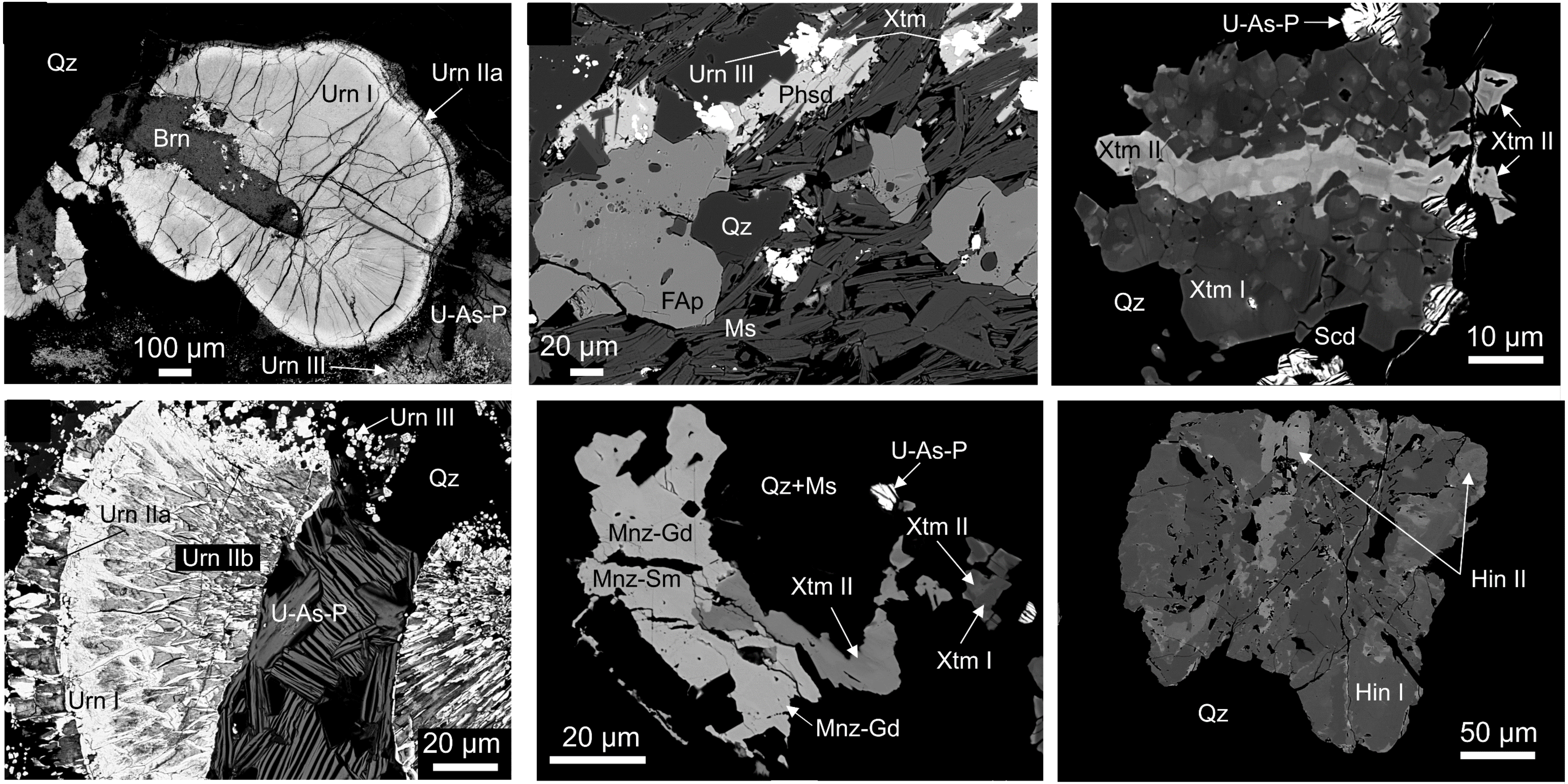
vein mineralization

Prakovce – Zimná voda

Gemeric unit

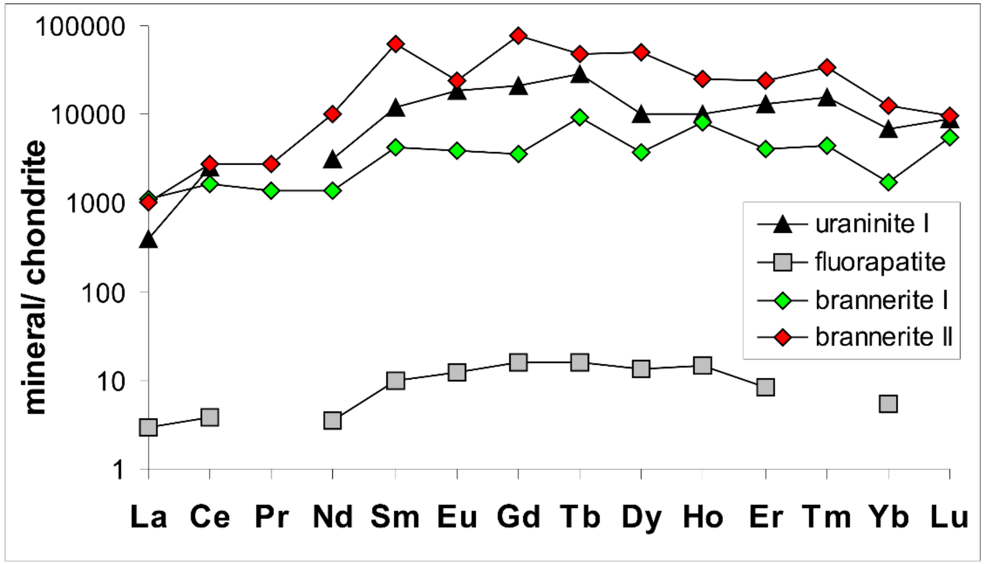


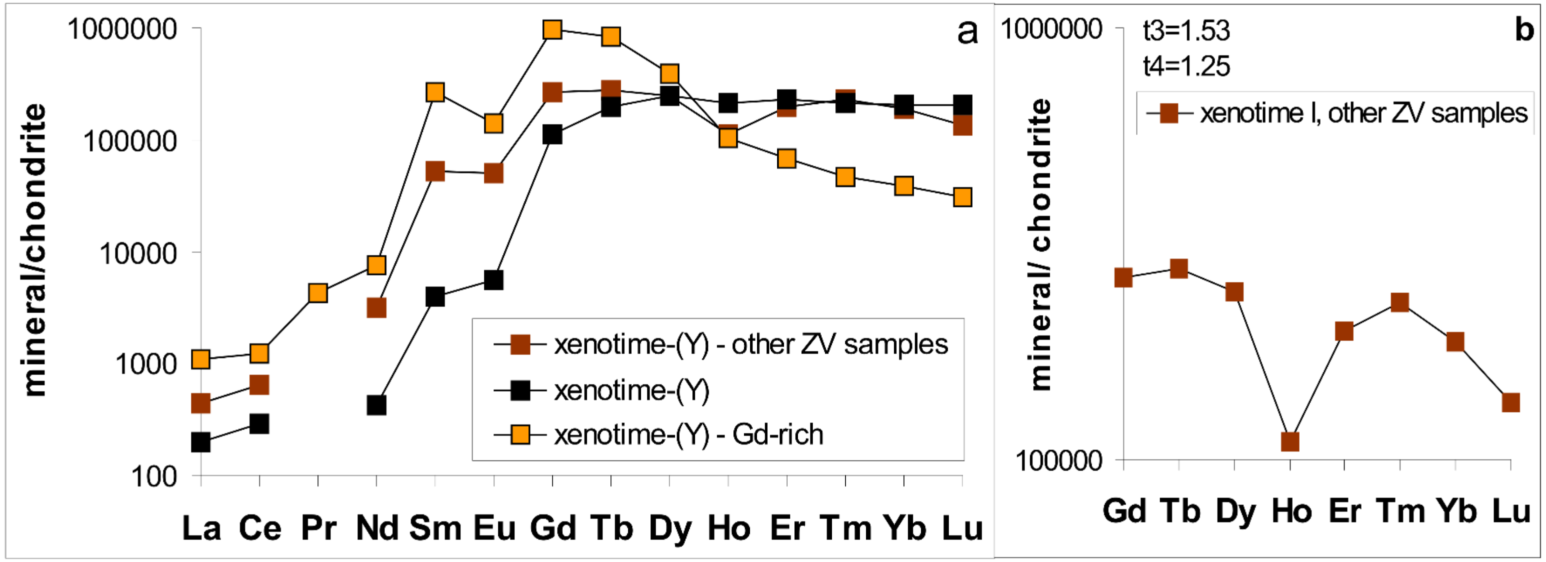
BSE microstructures

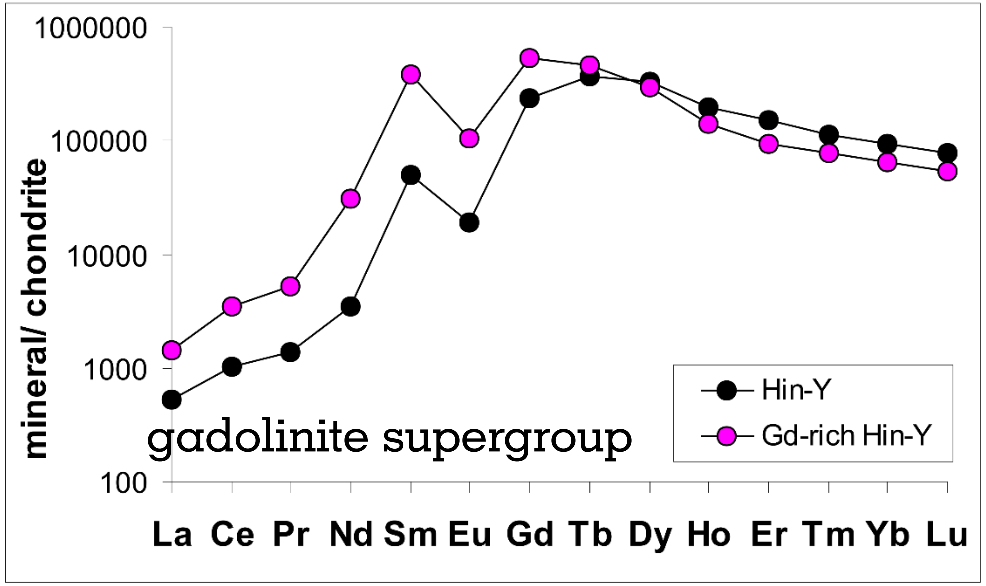


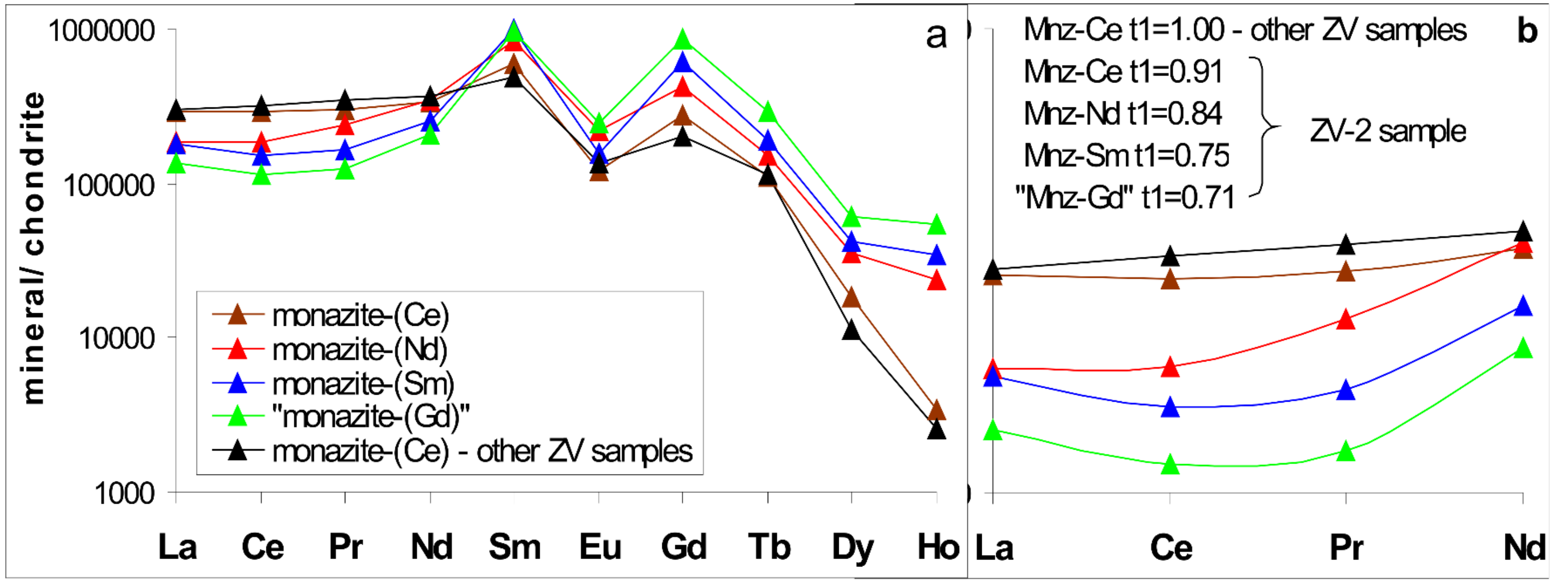
Gd (MREE) hump

M-type tetrad effect



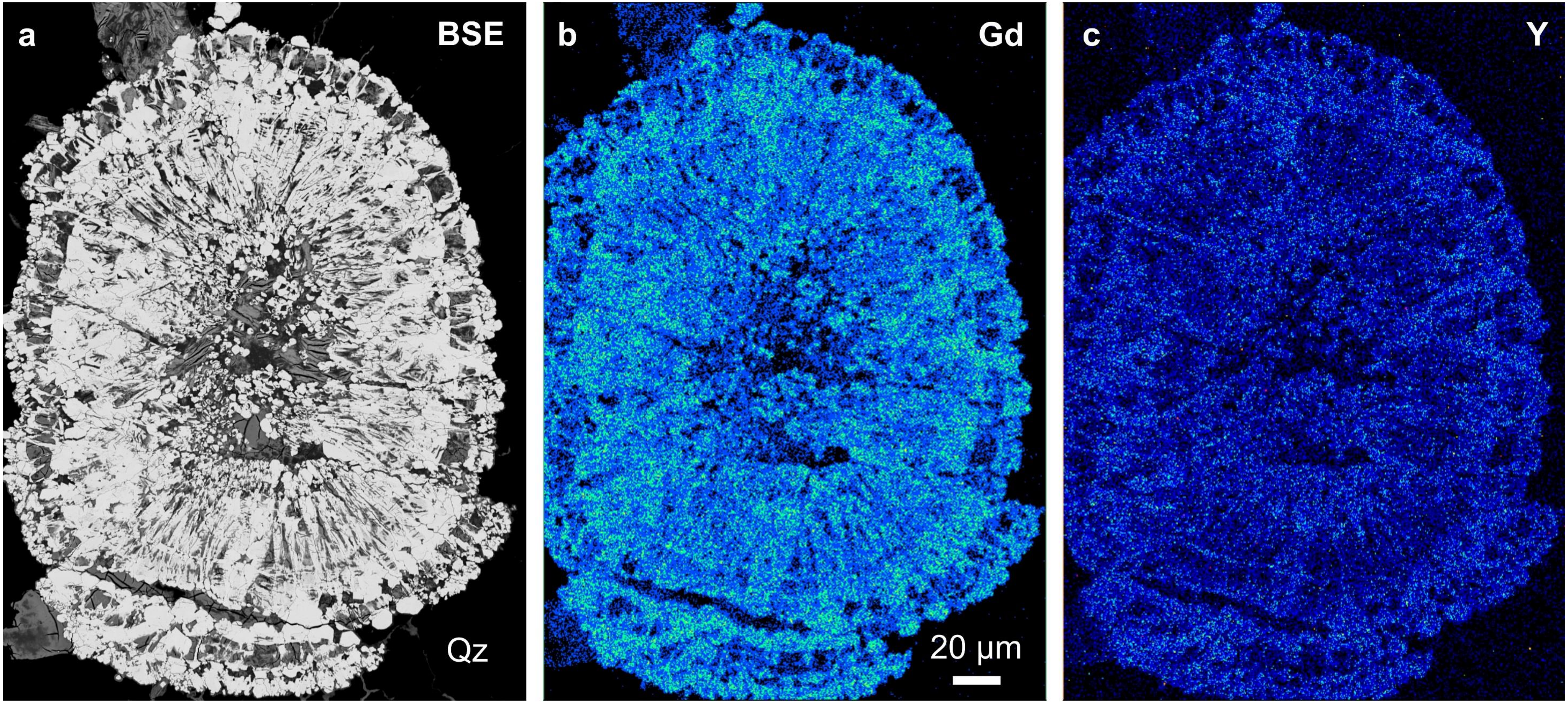






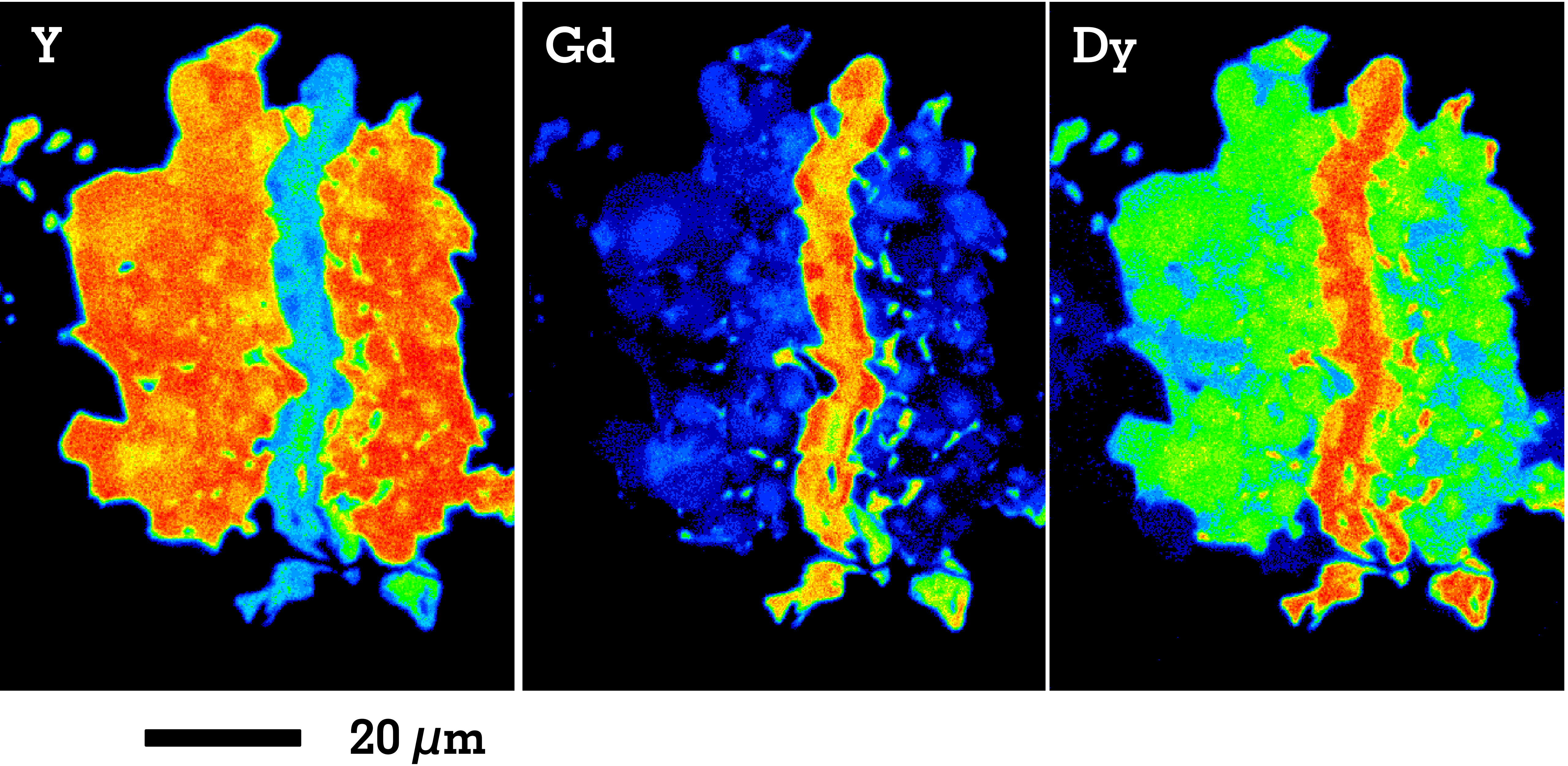
W-type tetrad effect

X-ray maps – botryoidal uraninite (pitchblende)

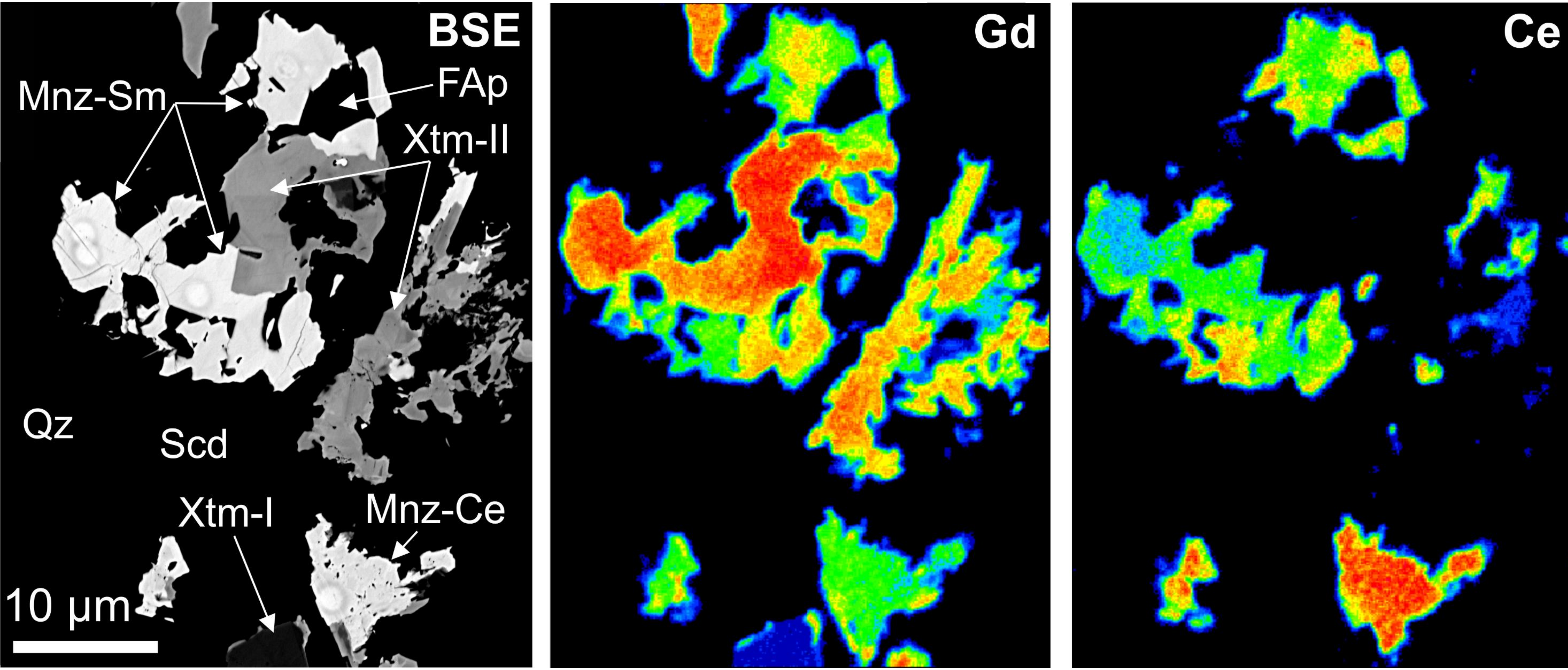


ionic radius of U^{4+} in eight-fold coordination (1.00 Å) is similar to that of Gd^{3+} (1.053 Å) - Shanon, 1976

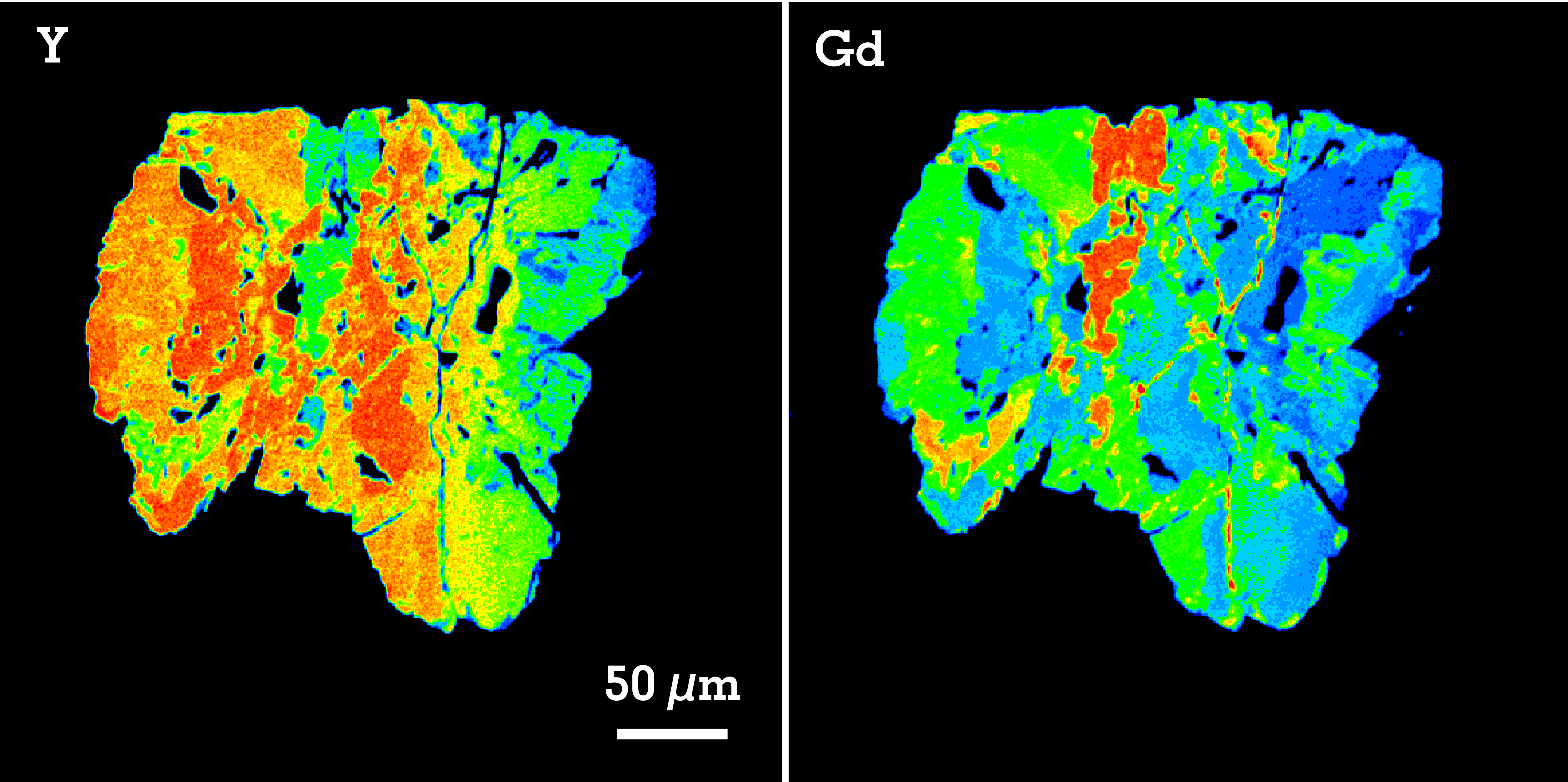
X-ray maps – xenotime I and II



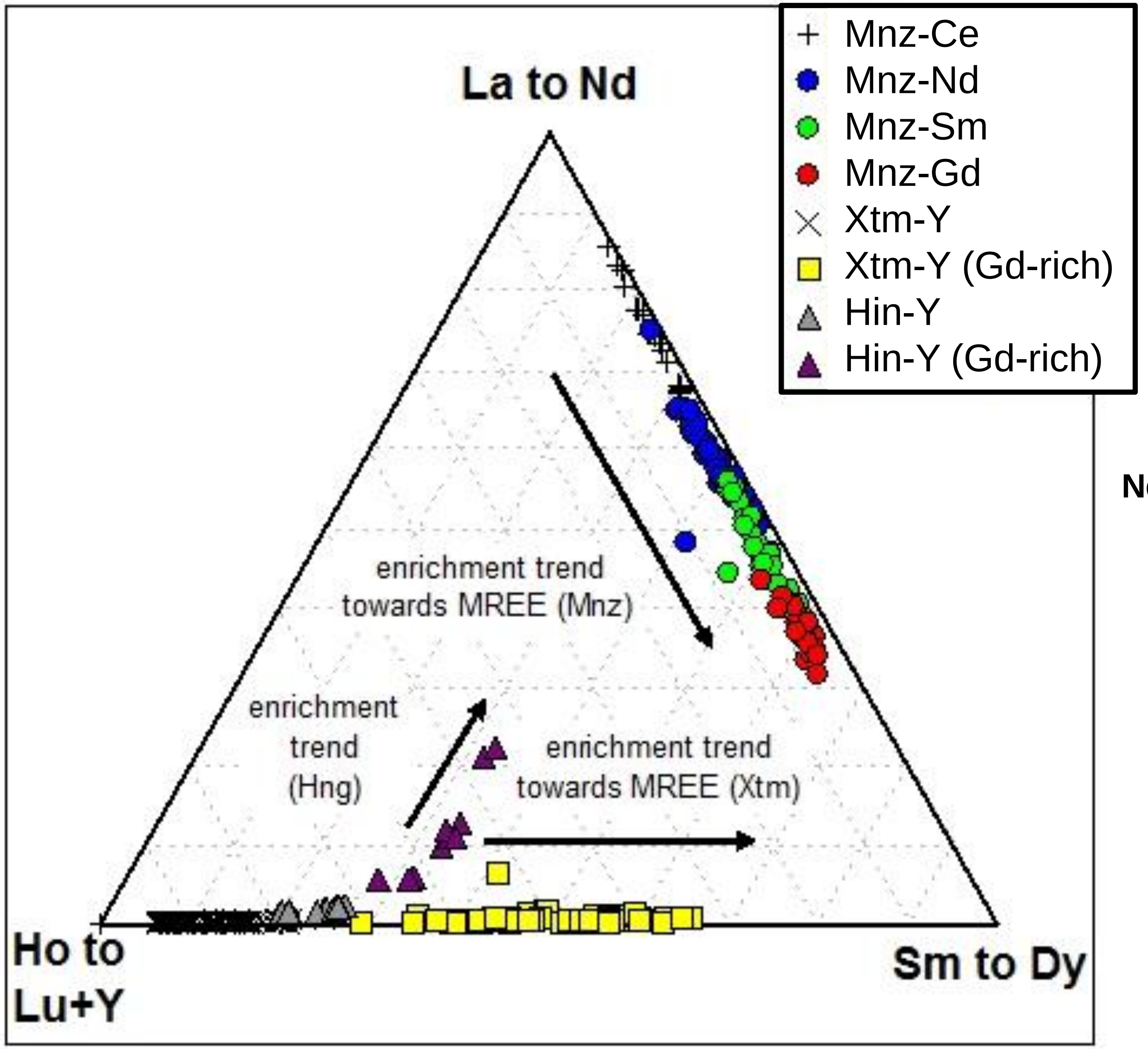
X-ray maps – monazite group

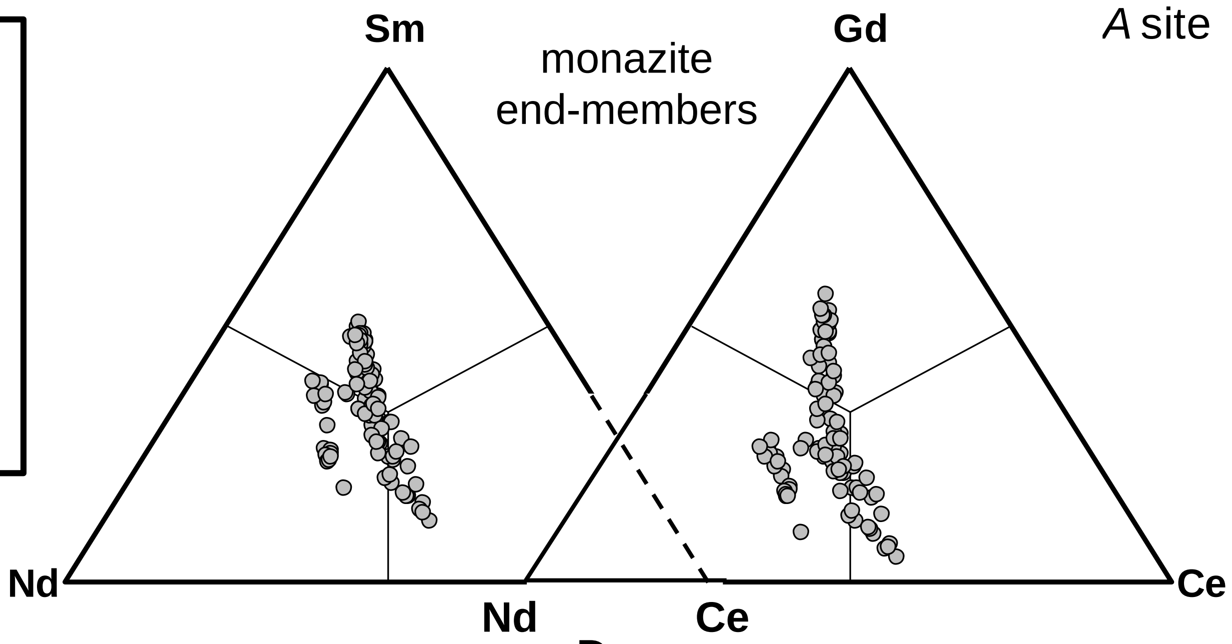


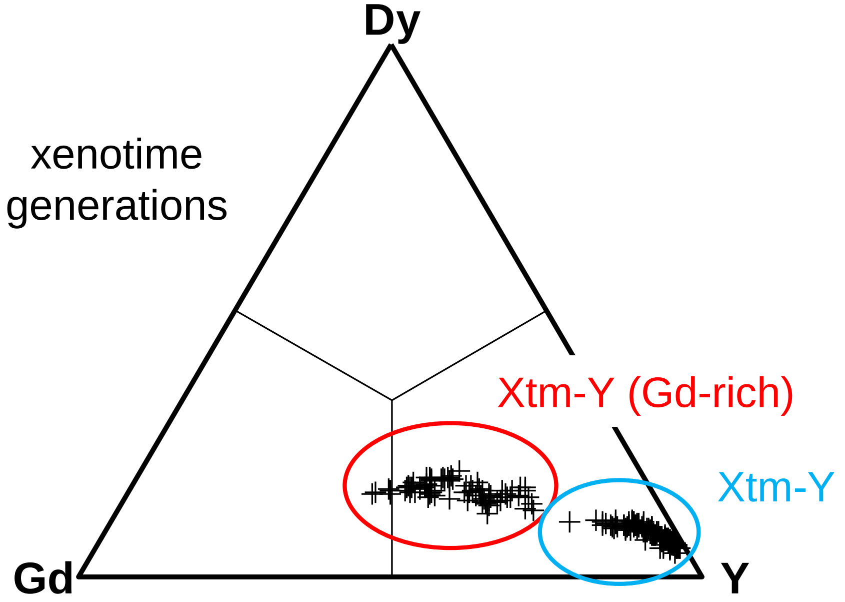
X-ray maps – gadolinite supergroup



Gd (MREE) supersaturation – general trends of fractionation





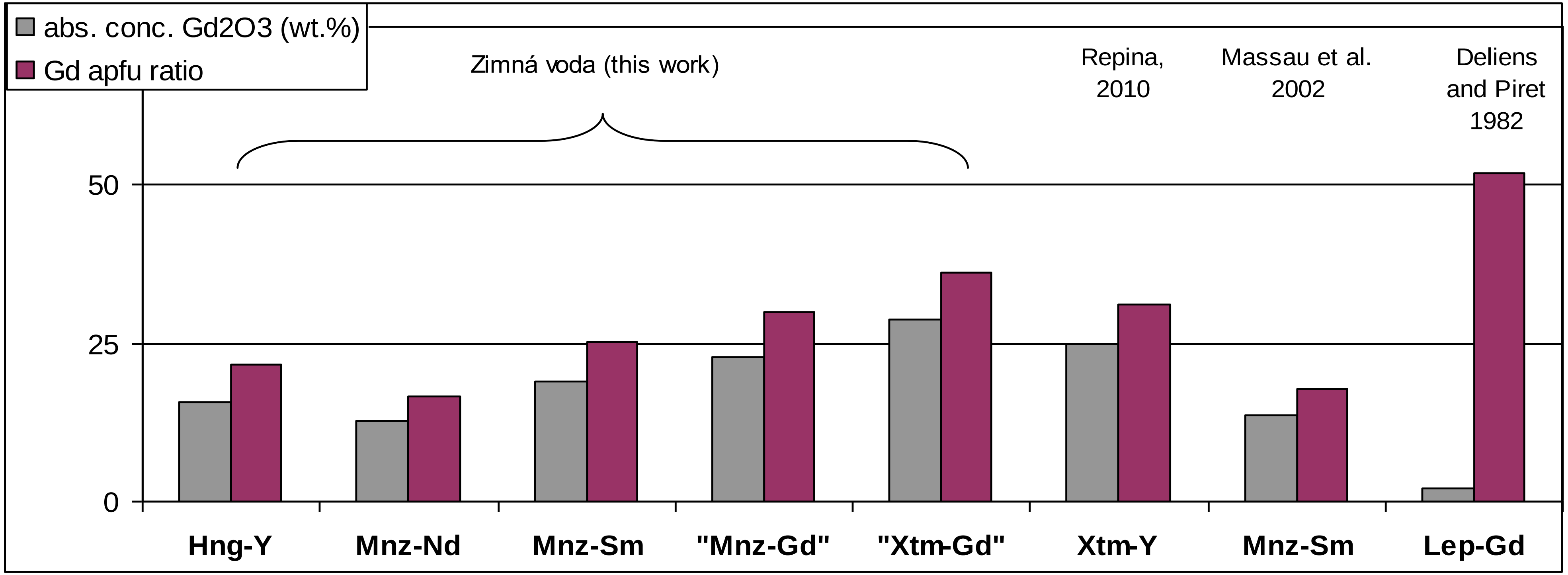


Gd distribution in nature

Lepersonite-(Gd): $Ca(Gd,Dy)_2(UO_2)_{24}(SiO_4)_4(CO_3)_8(OH)_{24}\cdot 48H_2O$ (Deliens and Piret 1982)
only valid Gd-dominant mineral on Earth

possible Gd-fractionated signatures – who other than Russians? ☺

- Gd-dominant phosphate: 42.5 wt.% Gd_2O_3 $(Gd_{0.55}Y_{0.25}Dy_{0.1}Sm_{0.05}Nd_{0.05}Th_0Ca_0)(PO_4)$, alkali-feldspar syenite pegmatite, Myanmar (EDX, Kartashov, web data at mineralienatlas.de; mindat.org).
- fine-grained authigenic unknown Gd- and Dy-bearing minerals: REE accumulations in coals, Russian Far East Pavlovka deposit (EDX, Seredin 1992).
- fractionated REE and Gd-dominant signature in the lunar regolith, Mare Crisium (EDX, Bogatikov et al. 2004; Mokhov et al. 2011)



Conclusions – part II.

Gd-dominant and Gd-rich minerals are very rare in nature due the low absolute abundance of Gd relative to other REE (esp. Ce, Nd, La, Y) in the Earth's upper crust and s**trongly coherent lanthanides partitioning** dependent mainly on the charge and ionic radius-controlled behavior (CHARAC).

Selective supersaturation of Gd, or other individual MREE and HREE is an **extremely rare process** which occurred as rather, localized anomaly = **Zimná voda is gonna be very famous !!!**

Gd-rich Mnz (LREE>HREE) and Xtm (HREE>LREE) suggest the substantial incorporation of Gd **into both REE-selective structures -** confirm lab-studies of differently sized REE^{3+} substitution in $REEPO_4$ s.s. and the stabilization of the Gd-rich Xtm-type structure by substitution of rest of the *A*-site cations for smaller HREE and Y and vice versa.

Gd supersaturation most likely results from a localized, but strong progressive decoupling of (LREE+HREE) and MREE on relatively small scales. The alteration of hypogene MREE-selective minerals (uraninite I, brannerite I ± fluorapatite) by late hydrothermal fluids/ groundwater solutions can be responsible for such REE remobilization and low-*T* MREE enrichment.
This scenario is likely only in an **isochemical system**, even **local mass transport** on a small spatial scale must occur during precipitation = **localized process in chemically closed system.**

An obvious connection of Gd (MREE) supersaturation with U ore occurrence and subsequent alteration of uraninite, e.g. lepersonite-(Gd), Shinkolobwe, D.R. Congo. The significant fractionation of REE with selective enrichment of MREE can occur via alteration and leaching of Urn ± Bnr ± FAp by low-*T*, F-rich aqueous fluids.

Thank you for your attention!

M. OndREEjka

Acknowledgments: *Thanx to my co-authors and dept. colleagues for their support and help... appreciate it.*

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